ANA EMANDI

PRACTICAL WORKS OF BASIC INORGANIC CHEMISTRY

Editura Universității din București
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Referenți științifici: Prof. dr. **Elena Cristurean**
Prof. dr. **Maria Negoiu**

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Șos. Panduri, 90-92, București - 76235; Telefon/Fax: 410.23.84
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SECTION I

WHAT IS A CHEMICAL TECHNICIAN?

The chemical technician is a professional in every sense of the word. He should look, think and act as professionals are expected to do. He is entitled to all privileges of a professional and at the same times 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 serious 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 composing 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 exists 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 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 technician should thoroughly understand, know how to use and be capable of using expertly 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 kow 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 facts, know the organization of 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 are:
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 of Elements. Minerals. Inorganic Compounds. Industrial Minerals. Chemical Analysis. Tables of Specific Properties. Solubility 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 and X-ray Data). Organic Compounds (Nomenclature, Physical constants, Melting Point, Boiling point, Miscibility, Amano Acids,

Carbohydrates, Waxes, Plastics). General Chemical (Azeotropes, Thermodynamic Constants, Reagents, Buffers, Indications, Flame Tests, Dissociation and Ionization Constants, Conductance, Specific Heats, Boiling Point and Melting Point Data, Thermometers, Vapor Pressure, Thermal Conductivity, Relative Humidity, Dielectric Constants, Permeability, Magnetism, X-ray Diffraction, Refractivity, Optical Rotation), Densities, Surface Tensions, Viscosity's, Conversion Tables, Wire Data, Electrical Data, Earth Composition and Analysis, Molecular and Crystal Data. Abbreviations.

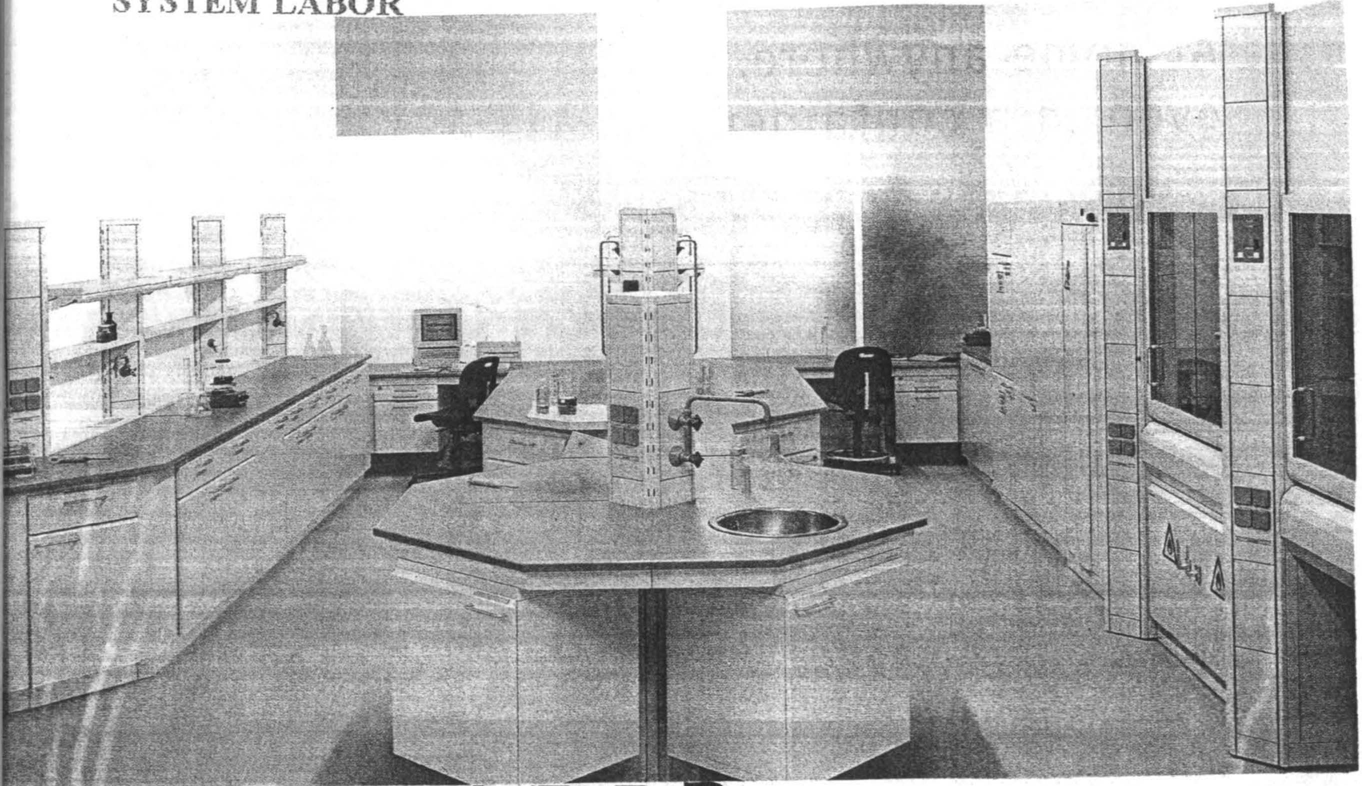
"Merck Index", Merek&Company, an encyclopedia of chemicals and drugs. Abbreviated Table of Contents: Nomenclature, Isotopes, Measurements, Densities, Conversion Tables, Solutions, Buffers, Mathematical Tables, Acids, Medical Isotopes, Monograph of chemicals and drugs, alphabetical arranged, identifying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

SYSTEM LABOR



LABORATORY USTENSILS

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

For caring out the laboratory working is necessary besides a series of substances, different kinds of laboratory ustensils are made of resistant materials both chemical agent action and to temperature variations.

The most used materials for laboratory vessels and aparatures are 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 composition depending on each utility are manufactured.

The glass is obtained: silica, borax, alumina, calin, feldspar, sodium carbonate, lithium carbonate, sodium sulfate, dolomite, magnetite, zinc oxide, etc; all this 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 composition for some well-known laboratory glasses.

We can notice that the glass composition includes considerable quantities of aluminum oxide, which have stabilization role.

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

Composition:

In per cents	Pyrom	Turda-Term	Medias	Jena	Pyre	Turingia	Duran	For thermometer
SiO_2	80	75.5	68	76	81	66	80	67.5
B_2O_3	12.9	7.5	2	16	12	--	12	2
Al_2O_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_2O	4	6.5	17	5.4	4.5	14.4	14	--
K_2O	1.4	--	--	0.6	--	3	--	--
Fe_2O_3	0.05	0.05	0.05	--	--	--	--	--
BaO	--	4.2	--	--	--	--	--	--

The apertures used 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 method of weighing, accuracy 0.0001 gram.

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

(c) Double-pen, analytical balance manual weight and rider adjustment, readout to 0.0001 gram.

(d) Laboratory and gold balances with the integral weighing mechanism placed onto the weighing mechanism through a calibration button.

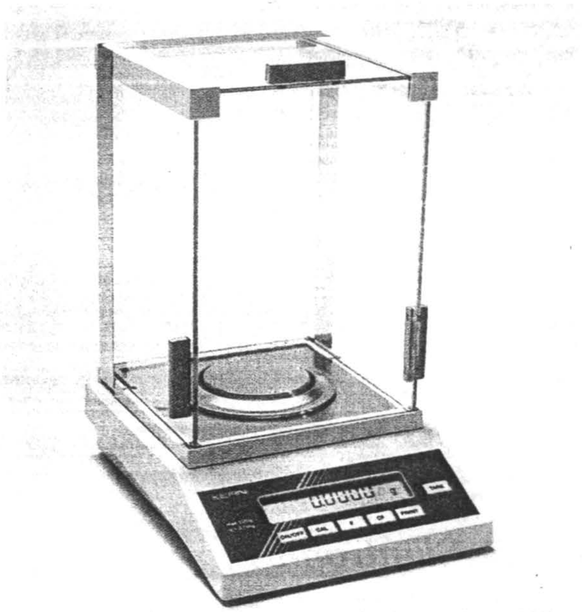
2. Balance weights

Analytical balance weights with forceps from 1 mg to 100 grams. Handle weights only with forceps. Handle with care because they are precision weights.

1-2.BALANCE AND BALANCE WEIGHTS

Electronic analytical balance

Automatic internal calibration with built-in and motor driven calibration weights. All-glass wind shield gives access from both left and right hand sides and top. Protection against dust and spray.

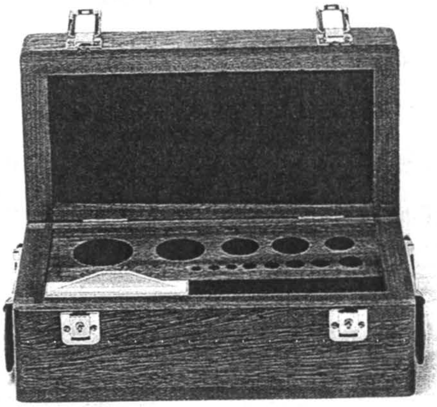


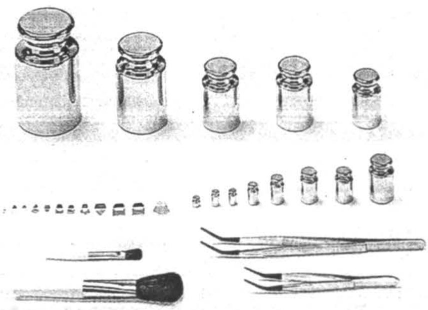
Laboratory and gold balances

Have calibration switch. The integral calibration weight is placed onto the weighing mechanism via a button for calibration processes. Protection against dust and spray.

Balance weights

1 mg and 500 mg disc shaped made of aluminum and nickel silver. 1g to 50 kg button shaped made of stainless steel.





3. Beaker

Beakers are available in sizes from 1 to 4000 cm^3 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

Liquid and solid storage for chemicals and samples; varied design, opening and closures.

Dropping bottle to dispense small volumes of liquids.

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-cm^3 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 haper and stopcock. Available models with volumes from 50 to 500 cm^3.

(c) Tittering assembly and attend with white base for easy color-change observations.

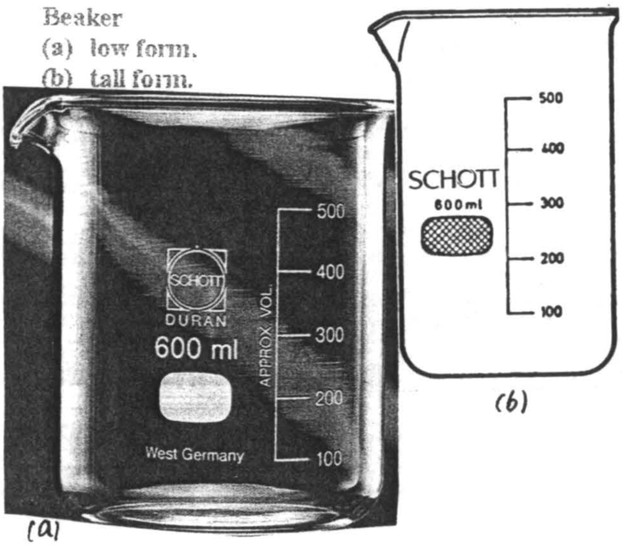
7. Burners

Bunsen burner, artificial gas, sleeve air inlet regulator.

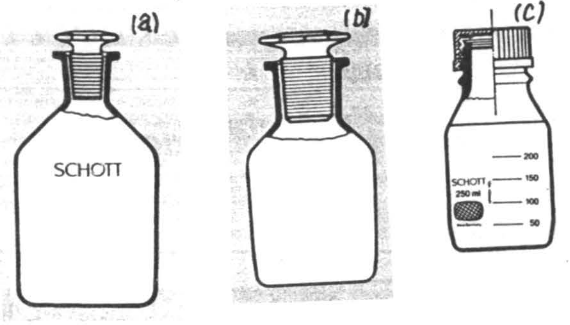
8. Capillary Tubes

Capillary tubes with scaled end for melting point determination.

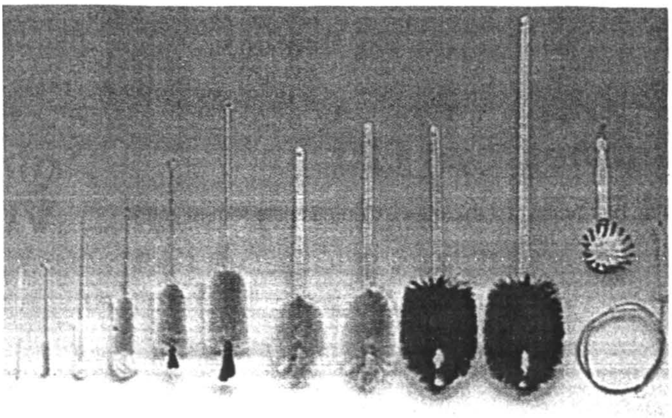
Beaker
(a) low form,
(b) tall form.



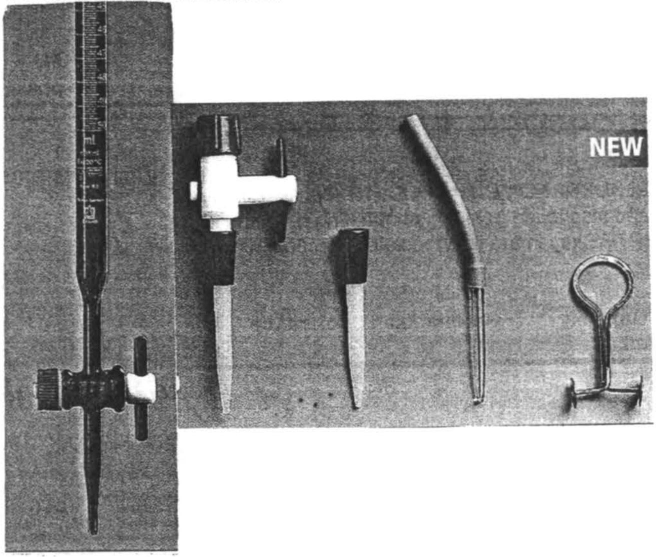
Bottles
(a) narrow neck,
(b) wide neck,
(c) laboratory bottles



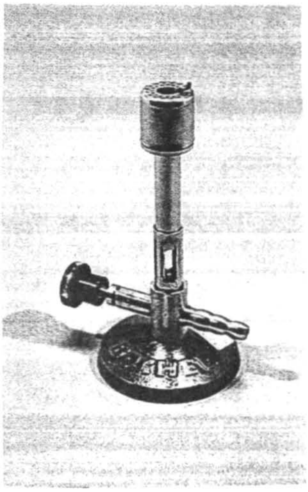
Brushes



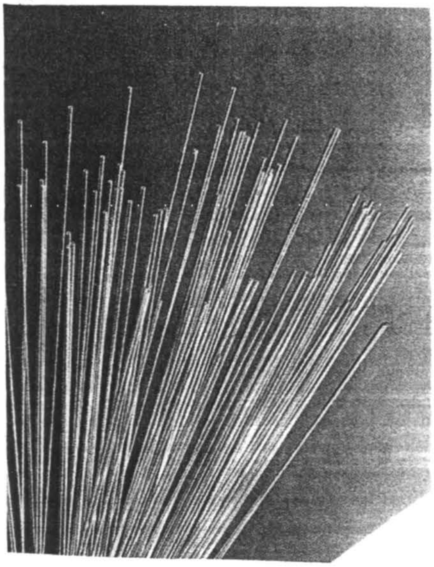
Burettes and accessories



Burner



Capillary tubes



9. Clamps

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

(b) Screw-type clamps with adjustable tension.

(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) Fixed-position clamps with vinyl or asbestos covered jaws.

(g) Spring–type clamps with positive closure.

(h) Clamp for holding spherical-ground standard-taper glass apparatus together.

(i) Tubing clamps for positive attachment of pressure or vacuum tubing.

9.1. Bossheads

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

(b) Screw-pinch clamps with adjustable closure for flexible tubing.

(c) Stopcock clamp prevents loss of plug due to pressure or vibration; fixes plug firmly into desired position.

(d) Test-tube holder clamps, spring activated.

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

10. Crucible

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

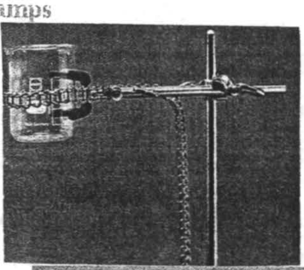
(b) Gooch crucible with perforated bottom. Filtering asbestos and water slurry usually forms filter bed.

11. Cylinders

Graduated cylinders of various sizes, shapes, openings and closures to meet special needs, capacities from 5 to 4.000 cm^3.

Clamps

(a)



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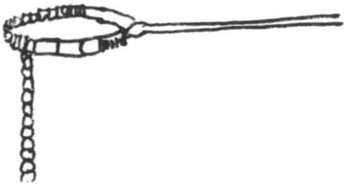

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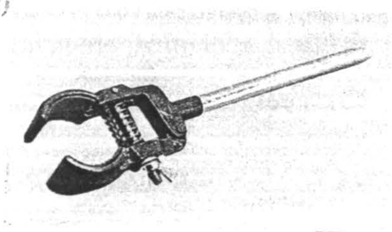

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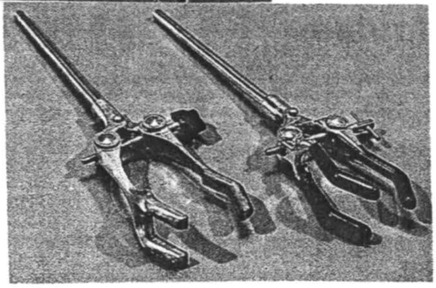

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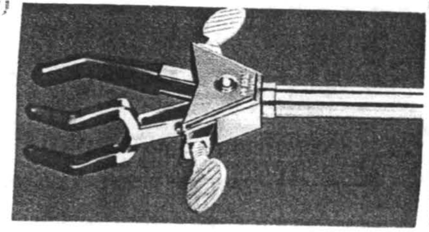
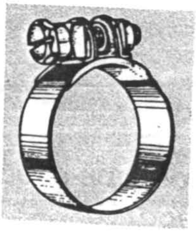
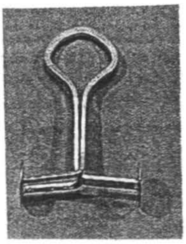


(I)



(f)

(g)



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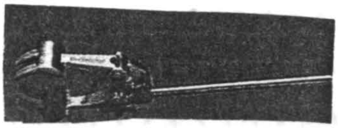
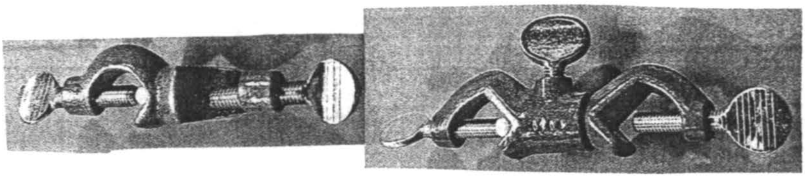


Bosshead

(a)



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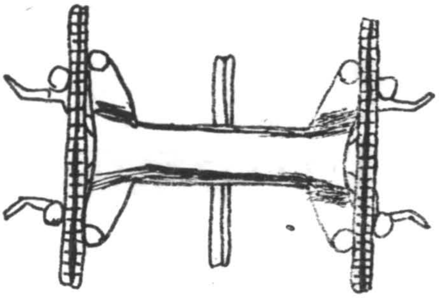

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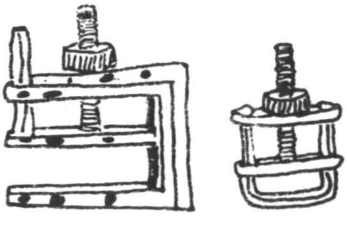

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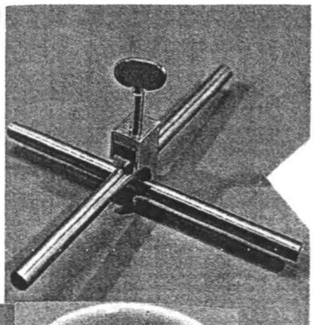

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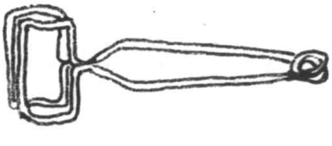
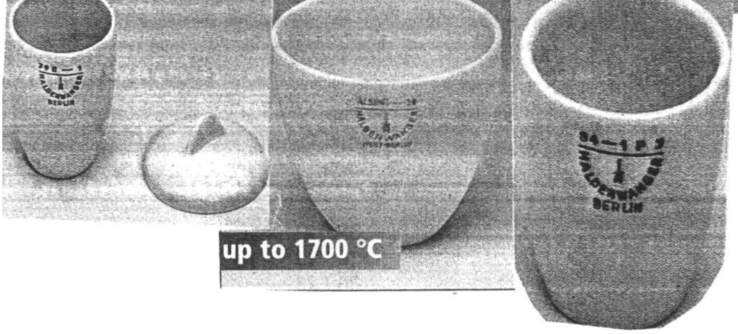
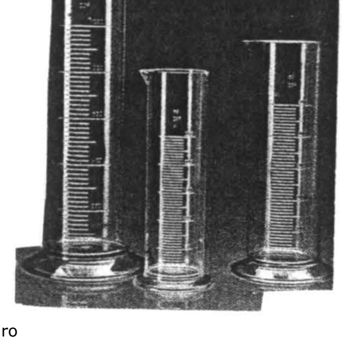


Crucibles



Cylinders



12. Desiccators

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

13. Dishes

Evaporating porcelain dishes with heavy rim and pouring spout. Used to evaporate liquids. Nickel evaporating dishes. Crystallizing dishes to hold or contain liquids, which are expected to crystallize. Culture dishes for bacteriological work.

14. Filter papers

(a) Filter paper is assorted sizes and porosities.

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

15. Filter pump and accessories

Water pump for suction filtrations, general vacuum manipulations and pipette cleaning. Accessories are used to couple to waterlines and prevent splashing to existing water.

16. Flasks

(a) One-neck distilling flask. Flat-bottom flask. Round-bottom flask with short or long neck for general relations.

(b) Erlenmeyer flask in various sizes, 10 to 6.000ml plain or graduated open or fitted with ground-glass stopper.

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

(d) Claisen distilling flask with side neck.

(e) Multineck flasks with one, two, three or four necks, sizes from 500 to 12.000 cm^3.

(f) Volumetric, standardized to contain stated volumes of liquid, available in various designs, capacities from 1 to 2000 cm^3; also made of actinic glass to prevent light decomposition of unstable solutions.

(g) Kjeldahl flask for analytical procedures. Available in different capacities.

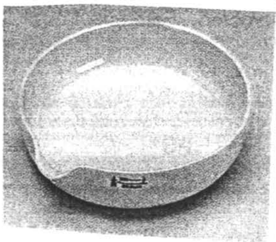
(h) Florence flask with cork-insulated neck for positive hold. Used to make wash bottles.

(i) Florence-type wash bottle with directional tip, breath operated.

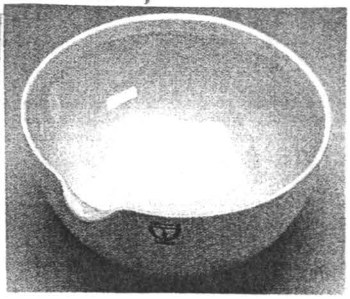
(j) Florence-type wash bottle, hand squeeze, pressure-bulb-operated.

Desiccator

Dishes -flat

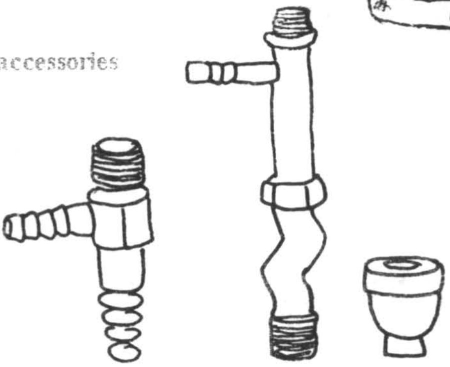


-hemispherical



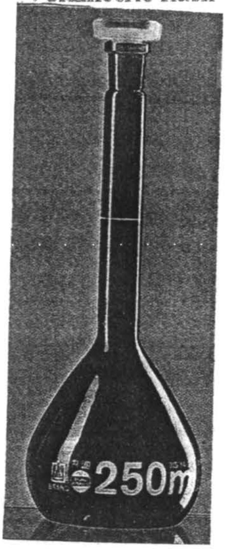
Filter papers

Filter pump and accessories



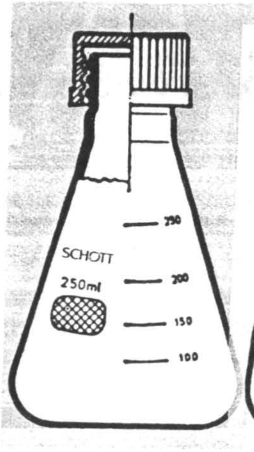
Flasks

Volumetric flask

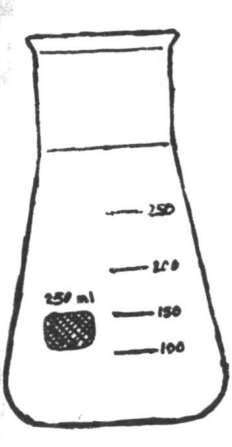


Erlenmeyer flask

–narrow neck

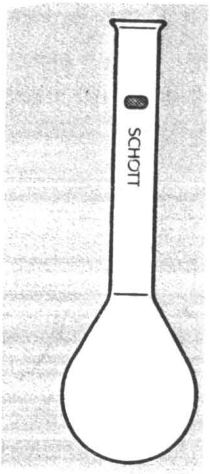


–wide neck



Round bottom flask

Kjeldahl flask



17. Forceps

Flexible forceps stainless steel or chrome-plated-steel. Use to pick up small objects and handle small screw and pins for laboratory equipment.

18. Funnels

(a) Buchner suctions funnel.

Buchner jacketed funnel for cooling or heating. Varied sizes.

Buchner plain funnel, available in sizes 14.5 to 308 mm (removable plate).

Buchner table tops model funnel for large volumes, from 50 to 308 mm diameters.

(b) Glass funnels varied sizes and steam length. Use for general filtration. Glass funnel with heavy ribbed construction; raised ribs on inner surface facilitate filtration.

(c) Fritted-disk glass funnel used in vacuum filtration with suction flask in operations where the filter paper of a Buchner funnel would be attacked; with stands temperatures to 500°C, available in four porosities.

(d) Separatory funnel graduated with ground-glass stopper. Available in different sizes, capacities from 30 to 6.000 cm^3.

19. Furnaces

(a)Muffle furnace, temperature indicating dial, adjustable rheostat heat control and automatic door closure.

