

ANCA EMANDI

GENERAL CHEMISTRY
PRACTICAL WORKS GUIDE

EDITURA UNIVERSITĂȚII DIN BUCUREȘTI



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GENERAL CHEMISTRY

- PRACTICAL WORKS GUIDE -

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SECTIUNEA I

What is a chemical technician?

The chemical technician is a professional in every sense of the words. He should look, think, and act as professionals are expected to do. He is entitled to all privileges of a professional and of the same time is expected to shoulder the responsibilities of a professional. In fact, the best definition of a technician can be obtained from an analysis of what the technician must know, what special abilities he must possess, and what he must be able to do.

The chemical technician is a mature individual with seriousness of a purpose and adequate technical knowledge. He is strongly motivated, possessing the requisite mechanical aptitude, curiosity, and ability to reason. He should be accurate in his work, objective in his approach to his work, patient, and persistent. He should have the physical stamina to stand at worktables for long periods of time to perform manipulation. He should have good or corrected eyesight in order to use precision equipment and have color vision to perform the many color tests which are used to determine chemical properties and analyze substances. Manipulative skills such as hand-eye coordination and finger dexterity are extremely important when using delicate equipment and when handling dangerous and toxic materials.

A professional technician is, when working, always serious and businesslike in the laboratory. There is a time to work and a time to play, and the two do not mix when there is a job to be done. Since he is a professional, his dress should be professional. He does not engage in horseplay, practical jokes, or frivolity while on the job, always observing the rules of good laboratory practice and safety. Those rules are commonsense rules. He is aware of the hazards that are involved in laboratory work, he recognizes their causes, and he follows directions for standardized laboratory procedures.

The professional technician has the important traits of good scientists. He has the ability to plan and perform precise experiments are neat and accomplish the objectives of the experiment. This ability can be attained even by those who feel they are clumsy and not mechanically inclined.

What should a technician know?

A scientist systematically accumulates many facts and organizes his knowledge so that he may effectively use it to predict future events. The chemical technician is an important part of the technical team comprising the scientist, the engineer, and the other members having expertise in their fields.

The chemical technician must:

1. Define the particular problem and know the goal of what he is doing.
2. Gather facts and verify them for accuracy under controlled condition in order to determine the relationship between the variables.
3. Classify the accumulated data and observe the relationship that exist between the data.
4. Formulate hypotheses, or reason why things behave as they do in a particular system.
5. Confirm his hypotheses by experimentation to formulate theories.

This is the scientific method of scientists who carefully carry out scientific experiments to collect all the pertinent facts, objectively recording data obtained by unbiased observation, who generalize from those collected facts, and who check generalizations by further observation and experimentation.

1. The chemical technician must use the disciplined and objective scientific method and inquiry and observations in the application of the basic principles, concepts, and laws of physics, chemistry, and/or biological science pertinent to the individual field of technology.

2. The chemical technician must have competence in mathematics because mathematics is the tool of scientist. His level of proficiency should cover those areas of mathematics in which he needs to be knowledgeable.

3. The chemical technician should thoroughly understand, know how to use, and be capable of using expertly all the materials, apparatus, processes, procedures, methods, and techniques commonly performed in the laboratory.

4. The chemical technician should have knowledge of the physical and biological science in his field and how it relates to the engineering, health, industrial processing, or research activities that distinguish the technology of his field of specialization.

5. The chemical technician should have the individual judgment, initiative, and resourcefulness to use the techniques and procedures and to perform the detailed or technical work outlined in general procedures and instructions.

6. The chemical technician should have communication skills, including the ability to record, analyze, interpret, and transmit ideas orally and especially in writing with complete objectivity. He should know how to locate and master new information pertinent to the technology. Technicians should be able to communicate easily with all persons, regardless of the technical level involved in their work.

7. The chemical technician should, as a professional, generally understand the broad aspects of social and economic factors, know the organization of the society in which he lives and works, and in particular, know his employer's organization. He should be aware of acceptable personal attitudes based on understanding of person-to-person relationship.

Information retrieval

Much of the information a technician needs to complete many laboratory procedures can be found in reference handbooks, encyclopedias, and manuals in his laboratory or library. Three of the most useful follow:

Dean, "Lange's Handbook of Chemistry", 11th ed., McGraw-Hill Book Company, New York, 1973. Abbreviated Table of Contents: Life and Fire Hazards, Chemical and Physical Properties of Elements, Minerals, Inorganic Compounds, Organic Compounds, Industrial Materials, Chemical Analysis, Tables of Specific Properties, Solubilities of

Gases, Solubility Product, Density, Electrical Properties, Refractivity, Crystallography, X-ray Tables, Hygrometry, Vapor Pressure, Thermal Properties, Surface Tension, Viscosity, Chemical Equations, Definition, Laboratory Arts, Conversion Factors.

"Handbook of Chemistry and Physics", The Chemical Rubber Co. Abbreviated Table of Contents: Mathematical tables of every conceivable kind, Elements and Inorganic Compounds (Periodic Table, Isotopes, Nomenclature, Gravimetric Factors, Solubility Constants, X-ray Data). Organic Compounds (Nomenclature, Physical Constants, Melting Point, Boiling Point, Miscibility, Amino Acids, Carbohydrates, Waxes, Plastics), General Chemical (Azeotropes, Thermodynamic Constants, Reagents, Buffers, Indicators, Flame Tests, Dissociation and Ionization Constants, Conductance, Specific Heats, Boiling Point and Melting Point Data, Thermometers, Vapore Pressure,, Thermal Conductivity, Relative Humidity, Dielectric Constants, Permeability, Magnetism, X-ray Diffraction, Refractivity, Optical Rotation), Densities, Surface Tensions, Viscosities, Conversion Tables, Wire Data, Electrical Data, Earth Composition and Analysis, Molecular and Crystal Data. Abbreviations.

"Merck Index", Merck & Company, an encyclopedia of chemicals and drugs. Abbreviated Table of Contents: Nomenclature, Isotopes, Measurements, Densities, Conversion Tables, Solutions, Buffers, Mathematical Tables, Acids, Medical Isotopes, Monograph of chemicals and drugs, alphabetically arranged, identifying the compound, alternative names, method of preparation, literature references, chemical and physical constants, medical data concerning use, potency, toxicity, medical use if any, incompatibilities, reactivities, solubilities, salts and derivatives, and other relevant data.

other common reference books that contain data on chemicals and their specific constants are:

- " Chemical Engineering Catalog", Reinhold Publishing Corporation
- "The Condensed Chemical Dictionary", Reinhold Publishing Corporation.
- "Chemical Buyers Guide", OPD, Schnell Publishing Co.
- Chemical Abstracts, American Chemical Society.
- Beilstein, Berichte von Deutsche Chemische Gesellschaft.
- Furman, "Standard Method of Analysis", D. Van Nostrand Company, Inc.
- Grant, "Hanckh's Chemical Dictionary", 4th ed. McGraw-Hill Book Company, New York, 1969.

LABORATORY USTENSILS

The accomplishment of the laboratory workings in good condition is possible only after a throughgoing study of the theoretical problems treated on the course or indicated in each work paper.

For carrying out the laboratory workings are necessary besides a series of substances, different kinds of laboratory utensils, the utensils are made of resistant materials both chemical agent action and to temperature variations.

The most used materials for laboratory vessels and apparatuses is glass. The glass has some advantages over other materials: it allows the visual observation of the reaction and it is resistant to the most usual reagents. Due to the demand of chemical stability both the acids and bases, different kind of glasses of different compositions depending on each utility are manufactured.

The glass is obtained : silica, borax, alumina, calin, feldspar, sodium carbonate, lithium carbonate, potassium carbonate, sodium sulphate, dolomite, magnesite, zinc oxide, etc; all these substances are molten at high temperature together with other auxiliary substances, and then, after the solidification yields complex mixture of silicates. The quality of the glass shows large variation with composition.

Table 1 contains the compositions for some well-known laboratory glasses.

We can notice that the glass composition includes considerable quantities of aluminium oxide which have a stabilisation role.

The most resistant from the chemical point of view (especially to acids) , and also resistant to thermal variations are borosilicate glasses (Pyrom, Turdterm, Jena, Pyrex, Duran). Extremely resistant to acids and to thermal shocks is the quartz glass.

Composition:

in per cents	Pyrom	Turdatern	Medias	Jena	Pyre	Turingia	Duran ***	
SiO ₂	80	75.5	68	76	81	66	80	67.5
B ₂ O ₃	12.9	7.5	2	16	12	-	12	2
Al ₂ O ₃	2	5	5	1.7	2	7.5	2.3	2.5
CaO	-	1.5	4.9	0.2	0.5	8	0.3	7
MgO	-	-	3.1	-	-	4.5	-	-
ZnO	-	-	-	-	-	-	-	77.1
Na ₂ O	4	6.5	17	5.4	4.5	1 4.4	14	
K ₂ O	1.4	-	-	0.6	-	3	-	-
Fe ₂ O ₃	0.05	0.05	0.05	-	-	-	-	-
BaO	-	4.2	-	-	-	-	-	-

where *** means " for thermometers" .

The apparatuses use in laboratory are made of different kinds of glasses , depending on uses. The simplest and more used are:

1. Balance

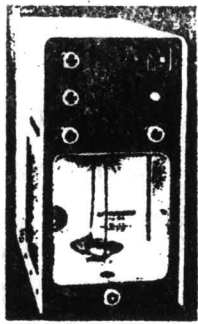
(a) Ainworth, accurate single-pan balance, digital in line readout, substitution metod of weighing, accuracy 0.0001 gram.

(b) Sartorius, accurate single-pan balance, digital in line readout, substitution metod of weighing, accuracy to 0.0001 gram.

(c) Double-pan, analytical balance manual weight and rider adjustment, readout to 0,0001 gram.

2. Balance weights

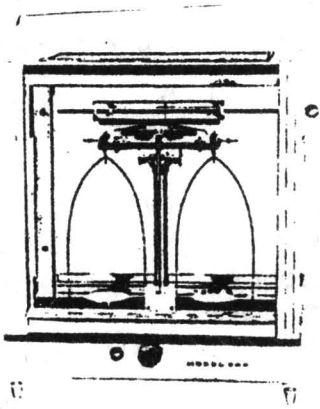
(a) Analytical balance weights with forceps from 1mg to 100 grams. Handle weights only with forceps.



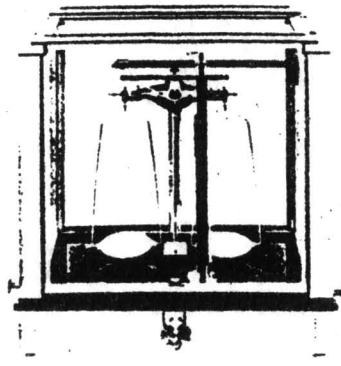
(a)



(b)



(e)



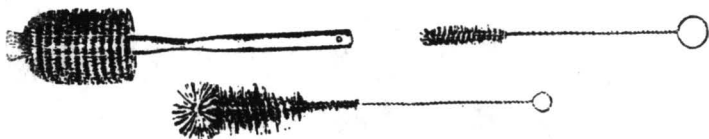
(f)



(a)



(b)



(f) Chemical-liquid storage bottles available for general laboratory acids, bases and reagents.

5. Brushes

Brushes for cleaning laboratory equipment in a varied selection of sizes and designs.

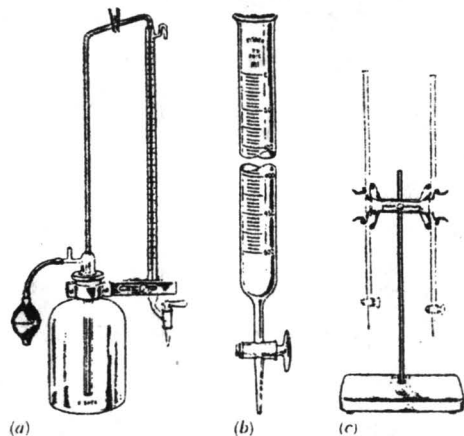
6. Burettes

(a) Automatic-filling burette. Pumping the rubber bulb fills it to a precise 0,0-cm³ graduation.

Overfill automatically returns to storage.

Used where many titrations with the same solution are to be made.

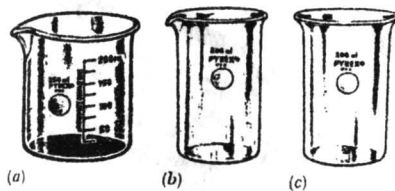
(b) Single-dispensing burette with graduated etched scale, standard taper,



Handle with care, because they are precision weights.

3. Beaker

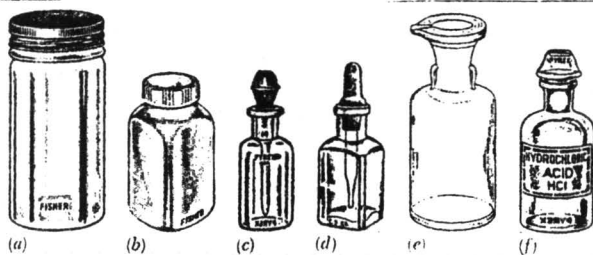
(a-c) Beakers available in sizes from 1 to 4000 cm³ in a variety of shapes, rims, lips, and designs graduated and plane. Used to heat liquids, solids, solutions and for general laboratory use as a versatile container.

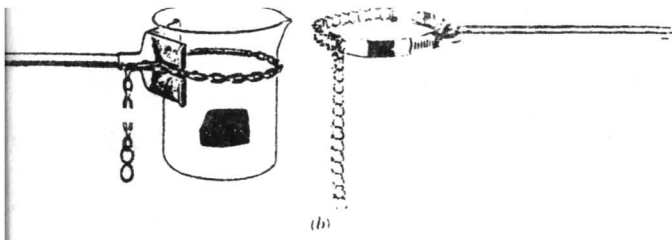


4 Bottles

(a,b) Liquid and solid storage for bottles for chemicals and samples; varied design, opening and closures.

(c,e) Dropping bottle to dispense small volumes of liquids.





(b)

9 Clamps

(a) Baker clamps; chain adjustable size; spring tension.

(b) screw-type clamps with adjustable tension.



(a)

10 Clamps

(c) Utility clamp with long handle.

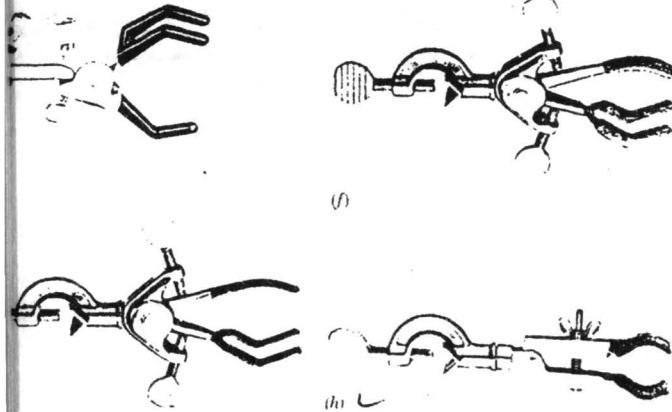
(d) Trigrip, double jaw, vinyl-covered clamps with long handle to hold equipment.

(e) Double-jaw clamp with three adjustable vinyl-covered prongs.

(f) Double-jaw, three prong, asbestos-covered clamps.

(g) Double-jaw, three-prong, vinyl-covered clamps.

(h) Fixed-position clamps with vinyl-covered jaws.

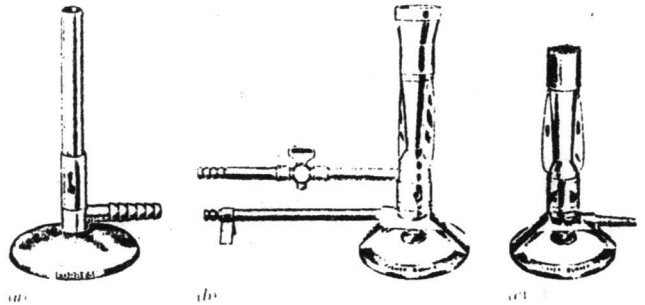


and stopcock. Available models with volumes from 50 to 500cm³.

(c) Titrating assembly and stand with white base for easy color-change observations.

7 Burners

(a) Bunsen burner, artificial gas, sleeve air-inlet regulator.



(a)

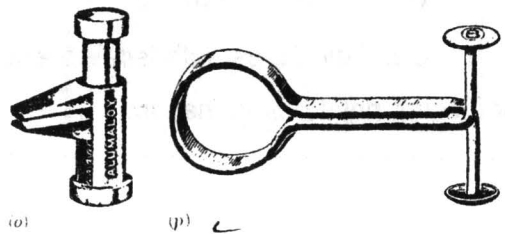
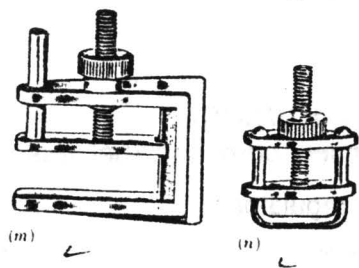
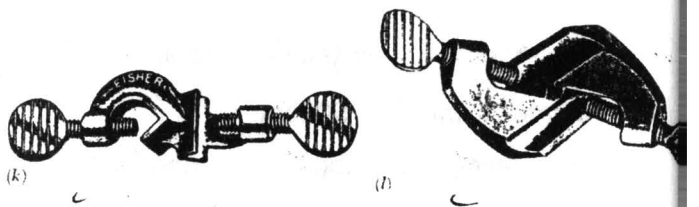
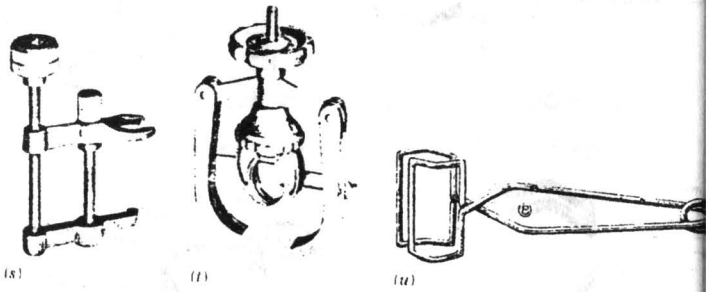
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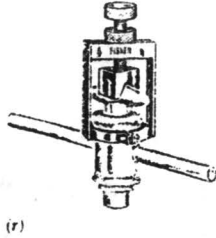
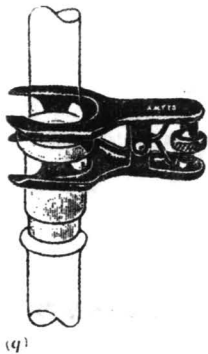
(c)

8. Capillary Tubes

Capillary tubes with sealed end for melting point determination.







(q) Clamps for holding spherical-ground standard-taper glass apparatus together.
 (r) Stopcock clamp prevents loss of plug due to pressure or vibration; fixes plug firmly into desired position.

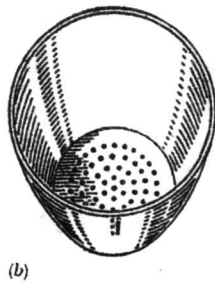


(s,t) Stopcock-removing clamp for frozen stopcocks and stoppers.

(u) Test-tube holder clamps, opruig-activated.

(v) Tulnig-clamp, for positive attachment of pressure or vacuum tubing.

11. Crucible



(a) porcelain crucibles, used for ignition of samples in analysis.

(b) Gooch crucible with perforates bottom. Filter bed is usually formed by filtering asbestos fiber and water slurry.

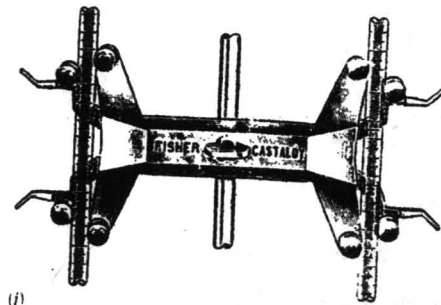
(i) Fixed-position utility clamp with asbestos-covered jaws.

(j) Burette clamp, double with screw to anchor to support rod.

(k,l) Clamp holder. Anchors securely rods t rods, support assemblies, and clamps to support assemblies, available in parallel (k), or right-angle direction.

(m,n) Screw-pinch clamps with adjustable closure for flexible tubing.

(o,p) Spring-type clamps with positive closure.





(a)

(b)

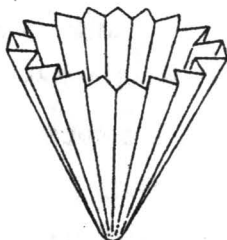


(c)

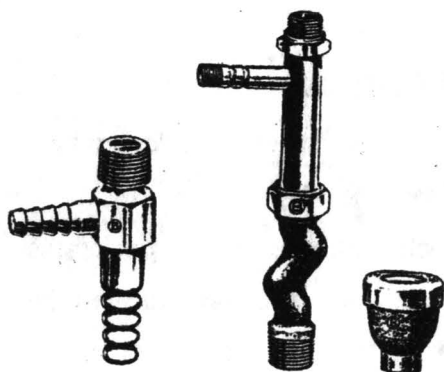
(d)



(a)



(b)



12. Cylinders

Graduated cylinders of various sizes, shapes, openings, and closures to meet special needs, capacities from 5 to 4000 cm³.

13. Desiccators

Desiccator with ground-glass top to provide positive seal with bottom, for drying and storing samples for analysis.

14. Dishes

(a) Evaporating porcelain dishes, with heavy rim and pouring spout. Used to evaporate liquids.

(b) Nickel evaporating dishes.

(c) Crystalizing dishes to hold and contain liquids which are expected to crystallize.

(d) Culture dishes for bacteriological work.

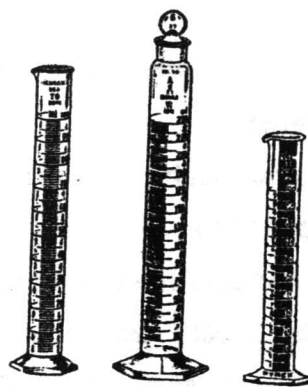
(d) Culture dishes for bacteriological work.

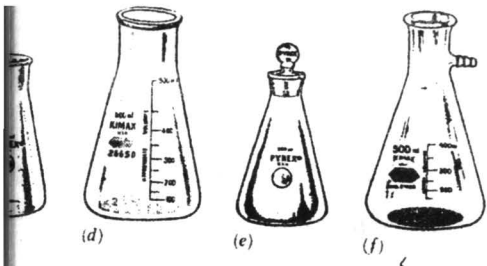
15. Filter papers

(a) Filter paper in assorted sizes and porosities.

(b) Fluted filter-paper in assorted sizes and porosities.

16. Filter pump and accessories.





(c-e) Erlenmeyer flask in various sizes, 10 to 6000 ml plain or graduated open or fitted with ground-glass stopper.

(f) Heavy-wall suction flask used for vacuum filtration.

(g) Claisen distilling flask with side neck.

(h) Round-bottom flask with short or long neck for general reactions.

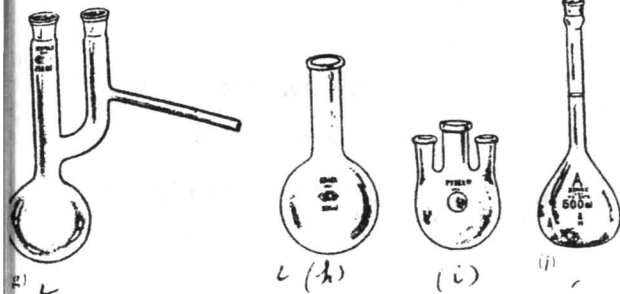
(i) Multineck flasks with one, two, three, or four necks, sizes from 500 to 12000 cm³.

(j) Volumetric, standardized to contain stated volumes of liquid, available in various designs, capacities from 1 to 2000cm³; also made of actinic glass to prevent light decomposition of unstable solutions.

(k) Kjeldahl flask for analytical procedures.

Available in different capacities.

(l) Florence flask with cork-insulated neck for positive hold. Used to make wash bottles.

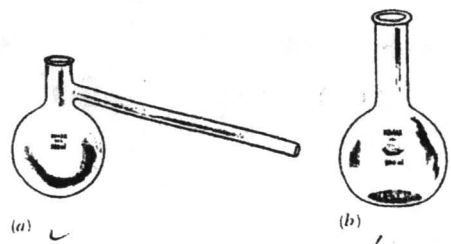
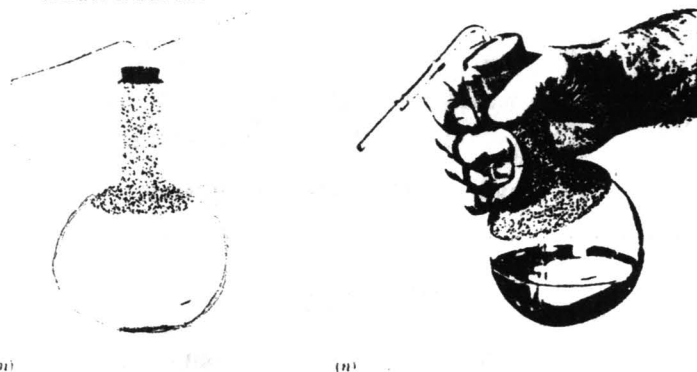


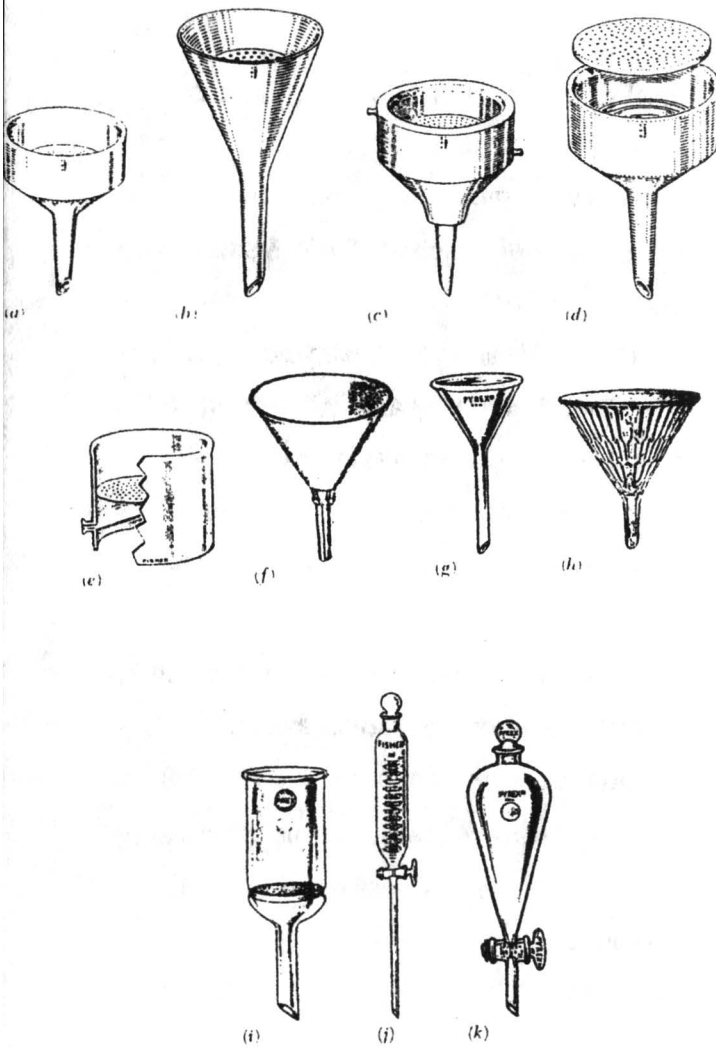
A water pump for suction filtrations, general vacuum manipulations, and pipette cleacleaning. Accessories are used to couple to water lines and prevent splashing to existing water.

17. Flasks

(a) One-neck disilling flask.

(b) Flat-bottom flask.





19. Funnels

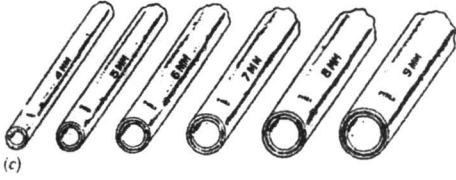
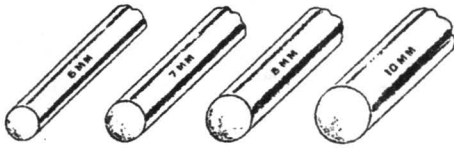
- (a,b) Buchner suction funnel.
- (c) Buchnerjackeded funnel for cooling or heating varied sizes.
- (d) Bucher plain funnel, available in sizes 14.5 to 308mm (removable plate).
- (e) Buchner table-top model funnel for large volumes,from 50 to 308mm diameter.
- (f),g Glass funnel,varied size and stem length.Use for general filtration.
- (h) Glass funnel with heavy ribbed construction; raised riles on inner surface facilitate filtrrion.
- (i) Fritted disk glass funnel used in vacuum filtration ewith suction flask in operations where for filter paper of a Buchner funnel would be atacked; with stands temperatures to 500^o, available in four prorsities.
- (j,k) Separatory funnel graduated with ground-glass stopper.Available in different sizes, capacities from 30 to 6000cm³.

(m) Florence-type wash bottle, hand-squeeze, pressure-bulb-operated.

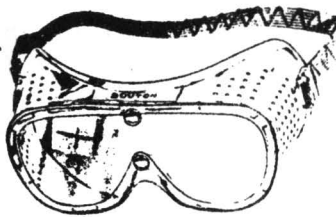
18. Forceps

Flexible forceps, stainless-steel or chrome-plated-steels.Use to pic up small objects and handle small serews and pins for laboratory equipment.





(c)

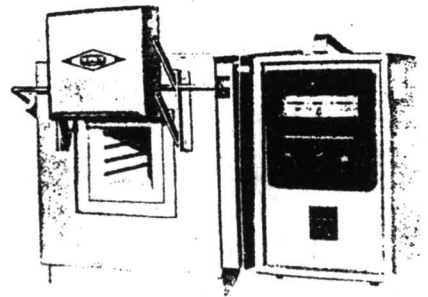


20. Furnances

(a) Muffle furnance, temperature-indicating dial, adjustable rheostat heat control, automatic door closing.



(a)



(b)

(b) Muffle furnace, temperature indicating dial, adjustable temperature, automatic door closing.

21. Glass Rods.

Pyrex or soft glass rod. Varied diameters available from 2 to 38 mm diameter.

22. Glass Tubing

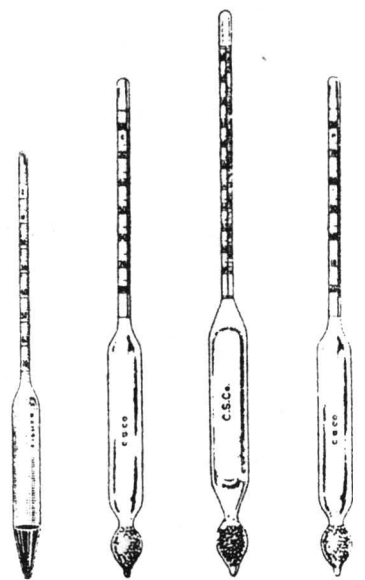
(a) Capillary wall thickness and diameter of hole varies. Bore from 1/4 to 3 mm diameter.

23. Gloves

Rubber gloves to protect hands against corrosive chemicals.

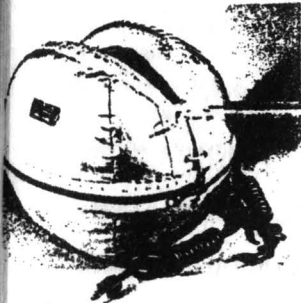
24. Goggles

Safety goggles, glass or plastic, for protection against flying objects and corrosive fumes and liquids, dependent upon construction. Select the protective goggle according to hazard potentially possible.

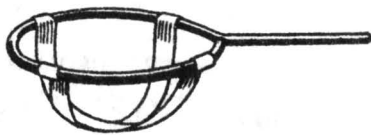




(b)



(d)



(f)

Heating mantles provide safe, intimate heat transfer, to heat most containers and are available in a variety of shapes and sizes. Heat is adjustable with variable transformer.

(a) Bottom, varied sizes and designs. Transformer varies voltage and temperature.

(b) Funnel - type heating mantle.

(c-f) Asbestos heating mantles with supports; thermocouple leads for temperature indicating. Usually safe for heating flammable liquids.

27. Hydrogen - ion test paper



28. Hydrometers

Glass hydrometers for specific - gravity determinations, weighted - bottom graduated direct - reading tube.



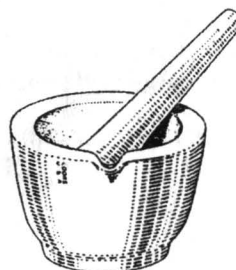
25. Graduates

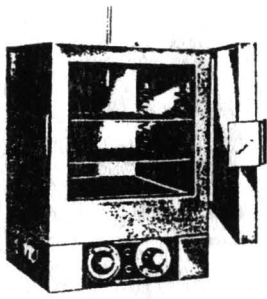
Glass graduates, pharmaceutical, graduated.

26. Heating mantles

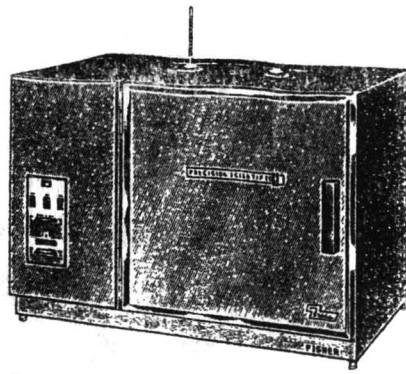
29. Mortar and Pestle

Porcelain or agate mortar and pestle used to grind solids to fine powder, available in sizes from very small to extremely large.





(a)



(b)

temperature controlled to maintain about a 2°C range.

(b) Constant - temperature oven, mechanical heat flow by fan, maintains temperature

$\pm 0,1^{\circ}\text{C}$ with temperature regulator.

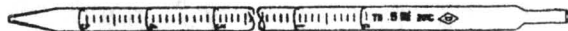


31. pH - Test Paper

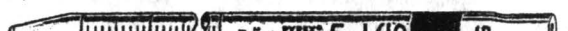
Immersion of strip of test paper yields color change in paper. Comparison with standard color chart gives the pH.



(a)



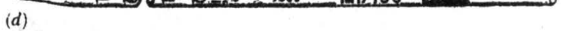
(b)



(c)



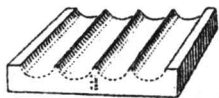
(d)



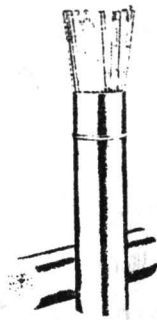
(e)

32. Pipetts

(a-d) Measuring pipetts, available from 0,2 to 50 ml permit to transfer of a measured amount of liquid. The deviation on the scale vary with the capacity of the pipette.



(a)



(b)



(c)

33. Pipette accesories

(a) Porcelain pipette rest, to rest pipettes upon securely, to prevent contamination, rolling, and breaking.

(b) Cylindrical cans color - coted top and bottom for storage of pipettes after cleaning and use.

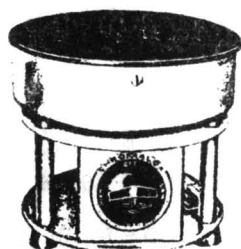
(c) Pipette filler, used to transfer sterile, corrosive, and toxic liquids

30. Oven

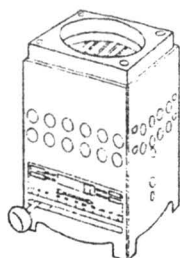
(a) Electrically heated oven for drying samples, baking, sterilizing. Automatic



(d)

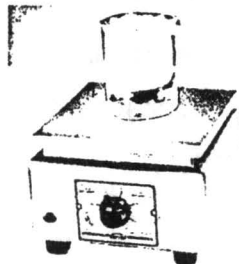


(a)



(b)

(d) Pipette filler fits over end of pipette to permit safe and easy filling of pipette containing toxic or corrosive liquids. Squeeze first, then immerse in liquid. Release pressure gradually as needed.



(c)

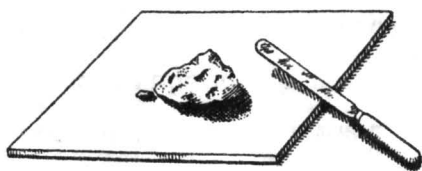


(d)

34. Plate, Hot

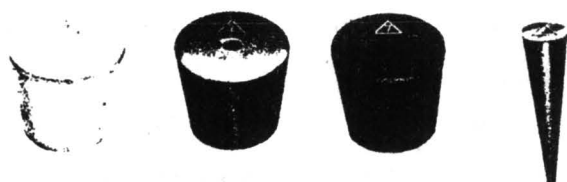
(a) An adjustable - temperature heavy - duty hot plate heating nonflammable materials.

(b) Hot plate with magnetic mixer, adjustable heat and of mixing. Multiple hot plate, magnetic mixer.



35. Plate, Porous

Wet samples can be partially dried by working the sample on the porous plate with a spatula. The plate absorbs the excess water.



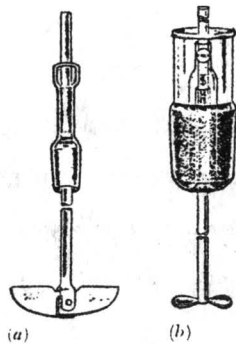
36. Rubber Stoppers

Various sizes, one, or two - hole.

37. Seals

(a) Glass seal, close fitting shoft to housing, lubricated with glycerin or silicone, provides isolation of system from atmosphere and contains very moderate pressure and vaccum conditions, while rotatting.

safely. Easily controlled by squeezing. Delivers quickly, precisely, and safely.



(b) Mercury - type seal provides a seal between the fixed standard - taper glass joint and the rotating shaft. The rotating tube is affixed to the shaft with flexible tubing and the mercury fills the well to isolate the system from the atmosphere and prevent the loss of volatiles.



(a)



(b)



(c)

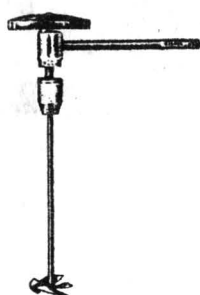


(d)

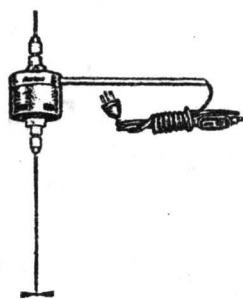
38. Spatulas

(a) Scoop - type spatulas used to transfer larger quantities of solids, especially from narrow - neck bottles or containers.

(b-d) Spatulas available in a variety of shapes, sizes, and designs to be used for special manipulations from micro size to very large for production poles.



