

CHEMICAL ENGINEERING MEASUREMENTS

Prepared for Students in C.M. 16

by

R. E. TOWNSEND

and

L. THOMASSEN

University of Michigan

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PURPOSE OF THE COURSE

The purpose of this course is to present and illustrate some of the principles of chemistry and physics as they apply to the problems of Chemical and Metallurgical Engineering measurements.

General Information

Cashier's Coupon

Each student must purchase the required chemical engineering coupons at the cashier's office. These coupons are to be presented to the instructor before the second meeting of the class.

Textbook

The text for this course is "Experimental Physical Chemistry" by Daniels, Matthews, and Williams, 3rd edition.

Reference Books

The books most frequently used as reference in this course are:

- "Gas and Fuel Analysis" by A. H. White, 2nd edition.
- "Pyrometry" by Wood and Cork, 2nd edition.
- "Electrical Measurements" by Smith, 3rd edition.
- "Experimental Electronics" by Muller, Garman, and Droz.

These books are available in the East Engineering Library.

Laboratory Record Book

All data are to be recorded in duplicate in a permanently bound (or spiral) $8\frac{1}{2}$ inch by 11 inch notebook. UNDER NO CIRCUMSTANCES ARE DATA TO BE TAKEN ON LOOSE PAPER. However, the sheets for the carbon copy may be report size paper inserted into record book.

Before recording measurements, the manufacturer's serial number and/or the department number is to be recorded to identify all meters, instruments and equipment used. All samples must be identified.

Line drawings of equipment and complete wiring diagrams, as well as the room temperature and barometric pressure are frequently invaluable in interpreting the results obtained.

The data must be recorded in a legible and orderly manner. All units of measurements must be clearly indicated. The importance of keeping a neat laboratory record book cannot be overemphasized. Like in an industrial laboratory the notes form the basis for writing the report. The record book is often the only tangible proof that an experiment has been performed and should therefore be completely intelligible to any other engineer. Granting of patents will in many cases depend on evidence presented in record book form, and the neater and more complete it is, the easier will be the task of convincing the judge.

DO NOT MAKE ANY ERASURES. When an error is made in recording observations or in calculations, draw a straight line through the portion in error and insert the correction so that it can be clearly recognized. Erasures and possible substitution of data will invalidate the work in the eyes of the law. Frequently the portions erased become the portion vital to the correct interpretation of the test.

Since the tests are short, all computation of results are to be included in the record books in this course.

The laboratory record book is subject to call at any time for review by the instructor.

Preparation

The student is expected to study the laboratory manual and reference reading before starting the assigned experiment. It is recommended that a tentative data sheet be prepared during this study to assist the student in more neatly arranging the data taken during the laboratory period.

Permission to work will be denied any student who is obviously not prepared.

Students are held responsible on examinations for the information contained in the reference assignments.

Use of Equipment

The student is only permitted the use of the apparatus to which he is assigned. Other equipment will be on the desks in the laboratory since some of the apparatus is not adapted to storage in lockers. Equipment, other than that assigned for the period, is not to be used or removed from location. Under no circumstances is it permissible to borrow pieces of apparatus from other installations. Any equipment shortage should be reported at once to the instructor.

The student will be expected to show reasonable dexterity in the use of equipment and to apply himself so that the work will be completed in the allotted time.

Any breakage or damage to equipment must be reported at once to the instructor.

Experiments

A total of 27 to 30 experiments will be performed in an average 15 week semester. Certain experiments covering gas density and analysis, colorimetry, physical and chemical measurements, and pyrometry are required. Optional experiments are presented so that a student may express his preference as to the type of experiments he will perform in addition to those required. The optional experiments are indicated by an asterisk in the list of experiments in this manual. Each student should submit a list of 8 optional experiments arranged in the preferred order of his choice at the second laboratory period of the semester.

Checking out of the Laboratory

The equipment is to be left clean and in good order at the end of every work period. Checking out consists of having the instructor inspect all equipment used, initial the data taken, and sign out the student on the daily report sheet.

The Report

Mechanical Details

The report is to be written in ink or typewritten on 8 1/2 inch by 11 inch paper, using one side of the paper only.

The student's name, the course, and section number, the date when the experiment was performed, and the date when the report is submitted, shall appear in the upper right-hand corner of the first page. The experiment number and title are to be centrally located across the upper section of this page. The student's name, section number and experiment number must also appear in the upper-right-hand corner of each succeeding page of the report together with the proper pagination. On graphs, this information is presented boxed in with other pertinent information. All graphs are to be inked in on standard graph paper. Since a graph is a visual presentation of data, all experimental points should be prominently shown. The graph should be as completely informative as possible, consistent with clarity.

Content

1. The content of the report should be presented in the following order:
 - (a) A tabulation of all pertinent results with weighted average of these results on the first page.
 - (b) Graphs, where applicable, to present results.
 - (c) Comparison of experimental results with accepted published data wherever possible.
 - (d) Wiring diagrams to illustrate clearly the principle of the test.
 - (e) Discussion of Method and Theory, errors, etc.
 - (f) Carbon copy of original data with all calculations clearly presented. These complete calculations should leave no doubt in the reviewer's mind as to the origin and meaning of the units used.

Experiment 1

CALIBRATION OF A GAS BURETTE AND FLUE GAS ANALYSIS

Reference: Gas and Fuel Analysis, 2nd edition, pp. 14-38, 65-68 (pp. 28-38 for procedure)

Purpose: To use the portable gas analysis apparatus to analyze a flue gas.

Equipment: Portable Gas Analysis Apparatus.

Discussion: Knowledge of the chemical composition of industrial gases is essential in many industries to determine the efficiency of the process, the purity of the product, or the degree of completion of reaction.

Orsat described a compact and portable gas analysis apparatus in 1875. It consisted of a graduated burette for storing and measuring the volume of a gas before and after successive chemical treatments in any one of several absorption pipettes connected by means of capillary tubing to the burette. Since that time many modifications to the "Orsat Apparatus" have been made, designed primarily to speed up the analysis, increase its accuracy, or extend its scope. Combustion tubes for the determination of CO, H₂, and CH₄ are now frequently included as part of the modern gas analyser.

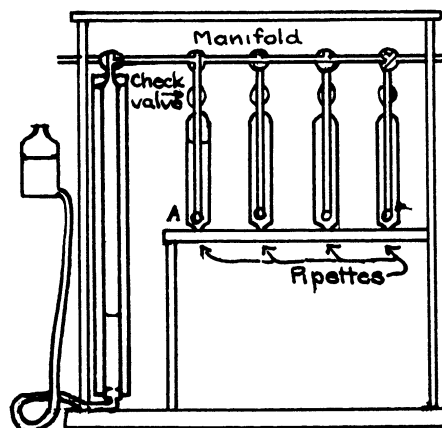


Fig. 1. Orsat Apparatus

The accuracy of this gas analysis may not always compare with that possible in gravimetric or certain other types of analysis, but because of its relative speed and simplicity, is admirably adapted to the control of many processes such as combustion, absorption, and purification.

Mercury is frequently used as the retaining liquid in the leveling bottle and burette, with a few drops of water over the mercury to saturate the gas in the burette. However, water may be used if slightly acidified with H₂SO₄, or saturated with Na₂SO₄, to lower the solubility of the gas sample in the water.

Procedure:

Calibration of the Burette

Before beginning an analysis with a burette of unknown history, it is important to see if the portion of the burette between the stopcock and the uniformly graduated portion contains the volume indicated. This upper portion of the burette may have been repaired by a glass-blowing operation which has changed its volume. The probability that the main portion of the burette is incorrect is very remote. The calibration, therefore, consists in transferring a known volume of gas into the upper portion of the burette being calibrated and observe the reading. Transfer a small portion (8 to 12

ml) of 20 to 30 ml of gas contained in one burette to the upper section of the burette being calibrated. If the volume as read on the burette being calibrated is different from the actual volume transferred, a correction must be applied to the volume as read. Make several check runs.

Analysis of the Gas

The usual constituents of a flue gas are: CO_2 , O_2 , CO , and N_2 , with almost negligible amounts of H_2 and CH_4 . The CO_2 is removed in the first pipette with a 33% by weight solution of KOH or NaOH . A rapid absorption of CO_2 may take place. However, in order to be sure of complete absorption, the gas must be run back and forth several times, and the volume read. Two successive readings should agree within 0.1 ml before absorption can be considered complete. The same procedure must also be used in other cases of absorption analysis.

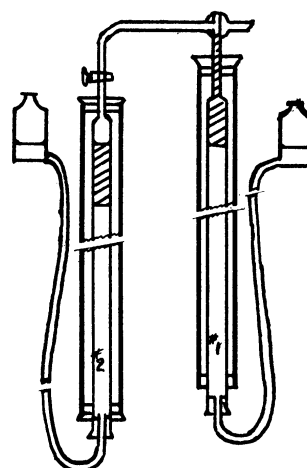


Fig. 2. Calibration of Burette

Oxygen may be removed with either alkaline pyrogallol, (pyrogallic acid dissolved in strong KOH) or phosphorous sticks. Absorption of oxygen in alkaline pyrogallol is rather slow unless the solutions are quite new. The maximum volume of oxygen that it is possible to absorb is rather small, being at best 8 to 10 times the volume of the solution. Old solutions have a tendency to give off carbon monoxide.

Absorption by reaction with phosphorous is also rather slow, especially if the sticks are covered with a deposit. Pure oxygen does not react with phosphorous and must be diluted. If ethylene is present in the gas, no reaction will take place, and it is therefore very important that this gas be removed before being analyzed by this method. The white smoke produced is not a gas and occupies a negligible volume.

Carbon monoxide may be absorbed in a solution of cuprous chloride. This solution oxidizes rapidly and must be protected from air. Oxygen not removed in the previous step will be absorbed along with the CO . It is frequently desirable to use two Cu_2Cl_2 pipettes, the solution in one to remove much of the CO from the gas, and a fresh solution in the other pipette to remove the balance of the CO .

Nitrogen is determined by difference.

The results of the analysis, corrected if necessary for the burette calibration, are reported in percent by volume of the original gas. List in tabular form the volume percentage of each constituent determined.