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

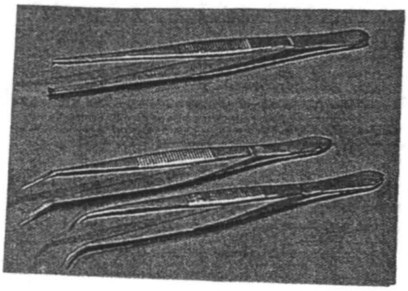
20. Glass Rods

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

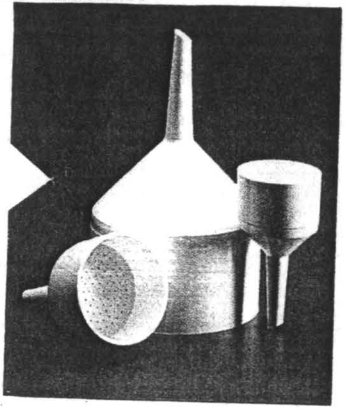
21. Glass Tubing

Capillary wall thickness and diameter of hole varies. Bore from ¼ to 3-mm diameter. Tubing in soft Pyrex or Vycor glass from 2 to 178mm.

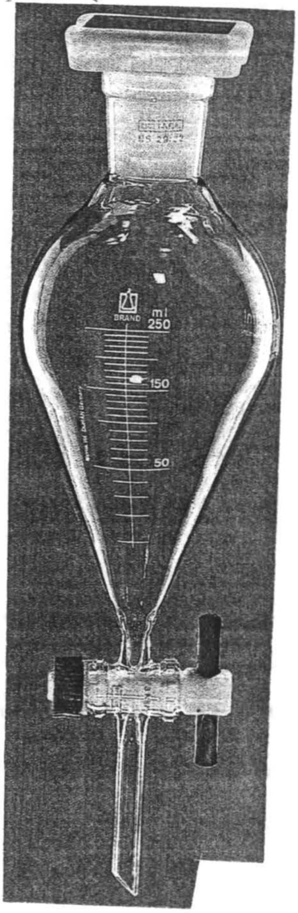
Forceps



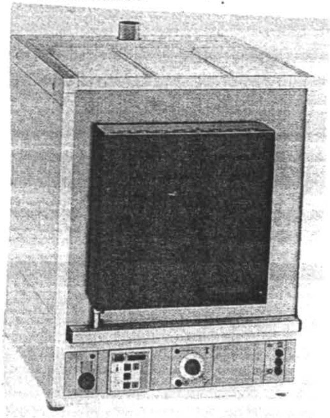
Funnels –Buchner



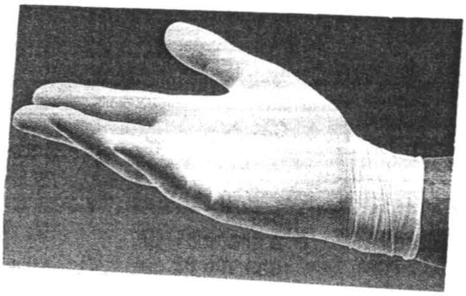
--Separatory



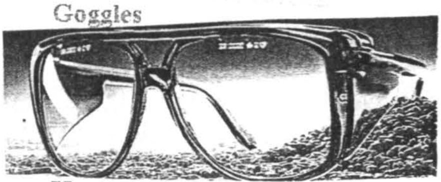
Furnance



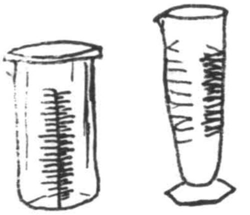
Gloves



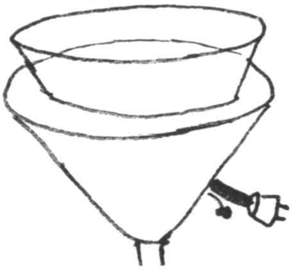
Goggles

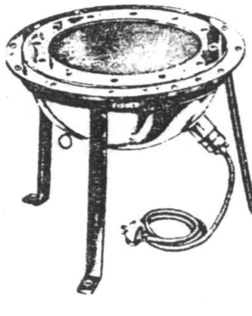


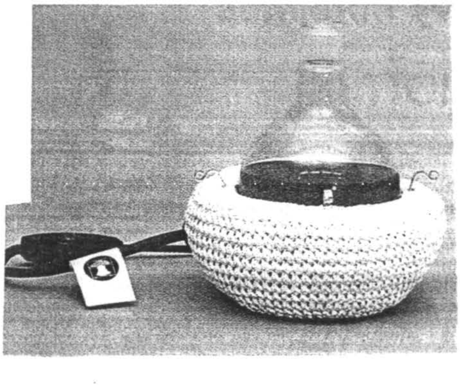
Graduates

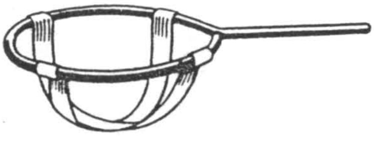


Heating mantles









22. Gloves

Rubber gloves to protect hands against corrosive chemicals.

23. Goggles

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

24. Graduated

Glass graduates, pharmaceutical graduated.

25. Heating mantles

Hearing mantles provides 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.

26. Hydrogen-ion test paper

27. Hydrometers

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

28. Mortar and Pestle

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

29. Oven

(a) Electrically heated oven for drying samples, baking, sterilizing temperature controlled to maintain about a 2°C range. Fitted with on/off switch and pilot light.

(b) Constant-temperature oven, mechanical heat flow by fan, maintains temperature ±0.1°C with temperature regulator.

30. PH-Test paper

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

31. Pipettes

Measuring pipettes, available from 0.2 to 5 ml permit the transfer of a measured amount of liquid. The division on the scale varies with the capacity of the pipette.

32. Pipette accessories

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

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

(c) Pipette filler used to transfer sterile, corrosive and toxic liquids safely. Easy controlled by squeezing. Delivers quickly, precisely and safely.

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

33. Plate, Hot

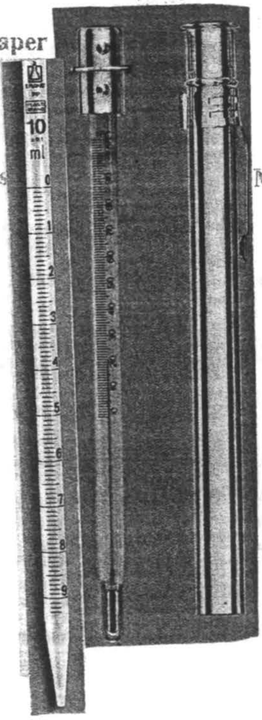
(a) An adjustable-temperature heavy dury hot plate for heating nonflammable materials.

(b) Open-coil adjustable-temperature hot plate for heating nonflammable materials.

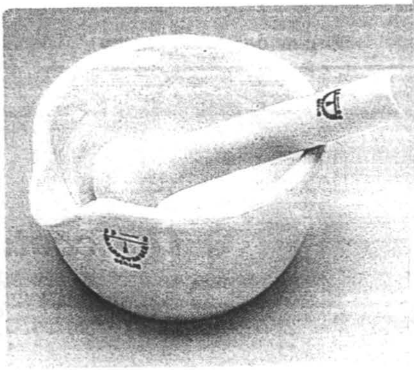
(c,d) Hot plate with magnetic mixer, adjustable heat and rate of mixing. Multiple hot plate, magnetic mixer.

H--ion test paper

Hydrometers

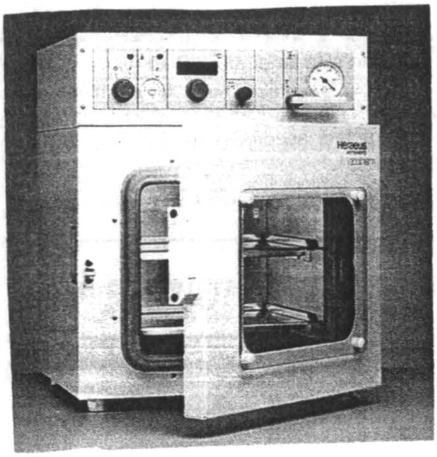


Mortar and pestle

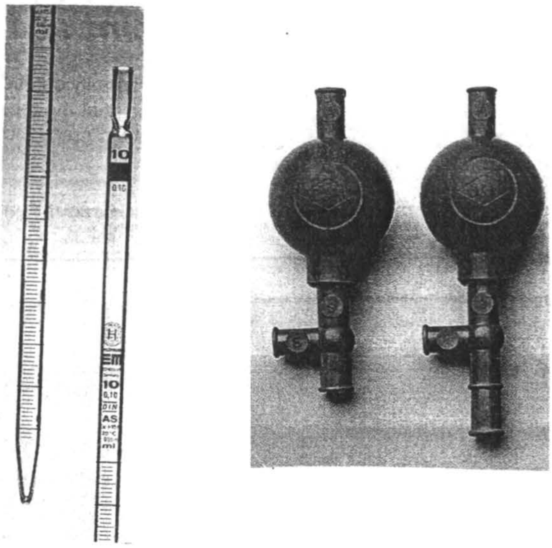


pH--test paper

Oven

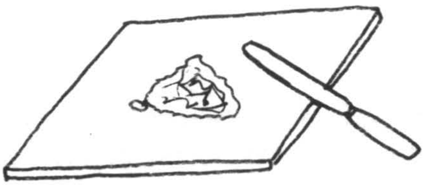


Pipettes and accessories



Hot Plate

Porous Plate



Rubber Stoppers

34. 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.

35. Rubber Stoppers

Various sizes, one- or two-hole.

36. Seals

(a) Glass seal, close fitting shaft to housing (standard taper joint), lubricated with glycerin or silicone, provides isolation of system from atmosphere and contains very moderate pressure and vacuum conditions, while rotating.

(b) Mercury-type seal provides a seal between the fixed standard-taper glass joint and the rotating shaft. The rotating tube is fixed to the shaft with flexible tubing (no shown) and the mercury fills the well to isolate the system from the atmosphere and prevent the loss of volatile. Not used for pressure or vacuum procedures.

37. Scissors

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

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 jobs.

39. Stirrer

(a) Air variable-speed stirrer derived by compressed air. Safe for explosive atmosphere.

(b) Light-dury electric stirrer with fixed speed. Shaft height adjustable through chuck.

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 monel, available in different shaft diameters and propeller designs, from tow-, 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 cutoff flow completely.

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

(a) 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) Flexible flame can be assembled from rods of various lengths to provide the support requirements for the apparatus. Provides steady base without use of multiple support stands. (c) Right-angle rod clamps.

(d) Rectangular single-rod support base. Fairly study on level areas.

(e) Tripods offer study support for apparatus may have two vertical rods.

(f) Support plate clamped to support base or flame with suitable clamp holder is used to hold flat-bottom containers.

(g) Electrically powered jack with remote control for hazardous areas

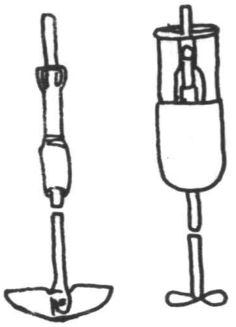
(h) Open-type support rings clamp with suitable clamp holder to frame support; opening allows easy removal of funnels and other supported glassware.

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

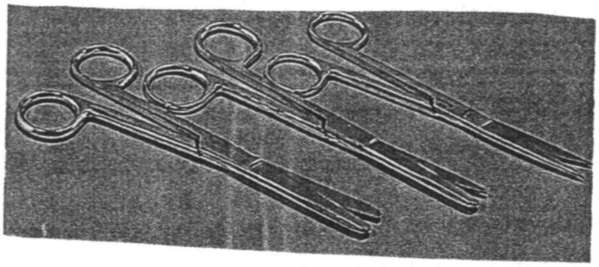
(j) Wooden adjustable-height funnel support in sizes and capacities for laboratory manipulations.

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

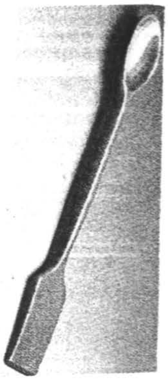
Seals



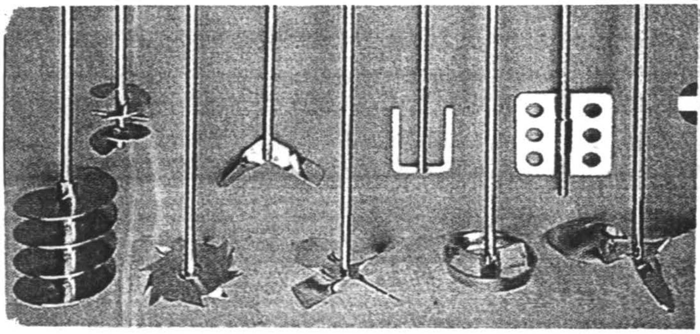
Scissors



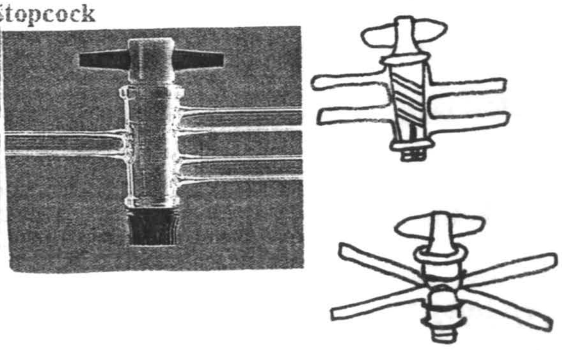
Spatulas



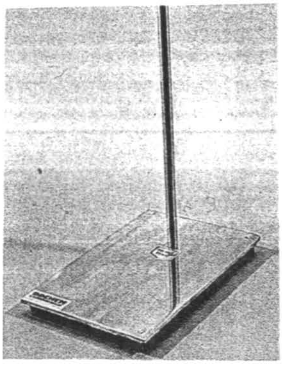
Stirrer

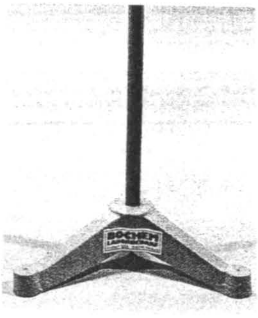


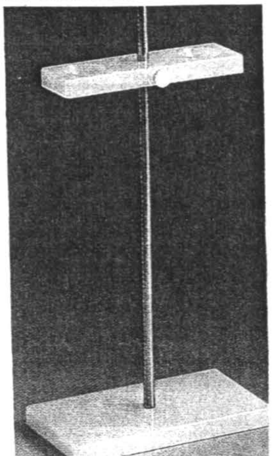
Stopcock

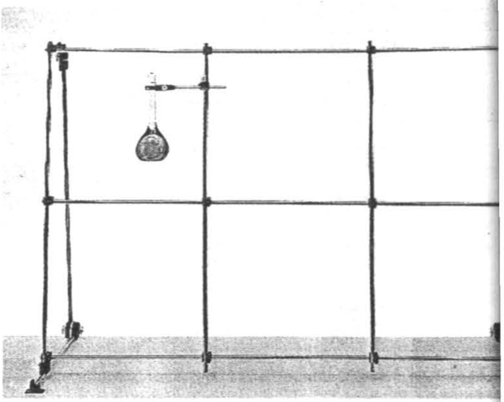


Supports

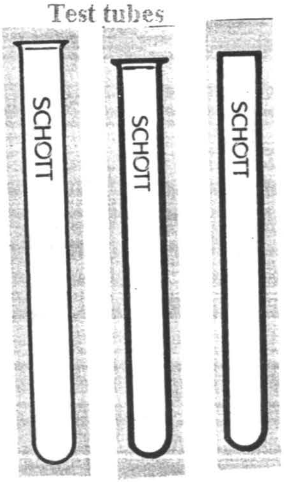




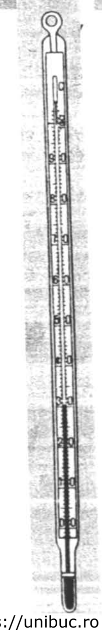




Test tubes



Thermometers



43. Test Tubes

Test tubes are available in soft, Pyrex, Vycor and actinic glass with or without rims or covers.

44. Thermometers

45. Tongs

Crucible tongs with flexible long length. Use to insert and remove hot crucibles from a muffle furnace and to avoid contact with crucibles in analytical procedures.

Utility tongs to handle hot, small apparatus and crucible.

Beaker-tongs to hold and carry small 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 separations or constructions to hold rubber or plastic tubing securely. (a) Plastic “Y”, (b) Glass “Y”, “T”, “U”, (c) Brass “T”, “Y”.

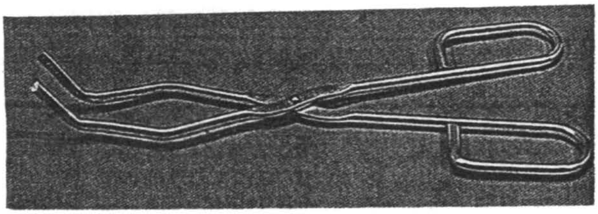
49. Water Bath

Steam-heated or electrically heated water bath used to heat solutions requiring temperatures not exceeding 100^{0}C

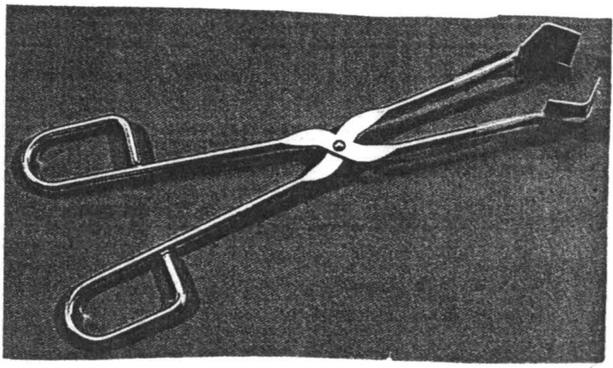
50. Wire Gauzes

Plain or asbestos centered wire gauze used to protect glasses–ware while being heated with gas-burner flame.

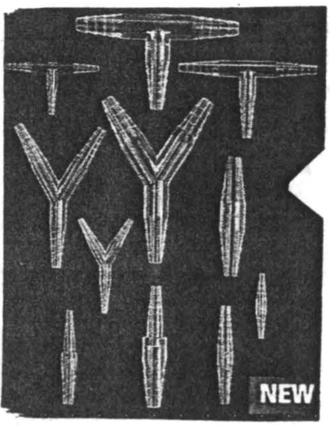
Tongs–Cruicible Tongs



Flask Tongs



Tubes

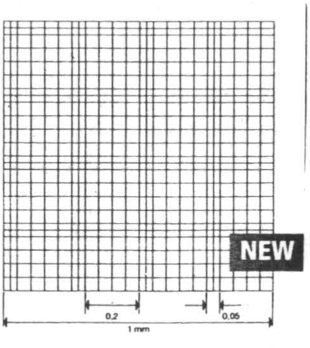


Triangles

Tripods

Water Bath

Wire Gauze



WHAT DOES A 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 on-the-job training program. He utilizes what he knows to operate specialized equipment and testing devices and to conduct experiments and analysis. He collects data and informations under the direction of scientists to assists to 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 system.

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, service 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 analysis of substances in the physical, agricultural, biological or health-related sciences and prepare appropriate reports such test.

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 informations 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 informations 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 excludes nor includes 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 engineering 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 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 project 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 capacity to represent ideas, concepts and data graphically through drawings, diagramming 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 think for granted; he questions, checks and verifies what he has experienced through his senses. The 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 forgot it. He takes several readings independently of each 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 taken 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 wrong 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 on procedure and sets forth its on format. If no formal procedure exists, however, these roles should 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 observation 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 the 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 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 charge, 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 and/or 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, how ever, 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-evidence 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 is some other logical fashion?
–Do we provide accessory equipment before we need it or it is 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 will 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 quality. 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 then 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 considered as mistabulations or miscalculations of figure. The guarantee against mistake is to check each item and computation. Time spent in checking is time well spent because it ensures accuracy, making unnecessary to redo a problem for sample. On the other hand, errors are usually random and can be determined or undetermined. It is therefore easier to eliminate mistakes then to detect and minimize random errors.

We should assume that everything done in the analytical laboratories is important to the research effort. A paradox, which some times evolve, is to be a sample with the comment "this is 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 truth. That is, we assume everything to be important unless otherwise stated. Hen techniques of the highest quality are released, 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 our goals are effective quantity rather than 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 marked the altered product rather than the raw product is the usable commodity? Such is a case with analytical data. Should adjustments or alternations 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 the 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 is usable quantity and high quality. The third factor we must consider is service. Service, by definition, is any result 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.

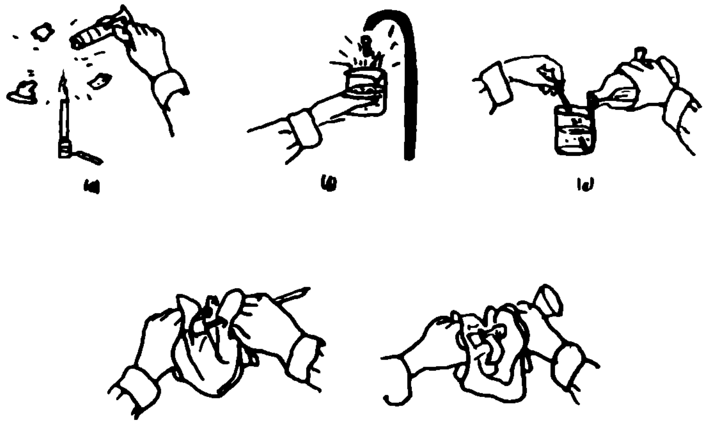
Procedure (See fig. A-1)

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 minimizes 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 tree sources of accidents: fire, cuts from broken glass equipment and contact with corrosive chemicals on clothing or person.

Every technician should know basic first-aid emergency equipment for minor injuries and also how to handle emergency equipment such as safety showers and fire extinguisher. Common sense is the best insurance against injury.

Figure A-1



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 handing 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 safely 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 that vaporize; its result can be toxic, nauseating, irritating or flammable or can have unpleasant side effects.

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.

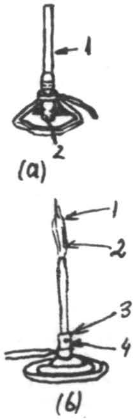
SECTION II

Laboratory techniques and procedures

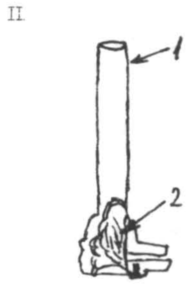
1. Open the gas cock on the gas inlet pipe wide.
2. Open the thumbscrew gas adjustment on the burner wide.
3. Close the air holes with a movable sleeve.
4. Light the burner with the match or striker.
5. Regulate the thumbscrew and the movable sleeve to produce nonluminous flame having a sharp-pointed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

FIGURE B-1
Gas burners

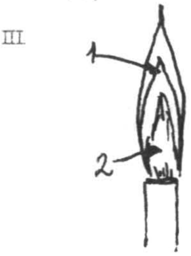
(a)1. Air adjustment tube. 2 Gas adjustment needle valve.
(b) 1 Violet. 2. Pale blue.
3. Movable sleeve.
4. Air inlet.
If the flame is like this, turn down gas.
1 Violet. 2 Flame rises off burner.



I If the flame is like this, turn down gas.
1 Violet. 2 Flame rises off burner.
II If the flame is like this, turn the gas off a moment and light again.
1. This gets very hot
2. Noisy flame inside



III 1 Oxidizing flame. Highest t⁰ 1560⁰C.
2. Cool region inside cone. Reducing flame 320⁰C.



IV. If the flame is like this, open air regulator.
1. Bright yellow tip.
2. Blue absent.

(a) Tirrill. (b) Bunsen.

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^{0}C; used in droppers glass rods, tubing for wash bottles, bottles; workable with a Bunsen or Tirrill burner; subject to attack by alkali does not withstand thermal shocks.

Pyrex glass: melting point 750 to 1100^{0}C; used for beakers, flasks common glass equipment; requires on oxygen torch to be worked; withstands alkali; resists thermal socks.

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

1. Scratch the tube or rode at the desired point with the three cornered file. Use only one or two strokes.
2. Raw the tubing in a protective clothes 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.

(fig. B-2 and B-3)

B-2

B-3 Proper method of holding glass tubing.

Fire polishing (fig. 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 back from the end being heated. It gets hot!

(fig. B-4 and B-5)

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

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

Dulling sharp glass edges (fig. B-6)

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

(fig B-6)

Glass bending (fig. 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.

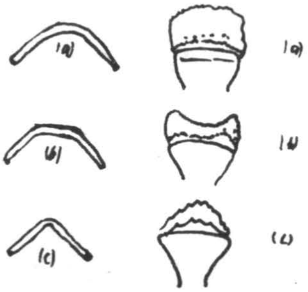
Caution

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

(fig B-7 and B-8)

B-7.Rotation of the work (wing tip).

B-8 Effects of flame adjustment on bends. (a) Good. (b) Poor. (c) Poor.



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 tube at an inclined angle.
4. Rotate the tube against the end to get the desired flare.

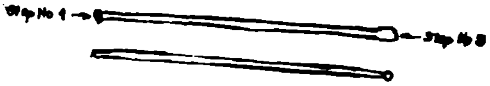
(fig B-9)

B-9 Flaring a tube end

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

1. Heat the 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 end, press the heated rod between two heated clean pieces of metal.

(fig B-10) B-10 Shaping glass rods.



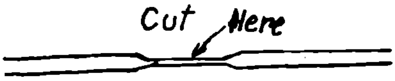
Making capillary tubes (fig B-11)

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 flame. Allow cooling slightly.
4. Pull the ends apart while rotating the cooling glass to get the desired capillary size.

5. Scratch with file then break.

(fig B-11)

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



Sealing ampoules (fig. B-12 and B-13)

PRINCIPLE

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

MATERIALS

Ampoules, filling pipette, gas burner.

PROCEDURE

1. Fill the ampoule or sellable glass bottle with a pipette (fig B-12) or with a funnel. (Do not fill more then two third full).
2. Gently insert the tip ampoule into a burner to constrict the opening.
3. Heat the tip of a piece of glass rod to redness and then tough it to the constricted tip of the ampoule, which is soft from the burner.
4. Remove the joined glass from the flame, allow cooling and pulling apart to get the final seal.

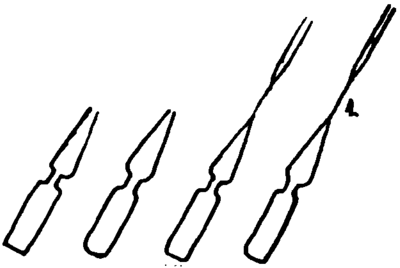
<u>Caution</u>

Practice with an empty ampoule 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 ampoule and the glass rod and the time the heated joined-glass items are allowed to cool before they are pulled apart.

(fig B-12 and B-13)

B-12.Filling the ampoule with a pipette

B-13.Sealing an ampoule with a torch.
Pull out soft glass with piece of scrop glass.
Construct opening in flame.
1. Final seal.