(a)

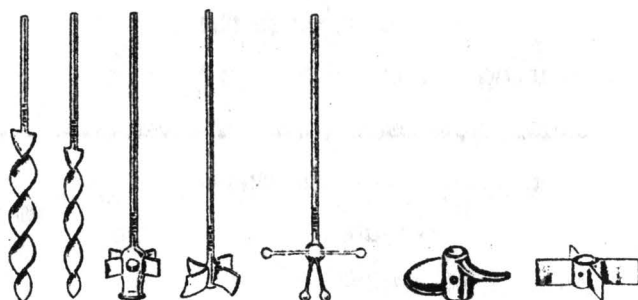


(b)

39. Stirrer

(a) Air available - speed stirrer driven by compressed air. Safe for explosive atmospheres.

(b) Light - duty electric stirrer with fixed speed, shaft height adjustable through chuck.



(a)

(b)

40. Stirrer Accessories

(a) Glass Stirrers in a variety of designs to mix thin to viscous solutions, to fit into narrow openings of containers.

(b) Propeller shaft stainless steel or neoneel, available in different shaft

diameters and propeller designs, from two-, three-, and four - blade or turbine type. Choose the type best suited for the procedure.

41. Stopcock

(a) three - way stopcock allows fluids to be channeled as desired in procedures or to cut off flow completely.

(b) Four - way oblique - bore stopcock with vent to the bottom of the plug.

(c) Four - way V - bore stopcock.

42. Supports

(a) Round, working - area - surface rest support base to support round bottom containers, available in a range of size.

(b) Right - angle rod clamps.

(c) Rectangular single - rod support base.

Fairly sturdy on level areas.

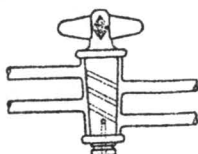
(d,e) Tripods offer sturdy support for apparatus, may have two vertical rod.

(f) Support plate clamped to support based or support frame with suitable clamp holder in used to hold flat - bottom containers.

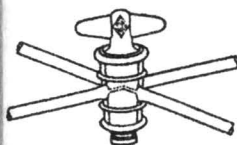
(g) Woadem adjustable - height support for funnels with deliver into separatory funnels in extraction procedures.



(a)



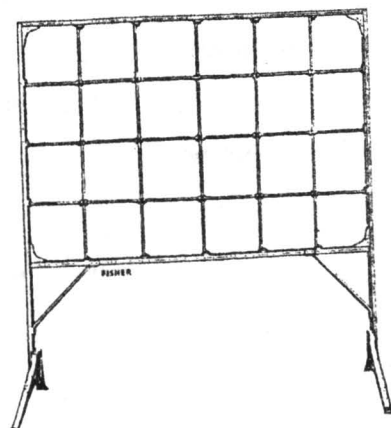
(b)



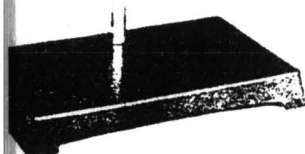
(c)



(e)



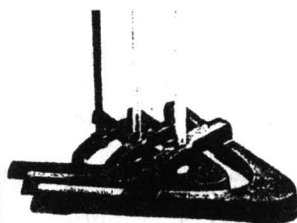
(f)



(g)

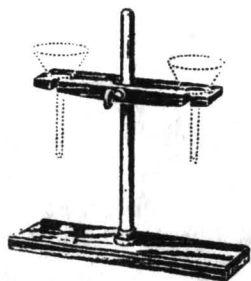


(h)

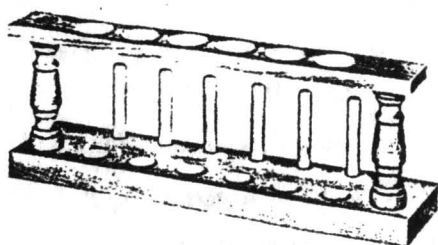


(j)





(k)



(l)

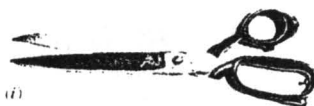
(h) Woadem - adjustable - height funnel support in sizes and capacities for laboratory manipulations.

(i) Test - tube holder, with drying pins to allow washed test tube to drain and dry.



43. Test tubes

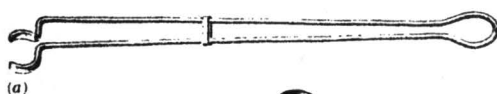
Test tubes are available in soft , Pyrex, Vycor and actinic glass with or without rims or covers in a variety of sizes and capacities.



(i)

44. Scissors to cut paper, asbestos, rubber, or any easily cut materials as needed.

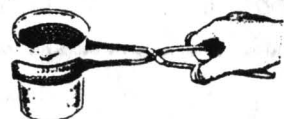
45. Tongs



(a)



(b)



(c)

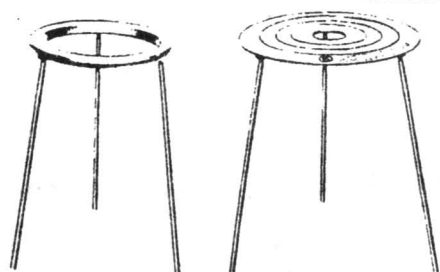
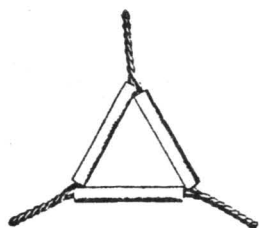
(a) Crucible tongs with flexible longlength.

Use to insert or remove hot crucibles from a muffle furnace and to avoid contact with crucibles in analytical procedures.

(b) Utility tongs to handle hot small apparatus and crucible.

(c) Braker - tongs to hold and carry smaller beakers in the laboratory.

46. Triangles



Triangles with or without porcelain cover support crucibles when heated over gas - burner flame. They normally rest upon a tripod or a support ring clamped to a support frame.

47. Tripods

Cast - iron tripods in various sizes and heights with concentric rings to reduce size of opening. Use to support containers being heated with gas - flame burner.

48. Tubes

Connecting tubes with serrations or constrictions to hold rubber or plastic tubing securely.

(a) Plastic "Y"

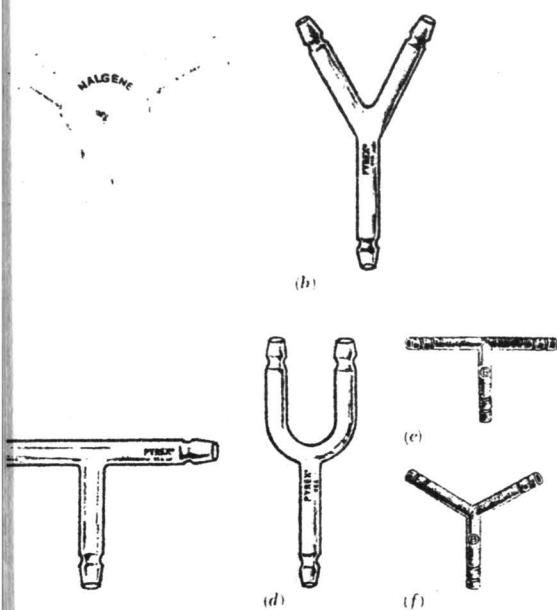
(b) Glass "Y"

(c) Glass "T"

(d) Glass "U"

(e) Brass "T"

(f) Brass "Y"

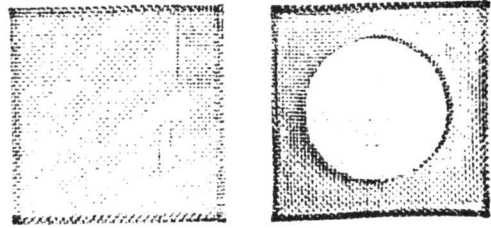


49. Water Bath

Steam - heated or electrically heated water bath used to heat solutions requiring temperatures not exceeding 100°C.



50. Wire Gauzes



Plain or asbestos centered wire gauzes used to protect glass - ware while being heated with gas - burner flame.

What does technician do ?

Basically, a chemical technician applies the principles of science and mathematics, in which he possesses a certain degree of proficiency, learned in either high school, technical school, trade school, junior college, or an on-the-job training program. He utilizes what he knows to operate specialized equipment and testing devices and to conduct experiments and analyses. He collects data and information under the direction of scientists to assist them in accomplishing their objectives.

Every technician must be prepared to perform some combination of the following activities:

1. Apply knowledge of science of mathematics extensively in rendering direct technical assistance to physical and/or biological scientists, engineers, or medical personnel engaged in scientific research and experimentation.

2. Design, develop or plan modification of new products, procedures, techniques, services, processes, or applications under the supervision of professional scientific, engineering, or medical personnel in applied research, design, and development.

3. Plan, supervise, or assist in installation, and inspect complex scientific apparatus, equipment, and control systems.

4. Advise regarding the operation, maintenance, and repair of complex apparatus and equipment with extensive control systems.

5. Plan production, operations, or services as a member of the management unit responsible for efficient use of manpower, materials, money, and equipment or apparatus in mass - production or routine technical or specialized personal service.

6. Advise, plan, and estimate costs as a field representative of a manufacturer or distributor of technical apparatus, equipment, services, and/or products.

7. Be responsible for the performance of test of mechanical, hydraulic, pneumatic, electrical, or electronic components or systems in the physical sciences; and/or determine, measure, and make specialized preparations. tests, or analyses of substances in the physical, agricultural, biological, medical, or health - related sciences; and prepare appropriate reports covering such tests.

8. Prepare or interpret engineering drawings and sketches, or write detailed scientific specifications or procedures for work related to physical and/or biological sciences.

9. Select, compile, and use technical information obtained from such references as engineering standards; handbooks; biological, agricultural, or medical and health - related procedural outlines; and technical digests or research findings.

10. Analyze and interpret information obtained from precision measuring and recording instruments and/or special procedure, determinations, and techniques, and make evaluations upon which technical decision can be based.

11. Analyze and diagnose technical problems that involve independent decisions. Judgment requires substantive experience in the occupational field in addition to knowledge of scientific principles and technical know-how.

12. Deal with a variety of technical problems involving many factors and variables which require an understanding of several technical fields. This versatility is a characteristic that relates to breadth of applied scientific and technical understanding, the antithesis of narrow specialization.

Some of the foregoing activities are broadly inclusive, while others describe specific function. They neither exclude nor include functions or activities that might be considered the special prerogatives of recognized professional or skilled worker groups.

The technician must comprehend the work of the professional scientists or engineers and the skilled workers in his technical field, since he usually works with either or both in performing his duties. Naturally, few, if any, technicians perform all 12 activities listed.

The chemical technician as a communicator

A most important requisite of a chemical technician is that he must be a competent communicator in all areas of communication. He must obtain information from a variety of sources. He must communicate with his coworkers and supervisors, make oral reports, prepare formal written reports, and keep accurate records of the results of his work, recording test data and services. As work on projects progresses, he must prepare and write reports for scientists who are supervising him or submit information compiled from the data he has acquired. He must learn to listen and speak and must have the competence to express himself in narrative or persuasive presentations. He

should possess the capability of representing ideas, concepts, and data graphically through drawings, diagraming, and sketching.

The ability or inability of a technician to communicate is immediately evident because everyone expects him to be able to communicate as an educated professional.

The recording of data

The competent technician does not see; he observes. He does not hear; he listens. This means that he does not take things for granted; he questions, checks, and verifies what he has experienced through his senses. The mere fact that an instrument gauge reads a certain value does not mean that the competent technician must accept it. He checks to see if the instrument is calibrated properly and if the readings indicated on the instrument are the identical readings that would be read on another similar gauge that has been calibrated or standardized. No technician should take it for granted that an instrument is correct.

Similarly, a competent technician does not merely take a reading, record it, and forget it. He takes several readings independently of each other separately and objectively, attempting to determine the most accurate reading each time.

The laboratory notebook

The laboratory notebook is the one place where the information the technician acquires is recorded. That means that all data are recorded directly into the notebook as they are obtained, not tacked down on stray sheets of paper.

The notebook is the diary and record of the technician. Because lawsuits may occur in which the notebook may play a key role in the decision of the court, it is imperative that the notebook record be above question. Many cases have been won or lost because of the credibility of the data contained in the notebook. Therefore it is of paramount importance that the following rules be observed (Of course, they are

provided solely as guidelines. Each company uses its own procedure and sets forth its own format. If no formal procedure exists, however, these roles could be used.)

1. The laboratory notebook should be a numbered, bound book, preferably with automatic carbon or other duplication method. The pages should be consecutively numbered, and no original pages should ever be ripped out. The data should be recorded in ink, in detail, and all observations and ideas should be included. By utilizing a duplicate-copy notebook, the technician may keep at his disposal for ready reference a copy of what he has recorded, while the original bound book can be placed in the proper place for security and ready reference by all other members of the staff. The cover of the record book should indicate the dates of the first and last entries made in that book.

2. All the information that is acquired should be entered, regardless of how trivial it may appear at the time.

3. Each page should be dated and signed by the technician accompanied by the signature of his supervisor.

4. The objective of the procedure should be stated on the top of the first page of the sequence of pages used.

5. The diagram of the apparatus or equipment to be used should be sketched, followed by a short summation of the procedure to be followed.

6. All raw data should be recorded neatly and directly in the notebook. Mistakes may be crossed out but never erased. All data should be entered in the notebook immediately. Delay leads to forgotten entries. All data regarding the starting materials should be recorded without delay and all changes in any data obtained from the samples should be entered.

7. Entries should always be specific. The technician should never generalize, so that no question can arise in the future. One of the objectives of a record book is to be able to duplicate what has been done, and the omission of relevant data can cause needless delays and costly repetitive work.

8. Information obtained from automatic recording devices, such as a chart, can be filed in an appropriate secure location, but all pertinent information should be noted from the charts and recorded in the notebook, and the appropriate reference should be indexed on the charts or recording paper so that the information can be retrieved easily when it is needed.

9. Calculation of the raw data may be carried out on other paper or on the calculator, and the results recorded. All calculation should be checked by either the person who performs the work or a competent coworker.

Planning an procedure

Planning

Each assignment requires some preparation. This is usually referred to as a plan or design. The plan may be either mental or physical, or mental and physical. Segments of a plan might be prearranged for us, e.g., American Society for Testing and Materials (ASTM) or other standard laboratory procedures. During the course of our career, however, it is inevitable that we will be required to plan our own assignments. If we accept the postulate "everything done requires a plan or design", let us explore what application it might have in planning an assignment. Question the assignment:

- Where is it done?
- When is it to be done?
- Why is it being done?
- Has it been done before?
- How is it done?
- How precise must the data be?

Answers to some of these questions are self-evident when we are familiar with our general assignments. The answers, of course, are the nucleus of a plan.

We have progressed with our plan and must now determine:

- Is it best to arrange our sequences chronologically or in some other logical fashion?
- Do we provide accessory equipment before we need it, or is it equally effective to stock as we proceed?
- Is a progress report necessary during the course of the assignment?
- At the conclusion of the project, how shall we report or record our data?

These are some of the mental processes required for planning our day -to-day assignments.

From these processes we conclude that planning is essential for any assignment. It is the foundation for providing a quality product of usable quantity. For example, planning to have all necessary equipment available at a test site when it is needed rather than making several additional trips to a stock room might reduce personal fatigue will increase our alertness to quality.

Analytical data: Quantity and quality

Quality

The quality of analytical data should be considered as the basic definition of quality rather than quality control. Quality control is an industrial arrangement completely independent of industrial quality. For example, if we use improperly zeroed balances when weighing, statistically we might produce an acceptable result. However, the general quality of our technique certainly is unacceptable. Much of quality might therefore be considered as the proper use of laboratory equipment and techniques. On the other hand quality control is used to permit a tendency or characteristics to present excel instable form. Therefore, the quality of technique should and must be constant, while statistics of quality control are inherently variable.

Mistakes vs. errors

Mistakes can be consider as mistabulatoins or miscalculation of figures. The guarante against mistake is to check each item and computation. Time spent inchecking is time well spent because it ensures accuracy, making unnecessary to redo a problem for sample. On the other hand, errors are usually random an can be determined or indetermined. It is therefore easier to eliminate mistakes then to detect and minimize random error .

We should assume that everything done in the analytical laboratories is important to the research effort. A paradox which some times evolves is to be given a sample with the comment " this very important " instead of " these samples data are relatively unimportant ". This type of approach leads us to believe that the importance of a project or a sample should be considered only when specifically stated. The reverse is actually the truth. That is, we assume everything to be important unless otherwise stated. When techniques of the highest quality are realized, the precision of our data is certain to be of the highest order. We therefore strive for greater uniformity of product through greater consciousness in the proper handling of equipment and proper techniques in the laboratory.

How does quality affect quantity?

As stated above, time used to check data is time well spent. It eliminates the need for redoing a sample or project, and quantity of data therefore follows logically. For, in fact, our goals are effective quantity rather than total volume. Quality is always more important and therefore is the barometer of effective quantity.

Planning: quantity, quality and efficiency.

The term production does imply quantity. However, production is not synonymous with effective quantity. A product is a salable commodity only when it is in its finished or usable form. Should a product need adjustments or alternations before it is marketed, the altered product rather than the raw product is the usable commodity. Such is a case with analytical data. The goal of our day-to-day operations is to provide finished or usable analytical data. Should adjustments or alterations of data be necessary, just as in the case of the adjusted salable product, the data in their altered form are in fact our product. The sum of usable products or data is the only measure of effective quantity.

Large quantities of low-quality data are valueless to the research effort. We must find the peak or optimum point of quantity vs. quality. This peak point is referred to as efficiency. Efficiency is attained when each of three concepts are usable quantity and high quality. The third factor we must consider is service. Service, by definition, is any results of useful labor which does not produce a tangible commodity. In the true sense of

analytical data, however, the definition of service might be applied to quantity and quality. For example, from the definition of service, the words " useful labor " imply quality. Also from definition, the words " produce a tangible commodity " imply quantity. Therefore, efficiency might be synonymous with service; when efficiency is guaranteed, good service is a natural occurrence.

Procedure (See fig. A-2)

The chemical technician knows the equipment and materials with which he works. He never treats them with contempt, even though he may be very familiar with them and have handled them many times. He treats them with the respect they deserve because he is aware of the hazards of laboratory work .

He minimize accidents by recognizing their causes and because he is alert at all times, following the rules for good laboratory practice. Accidents are usually the fault of the victim or his associates. Basically there are three sources of accidents: fire, cuts from broken glass equipment, and contact with corrosive chemicals on clothing or person.

Evey technician should know basic first - aid emergency equipment for monor injuries, and also the location of and how to handle emergency equipment such as safety showers and fire extinguishers. Common sense is the best insurance against injury.

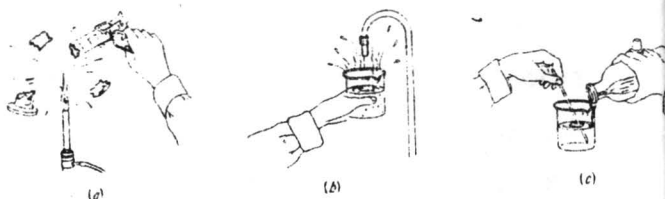
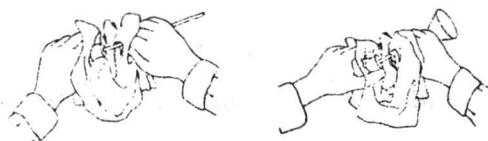


Figura A - 2



Self - protection - caution

The first rule of self - protection is to be alert at all times.

Protect for your eyes

Safety glasses should be worn at all times in the chemical laboratory. You have only one pair of eyes; protect them.

Protect your body

Wear laboratory coats or aprons and safety shoes. Keep ties or scarves secured with fasteners. Do not wear medallions or hanging objects. Tie long hair up out of the way. Avoid flammable clothing.

Fire

Handle fire with care. All burners should be placed safely away from all flammable materials, and the technician should not expose his hair, clothing, or flammable objects to them.

Corrosive liquids

Handle chemicals carefully so that none comes in contact with the skin. When pouring corrosive liquids, avoid spillage and avoid contact with the liquid that runs down the neck of the bottle.

Volatile liquids and gases

Never inhale volatile liquids and gases. When odors are to be observed, sniff a small portion by holding the container away from your nose and fanning a small amount toward you with your hand.

Chemicals

Always recheck the label of the chemical you are using. Use of the wrong chemical can cause an explosion or a ruined determination.

Disposal of wastes

When you have completed procedures and reactions, you will have residues, slurries (watery mixtures of insoluble matter, precipitates, pigments, etc.), and waste solutions which must be disposed of.

Caution:

Do not pour concentrated acids, bases or slurries into your sink without considering what you are doing. Think first !

Acid or basic solution wastes: Pour into your waste - disposal sink while running water continuously from the faucet to dilute the acid or base. When you have finished pouring the waste into the sink, flush with large volumes of water to dilute any corrosive effect.

Organic wastes, residues: These are insoluble in water. Discard the bulk of the residues in a waste - disposal safety container. Discard all volatile solvents into a waste-solvent receptacle which will contain the vapors and will not constitute a fire hazard. Volatile solvents are those solvents which vaporize which result can be toxic, nauseating, irritating, or flammable, or can have unpleasant side effects.

Caution:

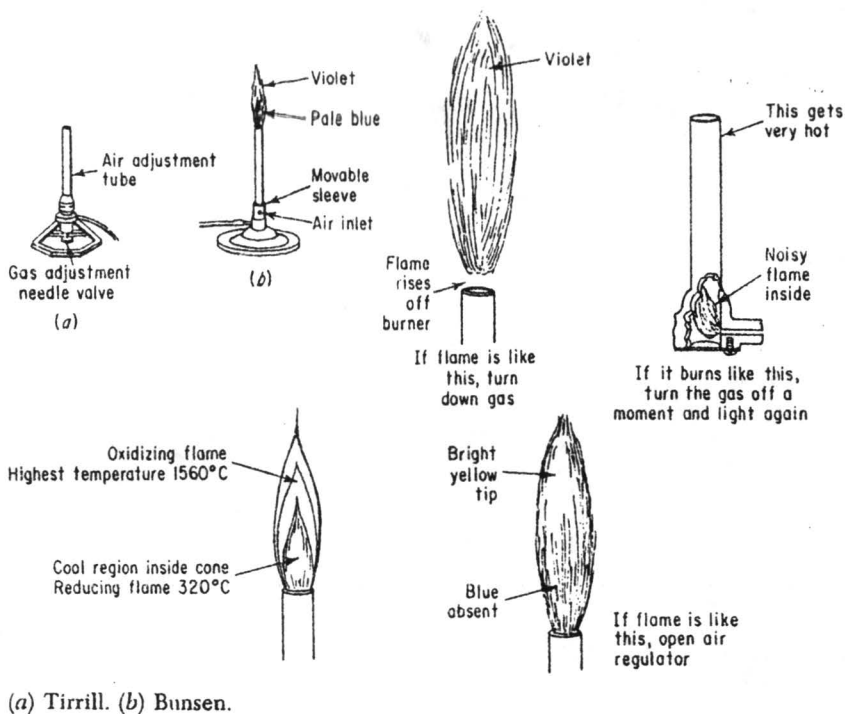
Avoid indiscriminate disposal of wastes. Always consider the possibility of spontaneous reactions, explosions, and fire. Waste receptacles are usually designated as to what should be put into them.

SECTION II

Laboratory techniques and procedures

1. Open the gas cock on the gas inlet pipe wide.
2. Open the thumbscrew gas adjustment on the burner wide.
3. Close the air holes with a movable sleeve.
4. Light the burner with the match or striker .
5. Regulate the thumbscrew and the movable sleeve to produce nonluminous flame having a sharp-pointed inner blue cone.

FIGURE B-1
Gas burners.



Laboratory glass equipment

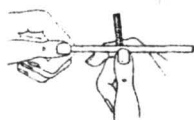
Most laboratory equipment is made of glass. The two types commonly found are either soft glass or Pyrex.

Soft glass : melting point 600 to 800°C; used in droppers glass rods , tubing for wash bottles , bottles; workable with a bunsen or tirrill burner; subject to attack by alkaly does not withstand termal shocks.

Pyrex glass: melting point 750 to 1100°C; used for beakers , flasks common glass equipment; requires on oxygen torch to be worked; withstands alkaly ; rezists temal socks.

Cutting glass tubing (figs. B-2 and B-3)

1. Scratch the tube or rode at the desired ponit with the three cornered file . Use only one or two strokes.
2. Raw the tubing in a protective cloth to avoid cutting your hands. Place thumbs together opposite scratch.
3. Using little force , pull back on the tube and push thumbs outward quickly to break the glass.



B-2



B-3 Proper method of holding glass tubing.

(figs. B-2 and B-3)



B-4 Fire polishing (note rotation of the work).



B-5 (a) After cut. (b) After fire polishing. (c) The end has been heated too long.

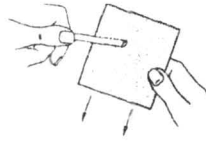
Fire polishing (Figs B-4 and B-5)

1. Round the sharp edges to prevent cut.
2. Insert the end into the hot nonluminous portion of burner flame and rotate smoothly and evenly.

Caution

Wear gloves or keep hands well back from the end being heated . It gets hot!

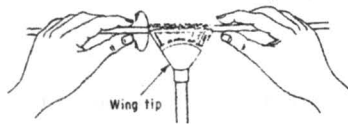
Fig B-4 B-5



B-5

Dulling sharp glass edges (Fig B-6)

1. Hold the glass article in the left hand and clean , new wire gauze in the right hand (nonasbestos).
2. Stroke the broken and with wire gauze softly while rotating the broken glass object.



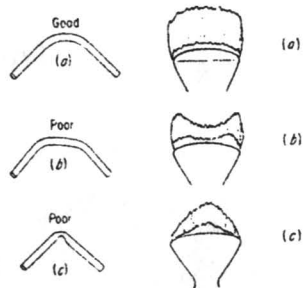
B-7 Rotation of the work.

Glass bending (Figs B-7 and B-8)

1. Use a flame spreader on the burner adjusted to give a nonluminous flame and well defined blue cone
2. Hold the tube lengthwise in the flame and rotate with the back enforce motion evenly until the glass becomes soft .
3. After the glass is soft (it bends under its own weight), remove it from the flame.
4. Band the glass to the desired shape , holding to position until it hardens.

Caution

Wear gloves or keep hands well back from the end of tube being heated. It gets hot!



B-8 Effects of flame adjustment on bends.



B-9 Flaring a tube end.

Annealing glass

1. Reduce internal thermal stresses by heating the worked glass in a smoky flame of the burner.
2. Permit the glass to cool slowly.

Flaring ends of glass tubing (Fig B-9)

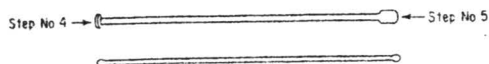
1. Insert the end of the tubing in the hot flame and rotate smoothly.
2. when the glass has softened, remove it from the flame.
3. Insert the heated end of a file in the tube at an inclined angle.
4. Rotate the tube against the file and to get the desired flare.

Shaping glass rods and tubes (Fig. B-10)

1. Heat the rod briefly in a nonluminous hot burner flame until it has softened.
2. Remove from the flame.
3. Heat a clean piece of metal.
4. Press the hot end of the glass perpendicularly against the hot metal.
5. To make a paddle and, press the heated rod between two heated clean pieces of metal

Fig B-10

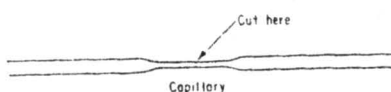
FIGURE B-10
Shaping glass rods.



Making capillary tubes

1. Use the burner without the wing tip.
 2. Heat the tubing or rod as under Glass Banding .
 3. When the glass softens , remove it from the fame. Allow to cool slightly.
 4. Pull the ends apart while rotating the cooling glass to get the desired capillary size.
- size.
5. Scratch with file then break.

Fig 11 - 12



B-11 Constructing the tip of a dropping pipette (making capillary tubes).



B-12 Filling the ampul with a pipette.

Sealing ampuls (Fig B-12 and B-13)

PRINCIPLE

Many organic compounds are decomposed on contact with air or moisture. They most be sealed against air to prevent decomposition.

MATERIALS

Ampuls , filling pipette , gas burner.

PROCEDURE

1. Fill the ampul or sealable glass bottle with a pipette (Fig B12, previous page), or with a funnel. (Do not fill more then two thirds full).

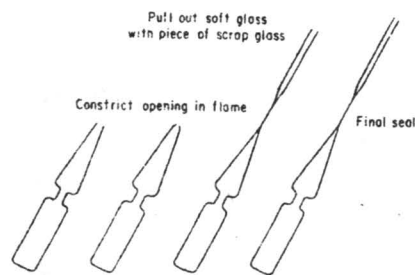
2. Gently insert the tip of the ampul into a bunsen burner to constrict the opening.
3. Heat the tip of a piece of glass rode to redness , and then tough it to the constricted tip of the ampul , which is soft from the burner.
4. Remove the joined glass glass from the flame ,allow to cool , and pull apart to get the final seal.

Caution

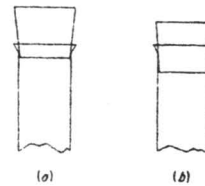
Practice with an empty ampul until you perfect your technique (refer to the discussion of capillary tubes under Glass Blowing).

Important variables are the temperature of the molten tip of the ampul and the glass rod , and the time the heated joined - glass items are allowed to cool before they are pulled apart.

FIGURE B-13
FIGURE B-14



B-13 Sealing an ampul with a torch.



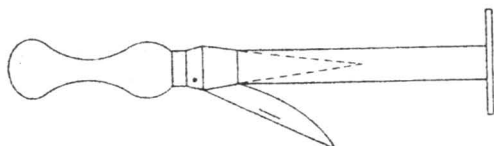
B-14 Rubber stoppers. (a) Correct size. (b) Too small.

Boring holes in cork and rubber stoppers (Figs B-14 and B-15)

1. Select a rubber or cork stopper of the correct size. (Fig B-14 above)
2. Select a borer sized slightly smaller than the hole to be bored.
3. Sharpen the borer with a sharpener, and wet borer with glycerin.
4. Hold the borer in the right hand and the stopper in the left hand supported by a cloth pad for palm protection.
5. Begin boring at the narrow end. Twist the borer and apply pressures.
6. Check the alignment after each twist.
7. Remove the borer when halfway through the stopper. Push out any plug in the borer.

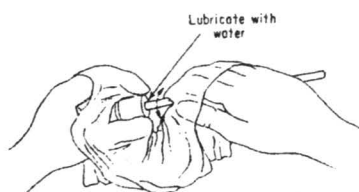
8. Begin boring the stopper from the other end; Check alignment.
9. Complete the boring operations.
10. Insert the glass tubing properly.

Figure B-15

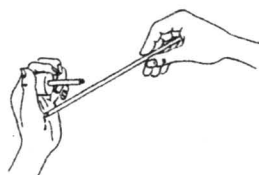


Inserting glass tubing in stoppers

1. Fire - polish the ends of the tubing.
2. Wet the tubing and stopper hole with water or glycerol.
3. Wrap hands in a towel for protection.
4. Grasp the tube near the point insertion.
5. Rotate the tube back and forth while gently pushing it into stopper.
6. Never attempt to push tubing through the stopper.



B-16 Proper way to insert glass tubing in a stopper.



B-17 Improper way to insert glass tubing in a stopper.

Removing glass tubing from stopper

1. Lubricate the tubing which is to be pulled through the stopper with water or glycerol.
2. Wrap the tubing with a towel.
3. Pull the tubing from the stopper with a gentle twisting motion.

4. If the tubing is stuck to the stopper, gently insert the end of the file between the tubing and the stopper and gently rotate, while lubricating with glycerin.

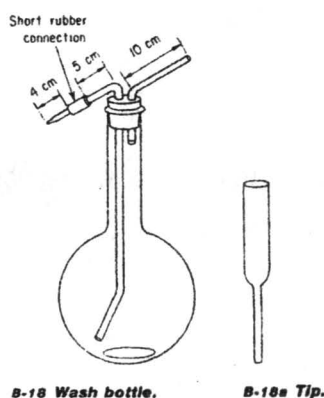
5. If procedure 4 fails, gently work the smallest - sized cork borer possible, which fits over the tubing, through the stopper.

Constructing a wash bottle

(Fig. B-18)

The wash bottle can be constructed as in fig. b 18. Dimensions need only be approximate. A 1 - liter flask is recommended.

Figure B-18



Making the tip

Roll the tube in a bunsen until it is soft. (Do not use a flame spreader.) Remove from the flame and slowly pull the ends apart until the softened region is as small as desired. After the glass has cooled, break it at the appropriate place and fire - polish the tip carefully so as not to close the opening.

To insert a glass tube in a stopper, first fire - polish both ends. After tube has cooled, wet both tube and stopper and twist the tube into the stopper with a screwlike motion.

1. Protect the hand with a towel.
2. Do not exert on a bend.
3. Refer to pages 14 and 18.

Plastic squeeze bottles are available.

Handling reagents and solutions

For successful analytical work, the availability of reagents and solutions of established purity is of prime importance. A freshly opened bottle of same reagents - grade chemical can be used with confidence in most application; whether the same confidence is justified when this bottle is half full depends entirely upon the care with which it was handled after being opened. The rules that are given here will be successful in preventing contamination of reagents only if there are conscientiously followed.

General rules

1. Select the best available grade of chemical for analytical work. If there is a choice pick the smallest bottle that will supply the desired quantity of substance.
2. Replace the top of every container immediately after removal of reagents; do not rely on having this done by someone else.
3. Stoppers should be held between the fingers and should never be set on the desk top.
4. Never return any excess reagents or solutions to a bottle; the minor saving represented by the return of an excess is indeed a false economy compared with the risk of contaminating the entire bottle.
5. Do not insert pipettes into a bottle containing a reagent chemical. Instead, shake the bottle vigorously with the cap in place to dislodge the contents; then pour out the desired quantity.
6. Keep the reagents shelf and the laboratory balances clean. Immediately clean up any spilled chemicals, even though others may be making the transfer of reagents in the same area

Removal of solid materials from glass- stoppered bottles

(Fig. B - 19)

1. If solid material is packed, gently tap the bottle against the desk top while gently rotating the bottle.
2. Tilt the bottle so that some of the material enters the hollow portion of the stopper.
3. Gently remove the stopper and transfer the material to weighing paper or container.
4. Repeat to get the required amount of solid.
5. Return to the bottle only that excess material which remain in the stopper. Discard any excess which has come in contact with anything else.
6. Replace the stopper in the bottle.

FIGURE B-19
Removal of a solid from a glass-stoppered bottle.



Figure B - 19

Alternative method

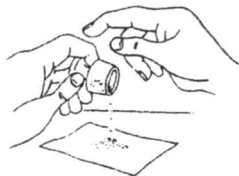
(Fig. B-20)

1. remove the glass stopper by gently twisting, tapping the stopper gently to loosen, if necessary.
2. Use an absolutely clean spatula and dig out material, always laying the stopper upside down on the desk top.

Figure B-20, B-21

FIGURE B-20

FIGURE B-21

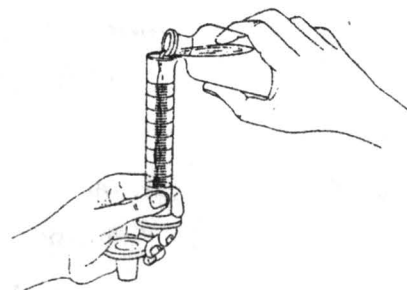


B-20 Alternative method.



B-21 Handling a glass stopper.

FIGURE B-22
Alternative method of
handling a glass stopper.



Pouring liquids from bottles

(Figs. B-21, B-22)

1. Loosen the stopper by gently twisting it.
2. Grasp the stopper either between the fingers of the hand as in fig. B-21 or between the palm and fingers as in fig. B-22.
3. Pour the liquid as needed.
4. Replace the stopper immediately in the bottle. Never lay it on the desk.

Figure B-22

Pouring liquids from beakers or other containers

(Fig. B-23)

1. Hold the glass stirring rod against the pouring lip of the beaker.
2. Tilt the container, allowing liquid to flow around the stirring rod which guides the liquid to the receiver.

3. When the desired amount of liquid has been poured, position the pouring beaker vertically allowing the last liquid to drain off the lip and down the rod.

Emergency hood

(Fig. B-24)

PRINCIPLE

When a hood is not available and noxious and corrosive fumes are emitted from a reaction flask or from a concentration - solution evaporation, assemble an emergency hood.

APPARATUS

Glass funnel, rubber tubing, aspirator, water pump.

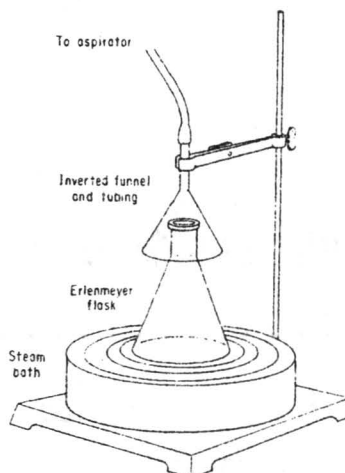
CAUTION

1. always use a hood when working with toxic or irritating chemicals.
2. The major source of accidents is spillage of corrosive chemicals on the clothing and skin. Immediately flood with excessive amounts of water and then consult the medical service.
3. Anything on any operation that must be forced should be examined very carefully. The application of excessive force. To make something work can lead to accidents and broken equipment. Always think! Always be on guard!

FIGURE B-23
FIGURE B-24



B-23 Use of stirring rod to guide liquid.



B-24 Emergency hood.

Thermometers

Temperature: Fahrenheit, Centigrade, Absolute (Kelvin), Rankine

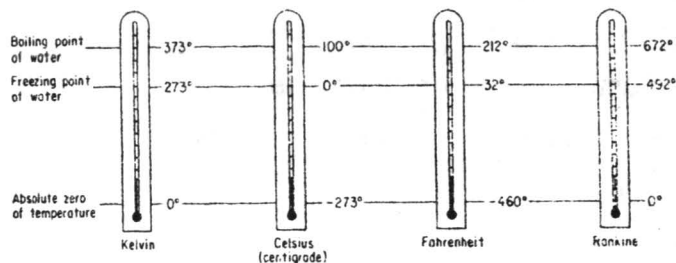
Temperatures are measured by instruments which indicate the intensity of the heat in a body. Heat will flow from a higher - temperature body to a lower - temperature body. The liquid thermometer, usually filled with mercury, is calibrated at the freezing point of water and when taken under 1 atm of pressure.

Definition of terms

(Fig. B-25)

There are four scales calibration: Fahrenheit , centigrade (Celsius), absolute (Kelvin), and Rankine. They are related as shown in Fig. B-25. The lowest temperature theoretically obtainable is called the absolute zero of temperature.

FIGURE B-25
Relationships of the four
scales of calibration.