- 1) What is the effect of pressure on the volumes observed in the calibration of the burettes.
- 2) Is the calibration expressed as a "correction" or as a "correction factor?"
- 3) What is the effect of hydrogen in the fuel on the ratio of oxygen containing gases ($\text{CO}_2 + \text{O}_2 + \frac{1}{2} \text{CO}$) to nitrogen in the flue gas?
- 4) The gas as measured in the burette is saturated with water vapor. Does this mean that the gas analysis must be reported on the "wet" basis? Explain.

Experiment 2

ANALYSIS OF A MANUFACTURED GAS

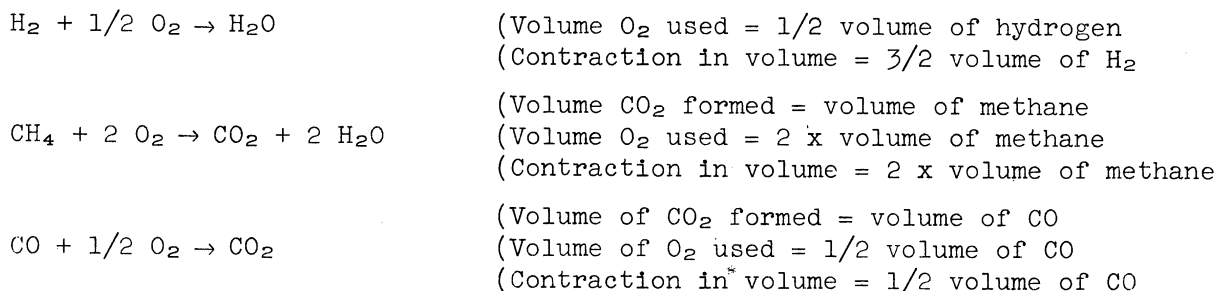
Reference: Gas and Fuel Analysis, 2nd edition, pp. 43-51.

Purpose: To determine the complete analysis of a coal gas, and use that analysis to calculate the heating value and gravity of the gas.

Equipment: Portable gas analysis apparatus, copper oxide combustion furnace, and explosion pipette.

Theory: The constituents usually found in a manufactured gas such as coal gas or carburetted water gas are CO_2 , C_nH_{2n} , O_2 , CO , H_2 , CH_4 , and N_2 . The first three of these constituents as listed can each be selectively and quantitatively removed from the rest of the gases by absorption methods. CO may be absorbed or it can be oxidized to CO_2 and this CO_2 determined by absorption. Hydrogen and methane may be determined separately by combustion, the H_2 oxidized to H_2O in the presence of hot copper oxide, the CH_4 , oxidized over a hot catalyst, or exploded in the presence of O_2 , to form CO_2 and H_2O . Frequently the H_2 and CH_4 are exploded simultaneously in the presence of O_2 . Nitrogen is determined by difference. The loss in volume in any pipette indicates the amount of the constituent removed in that step.

The reactions that may take place in the explosion pipette are as follows:



If CO has been completely removed, the volume of methane in the exploded samples can be readily determined. Equations in terms of volumes of hydrogen, methane, and CO , and the CO_2 formed, contraction in volume, and oxygen used can be set up and solved, thus determining the volumes of the constituents present.

Procedure: Carbon dioxide is removed with KOH solution as in Experiment 1. The illuminants or C_nH_{2n} compounds are removed by absorption in a saturated bromine water solution. The residual gas will contain some bromine vapor which must be removed before the loss in volume due to the removal of C_nH_{2n} can be measured. This bromine is removed by absorbing it in the KOH solution. Care must be taken to remove all of the bromine from the residual gas and the retaining liquid in the burette before proceeding with the analysis. The residual gas must be repeatedly passed through the KOH solution until the volume becomes constant. Oxygen and carbon monoxide are determined as in Experiment 1. (CO could also be determined by combustion over heated copper oxide or burned with O_2 to form CO_2).

The remaining gas should consist of H_2 and CH_4 and N_2 . Since there are no suitable absorbing solutions for hydrogen and methane, these gases are mixed with air or oxygen and exploded. The change in volume, the volume of CO_2 produced, and the oxygen used in the combustion are determined and used in calculating the amounts of hydrogen and methane (and sometimes CO) present in the gas.

Since the amounts of hydrogen and methane are usually too large to form an exploding mixture with all of this residual gas, and the explosion would be too violent,

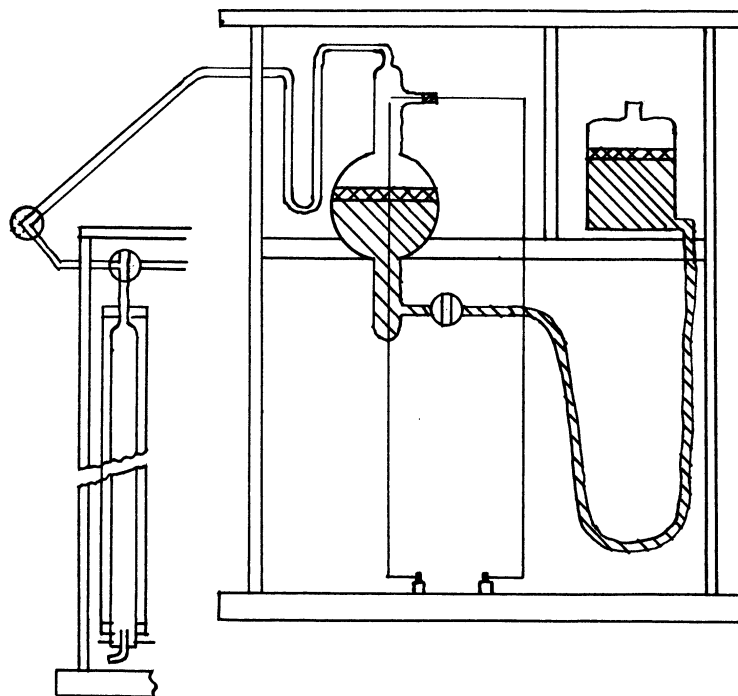


Fig. 3. Explosion Pipette and Connections

small portions of this residual gas are mixed with oxygen and exploded and the volumes of H_2 , CH_4 and N_2 determined are calculated back to their volumes in the original sample.

All but about 9-10 ml of the residual gas is stored in the cuprous chloride pipette. To this 9-10 ml of residual gas measured in the burette, air is added to bring the total volume to 75 to 95 ml, depending on the amount of H_2 and CH_4 present. The burette is securely connected to the explosion pipette connection and the gas - air mixture transferred completely to the explosion pipette after all other gases have been expelled from the explosion pipette system. Close the stopcock at the bottom of the explosion pipette only. Passage to the burette must be open because the retaining liquid in the burette serves as a buffer to cushion the force of the explosion. Be sure the stopper at the bottom of the burette is firmly in place. Explode the mixture by closing the circuit to the spark coil. A noticeable explosion should take place. Immediately, open the stopcock at the bottom of the explosion pipette and return the gas to the burette. Allow the gas to come to burette temperature. Record its volume. Determine the volume of CO_2 formed and the oxygen remaining after explosion. Discard this gas sample after the oxygen content of the exploded gas has been determined. Draw another 9 to 10 ml sample from the cuprous chloride pipette, dilute with air, and repeat the explosion process. Two or three, possibly four, explosions will be necessary before satisfactory data can be obtained.

Adjust the air-gas mixture as indicated by data from your previous explosions. The ratio of exploding to non-exploding gases (nitrogen plus excess oxygen) should be from 1: 3 to 1 : 5. At least one ml of excess oxygen should be present to assure complete combustion.

Results: Tabulated results will contain (1) the composition of the coal gas sample, (2) the total heating value, and (3) the specific gravity, all based on the analysis of one sample. This will include computations for two or three explosions. (Assume $n = 2$ for these computations). Calculate the percent of H_2 and CH_4 in two ways:

- 1) By means of the contraction and CO_2 formed in the explosion.
- 2) By means of the oxygen balance and CO_2 formed in the explosion.

Questions:

- (1) Why must the bromine be entirely removed from the gas?
- (2) If a small amount of CO was not removed before proceeding with the explosion, what effect would this have on the subsequent analysis?
- (3) If the volume of gas after explosion was observed before the gas had returned to the burette temperature, how would this affect the results obtained?
- (4) Nitrogen is usually calculated from the explosion data rather than by difference from 100%. Why?
- (5) Which method of calculating the percentage composition of the explosion sample should give the more reliable results?

Experiment 3

CALIBRATION OF MERCURY THERMOMETERS

Reading: Experimental Physical Chemistry, pp. 421-423.
Temperature, Its Measurement and Control in Science and Industry,
pp. 228-254 (general) pp. 240-244, 247-248.
Monograph: American Institute of Physics

Discussion: Mercury thermometers are frequently calibrated to read correctly, or nearly correctly, when the bulb and the entire liquid index in the stem are exposed to the temperature to be measured. Such a calibration is termed "total immersion." Other thermometers are calibrated so that they will read correctly or nearly correctly when the bulb and a short length of the stem only are in the bath. These thermometers are classed as "partial immersion" thermometers, and the length of the thermometer to be immersed is usually etched on the thermometer.

The error involved in using a "total immersion" thermometer so that the bulb and a short length of the stem only is immersed may be as large as 25°F. if the number of degrees emergent and the difference between the temperature of the bath and the space above it is large.

The general equation used in computing the correction for emergent stem is:

$$\text{stem correction} = Kn(t_1 - t_2)$$

where K = the differential expansion of mercury (or liquid in the thermometer)
and the particular kind of glass used making the thermometer

(K = 0.00016 for most mercury thermometers)

n = the number of degrees of mercury column emergent from the bath.

t₁ = the temperature of the bath

t₂ = the average temperature of the liquid column of n degrees

The value of t₂ is determined by means of an auxiliary thermometer fastened to the thermometer being observed at the midpoint of the emergent column of the liquid.

Two methods for calibration may be used, one using fixed points, the other comparing readings of thermometers with previously calibrated thermometers. The ice point and the boiling point of water and of many other pure liquids may be used in the fixed point, or primary, method. The Bureau of Standards certificate of calibration may be obtained for any well-constructed thermometer at a moderate cost. This calibrated thermometer can then be used for the secondary calibration of other thermometers by comparison of readings when each is properly immersed in close proximity to the other in a suitably stirred bath. Platinum resistance thermometers may be accurately calibrated and also used as a secondary standard.