Boring hales in cork and rubber stoppers (fig B-14 and B-15)

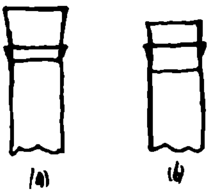
1. Select a rubber or cork stopper of correct size. (fig B-14)
2. Select a borer sized slightly then the hole to be bored.
3. Sharpen the burner with a sharpener and wet borer with glycerin.
4. Hold the borer in the right hand and the stopper in the left hand supported by a cloth pad for palm protection.
5. Being boring at the narrow end, twist the borer and apply pressures.
6. Check the alignment after each twist.
7. Remove the bore 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.

(fig B-14 and B-15)

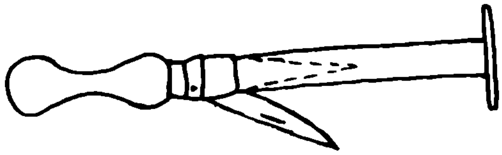
B-14 Rubber stoppers.

(a) Correct size.

(b) Too small



B-15.



Inserting glass tubing in stoppers (fig B-16 and B-17)

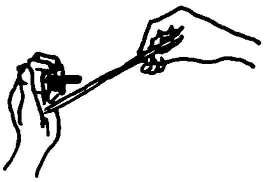
1. Fire-polish the ends of the tubing.
2. Wet the tubing and stopper hole with water or glycerol.
3. Wrap up hands in a towel for protection.
4. Grasp the tube near the point insertion.
5. Rotate the back and forth while gently pushing it into stopper.
6. Never attempt to push tubing through the stopper.

(fig B-16 and B-17)

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

1 Lubricate with water.

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

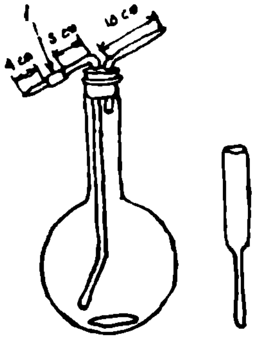


Removing glass tubing from stopper

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 falls, 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 one-liter flask is recommended.



(fig B-18)

B-18 Wash bottle; Tip

1. Short rubber connection

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 a small as desired. After the glass has cooled, break it at the approximate 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 the tube has cooled, wet both tube and stopper and twist the tube stopper with a screwlike motion.

1. Protect the hand with a towel.
2. Do not exert on a bend.

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 roles 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 desktop.

4.Never return any excess reagents or solutions to a bottle; the minor saving represented by the return of 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 safe and the laboratory balances clean. Immediately clean up any spled chemicals, even though others may be making the transfer of reagents in the same area.

Removal of solid materials from glass-stopper bottles (fig B-19)

1. If the solid material is packed, gently tap the bottle against the desktop 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.

(fig B-19)

B-19 Removal of a solid from a glass-stopper bottle.

Alternative method (fig B-20)

1. Remove the glass topper 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 desktop.

(fig B-20)

B-20. Alternative method.

Spatula must be clean.

1. Right. 2. Wrong.

Pouring liquids from beakers or other containers (fig B-21 and 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.

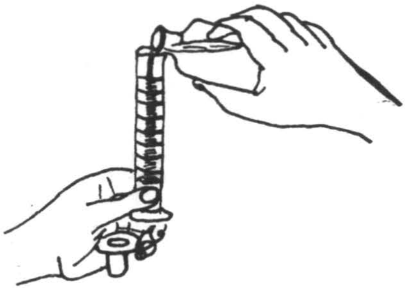
3. Pour the liquid as needed.

4. Replace the stopper immediately in the bottle. Never lay it on the desk.

(fig B-21 and B-22)

B-21 Handling a glass stopper.

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



Pouring liquids from beakers or other containers (fig. B-23)

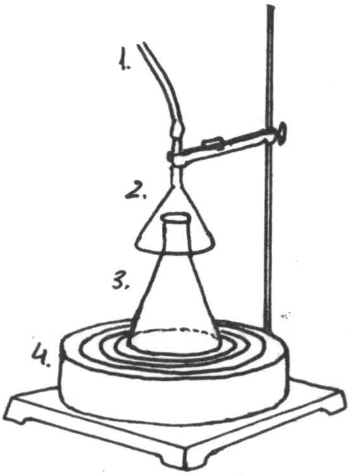
1. Hold the glass-stirring rod against the pouring lip of the beaker.
2. Tilt the container, allowing the liquid to flow around the stirring rod, which guides the liquid to the receiver.
3. When the desired amount of liquid as been pored, position the pouring beaker vertically allowing the last liquid to drain off the lip and down the rod.

(fig B-23)

B-23. Use of stirring rod to guide liquid.

(fig. B-24)

B–24. Emergency hood.
1. To aspire. 2. Insert funnel and tubing.
3. Erlenmeyer flask.
4. Steam bath.



Emergency hood (fig. B-24)

PRINCIPLE

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

APPARATUS

Glass funnels, rubber tubing, aspirator, water pump.

CAUTION

1.Alwaays uses 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 thing! Always be on guard!

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 high-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 is four scales calibration: Fahrenheit, centigrade (Celsius), absolute (Kelvin) and Rankine.

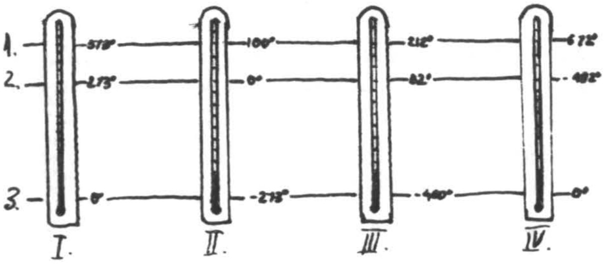
(fig. B-25) I. Kelvin. II. Celsius (centigrade). III. Fahrenheit. IV. Rankine.

B-25 Relationships of the four scales of calibration

1.Boiling point of water.

2. Freezing point of water.

3. Absolute zero of t^0.



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.Substract 32° from Fahrenheit reading.

2.Multiply the result by 5/9.

example: 212°F =?°C ?

solution: 212°F -32° =180°F

5/9 x 180° =100°

Centigrade to Fahrenheit

1.Multiply the centigrade reading by 9/5.

2.Add 32°.

example: 9/5 x 100°C =180°C

180°C +32° =212°F

Centigrade to Absolute (Kelvin)

1.Add the number 273 to the centigrade reading.

2.The value is the temperature reading in Kelvin.

example: 20°C =?°F ?

solution: 273 +20°C =293°K

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 the thermometer in a well stirred mixture of crushes ice and distilled water. The thermometer should read 0°C.

100°C: fix the thermometer above the surface of a beaker or 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:

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= Means the temperature of the exposed column (obtained by placing auxiliary thermometer along side with its bulb midpoint).

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

Example: the temperature 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 thermometers reads 50°C, Substituting:

$K = 0.00016$

$T_o = 250°C$

$T_m = 50°C$

$N = KN (T_o - T_m) = 0.00016 \times 250 (250 - 50) = 8.0°C$

The corrected temperature should be 250+ 8.0°C= 258.0°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 column cause error in thermometer readings.

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

Thermometer mercury column can be reunited by the following procedures.

Caution

Remember that 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 shocks. 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 gases 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 make 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. Heats expand the mercury in the upper expansion chamber.

Caution

Do not overfill the expansion reservoir.

SECTION III

WEIGHING

Chemistry is a science of precision, qualitative 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 which have determined ranges from kilograms to micrograms, the choice of the balance to be used for any determination is governed 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 instruments 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 balances) which are sensitive to 0.1 g to the analytical balances sensitive to fractions of a microgram.

Because balances are delicate instruments, the following comprehensive rules should be observed in caring for end using them. (Those are the general rules for all balances. Prudence will dictate which are not applicable in work with rougher measuring devices).

1.Level the balance.

2.Inspect the balance to be certain that it is working properly. Use calibrated undamaged weights.

3.Check the balance zero.

4.Be certain that the beam is locked before removing or changing weights or objects to be weighted.

5.Keep the balance scrupulously clean.

6.Work in front of the balance to avoid parallax error.

7.Handle all weight and object with forceps, never with fingers. Place the forceps as near as possible to the center of the pans.

8.Avoid weighting hot objects (if possible).

9.Release the locking mechanism slowly, avoiding jars.

10.Do not overload the balance.

11.Never weight moist objects or chemicals directly on the pans.

12.Close the balance case (if a part of balance).

13.Triple count all weights to avoid error. Separate weights.

14.Record weights in notebook for addition. Never add mentally.

MEASUREMENTS WITH THE ANALYTICAL BALANCE

Basic controls on most single-pan analytical balances

1.Pan-arrestment control

a. Assure constant position of the beam between and during weighing.

b. Protect the bearing surface for excessive wear and injury due to shocks.

2.Arestment 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 weightings 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 100 g.

5.Optical scale adjustment

Turn knob positions the optical scale relative to a reference line so that the final weight to 0.1 mg 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 1 g 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.

SECTION IV

Determination of Physical Properties

DENSITY

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

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

The density is expressed in the following units:

Grams per cubic centimeter	g/cc or g/cm^3
Grams per milliliter	g/ml
Pounds per cubic foot	lb/ft^3

The density of water at 4°C is 1000 g/cm^3=1000g/ml; therefore, the terms milliliter 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.D–1):

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

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

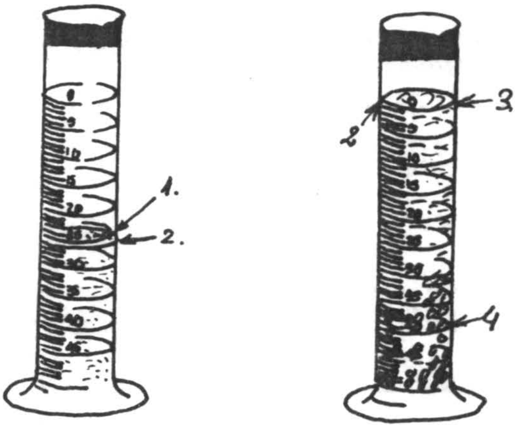
(c) Subtract the original volume from the final volume and obtain the volume of the object

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

(Fig.D–1)

D–1 A method of determining the volume of an irregular solid.

1. Original volume of water.
2. Difference=volume of solids.
3. Volume of pieces that were submerged.
4. Pieces of solid



Liquids

1.Use a calibrated-volume liquid container, filled 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.

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

The water standard is taken at 4°C (density of water is 1000 g/cm^3).

PROCEDURE

1.Weigh a pycnometer (Fig.D–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).

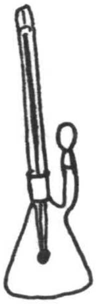
Hydrometer

A hydrometer is a floating glass container, weighted at the bottom, having a slender stem calibrated to a standard (Fig.D–3). The depth to which the container will sink in 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.

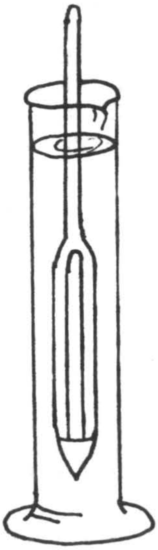
Hydrometers are calibrated in specific gravities (the weight of a liquid divided by the weight of an equal volume of water taken at certain temperature, such as 60°F or 70°F) or in arbitrary units such as degrees Baume (Be), degrees A.P.I. (American Petroleum Institute), or degrees Brix (also called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

(Fig.D–2 and D–3)

D–2 Pycnometer



D–3 Hydrometer.



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

—liquids lighter than water:

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

$$^{\circ}A.P.I. = \frac{140}{sp.gr.7\ 0^{\circ}F/60^{\circ}F} - 131.5$$

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

—liquids heavier than water:

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

°Brix= arbitrary graduated so that 1°Brix= 1% sugar in solution.

See Table 1 for conversion of degrees Baume to specific gravity

TABLE 1

Conversion Table, degrees Baume (American)- Specific Gravity at 60°F (15.55°C).

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

°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
90	0.636	0.633	0.631	0.628	0.625	0.622	0.619	0.617	0.614	0.611

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

SECTION V

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, particular in the case of solids, the water content is a variable quality 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 is weighted out for analysis; in this way his result can be corrected to a dry basis. In any event, most analysis is 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 a solid can hold water. Although developed primarily with respect to minerals, the classification of Hillenbrand 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 which is an integral part of the molecular or crystal structure of one of the compounds of the solid. It is present in that compound in stoechiometric quantities. Thus, the water of crystallization is stable solid hydrates (for example: $CaC_2O_4*2H_2O$, $BaCl_2*2H_2O$) 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. The processes typify this:

$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$

$Ca(OH)_2 \rightarrow CaO + H_2O$

Nonessential Water

Nonessential water is not necessary for the characterization of the chemical constitution of the sample and therefore does not occur in any sort of stoechiometric proportions. The solid as a consequence of physical forces retains it.

Absorbed 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. Absorption is general phenomenon that is encountered in some degree with all finely divided solids. The amount of moisture absorbed on the surface of a solid also increases with the amount of water in its environment. Quite generally, the amount of absorbed 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 absorbed 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 continuos increase in weight is observed unless the solid is contained in tightly stopper 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 absorbed 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 disposed 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 are 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, $CaSO_4 \cdot 2H_2O$, 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 are exposed to the atmosphere. A corresponding increase in absorbed water results. The magnitude of the effect is sufficient to alert appreciably the composition of solid. For example, the water content of a piece of porcelain in the form of coarse particles was zero, but after it has been ground for some time it was found to be 0.62 percent. Grinding a basaltic grindstone for 120 min. changed its water content from 0.22 to 1.70 percent.

Liquid Reagents Used for Dissolving or Decomposition 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 applications.

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-force 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 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; aluminum and chromium, which become passive to the reagent, are exceptions. Many of the common alloys can be decomposed by the 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 the temperature of decomposition and the 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. The hot acid attacks most metals and many alloys.

Perchloric Acid

Hot concentrated perchloric acid is a potent oxidizing agent. It attacks a number of ferrous alloys and stainless steel 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 results 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 marked as the 60 to 72 percent acids. 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

Most rapid 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 used 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 silica 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 action. Thus, for example, precipitation of aluminum 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 attraction 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 difficulty soluble steel. It can cause serious damage and painful injury 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 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 fort heir 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 undecomposition 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 the 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 unattached 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 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 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,		Pt (not with Na_2O_2)	For samples where an oxidizing agent is that is need, samples containing S, As, Sb, Cr...
$KClO_3$ or Na_2O_2		Ni	Powerful basic fluxes for silicates, KOH silica carbide and certain minerals; main limitation, purity of reagents.
NaOH or KOH	318-380	Au,Ag,Ni	
Na_2O_2	Decomposes	Fe,Ni	Powerful basic oxidizing flux for sulfides; acid–insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; platinum alloys; Cr, Sn, Zn minerals $K_2S_2O_7$
	300	Pt	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 determine.
$CaCO_3$+NH_4Cl		Ni	Upon heating of the flux, a mixture of CaO and $CaCl_2$ is produced; used for decomposing silicates for determining the alkali metals.

WEIGHING SAMPLES

Store and dry in weighing bottles, which have ground–glass contacting surfaces between the cover and the bottle.

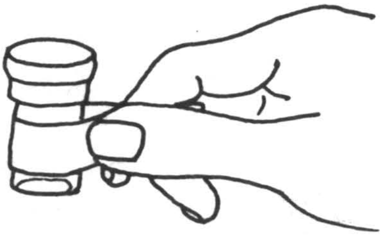
PROCEDURE

1.Use a clean weighing bottle filled with a ground–glass cover.

2.Handle the bottle with suitable tongs or with a strip of line-free paper (Fig.E–1)

(Fig.E–1)

E–1. Weighjng bottle and method of holding 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 titled weighing bottle.

3.Weigh the substance and the glazed paper or weighing dish.

4.Calculate the weigh 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.Qquantitatively 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.Substract the weight found in step 3 from the weight found in step 1. The difference in these tow weights is the amount of material transferred.

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

Use *weighing by differences* (Fig. E–2) when several samples of the same material are to be weighed. This method is preferable when weighing hygroscopic substances.

(Fig.E–2)

E–2.The weighing operations.

(a convenient method for transfer of a solid for weighing by difference).

DRYING SAMPLES

Heating at 105 to 100°C may direct dry samples, 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 beaker and the weighing bottle.

2.Place the weighing bottle in the beaker, which is covered by a watch glass supported on glass hooks (Fig.E–3).

3.Place in oven for required time at the temperature suggested.

DESICCATOR

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

PROCEDURE

1.Remove the cover by sliding sideways as in figure E–4.

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.

(Fig.E–3 and E–4)

E–3.Arrangement for drying samples.

E–4.Removing desiccator cover.

CLEANING AND RECHANGING 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 E--5).

5.Regrease the ground–glass lid.

6.Replace the porcelain support.

7.Slide the lid into position on the desiccator.

(Fig.E–5)

E–5. Filling the 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 cooling 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.

SECTION VI

COMMON HAZARDOUS CHEMICAL

Usual shipping container:

1.Acetic acid (glacial)–Glass carboys and barrels.

Expands on solidification and may burst container unless keep 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 which air flammable and explosive mixtures. Flashpoint -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 then 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 outstaying serious effect produced by ammonia in concentrations of 1/2% by volume for duration of exposure of the order half an hour is blindness. A concentration of 0.03% of ammonia in air for duration of exposure of the order half an hour to one hour 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 155 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. Incombustible packing should surround bottles.

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 burning unless adequate ventilation is provided.

b) Fire hazard--spontaneously ignitable when freshly calcimined 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 half an hour to one 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. Dangerous to neutralize chlorine in a room with ammonia.

7.Chromium Trioxide or Chromium Anhydride CrO_3 (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 box steel drums.

a) Life hazard–anaesthetic. See National Board of Fire Underwriters'. Recommended Safeguards for the Installation and Operation of Anaesthetic Apparatus Employing Combustible Anesthetics.

b) Fire hazard–a highly volatile liquid, giving off even at comparatively low temperature vapors which form with air or oxygen flammable and explosives mixtures. Explosive range is 1.85% to 36.5% (upward propagation). The ignition temperature is comparatively low, being approximately 180°C. (360°F). Spontaneously explosive peroxides sometimes form a 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% by weight)–glass carboys, aluminum drums, and aluminum tank cans (all containers must be vented).

a) Life hazard–prolonged exposure to vapor is 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, cooper, chromium and most metals or their salts.

11.Hydrogen Sulfide (Sulfured Hydrogen)–steel cylinders.

a) Life hazard–toxic. 0.05 to 0.07 percent by volume in air causes dangerous illness in half to one hour. 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–piosonous.

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 a fire, more readily extinguish.

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 burning. Contact of phosphorous 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 the presence of air). A cause 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–Classas with potassium hydroxide and calcium oxide.

20.Sulfur–sackes, boxes, barrel and box cars.

a) Life hazard--when burning form sulfur dioxide, which in concentration of 0.2% by volume with air may cause serious injury in half an hour or less.

b) Fire hazard–flammanle. Dust or vapor forms explosive mixtures with air. Hazardous in contact with oxidizing material.

21.Sulfuric Acid–corboys, 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 VII

PRACTICAL WORK

PHYSICAL CONSTANTS DETERMINATION

There are called **physical constants,** the physical properties of pure substances, which, with unchanged exterior conditions, have constant values. They serve at substance characterization.

Substance mixtures and impure substances have variable physical properties, depending on their composition. Physical constants can serve at substance's purity characterization.

Physical constants can also serve at theoretical and practical calculations.

The physical constants are:

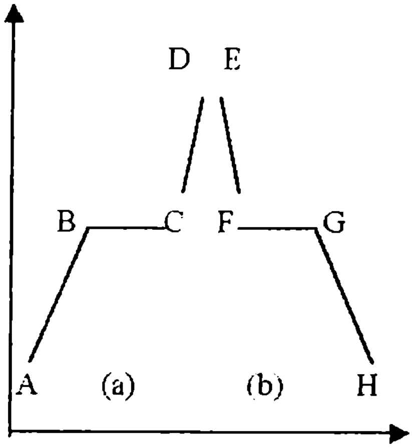
- Properties connected to the transition of substances from a state to another, in equilibrium conditions–melting, boiling, sublimation, polimorfic transformation, solidification, condensation temperatures, corresponding enthalpies (latent heats) to these temperatures, saturated vapors pressure etc.
- Density (specific gravity) in the aggregation states: solid, liquid and gaseous.
- Liquid viscosity.
- Optical properties–refraction index, UV spectral optics, visible and X–rays, X–rays spectra, X–rays and neutrons diffraction, etc.
- Electrical properties–dielectric constant, electric permeability, electric conductibility in solid state (metals and semimetals), in molten and solution, electro–chimic equivalent, etc.
- Magnetic properties–magnetic suscebility, RES and RMN spectrum, etc.
- Solubility with different solvents, ionization constant (acids and bases), hydrolysis constant (salts), etc.
- Atomic constants–atomic mass, molecular mass, chemical equivalent.
- Caloric constants–specific, molar heat, etc.

THEME I.

I.1.MELTING POINT DETERMINATION

Melting point represents the temperature at which a pure crystalline solid substance passes (isothermal), in equilibrium conditions, in liquid phase.

Substances which are not crystalline (amorphous or vitreous) have no melting point. They liquefiate in a temperature range and before melting, they soften.



a curve: AB–solid heating
BC–melting (isothermal)
CD–liquid heating

b curve: EF–liquid cooling
FG–solidification (crystallization from melt)
GH–solid cooling.

Fig.1–1.Melting (a) and solidification (b) diagram of pure crystalline substances.

Solidification point coincides with the melting one for majority of substances. Under exception are the viscous liquids (with hydrogen bonds).

The melting, respectively, solidification point is independent of pressure, liquids and solids being practically incompressible.

At crystallohydrates, melting is, actually, the result of two similar processes. Through heating, a part of crystallization water is degassed (efflorescence) and the crystal dissolves in the crystallization water. So, crystallohydrates melting has another mechanism as the actually melting which represents the crystalline lattice destruction under the temperature influence, after the thermal motion of vibration intensification of the particles from the crystal. The lose of the crystallization water begins, usually, at lower temperatures then the ones at which is taken place the crystal destruction and that's why, the crystallohydrates melt at lower temperatures then the anhydrite crystals.

Crystallohydrates at which this phenomena are produced at usual temperature are called delicvescents and the phenomena, delicvescence.

METHOD OF WORK:

It is worked with the apparatus represented in the figures1–2, 3 and 4.

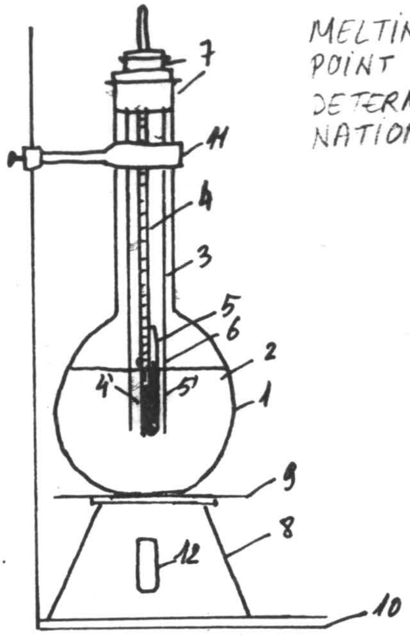
1.Figure 1–2 apparatus:

- It is mortared the crystalline substance until fine powder consistence, in a mortar with pestle.
- It is closed the narrow end of a capillary tube, putting it in a flame (in the superior con) for a short time. The powder is introduced in capillary, is settle through tapping in the capillary until the layer gets to the mercuric reservoir height of the thermometer.
- The capillary is fixed to the thermometer (with a rubber band), so that the inferior ends of the capillary and of the thermometer to be at the same level.
- The thermometer and the capillary is introduced in the liquid bath, protecting them with a test tube (it can be worked and without protection jacket), so that the liquid level to be above the mercury reservoir of the thermometer. In the case is worked without protection jacket (without test tube) it will watch that the liquid do not enter the capillary. For this, will work with a sufficiently long capillary.
- It is stetted under the liquid bath a tripod with asbestos sieve and under the tripod a gas burner with low flame which gives a slow heating, so that the temperature rising speed to be at least 3–5^{0}C/minut.
- It is followed, in the heating process, the temperature rising and the powder's state from the capillary. At the observation of a small modification in the powder's state, the temperature is quickly read, putting aside, in the same time, the heating source (the gas burner). It is put in the table the read temperature.
- The thermometer is taken out, the capillary is thrown, it is cooled carefully under water jet the liquid bath, it is prepared a new capillary with powder and the determination is resumed. It is repeated 3–4 times, putting the results in the table. The difference between two consecutive determinations must not be bigger then 0.5^{0}C.

- It is calculated the (arithmetical) average of the determinate temperatures and is labeled.
- It is done a report of the working manner and of the obtained results.

Figure.1–2.Laboratory installation for the determination of the melting point with capillary and liquid bath.

1.–Flat bottom and long neck balloon (liquid bath),
2.–Low volatility liquid (glycerin etc.),
3.–Test tube (protection jacket for thermometer and capillary),
4.–Laboratory thermometer (0–100 or 0–150°C),
4'.–Mercury reservoir of thermometer,
5.–Glass capillary closed at one end,
5'–Powder layer,
6.–Rubber band,
7.–Perforated and with air orifice. rubber stoppers,
8.–Tripod,
9.–Asbestos sieve,
10.–Test tube support,
11.–Clamp,
12.–Gas burner.



MELTING POINT DETERMINATION

TABLE OF RESULTS:

Nr of Determination	Melting point (^0C)	Medium melting point (^0C)	Determination errors	
			^0C	%
1	2	3	4	5
1 (X1)	$X = \frac{\sum Xn}{n}$			
2 (X2)				
3 (X3)				
N (Xn)				

- Are calculated the determination errors (X–Xn) and there are passed in 4. Are calculated the errors in % (X–Xn)/X.100 and there are passed in 5. Errors must not be greater then 2%.

2.Figure 1–3 apparatus:

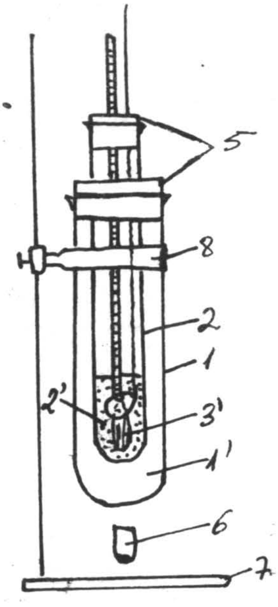
- It serves for the determination of melting and solidification (freezing) points. It is used also for determination of melting temperatures of mixtures, for melting diagram drawing of di– and policomponent systems (the melting temperature in function of composition).
- There are used quantities of order 2–5 g of substance.
- The pure substance (or the mixture of substance) is introduced in the test tube, so that, at thermometer fixation, it's mercury reservoir to be completely covered with substance. It is fixed then in the exterior test tube which serves as air bath (if is empty) or liquid bath (if is introduced in an involatile liquid). In the interior test tube, before the introduction of the substance, it is fixed a stirrer (a rigid wire dented at one end like a curl) of which straight end gets out of the test tube.
- The installation is fixed into a support (like in the figure 2 and 3) and is heated slowly, observing substance's state and temperature. At a small modification of the solid state, the temperature is recorded as being the melting temperature (the temperature corresponding to the beginning of melting) and is continuated the

heating until complete melting of the substance (is recorded the temperature corresponding to the end of the melting).