Conversion Between scales

Temperatures can be easily converted from one scale to another. Refer to Table B-1 for temperature conversions from centigrade to Fahrenheit and from Fahrenheit to centigrade.

Fahrenheit to centigrade

1. Subtract 32° from Fahrenheit reading.

2. Multiply result by 5/9.

Example: $212^{\circ}\text{F} = ?^{\circ}\text{C} ?$

Solution: 212°F

-32°

180°F

$5/9 \times 180 = 100^{\circ}\text{C}$ (Ans.)

Centigrade to Fahrenheit

1. Multiply centigrade reading by 9/5.

2. Add 32°

Example: $100^{\circ}\text{C} = ?^{\circ}\text{F} ?$

Solution: $9/5 \times 100^{\circ}\text{C} = 180^{\circ}\text{C}$

$+32^{\circ}$

212°F (Ans.)

Centigrade to absolute (Kelvin)

1. Add the number 273 to the centigrade reading.

2. The value is the temperature reading in Kelvin.

example: $20^{\circ}\text{C} = ?^{\circ}\text{K} ?$

Solution: $273 + 20^{\circ}\text{C} = 293^{\circ}\text{K}$ (Ans.)

Fahrenheit to Absolute

1. Convert Fahrenheit to centigrade

2. Convert centigrade to absolute.

Fahrenheit to Rankine

Add 460° to Fahrenheit temperature

Centigrade to Rankine

1. Convert centigrade to Fahrenheit.
2. Add 460° to Fahrenheit temperature.

Calibration of thermometers

Calibrate laboratory thermometers by testing at 0°C: Immerse thermometer in a well - stirred mixture of crushed ice and distilled water. The thermometer should read 0°C.

100°C: Fix thermometer above the surface of a beaker or flask of boiling water so that the mercury column is exposed to the vapor. The thermometer should read 100°C at a barometric pressure of 760 mm of mercury.

Laboratory thermometers, long-scale type, are calibrated for complete immersion of the mercury column in the liquid or vapor.

Stem correction

In melting-point or boiling-point determination, the entire mercury column is not completely immersed in the vapor or liquid. Therefore, corrections must be made.

At temperatures 0 to 100°C, error is negligible; around 200°C, error may be 3 to 5°C; and around 300°C, error may be 10°C.

Correct these values by using the following formula:

$$\text{Stem correction (in degrees)} = KN (T_o - T_m)$$

where N = length of the exposed thermometer in degrees (the length not being exposed to the vapor or liquid).

T_o = observed temperature on the thermometer

T_m = mean temperature of the exposed column (obtained by placing auxiliary thermometer alongside with its bulb midpoint)

K = constant, characteristic for the particular kind of glass and the temperature.

EXAMPLE

The thermometer reads 250°C on a thermometer. What is a correct reading?

Solution

The exposed column of the thermometer reads from 110 to 360°C, a difference of 250°C. The temperature of the auxiliary thermometer reads 50°C. Substituting:

$$K = 0.00016$$

$$T_o = 250^\circ\text{C}$$

$$T_m = 50^\circ\text{C}$$

$$N = KN (T_o - T_m)$$

$$= 0.0016 \times 250(250 - 50)$$

$$= 8.0^\circ\text{C}$$

The corrected temperature should be $250 + 8.0^\circ\text{C} = 258.0^\circ\text{C}$.

Reuniting the mercury column

Do not reject thermometers because the mercury column has become separated. Separation results from mechanical and thermal shock. Separated mercury columns cause error in thermometer readings.

Always inspect thermometers before using to detect separation of the capillary, bulb, and reservoir and to detect dispersed in the bore balls.

Thermometer mercury columns can be reunited by the following procedures.

Caution

Remember thermometers are made of glass; they are fragile and will break easily. The bulb is especially thin and fragile. Do not subject them to severe mechanical shock.

Reuniting procedure for mercury separation:

1. Immerse the bulb of the thermometer in a suitable freezing mixture of dry ice and acetone. All the mercury should be drawn into the reservoir by contraction. Remove and warm gently. The column should reunite. If unsuccessful, repeat this procedure several times.

2. Repeat procedure 1, but this time tap gently to dislodge gas bubbles.

3. Tap the thermometer at room temperature by holding the thermometer in your right hand, making a fist around the bulb (gently), then hitting your clenched fist into the palm of your other hand.

4. Turn the thermometer upside down, tap gently while heating the bulb intermittently, forcing the mercury downward. Turn right side up and repeat this procedure. Sometimes the mercury column will join together if there is a sufficiently large capillary.

5. Swing the thermometer rapidly in a circle. Centrifugal force may reunite the column. Do not "snap" your arm because the thermometer may break. The circular motion forces the upper section of the column to fall to the bottom.

6. Warm gently over a bunsen flame with the bulb at a reasonable height above the flame. Heat expands the mercury in the upper expansion chamber.

Caution

Do not overfill the expansion reservoir because the thermometer of them which will work.

SECTION III

Heating, Sublimation, Evaporation and Centrifuging

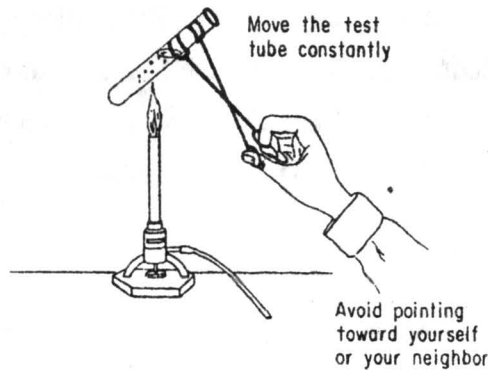
Heating nonflammable liquids

Test tubes

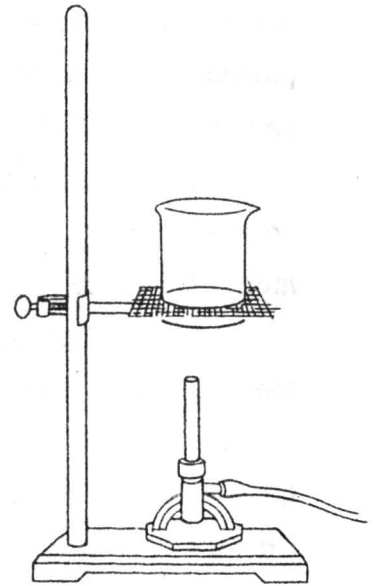
1. Fill the test tube one - half full maximum.
2. Hold the test tube with a test-tube clamp (Fig. C-1)
3. Point the mouth of the test tube away from you and anyone near you.
4. Place the test tube in the flame always moving the test tube constantly. If the test tube is not moved, the liquid will get very hot and vapor will form and eject liquid violently.

FIGURE C-1

FIGURE C-2



C-1 Heating a liquid in a test tube.



C-2 Assembly for heating solutions.

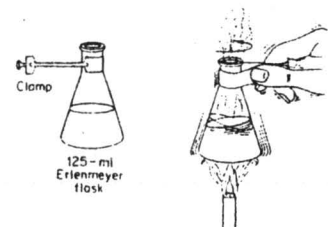
Beakers or flasks

1. Place the beaker on asbestos center wire gauze resting on a tripod or ring stand (Fig. C-2, previous page).
2. heat with a gas burner.

Alternative method

Grasp the neck of the flask as shown in Fig. C-3 and heat.

Figure C-3



Boiling stones

Boiling stones are essentially 99.6 percent pure silica, fused and bonded to form stones which have innumerable sharp projections for the release of vapor bubbles. They are chemically inert, and when they are used, they stop bumping, reduce the danger of breakage, and speed up distillation. They make possible sharper separations of fractions in distillations and are especially efficient Kjeldahl digestions. Boiling chips are microporous, chemically inert chips, made of carbon or other materials which are used for the same purpose as boiling stones.

When boiling stones are added to solutions which are heated to boiling to prevent bumping, they release small amounts of vapor at many points, and the bubbles rise to the surface, causing no trouble. Without them, large bubbles of vapor can form almost explosively, causing glass breakage and contamination and loss of the foamed boiling liquid.

Caution

Never add any boiling stones or boiling chips to hot liquids. Large amounts of vapor will be formed immediately, causing frothing, spraying, and ejection of the heated liquid from the flask. Always cool your solutions before you add the boiling stones.

HEATING FLAMMABLE LIQUIDS

Caution

Vapors of flammable liquids must be kept away from open flame. Never heat in open breakers or flasks with burner. The heavier - than - air vapors will descend and catch fire.

1. heat a sand bath or a very high - boiling mineral oil with gas burner.
2. Turn off the gas burner.
3. Immerse the beaker or flask in the heated bath to heat the material.

Alternative method 1

If temperatures up to 100°C are adequate, use a steam bath.

1. Seat the flask on the steam bath after removing the maximum number of supporting rings to give the maximum heating surface.
2. Pass steam into the top inlet.
3. Connect the bottom outlet to the drain to discharge steam condensate.

Alternative method 2

Place the flask in a heating mantle and adjust the temperature of the heating mantle with a transformer. Refer to Section 2 for Heating Mantles, Care and Operation.

HEATING ORGANIC LIQUIDS AND AQUEOUS SOLUTIONS

Practically all organic liquids are flammable. The lower the boiling point, the more flammable they are. If the identity of the liquid is known, check the reference handbook for the boiling point. Assume all organic liquids are flammable until you have determined otherwise.

Choose the heating system depending upon (1) the flammability of the liquid, (2) the vessel used, and (3) the presence of the hazard in the work area.

Beaker or open flask

Flammable:

1. Steam bath (for temperatures around 100oC).
2. Hot - water bath (for temperatures around 100oC).
3. Electric - heating mantles, variable transformer or rheostat (most convenient).

Refer to Section 2 Heating Mantles, Care and Operation.

Nonflammable:

Bunsen burner, direct or through oil or sand bath

Round - bottom flasks, closed - reaction assemblies

For reflux, distillation, and synthesis:

1. Bunsen burner, direct or through oil sand bath
2. Steam bath
3. Hot - water bath
4. Electric - heating mantle, with variable transformer or rheostat

Caution

1. Always place auxiliary thermometer in the oil or sand bath to guard against excessive heating.
2. Connect thermocouple leads to temperature - indicating meter to indicate heat of mantle to guard against excessive heating.

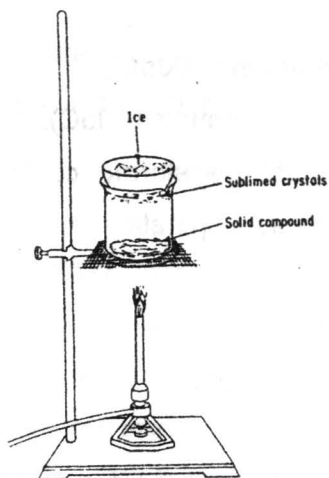
SUBLIMATION

Some solids go directly from the solid state to the vapor state when heated, and will go from that state back to the solid state when cooled.

PROCEDURE

Gently heat the sublimable compound in a container which has a loose - fitting cover chilled with cold water or ice (Fig. C-4).

FIGURE C-4
Sublimation.



EVAPORATION OF LIQUIDS

Small volumes

Evaporation of solvents is necessary at time concentrate solutions and to obtain crystallization of solutes.

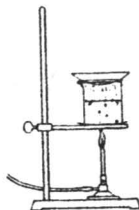
PROCEDURE

1. Pour the small volume of solution into the watch glass placed over a beaker of water (Fig. C-5).
2. Boil the water. The heat transfer through the steam formed evaporates the solvent of the solution.

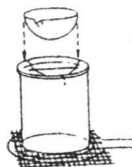
Alternative method

Use evaporating dish instead of a watch glass (fig.C-6).

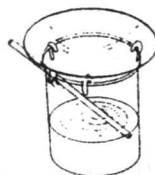
figure C-5



C-5 Evaporation over a water bath.



C-6 Alternative procedure using evaporating dish instead of watch glass.



C-7 Arrangement for the evaporation of liquids.

Large volumes of solvent

(Fig. C-7)

PRINCIPLE

Concentrate solutions by boiling off the desired volume of solvent. Refer to Heating flammable liquids and Heating nonflammable liquids.

PROCEDURE

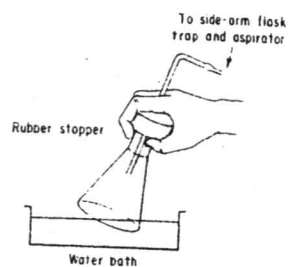
1. Pour the solution which is to be concentrated by boiling off solvent in a suitably sized beaker which is covered by a watch glass resting on glass hooks (Fig. C-7).
2. Heat the solution to evaporate the solvent.

Evaporation of solvent under reduced pressure

PRINCIPLE

Solvents can be evaporated more quickly by evaporating them at reduced pressure and gently heating (Fig. C-8). Refer to Fig. C-9 for trap bottle.

Figure C-8



PROCEDURE

1. Place the solution to be concentrated in a round - bottom flask or suction flask.

Caution: Do not use erlenmeyer flasks having volumes larger than 125 ml. there is a danger of implosion and collapse.

2. Connect with rubber tubing to a safety trap which in turn is connected to a water aspirator.

3. Apply vacuum by turning on water.

4. Swirl the flask to expose large areas of the liquid and speed evaporation.

Note: Swirling technique helps suppress bumping.

5. The flask cools as the solvent evaporates.

6. Heat the flask by immersing in a warm - water bath.

Evaporation under vacuum

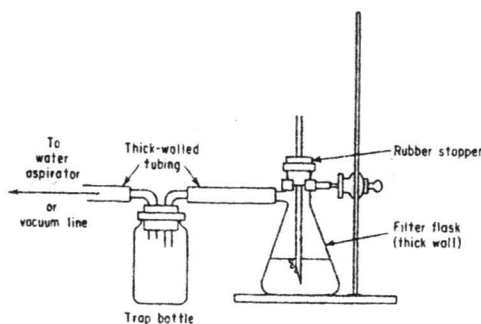
Water aspirator

1. Place liquid in a flask (fitted with a capillary air-inlet tube, Fig. C-9) which is connected to a water aspirator with tubing.

2. Turn on the water aspirator to apply vacuum; adjust the capillary in the flask.

3. Gently apply heat with a warm - water when evaporation is completed.

FIGURE C-9
Evaporation of solvent under reduced pressure.



Mechanical vacuum pump

1. Place liquid in a flask (fitted with a capillary air-inlet tube) connected to a dry - ice trap by tubing.

2. Connect the outlet of the trap to a vacuum pump. Refer to vacuum pumps in Section 1F.

3. Turn on vacuum pump; adjust capillary on flask to a fine-air-bubble stream.

4. Gently apply heat with a warm - water bath.

5. Disconnect the tubing, connecting the flask to the vapor trap before turning off the vacuum pump.

Commercial freeze -driers are available in some laboratories. They consist of a self-contained freeze - drying unit which effectively will remove volatile solvents. They may be simple ones, consisting merely of a vacuum pump, adequate vapor traps, and receptacle for the material solution. Others include refrigerator units to chill the solution plus more sophisticated instruments to designate temperatures and pressure, plus heat and cold controls and vacuum -release valves.

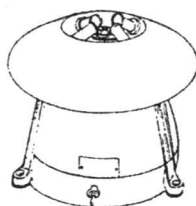
Freeze - driers, as the name indicates, are usually used to remove all the volatile solvents, but they can be used to remove smaller amounts as required.

CENTRIFUGES

See Fig. C-10. Use centrifuges to:

1. Clarify nonsettling solutions containing finely divided solids. (See Fig. C-11).
2. Break emulsions of two immiscible liquids.
3. Collect solids from a slurry.
4. Obtain a clear solution from a liquid - solid mixture.
5. Separate two immiscible liquids from each other.

FIGURE C-10
FIGURE C-11



C-10 Laboratory centri-
fuge.



C-11 Withdrawing liq-
uid after centrifuga-
tion of a mixture.

PROCEDURE: batch - type centrifuge

1. Divide the liquid to be centrifuged among the minimum number of centrifuge tubes. (See Fig. C-12)

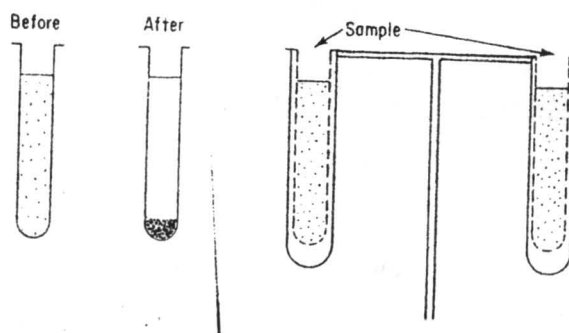
CAUTION

1. Use an equal number of tubes or fill one with counterbalancing solution. All tubes and contained liquid should be weighed and adjusted to the same weight.
2. Insert the tubes, equally spaced from each other.
3. Start the motor and run the centrifuge until the objective has been achieved.
4. Turn off the switch and allow the rotating centrifuge assembly to come to REST.

CAUTION

Do not attempt to stop the rotation manually when it is rotating at high speed. Use brake if available.

FIGURE C-12
Solid-liquid separation
through centrifugation.



SECTION IV

Chemistry is a science of precision, quantitativ science . The most important single piece of apparatus available to the chemist is the balance. It is as important to the chemist as the microscope is to the biologist. Balances are mechanical devices used to determine the mass of objects. Because the mass of the objects with are determinated rangs from kilograms to micrograms, the choice of the balance to be used for any determination is goverened by the total mass of the object and the sensitivity desired. Therefore the technician is always faced first with the decision of which to use. The precision required is his second decision. All balances are precision and expensive instrumentes and you should use extreme care when handling and using them. A great variety of balances are found in the chemical laboratory, ranging from rough measuring devices (the trip balances, the triple-beam balance) which are sensitive to 0.1 g to the analytical balances sensitive to frections of a micrograme.

Because balances are delicate instrumentes, the following comprehensive rules should be observed in caring for end using them. (This are general rules for all balances. Prudence will dictate whichare not aplicable in work with rougher mesuring devices).

1. Level the balance.
2. Inspect the balance to be ceertain that it is working properly. Use calibrated, undamaged weghts.
3. Check the balance zero.
4. Be certain the beam is locked before removing or changing weights or objects to be weighed.
5. Keep the balance scrupulously clean.
6. Work in front of the balance to avoid parallax error.
7. Handle all weights and objects with forceps, never with fingers. Place the forceps as near as possible to the center of the pans.
8. Avoid weighing hot objects. (If possible).
9. Release the locking mechanism slowly , avoiding jars.

10. Do not overload the balance.
11. Never weigh moist objects or chemicals directly on the pans.
12. Close the balance case (if a part of the balance).
13. Triple count all weights to avoid error. Separate weights.
14. Record weights in notebook for addition. Never add mentally.

MEASUREMENT

Introduction

The measure , by definition, is to determine the dimensions, capacity, or quantity of anything. A measurement is the extent, capacity , or amount of something as determined by measuring. Any of our life experiences are studied by a system of measures and communicated to others by transferring a stimulus to an instrument which measure its intensity. For example, we transfer aour feeling of temperature to others by comparing our body temperature with that of the surrroundings and saying we are hot , could , or comfortable. The stimulus is temperature and the instrument is our body's sense of feeling.

Laboratory instrumentes designed to measure our mere refinements for our body senses. For example , a balance permits us to determine the mass of an object more accurately than we could determine it by lifting.

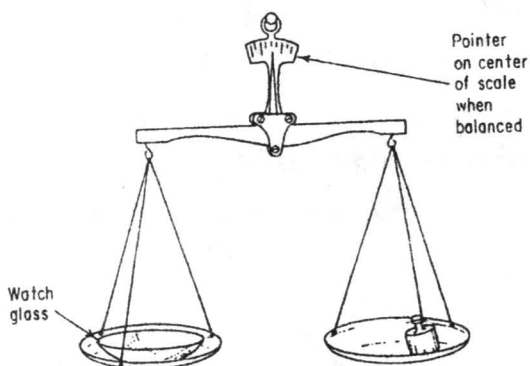
In a quantitative determination we are accurately measuring some part of the whole, some constituent of of the product. The amount of the constituent can be measured by a volumetric,instrumental, or gravimetric technique, and the percent of a constituent must be a ratio of the amount of contituent to the amount of product. The amount of product is usualy determined by weight, and the weight is measured by a balance.

Types of balances

Equal-arm balances - principle of operation

The equal-arm analytical balance (Fig. J1), acts as a first class lever.

FIGURE J-1
Equal-arm balance.



The addition of weight to one site of such a lever to rest (in equilibrium) will cause it to become unbalanced. The force at the point of load is a product of the mass involved and the horizontal distance from the fulcrum through which it is acting . The lever again achieves its position of equilibrium when the force at the load site is exactly balanced on the opposite side of the fulcrum.

$$F_1 = F_2$$

where F_1 and F_2 are opposing forces.

Since the force is dependent on the distance from the fulcrum, it is essential that the pans of the balance be exactly equidistant from the fulcrum.

The weighing operation on an equal -arm balance then consists of duplicating under load the equilibrium position of the unloaded balance.

Rider balances, chainomatic balances, and keyboard balances are examples of equal-arm balances.

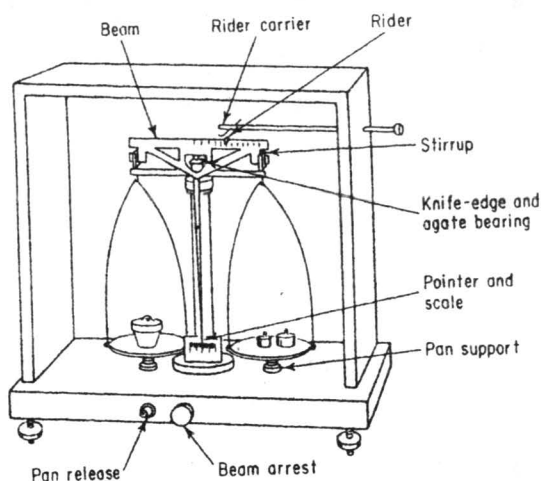
Two-pan equal-arm balances

(fig. J-2)

PROCEDURE:

1. Find the rest point of the balance when there is no load on either pan.
 - a) Raise the balance beam by turning the operating knob into the free - swinging position.
 - b) Start the balance swinging 10 to 20 division by air current.
 - c) Record 3 to 5 consecutive swing points of the pointer.
 - d) Return the balance to the supported position by reversing the position of the operating knob.
2. Place the weighing dish on the left pan of the balance. Handle with forceps.
3. Transfer the appropriate weights with forceps to the center of the right pan.
Adjust the weights on the right pan to 10 mg light.

FIGURE J-2
Controls and components of
a laboratory balance.



4. Move the " rider " to bring the swinging pointer to the *same rest point* as the original *no-load rest point*.
5. Record the total weight needed to achieve step 4.
6. You have obtained the weight of the weighed in the weighing dish.
7. Place the material to be weighed in the weighing dish.
8. Repeat operations 2 through 5.
9. You have obtained the weight of the substance and the weight of the weighing dish combined.

10. Subtract the weight in step 5 from that in step 9 to get the weight of the material.

WEIGHING

The triple-beam balance unequal arm

The capacity of a triple-beam balance is 2,610 g with attachment weights. Its sensitivity is 1.1 g. See figs. J-3 and J-4.

PROCEDURE

1. Observe all general weighing procedures.
2. Slide all poises or riders to zero.
3. Zero the balance, if necessary with balance-adjustment nuts.
4. Place the specimen on the pan of the balance.
5. Move the heaviest poise or rider to the first notch that causes the indicating pointer to drop; then move the poise back one notch, causing the pointer to rise.
6. Repeat procedure 4 with the next highest poise.
7. Repeat this procedure with the lightest poise, adjusting the poise position so that the indicator points to zero.
8. The weight of the specimen is equal to the sum of the values of all the poise positions, which are read directly from the position of the marked beams.

FIGURE J-3
Triple-beam balance.

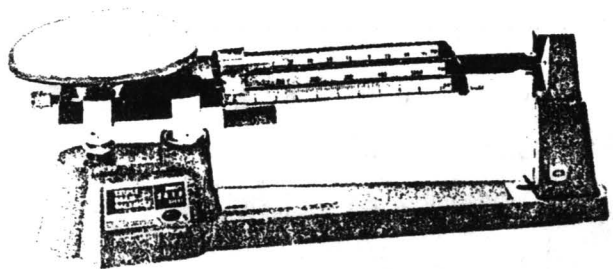
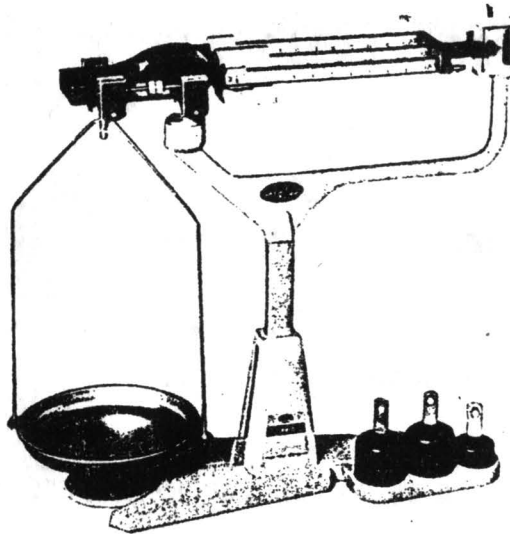


FIGURE J-4
Triple-beam balance.



The dial-O-gram balance unequal arm

The capacity of a Dial-O-Gram balance (fig. J-5) is 310 g. Its sensitivity is 0.01 g.

PROCEDURE

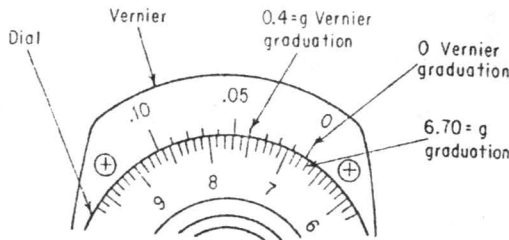
1. Observe all general weighing procedures, sliding poises to zero.
2. Rotate the dial to 10.0 g.
3. Move the 200 g poise on the rear beam to the first notch which causes the pointer to drop; then move it back one notch.
4. Move the 100 g poise to the first notch which causes the pointer to drop.
5. Rotate the dial knob until the pointer is centered.
6. Add the values of the 200 g poise, the 100 g poise, and the dial. Each graduation of the dial reads 0.1 g, with a vernier breaking the value down to 0.01g.

Two-pan equal-arm chainomatic balances

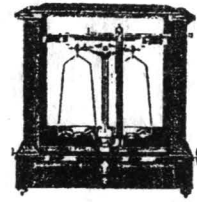
Adjustment of the height of the chain in this type of balance causes changes in the weight applied to the right-hand pan. It eliminates the use of weights less than 0.1 g. It will apply weights from 0 to 100 mg (0.1 g) to the right-hand pan. See Fig. J-6.

FIGURE J-5

FIGURE J-6



J-5 Dial-O-Gram control knob.



J-6 Ainsworth balance, chainomatic type.

PROCEDURE

1. Use the procedure given under Two-pan Equal-arm Balances except: When adding weights of 100 mg or less, adjust the height of the chain indicator to get the same rest point as that of the original with no load.
2. Read the calibrated vernier to obtain the weight portion 0 to 100 mg.

Using the Vernier on the Chainomatic Balance and Other Equipment

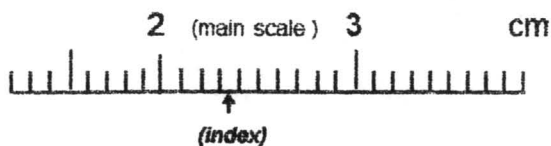
PRINCIPLE

The vernier is used to measure accurately a fraction of the finest division on the main scale of a measuring instrument.

Estimation without Vernier

On the main scale, without a vernier, the sliding index indicates the portion on the scale corresponding to the measurement.

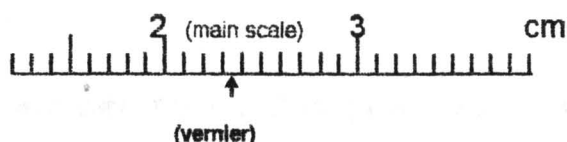
Example



1. The index points to a reading between 2.3 and 2.4 cm.
2. Estimate the index to be $\frac{8}{10}$ of a division ($\frac{8}{10}$ of 0.1 cm, or 1.08 cm).
3. The estimated reading of the index pointer = $2.3 + 0.08 = 2.38$ cm.

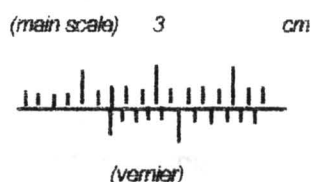
Exact reading with vernier

Example



1. The index point to a reading between 2.3 and 2.4 cm (the same as was obtained in the estimated procedure). The zero mark on the vernier equals the simple index pointer, indicating that reading is between 2.3 and 2.4 cm.
2. The division of the vernier scale which coincides with a division of the main scale indicates the exact reading.
 - a) The vernier division which coincides is 7, which is exactly 0.07 cm.
 - b) The accurate reading is the sum of 2.3 cm and the exact 0.07 cm to give 2.37.

ADDITIONAL EXAMPLE

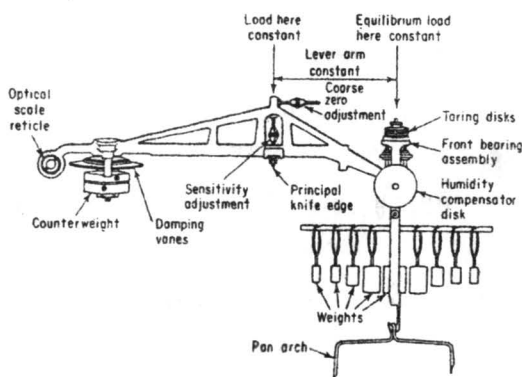


1. The vernier zero index is 2,7
2. The vernier reading is 0,01 cm (division 1 on the vernier coinciding with division 2,8 on the main scale).
3. The exact reading is $2,7 + 0,01 = 2,71$

Unequal-arm balance -substitution

The principle of operation of the unequal arm balance is substitution. The balance consists of an asymmetric beam. The maximum load is placed on both sides. On the shorter and are a pan and full complement of weight. A counterweight is used on the longer end to impart equilibrium on the system. When a load is placed on the pan, the analyst must remove an equivalent weight from the load side, within the range of the optical scale, to bring the balance into equilibrium. The total weights removed plus the optical scale reading equal the weight the on the pan. The Mettler single-pan balance operates on this principle. A diagram of the weight system appears in fig. J.7

FIGURE J-7
Diagram of the weight system of an unequal-arm balance.



Definition of terms to describe performance of balances

- **Mass** : an invariant measure of the quantity of matter in an object.
- **Weight** : the force of attraction exerted between an object and the earth. Weight equals mass times the gravitational attraction
- **Capacity**: the largest load on one pan for which the balance can be brought to equilibrium
- **Precision (standard deviation)** : degree of agreement of repeated measurements of the same quantity. It is a statistical value and is calculated :

$$S = \sqrt{\frac{\sum d^2}{f}}$$

where S = standard deviation

d = deviation between individual weighing and average

$f = n - 1$

Precision and reproducibility are synonymous.

- **Readability** : the smallest fraction of a division at which the index scale can be read with ease.

Accuracy : the agreement between the results of the measurement and the true value of the quantity measured.

Factors influencing accuracy

1. Magnitude of the lever arm error .
2. Magnitude of error in scale indication due to variable load.
3. Adjustment error of weights.
4. Uniform value of divisions throughout the optical scale.
5. Precision
6. Environmental

Factors 1 to 3 have no influence in the Mettler balance because of substitution.

- **Sensitivity** : the change in load required to produce a perceptible change in indication .
It is therefore a ratio and is not to be used to discuss the quality of a measurement.

Basic controls on most single-pan analytical balances

1. Pan-arrestment control
 - a. Assures constant position of the beam between and during weighing.
 - b. Protects the bearing surface for excessive wear and injury due to shocks.
2. Arrestment control-three positions

a. Arrest position is used when removing or placing objects on the pan, when the balance is being moved, and when the balance is not in use.

b. Partial arrest position is used to obtain preliminary balance.

c. Release position is used when the final weights are being made.

3. Zero-adjust knob

Positions the optical scale to read zero when the pan is empty, because of minute changes in beam position.

4. Weight-setting knobs-to which remove and replace weights from the beam.

a. One knob removes weights in 1- to 9-g increments.

b. The second knob removes weights in 10-g increments, load limit 100g.

5. Optical scale adjustment

Turn knob positions the optical scale relative to a reference line so that the final weight to 0.1mg can be obtained.

General steps to follow using single-pan analytical balance

1. Check to see that the balance is level.

2. Zero the balance in arrest position, with pans clear and all weight reading at zero.

3. Weigh the object.

a. Put the pan in arrest position.

b. Place the object on the pan

c. Set to semiarrest position

d. Adjust 1- and 10-g control knobs until the weight is within 1g of the object.

e. Return to arrest position, then to full release position with the arrestment control.

f. Obtain the final weight by adjustment of the optical system adjustment knob.

Types of single-pan analytical balances

Mettler model H-5 see fig. J-8

Sartorius series 2400 see fig J-9

Stanton unimatic CL2 see fig J-10

Ainsworth magni grad type 21 see fig. J-11

FIGURE J-8
The Mettler HF Gram-atic
single-pan analytical
balance.

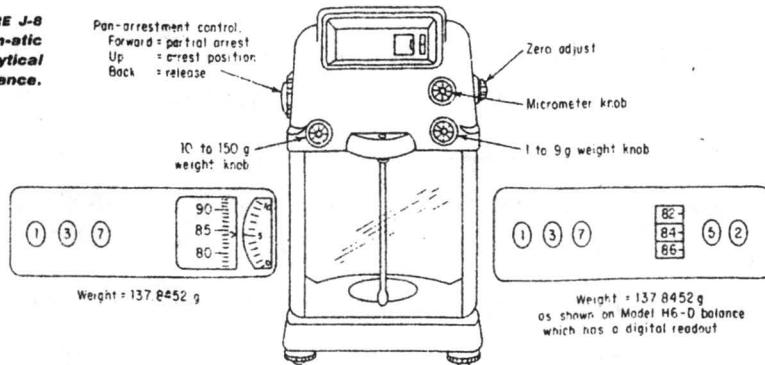


FIGURE J-9
The Sartorius 2400 Series
single-pan analytical
balance.

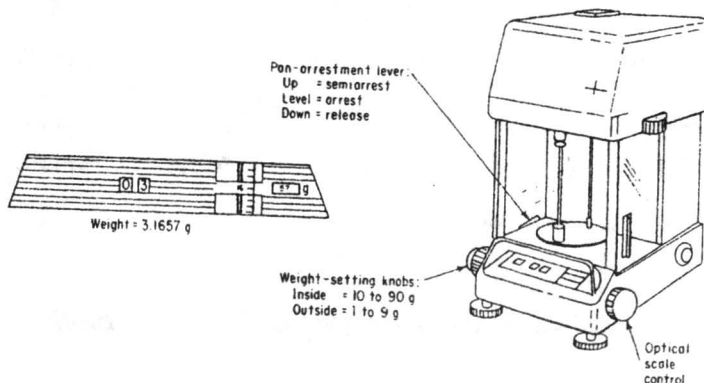


FIGURE J-10
The Stanton Unimatic CL2
single-pan analytical
balance.

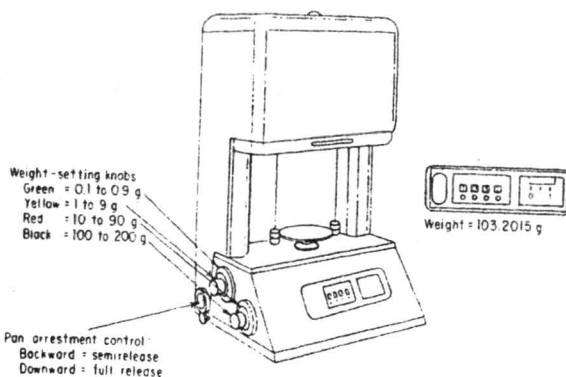
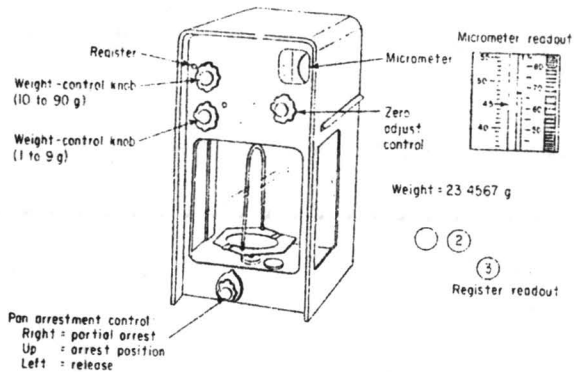


FIGURE J-11
The Ainsworth Magni Grad
Type 21 single-pan
analytical balance.



VOLAND MODEL POINTER See Fig. J-12.

160-A

TORBAL MODEL EA-1 See Fig. J-13

FIGURE J-12
The Voland Model Pointer
160-A single-pan analytical
balance.

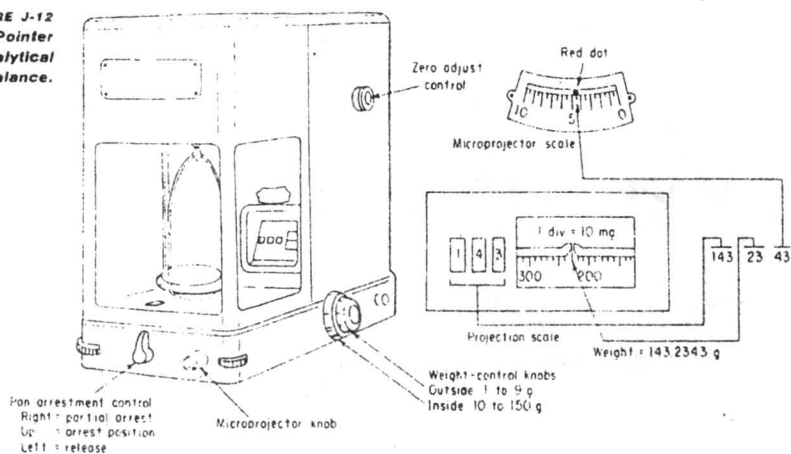
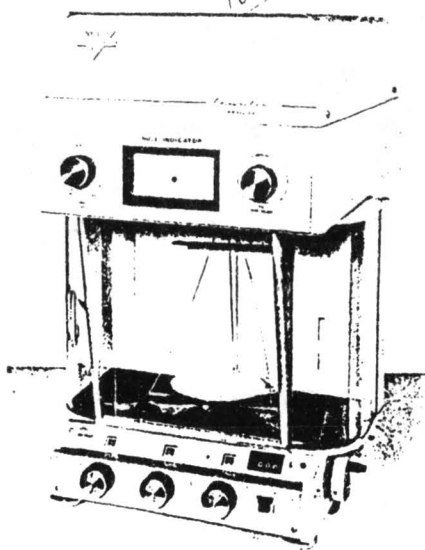


FIGURE J-13
The Torbal Model EA-1
single-pan analytical
balance.