Any calibration should be performed either with a rising stem (or mercury) or a falling stem. Frequently it may be desirable to calibrate a thermometer both with the mercury stem rising, and then with the stem falling, the calibration being reported as an average of the two calibrations.

Procedure: (Secondary Method)

(1) Calibration for total immersion

Suspend the standard thermometer and the thermometers to be calibrated in a bath so that the mercury stems will be totally immersed over the range through which the thermometer is to be calibrated. The thermometers should be grouped closely together

and no reading should be taken until the bath is uniformly heated. The upper range of calibration of the thermometers is limited by the flash point of the oil in the bath. This point is determined by the open cup method (A.S.T.M.D. 92-33) and the oil from this test may be returned to the bath. The current to the heating coil should be decreased for a few minutes each time before readings are taken to allow the bath to come to a uniform temperature.

Readings are to be taken at frequent intervals throughout the safe temperature range.

(2) Calibration for partial immersion

The standard thermometer is suspended as in part (1). The thermometers to be calibrated may be:

- (a) Flash and fire thermometer (used and calibrated for 1-inch immersion).
- (b) Low-range 40-580°F distillation thermometer (used at 3-inch immersion but originally calibrated for total immersion).
- (c) Thermometers as assigned by instructor.

Suspend the thermometers to the proper immersion point. Fasten an auxiliary thermometer to the thermometer being calibrated so that the average temperature of the emergent stem of mercury may be observed. Take readings on the standard thermometer, the auxiliary thermometers, and the thermometers being calibrated at frequent intervals throughout the calibration range.

(3) A Combination of total and partial immersion method

A combination of calibration methods, (1) and (2), may be made with a fair degree of accuracy provided some simple precautions are observed. All observations should be made with the mercury column either rising or falling between readings.

Suspend the thermometers for partial immersion calibration as described in (2) and observe the readings. Remove the auxiliary thermometers and completely immerse the thermometers. Allow time for the readings to become uniform and take readings for the "complete immersion" calibration.

Return the thermometers to the partial immersion position, and raise the bath temperature. Take readings when conditions are uniform.

Repeat the process at frequent intervals throughout the temperature range.

Report should include:

- (1) Identification of thermometers used.
- (2) Calibration curves for each thermometer.
- (3) Calculated value for K as determined from your data.
- (4) Your value of K compared with handbook values.
- (5) Observations and discussions.

Questions:

- (1) What are the three most important errors in reading thermometers?
- (2) Why should the direction of the movement of the mercury column affect the reading?
- (3) Explain why it is necessary to correct for the "exposed stem."

Experiment 4

THE CONTINUOUS FLOW CALORIMETER

Reference: White, pp. 92-118.

Purpose: To calibrate a wet test meter and to determine the calorific value of city (natural) gas.

Equipment: Calibrated 0.1 cubic foot test bottle, wet test meter, gas calorimeter, weighing buckets and balance.

Theory: The basic standard method for determining the calorific value of gas is by means of the continuous flow calorimeter, such as the Junkers or Sargent type, (Fig. 5). A stream of gas, accurately measured in a calibrated wet gas meter, (Fig. 4), is burned in this calorimeter which is so designed and adjusted that substantially all of the heat generated by the combustion is transferred to a measured quantity of water and the resultant temperature rise of the water determined.

Total Calorific Value is defined by the ASTM Committee D-3 on Gaseous Fuels as "the number of BTU evolved by the complete combustion, at constant pressure, of one standard cubic foot of gas with air, the temperature of the gas, air, and products of combustion being 60°F, and all of the water formed by the combustion reaction being condensed to the liquid state."

Net Calorific Value is "the number of BTU evolved by the complete combustion, at constant pressure of one standard cubic foot of gas with air, the temperature of the gas, air and products of combustion being 60°F, and all of the water formed by the combustion reaction remaining in the vapor state."

The net calorific value is lower than the total calorific value by the amount of heat equal to the latent heat of vaporization, at the same temperature as the gas, of the water formed by combustion. For most heating value calculations, the heat of vaporization of water may be taken as 2.3 BTU per cc. of water condensed.

In actual practice neither the total nor the net calorific value is usually determined directly. The water vapor in the gas and air entering the combustion chamber is rarely equal to the water vapor carried out in the exhaust gas. The amount of condensate collected is usually less than the amount of water formed by combustion. Therefore, the observed calorific value, obtained by multiplying the pounds of water heated in a calorific value test by its corrected temperature rise in degrees F., and dividing by the number of standard cubic feet of gas burned, usually represents a value between the total and the net calorific value of the gas.

Calibration of the wet test meter may be accomplished by (A) passing exactly 0.1 cubic foot of gas measured in a calibrated bottle through the meter, or (B) by collecting the water displaced by the gas passing through the meter during one complete revolution of the meter drum and determining the volume of this gas from the weight and density of the water displaced. In either method the temperature of gas and water must remain constant throughout the test, and the initial and final pressures must be the same.

Procedure: Calibration of the Wet Test Meter.

Method A: Be sure the meter is level before starting the test. In calibrating the meter with the 0.1 cubic foot bottle, the bottle is filled with gas saturated with water vapor at meter temperature and atmospheric pressure. The meter outlet is

open to the atmosphere. By means of the levelling bottle filled with water which is at meter temperature, force the 0.1 cubic foot of gas from the bottle into the meter. Record the reading of the indicating hand before and after each test. A correction factor may be calculated based on the relative volumes of gas actually passed through the meter and that indicated on the dials. A longer and more permanent procedure would be to adjust the water level in the meter so that on subsequent tests each 0.10 cubic foot of gas passing through the meter will rotate the indicating hand exactly one revolution.

Method B: A 0.3 cubic foot bottle is frequently used for the calibration of the wet meter. The bottle is filled with water which is at meter temperature. Gas is saturated with water vapor and passed through the gas meter, the gas collecting in the 0.3 cubic foot bottle. The water displaced by the gas passing through the meter during one complete revolution of the indicating hand is collected, weighed and the temperature noted.

$$\text{Meter C.F.} = \frac{\text{Weight of water collected during one revolution}}{\text{Weight of 0.1 cubic foot of water at temp. noted}}$$

Method A will be used to calibrate the meter used in this test.

Calorific Value Determination

The gas for the calorific value determination is passed through a water bottle to saturate it with water vapor. It then passes through a pressure regulator and the wet test meter and into the burner of the calorimeter. The gas flow is regulated so that about 3000 BTU are delivered to the calorimeter per hour. For manufactured (coal) gas this amounts to almost six cubic feet of gas per hour; for natural gas only three cubic feet per hour are required. Adjustment of the air mixer is set so that the gas burns with a steady blue flame, the yellow color due to incomplete combustion just disappearing.

Before the lighted burner is set securely in place in the calorimeter, a flow of room temperature water is started through the calorimeter. The water enters the instrument under constant head, and, in order to maintain this head, a small stream of water must always be overflowing the weir in the inlet line overflow cup. The burner is then inserted and carefully centered well up in the calorimeter. The temperature of the outlet water will rise rapidly, then soon become constant. The difference between inlet and outlet water temperature is then adjusted by regulating the water flow. A valve for this purpose is located in the inlet water line at a point where it enters the calorimeter. The difference between inlet and outlet water temperature must not be less than 13°F nor more than 18°F. When the calorimeter has reached thermal equilibrium, adjust the flue damper to give a maximum temperature reading at the water outlet thermometer. Preliminary readings may now be taken, recording:

- Barometer temperature in degrees Fahrenheit
- Barometer height to the nearest 0.01 inch of mercury
- Gas meter inlet pressure to the nearest 0.1 inch of water
- Gas meter temperature to the nearest 0.2 degree F