- The installation is removed from heating (the wire burner, the tripod with the asbestos sieve), the liquid is agitated through rising and lowering of the stirrer, following the liquid state and it's temperature. At the apparition of the first crystals (the liquid is easily disturbed) is read the temperature and is noted in the table. It is the solidification temperature. Intermittent stirring gives the cooling until the solidification of the whole mass. The temperature is noted (at the end of solidification). It is repeated the determination of the melting and solidification (crystallization) point 2–3 times. The results are noted in a table (see point 1). Calculations are made and it is written a report.

Figure 1–3. Laboratory installations for melting and solidification (crystallization) temperature.

1.–Test tube (air bath or liquid). It can be replaced with a Berzelius beaker (as liquid bath),
1'.–Air or liquid (glycerin etc.),
2.–Test tube with substance,
2'.–Substance layer,
3.–Laboratory thermometer,
3'.–Mercury reservoir of the thermometer,
4.–Stirrer,
5.–Perforated rubber stoppers and with air orifice,
6.–Gas burner,
7.–Support,
8.–Clamp.



3.Figure 1–4 apparatus:

- There are introduced the vials which contain a pure substance or mixture of substances in liquid bath, it is fixed into a support, at small distance from thermometer. The liquid bath is settled on a magnetic stirrer with electric heating (kitchen range).
- The stirrer is started and the heating. Is followed the state of substance from the vial and the temperature rising.
- At the observation of a small modification in the state of substance it is knotted the temperature as being the melting point (temperature) corresponding with the beginning of the melting. The process is continuated until the complete melting of the substance. The final temperature is knotted.
- The magnetic stirrer is removed; the liquid bath is left to cool, stirring carefully the liquid with a stirring–rod which has the end protected with rubber. At the apparition of the first crystals (the liquid is disturbed), it is noted the temperature. The cooling is continuated until the solidification of the entire mass of substance from the vial, after which, it is repeated the determination of the melting and solidification point (temperature) twice. The results are noted in a table (see point 1). Are made the calculations.
- The method serves at the melting point determination of pure substances that have large vapor tension at melting (it sublimates), for instance I_2, naphthalene, camphor, etc., and for mixtures of substances with components that sublimate, are hygroscopic or react with the environment components.

Figure 1–4.Laboratory installation for the determination of the melting and crystallization temperature of the volatile substances (that sublime).

1.–Closed vial,

1'.–Substance (volatile),

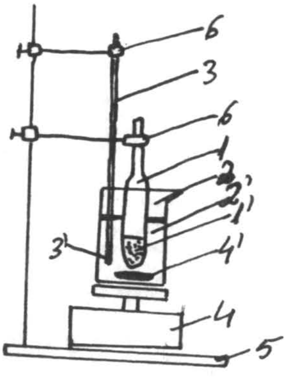
2.–Berzelius beaker (liquid bath),

2'.–Liquid (glycerin etc.)

3.–Laboratory thermometer,

3'.–Mercury reservoir of the thermometer,

4.–Magnetic stirrer with an electric kitchen range,
4'.–The iron core (with glass jacket) of the stirrer,
5.–Support,
6.–Clamp.



I.2. BOILING POINT DETERMINATION

The boiling point (temperature) represents the temperature at which the vapor pressure of a liquid becomes equal with the environment pressure, boiling being the phase transformation from liquid into vapors, which takes place in the whole liquid mass.

Unlike melting, the pressure powerful influences boiling, the boiling temperature is raised with the raising of the pressure and reverse. This why, the boiling point (temperature) is determinates at a constant, standard pressure which is, usually, one atmosphere (the standard boiling point or normal boiling temperature).

At homogeneous liquid mixtures (solutions), the boiling temperature varieties in function of composition, taking place, in general, a raising of boiling temperature of the solution towards the one of the pure solvent.

METHOD OF WORK:

For the determination of the boiling point there are used different construction apparatuses, like the one in the figure 2–1, which needs relative small quantities of liquid and distillation installation.

1.Figure 2–1 apparatus:

- In a clean and dried test tube (1) it is introduced the liquid that's boiling temperature is to be determined. Is added 1–2 bits of porous material (porcelain or glass shards) for assuring quiet, uniforms boiling of the liquid. The thermometer (4) is fixed through the rubber stopper (5), so that the mercury reservoir (6) to be at 3 cm above the liquid level (2). Next to the thermometer, through the rubber stopper specially perforated, is passed a capillary tube open at both ends (with the narrow end in interior), which makes the connection with the environment (7), for avoiding the pressure raising in the test tube. The test tube is fixed in the support (8) with the help of a clamp with muff (9), giving it a slight inclination (like in the figure). The contain of the test tube is heated in two ways:

- In the case of noninflammable liquids (carbon tetrachloride, aqueous solutions, etc.), the heating is done directly, using a small flame of a wire burner and protecting the test tube, not to break, with an asbestos sieve put on a tripod, the test tube being heated from the ascendant warm air.
- In the moment which, on the thermometer, is formed (on its mercury reservoir) the first drop of liquid, is read the temperature and written into the table. It represents the boiling temperature of the liquid determinate in vapor phase.
- The test tube and the liquid bath (if it was used) are cooled (under water jet) and the determination is repeated another 2–3 times. The results are noted in the table. It is calculated the average determinate values, which represents the experimental boiling temperature. It is comported with the value from the table. Is written rapport

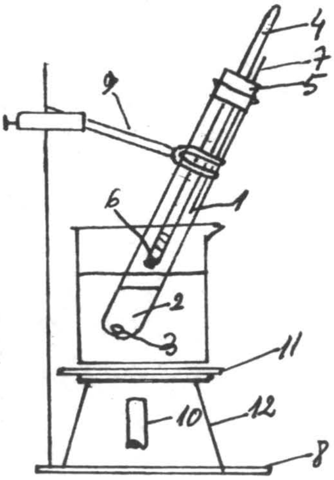
TABLE OF RESULTS:

Determination	Substance	Obtained values (⁰C)	Average value (⁰C)
Boiling temperature			

Figure 2–1.Apparatus for the determination of the boiling temperature in vapor phase, for small quantities of liquid.

1.–Test tube,
2.–Liquid with boiling temperature to be determinated,
3.–Porcelain or glass shard,
4.–Thermometer,

5.–Capillary tube,
6.–The mercury reservoir of the thermometer
7.–Capillary tube,
8.–Holder,
9.–Clamp with muff,
10.–Gas burner
11.–Asbestos sieve,
12.–Tripod,
13.–Liquid bath (Berzelius beaker).



2.Distillation apparatus:

In a clean and dried Würtz balloon is introduced 50 cm^3 of liquid and a few bits of porcelain or glass for assuring a quit boiling. The balloon is fixed in the holder with a clamp. The thermometer is fixed through the tight rubber stopper, so that the interior end of the mercury reservoir of the thermometer to be cca 0.5 cm lower then the lateral tube orifice. The tap water is opened, so that it flows with a reduce debit. Under the balloon is putted a tripod with an asbestos sieve and a gas burner with moderate flame. At the end of the refrigerant is fixed an along and a collecting vessel (a conical balloon).

During the heating, it is followed the vapor temperature. When the temperature is stabilized (it doesn't variate in the course of one minute), it is read and noted in the table, as being the determinate boiling temperature in vapor phase.

For the determination repeating it is cooled the balloons contain and the operations are made again. It is noted in the table the determinate boiling temperatures. It is calculated the determinations range as being the experimental boiling temperature, determinate in vapor phase. A report is written.

I.3. DENSITY DETERMINATION

It is called density, specific mass or volumetric mass, the volume unity mass of a homogeneous body. In the case of nehomogeneous bodies, the report between the m mass and volume V represents the average density.

The density (and average density): $\rho = m/V$ is expressed in kg/m^3 in IS (international system), but are kept also the tolerant measures g/cm^3 and kg/dm^3 for liquids and solids and g/dm^3 for gases.

The density depends on the nature of bodies (substances from which the bodies are made) and varieties insures proportionally with the temperature. If ρ_o is the density of a body at 0^{0}C, it's density at t^{0}C is, in the first approximation, $\rho_t = \rho_o/1+\alpha t$, where α is the dilution in volume coefficient. In the case of gases, the density depends in a sensitive way of the pressure.

It is sometimes used the relative density ρ_r, which is the report between the given substance density and the density of a reference substance: ρ_o, $\rho_r = \rho/\rho_o$. Reference substances are, in the case of liquid bodies, water–at 4.16^{0}C and normal pressure and, for gases, air–in normal physical conditions.

Because the density is sensitive influenced by the temperature, at the density determination (absolute and relative) the temperature must be maintained constant with strictness, indicating its value. Liquids and solids, not being practical compressible, the pressure does not influence their density. In the case of gases, which are easily compressible, it is taking into account the pressure and, when needed, there are made corrections at the determinate values, using the perfect gas equations.

For mixture and at impure substances, the density depends on the composition (for instance for acid, base, salt etc. solutions).

Density, which is a physical characteristic of pure substances, can serve for their characterization and, in the case of mixtures, density can serve at component concentration determination of a mixture (under the base of table data or parallel determinations on synthetic samples with known composition) or at purity determination.

There are used different experimental methods for the density determination for solids, liquids and gases.

1. Liquid density determination:

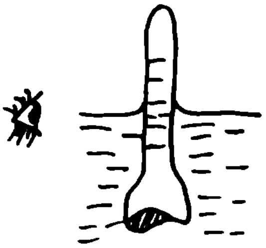
The most usual methods for determining liquid's density are:

- Free floating method (airmeters and densimeters),
- Pycnometer method,
- Hydrostatic weighting method.

1.1. Free floating method:

It is the simplest and spread method in practice and consists in the application of Arhimede's law for the density determination, by using some special instruments– airmeters (densimeters) which are introduced in liquid in such a way that they have a free floatation. Through their construction, airmeters keep their vertical position (have a ballast in the inferior part) and indicate the density with the aid of a scale etalonated in density units or in Be^0 degrees. Scale reading is made as in the figure below.

Figure. The correct reading of the airmeter's indications.



METHOD OF WORK:

- The liquid of which density is to be determinate, is introduced into a vessel with height and diameter sufficiently large to assure the free floating of the airmeter, best a graduated cylinder of corresponding capacity, in function of the airmeter dimension. Is left a sufficiently free space above the liquid that, at the introduction of the airmeter, it has a displaced liquid volume.
- It is choused an airometer whose scale to correspond to the liquid density. If the density is not known (with approximation), preliminary trials are made. It is taken an airmeter; it is taken from the superior end (with the big finger and the forefinger) and in sank slowly into the liquid. If he goes to the bottom of the vessel, the liquid density is too small and is tried, by repeating the operation, with a lighter densiometer. If the airmeter floats so that the liquid does not reach the scale, it means that the liquid density is too big and it is tried with a heavier densiometer.

- The corresponding airmeter (of whose scale corresponds to the measured density) is sunk in liquid in the way shown above. It is left a while until the vertical oscillation movements slow down. It is assured a central position of it (more close as possible to the vertical axis of the cylinder), so that doesn't touch and doesn't gets to close of the vessel walls. Is read the scale indication in the way shown in the figure (with the vessel in vertical and stable position–on the working table and with the right eye in the front of the read position). The result is noted.
- For repeating the determination, it is imprinted to the airmeter a slight vertical oscillation motions, then are repeated the operations descried above. The read values must, practically, coincide.

The disadvantage of the method is the necessity of using a relative large volume (50–100 cm^3) of liquid.

After the determination is complete, the airmeter is washed, is wiped with a clean, dried rope, and is put in its box. In the manipulation time, it is watched that the airmeter do not break. Being made from relative thin glass, it is fragile.

1.2. Pycnometer method:

It is based on the mass determination of a volume of liquid exactly measured. There are used pycnometers of different constructions, with or without thermometer. In stade of pycnometer, it can be used a quoted balloon of small capacity (25–50 cm^3).

METHOD OF WORK

- It is washed and well dried and weighted at the analytical balance. Empty pycnometer mass is noted m_o.
- The pycnometer is filled with distillated water so that it does not have air boles inside (the quoted balloon is brought to the sign) and is weighted. It is noted the pycnometer mass with water, m_a.
- The pycnometer is emptied of water, is washed 2 or 3 times with small portions from the liquid of whose density is to be determined and is filled with liquid (same as water). The pycnometer with liquid is weighted and the mass is noted m_x.
- The relative density is weighted ρ_r ($V_{liquid} = V = _{water}$):

$$\rho_r = \rho_{liquid} / \rho_{water} = m_{liquid} / m_{water} = (m_x - m_o) / (m_a - m_o)$$

and then: $\rho_{liquid} = \rho_r \times \rho_{water}$ –the density or the specific mass.

The water density at different temperatures (g /cm^3):

t(°C)	17	18	19	20	21	22	23	24	25	26
ρ water	0.99880	0.99862	0.99843	0.99823	0.99802	0.99780	0.99756	0.99732	0.99707	0.99681

The values from table are taken corresponding to the temperature from the laboratory.

2. Solids density determination:

The most usual method to determinate solid substance's density is pycnometer's method. The imposed condition is that the substance with the density to be determinate, not to be soluble in the used reference liquid, which is the usually water.

It is working with similar pycnometers used for liquid determination.

METHOD OF WORK

- It is weighted on the analytical balance the well cleaned and dried pycnometer. The empty pycnometer mass is noted as m_o.
- It is introduced in the pycnometer a some quantity of substance brought is powder state and is weighted again. The pycnometer mass with substance is noted m_s.
- It is filled the pycnometer that contains the substance with chosen liquid for determination (usually water) and it is weighted. Pycnometer mass with substance and liquid (water) is noted m_{sa}.
- The pycnometer is washed taking care it does not have solid substance left in it; it is filled with liquid (water) and weighted again. The pycnometer mass filled with distilled water is noted m_a.
- The relative density of the solid substance is calculated as is the following:

$$\rho_r = (m_a - m_0) / (m_a + m_s - m_0 - m_{sa})$$

If the reference liquid is water, the density or the specific mass is calculated as:

$$\rho_{liquid} = \rho_r \times \rho_{water}.$$

PRACTICAL WORK

I. 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 is 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 the thermometer, which is centered in a heating bath.

Setup of apparatus

Obtain commercially available capillary tubes or make them by drawing out 12-mm soft glass tubing. Fill the capillary tube with powdered compound to a height of 3 to 4 mm. Scrape the powder into a pile. Push the powder into the open end of the capillary tube. Shake the powder to the bottom of the tube by tamping lightly against the desktop or by gently scraping the tube with a file. Pack tightly. Attach the capillary to the thermometer with a rubber band and immerse in an oil bath. Heat the oil bath quickly to about 5 ^{0} C below the melting point, stirring continuously. Now heat slowly; raise the temperature about 5 ^{0} C / min, mixing continuously. Record the temperature when fusion is observed and record the melting – point range. Discard the capillary after the determination has been made.

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 an another crystalline form having a different melting point. Multiple melting points may be run simultaneously if their melting points differ by 10^0 C. Identify tubes to avoid mistakes.

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

Substance, which tends 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.

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

Clean the surface of the block;
Place a very small quantity of finely powdered material on the proper area;
Follow the heating procedure above;
When the determination is complete, turn off the electricity;
Multiple melting points may be determined simultaneously.

THEME II.

II.1. SOLUTIONS

Solutions are homogeneous mixtures of two or more substances; their properties vary with the ratio of components.

The homogeneous mixtures may be liquid, solid or gaseous. For the dispersed systems we may distinguish:

- Solution of gas into liquid
- Solution of liquid into liquid
- Solution of solid into liquid

Any solution has two components: the dissolvent substance called solvate, the solvent (the most used one is H_20)

Ideal Solution

The ideal solutions are homogeneous mixture of substances that has physical properties linearly related to the properties of the pure components. The classic statement of this condition is Raoult's law, which is valid for many highly dilute solutions and for a limited class of concentrated solutions, namely, those in which the interactions between the molecules of solute and solvent are the same as those between the molecules of each substance by itself. Solutions of benzene and toluene, which have very similar molecular structures, are ideal: any mixture of the two has a volume equal to the sum of the volumes of the separate components, and the mixing process occurs without absorption or evolution of heat. The vapor pressures of the solutions are mathematically represented by a linear function of the molecular composition.

When the components of nonideal solutions are mixed, the volume of the mixture ordinarily differs from the sum of the volumes of the pure components, and heat is evolved or absorbed. The properties of such solutions often are described in terms of their deviations from those of ideal solutions. Mixtures of acetone and chloroform, for example, are said to show negative deviations from ideality: their vapor pressures are lower than those calculated on the assumption of a linear relationship to the molecular composition. Solutions of acetone and carbon disulfide, on the other hand, have higher vapor pressures than those that would characterize an ideal **solution**.

Activity coefficients and excess functions

As has been explained previously, when actual concentrations do not give simple linear relations for the behavior of a **solution**, activity coefficients, symbolized by γ_i, are used in expressing deviations from Raoult's law. Activity coefficients are directly related to excess functions, and, in attempting to understand **solution** behavior, it is convenient to characterize nonelectrolyte solutions in terms of these functions. In particular, it is useful to distinguish between two types of limiting behavior: one corresponds to that of a regular **solution**; the other, to that of an athermal **solution** (*i.e.*, when components are mixed, no heat is generated or absorbed).

In a binary mixture with mole fractions x_1 and x_2 and activity coefficients Y_1 and Y_2, these quantities can be related to a thermodynamic function designated by G^E, called the excess Gibes (or free) energy. The significance of the word excess lies in the fact that G^E is the Gibes energy of a **solution** in excess of what it would be if it were ideal.

In a binary **solution** the two activity coefficients are not independent but are related by an exact differential equation called the Gibes-Durham relation. If experimental data at constant temperature are available for Y_1 and Y_2 as a function of composition, it is possible to apply this equation to check the data for thermodynamic consistency: the data are said to be consistent only if they satisfy the Gibes-Durham relation. Experimental data that do not satisfy this relation are thermodynamically inconsistent and therefore must be erroneous.

To establish a theory of solutions, it is necessary to construct a theoretical (or semitheoretical) equation for the excess Gibbs energy as a function of absolute temperature (T) and the mole fractions x_1 and x_2. After such an equation has been established, the individual activity coefficients can readily be calculated.

Gibbs energy, by definition, consists of two parts: one part is the enthalpy, which reflects the intermolecular forces between the molecules, which, in turn, are responsible for the heat effects that accompany the mixing process (enthalpy is, in a general sense, a measure of the heat content of a substance); and the other part is the entropy, which reflects the state of disorder (a measure of the random behavior of particles) in the mixture. The excess Gibbs energy G^E is given by the equation

$$G^E = H^E - TS^E,$$

where H^E is the excess enthalpy and S^E is the excess entropy. The word excess means in excess of that which would prevail if the **solution** were ideal. In the simplest case, both H^E and S^E are zero; in that case the **solution** is ideal and $Y_1 = Y_2 = 1$. In the general case, neither H^E nor S^E is zero, but two types of semi-ideal solutions can be designated: in the first, S^E is zero but H^E is not; this is called a regular **solution**. In the second, H^E is zero but S^E is not; this is called an athermal **solution**. An ideal **solution** is both regular and athermal.

In a pure liquid, the vapor generated by its escaping molecules necessarily has the same composition as that of the liquid. In a mixture, however, the composition of the vapor is not the same as that of the liquid; the vapor is richer in that component whose molecules have greater tendency to escape from the liquid phase. This tendency is measured by fugacity; a term derived from the Latin *fugere* ("to escape, to fly away"). The fugacity of a component in a mixture is (essentially) the pressure that the component exerts in the vapor phase when the vapor is in equilibrium with the liquid mixture. (A state of equilibrium is attained when all the properties remain constant in time and there is no net transfer of energy or matter between the vapor and the liquid.) If the vapor phase can be considered to be an ideal gas (*i.e.*, the molecules in the gas phase are assumed to act independently and without any influence on each other), then the fugacity of a component, i, is equal to its partial pressure, which is defined as the product of the total vapor pressure, P, and the vapor-phase mole fraction, y_i. Assuming ideal gas behavior for the vapor phase, the fugacity (y_iP) equals the product of the liquid-phase mole fraction, x_i, the vapor pressure of pure liquid at the same temperature as that of the mixture, P_i, and the activity coefficient, γ_i. The real concentration of a substance may not be an accurate measure of its effectiveness, because of physical and chemical interactions, in which case an effective concentration must be used, called the activity. The activity is given by the product of the mole fraction x_i and the activity coefficient γ_i. The equation is:

$$y_i P = \gamma_i x_i P_i Y.$$

Raoult's law

In a real solution, the activity coefficient, Y_i, depends on both temperature and composition, but, in an ideal solution, Y_i equals 1 for all components in the mixture. For an ideal binary mixture then, the above equation becomes, for components 1 and 2, $y_1P = x_1P_1^\circ$ and $y_2P = x_2P_2^\circ$, respectively. Upon adding these equations--recalling that $x_1 + x_2 = 1$ and $y_1 + y_2 = 1$--the total pressure, P, is shown to be expressed by the equation $P = x_1P_1^\circ + x_2P_2^\circ = x_1[P_1^\circ - P_2^\circ] + P_2^\circ$, which is a linear function of x_1.

Assuming $Y_1 = Y_2 = 1$, equations for y_1P and y_2P express what is commonly known as **Raoult's law**, which states that at constant temperature the partial pressure of a component in a liquid mixture is proportional to its mole fraction in that mixture (*i.e.*, each component exerts a pressure that depends directly on the number of its molecules present). It is unfortunate that the word **law** is associated with this relation, because only very few mixtures behave according to the equations for ideal binary mixtures. In most cases the activity coefficient, Y_i, is not equal to unity. When Y_i is greater than 1, there are positive deviations from **Raoult's law**; when Y_i is less than 1, there are negative deviations from **Raoult's law**.

Henry's Law

The **law**, which was first formulated in 1803 by the English physician and chemist William Henry, holds only for dilute solutions and low gas pressures.

In a very dilute solution, a solute molecule will (with rare exceptions) have only solvent molecules as near neighbors and the probability of escape of a particular solute molecule into the gas phase is expected to be independent of the total concentration of solute molecules. In this case the rate of escape of solute molecules will be proportional to their concentration in the solution, and solute will accumulate in the gas until the return rate is equal to the rate of escape. With a very dilute gas this return rate will be proportional to the partial pressure of solute. Thus, we expect that, for a solution very dilute in solute, in equilibrium with a gas at very low pressure, the gas pressure will be proportional to the amount of dissolved gas--the relation known as **Henry's law**. While the above argument is to be considered only suggestive, **Henry's law** is found experimentally to hold for all dilute solutions in which the molecular species is the same in the solution as in the gas. The most conspicuous apparent exception is the class of electrolytic solutions.

Classes of Solutions

Electrolytes and nonelectrolytes

Broadly speaking, liquid mixtures can be classified as either solutions of electrolytes or solutions of nonelectrolytes. Electrolytes are substances that can dissociate into electrically charged particles called ions, while nonelectrolytes consist of molecules that bear no net electric charge. Thus, when ordinary salt (sodium chloride, formula NaCl) is dissolved in water, it forms an electrolytic **solution**, dissociating into positive sodium ions (Na^+) and negative chloride ions (Cl^-), whereas sugar dissolved in water maintains its molecular integrity and does not dissociate. Because of its omnipresence, water is the most common solvent for electrolytes; the ocean is a **solution** of electrolytes. Electrolyte solutions, however, are also formed by other solvents (such as ammonia and sulfur dioxide) that have a large dielectric constant (a measure of the ability of a fluid to decrease the forces of attraction and repulsion between charged particles). The energy required to separate an ion pair (*i.e.*, one ion of positive charge and one ion of negative charge) varies inversely with the dielectric constant, and, therefore, appreciable dissociation into separate ions occurs only in solvents with large dielectric constants.

Most electrolytes (for example, salts) are nonvolatile, which means that they have essentially no tendency to enter the vapor phase. There are, however, some notable exceptions, such as hydrogen chloride (HCl), which is readily soluble in water, where it forms hydrogen ions (H^+) and chloride ions (Cl^-). At normal temperature and pressure, pure hydrogen chloride is a gas, and, in the absence of water or some other ionizing solvent, hydrogen chloride exists in molecular, rather than ionic, form.

Solutions of electrolytes readily conduct electricity, whereas nonelectrolyte solutions do not. A dilute **solution** of hydrogen chloride in water is a good electrical conductor, but a dilute **solution** of hydrogen chloride in a hydrocarbon is a good insulator. Because of the large difference in dielectric constants, hydrogen chloride is ionized in water but not in hydrocarbons.

Thermodynamics and intermolecular forces in solutions

The properties of solutions depend, essentially, on two characteristics: first, the manner in which the molecules arrange themselves (that is, the geometric array in which the molecules occupy space) and, second, the nature and strength of the forces operating between the molecules.

Energy considerations

The first characteristic is reflected primarily in the thermodynamic quantity S, called entropy, which is a measure of disorder, and the second characteristic is reflected in the thermodynamic quantity H, called enthalpy, which is a measure of potential energy--*i.e.* the energy that must be supplied to separate all the molecules from one another. Enthalpy minus the product of the absolute temperature T and entropy equals a thermodynamic quantity G, called Gibbs energy (also called free energy):

$$G = H - T S.$$

From the second law of thermodynamics, it can be shown that, at constant temperature and pressure, any spontaneous process is accompanied by a decrease in Gibbs energy. The change in G that results from mixing is designated by ΔG, which, in turn, is related to changes in H and S at constant temperature by the equation

$$\Delta G = \Delta H - T \Delta S.$$

At a fixed temperature and pressure, two substances mix spontaneously whenever ΔG is negative; that is, mixing (either partial or complete) occurs whenever the Gibbs energy of the substances after mixing is less than that before mixing.

The two characteristics that determine **solution** behavior, structure and intermolecular forces, are, unfortunately, not independent, because the structure is influenced by the intermolecular forces and because the potential energy of the mixture depends on the structure. Only in limiting cases is it possible, on the one hand, to calculate ΔS (the entropy change upon mixing) from structural considerations alone and, on the other, to calculate ΔH (the enthalpy change of mixing) exclusively from relations describing intermolecular forces. Nevertheless, such calculations have proved to be useful for establishing models that approximate **solution** behavior and that serve as guides in interpreting experimental measurements. Solutions for which structural considerations are dominant are called athermal solutions, and those for which the effects of intermolecular forces are more important than those of structure are called regular solutions (see below Theories of solutions: Regular and athermal solutions).