Choosing the correct balance

Criteria for choosing a balance

1. Is the balance suitable for making the desired measurement?

EXAMPLE

Is a Mettler model B-5 (four - place balance) suitable for weighing 10 mg of material?

The accuracy in the optical scale is ± 0.05 mg.

The error on a 10 mg sample is 0.5 percent error; therefore, a different balance must be chosen.

Conclusion: Analytical tests cannot tolerate ± 0.5 percent errors; therefore, a different balance must be chosen.

2. What balance is suitable to weigh 10 mg of material?

Model B-5 accuracy in the optical scale is ± 0.05 mg.

The error on a 10 mg sample is ± 0.5 percent (not tolerable).

Model B-6 accuracy in the optical scale is ± 0.02 mg.

The error on a 10 mg sample is ± 0.2 percent (tolerable).

Conclusion: Model B-5 is not suitable. Model B-6 is suitable.

Model calculation

Determination of chloride:

$$\text{Percent Cl} = \frac{V * N * \text{milliequivalent weight} * 100}{\text{weight of sample (g)}}$$

where: V = volume of titrant (2 ml)

N = normality of titrant (1N)

milliequivalent weight of chloride = 0.035

weight of sample, g = 0.010000 (no error assumed)

Assumption: The V and N of the titrant have no error.

$$\frac{2 * 0.1 * 0.035 * 100}{0.010000} = 70.0 \text{ percent}$$

$$\text{Four - place balance: } \frac{2 * 0.1 * 0.035 * 100}{0.01015} = 69.64 \text{ percent}$$

possible error = ± 0.37

$$\text{Five-place balance: } \frac{2 * 0.1 * 0.035 * 100}{0.01002^{\circ}} = 69.76 \text{ percent}$$

possible error = ± 0.24

$$\text{Microbalance: } \frac{2 * 0.1 * 0.035 * 100}{0.010002^{\circ}} = 69.98 \text{ percent}$$

possible error = ± 0.02

Fundamental rules for maintaining accuracy and reproducibility of balances

1. Set up the balance where it will be free from vibration. Preferably choose a room with constant temperature and humidity in which to set up the balance. a weighing table of adequate weight and stability will be a suitable base.

2. Load and unload the balance only when it is arrested. When arrested, the beam and suspension rest on three arrestment pins each. The knife-edges are thus fully unweighted and not liable to damage by sudden load changes such as are caused by laying on or removing the object to be weighted. The arrestment lever should be moved slowly until the scale illumination has been switched on.

3. Turn weight-setting knobs only with the balance semireleased. Partial release protects the knife-edges from damage during weight settings. Abrupt loading changes resulting from applying and removing the weights are to a large extent absorbed by the arrestment pins as, when semireleased, beam movement is limited.

4. Never place chemicals directly on the pan.

Weighing

Weighing requires the following operations.

1. Checking the level. Check the spirit level to ensure that the balance is properly leveled. If necessary relevel the balance.

2. Checking the zero point.

Unload the pan and clean it if necessary.

Close the side window.

Set all weights to 0.

Set the micrometer scale to 0.

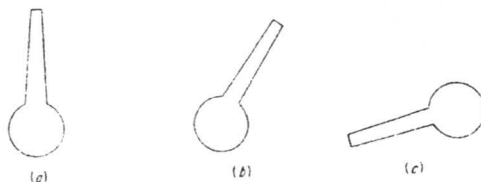
Release the balance fully.

When the projected scale is at rest, bring the zero line of the scale to read zero.

Arrest the balance as fig. J-14a.

3. Placing an object to be weighed on the balance. The object to be weighed may be placed on the balance only in the arrest state(fig. J-14a).

FIGURE J-14
Weighing positions for
Mettler balances.



(a) Balance arrested, loading and unloading of pan. (b) Balance semireleased, operation of weight-setting knobs. (c) Balance fully released, setting of zero point and reading of result.

Whenever possible use a pair of tweezers to avoid humidity and heat being transmitted by the hands to the objects to be weighed and inside the weighing chamber. Rubber causes static charges. After introducing the object to be weighed, close the side window immediately.

4. Weight setting.

Semirelease the balance (fig J-14b).The optical scale moves downward about seven graduations.

Turn the highest weight-setting knob clockwise. When the scale moves upward, turn the knob back one step.

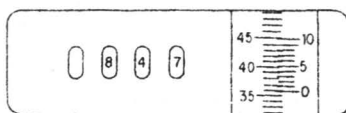
Repeat the same operation with the remaining weight setting knobs.

Arrest the balance after having set the weights. (In this position the pen becomes operative).

Release the balance fully and allow it to come to rest.

On model B-5 reading of the last decimal place is done with the aid of the vernier (fig. J-15). On semimicro balance B-6 and micro M-5 turn the micrometer knob

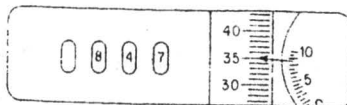
FIGURE J-15
Vernier on Mettler Model
B-5.



Weight = 84.7359

counterclockwise until the next lower scale graduation lies exactly in the center of the forked pointer (fig J-16)

FIGURE J-16
Micrometer knob (micro and semimicro balances).



Errors in weighing.

1. Changes in moisture or CO₂ content. Some materials take up H₂O or CO₂ from the air during the weighing process. Such material must be weighed in a close system.

2. Volatility of sample. Material which are volatile at room temperature will lose weight while on the balance. Such materials weighed in close system.

3. Electrification. An object carrying a charge of static electricity is attracted to various parts of the balance and an error in weight may occur. An antistatic brush might help in such cases.

4. Temperature. If an object is warm relative to the balance, convection currents cause the pan to be buoyed up and the apparent weight of air displaced by the object on the pan. This errors are quite small.

Performance data

	B-5 macrobalance	B-6 semimicro	M-5 micro
Capacity , g	200	100	20
Optical range , mg	115	115	20
Readability , mg	0.05	0.01	0.001
Accuracy of weights , mg	±0.1	±0.1	
Accuracy in optical range , mg	±0.05	±0.02	±0.002
Precision	±0.03	±0.01	±0.001
Suggested weight range , mg	<50	20-50	<20

SECTIUNEA V

VOLUMETRIC ANALYSIS

A volumetric analysis is one in which the analysis is completed by measuring the volume of a solution of established concentration needed to react completely with the substance being determined.

DEFINITION OF TERMS

Units of Volume

Liter: The volume occupied by 1,000g of water at 4°C at atmospheric pressure.

Milliliter (ml): One-thousandth of a liter.

Cubic centimeter (cm³): Can be used interchangeably with milliliter without effect; however, 1ml = 1.000028cm³.

Titration

A process by which a substance to be measured is combined with a reagent and quantitatively measured. Ordinarily, this is accomplished by the controlled addition of a reagent of known concentration to a solution of substance until reaction between the two is judged to be complete; the volume of reagent is then measured.

Back Titration

A process by which an excess of a reagent is added to a sample solution and then the excess is determined with a second reagent of known concentration.

Standard Solution

A reagent of known composition used in a titration. The accuracy with which the concentration of a standard solution is known sets a limit of the accuracy of the test.

Standard solutions are obtained by one of the following:

- Carefully measuring a quantity of a pure compound and calculating the concentration from measuring a quantity of a pure compound and calculating the concentration from the weight and volume measurement
- Carefully dissolving a weighed quantity of the pure reagent itself in the solvent and diluting it to an exact volume
- Using a prestandardized and commercially available solution

Primary Standard

A highly purified chemical compound used as a reference material in preparing a standard solution.

Characteristics of a primary standard are:

- It has high purity which has been tested.
- It is stable and therefore should not be attacked by atmosphere.
- It should not be hygroscopic.
- It is readily available.
- It has high equivalent weight.

Equivalence Point

The point at which the standard solution is chemically equivalent to the substance being titrated. The equivalence point is a theoretical concept. We estimate its position by observing physical changes associated with it in the solution.

End Point

The point where physical changes arising from alterations in concentration of one of the reactants at the equivalence point become apparent.

Titration Error

The inadequacies in the physical changes at the equivalence point and our ability to observe them.

Typical Physical Changes in Volumetric Analyses

- Color due to the reagent, the substance being determined, or an indicator substance
- Turbidity resulting from the formation or disappearance of an insoluble phase
- Conductivity changes in a solution
- Potential changes across a pair of electrodes
- Refractive index
- Temperature changes

Volumetric Flasks

Volumetric flasks are calibrated to contain a specified volume when filled to the line etched on the neck.

Direction for the Use of a Volumetric Flask

Before use, volumetric flasks should be washed with detergent and, if necessary, cleaning solution; only rarely need they be dried. Should drying be required, however, it is best accomplished by clamping the flasks in an inverted position and employing a mild vacuum to circulate air through them.

Weighing Directly into a Volumetric Flask

Direct preparation of a standard solution requires that a known weight of solute be introduced into a volumetric flask. In order to minimize the possibility of loss during transfer, insert a funnel into the neck of the flask. The funnel is subsequently washed free of solid.

Dilution to the Mark

After transferring the solute, fill the flask about half full and swirl the contents to achieve solution. Add more solvent, and again mix well. Bring the liquid level almost to the mark, and allow time drainage. Then use a medicine dropper to make such final additions of solvent as are necessary. Firmly stopper the flask and invert repeatedly to assure uniform mixing.

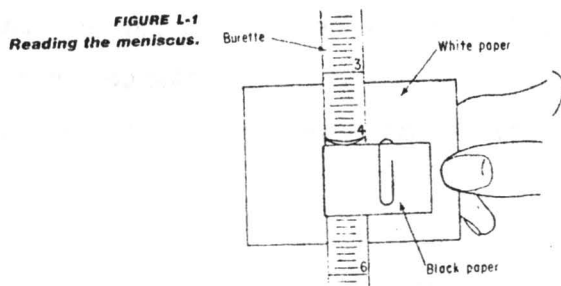
NOTE 1. If, as sometimes happens, the liquid level accidentally exceeds the calibration mark, the solution can be saved by correcting the excess volume. Use a gummed label to mark the actual position of the meniscus. After the flask has been emptied, carefully refill the mark with water. Then, using a burette, measure the volume needed to duplicate the actual volume of the solution. This volume, of course, should be added to the nominal value for the flask when the concentration of the solution is calculated.

2. For exacting work, the flask should be maintained at the temperature indicated on the flask.

READING THE MENISCUS

Volumetric flasks, burettes, pipettes, and graduated cylinders are calibrated to measure volumes of liquids.

The water meniscus should be carefully read to get the correct measurement, because water wets glass and the surface of water in glass tubes looks like Fig. L-1.



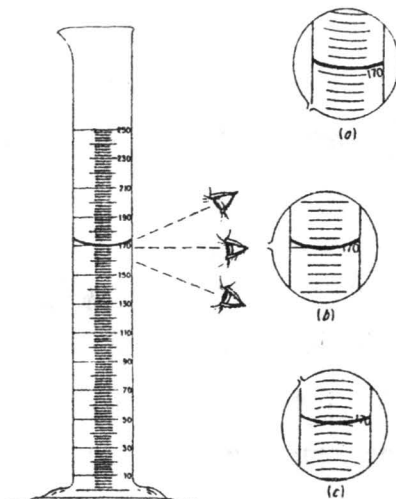
Special care must be used in reading the meniscus. Render the bottom of the meniscus, which is transparent, more distinct by positioning a black-striped white card behind the glass.

Location of the eye in reading a graduated cylinder:

1. With the eye above the meniscus, too small a volume is observed.
2. With eye on the same level as the meniscus, the correct volume is observed.
3. With the eye below the meniscus, too large is observed.

The eye must be level with the meniscus of the liquid to eliminate parallax errors (Fig. L-2).

FIGURE L-2
Avoiding parallax error in
reading the meniscus.



(a) Eye level too high; volume too high. (b) Eye level correct; volume correct. (c) Eye level too low; volume too low.

Then read the top of the black part the top of the black part of the card with respect to the graduations on the burette.

TOOLS OF VOLUMETRIC ANALYSIS

Pipettes, burettes, and volumetric flask are standard volumetric equipment. Volumetric apparatus calibrated to contain a specified volume is designated TC and apparatus calibrated to deliver a specified amount TD.

The Measurement of Volume

Only clean glass surfaces will support a uniform film of liquid; the presence of dirt or oil will tend to cause breaks in this film. The appearance of water breaks a certain indication of an unclean surface. Volumetric glassware is carefully cleansed by the manufacturer before being supplied with markings, and in order for these to have meaning, the equipment must be kept equally clean when in use.

As a general use, the heating of calibrated glass equipment should be avoided. Too rapid cooling can permanently distort the glass and cause a change in volume.

When a liquid is confined in a narrow tube such as a burette or a pipette, the surface is found to exhibit a marked curvature called a meniscus. It is common practice to use the bottom

of the meniscus in calibrating and using volumetric ware. This minimum can often be established more exactly if an opaque card or a piece of paper is held behind the graduations.

Pipettes

Pipettes are designed for the transfer of known volumes of liquid from one container to another. Pipettes which deliver a fixed volume are called volumetric or transfer pipettes (Fig. L-3). Other pipettes, known as measuring pipettes, are calibrated in convenient units so that any volume up to maximum capacity can be delivered (Fig. L-4).

FIGURE L-3

FIGURE L-4

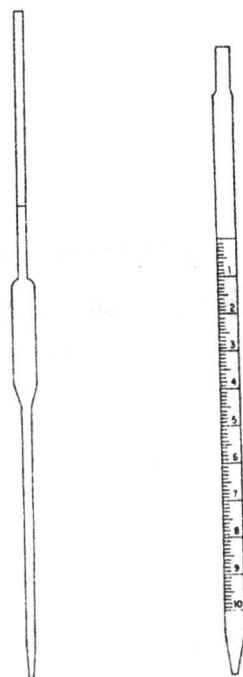


Fig.L-3

Fig.L-4

Cleaning

Pipettes may be cleaned with a warm solution of detergent or with cleaning solution. Draw in sufficient liquid to fill the bulb to about one-third of its capacity. While holding it nearly horizontal, carefully rotate the pipette so that all interior surfaces are covered. Drain inverted, and rinse thoroughly with distilled water. Inspect for water breaks, and repeat the cleaning cycle if necessary.

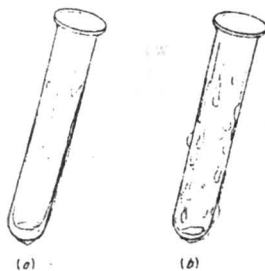
Cleaning of Volumetric Equipment

1. Always rinse volumetric glassware equipment three times with distilled water after you have emptied and drained it. This prevents solutes from drying on the glassware, which may be difficult to remove later.

2. Dry volumetric glassware at room temperature, never in a hot oven. Expansion and contraction may change the calibration.

3. The glass surfaces should be wetted evenly (Fig. L-5a). Spotting is caused by grease and dirt (Fig. L-5b). Grease removal: rinse and scrub with hot detergent solution followed by adequate distilled-water rinses. Dirt: Fillor rinse with dichromate cleaning solution. Allow to stand for several hours, if necessary. Flow with multiple distilled-water rinses.

FIGURE L-5
Water spreads out smoothly on clean glass (a) but stands in droplets on soiled glass (b).



Preparation of Cleaning Solution

In a 5000ml heat-resistant conical flask mix 10 to 15 g of potassium dichromate with about 15ml of water. Add concentrated sulfuric acid slowly and with thorough stirring between increments. The contents of flask will become a semisolid red mass; add just enough sulfuric acid to bring the mass into solution. Allow to cool somewhat before attempting to transfer to a soft glass bottle. The solution may be reused until it acquires the green color of chromium III ion, at which time it must be discarded.

Directions for the Use of a Pipette

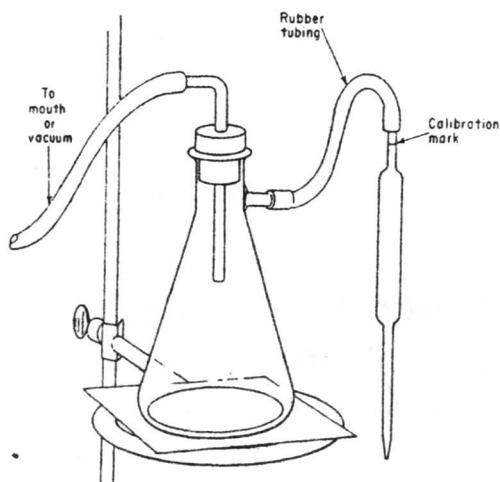
The following instructions pertain specifically to manipulation of transfer pipettes, but with minor modifications they may be used for other types as well. Liquids are usually drawn into pipettes through the application of a slight vacuum. The mouth should not be used for suction, since aside from the danger of accidentally ingesting liquids, there is possibility of contaminating the sample with saliva. Use of a rubber suction bulb or a rubber tube connected to a vacuum pump is strongly recommended (Fig. L-6).

FIGURE L-6
A pipette bulb.



1. Pipettes must be clean and rinsed with distilled water.
2. Drain completely, leaving no rinse-water drops inside. If the pipette is wet with water, rinse three times with solution to be used in the analysis.
3. Draw the liquid up in the pipette using:
 - a. The pipette bulb.
 - b. Suction: mouth or aspirator (Fig. L-7).

FIGURE L-7
Using a pipette with water aspirator.



CAUTION

Always use aspirator, pipette bulb, or safety flask when working with dangerous, poisonous, or corrosive liquids. (Figs. L-6 and L-7).

PROCEDURE

1. Keep the tip of the pipette below the surface of the liquid.
2. Draw the liquid in the pipette with a pipette bulb or suction.
3. Disconnect the suction when the liquid is above the calibration mark. Quickly remove the suction unit and place the index finger of the hand holding the pipette immediately over the exposed end of the pipette to the closed end.
4. Release pressure on the index finger to allow the meniscus to approach the calibration mark.
5. At the mark, apply pressure to stop liquid flow, and drain the drop on the tip by touching it to the wall of the liquid-holding container.

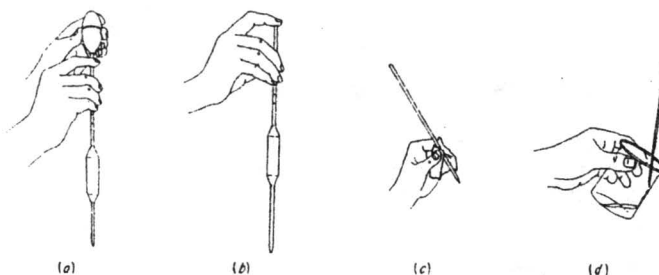
6. Transfer the pipette to be used and release pressure on the index finger. Allow the solution to drain completely, removing the last drop by touching the wall of the container (Figs. L-8d and L-9).

7. The calibrated amount of the liquid has been transferred. Do not blow out the pipette.

Measurement of an Aliquot

As in cleaning, draw in a small quantity of the liquid to be sampled and thoroughly rinse the interior surfaces; repeat this with at least two more portions. Then carefully fill the pipette somewhat past the graduation mark. Quickly place a forefinger over the upper end of the pipette to arrest the overflow of the liquid. Make certain that there are no air bubbles in the bulk of the liquid or as a foam at the surface. Tilt the pipette slightly from the vertical and wipe the exterior free of adhering liquid. Touch the tip of the pipette to the wall of a glass vessel (not the actual receiving vessel) and slowly allow the liquid level to drop by partially releasing the forefinger, halting further flow as the bottom of the meniscus coincides exactly with the graduation mark. Place the tip of the pipette well into the receiving vessel and allow the sample to drain. When free flow ceases, rest the tip against an inner wall for a full 10s or until time as indicated on the the pipette. Finally, withdraw the pipette with a rotating motion to remove any droplet still adhering to the tip. The small volume remaining inside the the tip is not to be blown or rinsed into the receiving vessel (Figs. L-8 and L-9).

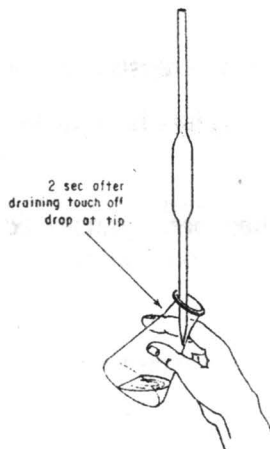
FIGURE L-8
Technique for using a
volumetric pipette.



(a) Draw liquid past the graduation mark. (b) Use forefinger to maintain liquid level above the graduation mark. (c) Tilt pipette slightly and wipe away any drops on the outside surface. (d) Allow pipette to drain freely.

FIGURE L-9

FIGURE L-10

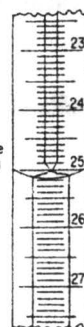


L-9 Draining the pipette.

Magnified view of tip



Blue stripe (magnified below)



L-10 Schellbach burette.

In the case of color-coded pipettes, a frosted ring indicates complete blow-out.

NOTE:

1. The liquid can best be held at a constant level in the pipette if the forefinger is slightly moist. Too much moisture, however, makes control difficult.
2. It is good practice to avoid handling the pipette by the bulb.
3. Pipettes should be thoroughly rinsed with distilled water after use.

Burettes

Burettes, like measuring pipettes, deliver any volume up to the maximum capacity. Burettes of the conventional type must be manually filled. Others with side arms are filled by gravity. For more accurate work, Schellbach burettes (Fig. L-10) are employed. These have a white background with a blue stripe and can be read at the point of least magnification. When unstable reagents are employed, a burette with a reservoir bottle and pump may be employed.

Directions for the Use of a Burette

Before being placed in service, a burette must be scrupulously clean. In addition, it must be established that the valve is liquid-tight.

Cleaning

Thoroughly clean the tube with detergent and a long brush. If water breaks persist after rinsing, clamp the burette in an inverted position with the end tipped in a beaker of cleaning

solution. Connect a hose from the burette tip to a vacuum line. Gently pull the cleaning solution into the burette, stopping well short of the stopcock. Allow to stand for 10 to 15 min and then drain. Rinse thoroughly with distilled water again inspect for water breaks. Repeat the treatment if necessary.

NOTE:

Grease films that appear unaffected by cleaning solution may yield to treatment with such organic solvents as acetone or benzene. Thorough washing with detergent should follow such treatment.

Filling

Make certain that the stopcock is closed. Add 5 to 10 ml of solution and carefully rotate the burette to wet the walls completely; allow the liquid to drain through the tip. Repeat this procedure two more times. Then fill the burette above the zero mark. Free the tip of air bubbles by rapidly rotating the stopcock and allowing small quantities of solution to pass. Finally, lower the level of the solution to, or somewhat below, the zero marking; after allowing about a minute for drainage, take an initial volume reading.

Holding the Stopcock

Always push the plug into the barrel while rotating the plug during a titration. A right-handed person points the handle of the stopcock to the right, the operates the plug with the left hand, and grasps the stopcock from the left side as shown in Fig. L-11.

FIGURE L-11
Preferred method for manipulating a stopcock.

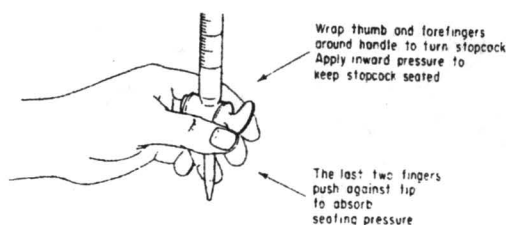
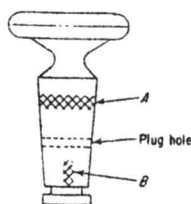


FIGURE L-12
How to grease a stopcock.



Titration is the preferred method for manipulation of a stopcock. Any tendency for lateral movement of the stopcock will be in the direction of firmer seatings.

Using the Burette

1. Test for cleanliness by clamping in an upright position and allow it to drain. No water drops should adhere to the inner wall. If they do, reclean the burette.
2. Grease the stopcock with clean grease, after cleaning it.
 - a. Remove the stopcock.
 - b. Clean the barrel and stopcock with a rag soaked in benzene.
- c. Regrease as in Fig. L-12. Improperly applied grease will spread and obstruct the holes, making recleaning necessary.

Making a Titration

1. Rinse the cleaned burette three times with the solution to be used, draining completely each time.
2. Fill the burette above the zero graduation.
3. Drain slowly until the tip is free of air bubbles and completely filled with liquid and the meniscus liquid is at the zero graduation.
4. Add the titrant slowly, while swirling the flask with the right hand until the end point is obtained.
5. For precision work, volumes of less than one drop can be rinsed off the tip of the burette with wash water.
6. Allow 30s to drain; then read the final position of the meniscus.

CAUTION

Never allow reagents to remain in burettes overnight. The stopcock may "freeze" because of prolonged contact, especially with bases such as KOH and NaOH

7. The difference between the "before" and "after" readings on the burette is the volume of liquid delivered.

To avoid error, with the tip well within the titration vessel, introduce solution from the burette in increments of a milliliter or so. Swirl (or stir) the sample constantly to assure efficient mixing. Reduce the volume of the additions as the titration progresses; in the immediate vicinity of the end point, the reagent should be added a drop at a time. When it is judged that only a few more drops are needed, rinse down the walls of the titration. Allow a minute or so to elapse between the last addition of reagent and the reading of the burette.

SYRINGE-HANDLING TECHNIQUES IN CHROMATOGRAPHY

In chromatography, your results are often only as good as the reproducibility of your sample. And the reproducibility of your sample quantity depends on many factors, among which are an accurate syringe and the operator.

To help chromatograph operators obtain the greatest reproducibility possible, we have compiled some syringe-handling techniques from experienced operators in the field. No suggestion or hint here is "the" answer to every problem, but perhaps you will find an answer to the problem that has been plaguing you.

Filling the Syringe

1. Be certain the syringe and plunger are clean before filling. Following is one recommended method of cleaning a syringe: Pump cold chromic acid solution through the syringe with the plunger, rinse both with distilled water, blow the syringe dry, and carefully wipe the plunger with lint-free tissue, being careful not to touch the plunger shaft with your finger.

The chromic acid solution does a good job of destroying organic detergent residues and fingerprints on the plunger. The more stubborn oxide stains in the syringe-body neck may

be removed with aqua regia, but it is recommended only as a last resort and should never contact the plunger or needle.

2. Pressurize your sample bottle using a gastight syringe filled with inert gas. Repeat as needed to build pressure in the bottle. This is particularly recommended for syringes with a detachable needle.

3. To assure an accurate measurement, wet the interior surfaces (barrel and plunger) of the syringe with the sample by pumping the plunger before filling. When properly done, this neutralizes the liquid movement by capillary forces.

4. Overfill the syringe in the sample bottle, and move the plunger to the desired calibration line, discharging the excess sample. This is your best assurance of a "full" sample. Discharging the excess sample while the needle is still in the sample bottle may cause a loss of sample upon withdrawing.

5. Read the syringe graduation from the same angle each time you fill the syringe. Recommended practice is to read the sample at the "top" (flange end) of the calibration line. This provides an accurate visual check and reduces the problems of "line thickness". Strive to develop a smooth uniform loading operation to minimize slight involuntary errors.

6. Take a visual check of syringe for bubbles or foreign matter in the sample.

7. Syringes with detachable needle require care filling because of the dead volume in the needle. (Refer to point 2)

8. Before injecting, wipe the needle clean with a lint-free tissue in a quick motion, taking care not to wipe sample out of the needle and not to transfer body heat from your fingers to the needle.

Injecting the sample

1. Develop a rhythm in your motion that is used each time you inject; i.e., do the same things in the same manner at the same time.

2. Hold the syringe as close to the flange (in the unmarked area) as possible. This will prevent the heat transfer that occurs when you hold the needle or barrel with your fingers. Another way to prevent heat transfer is to use a Kel-F syringe guide. The guide also makes septum penetration easier.

3. Handle the plunger by the button, not the plunger shaft. This reduces the possibility of damage or contamination.

4. Develop a smooth rhythm that allows you to inject the sample as quickly as you can with accuracy.

5. For greatest accuracy, it is recommended that the syringe not be used at maximum capacity.

SECTION VI

Determination of Physical Properties

DENSITY

The density of any substance can be found by dividing the weight of that substance by the volume that it occupies:

$$\text{Density} = \frac{\text{weight of the substance in grams}}{\text{volume of the substance in cubic centimeters}}$$

Density is expressed in following units:

Grams per cubic centimeter g/cc or g/cm³

Grams per milliliter g/ml

Pounds per cubic foot lb/ft³

The density of water at 4°C is $1000 \text{ g/cm}^3 = 1000 \text{ g/ml}$; therefore, the terms milliliters and cubic centimeters are usually interchangeable. (However, in British system the density of water at 4°C = 62.4 lb/ft^3)

PROCEDURE

Determine the weight and volume of the substance, and divide the weight by the volume.

Regularly Shaped Solids

1. Weigh the object
2. Measure the object and obtain relevant dimension.
3. Calculate the volume using mathematical formulas for box, sphere or cylinder.
4. Divide the weight by volume.

Irregularly Shaped Solids

1. Weigh the object.
2. Determine the volume by water displacement (Fig. F-1):

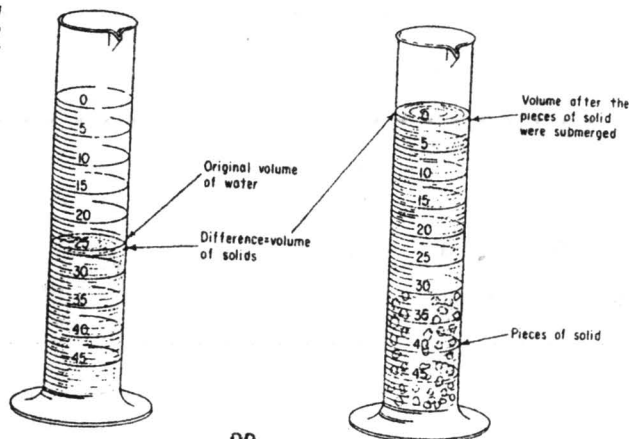
(a) Use a graduated cylinder containing a measured amount of water (original volume).

(b) Submerge the weighed solid completely in the cylinder containing the water and record the larger volume reading (final volume)

(c) Subtract the original volume from the final volume and obtain the volume of the object.

(d) Divide the weight of the object by the volume.

FIGURE F-1
A method of determining the volume of an irregular solid.



Liquids

1. Use a calibrated-volume liquid container, fitted with thermometer.
2. Weigh the empty container.
3. Weigh the filled container and record the temperature.
4. Obtain the weight by subtraction.
5. Divide the weight by the volume of the calibrated container.

SPECIFIC GRAVITY

Pycnometer

Specific gravity is numerically the same value as the density; it is the weight of the substance divided by the weight of an equal volume of water. Specific gravity is only a number; there are no units to it.

$$\text{Specific gravity} = \frac{\text{weight of given volume of substance}}{\text{weight of same volume of water}}$$

The water standard is taken at 4°C (density of water is 1000g/cm³).

PROCEDURE

1. Weigh a pycnometer (Fig.F-2), a calibrated-volume ground_glass fitting with closure and thermometer.
2. Weigh the pycnometer filled with water. Subtract the weight obtained in step 1 from this weight. This gives the weight of the water.
3. Weigh the pycnometer filled with the unknown liquid. Subtract the weight obtained in step 1 from this weight. This gives the weight of an equal volume of liquid.

4. Divide the weight obtained in step 3 by the weight obtained in step 2 to get the specific gravity. (Weights should be taken at the same temperature).

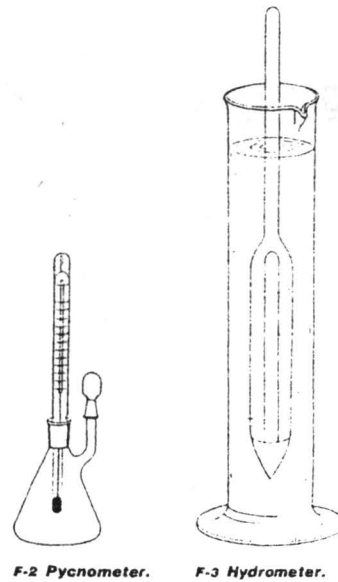
Hydrometer

A hydrometer is a floating glass container, weighted at the bottom, having a slender stem calibrated to a standard (Fig. F-3). The depth to which the container will sink in a liquid is a measure of the specific gravity of the liquid. Specific gravity is read directly from the calibrated scale on the stem of the container.

Hydrometers are calibrated in specific gravities (the weight of a liquid divided by the weight of an equal volume of water taken at certain temperatures, such as 60°F or 70°F) or in arbitrary units as degrees Baume (Be), degrees A.P.I. (American Petroleum Institute), or degrees Brix (also called Fisher).

FIGURE F-2
FIGURE F-3

Fig.F-2, F-3



Hydrometer readings given in specific gravities can be converted to these units by the following formulas:

Liquids lighter than water:

$$^{\circ}Be = \frac{140}{sp. gr. 60^{\circ} F / 60^{\circ} F} - 130$$

$$^{\circ}A.P.I. = \frac{141.5}{sp. gr. 70^{\circ} F / 60^{\circ} F} - 131.5$$

$$^{\circ}Brix = \frac{400}{sp. gr. 60^{\circ} F / 60^{\circ} F} - 400$$

Liquids heavier than water:

$$^{\circ}Be = 145 - \frac{145}{sp. gr. 60^{\circ} F / 60^{\circ} F}$$

$^{\circ}Brix$ = arbitrarily graduated so that $1^{\circ}Brix=1\%$ sugar in solution

See Table F-1 for conversion of degrees Baume to specific gravity

TABLE F-1

Conversion Tble, Degrees Baume (American)-Specific Gravity at 60°F (15.55°C)

For Liquids lighter than water, degrees Baume=140/sp.gr - 130

$^{\circ}Be$	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
10	1.000	0.993	0.986	0.979	0.972	0.966	0.959	0.952	0.946	0.940
20	0.933	0.927	0.921	0.915	0.909	0.903	0.897	0.892	0.886	0.880
30	0.875	0.870	0.864	0.859	0.854	0.848	0.843	0.838	0.833	0.828
40	0.824	0.819	0.814	0.809	0.804	0.800	0.795	0.791	0.786	0.782
50	0.778	0.773	0.769	0.765	0.761	0.757	0.753	0.749	0.745	0.741
60	0.737	0.733	0.729	0.725	0.722	0.718	0.714	0.711	0.707	0.704
70	0.700	0.696	0.693	0.690	0.686	0.683	0.680	0.676	0.673	0.670
80	0.667	0.664	0.660	0.657	0.654	0.651	0.648	0.645	0.642	0.639

For liquids heavier than water, degrees Baume=145-145/sp.gr.

°Be	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
0	1.000	1.007	1.014	1.021	1.028	1.036	1.043	1.051	1.058	1.066
10	1.074	1.082	1.090	1.098	1.107	1.115	1.124	1.133	1.142	1.151
20	1.160	1.169	1.179	1.188	1.198	1.208	1.218	1.229	1.239	1.250
30	1.261	1.272	1.283	1.295	1.306	1.318	1.330	1.343	1.355	1.368
40	1.381	1.394	1.408	1.422	1.436	1.450	1.465	1.480	1.495	1.510
50	1.526	1.543	1.559	1.576	1.593	1.611	1.629	1.648	1.667	1.686
60	1.706	1.726	1.747	1.768	1.790	1.812	1.835	1.859	1.883	1.908

MELTING POINTS

The melting point of a crystalline solid is the temperature at which the solid substance begins to change into a liquid. Pure organic compounds have sharp melting points. Contaminants usually degrade the melting point and extend it over a long range. The temperature of the melting point and sharpness of the melting point are criteria of purity. The melting-point range is the temperature range at which crystals begin to collapse and melt and the temperature when the material becomes completely liquid.

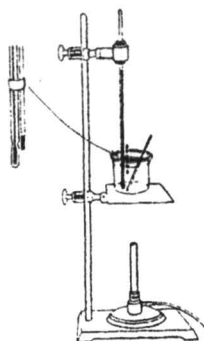
PROCEDURE

Determine melting points by introducing a tiny amount of the compound into a small capillary tube attached to the stem of a thermometer which is centered in a heating bath.

SETUP OF APPARATUS

1. Obtain commercially available capillary tubes or make them by drawing out 12mm soft glass tubing. (Refer to laboratory procedures, making capillary tubes).
2. Fill the capillary tube with powdered compound to a height of 3 to 4 mm.
 - (a) Scrape the powder into a pile.
 - (b) Push the powder into the open end of the capillary tube.
 - (c) Shake the powder to the bottom of the tube by tamping lightly against the desk top or by gently scraping the tube with a file. Pack tightly.
3. Attach the capillary to the thermometer with a rubber band and immerse in an oil bath.
4. Heat the oil bath quickly to about 5°C below the melting point, stirring continuously.
5. Now heat slowly; raise the temperature about 1°C/min, mixing continuously.
6. Record the temperature when fusion is observed and record the melting-point range.
7. Discard the capillary after the determination has been made.

FIGURE F-4
Laboratory setup.



CAUTION

Never determine the melting point by observing the temperature at which the melted substance solidifies when the bath cools. The substance may have decomposed, forming a new substance with a different melting point, or the substance may have changed into another crystalline form having a different melting point. Multiple melting points may be run simultaneously if their melting points differ 10°C. Identify tubes to avoid mistakes.

Substances which sublime: Seal both ends of the capillary tube.

Substances which tend to decompose: insert the capillary in the heating bath when the temperature is only a few degrees below the melting point.

Electrical Melting-point Apparatus

This is a metal block in which a thermometer is inserted into a close-fitting hole bored into the block, which is heated by electricity controlled by a variable transformer or a rheostat (Fig. F-5).

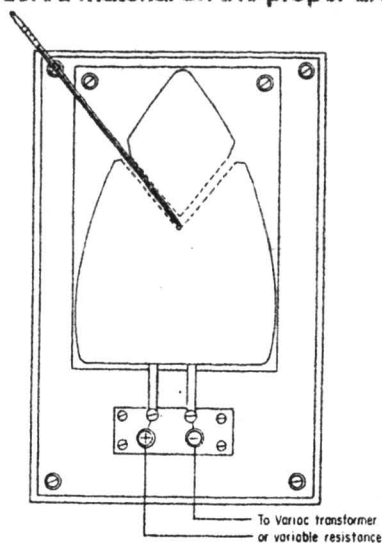
PRINCIPLE

The metal block is constructed so that the temperature of the thermometer indicates the temperature of the metal block on which the solid melts.

PROCEDURE

1. Clean the surface of the block.
2. Place a very small quantity of finely powdered material on the proper area.

Fig.F5, F-6



F-5 Electrical melting-point apparatus.