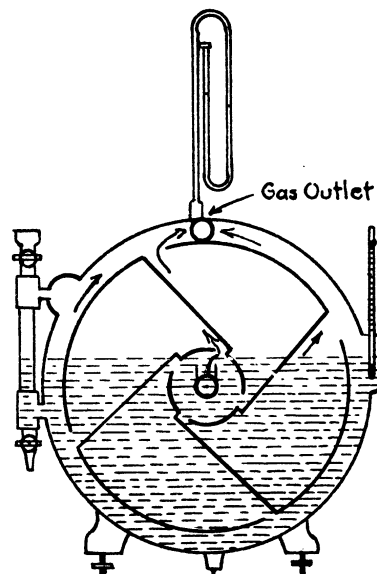


Fig. 4. Wet Test Meter

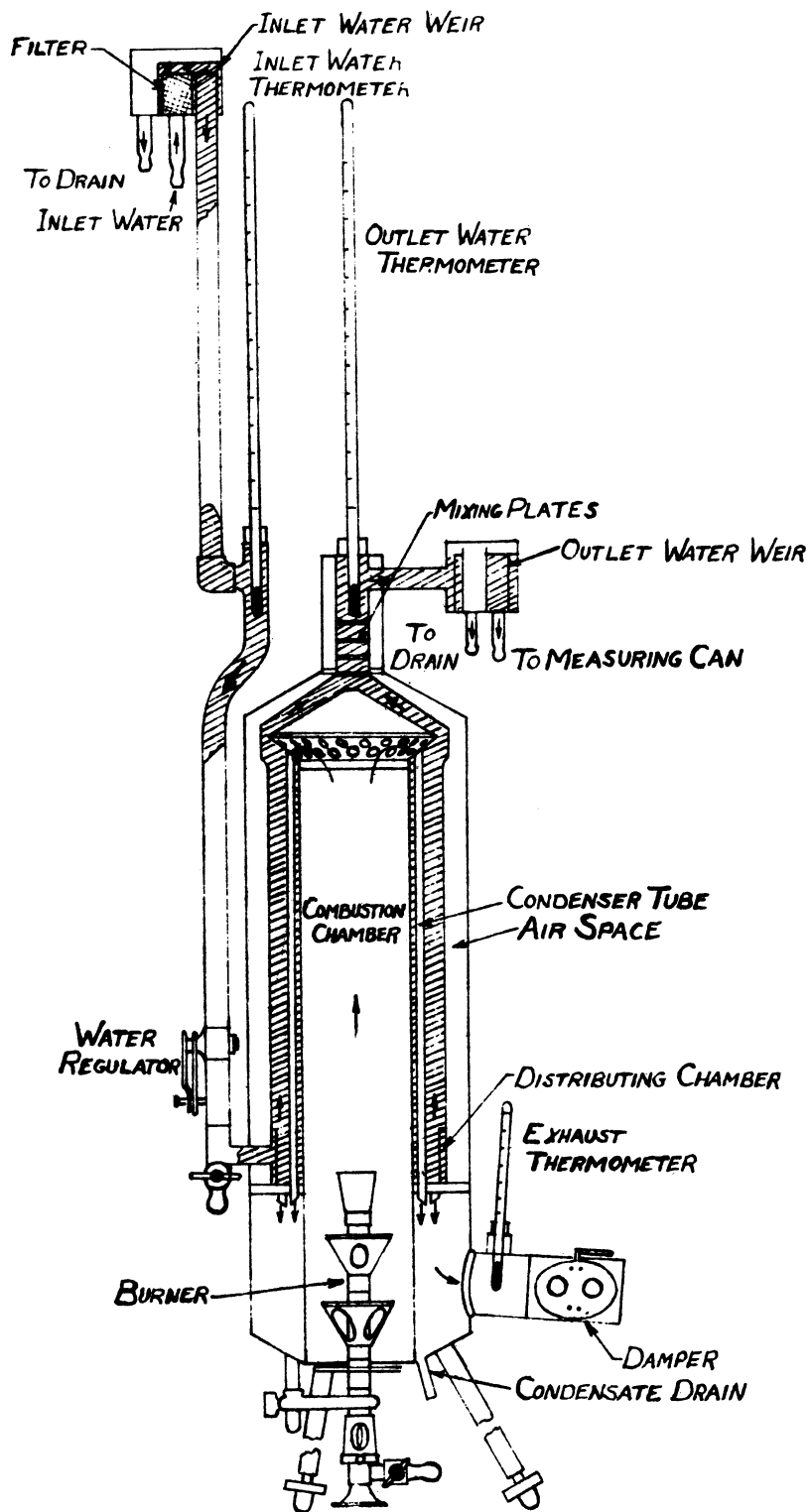


Fig. 5. Flow Calorimeter

Wet and dry bulb thermometer readings of the psychrometer, taken inside the calorimeter cabinet
Flue gas temperature. This temperature should approximate the room and inlet water temperature

By this time condensate from the products of combustion should be dropping at a constant rate from the condensate drain. Check the inlet and outlet water thermometers to make sure that the proper differential is being maintained.

The standard test consists in collecting the water heated and the condensate formed while exactly 0.2 cubic foot of gas, as measured by the meter, is burned.

A test is started by simultaneously reading the inlet and outlet thermometers, placing the 10 ml graduate under the condensate drain, and directing the outlet water into the tared collecting can as the indicating hand of the gas meter passes a zero mark. Continue reading the inlet and outlet thermometers at each quarter revolution of the indicating hand until eight pairs of readings have been taken. As the indicating hand passes the above zero point for the second time, the water is immediately diverted from the collecting can and the condensate receiver removed. The weight of water heated and volume of condensate collected are recorded. The test is repeated for two or three check runs. The preliminary readings are again taken to make sure that no radical changes have taken place in operating conditions.

Calculations and Results

Inlet and outlet water temperatures for each run are averaged. Their difference, with proper thermometer corrections applied is equal to ΔT .

$$\text{Observed Calorific Value (BTU/Cu.Ft.)} = \frac{\Delta T (\text{°F} \times 1 \times \text{pounds of water heated})}{0.2 \times \text{Meter C.F.} \times \text{C.F.T.P.}}$$

Meter C.F. is the correction factor calculated from the data obtained while calibrating the wet test meter.

The gas as measured in the meter is under a pressure substantially equal to atmospheric, which may vary considerably from day to day. The gas temperature may also vary. C.F.T.P. is the correction factor to reduce the gas volume burned to standard conditions, i.e., to 60°F and 30 inches of mercury and saturated with water vapor. This factor appears on a chart near the calorimeter cabinet.

For routine testing, many of the corrections usually applied in precision work may be neglected. The more important corrections are:

1. Thermometer calibration and emergent stem correction (see chart in calorimeter cabinet).
2. Radiation due to difference between inlet water and room temperature. At a room temperature of 70 degrees F., this amounts to 1.26 BTU for total calorific value and 0.82 BTU for net calorific value per cu. ft. per degree F. difference between inlet water and room temperature, when burning 0.2 cubic foot of a gas of about 1000 BTU heating value, (see chart near cabinet)
3. Humidity correction. Total calorific value is based on the condensation of all the water formed from combustion. If the gas and the air entering the calorimeter do not carry enough water vapor to saturate the flue gas some of the water formed in the combustion will be carried out with the flue gas as water vapor.

Report all of the data taken in the calibration of the gas meter.

The total and net calorific values of the gas are calculated for each of four tests at temperature differences assigned by the instructor.

Experiment 6

WATER EQUIVALENT OF THE BOMB CALORIMETER

Reference: White, pp. 258-67, 272-79; Daniels Mathews and Williams, 98-102, 342-50.

Purpose: To determine the water equivalent of a bomb calorimeter. This W. E. (water equivalent) must be known in order to determine the total calorific value of a solid or liquid fuel. (Experiment 7).

Equipment: The calorimetric bomb used in this laboratory (Fig. 6) is described fully in "White," pp. 259-61. The body, with a capacity of about 300 cc., has an octagonal belt around the center which fits into a recessed plate for holding during the process of assembly and filling; the head carries the needle valve for admitting oxygen after assembly, a lead gasket, a straight electrode, and a stirrup electrode for holding the fuel pan; the steel collar screws down over the head and makes the bomb gastight. This compact unit when assembled is immersed in 2,000 grams of water contained in a well-insulated bucket. A stirring device and thermometer graduated to 0.02 degree Centigrade are provided.

Theory: The bomb calorimeter method for the determination of the heating value of solid and certain liquid fuels consists essentially of completely burning a measured amount of the fuel with a large excess of oxygen in the bomb, absorbing the heat evolved by the combustion in the bomb by the water in which the bomb is immersed, and determining the resulting true temperature rise of the bomb and water. The weight of the water is measured. It is necessary to find how many calories are required to heat the metal parts of the bomb calorimeter through a temperature rise of one degree centigrade. This value, expressed as grams of water for convenience of calculation, is called the water equivalent (W.E.) of the bomb.

The water equivalent of the bomb calorimeter is best determined by burning a weighed amount of a substance of known heating value in the bomb, measuring the temperature rise of the bomb and the water in which it is immersed, calculating the amount of heat absorbed in the water and assigning the balance of the heat units available to heating the bomb through the same temperature rise. The calories required to heat the bomb one degree centigrade can then be readily calculated. Since the specific heat of pure water at room temperature is substantially one calorie per gram per degree centigrade, the number of calories required to heat the bomb one degree centigrade would also be the number of grams of water those calories could heat through the same temperature rise, i.e., the water equivalent of the bomb.

The substances usually used as standards of heating value are: sucrose, benzoic acid, and naphthalene. Benzoic acid is the substance best adapted to coal calorimetry and has an accepted total heating value of 6329 ± 2 cal./gram.

Procedure: Weigh accurately into the small crucible about 1.2 grams of fused benzoic acid. Wash the inside of the bomb thoroughly with water. Do not dry. The 5-6 cc. of water remaining in the bomb will thoroughly saturate the oxygen charged, assuring that all water formed during combustion is condensed to a liquid. The heating value obtained in the bomb calorimeter is then the total or higher heating value.

Measure about three (3) inches of the No. 34 iron fuse wire supplied. Fasten the ends securely to the cleaned electrodes in such a way that the wire bends in a half loop touching the benzoic acid only (Fig. 6). A poor contact between iron wire and electrodes usually results in failure to ignite the fuel. Check the continuity

of the firing circuit by means of the dry cell and voltmeter provided. If the same length of wire is burned in every test, the same number of calories will result from its combustion. The heat evolved by the combustion of the iron wire to Fe_3O_4 is 1600 calories per gram.

Assemble the bomb, using the spanner wrench to tighten the collar. Set the needle valve 1-1/2 turns open. Connect bomb to the source of oxygen, being careful to put no strain on the copper connection. Admit the oxygen slowly until the pressure in the bomb is about 20 atmospheres (300 psi.). Close the needle valve and the oxygen supply valve. Disconnect the bomb and test for leaks by immersing the bomb in room temperature water.

If the bomb does not leak, blow off most of the water with compressed air. Attach the copper lead wire to the binding post on the head of the bomb, but be sure that it does not contact the bomb. Set the bomb in the insulated bucket so that it is well centered. Weigh into the tared container exactly 2,000 grams of water the temperature of which is about 2.5 degrees C. below room temperature. Pour this into the bucket. Connect the stirrer. Then set the thermometer in position so that it hangs freely with the bulb about midway between water surface and bottom of bucket, and carefully centered in the space between the bomb and the side of the bucket. Moving the thermometer during test or failure properly to place the thermometer bulb is certain to lead to inaccurate results. Allow the stirrer to run at least three minutes before any temperature readings are taken.

Record the thermometer readings at minute intervals until readings over a five-minute period show a uniform temperature change. Fire the charge by closing the ignition circuit for a moment, observing carefully the time and the firing temperature. After firing, take twelve temperature readings at 1/4 minute intervals. Continue readings at even minute intervals until at least ten more temperatures have been recorded.

After the time-temperature readings have been taken, remove the bomb from the jacket, blow off the water, release the pressure, take the bomb apart, and wash the inside the bomb thoroughly. Loosen the friction rings and remove all particles of iron oxide from the electrodes after each test. The needle valve must never be open more than 1-1/2 turn. After the last test for the lab period, dry the equipment, giving special care to the needle valve which otherwise rusts and becomes leaky. Blow air through this valve, up and back, until it is thoroughly dry.