Properties of solutions

The concentration of a solution may be:

- Percentage concentration (%) - indicates the quantity (in grams) of dissolute substance contained into 100g of solution.

$c\% = m_d/m_s x 100$ where: m_d = mass of dissolute substance

m_s = the mass of solution

- Molar concentration (m = morality) - indicates the no. of molecules of solvate dissolute into one liter of solution.

$m = m_d/M \times v$ where: m_d = the mass of solvate

M = the molecular weight of the solvate

v = the volume of solution

Normal concentration (n normality) - indicate the number of equivalents of dissolute substance contained into one liter of solution

$n=m_d/Exv$ where: m_d = the mass of dissolute substance

E = the equivalent of the dissolute substance

v = the volume of the solution

Molar concentration (m = morality) - indicates the number of moles of dissolute substance contained into 1000g of solvent.

$m = m_d \times 1000 / M \times m_s$

where: m_d = the mass of solvate

M = the molecular weight of the solvate

m_s = the mass of solution

Besides these concentrations there is also the titre of a solution, which represents the amount of substance (in grams) contained into $1m^3$ of solution.

PRACTICAL WORK

PREPARATION OF SOLUTIONS

The preparation of a solution 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 classified in 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 theoretical value of this concentration is the titre.

In the 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 precisely concentration is called factor of the solution. (F)

$$\mathbf{F = T_{experimental} / T_{theoretical}}$$

Thus, F for standard solutions is 1.

The factor of solutions can be also obtained from the relation:

$$Va \times Fa = Vb \times Fb$$

where: Va & Fa are the volume & the factor for approximate solution

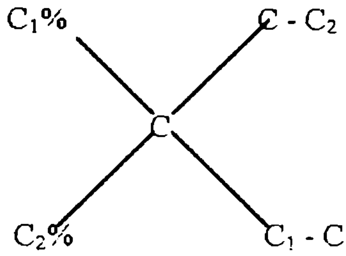
Vb & Fb are the corresponding values for standard solution

In the case of solutions obtained through dilution or through mixing solutions of different concentrations, the calculus of required quantities of solutions 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%).

$C_1\% > C\% > C_2\%$

The rule of mixture may be reduced to a simple scheme:



Thus, (C - C2) represents the weighed mass 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% & C_2%) we have to divide the masses (C - C_2) & (C_1 - C) by the densities of the solutions.

This rule is also applied for normal & molar concentrations.

II.1.1. PREPARATION OF CUPRIC SULPHATE SOLUTION 4.1%

We have to calculate the amount of cupric sulfate hydrated by five molecules of water ($CuSO_4$.x %H_20) necessary for the preparation of 60g solution 4.1%. The solid substance ($CuSO_4$ x %H_20) must be weighed at the analytical balance and the water must be measured in a graduated cylinder. The reaction is made in a Berzelius glass and the solution obtained is put into a bottle for reagents.

II.1.2. PREPARATION OF NATRIUM HYDRATE SOLUTION 0.1 N

We have to compute the quantity of NaOH solution necessary to prepare 200 or 250 cm^3 (depending on the quoted balloon) of NaOH solution 0.1 N.

The concentration will be approximately 0.1 N because of the hygroscopic properties of the substance. Its normal concentration will be better determined after establishing the titre and the factor.

Sodium hydrate is weighted on a glass plate at pharmaceutical balance and introduced into a quoted balloon.

II.1.3. PREPARATION OF SULPHURIC ACID SOLUTION 0.1 N

We need to compute the volume of sulfuric acid 96% (d = 1.8 g/cm^3) necessary for preparing 200 cm^3 (250cm^3) solution 0.1 N.

Fill a half of the balloon with distilled water and add drop by drop and under permanent stirring the required volume of H_2S0_4; fill the balloon with distilled water until it reaches the quotation (sign).

Since the solution has an approximate concentration, the following step is the determination of the titre and factor.

II.1.4. DETERMINATION OF SOME ACIDS AND BASES CONCENTRATION (TITRE)

This determination is carried out employing the volumetric analyses, which determine the volume of reagent B consumed, by the analyzed substance A during a certain chemical reaction (neutralization, oxidation-reduction or precipitation reactions).

The reagent, of precisely Known concentration is added in stoechiometric quantity. Using the chemical equations the amount of substance A may be determined.

The indicators are used in order to determine the end of the titration (point of equivalence). These are substances, which change their color at every small amount of reagent added.

II.1.5. DETERMINATION OF THE TITRE (CONCENTRATION) OF A NATRIUM HYDROXIDE SOLUTION

Necessary substances and tools:

0.2g oxalic acid;
NaOH solution;
Distilled water;
Phenolphthalein
Erlenmeyer glass of 250 cm^3;
Burette with a Mohr clamp.

WORKING MANNER:

Oxalis acid is used as standard substance. Into an Erlenmeyer glass introduce 0.2g of oxalic acid (weighed at the analytical balance) hydrated by two molecules of H_2O. Add 40 - 50 cm^3 of distilled water just boiled. After the dissolution add 2-3 drops of phenolphthalein and then carry out the titration with NaOH solution (prepared at experience 1.3) until a pink color appears. Repeat this operation until the difference between the results is about 0.05 cm^3.

For measuring the volume of sodium hydrate it's better to use a burette with Mohr clamp. Before using it, wash it with water and finally with the solution.

The titre T_1 of the sodium hydrate solution may be computed as follows:

ml (grams) = mass of oxalic acid (use four decimal fractions)

V1 (cm^3) = volume of NaOH solution 0.1 used.

$E_{H2C2O4 \times 2H2O} / m1 = E_{NaOH}/T_1 V_1 \Rightarrow T_1 = m_1 \times E_{NaOH}/E_{H2C2O4 \times 2H2O} \times V_1 = 40.005 \times m_1/ 163.034 \times V_1$

The factor F_1 is determined from the ratio:

$F_1 = T_1 / T_{theoretical}$

Where: $T_{theoretical} = 0.004$ g/cm^3

II.1.6. DETERMINATION OF THE TITRE OF A SULPHURIC ACID SOLUTION 0.1 N

Necessary substances and tools:

NaOH 0.1N

H_2S_4 0.1 N

Phenolphthalein

Distilled water

Erlenmeyer glass

Burette with a Mohr clamp

WORKING MANNER:

Is used a solution of sodium hydrate 0.1 N for which the titre and factor were determined. Introduce 20 cm^3 of NaOH solution 0.1 N measured with the burette into an Erlenmeyer glass. Dilute it with distilled water, washing the walls of the glass too. Add 2-3 drops of the phenolphthalein and carry out the titration with sulfuric acid solution 0.1 N until the colorless solution. Repeat the titration until the difference between the results is about 0.05 cm^3. The titre and the factor are calculated as follows:

$E_{H2SO4}/Xg_{H2SO4} = \mathbf{E_{NaOH} / V_{NaOH} \times T_{NaOH}}$

$X = 20 \times T_1 \times 49/40.005$

V2 (cm^3) = volume of H_2S0_4 0.1 N used

$T_2 = X / V_2$ (titre of H_2S0_4)

$F_2 = T_2 / T$ theoretical (factor of H_2S0_4)

Where T theoretical is 0.0040 g/cm^3

The titre and the factor can be computed using the relation:

V_{NaOH} X $F_{NaOH} = V_{H2SO4}$ x F_{H2SO4}

II.2. SOLUBILITY DETERMINATION

The dissolution of a substance into a solvent in order to form a solution (a liquid homogeneous mixture) is a complex process which supports the breaking of the old ligations between the particles of the solvent (the substance in whose volume the solvates particles spread through the process of diffusion) and, of course, the formation of the new ligations solvate. That can be made only if there is a structural chemical analogy between the solvent and the solvate, that means this thing is possible if the two components have same nature. For instance polar and ionic substances dissolves in polar solvents and not in anpolar solvents etc.

The solubility of a substance into a certain solvent it is quantitatively expressed through the concentration of the saturated solution (the solution which is into a dynamical equilibrium with the andissloved solvate). The concentration is given in many known ways. The solubility S is usually given in grams of solvate in 100 g solvent. From this point of view we can distinguish the following classes of substance reported to a certain solvent.

Substance	Solubility S (g solvate /100 g solvent)
Very soluble	10–100
Easy soluble	1–10
Soluble	0.1–1
Little soluble	0.01–0.1
Very little soluble	0.001–0.01
Practically insoluble	<0.001

Substances absolutely insoluble do not exist. There exist substances whose solubility being little is practically neglectible (these are called insoluble)

The solubility of a substance into a certain solvent is a constant measure if the temperature remains invariable and it represents a physical constant that characterizes the substance.

When the temperature alternates, the solubility changes at almost all the substances (reported to a certain solvent) once with the rising of the temperature, the solubility increases. There are substances at which this dependence is inverse (the solubility goes down when the temperature goes down like at the dissolvation of the natrium sulfate in water). There are also substances that have the solubility constant with the temperature (solubility does not practically alternate with the variation of the temperature, like in the case of natrium chloride dissolvation in water).

The solubility variation of a substance into a solvent with the temperature it is represented under the shape of a diagram that represents the "solubility curves". The points of discontinuity from certain curves (at the zinc, calcium, and ferum sulfate) represent the temperature of passing from the raising of the temperature making the hydration degree of the salt to go down.

Knowing the solubilities of the substances (at different temperatures) has a special practical importance. Based on the solubility data, there are drown out the tehnological processes of crystallization, purification, etc. of the substances.

PRACTICAL WORK

Solubility determination

There will be made determinations in order to make the curve of solubility for different substances using H_2O as a solvent. We will work with pure substances and with distilled water. The point of saturation of a substance into a given solvent can be determinate through two methods (for solid crystallized substances):

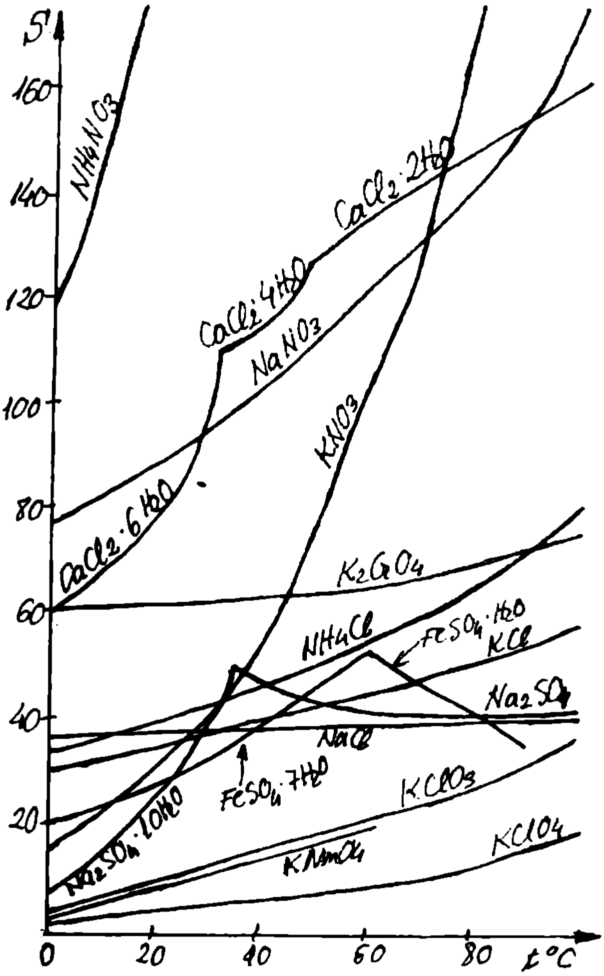
- Reading the temperature at which the entire quantity of solvent dissolves into the volume of solvent (the crystals of solid disappears).

- Reading the temperature at which appear the first crystals into a solution (the solution is not clear anymore).

Both temperatures (that of total solubilization and that of crystallization through cooling off) reflects the saturation of the substance, the first through the worming of the solution in the presence of an excess of solid substance (solvate), the second at the cooling of a saturated solution.

Figure II.1. Solubility curves of some substances in water.

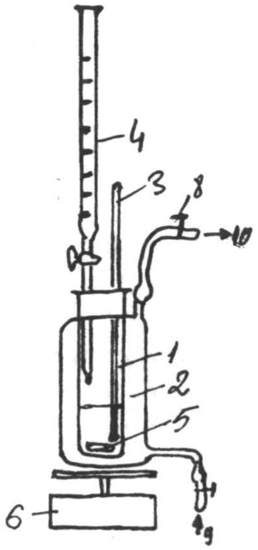
Solubility S (g substance /100 g water).



WORKING MANNER:

We will work with the apparatus shown below:

Figure II.2. Apparatus for determination of the solubility of solid substances in water at different temperatures.



1.–Glass vessel with double walls (water jacket),
2.–Water jacket,
3.–Thermometer,
4.–Burette,
5.–Magnet,
6.–Magnetic stirrer,
7.–Rubber connections with Hoffman clamp,
8.–Hoffman clamp,
9.–Water source for cooling (tap),
10.–Vessel for draining water used in cooling.

It will be weighted at the analytical balance a quantity of substance corresponding to the indications below:

Substance	Weighted mass (g)	cm^3 water
NH_4Cl	2.0000 – 2.5000	3.5
KNO_3	2.0000 – 2.5000	2.0
$K_2Cr_2O_7$	1.0000 – 2.0000	3.5
$KClO_3$	1.0000 – 2.0000	2.5
KCl	2.0000 – 2.5000	2.0

For quantitative transfer of the weighted substance in vessel 1, the weighing is made on a shiny paper (put on a watch glass), with the mass of the watch glass with the paper determinate before. It can also be made a weighting through difference (it is weighted a vial of weighing which can be replaced with a little box for medicines, containing the substance. The weighted mass is noted m_1. It is introduced a quantity of salt in vessel 1, which corresponds with approximation with the required quantity. The vial or the box is weighted again and the mass is denoted m_2. The salt quantity from the vessel 1 will be m_1-m_2. If the salt mass from vessel 1 is too small, it is added from the vial, then is weighted again. It is noted m_3. In this case, the substance mass from vessel 1 is m_1-m_3. The substance quantity must be taken in such a way that it covers the bottom of the vessel.

- In vessel 1 is introduced the magnet (an iron core protected by a glass jacket), there are fixed the thermometer and burette (3 and 4) through a perforated cork. The height of the thermometer from the vessel is adjusted such that the mercury reservoir to be immerged in solution but not to bother the magnet's working. In the burette is introduced distilled water until to a known division (best until zero division).
- The vessel is put on the magnetic kitchen range (6). The rubber tubes are connected to the tap of cold water and the other one is left free in the sink. The magnetic shaker is plugged to the electrical network and the stirring and heating are started.
- In the vessel 1 is introduced from the burette the water quantity indicated on the table.
- The dissolution process, that takes place in the vessel 1, is continuous observed and the temperature is read in the moment of the disappearance of the last crystals.
- The heating is stopped; the vessel 1 is isolated from the range through an azbest sieve. Opening the tap so that the water flows in a thin vein starts the cooling.
- During cooling process, the transparence of the substance is followed. When the first turbid aspect appears, the temperature is read.
- Both the temperatures are written (dissolution and crystallization) in the table below.
- The cooling is stopped (the cold water tap is closed and the water jacket is drained by detaching the water adduction tube). The azbest sieve is removed. Heating is started.
- From the burette is added in the vessel 0.5 cm^3 of distilled water. A dilution of the precedent solution takes place. It is calculated the new concentration of the saturated

solution. The experience for determining the solubility and crystallization temperatures is repeated as before. The results are noted in the table.

- The adding of distilled water (0.5 cm^3 each case) from the burette is repeated at least three times and then the determination operations for the crystallization temperatures, so that it exists at least four determinations through distilled water additions to the initial solution. Each time it is calculated the saturated solution's concentration. Experiment's dates are noted in the table below:

Solution	Solution's mass	Added water volume cm^3	Solution's (g/100g) concentration	Determined temperatures t_{sol}–t_{crys}	
				solubility tsol	crystallization t_{crys}

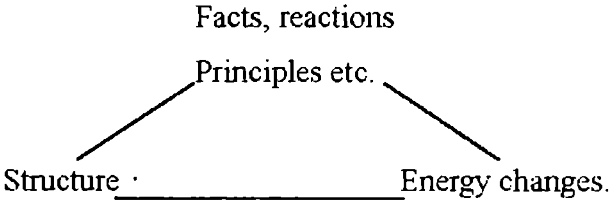
- With the obtained dates, the solubility curve is drowning for the value t_{sol} and separately for the value t_{crys} (on the same diagram). On the abscise axis are noted the temperatures and on the ordinate, the concentrations (g substance /100 g water). The abscissa and ordinate's modules are chosen so that they form a square.
- In the case of crystallohydrates it is calculated the solubility towards the anhydre solution.
-

THEME III.
THERMIC EFFECT

ENERGETICS

III.1. Introduction

A study of chemistry can be summarized by the following triangle:



The emphasis must be towards the learning of fact, principles and reactions, with structure and energy changes are introduced varies from one syllabus to another.

For example, the melting of ice to give water is a simple process and a straightforward topic which 0 level candidates should know. As an A level candidate you should appreciate that ice has an open crystal lattice with a tetrahedral structure. On heating, the water molecules in the lattice vibrate more and the structure breaks up on melting. The process requires energy:

e.g. ice + energy→ liquid water

This is an **endothermic** process and the energy required is called the **enthalpy change of fusion.**

You should always consider changes of structure and energy changes when answering questions. Nearly all chemical reactions involve energy changes and study changes is called **energetic.**

III.2. First law of thermodynamics

This law is equivalent of the law of conservation of energy. It states that **energy cannot be created or destroyed but may be converted from one form unto another:**

$q = \Delta U + w$

Where: ΔU is the change in the internal energy

q is the actual heat change and

w is the work done by the system.

The term w involves the gas produced expanding and pushing back the atmosphere. This can be established by using a syringe with a poison. The work done:

$w = P\Delta V$ where P is the external pressure and ΔV is the change in volume.

$P\Delta V$ (and hence w) only becomes significant when either P and/or ΔV is large.

For gases, ΔV is frequently large and w can be significant.

Reactions carried out at constant volume. In these cases $\Delta V=0$ (i.e. no change in volume) and $P\Delta V = w = 0$

$qv = \Delta U$

Where qv represents heat change at constant volume. Any heat change recorded corresponds to a change in the internal energy of the system.

Reactions carried out at constant pressure. Most reactions are carried out in the laboratory at a constant pressure e.g. in an open beaker. Any gas expanding against the pressure of the atmosphere does work.

$qv = \Delta U + P\Delta V$ where qv represents the heat change at a constant pressure.

$qv = (U\ final - U\ initial) + P((V\ final - V\ initial)$

$(U\ final + Pv\ final)(U\ initial + Pv\ initial)$

The term U + PV represents the energy possessed by the system and is called the **enthalpy B** or **heat content H:**

$qv = H\ final - H\ initial = \Delta H$

Substituting,

$\Delta H = \Delta U + \Delta V$

III.3. Enthalpy change of reaction

The equation for the reaction between carbon and excess oxygen is:

$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H = -393.5\ kJ\ mol^{-1}$

(Note: mol^{-1} means per quality shown in the equation *not* per mole of product.)

The combustion of 12 g of graphite in excess oxygen liberates 393.5 kJ. (the negative sign for ΔH, by conversion, tell us that energy is **liberated** or the reaction is **exothermic.**

The quantity of energy liberated or absorbed is given by the equation. ΔH is called the **enthalpy change of reaction.** Often standard enthalpy changes are quoted. These are the enthalpy changes at standard atmospheric pressure and at constant temperature, usually 25°C (or 298K). The reactions and products are in their usual or standard states at 25°C. Carbon is in the form of graphite and oxygen and carbon dioxide are gases. The standard enthalpy change of reaction is represented by ΔH°. If solutions are used they must have a concentration of 1 mol dm^{-3}.

It is impossible to estimate absolute enthalpies but only enthalpy changes. Elements in their standard states are regarded as having zero enthalpy.

There are a number of standard enthalpy changes, which are important and should be clearly defined.

III.4. Standard enthalpy change of formation

The standard enthalpy changes of formation of a compound is the energy give out or taken in when one mole of the compound is formed from its constituent elements in their standard states at 25°C.

For example, $\Delta H^{\circ}f = -393.5$ hJ mol^{-1} for the formation of carbon dioxide.

III.5. Standard enthalpy change of combustion

The standard enthalpy changes of combustion of a substance ΔH°c is the enthalpy change when one mole of the substance in its standard state undergoes complete combustion.

If the compound contains carbon, hydrogen and oxygen, the complete combustion will produce carbon dioxide and water.

e.g. $C_2H_{6\,(g)} + 3\frac{1}{2}O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{(l)}$ $\Delta H^{\circ}c = -1560$ kJ mol^{-1}.

In any chemical reaction the change of the enthalpy is:

$aA + bB \rightarrow cC + dD$

$\Delta H = \Delta h$ products – Δh reactants

$\Delta H = c\Delta HC + d\Delta HD - (a\Delta HA + b\Delta HB)$

$\Delta H = \sum npHp - \sum nrHr$

III.6. Standard enthalpy change of neutralization

The standard enthalpy change of neutralization is the enthalpy change when 1 mole of H_3O^+ ions is just neutralized by an alkali in dilute solution. The acid and base are in their standard states at 25°C and the acid and base are in solution containing 1 mol dm^{-3}.

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ $\Delta H^oc = -57.1$ kJ mol^{-1}

III.7. Enthalpy change of solution and enthalpy change of dilution

The enthalpy change of solution is the enthalpy change when 1 mole of substance is dissolved in a specified volume of solvent. The enthalpy change will depend upon the volume of solvent used.

The enthalpy change of dilution is the enthalpy change when 1 mole of substance is dissolved in a large volume of solvent such that further dilution process does not suffer enthalpy change.

III.8. Measuring enthalpy change

Enthalpy change is determined by simple calorimetry experiments. For example to determine the enthalpy change of neutralization of sodium hydroxide and hydrochloric acid, a known volume of sodium hydroxide solution of known concentration is placed in a vacuum flask and the temperature is accurately measured. The volume of hydrochloric acid of known concentration, required to neutralize the sodium hydroxide solution is rapidly added, the mixture stirred and the final temperature recorded.

If the initial temperature of both the acid and alkali is t_1°C and the final temperature is t_2°C, the temperature change is $t_2 - t_1$°C. If the mass of the mixture is *mg*, the specific heat capacity of the solution is 4.2 J deg^{-1} (dilute solutions can be assumed to have the same specific heat capacity as water), and the heat capacity of the vacuum flask is W, then

Heat evolved = $m \times 4.2 \times (t_2 - t_1) + W \times (t_2 - t_1)$ J

From these results the enthalpy change of neutralization can be calculated.

III.9. Hess's law

Hess's law can be used for calculating enthalpy changes, which can not be determined by experiment. The law states that the total enthalpy changes for a reaction is independent of the route taken. For example, if X is converted to Y and Y to Z, the total enthalpy change will be the same as when X is converted to Z.

Example. Calculate the standard enthalpy change of formation of carbon monoxide from the following information: enthalpy changes of combustion of carbon (graphite) and carbon monoxide are: -393.5 kJ mol^{-1} and -283 kJ mol^{-1}.

The following equation can be written:

$C_{(graphite)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$

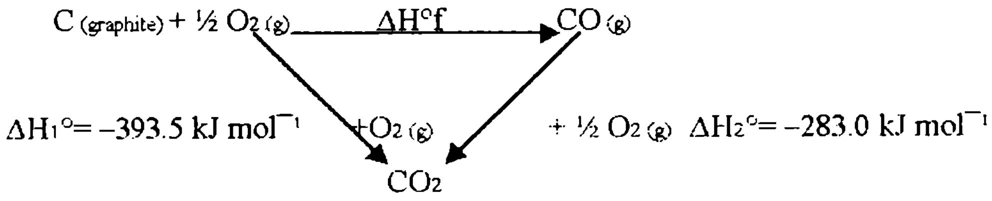
Required: enthalpy change of formation of carbon monoxide.

Given: the enthalpy change of combustion of graphite and carbon monoxide:

(i) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5$ kJ

(ii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^\circ = -283$ kJ

A diagram can be draw to summarize the situation:



$\Delta H^\circ_f = \Delta H_1^\circ - \Delta H_1^\circ = -393.5 + 283.0 = -110.5$ kJ mol^{-1}.

Alternatively, from equation (I) and (ii) above, the equation can be reversed when the enthalpy change is the same numerically but the sign is changed.

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5$ kJ

$CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2} O_{2(g)}$ $\Delta H^\circ = +283$ kJ

Adding these two equations together:

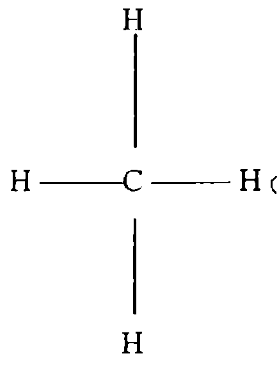
$$C_{(graphite)} + \frac{1}{2} O_{2\,(g)} \rightarrow CO_{(g)} \qquad \Delta H^{\circ}f = -393.5 + 283.0 = -110.5\ kJ\ mol^{-1}.$$

The **negative** sign shows, by convention, that the process is **exothermic.** A **positive** sign shows that the process is **endothermic.** Candidate loses many marks in this type of work by either getting a sign wrong or by missing out units. It is advisable when an enthalpy change is positive to put in a positive sign. This shows the examiner that you have thought about it and decided that the process is endothermic.

III.10. Bond enthalpies

During a chemical reaction a number of bonds will be formed or broken. **Forming bonds liberates energy and breaking bonds requires energy.** It would be useful to be able to attribute specific enthalpy changes to various bond changes. The sum of these enthalpy changes would equal the total enthalpy change.

Consider the breaking of the four C—H bonds in methane:



$$CH_{4\,(g)} \rightarrow C_{(g)} + 4H_{(g)} \qquad \Delta H^{\circ} = -393.5\ kJ\ mol^{-1}.$$

It is reasonable to assure that the energy required to break each C—H bond is the same and the same as is required to break a C—H bond in any other compound and for all practical purposes this can be taken as a true at his level.

For a diatomic molecule XY, the bond enthalpy is defined as the enthalpy change for the process:

$X—Y_{(g)} \rightarrow X_{(g)} + Y_{(g)}$

List of some of the average bond enthalpies at 25°C.