F-6 Separatory funnel for extraction.

3. Follow the heating procedure above.
4. When the determination is complete, turn off the electricity.
5. Multiple melting points may be determined simultaneously.

EXTRACTION

Extraction methods involve the use of two nonmiscible (immiscible) solvents and a solute which is soluble in each. Immiscible solvents are incapable of mixing with each other to attain homogeneity. They will separate each other into separate phases, such as oil and water. Miscible solvents are capable of being mixed in any ratio without separation into two phases, such as methyl alcohol and water.

Use extraction procedures to separate, purify, and analyze. Solvents usually involve water and an immiscible organic solvent such as the following:

- Diethyl ether
- Benzene
- Chloroform
- Petroleum ether
- Ligroin
- Ethylene dichloride

If two organic solvents are being used, they must be immiscible, or insoluble, in each other. The solubility of the solute in the solvent determines the selection of that solvent. The ease of removal of the solvent from the solute also is a factor in the choice of the extraction solvent.

EQUIPEMENT

Separatory funnel, solvent is extracted with another solvent which is immiscible with that solvent. The solute must be soluble in both solvents. Multiple extractions with smaller portions of the extractions with smaller portions of the extraction solvent are more effective than one extraction with a large volume.

PROCEDURE FOR HIGHER-DENSITY EXTRACTION SOLVENT

1. Use a clean separatory funnel (Fig.F-6), lubricating the barrel and plug of the funnel with a suitable lubricating. (Refer to procedures: lubrication of stopcock).
2. Pour the solution to be extracted into the funnel, which should be at least twice the total volume of the solution and the extraction solvent.
3. Pour in the extraction solvent.

4. Shake the funnel gently.
5. Invert the funnel and open the stopcock slowly to relieve the pressure built up.
6. Close the stopcock while the funnel is inverted and shake again.
7. Repeat steps 5 and 6.
8. Place the funnel in a ring-stand support and allow the two layers of liquid to separate. Remove stopper closure.
9. Open the stopcock slowly and drain off the bottom layer.
10. Repeat operations starting at step 3 with fresh extraction solvent as many times as desired.
11. Combine the lower layers which have been drawn off.

NOTE: The choice of extraction solvent determines whether the solute remains in the separatory funnel or is in the solvent which is drawn off. The solvent which has the greater density will be the bottom layer. Thus the less dense extraction solvent remains in the separatory funnel and more dense extraction solvent is drawn off.

The extraction solvent and the solute which it now contains are now processed to recover the solute wanted and, if practical, to reclaim the extraction solvent for economy reasons. (Refer to Fig.D-34e or procedures: evaporation of liquids).

Solvent Considerations

Like substances tend to dissolve like substances:

- Organic solvents tend to dissolve organic solvents
- Water tends to dissolve inorganic compounds and salts of organic acids and bases
- Organic acids, soluble in organic solvents can be extracted into water solutions by using bases (NaOH, Na₂CO₃, or NaHCO₃): (1) The base neutralizes the organic acid, converting it to a salt. (2) The salt, soluble in water, is extracted by the water.

NOTE: *Diethyl ether* is a commonly used organic solvent because:

1. It is easily removed from solutes because of its high volatility.
2. It is cheap.
3. It is an excellent high-power solvent.

However, it has disadvantages:

1. It is a fire hazard.
2. It has high solubility in water.
3. It has poor recovery because of high volatility.
4. It is an explosion hazard because peroxides form.

Emulsion Problems

Emulsions may form when aqueous solutions are extracted with organic solvents; therefore, the two separate and distinct layers do not form. Emulsions may be broken by:

1. Adding some NaCl.
2. Adding a few drops of silicone defoamer.
3. Adding a few drops of dilute acid (if permissible).
4. Drawing a stream of air over the surface with a tube connected to a water pump.
5. Placing the emulsion in a suitable centrifuge tube and centrifuging until the emulsion is broken. (Refer to procedures: centrifuges).

FILTRATION

Efficient filtration depends on the correct selection of the method to be used, the various pieces of apparatus available, the utilization of the filter medium most appropriate for the particular process, and the use of correct laboratory technique in performing the manipulations involved.

Filtration is a process by which a liquid is separated from a solid by pouring the liquid through a sieve, usually filter paper. The liquid passes through the paper, but the solid is retained. Gravity is employed to cause the liquid to pass through the paper. More rapid methods utilizing vacuum to hasten the separation are recommended.

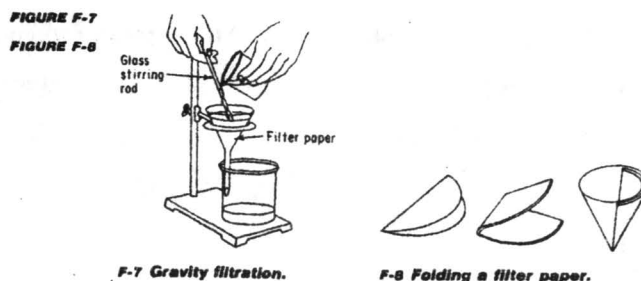
It may be necessary to filter materials from highly caustic or acidic media or under highly reactive conditions. A variety of filter media exist from which a selection may be made which best fits the particular objectives and conditions of a given process. The most common filters are:

- Paper
- Fiber-glass papers or mats

- Gooch crucibles
- Sintered-glass crucibles and funnels
- Porous porcelain crucibles
- Monroe crucibles
- All are available in various porosities.

Types of Filtration

There are two general methods of filtration: gravity and vacuum filtration. Gravity filtration is a procedure in which the filtrate passes through the filter medium under the force gravity and capillary attraction between the liquid and the funnel stem (Fig. F-7).



Vacuum filtration is a procedure in which a pressure differential is maintained across the filter medium by evacuating the air below the filter paper. Vacuum filtration provides a force on the solution in addition to that of gravity and increases the rate of filtration (see Fig. F-19).

Gravity Filtration

Gravity filtration using filter paper and the conical funnel is the most common procedure for filtration. The procedure is slow, but it is highly favored for gravimetric analysis over the more rapid vacuum filtration because there is better retention of fine particles of precipitate and less rupturing or tearing of the paper. Gravity filtration is generally the fastest and most preferred method for filtering gelatinous precipitates because these precipitates tend to clog and pack the pores of the filtering medium much more readily under the additional force supplied during a vacuum filtration.

Avoid the accumulation of precipitate on the filter paper at early stages of the filtration process. This is necessary for rapid filtering since the precipitate will be drawn into the pores of the paper where it will impede the passage of solution and retard the rate of filtration. The

precipitate should be allowed to settle to the bottom of the breaker before the filtration begins. The supernatant-liquid phase, free of most of the suspended precipitate, is then poured into the filter, leaving the precipitated solid essentially undisturbed. The bulk of precipitate is not added until the last stages of filtration, as part of the washing process (see Fig. F-16).

NOTE: Many precipitates will spread over a wetted surface against the force of gravity; this is known as creeping. To avoid loss of precipitate because of this phenomenon, a paper filter or filtering crucible is never filled more than three-quarters full at any time.

Optimum filtering speed is achieved in gravity filtration by proper folding and positioning of the paper in the funnel (Fig. F-8). If maximum speed is to be maintained, observe the following condition in gravity filtration:

1. Take maximum advantage of capillary attraction to assist in drawing the liquid phase through the paper. Use a long stem on the funnel; maintain a continuous column of water from the tip of the funnel stem to the undersurface of the paper. The tip of the funnel should touch the side of the vessel which receives the filtrate, which aids the filtration and minimises the loss of filtrate due to splashing. Maintain an airtight seal between the glass surface of the funnel and the top edge of the paper (Fig. F-9).

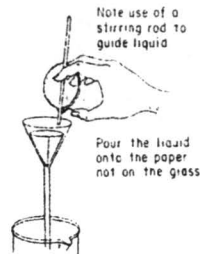
Fig.F-9, F-10, F-11



F-9 Alternative method of folding filter paper. Steps in folding filter paper for use in filtering with a regular funnel. The second fold is not exactly at a right angle. Note tear.



F-10 Seating of a filter paper.



F-11 Filtration.

2. Expose as much of the paper as possible to provide free flow of liquid through the paper. Fold the paper so that it does not coincide exactly with the walls of the funnel, permitting liquid to flow between the paper and the glass. Maintain an airtight seal between the top of the filter paper and the funnel (Fig. F-10).

3. Add solution until the paper cone is three-quarters filled. Never fill the cone completely. This offers protection against loss of precipitate due to creeping and overflow. It also provides an area near the top of the paper which is free of precipitate. By holding this "clean" portion, you can remove the cone from the funnel and fold it for ignition without loss or contamination (Fig. F-11).

Selection of the Filter Paper

There are several varieties or grades of filter paper for special purposes, qualitative grades, low-ash or ashless quantitative grades, hardened grades, and glass-fiber papers. For a given filtration, you must select the proper filter paper with regard to porosity. The choice of method to be used - gravity or vacuum filtration - depends upon the following (see Table F-2):

1. The nature of the precipitate
2. The time to be spend on the filtration
3. The degree to which it is necessary to retain all the precipitate
4. The extent to which one can tolerate the contamination of the precipitate with the filtrate

filtrate

The main objective is to carry out the filtration as rapidly as possible, retaining the precipitate in the paper with a minimum loss.

Table F-2 Commonly Used Filter Papers

W	SS	RA	Porosity	Speed	Use for
Qualitative- or regular-grade papers					
4	604	202	Coarse	Very rapid	Gelatinous precipitates
1	595	271	Medium	Medium	Ordinary crystalline precipitates
3	602	201	Medium	Slow	Fine precipitates; used with buchner funnels
Quantitative-grade papers (less than 0.1mg ash)					
41	589 blue ribbon	...	Coarse	Very rapid	Gelatinous precipitates
40 ribbon	589 white	...	Medium	Rapid	Ordinary crystalline precipitates
42	589 black ribbon	...	Fine	Slow	Finest crystalline precipitates

It is advisable to carry out precipitations in a beaker whenever possible because it has a pour spout to facilitate of liquids without loss.

Qualitative-grade papers will leave an appreciable amount of ash upon ignition (of order of 0.7 to 1 mg from a 9-cm circle) and therefore unsuitable for applications in quantitative analysis where precipitates are to be ignited on the paper and weighed. They are widely used

for clarifying solutions, filtration of precipitates which will later be dissolved, and general nonquantitative separations of precipitates from solution.

Low-ash or ashless quantitative-grade papers can be ignited without leaving an ash. The residue left by a 11-cm circle of a low-ash paper may be as low as 0.06mg; an ashless-grade paper typically leaves 00.09mg or less from an 11-cm circle. In most analytical procedures, this small weight can be considered negligible.

Hardened-grade papers are designed for use in vacuum filtrations and are processed to have great wet strength and hard lintless surfaces. They are available in low-ash and ashless as well as regular grades.

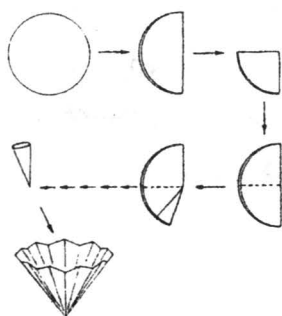
Fiber-glass papers are produced from very fine borosilicate glass, used in Gooch, buchner, or similar filtering apparatus to give a combination of very fine retention, very rapid filtration, and inertness to action of most reagents to an extent not found in any cellulose paper.

All grades of filter paper are manufactured in a variety of sizes and in several degrees of porosity. Select the proper porosity for a given precipitate. If too coarse a paper is used, very small crystals may pass through, while use of too fine a paper will make filtration unduly slow.

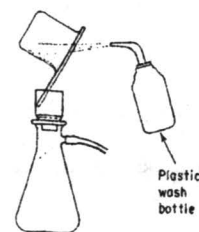
NOTE: Solutions of very volatile liquids, ether, and hot solutions are not filtered very conveniently with suction. The suction may cause excessive evaporation of the solvent, which cools the solution enough to cause precipitation of the solute.

Fluting the filter paper (Fig.F-12) increases the rate of filtration. Fluting makes more of the surface of the filter paper available for filtration. Fold the paper in half and then fold this half into eight equal sections, like an accordion. The fluted filter paper is then opened and placed in a funnel

(Fig.F-13).



F-13 A fluted filter paper in a funnel.



F-14 Washing the precipitate into the crucible with a squeeze bottle

Wash Bottles

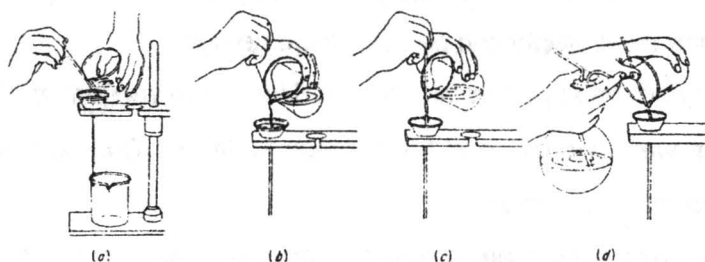
F-12 Folding a fluted filter.

Two types are generally used: (1) the Florence flask (see Fig.B-18), which operates on breath pressure (the stream of water is directed by moving the tip with the fingers) and (2) the plastic squeeze bottle (Fig.F-14).

Manipulations Associated with the Filtration Process

Whether one uses gravity or vacuum filtration, three operations must be performed: decantation, washing, and transfer (Fig.F-15).

FIGURE F-15
The filtering operation showing techniques for decantation and transfer of precipitates.



Decantation

When a solid readily settles to the bottom of a liquid and shows little or no tendency to remain suspended, it can be separated easily from the liquid by carefully pouring off the liquid so that no solid is carried along. This process is called decantation. To decant a liquid from a solid:

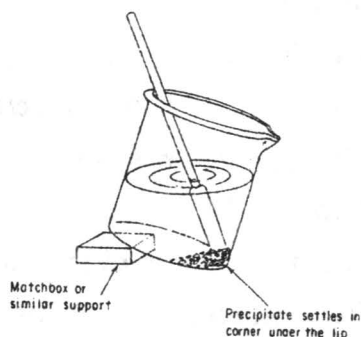
1. Hold the container (beaker, test tube, etc.) which has the mixture in it in the right hand and have a glass stirring rod in the left.
2. Incline the beaker until the liquid has almost reached the lip.
3. Touch the center of the glass rod to the lip of the beaker and the end of the rod to the side of the container into which you wish to pour the liquid.
4. Continue the inclination of the beaker until the liquid touches the glass rod and flows down it into the second container. The glass rod enables you to pour the liquid from the beaker slowly enough that the solid is not carried along and also prevents the liquid from running back along the outside of the beaker from which it is being poured.

Washing

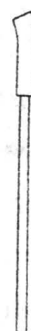
The objective of washing is to remove the excess liquid phase and any soluble impurities which may be present in the precipitate. Use a solvent which is miscible with the liquid phase but does not dissolve an appreciable amount of the precipitate.

Solids can be washed in the beaker after decantation of the supernatant-liquid phase. Add a small amount of the wash liquid and thoroughly mix it with the precipitate. Allow the solid to settle. Decant the wash liquid through the filter. Allow the precipitate to settle, with the beaker tilted slightly so that the solid accumulates in the corner of the beaker under the spout (Fig.F-16). Repeat this procedure several times.

FIGURE F-16
FIGURE F-17

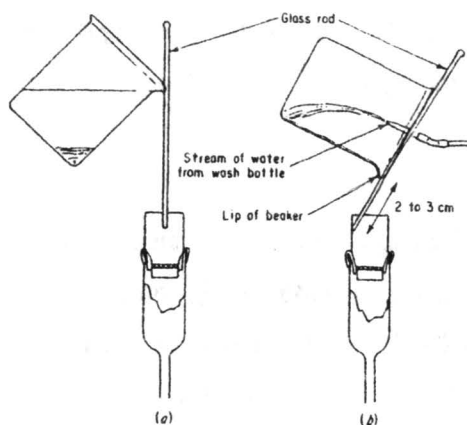


F-16 Supporting a beaker in a tilted position to allow the precipitate to settle prior to decantation.



F-17 Stirring rod with rubber policeman.

FIGURE F-18



(a) Filtration by decantation. (b) Transfer of last portions of precipitate.

Several washings with the small volumes of liquid are more effective in removing soluble contaminants than a single washing using the total volume.

Transfer of the Precipitate

Remove the bulk of the precipitate from the beaker to the filter by using a stream of wash liquid from a wash bottle. Use the stirring rod (Fig.F-17) to direct the flow of liquid into the filtering medium. The last traces of precipitate are removed from the walls of the beaker by

scrubbing the surfaces with a rubber policeman attached to the stirring rod. All solids collected are added to the main portion in the filter paper (Fig.F-18). If the precipitate is to be ignited, use small fragments of ashless paper to scrub the sides of the beakers; then add these fragments to the bulk of the precipitate in the filter with the collected solid.

Aging and Digestion of Precipitates

Freshly formed precipitates are left in contact with the supernatant for a period of time and are aged. There are frequently changes in the surface: a decrease in the total surface area or removal of strained and imperfect regions. Both effects are due to recrystallization because small particles tend to be more soluble than large ones, and ions located in imperfect and strained regions are less tightly held than normal and therefore tend to return to the solution. On aging they are deposited again in more perfect fashion. These changes cause a beneficial decrease in adsorbed foreign ions and more filterable but also a purer precipitate.

Increasing the temperature greatly enhances digestion. The precipitate is kept in contact with the supernatant at a temperature near boiling for a period of time. Flocculated colloids usually undergo rapid aging, particularly on digestion, and a major portion of the adsorbed contaminants may often be removed.

Vacuum filtration

A typical setup for carrying out a vacuum filtration is shown in Fig. F-19. The funnel or crucible is fitted to a suction flask. The side arm of the flask is connected to a source of vacuum such as a water aspirator. A trap bottle is inserted between the flask and the source of vacuum. When the vacuum is turned on, the pressure difference between the filter medium and atmosphere helps to speed up the filtration process.

CAUTION

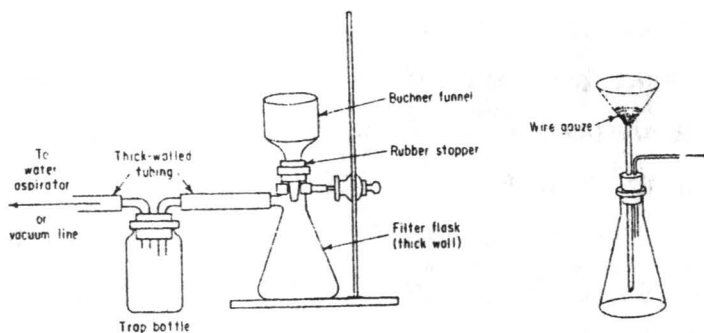
1. Wear glasses when the assembly is under reduced pressure.
2. Be careful that the liquid level or "safety trap" bottle is never as high as the inlet tubes.

Vacuum filtration is advantageous when the precipitate is crystalline. It should not be employed for gelatinous precipitates because the added pressure forces the particles into the pores of the filter medium, clogging them so much that no liquid can pass through.

Vacuum filtration can be used with filter papers as well as with the various crucibles. The common conical funnel paper is easily ruptured at the apex of the cone when under the added

stress of the vacuum. To strenght tthe cone at the apex, a small metal liner is often inserted (see Fig. F-20).

FIGURE F-19
FIGURE F-20



F-19 Complete vacuum-filtration assembly using a Buchner funnel.

F-20 Wire-gauze funnel.

Buchner funnels are often used for vacuum filtrations. They are not conical in shape but have a flat, perforated bottom. A filter-paper circle of a diameter sufficient to cover the perforation is placed on the flat bottom, moistened, and tightly sealed against the bottom by applying a slight vacuum.

When a buchner funnel is used, the precipitate is allowed to settle and the liquid phase is first decanted by pouring down a stirring rod aimed at the center of the filter paper, applying only a light vacuum until sufficient solid has built up over the paper to protect from breaking. The vacuum is then increased and remainder of the precipitate is added.

The precipitate ccan be washed by adding small amounts of wash liquid over the surface of the precipitate, allowing the liquid to be drawn through the solid slowly with the vacuum. Precipitation cannot be dried or ignited and weighed in buchner funnels.

Buchner funnels are not applicable for gravimetric analysis because they do permit rapid filtration of large amounts of cristallyne precipitates. They are extremely useful in synthetic works, however. Precipitates can be air-dried by following them to stand in the funnel and drawing a current of air from the room through the precipitate with the vacuum pump or water aspirator. Wash the last traces of water from precipitates with a suitable water-miscible, volatile solvent.

Sintered-glass Crucibles

Glass crucibles employ fitted-glass disks sealed permanently into the bottom and are available in a variety of porosities. With care they can be used for quantitative analyses requiring ignition to a temperature as high as 500°C.

Wire-gauze Conical Funnel

When a buchner funnel and filter flask are not available, The apparatus can be constructed and used for vacuum filtration. A small piece of wire gauze is bent into the form of a cone that fits into the funnel (Fig.F-20). The filter paper is then wetted and pressed against the side of the funnel to make a good seal with the glass. It may be necessary to use a double thickness of filter paper to prevent tearing. Wrap the flask with a towel before applying vacuum.

Porous Porcelain and Monroe Crucibles

Porcelain crucibles have porous ceramic disks permanently sealed in the bottom. They are used like sintered-glass crucibles, except they may be ignited at extremely high temperatures. The monroe crucible is made of platinum, with a burnished platinum mat serving as the filter medium. Advantages of these crucibles are:

1. Their high degree of chemical inertness
2. Their ability to withstand extremely high ignition temperatures

The Gooch Crucible

The gooch crucible is a porcelain thimble with a perforated base. The filtering medium is either a mat of asbestos or a fiber-glass paper disk. They are prepared by pouring a slurry of asbestos fiber suspended in water.

Asbestos mats permit precipitates to be quantitatively ignited to extremely high temperatures without danger of reduction by carbon. With fiber-glass mats, ignition temperatures above 500°C are not possible. Both filter media are resistant to attack by most chemicals.

The filter media used in these crucibles are quite fragile. Exercise care when adding the liquid, so that the asbestos or glass paper will not be disturbed or broken, allowing the precipitate to pass through. Use a small, perforated porcelain disk over the asbestos mat or glass paper to deflect any stream of liquid poured into the crucible.

The Hirsch Funnel and Other Funnels

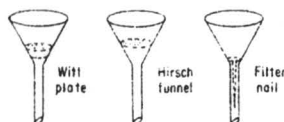
Hirsch funnels (Fig.F-21) are usually made of porcelain. The inside bottom of the funnel is a plate with holes in it which supports the filter paper. Buchner and Hirsch funnels can also be obtained in glass with sintered-glass disks. Other funnels are the Witt and filter nail (See Fig.F-22).

FIGURE F-21

FIGURE F-22

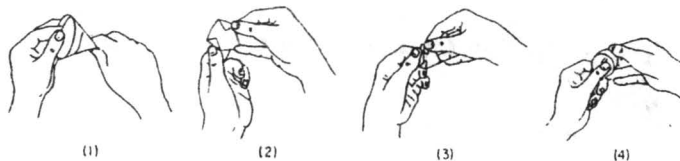


F-21 Suction filtration with a Hirsch funnel.



F-22 The Hirsch and other funnels for collecting small quantities of solids.

FIGURE F-23
Method for transferring a filter paper and precipitate to a crucible.



A rubber ring forms the seal between the funnel and the filter flask, which is connected to the vacuum line or to the aspirator. (A rubber stopper or cork can also be used instead of the rubber ring to fit the funnel to the filter flask).

Filtration and Ignition

Preparation of Crucibles

All crucibles employed in converting a precipitate into a form suitable for weighing must maintain a substantially constant weight throughout the drying or ignition process; you must demonstrate that this condition applies before you start.

1. Inspect each crucible for defects, especially where the crucible has previously been subjected to high temperatures.

2. Place the porcelain crucible upright on hard surface and gently tap with a pencil. You should hear a clear ringing tone indicating an intact crucible. A dull sound is characteristic of one that cracked and should be discarded.

3. Clean the crucible thoroughly. Filtering crucibles are conveniently cleaned by backwashing with suction.

4. Bring the crucible to constant weight, using the same heating cycle as will be required for the precipitate. Agreement within 0.2 mg between consecutive weighings is considered as constant weight.

Preparation of a Filter Paper

Fold a filter paper and seat it in a funnel. Fold exactly in half; Then make the second fold that the corners fail to coincide for about 1/8 in. in dimension. Tear off a small triangular sectionn from the short corner to permit a better seating of the filter in the funnel. Open the paper so that a cone is formed and then seat it gently in the funnel with the aid of water from wash bottle. There should be no leakage of air between paper and funnel, and stem of the funnel should be filled with an unbroken column of liquid, a condition that markedly increases the rate of filtration.

Transfer of Paper and Precipitate to Crucible

When filtration and washing are completed, transfer the filter paper and its contents from the funnel to a tared crucible (Fig.F-23). Use considerablecare in performing this operation. The danger of tearing can be reduced considerably if partial drying occurs prior to transfer from the funnel. First, flatten the conne along its upper edge; then fold the corners inward. Next, fold the top over. Finally, ease the paper and contents into the crucible so that the bulk of the precipitate is near the bottom.

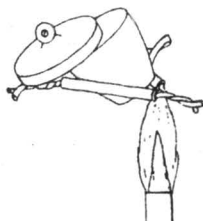
Ashing of a Filter Paper

If a heat lamp is available, place the crucible on a clean, nonreactive surface; an asbestos pad covered with a layer of aluminium foil is satisfactory. Then position the lamp about 1/2 in. from the top of the crucible and turn it on. Charring of the paper will take place without further intervention; the process is considerably accelerated if the paper can be moistened with no more than one drop of strong ammonium nitrate solution. Removal of remaining carbon is accomplished with a burner.

Considerably more attention must be paid the process when a burner is employed to ash a filter paper. Since the burner can produce much higher temperatures, the danger exists of expelling moisture so rapidly in the initial stages of heating that mechanical loss of the precipitate occurs. A similar possibility arises if the paper is allowed to flame. Finally, as long as carbon is present, there is also the possibility of chemical reduction of the precipitate; this is a serious problem where reoxidation following ashing of the paper is not convenient.

In order to minimize these difficulties, the crucible is placed as illustrated in Fig. F-24. The tilted position of the crucible allows for the ready access of air. A clean crucible cover should be located nearby, ready for use if necessary.

FIGURE F-24
Ignition of a precipitate
with access to air.



NOTE: Always place the hot cover or crucible on a wire gauze—never directly on the desk top. The cold surface may crack the crucibles, and dirt, paint, etc., are easily fused into the porcelain, thus changing the weight.

Heating is then commenced with a small burner flame. This is gradually increased as moisture is evolved and the paper begins to char. The smoke that is given off serves as a guide to the intensity of heating that can be safely tolerated. Normally it will appear to come off in thin wisps. If the volume of smoke emitted increases rapidly, the burner should be removed temporarily; this condition indicates that the paper is about to flash. If, despite precautions, a flame does appear, it should be snuffed out immediately with the crucible cover. (The cover may become discolored owing to the condensation of carbonaceous products; these must ultimately be removed by ignition so that the absence of entrained particles of precipitate can be confirmed.) Finally, when no further smoking can be detected, the residual carbon is removed by gradually lowering the crucible into the full flame of the burner. Strong heating, as necessary, can then be undertaken. Care must be exercised to avoid heating the crucible in the reducing portion of the flame.

Summary

1. Oxidize the paper completely to CO_2 and H_2O .
2. Arrange the crucible according to Fig.F-24.
3. Increase the temperature slowly until all black carbon residue is burned away.
4. Position the burner so that the reducing gases of the flame are not deflected into the crucible.
5. Reposition the crucible to expose fresh portions to the highest temperature of the burner.

6. Final ignition converts the precipitate to the anhydrous oxide: (a) Remove the crucible cover. (b) Ignite at red heat for 30 min with a fisher, meeker, or other high-temperature burner, or a muffle furnace.

7. The foregoing procedure must precede the final ignition.

Platinum

Platinum is useful in crucibles for specialized purposes. The chemically valuable properties of this soft, dense metal include its resistance to attack by most mineral acids, including hydrofluoric acid; its inertness with respect to many molten salts; its resistance to oxidation, even at elevated temperatures; and its very high melting point. With respect to limitations, platinum is readily dissolved on contact with aqua regia and mixtures of chlorides and oxidizing agents generally. At elevated temperatures, it is also dissolved by fused alkali oxides, peroxides, and to some extent hydroxides. When heated strongly, it readily alloys with such metals as gold, silver, copper, bismuth, lead, and zinc. Because of this predilection toward alloy formation, contact between heated platinum and other metals or their readily reduced oxides must be avoided. Slow solution of platinum accompanies contact with fused nitrates, cyanides, alkali, and alkaline-earth chlorides at temperatures above 1000°C; bisulfates attack the metal slightly at temperatures above 700°C. Surface changes result from contact with ammonia, chlorine, and volatile chlorides, sulfur dioxide, and gases possessing a high percentage of carbon. At red heat, platinum is readily attacked by arsenic, antimony, and phosphorus, the metal being embrittled as consequence. A similar effect occurs upon high-temperature contact with selenium, tellurium, and to a lesser extent, sulfur and carbon. Finally, when heated in air for prolonged periods at temperatures greater than 1500°C, a significant loss in weight due to volatilization of the metal must be expected.

Rules Governing the Use of Platinumware

1. Use platinum equipment only in those applications which will not affect the metal. Where the nature of the system is in doubt, demonstrate the absence of potentially damaging components before committing platinumware to use.

2. Avoid violent changes in temperature; deformation of a platinum container can result if its contents expand upon cooling.

3. Supports made of clean, unglazed ceramic materials, fused silica, or platinum itself may be safely used in contact with incandescent platinum; tongs of nichrome or stainless steel may be employed only after the platinum has cooled below the point of incandescence.

4. Clean platinumware with an appropriate chemical agent immediately following use; recommended cleaning agents are hot chromic acid solution for removal of organic materials, boiling hydrochloric acid for removal of carbonates and basic oxides, and fused potassium bisulfate for the removal of silica, metals, and their oxides. A bright surface should be maintained by burnishing with sea sand.

5. Avoid heating platinum under reducing conditions, particularly in the presence of carbon. Specifically, (a) do not allow the reducing portion of the burner flame to contact a platinum surface, and (b) char filter papers under the mildest possible heating conditions and with free access of air.

PURIFICATION OF SOLIDS BY RECRYSTALLIZATION

Solids are purified by recrystallization by dissolving them in hot solvents, filtering the solution, and then allowing the crystals to form in the filtrate, with the impurities remaining in solution.

Use crystallizing procedures to purify substances from soluble impurities and decolorize off-colored substances. Suitable solvents should:

- Not react with the compound
- Form desirable well-formed crystals
- Be easily removed from the purified crystals
- Have high solvency for the substance at high temperatures and low solvency for substance at low temperatures
- Have high solvency for impurities

Common Solvents

Water-soluble Solvents

	Boiling point, °C
Acetone	56.5
Methanol	64.7
95% ethanol	78.1
Water	100

Water-insoluble Solvents

	Boiling point, °C
Diethyl ether	34.6
Petroleum ether	40-60
Chloroform	61.2
Ligroin	65-75
Carbon tetrachloride	76.7
Benzene	80.1

Solvents Pairs

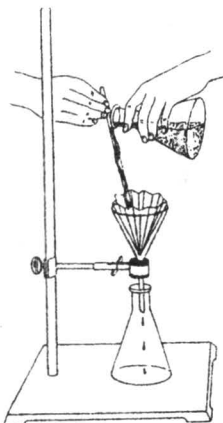
Miscible solvents of different solvent power yield a mixture which gives a usable solvent system.

Examples: Benzene-ligroin
Ether-acetone
Acetone-water
Ethanol-water
Methanol-water
Ether-petroleum ether

Decolorizing Substances

To remove colored contaminants, use finely powdered decolorizing charcoal, such as Norit, which adsorbs the contaminants. Soluble contaminants, not adsorbed, remain in solution in the mother-liquor filtrate (Fig.F-25).

FIGURE F-25
Recrystallization (decolorization filtration) experimental setup.



PROCEDURE: 1. Select the most desirable solvent; refer to solubility tables.

2. Place the solid substance in a suitably sized flask.

3. Add a determined volume of solvent (maximum two-thirds volume of vessel) and a few boiling stones.

NOTE: Add decolorizing carbon, 1 percent by weight of solid, if needed.

4. Boil until all solid has dissolved.

5. Filter as quickly as possible through a fluted filter in the funnel.

NOTE: Warm the filter funnel to prevent crystallization of hot filtrate in the funnel.

CAUTION

Observe all fire-hazard cautions because of volatile fumes.

6. Collect the filtrate in a beaker or flask; allow it to stand and cool. (a) Cool or chill rapidly in a cooling bath for small crystals. (b) Cool slowly to get large crystals.

7. Filter the crystals from the mother liquor in a gravity or suction filter. Further crystals can be obtained by evaporation and concentration of the mother liquor.

CAUTION

These crystals may be impure compared with the first crystallization.

8. Dry the crystals in a warm oven.

CAUTION

Be careful that the temperature of the oven is not excessive.

Problems Encountered

The solid sometimes fails to crystallize, and remains as an oil in the mother liquor. To induce crystallization:

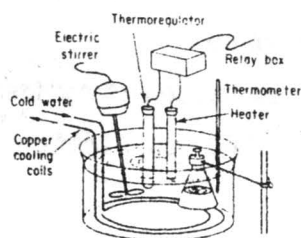
1. Scratch the oil against the side of the beaker with a glass stirring rod.
2. "Seed" the oil with some of the original material, finely powdered.
3. Cool the solution in a freezing mixture.
4. Add crumbs of dry ice.
5. Let stand for a long period.

CONSTANT-TEMPERATURE BATHS

PRINCIPLE

Investigations that require the maintenance of constant temperature for a procedure use constant-temperature baths (Fig.F-26).

FIGURE F-26
Constant-temperature bath.



APPARATUS AND PURPOSE

1. A sufficiently large glass or metal container is the bath.
2. Copper tubing through which cold water circulates, as required, is the cooling component.
3. Electric stirrers or circulating pumps give equalized heat distribution.
4. A thermoregulator permits temperature control to about 0.02°C .
5. The electric heater, activated by the thermoregulator, heats the solution as required.
6. A thermometer reads the temperature.
7. The temperature range is -15 to 70°C .
8. Oil is substituted for water for temperatures to 250°C .

COOLING BATHS

Various cooling baths for various laboratory operations requiring cold may be prepared as in Table F-3.

Thermos flasks or foam-insulated containers minimize heat transfer for maximum retention of cooling bath.

TABLE F-3

Temperature range	Components
0 to 5°C	Finely crushed ice-water slush
-5°C to -15°C	Finely crushed ice, 3 parts Sodium chloride, 1 part
-10° to -20°C	Ammonium chloride, 1 part Sodium nitrate, 1 part Ice, 1 part
-35° to -50°C	Finely crushed ice, 1 part CaCl ₂ ×6H ₂ O, 1 part
-72°C	Dry ice (CO ₂) in ethanol Dry ice (CO ₂) in acetone

CAUTION

Dry ice is dangerous. Handle with care! Do not handle with bare hands or fingers. It will cause severe cold burns.

DRYING ORGANIC LIQUIDS

Water can be removed from organic liquids and solutions by treating the liquids with a suitable drying agent to remove the water.

CAUTION

Select the drying agent which will not react with the compound or cause the compound to undergo any reaction but will only remove the water.

Classification

1. Those which form compounds with water of hydration (the hydrates can be regenerated to the anhydrous form by suitable heating to remove the water): Na_2CO_3 , Na_2SO_4 , anhydrous CaCl_2 , ZnCl_2 , NaOH , CaSO_4 , H_2SO_4 (95 percent), silica gel, CaO .

NOTE: Traces of acid residuals in wet organic-liquid reaction products are removed simultaneously with the water when basic drying agents are used: Na_2CO_3 , NaOH , $\text{Ca}(\text{OH})_2$.

2. Those which form new compounds by chemical reaction with water: metallic sodium, calcium carbide, phosphorus pentoxide.

CAUTION

These are extremely reactive and most efficient. Handle with care. They react with water to give sodium hydroxide, calcium hydroxide, and phosphoric acid, respectively.

Do not use where either the drying agent itself or the product that it forms will react with the compound or cause the compound itself to undergo reaction or rearrangement.

Use to dry saturated hydrocarbons, aromatic hydrocarbons, ethers.

CAUTION

The above compounds should not have functional groups such as OH and $-\text{COOH}$ which will react with the drying agent.

Do not dry alcohols with metallic sodium. Do not dry acids with NaOH or other basic drying agents. Do not dry amines (or basic compounds) with acidic drying agents.

PROCEDURE

1. Pour the organic liquid into a flask which can be stoppered. Add small portions of the drying agent, shaking the flask thoroughly after each addition. Add as much drying agent as is required.

2. Allow to stand overnight or for predetermined time.

3. Filter the solid hydrate from the liquid with a filter funnel and filter paper.

BOILING POINT OF LIQUIDS

PRINCIPLE

The boiling point of a liquid is the temperature at which the vapor pressure equals the pressure of the atmosphere on the surface of the liquid. (Refer to procedures: distillation of pure liquids)

EXPERIMENTAL SETUP

Ringstand, clamps, thermometer, burner.

PROCEDURE

1. Clamp a test tube containing 2 to 3 ml of the compound on a stand.

2. Suspend a thermometer with the bulb of the thermometer 1 in. above the liquid surface.

3. Apply heat gently until the condensation ring of the boiling liquid is 1 in. above the bulb of the thermometer.

4. Record the temperature when reading is constant.

Fig. F-27

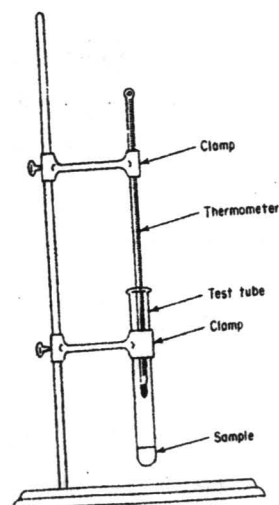
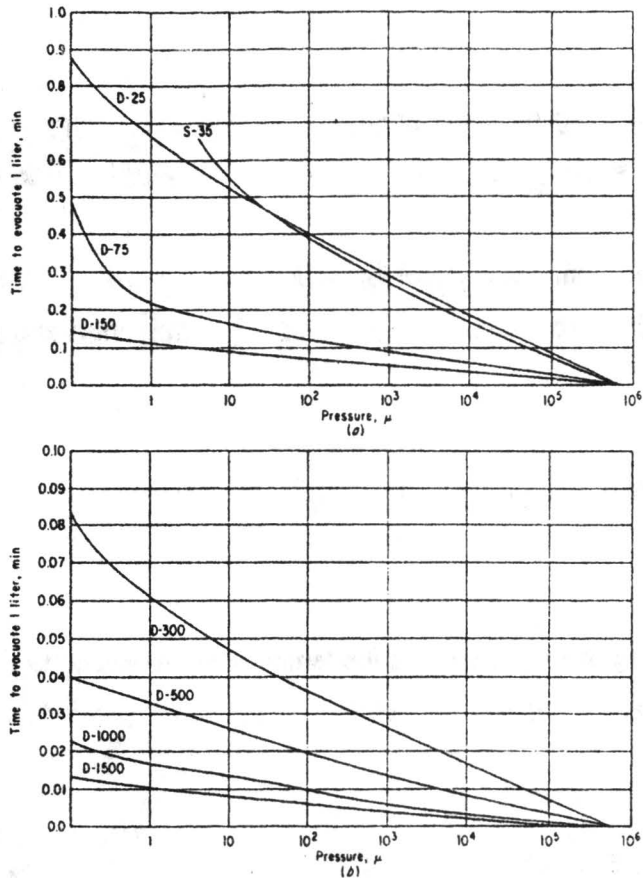


FIGURE F-28



(a) Pumps rated (free-air displacement) 25 to 150 liters/min. (b) Pumps rated (free-air displacement) 300 to 1,500 liters/min.