Calculations: The combustion of benzoic acid, or of coal, or oil, in the bomb calorimeter may take only a few seconds, but it requires several minutes for the heat to be transferred to the water and for the thermometer to register the rise in temperature. During this period heat may be absorbed from, or transferred to, the surrounding atmosphere. Correction must be made for this heat transfer, and the method of Dr. H. C. Dickinson, given in "White," pp. 272-73, for determining the true temperature rise is simple and accurate. This method divides the time of heat transfer from the fuel to the water into an initial and a final period. The duration of the initial period is equal to the time required for 60% of the total temperature rise due to combustion to register on the thermometer. The time from this 60% point until the readings again show a uniform change due to radiation alone is called the final period. The rate of radiation determined during the preliminary five minute period is used to correct for the radiation taking place during the initial period. The last six or seven readings of the test are used to determine radiation during the final period. Determine ΔT^0 graphically for this experiment. Plot the data, time versus temperature, using a good-sized scale especially for the temperature ordinate (Fig. 7). Locate the point of 60% temperature rise and erect a line through it parallel to the temperature ordinate. With the initial radiation period thus determined, the corrected initial temperature may be determined graphically along with the final temperature by extending the initial and final radiation period lines until they

intersect the 60% vertical line. The intersections will give the corrected initial and final temperatures, their difference being the temperature rise, ΔT , corrected for radiation.

The general formula used in calorimetry calculations is:

$$\text{Total Heating Value (cal./gm.)} = \frac{\Delta T (\text{grams water} + \text{bomb W.E.})}{\text{grams of sample}}$$

The water equivalent of the bomb may be calculated when the true temperature rise (ΔT), the weight of the benzoic acid and iron wire burned and the weight of water used, are known.

Report: The report must include the results from at least two good tests.

Questions:

- 1) What would be the effect of incomplete combustion on the W.E. obtained?
- 2) What would be the effect of using the bomb dry on the W.E. obtained?
- 3) Occasionally insufficient readings are taken during the final radiation period. How will this affect the W.E. obtained?

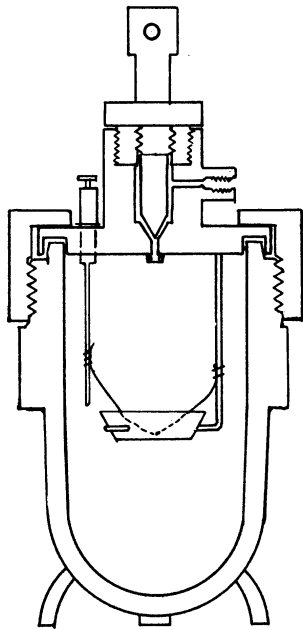


Figure 6. Bomb Calorimeter

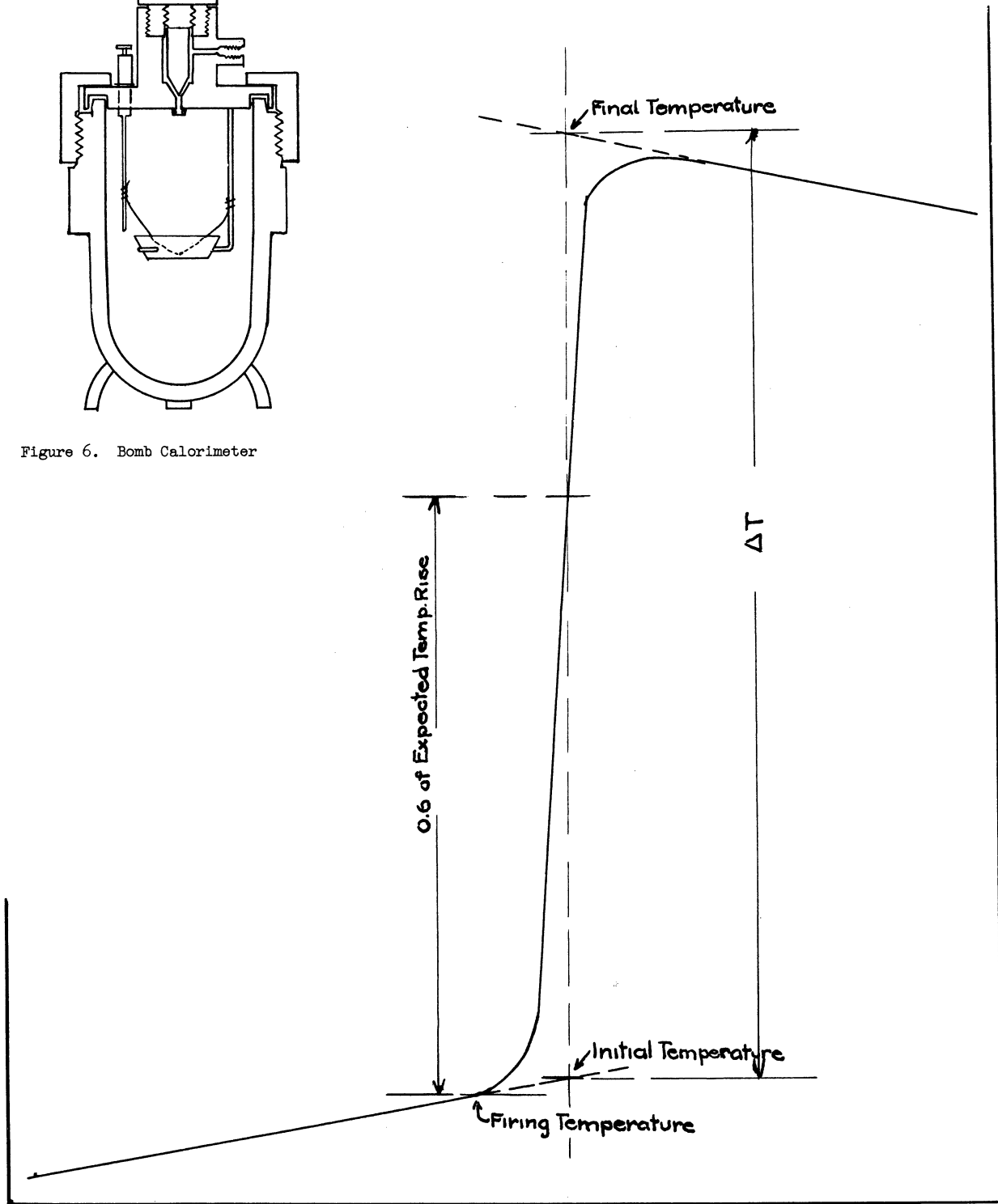


Fig. 7. Plot for Correcting ΔT

Experiment 7

HEAT OF COMBUSTION OF A SOLID OR LIQUID FUEL AND ITS TOTAL CARBON CONTENT

Reference: White, pp. 258-67; 272-81: Ind. Eng. Chem. 19, 1052-54, (Sep. 1927).

Purpose: To determine the total calorific value and total carbon content of coal.

Equipment: Bomb calorimeter, and thermometer as in Exp. 6.

Theory: After the water equivalent of the bomb calorimeter has been accurately determined (Experiment 6), the calorimeter is ready to be used for determining the heat of combustion for any solid or liquid material which can be burned completely in it. The procedure is, in general, similar to that used in determining the W. E. of the calorimeter, excepting that the heat of combustion now is the unknown quantity. A sufficient amount of the material to be tested is burned to give a temperature rise substantially equal to that obtained in the calibration runs, namely about 3 degrees C. Initial and final rates of radiation are measured and the temperature rise, ΔT , due to the combustion, is calculated.

The products of the combustion are CO_2 and water, the latter being condensed to a liquid. At the conclusion of the heat of combustion test, the contents of the bomb are released into a gasometer. The volume of gas from the combustion is measured, CO_2 content is determined, and from these data the total carbon content of the material is calculated.

Procedure:

A. Total Calorific Value

Weigh accurately into the small crucible approximately one gram of coal or 0.7 gram of oil sample. Wash the inside of the bomb thoroughly. Do not dry. (Why not?) Assemble the bomb, charge with oxygen, and conduct the test according to the method outlined on page 272 of the above reference. The algebraic method of the calculation of the corrected ΔT is to be used. The 'expected rise' in temperature for the first run may be obtained by calculations using the W. E. determined in Experiment No. 6 and an assumed T.H.V. for the fuel (14,000 BTU/lb. for an average coal, or about 19,000 BTU/lb. for an oil sample). The 'expected rise' in temperature is calculated by dividing the sum of the grams of water used plus the W.E. of the bomb into the calories available from the fuel weighed. Add 60% of this expected rise to the firing temperature and observe the time required for this reading to register on the thermometer after the charge is fired. This time would be the initial radiation period, and the rate of radiation determined during the first five minutes of reading multiplied by this time would be the amount to add to the firing temperature to obtain the initial temperature. Similarly the final temperature is calculated, and the corrected temperature rise (ΔT) is determined.

Use the calorific value determined in the first test to calculate the expected temperature rise for the second test.

B. Total Carbon Content

All of the products of combustion remain in the bomb after the calorific value test. The carbon is burned to form carbon dioxide, the sulfur is converted to sulfur dioxide or sulfur trioxide and dissolves in the water in the bomb, and the hydrogen burned to water is condensed. The contents of the bomb are expanded into a mercury sealed gas holder and measured at approximately atmospheric pressure and temperature. A sample of this gas is taken from the holder and the carbon dioxide content determined. Three check analyses should be made. The gram moles of carbon in the gas from the bomb is calculated from this, and then the percentage of carbon in the fuel is readily determined.

The Report:

Report the total heating value of the fuel in BTU/lb. and the percentage of carbon in the fuel by weight percent.

Questions:

- 1) What would be the effect of incomplete combustion on the H. V. obtained?
- 2) What would be the effect of using the bomb dry on the H. V. obtained?
- 3) Occasionally insufficient readings are taken during the final radiation period. How will this affect the H. V. obtained?
- 4) How could the calorific value of a volatile liquid be obtained?

Experiment 8a

GRAVITY OF LIQUIDS

Reference: Daniels, Matthews, and Williams pp. 321-325
A.S.T.M. Standards D 287, D 71, D 70.

Purpose: To present three commonly used methods for determining the gravity liquids.

Equipment: a) Hydrometers
b) Pycnometer
c) Westphal Balance

Discussion: Gravity is a property frequently used to identify and classify liquids. It is also used to determine the purity of materials or concentration of solutions.

a) Hydrometers, Fig. 8, depend on the Archimedes principle for their operation. The lower end of the instrument consists of a weighted bulb, the upper end carries a graduated scale. The dimensions of the connecting body will depend on the weight, scale, and purpose for which the hydrometer is designed.