TABLE 1:

Bond	ΔH kJ mol^{-1}
H——H	+436
C——C	+348
C═C	+612
C——F	+484
C——Cl	+338
C——Br	+275
C——I	+238

It must be remembered that bond enthalpies can only be used as a guide. The actual value of a bond enthalpy will depend upon the nature of other atoms or groups joined to it

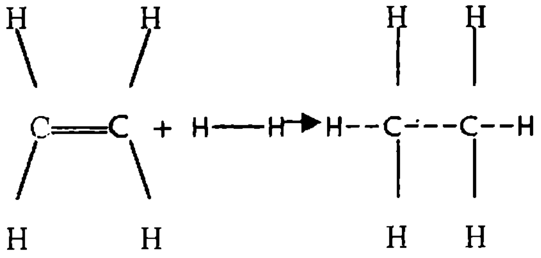
The enthalpy change is positive when a bond is broken and negative on making a bond. Bond enthalpies can be used to explain a number of facts from inorganic chemistry.

E.g. the increased reactivity of phosphorous compared with nitrogen or the increase rate of substitution reaction for iodoalkanes compared with other haloalkanes.

The enthalpy change for atomization can be established using bond enthalpies for example the atomization of ethane C_2H_6 involves the breaking of one C——C bond and six C——H bonds. The enthalpy atomization of these is:

$$\Delta H^{o} = 1(C{-}C) + 6(C{-}H = 348 + (6x412) = +2820 \text{ kJ mol}^{-1}.$$

Bond enthalpies can also be used to estimate likely enthalpy changes in chemical reactions, e.g. the hydrogenation of ethane:



Using the information in table 1:

Bond broken 1 (C——C) + 1(H——H) Enthalpy change =+612 +436=+1048 kJ

Bond formed 1 (C——C + 2 (C——H) Enthalpy change = −348 +2(−412)

Net enthalpy change = 1048 −1172 = −124 kJ.

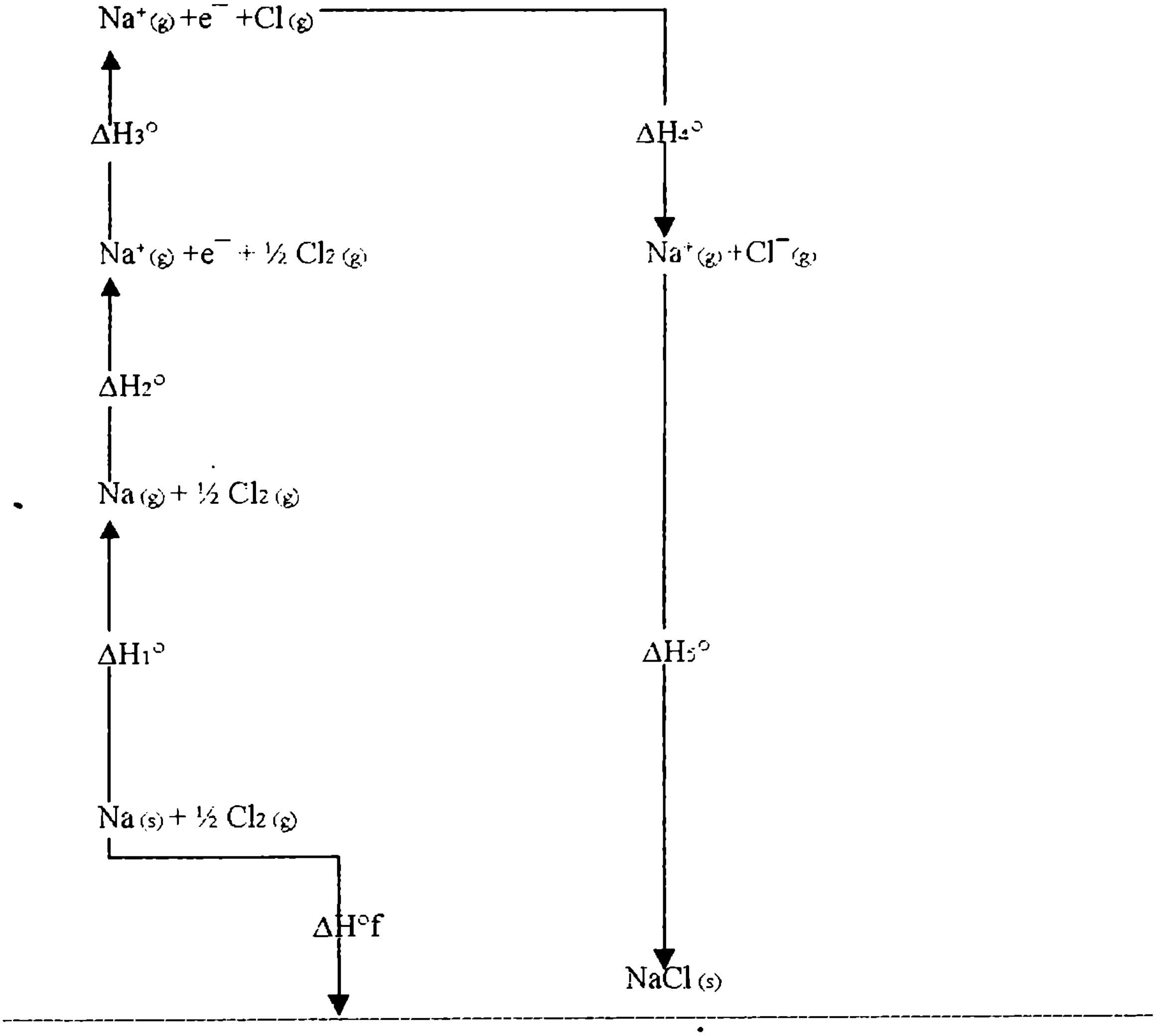
III.11. Born–Harber cycle

Lattice enthalpies cannot be determined directly but may b found indirectly by using an **energy diagram**. These diagrams are called **Born–Harber cycles**. The most common one seen on examination papers is the one for sodium chloride.

The standard enthalpy change when one mole of sodium chloride crystal is produced from sodium metal and chlorides gas can be determined experimentally and is, in fact, the standard enthalpy change of formation of sodium chloride.

$\Delta H^{o}f = -411\ kJ\ mol^{-1}$.

We can consider the various steps, which are required to bring about this change:



$\Delta H_1°$ corresponds to the **standard enthalpy change of atomization** of sodium. It is the enthalpy change when one mole of sodium is converted to free sodium atoms.
$\Delta H_1° = +108.4$ kJ mol^{-1}.

$\Delta H_2°$ corresponds to the **first ionization energy** of sodium e.g. the enthalpy change when one mole of electrons in their ground state is totally removed from 1 mole of sodium atoms in their gas phase. $\Delta H_2° = +500$ kJ mol^{-1}.

$\Delta H_3°$ corresponds to the **standard enthalpy change of atomization** of chlorine. This is the enthalpy change when one mole of gaseous chlorine atoms is produced from chlorine molecules. $\Delta H_3° = +121$ kJ mol^{-1}.

$\Delta H_4°$ corresponds to the **first electron affinity** of chlorine. This is the enthalpy change when one mole of chlorine atoms each accepts one electron to form one mole of chlorine ions. $\Delta H_4° = -364$ kJ mol^{-1}.

$\Delta H_5°$ corresponds to the **lattice enthalpy** sometimes called **lattice energy** of sodium chloride. $\Delta H_5° = -776.4$ kJ mol^{-1}.

By Hess's law: $\Delta H°f = \Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4° + \Delta H_5°$.

An understanding of lattice enthalpy is extremely useful in various ways at A level:

(i) Substances with high lattice enthalpies will have melting points.

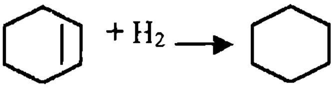
(ii) The solubility of an ionic compound will depend upon the relative values of the lattice and hydration enthalpies or energies.

(iii) Comparison of the calculated and experimental values lattice enthalpy gives an indication of the degree of covalent bonding in a compound.

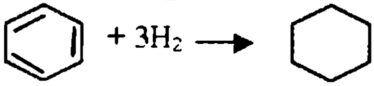
(iv) Lattice enthalpies can be used to explain the non-existence of some compounds.

III.12. The stability of benzene

The enthalpy change of hydrogenation is the enthalpy change when one mole of hydrogen molecules is added to one mole of alkene. The enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1}.



If it is assumed that benzene contains three double bonds i.e. it is a triene. The enthalpy change of hydrogenation should be 3 x (–120) kJ mol^{-1} i.e. –360 kJ mol^{-1}.



The experiment value for the enthalpy change of hydrogenation of benzene is –208 kJ mol^{-1}. The difference between these two values (125 kJ mol^{-1}) again is a measure of the stability of benzene. The difference between this value and the one obtained previously from hydrogenation calculations is probably due to the use of average values for bond enthalpies.

III.13. Second law of thermodynamics–entropy

The majority of reactions are exothermic and it was once believed that only exothermic reactions could take place. There is another factor, which governs the feasibility of reaction.

The second factor is **entropy**, which is related to the degree of randomness or disorder in the system. If two gases in separate bulbs are allowed to come into contact, the gases mix and there is an increase in the disorder.

Given an opportunity, the disorder of a system and hence its entropy, will spontaneously increase. The dissolving of an ionic crystal in water produces an increase in entropy. In the lattice the ions are regularly arranged. The dissolving of ammonium nitrate is an endothermic process divided by the temperature at which the process occurs:

$$\Delta S = \frac{q}{T}$$

Systems having perfect order i.e. the perfect ionic crystal lattice at 0 K, posses zero entropy. The entropy of a given mass of matter increases in the order:

Solid → liquid → gas.

The entropy of substances not possessing perfect order and all substances at temperature above 0 K will be greater than zero, e.g. the standard entropy S° (at 298 K and 1 ATM pressure) of water–70 kJ mol^{-1}.

The entropy change in a reaction can be found.

Example: Find ΔS° for the reaction:

$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2HI_{(g)}$

Given that the standard entropies of hydrogen, gaseous iodine and hydrogen iodine are +131, +261 and +207 J $mol^{-1}K^{-1}$ respectively.

$\Delta S^\circ = 2 \times S^\circ_{HI} - S^\circ_{H_2} - S^\circ_{I_2} = 414 - 131 - 261 = +22$ J $mol^{-1}K^{-1}$.

There is an increase in entropy and a spontaneous reaction is feasible, although no indication is given of the possible rate of reaction.

III.14. Free energy G

This is a measure of the useful work, which can be obtained from a system (apart from volume changes).

A reaction can only proceed spontaneously ΔH and ΔS and they are related by the equation: $\Delta G = \Delta H + T\Delta S$

Since for a reaction to proceed Δg must be negative, for an endothermic reaction (ΔH positive), a reaction will take place only if $T\Delta S > \Delta H$. If ΔG is possible, no useful work can be obtained and the reaction is not feasible. If $\Delta G = 0$ the system will be in dynamic equilibrium.

PRACTICAL WORK

THERMIC EFFECTS

The variation of the internal energy and of the enthalpy which accompany the reverse chemical process (**isochoric** or **isobaric**) are taking place accompanied by exchange of energy (heat) with exterior.

Thus, in case of some chemical processes, the system yields heat to his neighborhood (**endothermic processes**). The thermic amount of heat, which is given off or accepted during a process, is called **thermic effect**.

Depending of the nature of the process, the thermic effect may be formation heat, reaction heat, hydration heat, and evaporation heat.

The quantity of heat changed during a chemical reaction is called **reaction heat**. 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 negative variation of volume ($\Delta V = 0$), the energy of reaction is equal to the enthalpy of reaction (ΔH).

If during the reaction intervene gaseous reacting substances to $n_2$moles of gaseous reaction products (so a variation of moles number $n = n_1 - n_2$) and for the volume V of one mole, we can write:

$$\Delta U = \Delta H - pdV\Delta n$$

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) 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 accusing which allows no change of heat (**adiabatic calorimeters**).

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. The constant is experimentally determined and corresponds to the sum of the products between masses and specific heats of all components of the calorimetric system.

DETERMINATION OF THE CALORIMETER'S CONSTANT

Introduce into calorimeter 50 cm^3 of distillated water, after 2–3 minutes its temperature must be measured. Over the water having the temperature t_1, suddenly introduce 30 cm^3 of distillated water with temperature t_2 (about 90°C). Stir 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 cm^3 of distillated water, $30(t_2 - t_1)$ was taken by $(50 + K)$ grams of water (K is the calorimeter's constant) and results an increasing of the whole system's temperature equal to $(t_2 - t_1)$°C. Considering the specific heat and water's density equal to unit, we may write:

$$30\,(t_2 - t_3) = (t_3 - t_1)\,(50 + K).$$

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 lattice is higher than the energy stetted free as a result of molecules or ions interactions with the solvent. The dissolution process is exothermic when the energy absorbed is lower than the energy stetted free.

EXP.III.1. In the experimental work we shall determine the molar dissolution and hydration heats for $CuSO_4$ (the heat evolved 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 $CuSO_4$, which is given by the sum between the hydration heat 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, which remains invariable (t_1°C). Over the water from colorimeter add 2.5 cm^3 anhydrous $CuSO_4$ (precisely measured at the analytical balance).

Stir the solution to accelerate the dissolution process and write down the temperature every 30 seconds until it remains invariable (t_2°C). The specific heat of the obtained solution is equal to unit. The solution's mass (m_1) consists of sum between water's mass heat q_1 can be obtained from the calorimeter relation:

$q_1 = m_1 c (t_2 - t_1) + k(t_2 - t_1)$.

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 $CuSO_4 * 5H_2O$.

EXP.III.2. Another experiment allows the determination of thermic effect for the dissolution process of $CuSO_4 * 5H_2O$. The result is the molar dissolution heat q_2* ($q_1 - q_2$) represents the "molar hydration heat".

You have to repeat the experience above, using now 3 g of $CuSO_4 * 5H_2O$. You must write down the temperature every 30 seconds until it remains invariable (t_2°C). Taking into account the initial temperature t_1 measured for the 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:

$q_2 = m_2 c(t_2' - t_1')k$.

Where q_2 is the dissolution heat for $CuSO_4 * 5H_2O$. Divide q_2 by a mole of $CuSO_5 * 5H_2O$ and you have the molar dissolution heat.

THE DETERMINATION OF THE NEUTRALISATION HEAT

EXP.III.3. Into a calorimeter bomb (having his calorimetric constant already determined) introduce 100 cm^3 of hydrochloric acid solution (0.5 N) and into another calorimeter bomb introduce 100 cm^3 of sodium hydrate solution (0.5 N). Write down the temperature t_1 (for NaOH) and t_2 (for HCl). Put 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:

$q = (t_3 - t_2) * 100 + (t_3 - t_2)(50 + K)$.

The specific heat of the solutions is considered equal to unit. Dividing q by a mole of acid (or of base) you can obtain the molar neutralization heat.

THEME IV.

CHEMICAL KINETICS

IV.1. THE FACTORS THAT INFLUENCE THE REACTIONS SPEED

The reaction speed depends not only on the concentration of the reactants, but on the factors that influence the speed constant k.

Experimentally it was established that the temperature, contact surface and catalizator influence the specific speed.

The dependence of the speed constant is given through Arrhenius relation:

$$k = A\,e^{\frac{Ea.}{RT}}$$

Where: Ea. is the energy of activation. T is the absolute temperature. R is the constant of ideal gases.

IV.2. REACTION KINETICS

Most 0 level courses now contain same work on rates of chemical reactions and the factors, which affect the rate of reaction. The work on reaction kinetics becomes more significant at A level, because it is closely related to structure and to the mechanisms of reactions.

The factors, which can affect the rate of reaction, include:

(i) Physical state of reactants.

(ii) Concentration (and gas pressure).

(iii) Temperature.

(iv) Catalysts.

(v) Light.

These factors will be considered in turn.

PHYSICAL STATE OF REACTANTS

The reaction between calcium carbonate and dilute hydrochloric acid is:

$$CaCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2\,(aq)} + H_2O_{(l)} + CO_2$$

It reacts separately equal volumes of dilute hydrochloric acid and excess with calcium carbonate with the same concentration as the acid. The volume of carbon dioxide collected in each case is the same because equal masses of calcium carbonate were used. It is produced very quickly with power and more slowly with lamps. The reaction with power is faster because the power has a larger area and the reaction takes place when the acid comes in contact with the surface.

CONCENTRATION

This is probably the most important factor to understand at A level. During a reaction, the reactants are used up and so the rate of reaction decreases.

The exact relationship between the rate of reaction and the concentration of the reactants in a particular reaction can only be determined experimentally. Most reactions take place in a series of steps and the rate of the overall reaction depends upon the rate of the slowest step, called the **rate-determining step**.

It is vital for you to distinguish clearly the meaning of the terms **order of reaction** and **molecularly**. Few candidates understand the distinction and many questions test this. The order of reaction is determined experimentally. In the reaction:

$$A + B \rightarrow C + D$$

Experiment may show that the rate of reaction is proportional to the concentration of A to the power of x i.e. rate $\alpha[A]^x$ and also the rate of reaction may also be proportional to the concentration of B to the power of y i.e. rate$[B]^y$.

The overall equation is therefore:

$$Rate = k\,[A]^x\,[B]^y$$

K is the **rate constant** and overall equation is called the **rate equation**. In this example, the order of the reaction with respect to A is x and the order with respect to B is y and the total order of reaction is x +y.

The reaction between peroxodisulphate and iodide ions is:

$$S_2O_8^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow S_2O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$$

The rate equation determined experimentally is:

$$\text{Rate} = k\,[S_2O_8^{2-}]\,[I^-]$$

And the total order is 2. The order is not related to the equation. The order may be integral i.e. 1,2 or 3 etc. but it also can be fractional.

CATALYSTS

A **catalyst** is a substance, which alters the rate of a chemical reaction without being used up. The catalysts may be changed physically but the mass of catalysts is unchanged at the end of reaction.

An example of catalyst is manganese (IV) oxide in the decomposition of hydrogen peroxide.

$$2H_2O_{2\,(aq)} \rightarrow 2H_2O_{(l)} + O_{2\,(g)}$$

This is an example of catalyst, which speeds up a chemical reaction. A substance, which slows down the rate of a reaction, is called an inhibitor.

A catalyst does not alter the position of equilibrium or increase the yield of products. It merely alters the rate at which the equilibrium is achieved or the products are obtained. A catalyst provides an alternative route with a lower activation energy barrier for the reaction. More molecules possess the lower activation energy and so the reaction is speeded up.

$$2HI \rightarrow H_2 + I_2$$

activation energy without catalyst 183 kJ mol^{-1}
with gold catalyst 105 kJ mol^{-1}
with platinum catalyst 58 kJ mol^{-1}.

There are two types of catalyst –**homogeneous catalysts** and **heterogeneous catalysts**. A homogeneous catalyst is in the same phase as the reactants; the reaction between an organic acid and an alcohol is catalyzed by the presence of hydrogen ions. A heterogeneous catalyst is not in the same phase: manganese (IV) oxide is solid and hydrogen peroxide is a liquid. There are two theories of catalysis.

1.Intremediate compound theory

The catalyst reacts with one of the reactants to produce an intermediate compound, which eventually produces the required product and regenerates the catalyst: manganese (IV) oxide and hydrogen peroxide.

The intermediate compound theory explains most examples of homogeneous catalysis.

2.Absorotion theory

A gas is absorbed when its particles collide with and adhere to the catalyst surface. When gas molecules are absorbed they are brought close together and in a state which enables them to react together. On description the catalyst surface is available for further reaction. An example is the reaction of an alkene with hydrogen using a nickel catalyst.

In the same reaction one of the products of the reaction acts as a catalyst for the reaction. For example, in the reaction of an ethanediodate (oxalate) which acidified potassium manganate (VII), the reaction has to be heated to about 60° to get the reaction to start but the manganese (II) ions produced catalyze. The reaction continues even if the solution is cooled to room temperature. This is an example of what is called **autocatalysis.**

LIGHT

Some reactions are greatly affected by light. For example the reaction of hydrogen and chlorine is explosive in sunlight. The ultraviolet light in the sunlight splits some of the chlorine molecules into free chlorine atoms or chlorine **free radicals**.

$Cl_2 \rightarrow 2Cl^{\circ}$

Then a free radical chain reaction takes place producing hydrogen chloride.

$Cl^{\circ} + H_2 \rightarrow HCl + H^{\circ}$

$H^{\circ} + Cl_2 \rightarrow HCl + Cl^{\circ}$

The reaction between chlorine and methane is another reaction affected by light.

METHODS OF FOLLOWING THE PROGRESS OF A REACTION

There are a number of methods, which can be used to follow the progress of a reaction. These include:

(i) Measuring the volume of gas evolved at intervals of time using a gas syringe; in the reaction between calcium carbonate and hydrochloric acid.

(ii) Measuring the electrical resistance of the solution.

(iii) Measuring the change color in the solution with a colorimeter.

(iv) Removing samples from the reacting mixture and titration: the hydrolysis of ethanoate whit alkali. Portions of the reaction mixture are removed at intervals of time and titrated with dilute hydrochloric acid using phenolphthalein as indicator.

Another factors that affect the rate of reaction are:

(i) Equilibrium.

(ii) Acids and bases.

(iii) Salt hydrolysis and buffer solutions

(iv) Oxidation and reduction

EQUILIBRIUM

The equilibrium is established when the rate of the forward reaction is equal to the rate of the reverse reaction.

$$3Fe_{(s)} + 4H_2O_{(g)} \underset{(v2)\ \leftarrow}{\overset{(v1)\ \rightarrow}{\qquad}} Fe_3O_4{}_{(s)} + 4H_2{}_{(g)}$$

V1= the speed of the forward reaction.

V2= the speed of the reverse reaction.

–the **law of mass action** –states that, at constant temperature, the rate of reaction is proportional to the active mass of the reacting substances. For A level purposes, active mass is the same as concentration in mol dm^{-3}. The law of mass action applies to equilibrium in a homogeneous system. The sign ↔ shows the system can reach equilibrium.

In the equilibrium:

$$aA + bB \leftrightarrow cC + dD$$

the equilibrium constant is:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at constant temperature.}$$

By convention, the concentrations of products are divided by reactants.

Equilibrium constants can be calculated using concentrations in mol dm^{-3} and the equilibrium constants is represented by K_c Partial pressures can also be used to calculate equilibrium constants and the equilibrium constant is then represented by K_p

The law of mass action can be modified to include heterogeneous systems. The common example is the heating of calcium carbonate in a closed system to prevent the escape of carbon dioxide:

$$CaCO_{3\,(s)} \leftrightarrow CaO_{(s)} + CO_{2\,(g)}$$

The vapor above the solid is a homogeneous system and

$$\frac{P_{CaO}}{P_{CaCO_3}} \times P_{CO_2} = \text{constant}$$

where p represents partial pressures. Thus at constant temperature the partial pressures of calcium carbonate and calcium oxide are constant. This is because the vapor pressures of solids are constant at constant temperature:

$$K_p = P_{CO_2}$$

From this it follows that at any particular temperature, the partial pressure of carbon dioxide is constant.

– **Le Chatelier's principle** –states that if one of the conditions is changed, the position of equilibrium will alter in such a way as to tend to restore the original conditions.

Consider the equilibrium:

$$A + B \leftrightarrow C + D$$

At equilibrium A, B, C and D are present and the concentrations of these substances remain constant if the providing conditions are unchanged. If the forward reaction is encouraged, a new equilibrium will be set up. In this equilibrium [C] and [D] will have decreased. The equilibrium is said to have 'moved to the right'. A system 'moves to the left' if the new equilibrium established contains higher concentrations of A and B and lower concentrations of C and D.

The conditions, which are commonly changed, are:

(1) Concentrations of reactants or products.

(2) Temperature.

(3) Pressure. This is only important in reactions involving gases.

These conditions are considered separately.

(1) Concentration

If the product C is removed by liquefaction, escape into the atmosphere etc. the reverse reaction cannot occur. The position of the equilibrium moves to the right. If the concentration of A and B is increased, again the forward reaction is encouraged and again the equilibrium moves to the right.

(2) Temperature

The change that takes place in equilibrium when temperature is altered depends upon whether the forward reaction is exothermic or endothermic. If the forward reaction is exothermic, the reverse reaction will be endothermic. The equilibrium can be written:

$$A + B \leftrightarrow C + D \qquad \Delta H \text{ is negative.}$$

If the temperature of the system is raised, the equilibrium moves to the left, as the endothermic process will tend to reduce the temperature, i.e. restore the initial conditions. Conversely if the temperature is decreased, the equilibrium moves to the right.

(3) Pressure

For a reaction involving gases, altering the pressure may cause a change in the position of the equilibrium.

For the reaction:

$$H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2HI_{(g)}$$

At 700°C, the number of moles of reactants and products are the same. Pressure has no effect on the position of the equilibrium.

For a reaction where there is an increase in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the left. Where there is a decrease in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the right.

ACIDS AND BASES

- definition

Bronsted and Lowry defined an **acid** as a **proton donor** and a **base** as a **proton acceptor**. A proton in the same as a positively hydrogen ion (H^+). In practice, H^+ ions do not exist in solution and are more likely to exist as H_3O^+.

The equation for the ionization of hydrochloric acid is:

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Hydrochloric acid is an acid because it loses an H^+ ion to form a Cl^- ion. Water is a base because it accepts H^+ ions to form H_3O^+ ions.

Looking at the reverse reaction, H_3O^+ ions lose H^+ ions in forming H_2O and therefore H_3O^+ is acting as an acid. Chloride ions accept H^+ ions to form HCl and therefore, act as a base. The H_3O^+ is called the **conjugate acid** and Cl^- the **conjugate base** (i.e. the acid and base for the reserve process).

In the case of a general acid HA:

$$HA_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

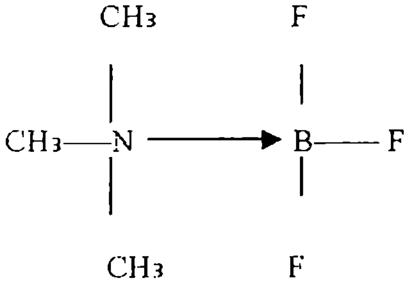
The position of this equilibrium depends upon the strength of the acid. For a strong acid such as HCl, the equilibrium lies well to the right, i.e. the acid may be considered as completely ionized. In such a case the base Cl^- is very weak base. With a weak acid the equilibrium lies well to the left. A^- is a fairly strong base.

Water can act as an acid:

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$

Base	acid	conjugate acid	conjugate base

Lewis widened the definition of acid and base by defining an acid as an **electron pair acceptor**. This definition includes examples of acids and bases, which would not be recognized using the other definitions. For example the reaction between trimethylamine and boron trifluoride forms a solid salt.



Trimethylamine has an electron pair that can be donated to the boron trifluoride that electron deficient because it only has six electrons in the outer shell.

Trimethylamine acts as a Lewis base and Boron trifluoride is a Lewis acid. Aluminum chloride acts as a Lewis acid.

– **Ostwald's dilution law**– since the ionization of weak acids and bases are equilibrium processes, the law of mass action can be applied to them at constant temperature.