FIGURE F-29
Schematic of a single-stage regulator (typical construction).

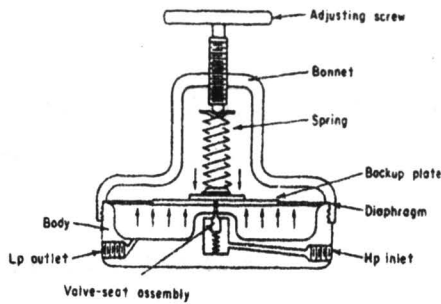
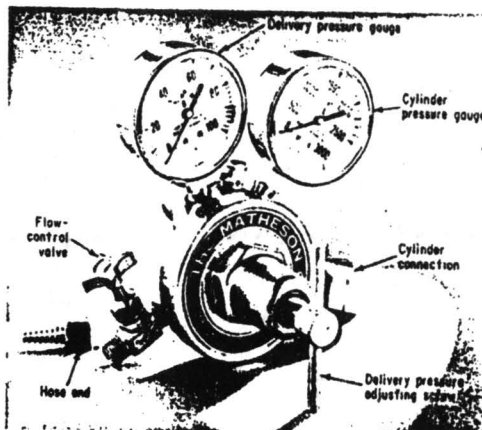


FIGURE F-30
Gas regulator.



SIMPLE DISTILLATION

Distillation is used to purify liquids and to separate one liquid from another. It is based on the difference in the physical property of liquids called volatility. Volatility is a general term used to describe the relative ease with which the molecules may escape from the surface of a pure liquid or a pure solid. The vapor pressure of a substance at a given temperature expresses this property.

1. A volatile substance is one which exerts a relatively high pressure at room temperature.

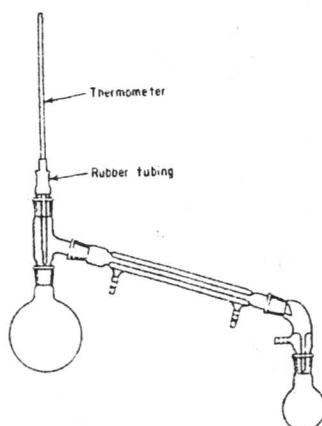
2. A nonvolatile substance is one which exerts a low vapor pressure.

The more volatile the substance, the greater its vapor pressure and the lower its boiling point. The less volatile a substance, the less its vapor pressure and the higher its boiling point.

Distillation is a process in which the liquid vaporized, recondensed, and collected in a receiver. The liquid which has not vaporized is called the residue. The condensed liquid, the condensed vapor, is called the condensate or distillate.

An experimental setup for simple distillation is shown in Figs.F-31 and F-32.

FIGURE F-31
Distillation, simple
atmospheric pressure.



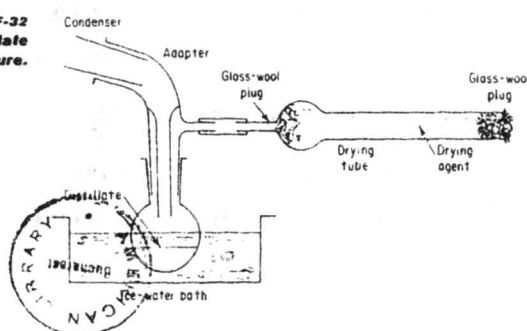
EQUIPEMENT

The glass equipment may be standard and require corks or may be ground-glass fitted joints.

POINTERS

1. The distilling flask should contain twice the volume of the liquid to be distilled.
2. The thermometer bulb should be slightly below the side-arm opening of the flask.
3. All glass-to-glass or glass-to-cork connections should be firm and tight.
4. The flask, condenser, and receiver should be clamped independently in their proper relative position on a steady base.
5. The upper outlet for the cooling exiting from condenser can point upward to keep the condenser full of water.

FIGURE F-32
Protecting the distillate from atmospheric moisture.

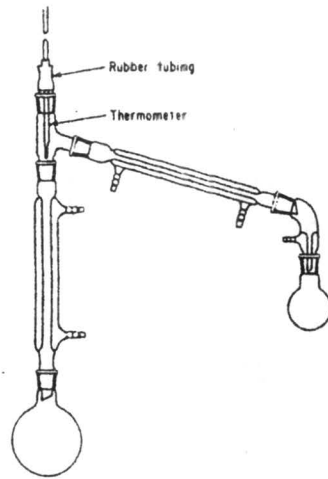


PROCEDURE

1. Pour the liquid into the distilling flask with a funnel which extends below the side arm.
2. Add a few boiling stones to prevent bumping.
3. Insert the thermometer.
4. Open the water valve for condenser cooling.
5. Heat the distilling flask until boiling begins; adjust the heat input so that the rate of distillate is a steady 2 to 3 drops per second.
6. Continue distillation until only a small residue remains. Do not distill to dryness.
7. Collect the distillate in the receiver.

Distillation of Pure Liquids

FIGURE F-33
Fractional distillation,
vacuum or atmospheric
pressure.



Column should be packed with stainless-steel sponge.

FIGURE F-34
Fractional distillation.

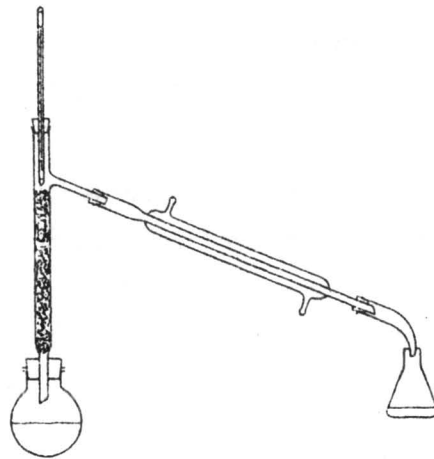
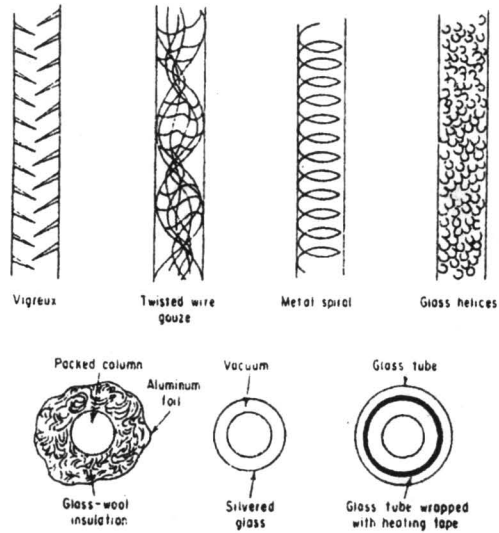


FIGURE F-35
Fractionating columns.



The experimental setup for pure liquids is the same as that shown in Figs. F-31 and F-32.

1. The composition of the condensate is necessarily the same as the original liquid and is the same as the residue.
2. The composition does not change.
3. The boiling temperature remains constant throughout the distillation.
4. Distillation establishes only the purity of the pure liquid and the boiling point.

Distillation of a Solution

This process effects the separation of the nonvolatile dissolved solids because they remain in the residue and the volatile liquid is distilled, condensed, and collected.

1. The temperature of the distilling liquid is constant throughout the distillate because it is pure.
2. The temperature of the boiling solution increases gradually throughout the distillation. The boiling solution becomes saturated with the nonvolatile solids.

AZEOTROPIC DISTILLATION

Azeotropic mixtures distill at constant temperature without change in composition.

NOTE: You cannot separate azeotropic mixtures by normal distillation methods.

EXAMPLES

95.5 percent ethyl alcohol (boiling point 78.1°C) composed of 95.5 percent by weight ethyl alcohol (boiling point 78.4°C) and 4.5 percent water (boiling point 100°C)

Mixture of 32.4 percent ethyl alcohol and 67.6 percent benzene (boiling point 80.1°C) boils at 68.2°C

Ternary azeotrope (boiling point 64.9°C) composed of 74.1 percent benzene, 18.5 percent ethyl alcohol, and 7.4 percent water

USES

Absolute ethyl alcohol can be obtained by distilling azeotropic 95.5 percent ethyl alcohol with benzene. The water is removed in the volatile azeotrope formed.

The procedure is the same as that described above under Distillation of Pure Liquids.

VACUUM DISTILLATION

PRINCIPLE

Many substances cannot be distilled satisfactorily at atmospheric pressure because they are sensitive to heat and decompose before the boiling point is reached. Distillation under reduced pressure, vacuum distillation, makes it possible to distill at much lower temperatures. The boiling point of the material is affected by the pressure in the system. The lower the pressure the lower the boiling point. The higher the pressure the higher the boiling point.

CAUTION

Glass equipment under reduced pressure may collapse. Use safety glasses and a safety shield.

The experimental setup is shown in Fig. F-36.

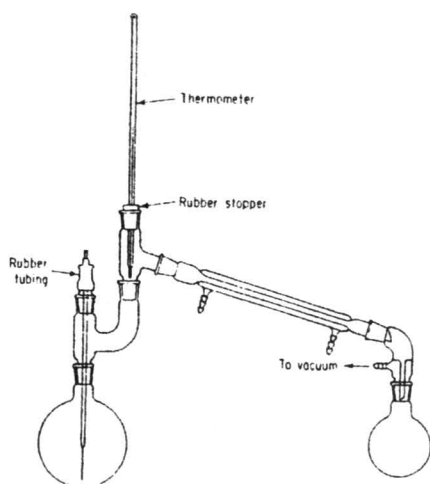
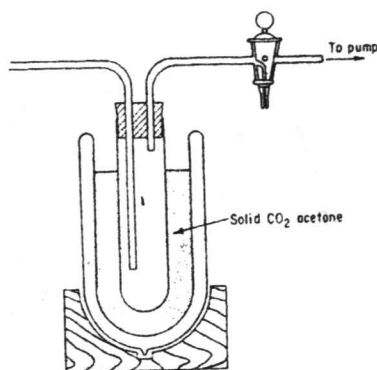
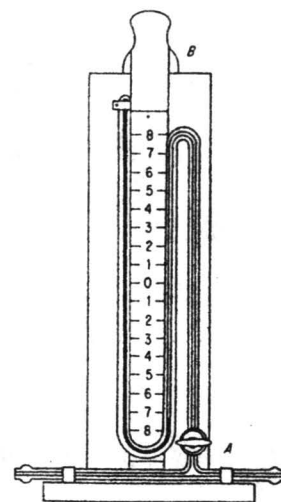


FIGURE F-36
Vacuum distillation with
gas-capillary bubbler.



F-37 Dry-ice vapor trap.



F-38 Manometer.

GENERAL REQUIREMENTS

1. A source of vacuum. Efficient water pumps, aspirators, will theoretically reduce the pressure in the system to the vapor pressure of the water passing through the pump. In practice, the pressure is usually about 10mm higher. (a) Oil mechanical vacuum pumps. (b) Use "pressure" rubber tubing. (c) The entire distillation system should be airtight, free from leaks. (d) Lubricate all joints and connections.

2. Safety trap to protect manometer and vacuum source from overflow-liquid contamination (Fig.F-37)

3. Pressure gauge (manometer, Fig.F-38). Exercise great care when allowing air into the evacuated system. It must be done slowly to avoid breakage when the mercury column rises to the top of closed tube.

4. Manostat (pressure regulator). To maintain constant pressure in the system, it automatically opens and closed needle valves, permitting air to enter or keeping the system airtight because of vacuum variations.

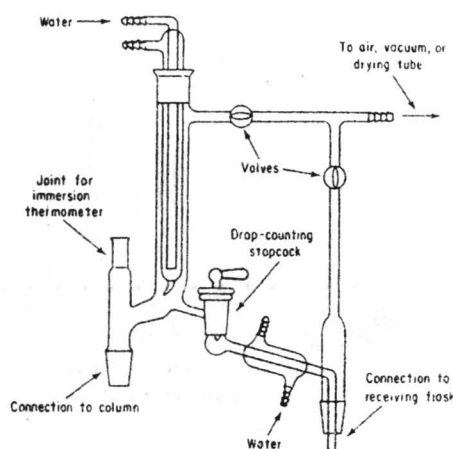
5. Capillary air inlet (Fig.F-39).

FIGURE F-39

FIGURE F-40



F-39 Capillary air- or gas-inlet tube.



F-40 Partial-takeoff distillation head.

6. Special vacuum distillary flasks to minimize contamination of distillate because of boiling-solution frothing.

7. Heating baths, electric mantles and fusible alloy or sand baths.

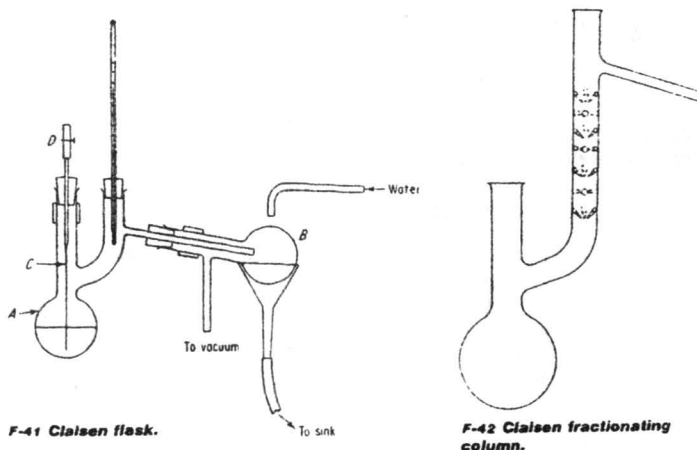
8. Special distilling heads (Fig.F-40) to permit removal of distillate fractions without interrupting the distillation.

Assemblies for Simple Vacuum Distillation and Fractionation

A claisen flask for use in this process is shown in Fig.F-41.

FIGURE F-41

FIGURE F-42



PROCEDURE

1. Fill the claisen flask one-third full.
2. Apply vacuum; adjust the capillary air inlet with the pinch clamp.
3. Heat bath about 20°C higher than the temperature at which the material will distill.
4. Cooling water over the receiver condenses vapors to give distillate.
5. A safety trap prevents any condensate from contaminating pump or manometer.

CAUTIONS

When distillation is completed:

1. Remove the heating bath; allow the flask to cool.
2. Remove the capillary pinch clamp.
3. Cut off the cooling water.

4. Turn off the vacuum pump.

A claisen fractionating column is shown in Fig.F-42.

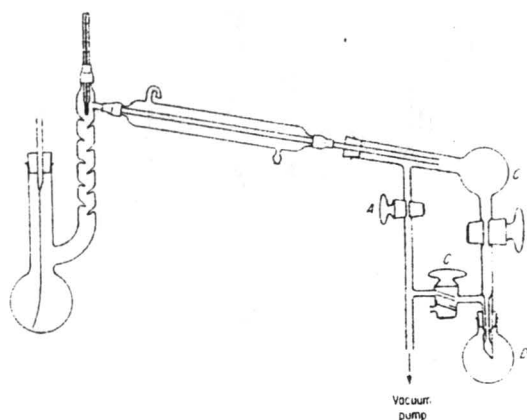
PRINCIPLE

The distillation neck of the claisen flask serves as a fractionating column because of the indentations. The receiver makes it possible to remove distillate fractions without interrupting the distillation or breaking the vacuum.

PROCEDURE

Follow the steps listed and observe the cautions given above. To remove distillate fractions during distillation (Fig.F-43):

FIGURE F-43
Apparatus for fractional distillation in a vacuum.



1. Close stopcock B.
2. Close stopcock C.
3. Reverse rotation stopcock C so that the air flows into flask D.
4. Gently remove flask D, empty into bottle, and replace.
5. Rotate stopcock C 180° so that D is now under vacuum.
6. Open stopcock B to allow collected distillate to drain into D.

Complete the fractional distillation and disconnect the equipment as recommended above.

STEAM DISTILLATION

PRINCIPLE

Steam distillation is a means of separating and purifying organic compounds by volatilization. The organic compound must be insoluble or slightly soluble in water. When steam is passed into a mixture of the compound and water, the compound will distill with the steam. In the distillate, this distilled compound separates from the condensed water because it is insoluble in water.

USES

Most compounds, regardless of their normal boiling point, will distill by steam distillation below that of pure boiling water.

EXAMPLE

Naphthalene is a solid with a boiling point of 218°C . It will distill with steam and boiling water at a temperature less than 100°C .

Some high-boiling compounds decompose at their boiling point. They can be distilled at low temperature by steam distillation.

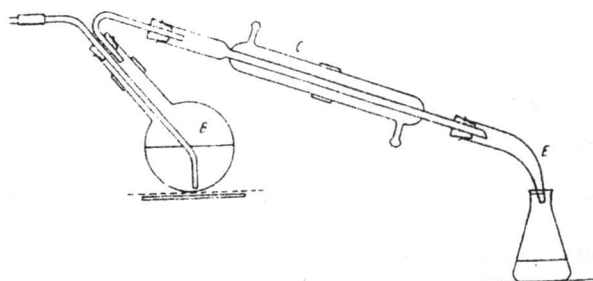
Steam distillation can be used to purify substances from contaminants because some water-insoluble substances are steam-volatile and others are not.

For separation of nonvolatile solids from high-boiling organic solvents steam distillation will remove all solvents (water insoluble).

PROCEDURE

1. Place the compound or mixture in the distilling flask with a little water. Pass cooling water through the condenser (see Fig.F-44).

FIGURE F-44
Steam-distillation
experimental setup.



2. Pass steam into the distilling flask, with the steam outlet below the surface of the liquid. The distilling flask itself may be heated gently with a burner.

3. Continue passing steam into the flask until no appreciable amount of water-insoluble material appears in the condensate.

CAUTION

1. Steam will cause severe burns. Handle with care.

2. If the substance crystallizes in the condenser, it will close the tube.

3. Steam pressure could build up when the tube closes and cause an explosion. *Use care!*

DANGER

Drain the condenser of cooling water. The material will melt and pass into the distillate.

When clear, slowly pass the cooling water through the condenser.

4. Always disconnect the steam-inlet tube from the flask.

REFLUXING

The reflux procedure allows you heat a reaction mixture for an extended period of time without loss of solvent. The condenser, which is fixed in a vertical position directly above the heated flask, condenses all vapors to liquid. Because none of the vapors escape, the volume of liquid remains constant.

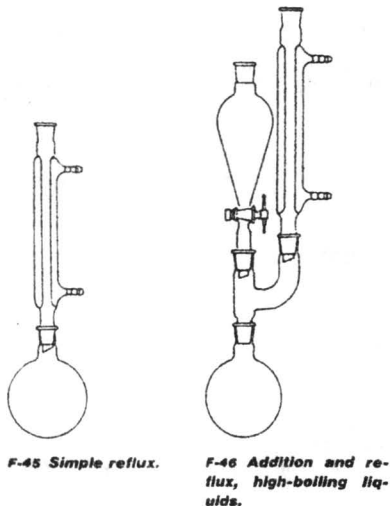
Reflux procedures are carried out in neutral, acid, or basic solution, depending upon the reaction.

Hydrolysis-saponification is used to split organic molecules (which are made by combination of two or more compounds) into the original compound.

Typical operations include hydrolysis-saponification of acid amides, esters, fats, nitriles, substituted amides, and sulfonamides.

Experimental setups are shown in Figs.F-45 to F-48.

FIGURE F-45
FIGURE F-46



1. The water inlet to the condenser is the lower one. The water outlet to the condenser is upper one.
2. Fill the heating flask, maximum half full; add a few boiling stones.
3. Turn on the cooling water.
4. Heat to reflux for desired period of time.

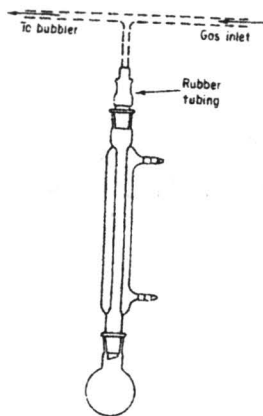
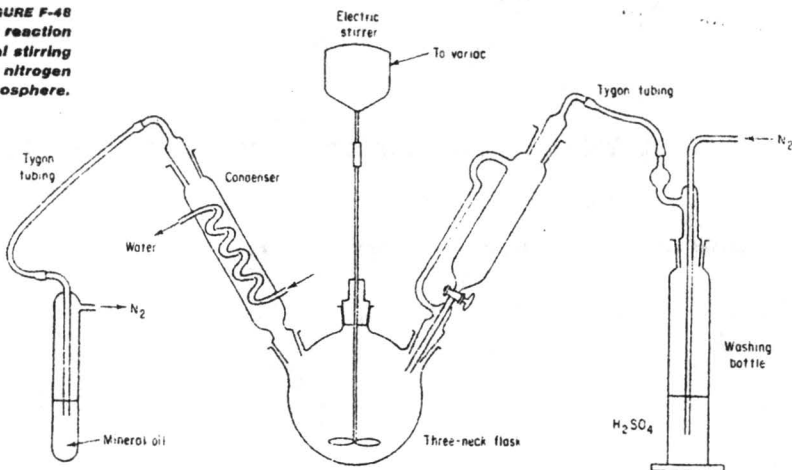


FIGURE F-47
Reflux, inert atmosphere.

FIGURE F-48
Apparatus for a reaction with mechanical stirring under a nitrogen atmosphere.

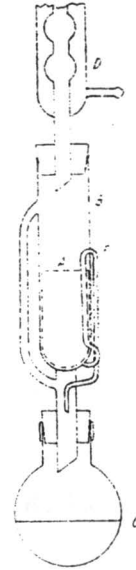


SOXHLET EXTRACTION

Solid materials can be extracted with hot solvent by using a soxhlet extractor.

The solvent is vaporised. When it condenses, it drops on the solid substance contained in a thimble and extracts soluble compounds. When the liquid level fills the body of the extractor, it automatically siphons into the flask. This process continues repeatedly as the solvent in the flask is vaporised and condenses.

FIGURE F-49
Soxhlet extractor.



PROCEDURE

Set up apparatus as illustrated in Fig.F-49.

Fig. F-49

1. Put the solid substance in the porous thimble and place the partially filled thimble in the soxhlet inner tube
 2. Fill the flask one-half full of extracting solvent.
 3. Assemble the unit.
 4. Turn on the cooling water.
 5. Heat.
 6. When the extraction is complete, turn off the heat and cooling water.
 7. Dismantle the apparatus, and pour the extraction solvent and solute into breaker.
- Isolate the extracted component by evaporation method.

SECTION VII

The Technician and His Sample

MOISTURE IN SAMPLES

The presence of water in sample represents a common problem that frequently faces the analyst. This compound may exist as a contaminant from atmosphere or from the solution in which the substance was formed, or it may be bonded as a chemical compound. Regardless of its origin, however, water plays a part in determining the composition of the sample. Unfortunately, particularly in the case of solids, the water content is a variable quantity that depends upon such things as humidity, temperature, and state of subdivision. Thus, the constitution of sample may change significantly with environment and method of handling.

In order to cope with the variability in composition owing to the presence of moisture, the analyst may attempt to remove drying prior to weighing samples for analysis. Alternatively he may determine the water content at the time his sample are weighed out for analysis; in this way his results can be corrected to a dry basis. In any event most analyses are preceded by some sort of preliminary treatment designed to take into account the presence of water. This accounted for many established tests.

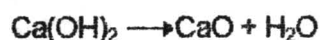
Forms of Water in Solids

It is convenient to distinguish among the several ways in which water can be held by a solid. Although developed primarily with respect to minerals, the classification of Hillebrand and his collaborators may be applied to other solids as well and forms the basis for the discussion that follows.

Essential Water

The essential water in a substance is that water which is an integral part of the molecular or crystal structure of one of the components of the solid. It is present in that component in stoichiometric quantities. Thus, the water of crystallization is stable solid hydrates (for example, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) quantities as a type of essential water.

A second form is called water of constitution. Here the water is not present as such in the solid but rather is formed as a product when the solid undergoes decomposition, usually as a result of heating. This is typified by the processes



Nonesential Water

Nonesential water is not necessary for the characterization of the chemical constitution of the sample and therefore does not occur in any sort of stoichiometric proportions. It is retained by the solid as a consequence of physical forces.

Adsorbed water is retained on the surface of the solids in contact with a moist environment. The quantity is dependent upon humidity, temperature, and specific surface area of the solid. Adsorption is general phenomenon that is encountered in some degree with all finely divided solids. The amount of moisture adsorbed on the surface of a solid also increases with the amount of water in its environment. Quite generally, the amount of adsorbed water decreases with temperature increases, and in most cases it approaches zero if the solid is dried at temperatures above 100°C .

Equilibrium, in the case of adsorbed moisture, is achieved rather rapidly, requiring ordinarily only 5 or 10 min. This often becomes apparent to the chemist when he weighs finely divided solids that have been rendered anhydrous by drying; a continuous increase in weight is observed unless the solid is contained in tightly stoppered vessel.

A second type of nonessential water is called sorbed water. This is encountered with many colloidal substances such as starch, protein, charcoal, zeolite minerals, and silica gel. The amounts of sorbed water are often large compared with adsorbed moisture, amounting in some instances to as much as 20 percent or more of the solid. Interestingly enough, solids containing even this much water may appear as perfectly dry powders. Sorbed water is held as

a condenses phase in the interstices or capillaries of the colloidal solids. The quantity is greatly dependent upon temperature and humidity.

A third type of nonessential moisture is occluded water. Here, liquid water is entrapped in microscopic pockets spaced irregularly throughout the solid crystals. Such cavities often occur naturally in mineral and rocks.

Water may be dispersed in a solid in the form of a solid solution. Here the water molecules are distributed homogeneously throughout the solid. Natural glasses may contain several percent of moisture in this form.

Effect of Grinding on Moisture Content

Often the moisture content, and thus the chemical composition, of a solid is altered to a considerable extent during grinding and crushing. This will result in decreases in some instances and increases in others.

Decreases in water content are sometimes observed in grinding solids containing essential water in the form of hydrates; thus the water content of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is reduced from 20 to 5 percent by this treatment. Undoubtedly the change is a result of localized heating during the grinding and crushing of the particles.

Losses also occur when samples containing occluded water are reduced in particle size. Here, the grinding process ruptures some of the cavities and exposes the water so that it may evaporate.

More commonly perhaps, the grinding process is accompanied by an increase in moisture content, primarily because of the increase in the surface area exposed to the atmosphere. A corresponding increase in adsorbed water results. The magnitude of the effect is sufficient to alter appreciably the composition of a solid. For example, the water content of a piece of porcelain in the form of coarse particles was zero, but after it had been ground for some time it was found to be 0.62 percent. Grinding a basaltic greenstone for 120 min changed its water content from 0.22 to 1.70 percent.

Liquid Reagents Used for Dissolving or Decomposing

Samples

The most common reagents for attacking analytical samples are mineral acids or their aqueous solutions. Solutions of sodium or potassium hydroxide also find occasional application.

Hydrochloric Acid

Concentrated hydrochloric acid is an excellent solvent for many metals oxides as well as those metals which lie above hydrogen in the electromotive-forces series; it is often a better solvent for the oxides than the oxidizing acids. Concentrated hydrochloric acid is about 12N, but upon heating, hydrogen chloride is most until a constant-boiling 6N solution remains (boiling point about 110°C).

Nitric Acid

Concentrated nitric acid is an oxidizing solvent that finds wide use in the attack of metals. It will dissolve all the common metallic elements; aluminium and chromium, which become passive to the reagent, are exceptions. Many of the common alloys can also be decomposed by nitric acid. In this connection it should be mentioned that tin, antimony, and tungsten form insoluble acids when treated with concentrated nitric acid; this is sometimes employed to separate these elements from others contained in alloys.

Sulfuric Acid

Hot concentrated sulfuric acid is often employed as a solvent. Part of its effectiveness arises from its high boiling point (about 340°C), at which temperature decomposition and solution of substances often proceed quite rapidly. Most organic compounds are dehydrated and oxidized under these conditions; the reagent thus serves to remove such components from a sample. Most metals and many alloys are attacked by the hot acid.

Perchloric Acid

Hot concentrated perchloric acid is a potent oxidizing agent and solvent. It attacks a number of ferrous alloys and stainless steels that are intractable to the other mineral acids; it is frequently the solvent of choice. This acid also dehydrates and rapidly oxidizes organic materials. Violent explosions result when organic substances or easily oxidized inorganic compounds come in contact with the hot concentrated acid; as a consequence, a good deal of care must be employed in the use of this reagent. For example, it should be heated only in hoods in which the ducts are clean and free of organic materials and where the possibility of contamination of the solution is absolutely nil.

Perchloric acid is marketed as the 60 to 72 percent acid. Upon heating, a constant-boiling mixture (72.4 percent HClO_4) is obtained at a temperature of 203°C . Cold concentrated perchloric acid and hot dilute solutions are quite stable with respect to reducing agents; it is only the hot concentrated acid that constitutes a potential hazard. The reagent is a very valuable solvent and is widely used in analysis. Before it is employed, however, the proper precautions for its use must be clearly understood.

Oxidizing Mixtures

More rapid solvent action can sometimes be obtained by the use of mixtures of acids or by the addition of oxidizing agents to the mineral acids. Aqua regia, a mixture consisting of three volumes of concentrated hydrochloric acid and one of nitric acid, is well known. Addition of bromine or hydrogen peroxide to mineral acids often increases their solvent action and hastens the oxidation of organic materials in the sample. Mixtures of nitric and perchloric acid are also useful for this purpose.

Hydrofluoric Acid

The primary use of this acid is for the decomposition of silicate rocks and minerals where silica is not to be determined; the silicon is, of course, evolved as the tetrafluoride. After decomposition is complete, the excess hydrofluoric acid is driven off by evaporation with sulfuric acid or perchloric acid. Complete removal is often essential to the success of an analysis, because of the extraordinary stability of the fluoride complexes of several metal ions; the properties of some of these differ markedly from those of the parent cation. Thus, for example, precipitation of aluminium with ammonia is quite incomplete in the presence of small quantities of fluoride. Frequently removal of the last traces of fluoride from sample is so difficult and time-consuming as to negate the attractive features of this reagent as a solvent for silicates.

Hydrofluoric acid finds occasional use in conjunction with other acids in the attack of some of the more difficultly soluble steels.

Hydrofluoric acid can use serious damage and painful injury when brought in contact with skin; it must be handled with respect.

Decomposition of Samples by Fluxes

Quite a number of common substances - such as silicates, some of the mineral oxides, and a few of the iron alloys - are attacked slowly, if at all, by the usual liquid reagents. Recourse to more potent fused-salt media, or fluxes, is then called for. Fluxes will decompose most substances by virtue of the high temperature required for their use (300 to 1000°C) and the high concentration of the reagent brought in contact with the sample.

Where possible, the employment of a flux is avoided, for several dangers and disadvantages attend its use. In the first place, a relatively large quantity of the flux is required to decompose most substances - often ten times the sample weight. The possibility of significant contamination of the sample by impurities in the reagent thus becomes very real.

Furthermore, the aqueous solution from the fusion will have a high salt content, and this may lead to difficulties in the subsequent steps of the analysis. The high temperatures required for a fusion increase the danger of loss of pertinent constituents by volatilization. Finally, the container in which the fusion is performed is almost inevitably attacked to some extent by the flux; this again can result in contamination of the sample.

In those cases where the bulk of the substance to be analyzed is soluble in a liquid reagent and only a small fraction requires decomposition with a flux, it is common practice to employ the liquid reagent first. The undecomposed residue is then isolated by filtration and fused with a relatively small quantity of a suitable flux. After cooling, the melt is dissolved and combined with the majority of the sample.

Method of Carrying Out a Fusion

In order to achieve a successful and complete decomposition of a sample with a flux, the solid must ordinarily be ground to a very fine powder; this will produce a high specific surface area. The sample must then be thoroughly mixed with the flux; this operation is often carried out in the crucible in which the fusion is to be done by careful stirring with a glass rod.

In general, the crucible used in a fusion should never be more than half filled at the outset. The temperature is ordinarily raised slowly with a gas flame because the evolution of water and other gases is a common occurrence at this point; unless care is taken there is the danger of loss by spattering. The crucible should be covered as an added precaution. The maximum temperature employed varies considerably depending upon the flux and the sample; it should be no greater than necessary, however, to minimize attack of the crucible and decomposition of the flux. The length of the fusion may range from a few minutes to one or two hours depending upon the nature of the sample. It is frequently difficult to decide when the heating should be discontinued. In some cases, the production of clear melt serves as a signal for the completion of the decomposition. In others the condition is not obvious, and the analyst must base the heating time on previous experience with the type of material being analyzed. In any event, the aqueous solution from the fusion should be examined carefully for particles of unattacked sample.

When the fusion is judged complete, the mass is allowed to cool slowly; then just before solidification the crucible is rotated to distribute the solid around the walls of the crucible so that the thin layer can be readily detached.

Types of Fluxes

With few exceptions the common fluxes used in analysis (Table K-1) are compounds of the alkali metals. Basic fluxes, employed for attack of acidic materials, include the carbonates, hydroxides, peroxides, and borates. The acidic fluxes are the pyrosulfates and the acid fluorides as well as boric oxide. If an oxidizing flux is required, sodium peroxide can be used. As an alternative, small quantities of the alkali nitrates or chlorates are mixed with sodium carbonate.

Table K-1 : The Common Fluxes

Flux	Melting point °C	Type of crucible for fusion	Type of substance decomposed
Na_2CO_3	851	Pt	For silicates and silica-containing samples; alumina-containing sample; insoluble phosphates and sulfates
Na_2CO_3 +an oxidizing agent such as KNO_3 , KClO_3 , or Na_2O_2 NaOH , or KOH	318-380	Pt (not with Na_2O_2) Ni Au,Ag,Ni	For samples where an oxidizing agent is needed; that is, samples containing S, As, Sb, Cr, etc. Powerful basic fluxes for silicates, KOH silicon carbide, and certain minerals; main limitation, purity of reagents
Na_2O_2	Decomposes 300	Fe, Ni Pt	Powerful basic oxidizing flux for sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; platinum alloys; Cr, Sn, Zn minerals $\text{K}_2\text{S}_2\text{O}_7$ Acid flux for insoluble oxides porcelain and oxide-containing samples
B_2O_3	577	Pt	Acid flux for decomposition of silicates and oxides where alkali metals are to be determined
$\text{CaCO}_3+\text{NH}_4\text{Cl}$		Ni	Upon heating of the flux, a mixture of CaO and CaCl_2 is produced; used for decomposing silicates for determination of the alkali metals

WEIGHING SAMPLES

Store and dry in weighing bottles which have ground-glass contacting surfaces between the cover and the bottle (Fig.K-3).

Fig. K-3

PROCEDURE

1. Use a clean weighing bottle fitted with a ground-glass cover.
2. Handle the bottle with suitable tongs or with a strip of lint-free paper (as illustrated in

Fig.K-4).

FIGURE K-4
*Weighing bottle and method
of handling it.*



3. Do not touch the weighing bottle with your finger. Weighing data will be significantly affected by moisture and grease on your fingers.

Direct Weighing

1. Weigh a clean receiving vessel or dish or a piece of glazed paper.
2. Transfer the desired quantity of substance with a clean spatula or by gently tapping the titted weighing bottle.
3. Weigh the substance and the glazed paper or weighing dish.
4. Calculate the weight of the sample by subtracting the weight of the paper or dish from the weight of the material and dish found in step 3. The difference in these two weights is the weight of the substance.

Weighing by Difference

1. Weigh the weighing bottle which contains the sample.
2. Quantitatively remove the desired amount of the substance to the receiving container by gently pouring the material out of the weighing bottle.
3. Reweigh the weighing bottle.

4. Subtract the weight found in step 3 from the weight found in step 1. The difference in these two weights is the amount of material transferred.

Use *direct weighing* when an exact quantity of substance is needed.

Use *weighing by difference* (Fig.K-5) when several samples of the same material are to be weighed. This method is preferable when weighing hygroscopic substances.

FIGURE K-5
The weighing operation.



A convenient method for transfer of a solid for weighing by difference.

DRYING SAMPLES

Samples may be dried by heating at 105 to 100°C, if the melting point of the material is higher and the material will not decompose at that temperature. This procedure will remove the moisture bound to the surface of the particles.

METHOD

1. Label the breaker and the weighing bottle.
2. Place the weighing bottle in the breaker, which is covered by a watch glass supported on glass hooks (Fig.K-6).
3. Place in oven for required time at the temperature suggested.

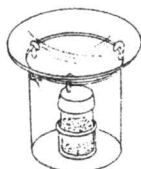
DESICCATOR

This is a glass container filled with a desiccant which adsorbs water, used to provide a dry atmosphere for objects and substances.

PROCEDURE

1. Remove the cover by sliding sideways as in Fig.K-7.
2. Place the object on the porcelain platform plate.
3. Regrease the ground-glass rim with petroleum jelly if necessary.
4. Slide the lid back in position.

FIGURE K-6
FIGURE K-7



K-6 Arrangement for the drying of samples.



K-7 Removing desiccator cover.

CLEANING AND RECHARGING DESICCATOR

1. Remove the cover and the porcelain support plate.
2. Dump the waste desiccant in a refuse pail.
3. Wash and dry the desiccator.
4. Refill with fresh desiccant (Fig.K-8).
5. Regrease the ground-glass lid.
6. Replace the porcelain support.
7. Slide the lid into position on the desiccator.

FIGURE K-8
Filling desiccator with fresh desiccant.



Storage of Samples in Desiccators

Desiccators are vessels which are used to *achieve and maintain* an atmosphere of low humidity for the storage of samples, precipitates, crucibles, weighing bottles, and other equipment

Vacuum desiccators are equipped with side arms, so that they may be connected to a vacuum rather than dried air.