Some hydrometer scales have general application, as specific gravity scales, Baume scales for liquids lighter and heavier than water, and Twaddle, for liquids heavier than water. Other hydrometers are designed and calibrated for a particular purpose or have application in a special industry. In this latter group are found the American Petroleum Institute scale, (A.P.I. Degrees) Salimeter degrees (for reading the percentage of salt in brine), the Brix scale (for sugar,) Balling scale (for the brewing industry), Tralle and Proof scales (for the alcohol industry and the U. S. Customs), and others.

The proper range hydrometer is chosen so that when the hydrometer is carefully immersed in the liquid it rises slightly and the meniscus cuts the scale of the hydrometer. The reading of the scale is made on the line of the bottom of the meniscus.

The temperature at which the gravity measurement is made is observed by means of the thermometer incorporated in the hydrometer, or by the use of a supplementary thermometer.

b) Pycnometers, (weighing bottles,) are used to get comparable weights of equal volumes of liquids. The liquid usually used as a basis for comparison is water, at a specified temperature. The size and design of the pycnometer is determined by the physical properties and the amount of material available for test.

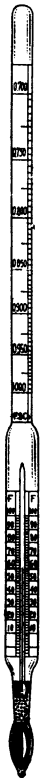


Fig. 8

c) Westphal balance, Fig. 10, consists of a balance with suitable weights or riders, and a plummet. The plummet is completely submerged in the liquid being tested and the buoyant effect of the liquid is measured by balancing the beam with the riders. Calibration is made, using water at a specified temperature as a base or reference point.

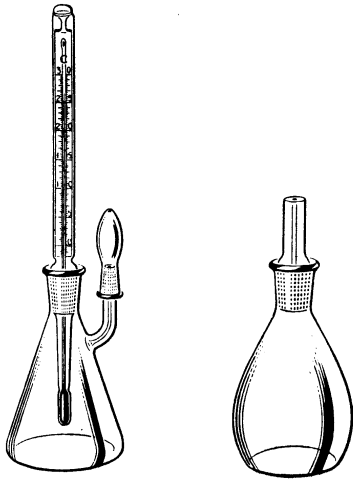


Fig. 9

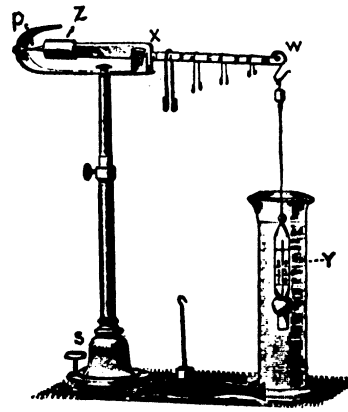


Fig. 10

Experiment 8b

DISTILLATION OF A PETROLEUM PRODUCT

Reference: A.S.T.M. Standards on Petroleum Products and Lubricants, Test Designation D 86-40.

Discussion: The A.S.T.M. Distillation Test of a petroleum product such as gasoline, naphtha, kerosene, or similar products is an empirical method used to measure the boiling characteristics of a material which consists of a mixture of a number of hydrocarbons and therefore has no definite boiling point. A motor fuel suitable for use in hot weather would not have satisfactory starting qualities for use in cold weather. A motor fuel designed to give excellent starting qualities for cold weather use would contain light hydrocarbons in such quantity that use of this fuel in warm weather would result in serious vapor lock in the fuel supply lines and pump. The A.S.T.M. distillation curve is used to differentiate between the various classifications of fuels.

The apparatus used consists of a flask, thermometer, shield and support, heater (gas or electric), condenser, and receiver, or graduate. Each item must conform rigorously to dimensions specified under the A.S.T.M. test designation D 86-40.

Procedure: The condenser is prepared by swabbing dry the inside of the tube and filling the jacket with crushed ice and water. A blotting-paper shield fits over the lower end of the condenser tube to absorb water condensing from the atmosphere and to serve as a cover for the receiver when in place.

The sample, exactly 100 ml. is measured in the graduated cylinder at 55° to 65°F and transferred to the flask. The graduated cylinder is set in place, without drying, to receive the distillate at the lower end of the condenser. The graduated cylinder must not be in contact with the end of the condenser tube until after the Initial Boiling Point has been observed. A bath may be used to maintain the distillate at the same temperature as that at which the sample was measured.

The 100 ml distillation flask is fitted with a well-rolled cork stopper carrying the thermometer. The thermometer, either low range (+30°F to 580°F) or high range + 30°F to 760°F) depending on the boiling range of the product to be tested, is fitted concentrically into the neck of the flask so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapor outlet tube. The flask is supported inside of the shield with the side outlet of the flask fitted snugly into the condenser tube, extending from 1 to 2 inches into the tube.

Heat is applied at a uniform rate so regulated that the first drop of condensate falls from the condenser in not less than 5 nor more than 10 minutes. When this first drop falls from the end of the condenser the reading of the distillation thermometer is recorded as the Initial Boiling Point (I.B.P.)

The graduated cylinder is now moved so that the end of the condenser tube touches the side of the cylinder. The heat is so regulated that distillation proceeds at a uniform rate of from 4 to 5 ml per minute. The temperature and the volume recovered are recorded at regular intervals throughout the distillation. The volume recovered at multiples of 18°F may be recorded. If preferred, the reading of the distillation thermometer may be observed and recorded when the level of the distillate reaches each 10 ml mark on the graduate. This latter procedure is to be followed. No adjustment of the heat shall be made after the liquid residue in the flask is approximately 5 ml

unless the time necessary to bring over the last 5 ml and reach an end point exceeds 5 minutes. The End Point is the maximum temperature observed on the distillation thermometer and is usually reached after the bottom of the flask has become dry.

When the end point is reached the heat is removed and the condensate in the condenser tube allowed to drain into the cylinder. The total volume of distillate collected in the cylinder is recorded as the recovery.

The contents of the flask are condensed, cooled, and then measured in a small graduated cylinder, and the volume recorded as flask residue.

The difference between 100 ml and the sum of the recovery plus residue is recorded as distillation loss.

The sum of the distillation loss plus the recovery is called the volume evaporated or volume distilled.

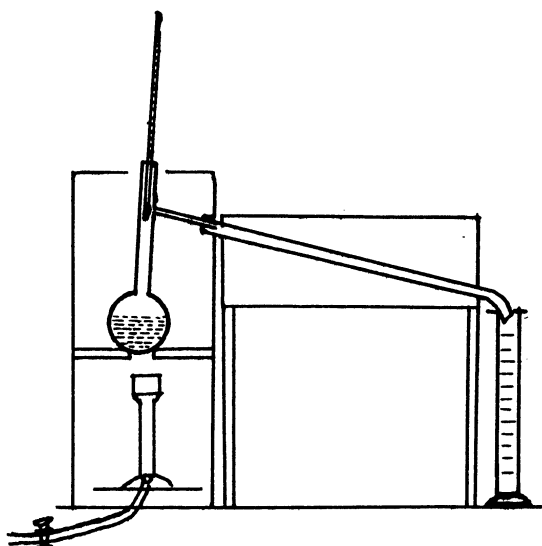


Fig. 11. A.S.T.M. Distillation Apparatus

Results:

Record Time-Temperature-Volume data including Initial Boiling Point, End Point, and all intervening readings. Plot temperature versus volume distilled, taking the distillation loss to occur before the actual distillation begins. Report the gravity of the sample in degrees A.P.I. and also as specific gravity at 60°/60°F

Questions:

- 1) The distillation curve rarely starts at 0% distilled, and rarely ends at 100% distilled. Explain.
- 2) What will be the effect of increasing the rate of distillation?

Experiment 10

VISCOSITY OF LIQUIDS

Reference: ASTM Standards for Petroleum Products, D446, D567, D445 Method B, and D88. Daniels, Matthews and Williams, pp. 35-38, 325-27.

Purpose: To determine the effect of temperature on the kinematic viscosity of a liquid, to measure the density of a liquid and to calculate its absolute viscosity.

Equipment: Electric chronometers marked in 0.2 second, constant temperature baths, and Cannon-Fenske modified Ostwald viscometers.

The viscometer used consists essentially of a capillary through which the liquid being tested is allowed to flow. Two bulbs of reservoirs are above the capillary and a larger one below it. Dimensions of the viscometer are specified in ASTM Standards; Test Designation D-445. These standards specify that a series of viscometer tubes be obtained with varying capillary diameters for use with liquids over a range of viscosities. The diameter of the capillary and the viscosity of the liquid at the test temperature determine the efflux time which must be greater than 300 seconds for viscometers with capillary diameters between 0.5 mm and 0.75 mm., and 100 seconds for capillary diameters greater than 0.75 mm.

Note: The Saybolt Viscometer and the Ball and Bucket Viscometer are available for students wishing to conduct additional experiments in viscosity measurement.

Theory: The viscosity of a fluid is that property of a fluid which determines its resistance to shearing stress. It is due to the internal resistance offered to motion of any portion of that fluid having a velocity different from that of a contiguous portion.

The absolute viscosity, η , of a liquid is defined as the force required to move a plane of unit area at unit velocity with respect to another parallel plane separated by unit distance, the space between being filled with the fluid under observation. This unit of force is termed poise when the unit velocity is one centimeter per second between layers of one square centimeter area and a distance of one centimeter apart. This unit, or its English equivalent, is used in all calculations involving flow. Absolute viscosity may be measured directly using instruments, such as the Ball and Bucket, or the Rolling Ball Viscometer, in which the density of the fluid contributes little or none of the driving force.

Kinematic viscosity, V , expressed as stokes, is defined by the equation:

$$V = \frac{\eta}{d} \quad (1)$$

in which d is the density of the fluid in grams per ml at the temperature of the test and η is the absolute viscosity in poises.

Kinematic viscosity is determined in flow or pipette viscometers such as the Ubbelohde, Ostwald, or Ostwald as modified by Cannon and Fenske.

The kinematic viscosity of a fluid can usually be measured with ease. For this reason it serves primarily as a numerical means for the comparison of the "flow property" of fluids.