For example, consider the dissociation of 1 mole of a weak acid HA. If the volume of the solution containing one mole of acid is V dm^3 and α is the degree of dissociation, then:

	HA	$\longrightarrow$ H^+	+ A^-
Before ionization	1 mole	0	0
After ionization	$1-\alpha$ mole	α mole	α mole

$$[HA] = \frac{1-\alpha}{V} \text{ mol dm}^{-3};\ [H^+] = \frac{1-\alpha}{V} \text{ mol dm}^{-3};\ [A^-] = \frac{1-\alpha}{V}$$

Applying the law of mass action:

$$K = \frac{[H^+]\,[A^-]}{[HA]}$$

$$K = \frac{\alpha^2}{(1-\alpha)\,V}$$

The expression is called **Ostwald's dilution law**. The equilibrium constant in this case is the **dissociation constant**. For very weak electrolytes, where little dissociation takes place, $(1-\alpha)$ is approximately equal to 1 and the expression simplifies to:

$$K = \frac{\alpha^2}{V} \quad \text{or} \quad K = \alpha^2 c$$

Where V is the volume containing one mole and c is the concentration in mol dm^{-3}.

Although the degree of dissociation of the acid changes with dilution, the value of K is unchanged at constant temperature.

– **ionic product of water–** even if water is purified by repeated distillations, the electrical conductivity never falls to zero. This is because of **self–ionization** of water. This can be represented either by:

$$2\,H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + OH^-_{(aq)} \qquad \text{or} \qquad H_2O_{(l)} \longleftrightarrow H^+_{(aq)} + OH^-_{(aq)}$$

Using the simpler equation:

$$K = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

Only a few molecules of water ionize and [H_2O] can be regarded at constant at a constant temperature.

$K_w = K_w \times \text{constant} = [H^+] [OH^-]$

This is called the **ionic product of water**.

At 25°C, $K_w = 1 \times 10^{-14}$ mol² dm⁻⁶ and because, from the equation, the concentrations of H^+ and OH^- are equal;

$[H^+] = [OH^-] = 1 \times 10^{-7}$ mol dm $^{-3}$

In any aqueous solution the product of the concentration of H^+ and OH^- is 1×10^{-14} mol^2 dm^{-6}. In a neutral solution both $[H^+]$ and $[OH^-]$ are equal to 1×10^{-7} mol dm^{-3}.

–**indicators and acid –alkali titrations**– most indicators for acid–alkali titrations are weak acids or bases.

Phenolphthalein is a weak acid and it dissociates:

$H_2O + HA \rightarrow H_3O^+ + A^-$

Colorless pink

HA exists in acid solution and A^- in alkaline solution. If acid is added to the equilibrium mixture, the equilibrium moves to the left and the solution turns colorless. Addition of alkali removes H_3O^+ ions and moves the equilibrium to the right turning the solution pinks.

Methyl orange is a weak base, which dissociates:

$BOH \rightarrow B^+ + OH^-$

yellow red

BOH exists in alkaline solution and B^+ in acid solutions. For a substance to be a good indicator, the two forms (HA and A^- for phenolphthalein and BOH and B^+ for methyl orange) must be different colors for the indicator to function adequately.

The indicators change their color in function of pH value.

Indicator	*acid solution*	*approx. pH*	*alkali solution*
Methyl orange	orange	4	yellow
Methyl red	red	5	yellow
Litmus	red	7	blue
Phenolphthalein	colorless	9	red

SALT HYDROLYSIS AND BUFFER SOLUTIONS

–**salt hydrolysis**– when a salt is dissolved in water, the resulting solution may be acid, alkaline or neutral. This is because the salt may have reacted to some extent with the water. This hydrolysis produces an acid and an alkali but they may not be of equal strength. There are four types of salts that should be considered.

(a) salt of a strong acid and a strong base

E.g. sodium chloride. Is completely ionized in solution to form Na^+ (aq) and Cl^- (aq). H_3O^+ (aq) and OH^- (aq) are also present from the ionization of a few of the water molecules. There is no interaction between the sodium and chloride ions and the water and as a result the concentrations of H_3O^+ (aq) and OH^- (aq) are the same and the solution is exactly neutral.

(b) salt of a strong acid and a weak base

E.g. ammonium chloride or iron (III) chloride. In a solution of ammonium chloride, there is a reaction between ammonium ions in the solution and the solvent to produce additional H_3O^+ (aq) ions: $NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

And $NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrow NH_3{}_{(aq)} + H_3O^+{}_{(aq)}$

The resulting solution is acidic because of an excess of H_3O^+ (aq) ions over OH^- (aq) ions.

A solution of iron (III) chloride in water is appreciably acidic. It will react rapidly with magnesium to produce hydrogen.

(c) salt of a weak acid and a strong base

E.g. sodium ethanoate. The ionization of sodium ethanoate produces CH_3COO^- (aq) and Na^+ (aq). The resulting solution is alkine, however, because of reaction between the ethanoate ions and the water to produce an excess of OH^- (aq) ions.

$$CH_3COONa_{(s)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-_{(aq)}$$

(d) salt of a weak acid and a weak base

E.g. ammonium ethanoate. Is ionized in solution to produce NH_4^+ (aq) and CH_3COO^- (aq) ions. Both of these ions react with water:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_3{}_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Whether the final solution is slightly acidic, slightly alkaline or neutral depends upon the position of the two equilibrium. In this solution is almost neutral.

–**buffer solutions**– is a solution of constant pH. The pH of the solution will not change appreciably if the solution is contaminated with traces of acid or alkali.

An acidic buffer solution (i.e. with pH less than 7) is prepared by mixing together definite amounts of a weak acid and the sodium or potassium salt of the same acid, e.g. ethanoic acid and sodium ethanoate.

An alkaline buffer (i.e. with pH greater than 7) is prepared by mixing a weak base and a soluble salt of the base, e.g. ammonia solution and ammonium chloride.

The most frequent mistake at a level is to fail to appreciate that a weak acid or base is required to make a buffer solution. Statements such as 'hydrochloric acid and sodium chloride can be used to make a buffer solution' are common.

--**solubility product**– the ideas of equilibrium can be applied to the equilibrium between an almost insoluble solid and its ions in solution. This leads to the concept of **solubility product**, which explains the conditions under which precipitation from a solution will occur.

For example, silver chloride AgCl is a suitable sparingly soluble salt.

$$AgCl_{(s)} \leftrightarrow AgCl_{(aq)} \leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$$

Equilibrium is established when sliver chloride is added to water. Using the ideas of equilibrium, the following expression can be obtained:

$$K_s = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

[AgCl] strictly represents the concentration of silver chloride in solution and this remains constant at constant temperature, as long as any solid remains in contact with the solution.

$$K_s = [Ag^+]\,[Cl^-] = 2 \times 10^{-10}\ mol^2\ dm^{-6}$$

Where K_s are called the **solubility product**. The solubility product is the maximum value of the ionic product of Ag^+ and Cl^- ions that can exist in solution without precipitation occurring. If the product of the ionic concentrations exceeds this maximum value, precipitation will occur.

For the sparingly soluble electrolyte AxBy the equilibrium is:

$$AxBy_{(aq)} \leftrightarrow xA^{z+}{}_{(aq)} + yB^{y-}{}_{(aq)}$$

And the solubility product is:

$$K_s = [A^{y+}]^x\,[B^{x-}]^y$$

The most frequent mistake with solubility product is to try to apply it to solids that are readily soluble.

OXIDATION AND REDUCTION

Oxidation and reduction occur together and the term **redox reaction** means a reaction where oxidation and reduction take place. **Oxidation** is a process where electrons are lost and **reduction** where electrons are gained. A reducing agent is an electron donor and an oxidizing agent is an electron acceptor.

For example, the reaction of iron (II) chloride solution which is not obviously a redox reaction. The equation is:

$2FeCl_2\,_{(aq)} + Cl_2\,_{(g)} \rightarrow 2FeCl_3\,_{(aq)}$

Writing this equation as an ionic equation gives:

$2Fe^{2+}\,_{(aq)} + Cl_2\,_{(g)} \rightarrow 2Fe^{3+}\,_{(aq)} + 2Cl^-\,_{(aq)}$

There are two processes taking place here:

(i) Iron (II) ions Fe^{2+} are losing electrons to form iron (III) ions:

$Fe^{2+}\,_{(aq)} \rightarrow Fe^{3+}\,_{(aq)} + e^-$

(ii) Chlorine ions are gaining electrons to form chloride ions:

$Cl_2\,_{(g)} + 2e^- \rightarrow 2Cl^-\,_{(aq)}$

During the reaction, iron (II) ions lose electrons and are therefore oxidized and chlorine, which gains electrons, is reduced. Chlorine is the electron acceptor and is therefore the oxidizing agent and the iron (II) ions the reducing agent (electron donor).

From this example it should be noted that ionic equations and the simple equations (like (i) and (ii) above), called **half reactions**, are useful when considering oxidation and reduction.

–**common oxidizing agents**– in the following reactions, electrons will be shown on the left hand side since all oxidizing agents are electron acceptors. (NB: for the sake of simplicity the ion H_3O^+ is represented in these equations by H^+ (aq).).

–oxygen $O_2\,_{(g)} + 4e^- \rightarrow 2O^{2-}\,_{(s)}$

–chlorine $Cl_2\,_{(g)} + 2e^- \rightarrow 2Cl^-\,_{(s)}$

–bromine $Br_2\,_{(g)} + 2e^- \rightarrow 2Br^-\,_{(s)}$

–iodine $I_2\,_{(aq)} + 2e^- \rightarrow 2I^-\,_{(aq)}$

–manganate (VII) in acid solution

$MnO_4^-\,_{(aq)} + 8H^+ + 5e^- \rightarrow Mn^{2+}\,_{(aq)} + 4H_2O\,_{(l)}$

–manganate (VII) in alkaline solution

$MnO_4^-\,_{(aq)} + 2H_2O\,_{(l)} + 3e^- \rightarrow MnO_2\,_{(s)} + 4OH^-\,_{(aq)}$

–dichromate (VI) in acid solution

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$$

–iron (II) salt $Fe^{3+}{}_{(aq)} + e^- \rightarrow Fe^{2+}{}_{(aq)}$

–hydrogen ions

$$2H^+{}_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

–hydrogen peroxide (in the absence of another oxidizing agent)

$$H_2O_{2(aq)} + 2H^+{}_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$$

–manganese (IV) oxide (in the presence of acid)

$$MnO_{2(aq)} + 4H^+{}_{(aq)} + 2e^- \rightarrow Mn^{2+}{}_{(aq)} + 2H_2O_{(l)}$$

–concentrated sulfuric acid

$$2H_2SO_4^{2-}{}_{(l)} + 2e^- \rightarrow SO_4^{2-}{}_{(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

–**common reducing agents**– in all of these half equations, electrons appear on the right side hand of the equation as reducing agents are electron donors.

–metals $M_{(s)} \rightarrow M^{n+}{}_{(aq)} + ne^-$

E.g. $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

–iron (II) salts

$$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e^-$$

–acidified potassium iodide

$$2I^-{}_{(aq)} \rightarrow I_{2(aq)} + 2e^-$$

–tiosulphate $2S_2O_3^{2-}{}_{(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2e^-$

–ethanedioic acid and ethanedioates (oxalic acid and oxalates)

$$C_2O_4^{2-}{}_{(aq)} \rightarrow 2CO_{2(g)} + 2e^-$$

–hydrogen sulfide and sulfides

$$S^{2-}{}_{(aq)} \rightarrow S_{(s)} + 2e^-$$

–sulphurous acid (sulfuric (IV) acid)

$$SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} + 2e^-$$

–hydrogen peroxide (in the presence of a strong oxidizing agent)

$$H_2O_2{}_{(aq)} \rightarrow O_2{}_{(g)} + 2H^+{}_{(aq)} + 2e^-$$

–tin (II) ions in hydrochloric acid

$$Sn^{2+}{}_{(aq)} \rightarrow Sn^{4+}{}_{(aq)} + 2e^-$$

–hydrogen $H_2{}_{(g)} + O^{2-}{}_{(s)} \rightarrow H_2O_{(l)} + 2e^-$

–carbon $C_{(s)} + O^{2-}{}_{(s)} \rightarrow CO_{(g)} + 2e^-$

–carbon monoxide

$$CO_{(g)} + O^{2-}{}_{(s)} \rightarrow CO_2{}_{(g)} + 2e^-$$

–**using ionic half equation to write full ionic equations**– combination of two ionic half equations, one representing an oxidizing action and one representing a reducing action, will produce a full ionic equation.

E.g. reaction of acidified potassium manganate (VII) with iron (II) sulfate solution.

OA $MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

RA $Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e^-$

On combining these equations, the electrons must cancel out. Multiply the RA equation by 5 and add:

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$

In this reaction, manganate (VII) acts as the oxidizing agent and iron (II) ions as the reducing agent.

–**oxidation states (or oxidation number)**–without direct chemical foundations, but is extremely useful, being appropriate to both ionic and covalent bonded species.

The oxidation states can be defined simply as the number of electrons, which must be added to a positive ion to get a neutral atom or removed from a negative ion to get a neutral atom.

E.g. Fe^{2+} (aq)–two electrons have to be added and the oxidation state is +2.

Cl^- (aq)–one electron has to be removed and the oxidation state is –1.

It is relatively easy to understand for simple ions because the electrons are definitely associated with certain ions.

For covalent species it is assumed that the electrons in the covalent bond actually go to the atom which is most electronegative. For example, in ammonia, NH_3, nitrogen is the more electronegative element and it is assumed that the three electrons (one from each hydrogen atom) are associated with the nitrogen atom. Nitrogen therefore (like nitrogen in N^{3-}) has an oxidation state of –3 and hydrogen +1.

The system will be clear with practice, but the following rules are worth remembering.

(i) The oxidation state of all elements uncombined is zero. Therefore, the oxidation state of oxygen in oxygen gas is zero.

(ii) The algebric sum of the oxidation states of the elements in a compound is always zero.

E.g. in NH_3	N	OS	–3
	H	OS	+1
	H	OS	+1
	H	OS	+1

(iii) The algebraic sum of the oxidation states of the elements in an ion is equal to the charge on the ion algebraic.

E.g. in CO_3^{2-}	C	OS	+4
	O	OS	–2
	O	OS	–2
	O	OS	–2

(iv) The oxidation state of oxygen is –2 (except in oxygen gas and peroxides).

(v) The oxidation state of hydrogen is +1 (except when combines with Group I or II metals as hydrides).

In chemical names the oxidation state of a particular species may be shown in Roman numerals in brackets if there is chance of any uncertainty. In these cases the sign is not given.

E.g. iron (III) chloride--iron is in oxidation state +3

tetracarbonylnickel (0)--nickel is in oxidation state zero.

If during a chemical reaction a species changes its oxidation state, then oxidation and reduction are taking place. An increase in oxidation state corresponds to oxidation and a decrease to reduction. E.g. the reaction of chlorine with hydrogen sulfide

$Cl_{2(g)} + H_2S_{(g)} \rightarrow 2HCl_{(g)} + S_{(s)}$ OA $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(g)}$

OR $S^{2-}_{(g)} \rightarrow S_{(s)} + 2e^-$

And add: $Cl_{2(g)} + S^{2-}_{(g)} \rightarrow 2Cl^-_{(g)} + S_{(s)}$

The oxidation state of chlorine in Cl_2 is zero (because it is an element) and in HCl is –1 (remember H is usually in OS +1 and the sum must be zero).

The chlorine therefore is reduced because the oxidation state is reduced from 0 to –1. Similarly, the oxidation state increases from –2 in H_2S to zero in S. The sulfur is oxidized as there is an increase in oxidation state.

With *d*–block elements, a variety of oxidation states are possible for each element.

PRACTICAL WORK

At the practical work it will be determined the activation energy of the disproportionate reaction of the ion of tiosulphate in an acid environment.

$S_2O_3^{2-} + 2H_3O^+ \rightarrow S + SO_2 + 3H_2O$

This reaction is enough slowly and it can be watched with eye–free.

THE QUALITATIVE REACTION

In a beaker which contains 10 cm^3 solution of sodium tiosulphate 0.1 M and it's adding 10 cm^3 H_2SO_4 0.1 M. After a few seconds it's finding that the solution from the beaker is distorted and after 1–2 minutes it's notice the formation of a yellow precipitate of colloidal sulph, which is deposed on the bottom of the beaker.

For the determination of the activation energy the reaction it will be made for four temperatures, each time measuring the time which passes from the apparition of the colloidal sulph. The reaction it will be made in two beakers of glass with double walls, in which travels water from the thermostat, which has the role to maintain a constant temperature of the water during reaction.

IV.3. ELECTRIC CONDUCTIBILITY DETERMINATIONS

Electric conductibility represents the property of some bodies to be passed by electric current under the influence of a continuos electric tension applied from exterior.

Substances are bat electricity conductors, dielectrics or insulators and good conductors of electricity or electric conductors.

Electric conductor is a body characterized by a small electric resistance, trough the electric current of conduction may pass.

From quantitative point of view, the electric conductibity can be expressed by the electric conductivity, a measure that characterizes the electric conductibility of bodies, equal with the inverse of resistance. In the international system, it is measured by 1 ohm–meter ($1/\Omega\cdot m$ or $\Omega^{-1}\cdot m^{-1}$). It is noted σ (sigma).

From the point of view of the mechanism of electric current passing and electric conductivity value σ, there are distinguished:

- First order conductors (electronic)–the electricity transport is made through free electrons (without a supplementary exterior excitation, only under the influence of the electric field). Is the case of metals and their alloys.
- Second order conductors (ionic)–through the free ions and with mass transport. Is the case of melting and electrolyte solutions (the electrolytes are the substances that transport, in molten state or in solution, the electric current with mass transport).
- Semiconductors– solid bodies with electric conductivity between the one of metals and the one of insulators (dielectrics) and the energy transport is made the same as at metals, without mass transport. The electric properties depend on the exterior factors

like temperature, pressure, electric and magnetic field, controlled presence of impurities. Electricity transport is due to the crystalline lattice flaws (existent and provocated). Is the case of semimetals (Si, Ge, Se) and compounds like oxides, sulfides, etc.

From electric conductivity value, the electric substances are>

- Conductors: $\sigma = 10^{6} \ldots 10^{8}\ \Omega^{-1}m^{-1}$
- Semiconductors: $\sigma = 10^{6} \ldots 10^{-8}\ \Omega^{-1}m^{-1}$
- Dielectrics $\sigma \leq 10^{-8}\ \sigma^{-1}m^{-1}$

The electric conductibility of electrolyte solutions:

After their behavior in an polar solvent like water, substances are:

- Substances that are formed by nepolar molecules and don't give ions to the solution and their solution do not conducts electric current.
- Substances formed by ions, that under the influence of the polar solvent pass in solution (if the substance is soluble in solvent), form great electrolyte solutions.
- Substances formed by polar molecules that, in the presence of the polar solvent, ionizes. Can form, after the ionization degree, great or weak electrolyte solutions.

The electrolytes can be:

- Great electrolytes, which, in aqueous solution (or polar solvent), or found as ions solvated (anions or cations). Is the case of ionic substances and molecular polar substances that totally ionize (the chemical equivalent law can not be applied): the majority of salts, great bases, hydracids and great oxoacids.
- Weak electrolytes, that ionize partially in solution in an equilibrium reaction. Is the case of polar substances that doesn't totally ionize in a polar solvent medium: hydracids and weak oxoacids, organic acids, weak bases.

The electric conductivity of electrolyte solutions depends on ion's nature, temperature and concentration.

It is presumed a constant temperature.

Ion's influence is their mobility, meaning their speed in an accelerator electric fields of intensity equal with unity. It is noted with μ and it is measured in $m^2/V \cdot s$ in IS.

To compare the electric conductivity of the electrolyte in different concentrations, it is defined: the equivalent conductibility λ, that represents the conductivity of all active ions from the volume V of solution: $\lambda = \sigma \cdot V\ \Omega^{-1}m^{2}$.

If in the volume V there exists an equivalent of electrolytes, the concentration is $c = 10^{-3}/V$ equivalents/l and $\lambda = 10^{-3}\ \sigma/c$.

For great electrolytes, which are completely ionized in solution, equivalent conductibility has a big value even in concentrated solutions and it varieties little with concentration.

PRACTICAL WORK

CHEMICAL KINETICS

Chemical kinetics studies the speed of the chemical reactions, the factors that influences the speed and the mechanisms of these reactions.

It is known that some reactions are momentary. Others, like the reactions between hydrogen and oxygen, won't take place at the room temperature.

The fact that the same substance or couple of substances, at different temperatures and pressure conditions react with different speeds, leads to the idea that chemical reactions follow an specific reaction mechanism and the molecules, for reacting, need a special energy, that takes them out from their chemical inertia named activation energy.

In chemical kinetics it is admitted that the reaction speed is proportionally with the product between the reactions concentrations and independent of the components that don't take place in reactions, these being even product.

For a general reaction like:

$$aA + bB + cC + \ldots = lL + mM + nN + \ldots$$

The reaction speed might be defined as the variation of the concentrations in rapport with time:

$$v=-\frac{dC_A}{dt}=\frac{dC_B}{dt}=\ldots=k\,C_A^aC_B^b\ldots=k[A]^a[B]^b$$

Where k is the specific speed or the speed constant; C_A, C_B, ... or [A], [B], ... are the molar concentrations of the reactions: a, b, the stoechiometrical coefficients.

THE FACTORS THAT INFLUENCE THE REACTIONS SPEED

The reaction speed depends not only on the concentration of the reactants, but on the factors that influence the speed constant k.

Experimentally it was established that the temperature, contact surface and catalizator influence the specific speed.

The dependence of the speed constant is given through Arrhenius relation:

$$k=A\,e^{\frac{Ea.}{RT}}$$

Where: Ea. is the energy of activation. T is the absolute temperature. R is the constant of ideal gases.

At the practical work it will be determined the activation energy of the disproportionate reaction of the ion of tiosulphate in an acid environment.

$$S_2O_3^{2-}+2H_3O^+\rightarrow S+SO_2+3H_2O$$

This reaction is enough slowly and it can be watched with eye–free.

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For the determination of the activation energy the reaction it will be made for four temperatures, each time measuring the time which passes from the apparition of the colloidal sulph. The reaction it will be made in two beakers of glass with double walls, in which travels water from the thermostat, which has the role to maintain a constant temperature of the water during reaction.

WORKING MANNER

The thermostat must contain water till ¾ from high. This is noticed at the bulb of level from the lateral part. It's connecting the thermostat at the network and the switch is moving in the start position (P). The temperature at which we want to make the reaction is fixing at the Wertex thermometer (this is manipulated by the didactic cadre). The flame must be open if the water's temperature from thermostat is under the value fixed at Wertex thermometer and is extinguished for a short time when the water's temperature touch this value.

Is pouring in the beaker of glass of the thermostat (with $Na_2S_2O_3$ label) 15 ml. Solution $Na_2S_2O_3$ 0.1 M and in the other bottle 15 ml. Solution H_2SO_4 0.1 M.

It's waiting that the solutions to touch the fixed temperature of the Wertex thermometer of the thermostat. It's measuring this with a thermometer, which is introduced in thermostat bottles.

When the temperature from the bottles is identical with the one fixed in the thermostat, is pouring suddenly the bottle contain on of other bottle contain and is mixing easily with the thermometer. It's measuring the time, t, from the mixing of the solutions till at the apparition of the colloidal sulph.

The experience it's repeated at 3–4 temperatures.

The results will be passed in the next table:

No	T(K)	1/T	Time (t) (seconds)	Lg (1/t)= –lg(t)

The calculation of the activation energy will be made on basis of Arrhenius relation, which under logarithm give:

$$Lg(k) = lg(a) - \frac{Ea.}{2.303\,R\,T}$$

Which represents the equation of a straight equation with coordinates lg (k) and 1/T. We may approximate lg (k) with lg (1/t) so that representing graphically lg (1/t) function of 1/T from the straight angle we can calculate the activation energy.

THEME V. MOLECULAR MASS DETERMINATION

MOLECULAR WEIGH

A. The molecular weight of compound is the number of times its molecule is as heavy as one sixteenth of the oxygen atom.

B. It is also the sum of atomic weights of all the atoms of the molecule.

DETERMINATION OF MOLECULAR WEIGHTS

The molecular weight of compound is the sum of the atomic weights of all the atoms presents in the molecule.

Gases

Vapor density method. (Hydrogen standard)

Since hydrogen has a molecular weight of 2, the molecular weight of other gases may be determined by multiplying their vapor densities, relative to hydrogen, by 2.

Avogadro's Hypothesis method.

a) The molecular weight of a gas is numerically equal to the weight in grams of 22.4 liters of the gas measured at standard condition.

b) Or the molecular weights may be found by multiplying the weight of 1 liter of gas by 22.4.

Other methods for molecular mass determination of gases:

Regnault method

It is used in molecular mass determination for not easy condensable gases, the so-called permanent gases. At the usual temperature, they have above their critical temperature. Is the case of oxygen, nitrogen, hydrogen, etc.

Liquids.

1) If the compound, whose molecular weight is to be determined is volatile liquid, a weighed sample is heated to a temperature above it's boiling point.

2) The volume of the vapor is measured and recalculated to standard conditions.

3) From this information the weight of 22.4 liters of the vapor, under standard conditions, is calculated.

a) Victor Meyer Method.

It is used for molecular mass determination of liquid or solid substances that can be transformed in vapors without being decomposed.

1) A small weighed sample of the volatile liquid is introduced into the closed, heated tube.

2) The vapor formed displaces an equal volume of air from the gas measuring tube.

3) From the known weight, volume of vapor, temperature, and pressure, the weight of 22.4 liters of vapor, at standard condition, is made.

b) Duma's Method.

It is applied to the molecular mass determination of easily volatile substances like: carbon tetrachloride, chloroform, alcohol, ethers, etc.

1) A small vessel of known capacity is weighed when filled with air.

2) Next, a small amount of the volatile liquid is introduced into the vessel and the whole is heated to a known temperature above the boiling point of the liquid.

3) The vessel, when filled with the vapor, is weighed.

4) From the known volume, weight of vapor, temperature, and pressure, the weight of 22.4 liters of vapor, at standard conditions, is calculated.

Solids. (Non- electrolytes)

1) The molecular weight of a non-volatile, non-ionized, solute may be determined by its depression of the freezing point, elevation of the boiling point, or lowering of the vapor pressure of the solvent.

a) Freezing Point Method.

1) The freezing point lowering in a dilute solution, when water is the solvent, are 1,86°C for 1 mole of nonionized solute in 1,000 g. of solvent.

2) Many other solvents show different but consistent moll freezing point depressions.

b) Boiling Point Method.

1) The boiling point evaluation in a dilute solution when water is the solvent, is 0,52° C., for 1 mole of nonvolatile, non-ionized solute in 1,000 g. of solvent.

2) Many other solvents show different but consistent molar boiling point elevations.

V.1. MOLECULAR MASS DETERMINATION FOR GASES

MOLECULAR MASS DETERMINATION OF CARBON DIOXIDE

The molecular weight of a substance is the number, which shows us how many times is the molecule of that substance heavier than the hydrogen atom or than the sixth part of oxygen atom weight or than the 12 part of the isotope ^{12}C weight.