CAUTION

Hot crucibles should never be inserted immediately in the desiccator. Allow to cool in air for 1 min prior to insertion. If this caution is not observed, the air will be heated in the desiccator when it is closed. On cooling, a partial vacuum will result. When the desiccator is opened, a sudden rush of air may spill the sample.

COMMON HAZARDOUS CHEMICAL

Usual shipping container:

1. Acetic acid (glacial) - Glass carboys and barrels

Expands on solidification and may burst container unless kept at a temperature above 16°C (60.8 ° F).

a) Life hazard - may cause painful burns of skin

b) Fire hazard - Dangerous in contact with chromic acid, sodium peroxide or nitric acid; yields moderately flammable vapors above flash point 104°F

2. Acetone - Carboys, steel drums, tank cars.

a) Life hazard- toxicity of a comparatively low order.

b) Fire hazard - a volatile liquid. Gives off vapors from with air flammable and explosive mixtures. Flash point -16 °C. Explosive range 2.55% to 12.8% (upward propagation). The ignition temperature is comparatively high, being within the range 538°C (1000° to 1050°F).

the vapors are heavier than air (vapor density 2). Fire hazard slightly less than that of gasoline.

3. Ammonia (anhydrous) - Steel cylinders or steel tank cars.

a) Life hazard - irritant

An outstanding serious effect produced by ammonia in concentrations of the order of 1/2 % by volume for duration of exposure of the order 1/2 hour is blindness. A concentration of 0.03 % of ammonia in air for duration of exposure of the order of 1/2 to 1 hour, according to Lehmann, does not cause serious effect.

b) fire hazard - gas density 0.60 (air = 1).

Not flammable in air except in comparatively high concentration, which is seldom encountered under practical conditions, the low limit of the flammable or explosive range being about 15.5 to 16% and the upper limit about 26% by volume (horizontal propagation). The presence of oil will increase the fire hazard. Ammonia aqua does not burn.

4. Bromine - Glass bottles; earthen jugs. Bottles should be surrounded by incombustible packing.

a) Life hazard - corrosive; at ordinary temperature gives off poisonous suffocating vapors.

b) Fire hazard - causes oxidizing effect, resulting in heating and may cause fire when in contact with organic material.

5. Charcoal (wood) - boxes, barrels, bags, or bulk

a) Life hazard - there is danger from carbon monoxide poisoning during burning unless adequate ventilation is provided.

b) Fire hazard - Spontaneously ignitable when freshly calcined and exposed to air, or when wet; hazardous when freshly ground and tightly packed.

6. Chlorine - steel cylinders and tank cars.

a) Life hazard - corrosive

Irritating to eyes and mucous membrane.

Toxic - 0.0045 to 0.006% by volume in air causes dangerous illness in 1/2 to 1 hour.

b) Fire hazard - Is not combustible in air but reacts chemically with many common substances and may cause fire or explosion when in contact with them. See remarks under "Storage".

Dangerous to neutralise chlorine in a room with ammonia.

7. Chromium Trioxide or Chromium Anhydride CrO₃ (often called "Chromic Acid") - Iron drums and glass bottles. It is used in chromium plating, in electric batteries, and in photography.

a) Life Hazard - Irritating to skin. Poisonous.

b) Fire Hazard - Oxidizing material; will ignite in contact with acetic acid and alcohol. Chars organic material such as wood, sawdust, paper, or cotton, and may cause ignition. Combustible material in presence of chromium trioxide when ignited burns with great intensity. May cause explosion in fire.

8. Ethyl Ether - Glass bottles or tin cans in boxes, steel drums.

a) Life Hazard - Anaesthetic. See National Board of Fire Underwriters' Recommended Safeguards for the Installation and Operation of Anaesthetical Apparatus Employing Combustible Anaesthetics.

b) Fire Hazard - A highly volatile liquid, giving off even at comparatively low temperatures vapors which form with air or oxygen flammable and explosive mixtures. Explosive range 1.85% to 36.5% (upward propagation). The ignition temperature is comparatively low, being approximately 180°C. (360°F). Spontaneously explosive peroxides sometimes form on long standing or exposure in bottles to sunlight. The vapors are heavier than air (vapor density 2.6) and may travel a considerable distance to a source of ignition and flash back. More hazardous than gasoline.

9. Hydrochloric Acid (Muriatic Acid) - Tank cars (rubber-lined), carboys, and glass bottles.

a) Life Hazard - Aqueous solution is corrosive, irritating, and poisonous. Fumes are corrosive and irritating to mucous membranes.

b) Fire Hazard - Not combustible (in air) but if allowed to come in contact with common metals hydrogen is evolved, which may form explosive mixtures with air.

10. Hydrogen Peroxide (27.5 per cent by weight) - Glass carboys, aluminum drums, aluminum tank cars (all containers must be vented).

a) Life Hazard - Prolonged exposure to vapor irritating to eyes and lungs. Causes skin irritation. Use goggles to protect eyes from splash.

b) Fire Hazard - Oxidizing liquid. May cause ignition of combustible material if left standing in contact with it.

May decompose violently if contaminated with iron, copper, chromium, and most metals or their salts.

11. Hydrogen Sulfide (Sulfuretted Hydrogen) - Steel cylinders.

a) Life Hazard - Toxic. 0.05 to 0.07 per cent by volume in air causes dangerous illness in 1/2 to 1 hr. Should be used under hood in chemical laboratories to avoid danger of breathing dangerous concentrations.

b) Fire Hazard - Flammable gas. Forms flammable and explosive mixture with air or oxygen. Explosive range in air (upward propagation) 4.3 (low limit) to 46. Heavier than air . Specific gravity 1.19(air=1). Ignition temperature 346°-379°C.(655°-714°F).

12. Nitric Acid - Carboys and glass bottles.

a) Life Hazard - Corrosive; causes severe burns by contact; deadly if inhaled.

b) Fire Hazard - May cause ignition when in contact with combustible materials; corrodes iron or steel; may cause explosion when in contact with hydrogen sulfide and certain other chemicals.

13. Phenol

a) Life Hazard - Poisonous.

b) Fire Hazard - When heated yields flammable vapors. Flash point 172.4° F.

14. Phosphorus , Red - Hermetically sealed tin cans inside of wooden boxes.

a) Life Hazard - Yields toxic fumes when burning.

b) Fire Hazard - Flammable. Explosive when mixed with oxidizing materials.

Not as dangerous to handle as white phosphorus, and when afire, more readily extinguished.

15. Phosphorus, White (or Yellow) - Under water usually in hermetically sealed cans enclosed in other hermetically sealed cans with outside wooden boxes, or in drums or tank cars.

a) Life Hazard - Poisonous. Serious under fire conditions. Yields highly toxic fumes when burning. Contact of phosphorus with the skin causes severe burns.

b) Fire Hazard - Highly flammable. Explosive in contact with oxidizing material. Ignites spontaneously on contact with air.

16. Potassium (Metallic Potassium) - Hermetically sealed steel drums , tin cans, and tank cars.

a) Life Hazard - Strong caustic reaction. Dangerous.

b) Fire Hazard - Oxidizes rapidly on exposure to atmosphere, igniting spontaneously if warm enough.

Water is decomposed suddenly by contact with potassium, sufficient heat being generated to ignite spontaneously the evolved hydrogen (in the presence of air). Its reaction with water is more violent than that of sodium.

17. Potassium Hydroxide - Wooden barrels, glass bottles.

a) Life Hazard -

b) Fire Hazard - In contact with organic materials causes violent combustion on ignition. Classes with sodium nitrate.

18. Sodium - Hermetically sealed steel drums , tin cans , and tank cars.

a) Life Hazard - Strong caustic reaction. Dangerous.

b) Fire Hazard - Water is suddenly decomposed by contact with sodium with the evolution of hydrogen, which may ignite spontaneously (in presence of air). Cases with potassium in respect to fire hazard but its reaction with water is less violent than of potassium.

19. Sodium Hydroxide - Bags, tins, and glass bottles.

a) Life Hazard -

b) Fire Hazard - Classes with potassium hydroxide and calcium oxide.

20. Sulfur - Sacks, boxes, barrels, and box cars.

a) Life Hazard - When burning forms sulfur dioxide, which in concentration of 0.2% by volume with air may cause serious injury in 1/2 hour or less.

b) Fire Hazard - Flammable. Dust or vapor forms explosive mixtures with air. Hazardous in contact with oxidizing material.

21. Sulfuric Acid - Corbys, iron drums, glass bottles, and tank cars.

a) Life Hazard - Corrosive; dangerous fumes under fire condition.

b) Fire Hazard - May cause ignition by contact with combustible materials. Corrodes metal.

SECTION VIII

REACTIONS WITH MODIFICATION OF ELEMENTS OXIDATION STATE

First, oxidation refers to those chemical reactions during which oxygen was caught to (or hydrogen was removed from) an element or a compound. After that, a new conception was accepted. This theory considers that the oxidation proces corresponds to a giving of electrons by an atom or an ion, and the reduction process means an acception of electrons. Thus, during a chemical reaction a substance suffers an oxidation process in the presence of a substance which suffers a reduction. The substance which gives electrons is the reducing agent and the one which accepts electrons is the oxidizing agent.

For a better understanding of this problem we must take into account the electrode potentials. The standard potential of a system may define its oxidizing or reducing properlies in presence of another redox system. Thus, a lower electrod potential means a higher reducing character and a higher electrod potential involves a higher oxidizing character.

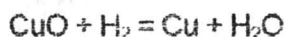
Now we all discuss about a few redox systems.

1. REACTIONS INITIATED BY REDUCING AGENTS

1.1. THE REDUCTION OF CUPRIC OXIDE WITH MOLECULAR HYDROGEN

Into a porcelain gondola 5-7 cm in lenght introduce 0,1-0,2 g of cupric oxide (precisely weighted at the analytical balance). Put the gondola into a combustion tube made heavily fusible glass, 30cm in lenght and with $f=1,5\text{cm}$. One end of the tube must be conected at a source of pure hydrogen. At the other end fix a glass tube small in diameter, curved after an angle of 90° and having an thin end. Now you have to adjust the hydrogen's debit so that the number of hydrogen bubbles can counted into a washig vessel filled with sulphuric acid. This vessel has to be settled between the source of hydrogen and combustion tube.

ATTENTION! The combustion tube may be heated only after you have verified the completely evicton of the air from the apparatures (with the detonating test) and you have lit the hydrogen stream at the thin end of the glass tube (by using the test tube from the detonating test). The equation of teh reaction is:

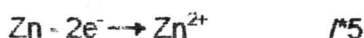
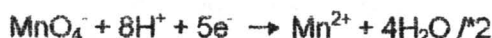


After the reaction's end, weight the gondola with copper and using the reaction's stoichiometry you can compute the yield (h%).

1.2. REDUCTIONS WITH ACTIVE HYDROGEN

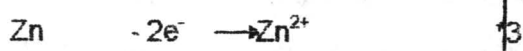
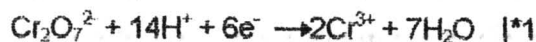
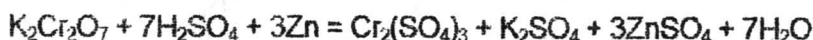
1.2.1. REDUCTION OF KALIUM

Introduce into a test tube 2-3 ml of KMnO_4 solution n/200 (violet), the same volume of H_2SO_4 solution 20% and a few granules of zinc. It is now observable the change of colour from violet to pale-pink, which is characteristic to ion Mn^{2+} . H_2SO_4 reacts with zinc and result is active hydrogen which is reducing the kalium permanganate:



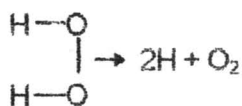
1.2.2. REDUCTION OF KALIUM DICHROMATE

Introduce into a test tube 3-4cm³ of $\text{K}_2\text{Cr}_2\text{O}_7$ solution n/100 (orange), the same volume of H_2SO_4 (1:5) and a few granules of zinc. The colour is changing from orange to green (characteristic for Cr^{3+} ion). The active hydrogen which results, is reducing the kalium dichromate as follows:

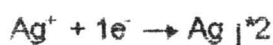
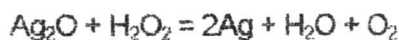


1.3. REDUCTIONS WITH HYDROGEN PEROXIDE

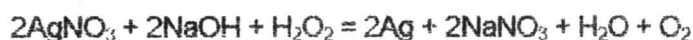
In the presence of strong oxidizing agents, hydrogen peroxide function as a reducing agent, both in acid or alkaline medium. As a reducing agent, hydrogen peroxide decomposes as follows:



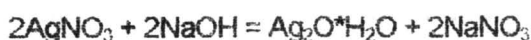
1.3.1. REDUCTION OF SILVER OXIDE TO METALLIC SILVER



Introduce into a test tube 2-3cm³ of dilute solution of silver nitrate, 4-5cm³ of hydrogen peroxide solution 3% and 2-3cm³ of dilute NaOH. A black precipitate of metallic silver is obtained:



While the NaOH solution is added, the dark silver oxide precipitates:

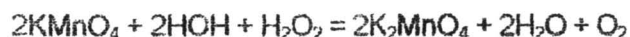
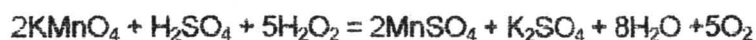


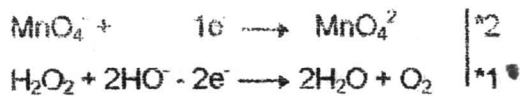
because of the instability of silver hydroxide which it is formed in the first step.

Gradually, the silver oxide is reduced by H₂O₂ to metallic silver.

1.3.2. REDUCTION OF KALIUM PERMANGANATE INTO ACID, NEUTRAL OR BASIC MEDIUM

The reactions are:



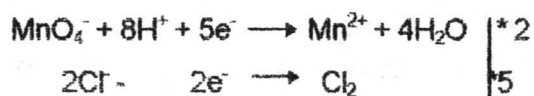


These reactions are carried out into test tubes.

Introduce 2-3 cm³ of H₂O₂ 3%, 3-5 cm³ of KMnO₄ n/200, and add 2-3 cm³ of natrium (kalium) hydrate or sulphuric acid 20%.

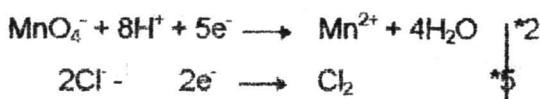
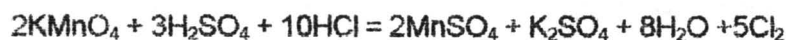
1.4. REDUCTIONS WITH HYDRACIDS

1.4.1. REDUCTION OF KMnO₄ WITH HCl



An excess of HCl is necessary because besides the fact that HCl is the reducing agent, it is also supplying the hydrogen ions.

Instead kalium permanganate can be used natrium permanganat, and H₂SO₄ 20% together with HCl. The reaction is:

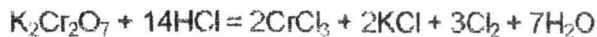


This reaction is carried out under the niche.

We need a Wurtz baloon (1), a dripping funnel (2) (with a tap), a washing vessel (3) and a vessel (4) for collecting the chlorine. (see figure 1).

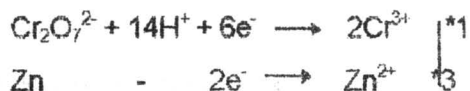
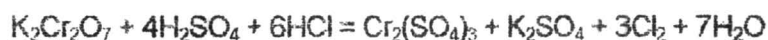
Introduce KMnO₄ (the oxidizing agent) into the baloon (1). The reducing agent (HCl) is introduced into the funnel (2) and it is dripped into the baloon. The chlorine obtained it is passed through the washing vessel (3) where the water washes the HCl gaseous traces, and than it is collected into the vessel (4) where there is water. The result is chlorine water which has an oxidizing character.

1.4.2. REDUCTION OF K₂Cr₂O₇ WITH HCl



The reagents are $\text{K}_2\text{Cr}_2\text{O}_7$ and HCl 37%; the reaction occurs on heating. The apparatuses are the same as above. (see figure 1).

It may be used also H_2SO_4 together with HCl :



These reactions are used to obtain chlorine in laboratory. For small amounts of chlorine the experiences may be carried out into a test tube closed by a rubber cork and equipped with a glass tube (see figure 2).



1.5. REDUCTIONS WITH NITROUS ACID

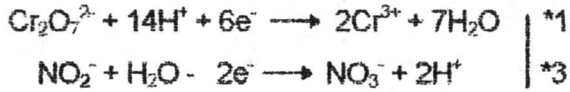
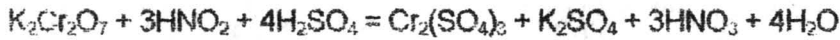
The nitrous acid is known only in diluted and cold aqueous solutions. Its salts (nitrous salts) are stable and toxic, but in aqueous solutions are changing into nitrites. The nitrous acid and its salts have both reducing and oxidizing properties.

1.5.1. REDUCTION OF KALIUM PERMANGANATE WITH NITROUS ACID OR NITROUS SALTS IN ACID MEDIUM



The experience is carried out into a test tube, adding a solution of nitrous sodium or kalium over a solution of KMnO_4 n/200 acidulated with H_2SO_4 20%.

1.5.2. REDUCING OF KALIUM DICHROMATE

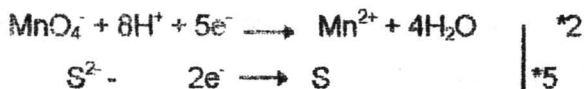
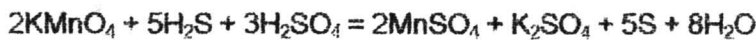


Into a test tube introduce a $\text{K}_2\text{Cr}_2\text{O}_7$ solution n/100 (orange) acidulates with H_2SO_4 20% and add nitrous sodium or kalium. The colour changes from orange to green (characteristics for Cr^{3+} ion).

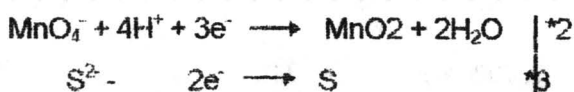
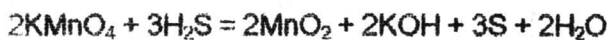
1.6. REDUCTION WITH SULPHURETTED HYDROGEN (H_2S)

1.6.1. REDUCTION OF KALIUM PERMANGANATE

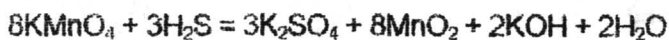
Introduce sulphuretted hydrogen into a KMnO_4 solution n/200 acidulated with H_2SO_4 20% or add sulphuretted hydrogen water to a dilute solution of KMnO_4 acidulated with H_2SO_4 . The kalium permanganate is reducing and sulphuretted hydrogen is oxidizing to colloidal sulphur.

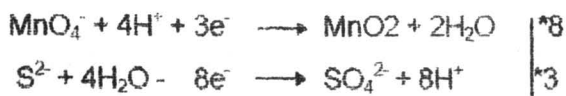


The sulphuretted hydrogen has acid properties and can react even in absence of H_2SO_4 :



Kalium permanganate can oxidize the sulphuretted hydrogen also in following way:

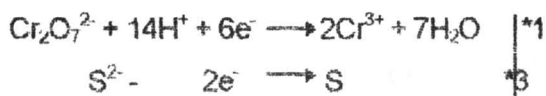
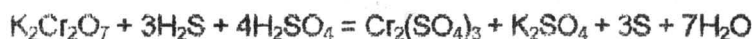




The experiences are carried out into test tubes, and are accompanied by a colour change (from violet to pale-pink-characteristic for Mn^{2+} ion, and to black- MnO_2)

1.6.2. REDUCTION OF KALIUM DICHROMATE

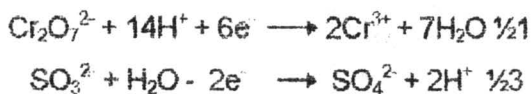
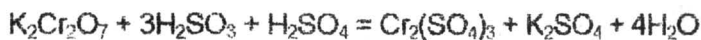
Occurs in acid medium after the equation:



You have to carry out the reaction between a $\text{K}_2\text{Cr}_2\text{O}_7$ solution n/100 acidulated with H_2SO_4 20%, and sulphuretted hydrogen water or gaseous H_2S . The apparition of colloidal sulphur as turbulense and a change of colour from orange to green are observed.

1.7. REDUCTIONS WITH SULPHUR DIOXIDE

1.7.1. REDUCTION OF KALIUM DICHROMATE IN ACID MEDIUM



Into a test tube introduce a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ n/100 acidulates with H_2SO_4 20% and add an aqueous solution of sulphur dioxide or sodium sulphite or introduce gaseous sulphur dioxide. The change of colour from orange to green can be observed.

1.7.2. REDUCTION OF KALIUM PERMANGANATE

It is made in acid medium, with sulphur dioxide, sodium sulphite or acide sodium sulphite:



The electronic balance for each reaction is:

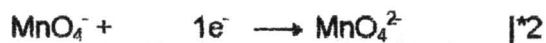
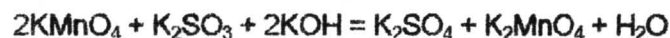
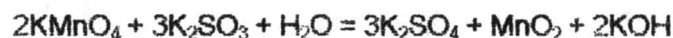


Reagents: - gaseous SO_2 , solution of SO_2 , or solution of sulphites

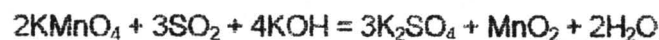
- solution of KMnO_4 n/200

The colour changes from violet to colourless (Mn^{2+} ion).

The kalium permanganate may be reduced by neutral sulphites in acid, neutral or alkalin medium,



or by sulphur dioxide in alkalin medium:



The experiences must be carried out into test tubes.

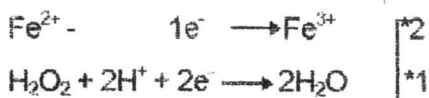
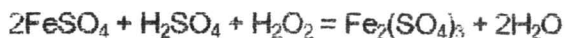
2. REACTIONS INITIATED BY OXIDIZING AGENTS

2.1. OXIDATIONS WITH HYDROGEN PEROXIDE

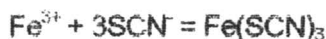
In presence of reducing agents, hydrogen peroxide acts as an oxidizing agent and decomposes into atomic oxygen and water. The atomic oxygen turns into the ion O^{2-} .



2.1.1. OXIDATION OF Fe(II) AND Fe(III) SALTS

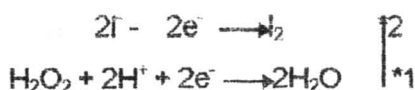


Into a test tube prepare a solution of ferrous sulphate and add H_2SO_4 20% and H_2O_2 3%. During the adding of hydrogen peroxide a change of colour to yellow occurs (because of the oxidizing process of Fe(II) to Fe(III)). The presence of the Fe(III) ion can be determined with the SCN^- ion; an intense red colour is obtained.



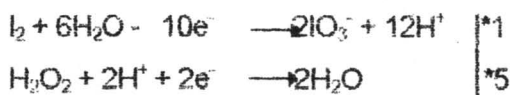
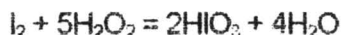
Therefore, add a dilute solution of ammonium or kalium sulphocyanate into the tube.

2.1.2. OXIDATION OF KALIUM IODIDE IN ACID MEDIUM

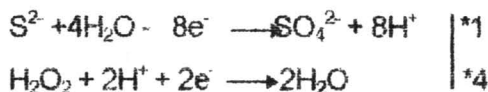
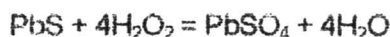


Into a tube introduce 3-4 cm^3 of KI, 2 cm^3 of H_2O_2 3% and 2-3 cm^3 of H_2SO_4 1:5. The iodide can be emphasize by its characteristic solution's colour (brown-red) or by the blue colour in presence of starch.

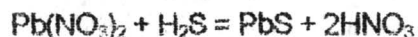
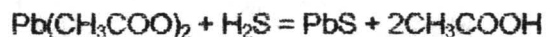
For an excess of hydrogen peroxide, the molecular iodine is oxidizing to iodate:



2.1.3. OXIDATION OF LEAD SULPHIDE

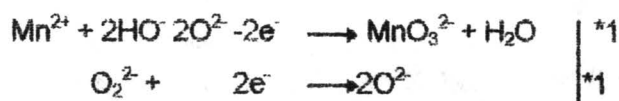
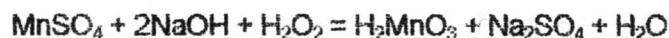


Add over an aqueous solution of lead nitrate or acetate an aqueous solution of sulphuretted hydrogen (obtained by the introducing of gaseous H₂S in water). A black precipitated of lead sulphide is obtained.

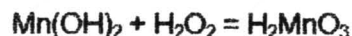


If over the black precipitate of PbS (washed by decantation with water), a solution of H₂O₂ 3% is added, a whiten of the precipitate can be observed, since the sulphide is oxidized to sulphate.

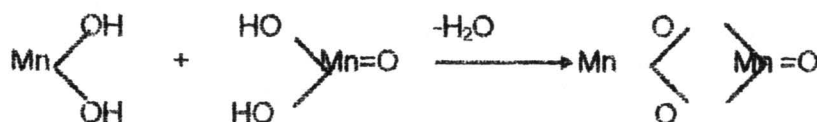
2.1.4. OXIDATION OF MANGANOUS SALTS IN BASIC MEDIUM



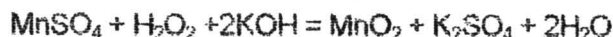
By treating a colourless solution (or pale pink) of manganese (II) with a hydrated oxide, yields a white precipitate of Mn(OH)₂ which is not stable and it is oxidizing in presence of oxygen to manganous acid (a brown precipitate). In presence of hydrogen peroxide, the reaction occurs faster.



Mn(OH)₂ in presence of manganous acid leads to manganous manganites.



On heating, the oxidation of manganous salts with H₂O₂ yields manganese dioxide:

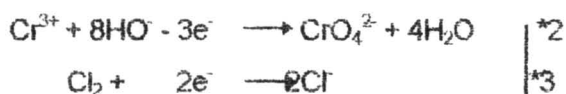


This reaction must be carried out into a test tube.

2.2. OXIDATIONS INTO AQUEOUS SOLUTIONS WITH HALOGENS

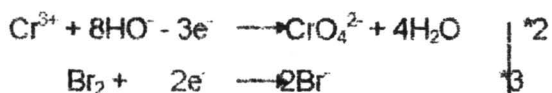
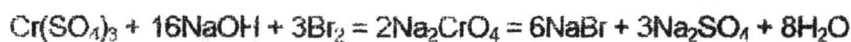
2.2.1. OXIDATION OF Cr(III) ION IN ALKALINE MEDIUM WITH CHLORINE WATER

In test tube introduce a solution of chromic sulphate, add kalium hydrate and an excess of chlorine water and observe the change of colour from green to yellow (characteristic for chromate ion).



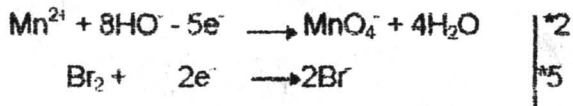
2.2.2. OXIDATION OF CHROME(III) ION TO CHROMIC ION, IN ALKALINE MEDIUM WITH BROMINE WATER

Into a test tube introduce a solution of chromic sulphate, add in excess of sodium hydrate and bromine water, and observe the colour's change from green to yellow.



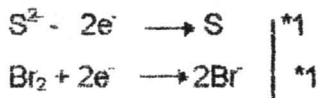
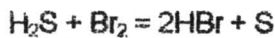
2.2.3. OXIDATION OF MANGANESE(II) ION TO PERMANGANIC ION, IN ALKALINE MEDIUM WITH BROMINE WATER

Into a test tube introduce a solution of MnSO_4 , an excess of potassium hydroxide solution, and add bromine water and a few drops of cupric sulphate (the catalyst). A change of colour from colourless-pink to violet is observed.



2.2.4. OXIDATION OF SULPHURETTED HYDROGEN WITH BROMINE WATER

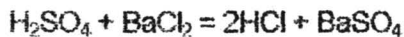
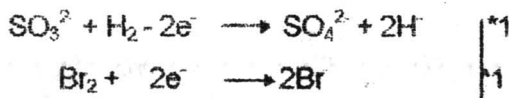
Over an aqueous solution of bromine water add under stirring sulphuretted hydrogen water (drop by drop). You can observe the disappearance of brown colour specific to bromine water and appearance of yellow opalescence characteristic for colloidal sulphur. Use a tube test.



2.2.5. OXIDATION OF SULPHUROUS ACID WITH BROMINE WATER

Into two test tubes introduce 5ml of sulphurous acid (5ml in each one) just prepared (through introducing gaseous sulphur dioxide into water) and then, in the first test tube add 2ml of bromine water and shake up the content. Into both test tubes add 2-3ml of barium chloride (BaCl_2) acidulates with dilute HCl. For the first experience (with bromine water) a white precipitate (BaSO_4) appears, while for the second experience no precipitate is formed.

The reaction for the first experience are:



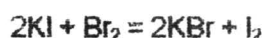
The sulphur dioxide required for the sulphurous acid preparation is obtained from the reaction of neutral or acid sulphites, carried out into the installations showed in figure no.1 (chapter 1.4.1) or in figure 2. The Wurtz balloon contains sodium sulphite and concentrated

H₂SO₄ is dripped by the funnel in small amounts, after every emission of gaseous sulphur dioxide.

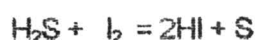
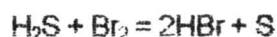
You may use other reagents, too, acid sodium sulphite (solution 40%) and sulphuric acid (45%).

2.2.6. OXIDATION OF IODIDES WITH BROMINE WATER

Add bromine water over a colourless solution of an iodide and observe the brown colour specific to aqueous solutions of iodine. Carry out the reaction into a test tube:



2.2.7. OXIDATION OF SULPHURETTED-HYDROGEN WITH CHLORINE AND BROMINE WATER AND WITH A SOLUTION OF IODINE IN IODIDE



Use test tubes. The result is the appearance of colloidal sulphur.

3. ANODIC OXIDATIONS

ANODIC OXIDATION OF CHROME TO CHROMATE AND OF MANGANESE TO PREMANGANATE

Chrome and manganese are transitional metals which may have multiple oxidation states. The following experience shows how chrome (0) turn into Cr(VI) and Mn(0) turns into Mn(VII). The metals are functioning as anodes, and in the electric field created by electrodes, they will oxidize to their superior states:

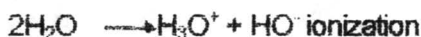
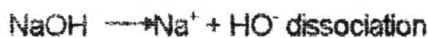


Cr(VI) stabilizes as CrO₄²⁻ ion (in alkaline medium)

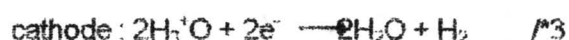
Mn(VII) stabilizes as MnO₄⁻ ion (acid medium)

The electrochemical processes from the electrodes are:

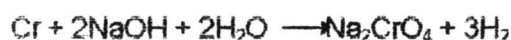
- for the electrolyse of a NaOH solution using metallic chrome as an anode:



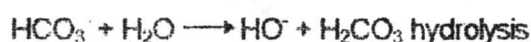
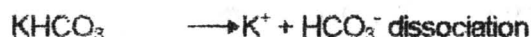
At the anode in the presence of the hydroxyl ions, the chrome oxidizes to CrO_4^{2-} and at the cathode, the hydronium ions are reducing because of their electrode potential, lower than sodium ions:



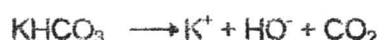
The total reaction is:



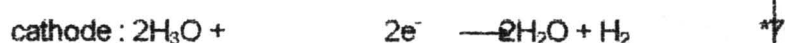
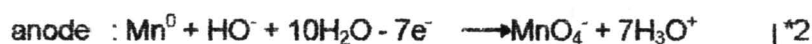
- for the electrolyse of an acid kalium carbonate using manganese as anode:



In solution we have:



At the anode, the manganese(0) oxidizes to MnO_4^- . At the cathode, H_3O^+ which results from water's ionization process and from anodic process, reduces to H_2 and H_2O .



Taking into account that two HO^- ions came from 2KHCO_3 , the total reaction will be:



The chromate and permanganate ions formed at the anode can be recognized after their characteristic colours (yellow for chromate and violet for permanganate).

The electrolytic installation consists of two cells linked parallel on to another. The anods are made of metals (chrom or manganese) and cathodes of iron. $U=5-10\text{V}$; $I=1-3\text{A}$. Reagents: NaOH solution 10% for chrom and solution of acid kalium carbonate 10% (for manganese).

The obtained solution is titrated with the KMnO_4 solution 0,1n (with titre T just determined), under stirring and drop by drop, until the pink colour is persistent.

The reaction is:



$$1E_{\text{KMnO}_4} = 31,606\text{g} \dots\dots\dots 1E_{\text{Fe}} = 55,84\text{g}$$

$$V_2 \text{ cm}^3 \times T \text{ g/cm}^3 \dots\dots\dots y \text{ g Fe}$$

where V_2 = volume of KMnO_4 0,1n used

T = titre

$$\rightarrow \text{the amount of iron from sample} = \frac{V_2 \times T \times 55,84}{31,606}$$

4. REDOX TITRATIONS

Redox titrations have a lot of practical applications. Knowing the quantity of standard reagent necessary for the titration of an element (see the chapter "Solutions") which is changing its oxidation state, the quantity of substance existent into a sample can be determined. Such a method of analyse uses manganic permanganate as oxidizing agent.

Kalium permanganate acts as an oxidizing agent and suffers a reduction process:



Thus, the gram-equivalent of KMnO_4 is 31,606

(E = Molecular weight) number of changed electrons = 158,03/5

The end of the titration may be exactly determined because of the colour's change. As long as the solution which is subdue to titration, still contains reducing substances, the solution of kalium permanganate added drop by drop will be discoloured; when the titration is finished, a single drop of KMnO_4 added in excess changes the colour the colour to pink.

The solution of KMnO_4 used has the normality 1/100.

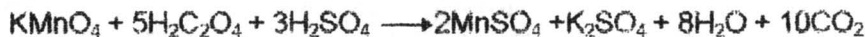
4.1. DETERMINATION OF TITRE OF KMnO_4 SOLUTION 0,1n

- Preparation of the solution

Dissolve 3,2-3,3g of KMnO_4 in 1000cm^3 distilled water and let the solution 2-3 days for the stabilization of its titre

• Determination of the titre

The method is based on the reducing action of the oxalic acid



Weight at the analytical balance about 0,22 of oxalic acid and introduce them into a conic glass (250cm³); pour 50-60cm³ of distilled water. Add 20-30cm³ of H₂SO₄ solution 20%, wash the glass walls with distilled water and heat the glass at 60-70°C. Now you can carry out the titration with kalium permanganate solution.

First, the reaction occurs slowly but then faster (because of the product MnSO₄ which has a catalytic role). To accelerate the oxidation process it is better to heat at 60-70°C.

The titration has to be made under stirring, and drop by drop (so take care of this rules!). The temperature may not exceed 60-70°C, because up to 70-80°C the oxalic acid decomposes:



The titre is calculated after the following reasoning:

- one gram-equivalent of H₂C₂O₄*2H₂O (63,034g) reacts with one gram-equivalent of KMnO₄ (31,606g)

- "m" grams of oxalic acid weighed will react with "x" grams of KMnO₄:

$$x = \frac{31,606 * m}{63,034}$$

- "x" grams of KMnO₄ are contained into V₁ cm³ of solution 0,1 n used for titration, so the titre is:

$$T = \frac{x(\text{g KMnO}_4)}{V_1(\text{cm}^3)}$$

4.2. DETERMINATION OF IRON FROM FERROUS SALTS

The experience uses as an oxidizing agent the solution of kalium permanganate 0,1n (with the titre determined above).

The sample of Mhor salt (10ml; 15ml; 20ml) will be diluted with 50-60cm³ of distilled water (washing also the glass'walls) and aciduated with 20-30cm³ of H

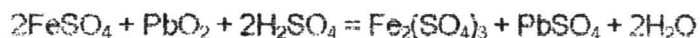
SECTION IX

The copper(II)sulphate purification from an mixture of copper(II) sulphate and iron (II) sulphate

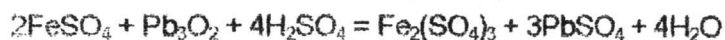
The copper(II) and iron(II)sulphates are izomorphous salts and crystalize together, so their separation by recrystalization it's impossible. These salts are separated,, by a chemistry method of oxidation of Fe(II) to Fe(III). The Fe(III) ion is removed as iron(III) hydroxide precipitate.

The chemical reactions are relised in a backer of 150cm³ where are introduced 40-50cm³ distilled water, 2g mixture of CuSO₄ and FeSO₄, 0,5g PbO₂ or 1,5g Pb₃O₄ and 2-3cm³ H₂SO₄ 20%.

This mixture is heating and take place the following reactions:



respectively

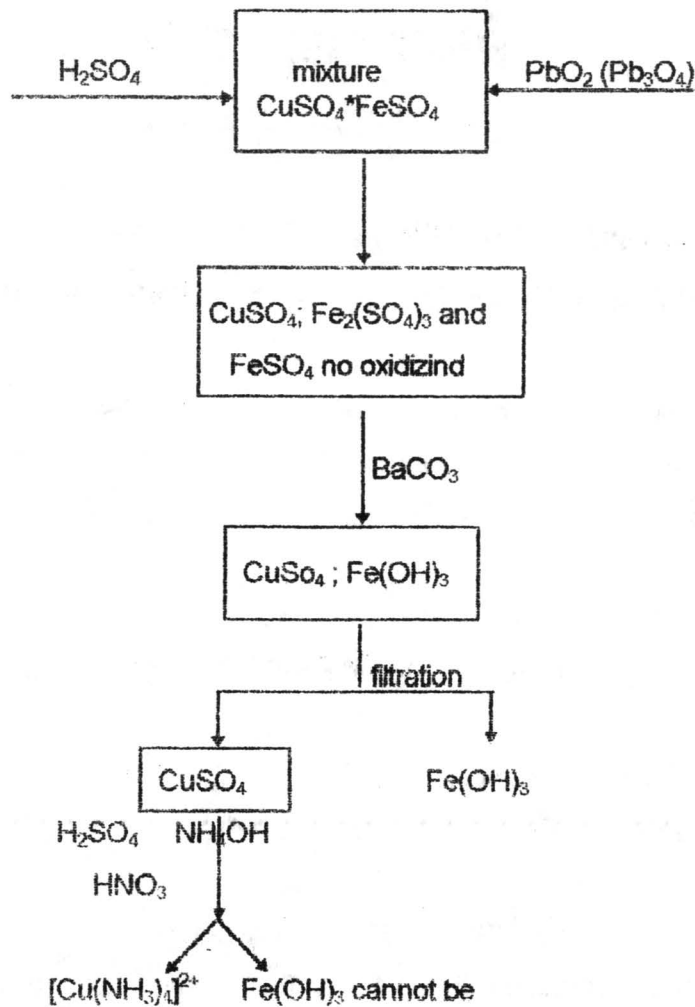


The iron(III) is precipitated with a 5-10cm³ BaCO₃ suspension as Fe(OH)₃, then Cu²⁺ and Fe²⁺ rested in the initial solution. The Fe(OH)₃ is remoted by filtration.