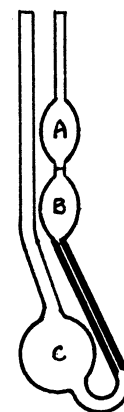


Fig. 12. Modified Ostwald Viscometer

Relative viscosity is the ratio of the absolute viscosity of a fluid to the viscosity of a known standard. If the fluid is a liquid, and the standard is water, the relative viscosity is given by the expression:

$$\frac{\eta}{\eta_w} = \frac{d \times t}{d_w \times t_w} \quad (2)$$

Viscosity may also be expressed in other units, such as the British Redwood viscosity units I and II, the German "Engler Viscosity," and the United States "Saybolt Universal" and "Saybolt Furol" units.

Procedure: Exactly 10 ml of the liquid to be tested is pipetted into bulb C of the tube.¹ Immerse the tube in the constant temperature bath at test temperature so that bulb A will be immersed and the tube fixed in a vertical position. After the liquid has drained into bulb C, and has come to the bath temperature (10 - 15 minutes), suction is applied so that the liquid rises in bulb A about 5 mm above the mark between the bulbs. The suction is released and the time for the meniscus to pass from the upper mark to the lower mark of bulb B is measured. The viscosity of the oil in centistokes is then obtained by multiplying the efflux time by the viscometer constant, C. ($V = C t$)

The constant C is determined by measuring the efflux time for a liquid of known viscosity, usually at 100 degrees F, and substituting the values of V and t in the above equation.

Make several check runs at each assigned test temperature both for the calibration of the pipette and with the unknown sample. Determine the gravity of the unknown sample using the API hydrometers. Convert the gravity reading at room temperature to API at 60°F and to specific gravity by means of the National Petroleum Tables.

The Report

- 1) Calculate the value of the constant C, explaining how it was determined.
- 2) Calculate the viscosity of the samples:
 - a) Kinematic (at two temperatures)
 - b) Absolute (at test temperature and room temperature)
- 3) Draw a graph of logarithm of kinematic viscosity (ordinate) versus the reciprocal of the absolute temperature (abscissa) between $t = 60^\circ\text{F}$ and $t = 210^\circ\text{F}$.

This relationship is substantially a straight line function and the line drawn between the two experimentally determined points on this graph can be used to determine the viscosity of the liquid at other points between, and near to, the test temperatures. Set up a table giving the kinematic and the absolute viscosity of the liquid tested at (about room temperature, at 100°F, at 180°F and 210°F).

- 4) Calculate the specific gravity 60°/60° F for a liquid having a gravity of 0° A.P.I.
- 5) Calculate the specific gravity 60°/60° F for a liquid having a gravity of 100° A.P.I.

1. This deviation from A.S.T.M. procedure is justifiable.

Experiment 21a

GAS DENSITY

Reference: Daniels, Matthews, and Williams, pp. 3-7, 303-11.

Purpose: To determine the density, specific gravity, and molecular weight of gases by the direct weighing method (Dumas).

Equipment: Two weighing bulbs (200 - 300 ml capacity), vacuum pump, analytical balance, calcium chloride drying tubes.

Theory: Equal volumes of gases at the same temperature and pressure contain the same number of molecules, and their weights are, therefore, proportional to their molecular weights. The weights of controlled volumes of various gases are compared to the same volume of a standard gas at the same temperature and under the same pressure.

Procedure: Flush the heavier bulb by evacuating it to less than one mm of mercury pressure (or for four minutes if a manometer is not available) and opening it carefully to air through a drying tube. Repeat this procedure two or three times. Immerse the bulb, but not the stopcock, in the 25°C. constant temperature bath and allow the air to come to bath temperature. Open the stopcock momentarily to allow the pressure of the air to come to atmospheric pressure. Dry the bulb carefully. Place in the balance for 4 to 7 minutes to come to constant weight. Weigh, using a counterpoise bulb which has been similarly immersed and dried.

Evacuate the bulb. Again, fill with dry air, adjust to 25°C, and atmospheric pressure, and weigh. A good check should be obtained.

Obtain the weight of the evacuated bulb, bringing the bulb to 25°C. and drying as before.

Determine the weights of two other gases, being sure that all of the gas from the preceding test has been removed from bulb. Allow the gas to enter the evacuated bulb until a pressure slightly above atmospheric exists in the bulb before immersing in the constant temperature bath.

Extreme care must be taken to prevent any liquid or solid from entering the bulb. If drying tubes are used, solid particles must be filtered from the gas and air supplied. Open the cocks slowly to prevent drawing particles of dust into the bulb. Handling the bulbs excessively will increase the weight. Use a clean cloth for handling the bulbs at all times during the determinations.

Calculations: For purposes of this experiment dry air will be used as the standard gas. The composition of dry air may be assumed to be 20.9% O₂ and 79.1% N₂ by volume. The volume of the bulb is then calculated from the equation:

$PV = (g/M)(RT)$, where g is the weight in grams of the dry air and R is 82.06 ml atm. per degree K per mole. Calculate the density, molecular weight, and specific gravity at standard conditions of each gas.

Questions:

- 1) Should the stopcock on the counterpoise bulb be open or closed between weighings?
- 2) Why should the gas bulb be evacuated and filled several times between tests?
- 3) What, if any, limitations does this method have?

Experiment 21b

GAS DENSITY AND SPECIFIC GRAVITY BY THE EDWARD'S GAS DENSITY BALANCE

Reference: Daniels, Matthews and Williams, pp. 16-19 Technical Paper of the Bureau of Standards, No. 89. "A Specific Gravity Balance for Gases."

Theory: According to Boyle's Law, the density of a gas is proportional to its pressure. The buoyant force exerted upon a body suspended in a gas is proportional to its density, and therefore to the pressures.

Therefore, if the buoyant force exerted upon a body is made the same when suspended successively in two gases, the densities of the two gases must be the same at these pressures; or the densities of the two gases at normal pressure are in inverse ratio to the pressures when of equal buoyant force.

Equipment: The apparatus consists of a balance beam carrying a sealed globe on one end and a counterweight on the other. The balance beam is mounted on its support in an air tight chamber to which is attached a mercury manometer.

Procedure: The chamber and connections are filled with dry air and the pressure adjusted until the beam is balanced as judged by observation through the telescope.

The chamber is then filled with the gas to be tested and the pressure adjusted until the beam again balances at the same zero point.

Calculations: Let d_a be the density of air at some standard pressure P_0 , and d_g the density of the gas to be tested at the same pressure P_0 . Let P_1 be the pressure at which the beam balances in air and P_2 the pressure at which it balances in the gas. The buoyant effect of the air displaced by the globe equals

$$kd_a \frac{P_1}{P_0}$$

The buoyant effect of the gas displaced by the globe equals $kd_g \frac{P_2}{P_0}$, k being a constant which depends upon the difference in external volume of the balance globe and of its counterweight. These forces are equal, since the buoyant force must have been the same to bring the beam to the same position.

or:

$$kd_a \frac{P_1}{P_0} = kd_g \frac{P_2}{P_0}$$

and $\frac{P_1}{P_2} = \frac{d_g}{d_a}$ = specific gravity of the gas.

Experiment 22

EFFUSION OF GASES

Reference: Daniels, Matthews and Williams, pp. 11-16, 311-315; Ind. Eng. Chem., Anal. ed., 15, 647.

Purpose: To demonstrate the molecular properties of gases, and from these compute molecular weights, molecular diameters, and the number of collisions per second per milliliter.

Equipment: Effusion apparatus and timer.

Theory: The theory of this experiment is treated fully on pp. 11-15 of Daniels, Matthews and Williams. This must be read carefully before proceeding with the experiment.

Procedure: The levelling bottle filled with mercury is used to regulate the flow of gas in and out of the calibrated bulb. The capillary tube attached with a piece of rubber tubing is taken off and that opening used as a vent when gases are introduced into the glass bulb. The other opening having the fine hole must not be touched. When introducing gases that may be wet, a drying tube must be used. All gases must be introduced very carefully and slowly.

The bulb is flushed thoroughly with a gas whose molecular weight is known. In this experiment, oxygen will serve for this purpose. The levelling bottle is placed on the stand so that the mercury can displace the gas from the bulb. The time required for the mercury meniscus to pass from the lower mark to the higher mark on the bulb is recorded.

Five successive determinations are made for gas escaping through the pin hold and five for the capillary tube. The same determinations are then made on air and carbon dioxide, keeping the levelling bottle at the same height while timing the flow. It is necessary to exercise considerable care in working with carbon dioxide since it cools rapidly on expansion and it may be necessary to let it stand in the tube till it warms to room temperature.

The Report: Oxygen gas is used as the standard in this experiment. Its molecular weight is 32.00 and its molecular diameter is 2.98×10^{-8} centimeter. Make all calculations on the basis of a temperature of 25 degrees C and a pressure of 760 mm of mercury. Using equations (3), (4), and (5) in the textbook, calculate the following quantities:

- (1) Molecular weight of air and carbon dioxide.
- (2) Molecular diameter of air and carbon dioxide.
- (3) Number of collisions per second per milliliter for oxygen, air, and carbon dioxide. List all these quantities in tabular form. Answer the following questions:
 - (1) List three practical applications of this experiment.
 - (2) Why is the time for flow of carbon dioxide compared to oxygen in the pinhole reversed when flowing through the capillary?

3. What property of a gas makes its flow through capillary tubing a fundamentally different phenomenon to flow through a pin hole?

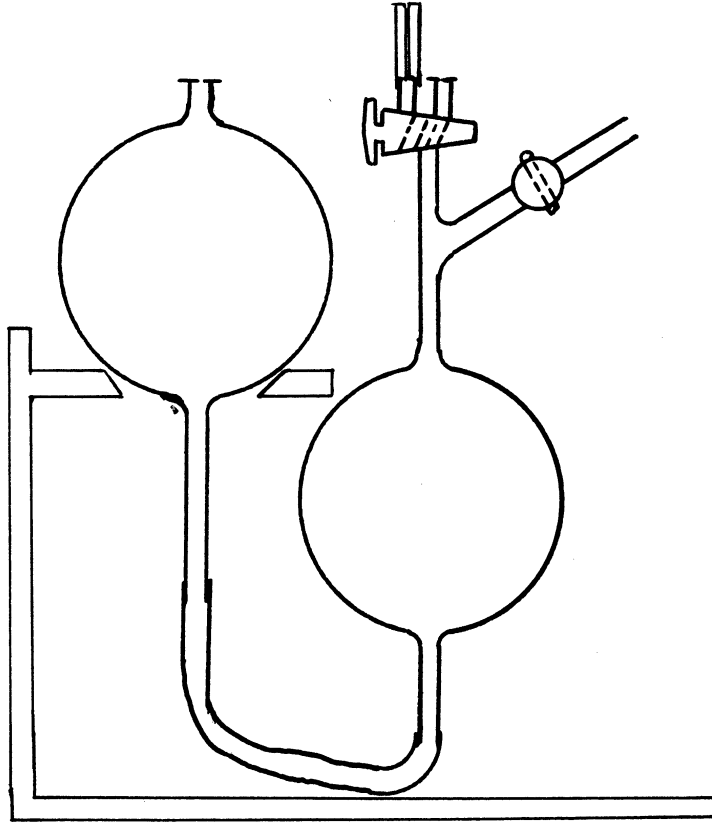


Fig. 13. Gas Diffusion Apparatus

Experiment 23

VAPOR PRESSURE OF LIQUIDS, MODIFIED RAMSAY-YOUNG METHOD

Reference: Daniels, Matthews, and Williams, pp. 20-23, 319-320.