From the easier methods for molecular weight determination of a gas is that which uses the relative density of the gas in front of other taken as reference gas.

The relative density D of a gas in front of other gas represents the ratio between the weights of the two gases taken in equal volumes in same conditions:

$M_A = M_B \cdot D$

The molecular weight of a gas is equal with its density in ratio of other gas multiply with the molecular weight of this gas.

The relative density is usually determined in ratio with hydrogen or with the air. The molecular weight of hydrogen is 2.016. The air is 14.38 times heavier than the hydrogen. The average molecular weight of air is 28.99. That is why the formulas for molecular weight determination are:

$M = 2.016 \cdot D_H = 2 \cdot D_H$

$M = 28.99 \cdot D_{air} = 29 \cdot D_{air}$

There can be calculated the molecular weights of gaseous substances and of that liquid substances or solid which can transform themselves in vapors at not very high temperatures without suffering a chemical decomposition.

The molecular weight is a very important constant of a pure substance, the impurities altering the vapor density, which causes erroneous results. At the experimental molecular weight determination of a gas it must be taken the

necessary measures for purification of the gas by the eventual impurities. At the molecular weight determination of some liquid substances and volatile solid substances it must be used chemical pure products.

WORKING MANNER:

Carbon dioxide is obtained in the Kipp device, from marble and hydrochloric acid.

Laboratory accessories: one Kipp device for obtaining CO_2, two vessels for washing, round bottom flask (50 ml) and cylinder.

WORKING MANNER

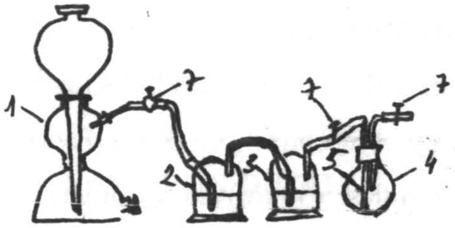
Weight at the analytical balance a dry balloon, with air, closed with a cork (g_1). The cork must be introduced in the balloon's neck ill some sign. In the balloon is introduced a small glass tube through which passes the CO_2 from the Kipp device. For washing and drying the gas, this is passed through some washing vessels with sodium bicarbonate and concentrated sulfuric acid. Start the Kipp device and introduce slowly the dioxide, 7 or 8 minutes. Close the balloons with a cork till the sign and weight it (g_2). Then the dioxide is passed again, 2 or 4 minutes, then the balloon is weighted again (g_3). If the weight g_2 and g_3 are equal or differ with less then 0.01 g, the balloon is completely filled. In the other case is continuated the filling and the thing that we look for is the balloon's constant weight. Write the temperature reached by the room thermometer and the pressure shown by the barometer. Fill with water the balloon till the sign and then pour it is a graduated cylinder for the volume of the balloon.

Using the gas equation, the gas's volume from the balloon is reduced to normal conditions (Vo). Knowing that in normal conditions one litter of air weights 1.2939 g determines the weight of the air from the balloon (g_4). From the difference $g_1 - g_4$ is calculated the empty balloon's weight with the cork (g_5). From the difference $g_3 - g_5$ is found the weight of CO_2 from the balloon (g_6). From g_6 and g_4 is determined the relative density of CO_2 toward air and is calculated the molecular mass.

The balloon's weight with air and cork	The balloon's weight with carbon dioxide and cork	The balloon's volume in ml	t°C	The pressure (mm Hg)
g_1	$g_2 = g_3 = \ldots$			

FIGURE V.1. Apparatus for molecular mass determination of CO_2 (Kipp device):

1.–Gas generator (Kipp apparatus),
2.–Washing vessel with sodium bicarbonate solution,
3.–Washing vessel with concentrated sulfuric acid,
4.–Flat bottom flask with perforated cork through which pass two glass tubes,
5.–Glass tube for balloon filling,
6.–Glass tube for gas evacuation,
7.–Taps.



V.2. Molecular mass determination in liquid phase

A solution is a homogeneous mixture, liquid, of two or many components, in which it is, distinguished the solvent–the component in whose volume the solute particles are uniformly distributed (dissolvent substance). If the two components are in equal proportions, the distinction between solvent and solute disappears. When one of the components is water, no matter of the it's proportion, it is considered to be the solvent.

Solutions respect Raooult's law in which it states that: for solutions in which the solute has negligible vapor pressure, the vapor pressure of the solution p is smaller then the vapor pressure p^0 of the pure solvent. The relationship is variable: $p^0 - p = x\,p^0$, meaning that the vapor pressure of the solution is direct proportional with the molar fraction x of the solute. This law is available for ideal solutions, but it is exact applied to not ideal solutions with small concentration.

Replacing: $x = n_2/(n_1 + n_2)$, where n_1–solvent moles and n_2–solute moles, it is obtained: $p^0 - p = n^0\,n_2/(n_1 + n_2)$, where, the solution being considered diluted, the value of n_2 from the denominator can be neglected. It can be written: $p^0 - p \approx p^0\,n_2/n_1$ meaning that the decreasing of vapor pressure of a (diluted) solution towards the one of the pure solvent is (approximately) proportional with solute–solvent moles report.

Considering $n_1 = m_1 \cdot M_1$ and $n_2 = m_2 \cdot M_2$, where m_1 and m_2 are the solvent and solute mass and M_1 and M_2 are the corresponding molecular masses, it can be written:

$$(p^0 - p)/p^0 = m_2 M_2/m_1 M_1.$$

So, measuring the decrease in vapor pressure of the solution in report to the solvent one, the other dimensions p^0, M_1, m_1 and m_2 being known it can be determinate the molecular mass of the dissolvated solution M_2.

Experimental determination of the vapor pressure is extremely difficult. It is preferred the determination of some physical parameters which are in tight connection with the vapor pressure and whose variation respects the Raoult's law. Is the case of boiling temperature determination (ebullioscopic method) of some volatile substances, in solvents of whose physical parameters are known.

V.2.1. DETERMINATION OF THE MOLECULAR MASS THROUGH THE EBULLIOSCOPIC METHOD

A liquid boils when his vapor pressure equals the exterior pressure.

When a nonvolatile substance in dissolved into a solvent, the vapor pressure of the resulting solution is smaller then the one of the pure solvent at the same temperature.

According to Raoul's law, the relative decreasing of the vapor pressure of a diluted solution is proportionally direct with the concentration of the solution:

$$\frac{P - P'}{P} = K \cdot c$$

Where: P–is the vapor pressure of the pure solvent.

P'–is the vapor pressure of the solution,

c –the concentration of the solution.

The k constant depends on the nature of the solvent, being independent of the nature of the dissolved substance. It is obvious that the numeric value of the constant k depends on the way the concentration is expressed.

Raul's law is valid for diluted and non-–electrizable solutions.

Let's consider a pure solvent in boiling process; its vapor pressure equals the atmospheric pressure. If in this volume of solution substance, then the pressure will decrease and the boiling will stop. For making the liquid boiling again its vapor pressure must be increased and so the temperature to be raised.

As consequence of the vapor pressure decreasing by nonvolatile substance dissolved into a solvent, **the boiling point of the solution**, meaning the temperature at which the vapor pressure equals the exterior pressure, **is higher then the boiling point of the pure solvent**.

The difference between the solution boiling temperature and that of the pure solvent (the ebulliometric rise of solution boiling point) is proportional with the concentration of the solution:

$$T_{solution} - T_{solvent} = \Delta Tb = k \cdot c$$

c– is the molar concentration of the solution (expressed in moles of substance dissolved in 1000 g of solvent)

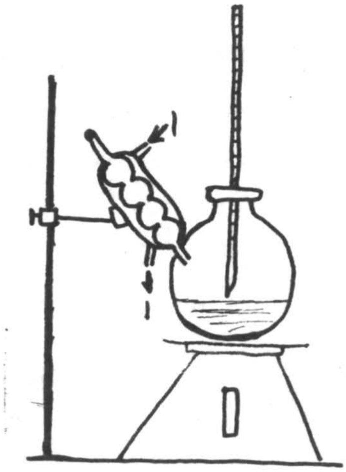
If g1 is the quantity of substance dissolved in g2 grams of solvent and M is the molecular mass of the dissolved substance, then the molar concentration c will be equal to 1000 ***g1 /M** *g2. So, it follows:

$$\Delta Tb = \frac{k \cdot 1000 \cdot g1}{M \cdot g2}$$

The molecular mass M of the dissolved substance could be determined by measuring the difference between solution boiling temperature and the one of the pure solvent (ΔTb)

PRACTICAL WORK

In this experiment we will determine the molecular mass of a pure nonvolatile substance using as solvent the distillate water which has an ebulliometric constant equal with 0.52°. The boiling temperatures of the solution and of the solvent will be determined using a device like:



In the balloon is introduced 50 ml of distilled water and it is heated until it boils.

After the liquid begun to boil, the heat intensity must be maintained such that the vapors formed in the balloon are sprinkling the thermometer. The vapors are condensed in the refrigerant.

The condensed drain in the balloon, if the number of draining drops is too small, the heat is not enough to maintain the water in the balloon at the boiling temperature.

It has been found experimentally that in the balloon, the liquid is overheated with 0.03 till 0.05 degrees above its boiling point. Only after the liquid sprinkling of the thermometer, the excess of heat consummated by the evaporation of a small quantity of liquid.

Because of this fact, in the upper part of the ebulliometer is reached the thermodynamic equilibrium between the liquid and the vapors that fill this part of the ebulliometer. It has been found experimentally, that the intensity of the heating is enough when trough the refrigerant are dripping 8 drops/min because in this case, the read temperature is corresponding to liquid boiling temperature and has no variations.

If the heating is increased, we observe that the temperature is not modifying until we have 25 drops/min, after that the temperature begins to rise, because the overheating becomes too strong and the thermodynamic equilibrium can not be maintained. Because of the difference between the boiling temperatures of the solution and the pure solvent is very small (tenths or hundredths of Celsius degrees) the temperature reading is done with a differential thermometer (Beckman). This thermometer has two reservoirs of mercury (one superior and one inferior). The quantity of mercury inside the inferior reservoir is adjusted such that at the boiling temperature of the solvent the mercury level matches the scale of the thermometer.

The temperature readings will be done with two decimal fractions. The read temperature does not represent a real boiling temperature (physical meaning: it has only the difference between two temperatures ΔTb –which is why is called differential thermometer).

After reading the water boiling temperature, the heating is stopped and in the balloon is introduced a tablet of substance of which we want to determine its molecular mass. The heating is started again and this time is determined the solution boiling temperature.

Knowing the boiling temperatures of the pure solvent and of the solution, well the quantities of the solvent and of the dissolved substance, we can compute the molecular mass of the dissolved substance.

THEME VI. CHEMICAL EQUIVALENT DETERMINATION

VI.1. ATOMIC WEIGHT VERSUS EQUIVALENT WEIGHT

The key to early periodic systems was the ordering of the elements by their atomic weight. The concept of atomic weight originated with the English scientist and teacher, John Dalton, in 1803. Dalton was attempting to explain why different amounts of various gases dissolve in a liquid by comparing the relative weights of these substances. His scale assigned a weight of 1 to hydrogen. When Dalton published his atomic theory, he included tables of atomic weight values. However, when tow elements combine in a compound, it is insufficient merely to determine the percentage of each element present to obtain correct atomic weights. One must also determine the valence of each element in the compound. Valence is a measure of how many atoms of one element combine with an atom of the other element, e.g. is water HO or H2O? Unfortunately, it cannot be determined until the atomic weight is known. Early experiments assumed, in the absence of evidence to the contrary, that a compound was made up of molecules containing one atom of each element. This monatomic hypothesis created difficulties in understanding reactions. The rule worked in many situations, but there were a large number of cases in early atomic weight tables where the assumed valence was not correct. Thus, equivalent weights (or proportional numbers as they were called, since they were ratios of elements) were quoted rather than the atomic weight.

This problem of listing atomic weights for some elements and fractions of atomic weights for other elements obscured the true periodicity of the elements.

In 1811, the Italian lawyer and physicist, Amedeo Avogadro, solved this problem by using the results of the French scientist Joseph Louis Gay–Lussac on combining volumes. Gay–Lussac determined that gaseous elements combined in chemical reactions in simple (numerical) volume ratios. Avogadro, then, hypothesized that equal volumes of different gases under the same conditions contain equal numbers, of molecules, a possibility that Dalton had considered and rejected, although without the benefit of Gay–Lussac's data. Avogadro also assumed that common gaseous elements consisted of two–atom molecules.

A table with the atomic weight was provided then by Mendeleyev. He and Lothar Meyer corrected equivalent weights values to atomic weights.

VI.2. CHEMICAL EQUILIBRIUM DETERMINATION

We define the equivalent as the equivalent as the quantity from an element, chemical compound or radical which combines with an equivalent of Hydrogen (1 g H), an equivalent of oxygen (8 g O), an equivalent of nuclidium ^{12}C (3g ^{12}C) or an equivalent of any substance which could replace these quantities.

For determining the equivalent, we start from the fact that for elements the equivalent represents the ration between the atomic mass A and the valance V of the element (A/V), so that, for H=1/1=1, for O=16/2=8, for ^{12}C (nuclidium)=12/4=3.In the case of chemical compounds; the equivalent can be computed knowing the molecular mass M.

–a) For ACIDS, it is the ratio between N and number of substituted hydrogen atoms C in each particular reaction and it is equal to: M acid /H replaced.

E.g.: Knowing the fact that at the HCl analyses it is obtained 2.74% H and 97.2% Cl;

--determine the equivalent of chlorine.

Knowing the relation which show that the ratio of equivalents is equal with the mass ratio; we can compute the equivalent of chlorine (Cl).

$$E_{Cl} = E_H x \frac{m_{Cl}\%}{m_H\%} = 1x \frac{97.26}{2.74} = 35.4$$

Also, this relationship results at the simple three rules: if 97.26g chlorine combine with 2.74 g hydrogen then x g chlorine combine with 1 g hydrogen.

If 97.26 g Cl _ _ _ _ _ _ _ _ _ _ 2.74 g H
x g Cl _ _ _ _ _ _ _ _ _ _ 1 g H
↔ x= 35.5

The stoechiometry calculus is used in chemically synthesis. For example, how many liters of hydrogen are necessary for obtaining 350 g water through burning?

By burning the hydrogen in air, it results the following reaction:

$$2H_2 + O_2 \rightarrow 2\,H_2O$$

So, 2 moles of hydrogen correspond at 2 moles of water. What hydrogen quantity is necessary for obtaining 350 g water?

$$\frac{36}{350} = \frac{4}{x} \rightarrow x = \frac{350 \times 4}{36} = 38.88 \text{ g } H_2.$$

Knowing that, 1 mole hydrogen (2 g) occupies, at 0°C and 760 mm Hg, 22.41 1, then 38.88 g hydrogen will occupy x volume:

$$\frac{2}{38.88} = \frac{22.41}{x} \rightarrow x = \frac{38.88 \times 22.41}{2} = 435.62 \text{ l } H_2$$

-b) For BASES, it is the ratio between M and the number of HO^-, being equal with:

M_{BASE} / number of HO^-.

–c) For SALTS, the equivalent is the ratio between the molecular mass and the valance of the cations times the number of cations:

$E_{SALT} = M_{SALT}$/ number of cations x V_{CATION}

–d) In the case of redox reactions, the equivalent is calculated taking into account the number of electrons displaced in the reaction, which we short write: M/ number of e^- (electron) displaced.

In accordance with the "EQUIVALENTS' LAW" (J. B. Richter), the elements and their chemical combinations react between themselves or replace one–another in quantities proportional with their chemical equivalents.

For the experimental determination of the chemical equivalent, chemical methods are used (combination reactions) and also electrochemical methods.

The value of the chemical equivalent, expressed in grams, is called 'weight–equivalent' (Eg). Multiples and submultiples of this value can also be used.

PRACTICAL WORK

Making chemical reactions of one element by combining it with another element or by it's substitution with another element with known chemical equivalent and mass, it can be determined, on the base of equivalent's law, the element's equivalent: $E_1/E_2 = m_1/m_2$, where m_1 and m_2 are experimental determined.

VI.1. DETERMINATION OF ZINC'S EQUIVALENT

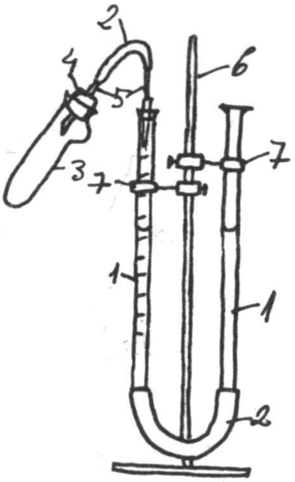
The equivalent of an element can be found chemically determining the quantity of H, O and other elements or substances with known equivalent which the desired substance combines or which it replaces.

Necessary materials: two glass tubes (burettes), a bubble test tube, rubber linkage tubes, thermometer, metallic test tube holder, clamps, zinc and HCl (1:3 solution)

WORKING MANNER

We install the device as in the following sketch; with one of the branches open in order to measure the pressure from the reaction tube.

1.–Glass tubes (one gradated burette),
2.–Rubber connecting tubes,
3.–Test tube with godeu,
4.–Rubber corks for tight closure,
5.–Small diameter test tubes,
6.–Holder,
7.–Clamps.



We fill the tubes with water. Before commencing the experiment, we have to make sure the apparatus is waterproof. That is why we lift and lower the open tube; the water level in the other tube must not vary suddenly, but very little. If it is not, the cork of both the tube and the test tube must be better screwed on. In case the apparatus is waterproof, the water level in both tubes must be brought to the same height and the tubes should be arranged in the test tube holder in that precise position. We write down the water level in the graded tube (V1) with a 0.05 ml precision (we take into account the lower meniscus). We pour 10 ml of HCl (diluted to 1:3) into the reaction test tube, through a long funnel, such that the walls do not get wet.

We weigh a quantity of Zn (0.05 up to 0.08g) and we carefully place it into the lower part of the tube–which we hold in a horizontal position–represented with a dotted line into the sketch. In this position we plug the test tube as well as possible (it has to be waterproof) and we move it to a vertical position. The metal falls down into the acid and we obtain the reaction.

$Zn + HCl \rightarrow ZnCl_2 + H_2$

Due to the pressure of the hydrogen obtained in this reaction, the liquid from the burette passes in the other tube. After the reaction is completed, we let the test tube to cool down (because the reaction is slightly exothermal) and wee bring the water in the tubes at the same level by heating the open tube down. We write down very precisely the new position of the liquid in the graded tube (the tube on the right) V2 and the indications of the thermometer and the barometer (be very careful in reading all these indications from the tube on the right).

All the data from the experiment will be written down in a table and we calculate the equivalent of zinc. Our calculation must take into account the partial pressure of the water vapors because the gas was obtained above the water. The equivalent of Zn will be smaller or bigger depending on the proportion of insolvable impurities in the acid and whether or not we make the pressure adjustment in our computations.

The results of the experiment will be written down in the following table:

Sample no.	Quantity of zinc	Water initial level	Water final level	Yielded H_2 volume	T° C	Atom pressure mm Hg	Water vapors tension	H_2 pressure	H_2 volume in c.n.
№	M Zn	V_1	V_2	$V=V_1-V_2$	t	p_1	p_2	$P=P_1-P_2$	V_0
1.									
2.									
3.									

T °C	20	21	22	23	24	25	26	27	28	29
P_{H_2O}	17.54	18.65	19.83	20.07	23.38	23.76	25.21	26.75	28.35	30.04

VI.2. DETERMINATION OF THE EQUIVALENT OF A METAL IN RESPECT TO OXYGEN (Mg)

The defined proportion low followed to the conclusion that the substances react in equivalent quantities. The quantity in grams from an element which combines to 1 g of hydrogen or 8 g of oxygen or which can replace this quantities of hydrogen or oxygen in their combinations, is called chemical equivalent or just the equivalent of the element.

Analysis of a great number of compounds containing hydrogen reached to this motion. It had been noticed that this element takes part always in these combinations in a small percent that the elements which is combined to. So, water analysis shows that in this combination 1 g of hydrogen is combined with 8 g of oxygen; in ammonia 1 g of hydrogen is combined to 4.67 g of nitrogen; in sulfur hydride, the percent between hydrogen and sulfur is 1:16; in HCl, the percent between hydrogen and Cl is 1:35.5.

Many elements don't combine to hydrogen, but they combine to oxygen. In this case, it is called the equivalent that is the quantity in grams of that element which combines to 8 g of oxygen. So, 28 g of iron combines to 16 g of sulfur and is reached the conclusion that the sulfur has the equivalent 16.

The quantity in grams of the substances is equal to the chemical equivalent called equivalent gram.

In the case of a binary compound, the value of an element equivalent is easily find out if it is known the percentile composition and the value of one of the equivalents. So, for instance the percentile composition of water is 11.1% hydrogen and 88.9% oxygen. The reasoning is the following: if 11.1 g of hydrogen corresponds 88.9 g oxygen, then to 1 g of hydrogen corresponds how many grams of oxygen (the oxygen equivalent)?

$$\frac{E_{OXYGEN}}{E_{HYDROGEN}} = \frac{88.9}{11.1} \leftrightarrow E_{OXYGEN} = 1 \times 88.9 / 11.1 = 8$$

In analogy, the sulfur equivalent is obtained from sulfur hydroxide:

$$\frac{E_{SULFUR}}{E_{HYDROGEN}} = \frac{94.1}{5.9} \leftrightarrow E_{SULFUR} = 1 \times 94.1 / 5.9 = 16$$

The elements have more equivalents in function of the combination they belong to. For instance, sulfur has combinations with oxygen, which are SO_2 and SO_3. The sulfur equivalent in this combination is:

$$\frac{E_{SULFUR}}{E_{OXYGEN}} = \frac{50}{50} \leftrightarrow E_{SULFUR} = 50 \times 8 / 50 = 8$$

$$\frac{E_{SULFUR}}{E_{OXYGEN}} = \frac{40}{60} \leftrightarrow E_{SULFUR} = 40 \times 8 / 60 = 5.3$$

The same for capper equivalents, from CuO is 31.8 and Cu_2O is 63.6.

WORKING MANNER

Necessary materials: crucible, Mg, HNO_3 sol 1:1, exicator, wire gases, Bunsen burner.

A crucible is weighted, empty until a constant weight G1 (by calcination and cooling in the exicator). In the crucible are weighted 0.05–0.10 g of Mg. The following operations are made in a niche. It is pursed in the crucible small portions of HNO sol 1:1 (1–2 ml) until the magnesium is completely dissolved. Than the crucible is laid on a wire gases and the solution are evaporated, carefully, until drying, after which the wire is removed and the calcination takes place directly to the flame. It takes place the decomposition of the resulted salt. The decomposition is considered finished when no vapors are degassed. The calcination is continued; the crucible is introduced into the exicator and it is left in it for a half an hour to become cold. Then the crucible is weighted again and the mass m_3 is noted. The calcination is repeated for fifteen minutes, then it is put in the exicator for half an hour and weighted again. The difference between the two experiments it must not be more then 0.002 g.

The results can be written in the following table:

The crucible Mass empty	The crucible mass with metal	The crucible mass with oxide	Metal mass	Oxide mass	Oxygen mass	E_{Mg}
M_1	m_2	m_3	(m_2-m_1)	(m_3-m_1)	$(m_3-m_1)-(m_2-m_1)$	

VI.3. DETERMINATION OF THE EQUIVALENT OF THE OXALIC ACID

Required materials: a solution of NaOH 5% (d=1.042 g/cm^3), a solution of oxalic acid 3% (d=1.023 g/cm^3), burettes, Erlenmeyer beaker.

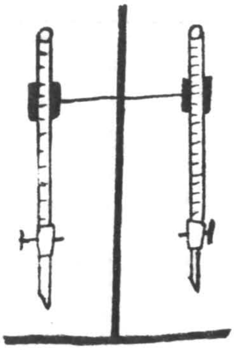
For the determination of the gram–equivalent of oxalic acid, the oxalic acid is treated with sodium hydroxide. It takes place a neutralization reaction. Knowing that the gram equivalent of NaOH (40 g) and the quantities in weight of two substances that react, it can be determined the gram–equivalent of the oxalic acid.

WORKING MANNER

The burettes are washed with water and then with 10–15 ml from the solution with which it will be filled because the concentration of the solution must not be changed. The burettes are placed on a frame as in the figure below. In one of them we introduce

$K_2C_2O_4$ and in the other NaOH. The level of the solution is established in each of the burettes so that the meniscus to be tangent to the zero division of the burettes. At the filling of the two burettes we will see that there bottom end to be full with solution. In an Erlenmeyer beaker we introduce 20 ml of oxalic acid and add 2--3 drops of methylorange as indicator and we perform titration with NaOH until we observe the orange coloration of the solution. The volume of NaOH used is very accurately red and noted. Knowing the solution's density we can determine the quantities of NaOH and $H_2C_2O_4$ ($H_2C_2O_4 * 2H_2O$) from the volumes used in neutralization reaction. In this way we determine m_1 and m_2 which are introduced in the reaction.

FIGURE VI.3.



$$E_{H_2C_2O_4 * 2H_2O} = E_{naOH} * m_1/m_2$$

Knowing that the gram–equivalent of NaOH is 40, we compute the equivalent of the oxalic acid by dividing the gram–molecule to the number of hydrogen ions replaceable through the metal.

VI.4. DETERMINATION OF THE CHEMICAL EQUIVALENT OF SOME COMPOSED SUBSTANCES

THE DETERMINATION OF CALCIUM CARBONATE EQUIVALENT

Necessary materials: a Berzelius beaker (capacity 100 ml), pieces of marble, HCl solution 1N.

WORKING MANNER

We weight at the analytical balance a clean Berzelius beaker of 100 ml capacity (g_1). We introduce in it some pieces of marble and is weighted again (g_2). We take a quantity of approximately 2.5–3 grams.

We measure with the burette 15 ml of solution of HCl 1N. To perform this task we have to wash the burette's walls with acid and then we throw it out. We fill up the burette in such manner that inside it does not have air bubbles and the level of the liquid to pass a little bit over the zero division. Through opening the top we bring the liquid to the zero division.

The beaker with the measured marble sample is placed under the burette and we add 15 ml of acid. After the emerging of the CO_2 bubbles stops the beaker is put into a sand bath at 60–70°C. At the beginning the bubbling intensifies and then stops. In that moment we consider the reaction complete. The solution present on the top of the excess of the carbonate is drained and the carbonate is washed a few times with distilled water using decantation.

The beaker with the rest of the marble is dried in the sand bath and after the cooling in the exicator is weighted again (g_3).

The experiments data is put into the table below and we compute the equivalent of the calcium carbonate.

The beaker's weight (g)			The marble's weight (g)		Grams of marble reacted	The acid (ml)
Empty	With marble					
	Before exp.	After exp.				
G_1	g_2	g_3	g_2-g_1	g_3-g_1	g_2-g_3	

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