In the filtrat Cu^{2+} rested as CuSO_4 . 10ml filtrat are treated with 1cm³ H_2SO_4 20% and some HNO_3 conc, NH_4OH conc until CuSO_4 is solubilized as $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

NH_4OH conc precipitats Fe^{3+} rested in the filtrat and it rested on the paper test, and indicates that the oxidization process of initial Fe^{2+} isn't finish and have to be repeted.

The outline of the CuSO_4 purification



DETERMINATION OF SUBSTANCES PURITY DEPENDING ON THE VOLUME OF GAS FORMED DURING THE REACTION

This method employs the following proceeding: the substance is treated with a reactive which determines a gas emission; this gas is reaped under the water and his volume is measured. The volume is reduced to normal conditions and from the equation of reaction, the purity of initial substance is determined.

DETERMINATION OF ZINC'S PURITY

For the determination of zinc's purity are employed the apparatuses presented in figure 1. Into the baloon (1) are introduced 10 ml of H_2SO_4 (30% concentrated together with a few drops of dilute solution of $CuSO_4$ 0.2 g of zinc (exactly weighted) are introduce into the neck of the baloon which is setted in a horizontal position (see the dotted part on the figure). The vessel no.3 and the graduated cylinder (2) are filled up with water. The cylinder is coveredby a glass plate and it is overturned into the vessel. The tightness apparatus must be verified. Then, the baloon is setted vertically, so zinc falls into the baloon, and the hydrogen which yields is reaped into the cylinder.

After the end of the reaction, the tube through which the gas is going out is taken from the vessel, the volume of gas, level into the cylinder is wried down and the distance from the liquid's level into the vessel, to the liquid's level into the cylinder (height no.1) is measured. The temperature and the pressure are wrien down.

Using the law of gases :

$$\frac{p * V}{T} = \frac{p_0 * V_0}{T_0} \quad (1)$$

the hydrogen's volume is reduced to normal conditions. The pressure of hydrogen (p) is :

$$p = p_{bar} - \left(h - \frac{l}{13,6}\right) \quad (2)$$

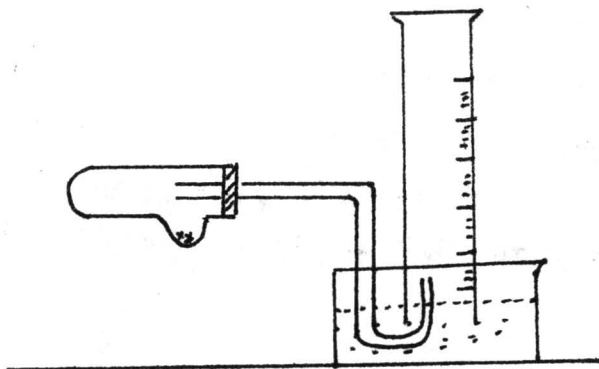
where h is the vapour pressure of water, and 13.6 represents dHg.

Values for the vapour pressure of water (h, mm Hg) depending on temperature (t, °C):

t°C	h	t°C	h	t°C	h	t°C	h
10	9.2	16	13.6	22	19.8	28	28.3
11	9.8	17	14.5	23	21.1	29	30.0
12	10.5	18	15.5	24	22.2	30	31.8
13	11.2	19	16.5	25	23.8	40	55.3
14	12.0	20	17.5	26	25.2	50	92.5
15	12.8	21	18.6	27	26.7	100	760

Using the equation of the reaction, may be measured the volume of the hydrogen resulted from the reaction between H_2SO_4 and pure Zn contained into the impure Zn taken for analyse.

Now, zinc's purity may be calculated.



THE OBTAINING OF SOME CUPROUS CHLORIDE

1. THE OBTAINING OF CUPROUS CHLORIDE

The method is based on the reduction of cupre sulphate by the metallic copper, in presence of natrium chloride:



A mixture of 2.5 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, 1g of copper chip and 5 g of NaCl together with 25 cm³ of water is heated about 20-30 minutes. The obtained solution is immediately filtered or decanted into 20-25 cm³ of acetic acid solution 2-3%.

The tetraedric crystals of cuprous chloride, which are stable in acetic acid are filtered on the Buchner funnel, washed with alcohol and ether, and dried in the oven.

2. THE PREPARATION OF CUPROUS OXIDE

The method is based on the reduction of cupric salts by organic reducers.

A mixture of 25cm³ of solutions I and II (the components of the Fehling solution - see below) and 40 cm³ of glucose solution 1% (the reducing agent is boiled. Yields a red precipitate (Cu_2O).

The equation of the reaction is:



The red product is filter on Buchner, it is washed with watert, alcohol and ether.

The solution I contains : 3.46 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ in 50 cm³ of water.

The solution II contains : 5.2 g of NaOH and 17.3 g sodium and kalium tartrat in 50 cm³ of water.

SOLUTIONS

Solution are homogenous mixtures formed of two or more substances; their properties are varying continuously with the ratio of components.

The homogenous mixtures may be liquid,solid or gaseous. As regard dispersed systems we may distinguis:

- solution of gas into a liquid
- solution of liquid into a liquid
- solution of solid into a liquid

Any solution has two main components; the dissolved substance called solute and the solvent (the most used solvent is water). The concentration of a solution indicates the amount of solute dissolved into a certain amount of solvent.

The solution's concentration may be:

-percentage concentration(%) - indicates the quantity in grams of dissolved substance which are contained into 100g of solution

$$c\% = \frac{m_d}{m_s} * 100$$

where m_d =mass of dissolved substance

m_s =solution's mass

- molar concentration (m = molarity) -indicates the number of molecules of solute dissolved into one liter of solution.

$$m = \frac{m_d}{M * V}$$

where: m_d =solute's mass (having the molecular weight M) dissolved into V liters of solution.

- normal concentration (n = normality) - indicates the number of equivalents of dissolved substance contained into one liter of solution:

$$n = \frac{m_d}{E * V}$$

- molal concentration (m = molality) -indicated the number of moles of dissolved substance contained into 1000 g of solvent.

$$m = \frac{m_d * 1000}{M * m_s}$$

Besides the concentration presented above, there is also another one: the titre of a solution, which represents the amount of substance (in grams) contained in 1 m³ of solution.

1. SOLUTION'S PREPARATION

Can be carried out in several ways:

- using a weighed sample of substance and water;
- using a solution of a certain concentration and water;
- using two solutions of different concentrations.

The solutions obtained from a weighed sample of solid substance are divided into standard solutions and approximate solutions. Standard solutions are prepared from very pure substance, non-alterable by air (for example the solution of oxalic acid). The titre corresponds to the theoretical value.

In case of approximate solutions, the titre is experimentally determined using standard solutions. The number which indicates how many times a solution is more concentrated or diluted than the solution of precise concentration is called factor of the solution (F).

$$F = \frac{T_{\text{experimental}}}{T_{\text{theoretical}}}$$

Thus, F for standard solutions is 1.

The solution's factor can be obtained both from the ratio $T_{\text{exp}}/T_{\text{theoretic}}$, or from the subsequent relation:

$$V_a \cdot F_a = V_b \cdot F_b$$

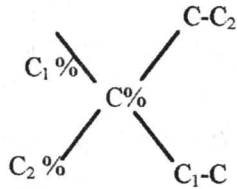
where V_a and F_a are volumes and factor for approximate solution and V_b , F_b are the corresponding values for standard solution.

In case solutions obtained through dilution or through mixing solutions of different concentrations, the calculus of required quantities of solution is made by the rule of mixtures.

Let's suppose that we have two solutions of different concentrations ($C_1\%$ and $C_2\%$). Starting from these solutions we want to prepare a certain amount of solution having an intermediate concentration between C_1 and C_2 ($C\%$).

$$C_1\% > C\% > C_2\%$$

We have to apply the rule of mixtures which may be reduced to a simple scheme:



Thus, $(C-C_2)$ represent weight parts of the $C_1\%$ solution which must be mixed with (C_1-C) parts of $C_2\%$ solution, to yield a solution $C\%$. To obtain the volumes of the two solutions ($C_1\%$ and $C_2\%$) we have to divide the masses $(C-C_2)$ and (C_1-C) by the densities of the solutions. The rule is also applied in case of normal and molar concentrations.

1.1 PREPARATION OF CUPRIC SULPHATE SOLUTION 4.1%

We have to calculate the amount of cupric sulphate hydrated by five molecules of water ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) necessary for the preparation of 60 g a solution 4.1%. The solid substance ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) must be weighted at the analytical balance and water measured by a graduated cylinder. Are needed a Berzelius glass and a rod. The obtained solution is introduced into a bottle for reagents.

1.2 PREPARATION OF A NATRIUM HYDRATED SLUTION 0.1n

We have to compute the quantity of NaOH solution necessary for the preparing of 200 or 250 cm^3 (depending on the quoted balloon) of NaOH solution with normal concentration 0.1. The concentration will be approximately 0.1n because of the hygroscopic properties of the substance. Its precisely normality will be determined afterwards, by the experimental establishing of titre and factor.

Sodium hydrate has to be weighted on a glass plate at pharmaceutical balance and will be introduced into the quoted balloon.

1.3 PREPARATION OF SULPHURIC ACID SOLUTION 0.1n

We need to compute the volume of sulphuric acid 96% ($d = 1.84\text{g/cm}^3$) necessary for the preparation of 200 cm^3 (250 cm^3) of solution 0.1n.

Fill a half of the balloon with distilled water and then add in drops and under permanent stirring, the required volume of H_2SO_4 ; fill up the balloon with water until you reach the quotation.

Since the solution has an approximate concentration, the following step is the determination of titre and factor.

2. DETERMINATION OF SOME ACIDS' AND BASES' CONCENTRATION (TITRE)

It is carried out employing the volumetric analyses, which determines the volume of reagent B consumed by the analysed substance B during a certain chemical reaction (a neutralization, oxidation - reduction or precipitation reaction).

The reagent of precisely known concentration, is added in stoichiometric quantity. Using the chemical equation the amount of the substance A may be determined.

The establishing of the reaction's end (the points of equivalence) is made by the indicators. These are substances which change their colour at every small amount of reagent added.

2.1 DETERMINATION OF THE CONCENTRATION (TITRE) OF A NARIUM

For this purpose can be used as standard substance oxalic acid. Introduce 0.2 g of oxalic acid hydrated by two molecules of water (precisely weighted at the analytical balance) into an Erlenmeyer glass of 250 cm³. Add 40-50 cm³ of distilled water just boiled. After the dissolution and 2-3 drops of phenolphthalein and then carry out the titration with the sodium hydrate solution (prepared at experience 1.3) until a pale pink colour appears. This operation must be repeated until the difference between the results is about 0.05cm³.

It is better to use a biuret with a mohr clamp for measuring the sodium hydrate solution's volume. Before its using, the biuret must be washed with water and finally with the solution.

The titre T_1 of the sodium hydrate solution may be computed as follows:

m_1 (grams) = mass of oxalic acid (use four decimal fractions)

V_1 (cm³) = volume of NaOH solution 0.1n used.

$$\frac{E(H_2C_2O_4 \cdot 2H_2O)}{m_1} = \frac{E(NaOH)}{T_1 V_1}$$

$$T_1 = \frac{m_1 * E(NaOH)}{E(H_2C_2O_4 * 2H_2O) * V_1} = \frac{40.005 * m_1}{63.034 * V_1}$$

The factor F_1 is determined from the ratio:

$$F_1 = \frac{T_1}{T_{theoretical}}$$

where $T_{theoretical} = 0.004 \text{ g/cm}^3$

2.2. DETERMINATION OF THE CONCENTRATION (TITRE) OF A SULPHURIC ACID SOLUTION 0.1n

It is used the solution of sodium hydrate 0.1n for which the titre and factor were determined.

Introduce 20 cm³ of NaOH solution 0.1n measured by the biuret, into an Erlenmeyer glass. Dilute with distilled water washing the walls of the glass, too. Add 2-3 drops of phenolphthalein and carry out the titration with solution of sulphuric acid 0.1n until

colourless solution. The titration must be repeated until the the difference between the results is about about 0.05 cm³

The titre and factor are calculated as follows:

$$\begin{aligned} E(\text{H}_2\text{SO}_4) & \text{-----} E(\text{NaOH}) \\ x \text{ g}(\text{H}_2\text{SO}_4) & \text{-----} V(\text{NaOH}) * T(\text{NaOH}) \end{aligned}$$

$$x = \frac{20 * T_1 * 49}{40.005}$$

V_2 (cm³) = volume of H₂SO₄ 0.1n used

$$T_2 = \frac{x}{V_2} \quad (\text{titre of H}_2\text{SO}_4)$$

$$F_2 = \frac{T_2}{T_{\text{theoretical}}} \quad (\text{factor of H}_2\text{SO}_4)$$

where T theoretical=0.0049 g/cm³

Another relation may be used for computing the titre and the factor:

$$V(\text{NaOH}) * (F(\text{NaOH})) = V(\text{H}_2\text{SO}_4) * F(\text{H}_2\text{SO}_4)$$

THERMIC EFFECTS

The variation of the internal energy and of enthalpy which accompany the reversible chemical processes (isochoric or isobaric) are taking place accompanied by exchange of energy (heat) with the exterior.

Thus, in case of some chemical processes, the system yields heat to its neighbourhood (exothermic processes) and in other case, the system accepts heat from its neighbourhood (endothermic processes). The amount of heat which is given off or accepted during a process, is called thermic effect.

Depending on the nature of the process, the thermic effect may be: formation heat, reaction heat, hydration heat, evaporation heat.

The quantity of heat changed during a chemical reaction is called reaction. It may be considered at invariable pressure or volume.

According to the first principle of thermodynamics:

$$\Delta U = Q + L$$

For a reaction which takes place at invariable pressure, the mechanic work (L) effectuated by the system is:

$$L = -pdV$$

therefore:

$$\Delta U = Q - pdV$$

As regards liquid and solid substances, which have a negligible variation of volume ($\Delta V=0$), the energy of reaction (ΔU) is equal to the enthalpy of reaction (ΔH).

If during the reaction intervene gaseous substances we must consider also the possible variation of volume.

Thus, for system which advances for n_1 mole of gaseous reacting substances to n_2 mole of gaseous reaction products (so a variation of moles' number $n = n_2 - n_1$) and for the volume V of one mole, we can write:

$$\Delta U = \Delta H - p\Delta V$$

For an ideal gas:

$$\Delta U = \Delta H - RT\Delta n$$

If the reaction occurs without a variation of volume ($\Delta n = 0$) the result is $\Delta U = \Delta H$.

The reaction heat at invariable pressure (ΔH) it is measured by an open calorimeter. The calorimetric measurements are based on the determination of temperature variations of the systems which are investigated into special calorimeters, equipped with a casing which allows no change of heat (adiabatic calorimeters).

1. THE CONSTANT OF THE CALORIMETER

When a warm body is introduced into a calorimeter's water, the heat of this body is taken over not only by the water, but also by the calorimeter bomb, by the stirrer and by the thermometer.

therefore, appears the need to determine the caloric capacity, known as the constant of the calorimeter (K) or the water equivalent of the calorimeter. This constant is experimentally determined and corresponds to the sum of the products between masses and specific heats of all components of the calorimetric system.

1.1.DETERMINATION OF THE CALORIMETER'S CONSTANT

Introduce into the calorimeter 50 cm³ of distilled water, after 2-3minutes its temperature must be measured.. Over the water having the temperature t_1 , suddenly introduce 30 cm³ of distilled water temperature t_2 (about 90°C). Stirr by the thermometer and read the temperature (by the same thermometer) every minute, until you establish the highest temperature reached by the system (t_3 °C).

The heat given off by 30 cm³ of distilled water, $30(t_2 - t_1)$ was taken by $(50 + K)$ g of water (K is the calorimeter's constant) and results an increasing of the whole system's temperature equal to $(t_3 - t_1)$ °C.

Considering the specific heat and water's density equal to unit , we may write:

$$30(t_2-t_3) = (t_3-t_1)(50+K)$$

It is easy now to obtain the value for K.

1.2. DETERMINATION OF DISSOLUTION AND HYDRATION HEAT

The dissolution heat is the heat which evolves or is absorbed during the dissolution of a substance.

The dissolution process is endothermic when the energy consumed for taking out the ions or molecules from the network is higher than the energy setted free as a result of molecules' or ions' interactions with the dissolvent. The dissolution process is exothermic when the energy absorbed is lower than the energy setted free.

EXP.1 In the experimental work we shall determine the molar dissolution and hydration heats for CuSO_4 (the heat during the dissolution of 1 mole of substance).

For this purpose , we must initially determine the thermic effect of the dissolution reaction of the anhydrous CuSO_4 , wich is given by the sum between the hydration head of CuSO_4 and the dissolution heat of CuSO_4 hydrated by five molecules of water. The subsequent determination of the thermic effect for the dissolution reaction of hydrated CuSO_4 , allows the calculation of the hydration heat.

Into the calorimeter, after his constant is determined, introduce 75 cm^3 of distilled water. Write down the temperature wich remains invariable ($t_1^\circ\text{C}$). Over the water from calorimeter add 2.5 cm^3 of anhydrous CuSO_4 (precisely measured at the analytical balance). Stirr the solution to accelerate the dissolution process , and write down the temperature every 30 seconds until it remains invariable ($t_2^\circ\text{C}$). The specific heat of the obtained solution is equal to unit, the solution's mass (m_1) consists of sum between waters's mass (75 g) and mass of anhydrous CuSO_4 introduced, so finally the quantity of heat q_1 can be obtained from the calorimeter relation:

$$q_1 = m_1c(t_2-t_1)+k(t_2-t_1)$$

where q_1 is the sum between the hydration and dissolution heats for the anhydrous CuSO_4 introduced, and K is the constant of the calorimeter.

Dividing the value q_1 by mole, you can obtain the sum between the molar hydration heat of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

EXP.2 Another experiment allows the determination of thermic effect for the dissolution process of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The result is the molar dissolution heat q_2 .

$q_1 - q_2$ represent "molar hydration heat".

You have to repeat the experience above, using now 3g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. You must write down the temperature every 30 seconds until it remains invariable ($t_2^\circ\text{C}$). Taking into account the initial temperature t_1 measured for 75 cm^3 of distilled water, the solution's mass m_2 and the value for calorimetric constant you can obtain the value q_2 :

$$q_2 = m_2 c (t_2' - t_1') + (t_2' - t_1') K$$

where q_2 is the dissolution heat for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Divide q_2 by a mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and you have the molar dissolution heat.

1.3. THE DETERMINATION OF THE NEUTRALIZATION HEAT

EXP.3 Into a calorimetric bomb (having his calorimetric constant already determined) introduce 50 cm^3 of chloric acid solution (0.5n) and into another calorimetric bomb 50 cm^3 of sodium hydrate solution (0.5n). Write down the temperature t_1 (for NaOH) and t_2 (for HCl). Pour NaOH over HCl. Write down the highest temperature t_3 obtained as a result of the neutralization process. The amount of heat which is given off, can be calculated in this way:

$$q = (t_3 - t_1) \cdot 50 + (t_3 - t_2) (50 + K)$$

The specific heat of the solutions are considered are considered equal to unit. Dividing q by a mole of acid (or of base) you obtain the molar neutralization heat.

COMPLEX COMBINATIONS

Known also as coordination compounds, they generally consist of a central metallic ion, surrounded by a great number of ions or molecules, which are called ligands. The complex compound may be a cation, an anion or a neutral molecule depending on the of the components charges. We can speak about determined structures when we know the coordination number of the metallic ion the stereochemistry of the complex molecule or ion, its conformation and the nature of the metal-ligand bond.

The complex compounds may be obtained using the following methods:

- the direct reaction between metallic salt and ligand;
- the partial or total substitution of the ligands from the coordination sphere;
- the substitution of the uncoordinated ligands (from the ionization sphere);

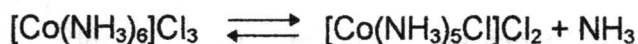
The following experiences will show how the first method can be used to obtain some ammine compounds.

1. HEXAAMMINO COBALT (III) CHLORIDE



Over the solution obtained from 2,5 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved into minimum amount of water are added 5 ml of ammonium hydroxide 25% in which are dissolved 1.5 g ammonium chloride. Finally, 0.2 g of active coal dust are added.

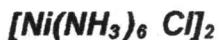
The brown solution has to be cooled on ice and after 15 minutes must be treated with 2 ml of hydrogen peroxide and kept on ice for another 15 minutes. The excess of hydrogen peroxide is eliminated on steam bath (until is free of oxygen bubbles). The solution must be now neutralized with HCl (pH = 7). Pay attention to the pH, because at a lower value the pentaammine forms, as follows :



After the solution is cooled, a simple filtration is made, using a filtering paper with small pores. The coal together with the hexaammine remain on the paper and the filtrate contains the secondary products.

For the hexaammine separation, the coal residue is treated with warm water acidulated with HCl (small amounts are needed). The solution is heated on steam bath until a turbidity appears. After the solution is cooled on ice, the hexaammine crystallized and is filtered on a Buchner funnel and washed with alcohol.

2. HEXAAMMINO Ni(II) CHLORIDE



1 g of nickel(II) chloride is dissolved into minimum amount of water and an excess of ammonium hydroxide is added. Another solution is prepared from 1 g of ammonium chloride and 2.5 ml of concentrated ammonium hydroxide and it is added to the first solution. The precipitate is washed through decantation and then is filtered on Buchner funnel and washed with alcohol.

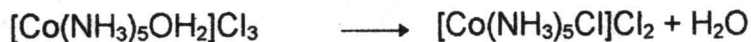
3. CHLOROPENTAAMINO Co(III) CHLORIDE



2.5 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are dissolved into minimum amount of water. Another solution is prepared from 15 ml of NH_4OH 25% and 5 g of NH_4Cl and it is added to the first solution. The reaction mixture is cooled on ice for 15 minutes, 2 ml of hydrogen peroxide are gradually added and then is kept for another 15 minutes on ice.

After the oxidizing process is finished (a brown mass is formed), the excess of H_2O_2 is eliminated on steam bath until the solution is free of oxygen bubbles. The solution is now cooled and neutralized with concentrated HCl (pH = 7) and then an excess of HCl is added (pH = 5). The solution is concentrated on steam bath until the first crystals appear and then is cooled on ice for a total crystallization. The filtration is made on the Buchner funnel and the the crystals are washed with some cold water. The crystals are purple-violet.

The reaction are supposed to be as follows :



ELECTROLYTIC CONDUCTIBILITY

Depending on their behavior to the electric current's passing over, there are two kinds of substances: substances having solutions through which, the electric current may pass over (the electrolytes and substances having solutions which not allow the passing of the electric current (non-electrolytes).

The dilute solutions of non-electrolytes demonstrate properties which are depending on the number of molecules from the system. This kind of solutions which

are respecting the Raoult and Van't Hoff laws are called ideal solutions and those which present deviations from these laws are the real solutions.

In 1887 Arrhenius elaborated the theory of the electrolytic dissociation.

In essence, it is considered that on their dissolution in water, the acids, bases and salts dissociate total or partial into ions with opposite charges, as a result of the interaction between the solvent and the dissolved substance.

Depending on the mechanism of the ions formation into the solution, the electrolytes are divided into:

- real electrolytes, having an ionic network; because of the ion-dipole interaction the ions from the network pass into the solution, suffer a solvation and a free diffusion into the solution's mass;
- potential-electrolytes-substances having polar covalent bonds which allow the ionization on the dissolution process;

The dissociation of a substance through its dissolution into a solvent or through its melting, may be expressed by the dissociation degree, α , which represents the fraction of molecules dissociated into ions, reported to the total number of molecules from the dissolution or molten:

$$\alpha = \frac{\text{numero_of_dissociated_molecules}}{\text{total_number_of_molecules_into_the_solution}} = \frac{N_{diss}}{N_{init}} \quad (1)$$

α has values from 0 to 1.

Usually α is expressed in percents:

$$\alpha = \frac{N_{diss}}{N_{init}} * 100 \quad (2)$$

The dissociation degree, α , depends on the electrolyte's and solvent's nature and on the concentration of the solution. α is obtained by conductivity measurements.

Depending on the values for α , the electrolytes were divided into two categories: strong electrolytes which dissociate almost total (α is close to 1), and weak electrolytes

which show a low dissociation (α is close to 0). Between these, there are the electrolytes with an intermediate behaviour.

1. THE IONS' MOBILITY

Under the action of an electric field, created by application of a potential difference between two electrodes, the ions migrate to these electrodes, depending on their charge. The rate of migration for different ions is not the same. Because of this, different concentration of electrolyte appear near the electrodes.

The distance (in cm) by the ions during a second, represents the rate of migration, which depends for a certain temperature, on the distance between the electrodes and on the potential difference. For this reason, the ionic mobility (u) is used instead of the rate of migration.

The ionic mobility represents the rate of the ions displacement because of an electric field (1 V/cm). Thus, the mobility u is given by the ratio between the rate of migration V (cm/sec) and the intensity of the field E (V/cm):

$$u = \frac{V \text{ cm/s}}{E \text{ V/cm}} \quad (3)$$

The mobility for one ion is equal to the rate of this ion, for a potential difference of 1 V, applied between two electrodes placed at 1 cm one from another.

The electricity amount transported by each ion is proportional to the mobility u_+ and u_- of the ion.

J.W.Hittorf has introduced the transport number t , which is the ratio between the electricity amount transported by an ion and the electricity amount transported by all ions from the solution:

$$t_+ = \frac{\text{lost_equivalents_from_catodic_space}}{\text{lost_equivalents_in_both_spaces}} = \frac{(u_+)}{(u_+) + (u_-)} \quad (4)$$

The transport number of the anion is:

$$t_- = \frac{(u_-)}{(u_+) + (u_-)} \quad (5)$$

It is obvious that $(t^+)+(t^-) = 1$

2. SPECIFIC ELECTRIC CONDUCTIBILITY OF THE ELECTROLYTES

The specific resistance or the resistivity ρ is the resistance of a column of substance ($l = 1 \text{ cm}$, $S = 1 \text{ cm}^2$). The resistance R of a substance is:

$$R = \rho \frac{l}{S} \quad (6)$$

where l is the length of the conductor and S is its section.

For the electrolytes solutions, the resistivity ρ is the resistance of the solution content between two electrodes having a surface of 1 cm^2 and placed at 1 cm one from another.

In electrochemistry, instead of resistivity is used specific electric conductivity or the conductivity γ , which is the reverse of the resistivity:

$$\gamma = \frac{1}{\rho} \Omega^{-1} \cdot \text{cm}^{-1} \quad (7)$$

3. EQUIVALENT CONDUCTIBILITY OF THE ELECTROLYTES Λ_c

The specific electric conductibilities of the electrolytes solutions depends on the concentration. Thus, the values for the specific electric conductivity are diminishing along to the diminishing of the concentration since the dilute solution contain a lower number of ions able to transport the electric current, than concentrated solutions.

The comparison of the conductibilities of different electrolyte solutions has determined the introduction of a new parameter, which refers to a certain amount of electrolyte. This parameter is the equivalent conductivity:

$$\Lambda_c = \gamma * V = \frac{\gamma}{c} \quad \frac{\Omega^{-1}cm^{-1}}{1/cm^3} = \Omega^{-1}cm^2val^{-1} \quad (8)$$

where V is the volume, in cm³, which contains one equivalent of electrolyte and c is the concentration of the solution expressed in number of equivalents into 1cm³ of solution.

The equivalent conductivity Λ_c represents the conductivity of a solution which contains an equivalent-gram of dissolved substance contained between two plane electrodes, with a surface of 1cm², placed at 1cm one from another. In other terms, Λ_c is the ratio between the specific conductivity and the concentration of the solution (val./ml).

4. EQUIVALENT CONDUCTIBILITY AT INFINITE DILUTION, Λ_∞

The equivalent conductivity, Λ_c , shows an increase along with the diminishing of the solution's concentration, tending to a maximum value at infinite dilution, which is a constant for each electrolyte, called equivalent conductivity at infinite dilution Λ_∞ .

To determine this parameter, the equivalent conductibilities at lowerer concentration are measured and the value is extrapolated for concentration zero.

The ratio between the equivalent conductivity and the equivalent conductivity at infinite dilution, allows the calculation of the dissociation degree:

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty} \quad (9)$$

Λ_∞ is given by the sum of the equivalent conductibilities at infinite dilution for each ion:

$$\Lambda_{\infty} = \lambda_{+\infty} + \lambda_{-\infty} \quad (10)$$

At infinite dilution, the ionic conductibilities are direct proportional with the ions mobilities:

$$\lambda_{+\infty} = k * u_{+} \quad ; \quad \lambda_{-\infty} = k * u_{-} \quad (11)$$

$$\Lambda_{\infty} = \lambda_{+\infty} + \lambda_{-\infty} = k(u_{+} + u_{-}) \quad (12)$$

where k is Faraday constant.

EXPERIMENTAL PART

The resistance R of a conductivity cell is:

$$R = \frac{l}{\gamma S} ; \quad \gamma = \frac{l}{R} * \frac{l}{S} = \frac{k}{R} \quad (13)$$

The ratio $l/s = k$ is the constant of the cell.

k is determined at the beginning through the introduction into the cell of an electrolyte's solution of known concentration and specific conductivity (at work temperature). A solution of KCl is used.

The conductometer is an OK -102/1 type. The function principle is based on measurement of the voltage fall which appears into the solution between two electrodes geometrically well defined.

1. DETERMINATION OF CELL S CONSTANT

A solution of KCl 0.1 n is used.

c / T°C	0	18	20	25
0.1 n	0.00715	0.01119	0.01167	0.01288

The electrode, washed with distilled water and alcohol, and then perfectly dried (using an air trend is introduced into the vessel which contains the solution of KCl 0.1 n. The bottom S_5 is fixed at 500 mS and then is turned round to higher values until on the scale a value easy to be readed is obtained. The calibration is then controlled once again by pressing the button S_3 . If the pointer is not perfectly overlapped over the red sign, button S_4 is used to fix it. Only after the button S_3 is free, the conductivity value may be readed.

There are two scales: one from 0 to 5, and another from 0 to 15 divisions.

After the value for specific conductivity of KCl solution is readed, the cell's constant can be determined as follows:

$$\gamma = \frac{1}{R} * \frac{l}{S} \Omega^{-1} cm^{-1} = \frac{1}{R} * k \quad (14)$$

where : R = cell's resistance

$1/R$ = conductance - the value which is readed on the scale

l = distance between the electrodes

γ = specific electric conductivity for KCl sol. 0.1 n

l/S = constant (k)

2. DETERMINATION OF SPECIFIC CONDUCTIBILITY(γ), EQUIVALENT CONDUCTIBILITY(Λ_c), EQUIVALENT CONDUCTIBILITY AT INFINITE DILUTION(Λ_∞), DISSOCIATION DEGREE (α) AND ACIDITY CONSTANT(K_a) FOR AN ACETIC ACID SOLUTION

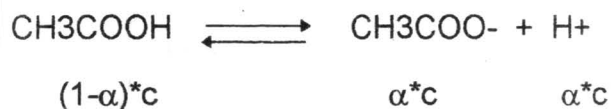
Starting from a solution of pure acetic acid ($\rho = 1.055 \text{ g/cm}^3$), 200 cm^3 of solution 0.1n; 0.01 n and 0.001 n will be prepared by dilution.

For these solutions, specific conductivity γ will be established. By an extrapolation for concentration zero, the equivalent conductivity at infinite dilution, Λ_∞ , is obtained.

Knowing Λ_{∞} for acetic acid and the equivalent conductivity at infinite dilution for a protone ($315 \Omega^{-1}\text{cm}^2/\text{vol}$), the equivalent conductivity at infinite dilution for acetate ion may be obtained (with the relation no.10).

Talking into account the equivalent conductivity Λ_c and also the value for Λ_{∞} previously determined, the dissociation degree α for acetic acid solution 1 n is determined (with 9).

In case of a weak acid as acetic is, its ionization process may be expressed depending on the dissociation degree α .



where c is the initial concentration of the acid (mole/l)

The acidity constant is:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \qquad (15)$$

The concentraion on equilibrium, depending on the dissociation degree are:

$$[\text{H}^+] = \alpha*c; \qquad [\text{CH}_3\text{COO}^-] = \alpha*c; \qquad [\text{CH}_3\text{COOH}] = (1 - \alpha)*c$$

The Oswald law may be now obtained:

$$K_a = \frac{\alpha^2}{(1 - \alpha)} * c \qquad (15)$$

Using $\alpha = \Lambda_c/\Lambda_{\infty}$, the dilution law becomes:

$$K_a = \frac{(\Lambda_c)^2 * c}{\Lambda_{\infty}(\Lambda_{\infty} - \Lambda_c)} K_a = \frac{(\Lambda_c)^2 * c}{\Lambda_{\infty}(\Lambda_{\infty} - \Lambda_c)} \qquad (16)$$

Using this relation for the experimental dates obtained of the previously, results the value for the acidity constant of the acetic acid.

THE ACTIVITY EXPONENT, THE pH

Water behaves both as a base or as an acid, so is an amphoteric substance. Thus, it suffers an autoionization:



$$K = \frac{a_{\text{H}_3\text{O}^+} * a_{\text{HO}^-}}{a_{\text{H}_2\text{O}}^2} \quad (2)$$

For pure water, the activities of the ions may be considered practically equal to their molar concentrations:

$$K = \frac{[\text{H}_3\text{O}^+][\text{HO}^-]}{[\text{H}_2\text{O}]^2} \quad (3)$$

Since the equilibrium (1) is strongly displaced to the left, the term $[\text{H}_2\text{O}]^2$ is almost constant, so the equation (3) becomes:

$$k * [\text{H}_2\text{O}]^2 = k(\text{H}_2\text{O}) = [\text{H}_3\text{O}^+][\text{HO}^-] \quad (4)$$

$k(\text{H}_2\text{O})$ = the ionic product of water

At 25°C, $K(\text{H}_2\text{O}) = 1 * 10^{-14}$, so:

$$[\text{H}_3\text{O}^+] = [\text{HO}^-] = 10^{-7} \text{ ions} * \text{g/l} \quad (5)$$

For the determination of these parameters the conductometric method is used.

The specific conductivity γ of pure water at 25°C is $5.54 * 10^{-8}$. Since for the autoionization reaction $[\text{H}_3\text{O}^+]$ and $[\text{HO}^-]$ are very low, the equivalent conductibilities (Λ_c) can be assimilated to equivalent conductibilities at infinite dilution (Λ_∞).

$$\Lambda_{\infty} = \lambda_{+\infty} + \lambda_{-\infty} = 350 + 198.5 = 548.5 \Omega^{-1} \text{ cm}^2 \quad (6)$$

where Λ_{∞} is the conductivity at infinite dilution of H_3O^+ ion.

Λ_{∞} is the same parameter for the $[\text{HO}^-]$ ion. It is obvious that into 1000 cm^3 of water (at 25°C) the concentration of $[\text{H}_3\text{O}^+]$ ion is:

$$[\text{H}_3\text{O}^+] = \frac{1000}{\Lambda_{\infty}} = \frac{6.54 \cdot 10^{-5}}{548.5} = 1 \cdot 10^{-7} \text{ mol} \cdot \text{ions} / \text{l} \quad (7)$$

When an acid is added to water, the activity (concentration) of the hydronium ion is decreasing because the ionic product of water is constant. The solution has an acid character. In their dilute solution, strong acids and bases are completely ionized.

When a strong electrolyte (inert), which not gives the hydrolysis, such as NaCl, the concentration of hydronium ions is the same as in pure water.

In 1909, S. Sorensen has proposed an expression which uses a logarithmic scale.

The pH was defined as the logarithm of hydronium ions concentration into the solution, taken with changed sign.

For concentrated solutions, the concentration was replaced with the "activity" of the ions. As a result:

$$\text{pH} = -\lg c_{\text{H}_3\text{O}^+} = -\lg c_{\text{H}^+} = \lg 1 / c_{\text{H}^+} \quad (9)$$

$$\text{pH} = -\lg a_{\text{H}_3\text{O}^+} = -\lg a_{\text{H}^+} \quad (10)$$

A similar parameter can be defined for hydroxyl ions:

$$\text{pOH} = -\lg C_{\text{OH}^-}$$

$$-\lg c_{\text{H}^+} - \lg C_{\text{OH}^-} = -\lg K_{\text{H}_2\text{O}} \quad (11)$$

$$\text{pH} + \text{pOH} = 14 \text{ or } \text{pH} = 14 - \text{pOH} \quad (12)$$

An aqueous solution is neutral when $[\text{H}_3\text{O}^+] = [\text{HO}^-] = 10^{-7}$ ion g/l ($\text{pH} = 7$). A solution with pH lower than 7 has an acid character, one with pH higher than 7 has a basic character.

METHODS FOR THE pH DETERMINATION

1. THE CALORIMETRIC METHOD

This method is used in case of indicators. The indicators colour depends on the pH of the liquid in which they are dissolved.

2. THE POTENTIOMETRIC METHOD

This method consists of the determination of the potential for an electrode in case that this potential is depending on the pH value of the studied solution. The compensation method is used: the potential of the electrode is measured in comparison with a reference electrode, which is usually the hydrogen or calomel electrode. It is preferred the saturated calomel electrode, which is made of a mercury layer covered by a calomel paste (Hg_2Cl_2) mixed with a little mercury, in contact to a saturated solution of KCl, 1 n. The potential of the calomel electrode in comparison with normal hydrogen electrode, at 20°C, is 0.2471 V.

As a measurement electrode a glass electrode is used. It is made of thin glass and it is filled with a buffer solution having a well determined pH value. Before the measurements, the glass electrode has to be etalonat with buffer solution of known pH.

EXPERIMENTAL PART

The unknown pH values for several solutions will be determined, and than the molar concentrations of the hydronium ions is calculated.

The pH-meter has to be etalonat and than the pH will be measured.

Before of their introduction into the solution, the electrodes will be washed with distilled water. At the end of the experiment, the electrodes will be washed again and will be introduced into initial solutions.

OBSERVATIONS

For the measurements, the electrodes has to be maintained for an hour into a solution of HCl 1 N or for 24 hours into a solution of HCl 0.1 n, followed by keeping in distilled water.

Be sure that there is solution into the eletrode.

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