Purpose: To study the effect of pressure on the boiling point of a liquid and to correlate the ratio of change of pressure with temperature and the latent heat of this liquid by means of the Clausius-Clapeyron equation.

Equipment: Modified Ramsay-Young apparatus, thermometers, heater, aspirator, and manometer.

Theory: Some molecules of a liquid, due to their kinetic energy, tend to leave the liquid and escape into space, moving about freely as gaseous molecules. If the liquid is placed in a closed vessel so that the molecules cannot leave the confining space, a pressure is produced and some of the molecules in the vapor space will return to the liquid (condensing) while other molecules are entering the vapor space (evaporating)

When the rate of condensing just equals the rate of evaporation a state of dynamic equilibrium is established, the pressure read on the manometer is equal to the vapor pressure of the liquid, and the liquid boils steadily.

If the pressure on the liquid (in the vapor space) is increased the liquid will stop boiling. When the temperature of the liquid is increased the vapor pressure increases. More and more molecules leave the liquid due to their increased kinetic energy and a state of equilibrium can again be established when the pressure exerted by the vapor becomes equal to the pressure exerted on the liquid.

The ratio of the change of vapor pressure with the temperature is closely related to the latent heat of vaporization of the liquid. This relationship is expressed approximately by the Clausius-Clapeyron equation.

Procedure: Evacuate the apparatus until the liquid being studied begins to boil. Shut off the system (flask, condenser, manometer, etc.) so that the pressure in the system is maintained, and the aspirator is left vented. Gently increase the temperature of the liquid. When the liquid is boiling smoothly and the pressure remains constant, record manometer reading and the temperature. Increase the pressure on the liquid slightly. Raise the temperature as before and observe the temperature and pressure when dynamic equilibrium has been reached.

Repeat this process covering the range of pressures from the vapor pressure of the liquid at room temperature to that at one atmosphere.

Note: Will it be necessary to apply emergent stem corrections to some of the temperature readings? (See Experiment 3, Calibration of Mercury Thermometers).

The Report:

- (1) Plot the experimental vapor pressure against temperature.
- (2) Plot accepted vapor pressures (taken from tables) on this graph for comparison.
- (3) Plot the logarithms of the vapor pressure against the reciprocals of the absolute temperatures. This should give a nearly straight line, the equation having the general form

$$\log P = \frac{-A}{T} + B$$

- (4) Calculate values for $-A$ and B . Test by substituting into this equation two or three observed temperatures and solving for the corresponding vapor pressures.
- (5) Compute the latent heat of vaporization of the liquid at two temperatures, one at room temperature, and one at one atmosphere of pressure.

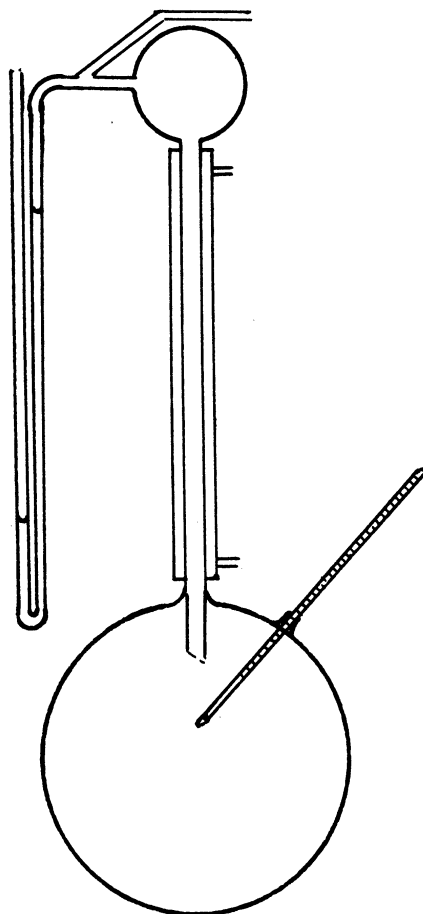


Fig. 14. Vapor Pressure Apparatus

Experiment 24

VAPOR DENSITY OF LIQUIDS--VICTOR MEYER METHOD

Reference: Daniels, Matthews and Williams, pp. 7-11, 303-304.

Purpose: To determine the molecular weight and vapor density of a volatile liquid by finding the volume occupied by a definite weight of the liquid under observed temperature and pressure. These properties are important in industry and research to identify and determine the purity of certain liquid materials.

Equipment: The apparatus used is the Weiser modification of Victor Meyer's apparatus. The assembled apparatus is shown in Fig. 9.

Theory: Equal volumes of ideal gases at the same temperature and pressure contain the same number of molecules, and their weights are, therefore, proportional to their molecular weights. The weight of the material is determined in the liquid state and the material is then vaporized. This vapor displaces an equal volume of air from the vaporization tube. By measuring the air displaced under known conditions of temperature and pressure, the volume of vapor formed from the liquid sample can be determined.

Procedure: Place the vaporizing tube in the steam jacket and bring to constant temperature. The water in the steam jacket must be kept boiling at a uniform rate throughout each test. Pass a stream of dry air through the vent into the vaporization tube so that all of the vapor is removed from the tube. Close the vent clamp. The dry air in the tube is at constant temperature when no bubbles are displaced through the delivery tube at the water seal.

A small glass ampule with a tight-fitting glass stopper is used for weighing the sample to the nearest 0.5 mg.

When constant temperature has been established, place the endiometer tube filled with distilled water over the tip of the delivery tube, but not resting on it. Open the clamp at the vent slightly. Remove the rubber stopper at the top of the vaporization tube, and drop in the ampule followed by its glass stopper which has previously been loosened. The rubber stopper must be replaced immediately and the clamp must also be closed at the same time. If too much time is consumed in this operation, part of the vaporized sample will be lost. It requires a very few seconds for the vapor pressure of the liquid sample to be made sufficiently high to cause a serious loss of gas from the system.

As the liquid is heated, it will vaporize and will displace some of the air which will bubble into the eudiometer tube. Since care has been taken to keep the temperature of the vaporization tube constant, the volume of air displaced into the eudiometer tube

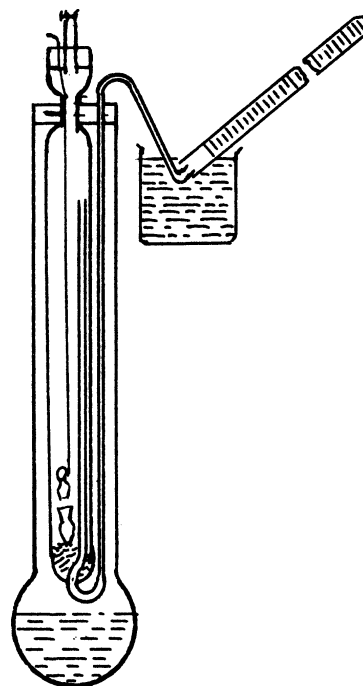


Fig. 15. Vapor Density Apparatus

will be equal to the volume of vapor formed from the vaporized liquid. After 6 minutes have elapsed from the time of the last observed air bubble delivered, the eudiometer tube may be transferred carefully to a water bath in which it is submerged. Allow time for the gas to come to the temperature of the water bath. Record the temperature of the water bath. Adjust the eudiometer tube so that the volume in the eudiometer tube is at atmospheric pressure. Read and record this volume. Repeat the test until three trials are obtained which check within 2% of each other as shown by rough calculations. Do not attempt to recover any of the ampules from the vaporization tube. Leave the vaporization tube dry.

Cautions:

1. When heat is removed from the boiling tube, the tip of the delivery tube must be raised above the water level else cooling will suck water into vapor tube.
2. Weigh the sample not more than 10 minutes before use to minimize error.
3. The apparatus is fragile. Do not turn the steam jacket stopper or else the delivery tube will be twisted and broken.

The Report:

The report will include the molecular weight and vapor density at STP for each trial.

Questions:

1. Why is it essential that all water vapor be removed from the vaporization tube?
2. What property of the liquid limits the application of this method of determining molecular weight?

Experiment 25

SURFACE TENSION

Reference: Daniels, Matthews, and Williams. pp. 24-35, 415.

Purpose: To demonstrate a method for determining surface tension and to study the effect of varying concentrations of solutes on the surface tension of a solvent.

Equipment: DuNuoy Surface Tension Apparatus.

Theory: The phenomenon of surface tension is a manifestation of molecular attraction. It is apparent that the molecules lying in the surface of a liquid are uniquely situated with respect to the forces of attraction due to other molecules. As a result of molecular attraction the molecules at the surface are pulled inward by other molecules of the liquid and tend to form a minimum surface area. This behavior is apparent in drops of liquid which tend to form a spherical shape, in the capillary rise of liquids, and in the wetting effect.

The surface tension of a liquid, γ , is the force, usually expressed as dynes per centimeter, on the surface of a liquid which opposes the expansion of the surface area.

The surface tension of a liquid can be measured by pulling a wire, straight or circular, through the surface of the liquid being examined. The pull M in grams is measured by any suitable instrument. The length l of the surface upon which the pull is exerted equals twice the mean length L of the wire. From this, surface tension is calculated by:

$$\gamma = \frac{Mg}{2L}$$

where g is the gravitational constant.

Procedure: Torsion (Ring) Method: Calibration of the instrument is obtained by first setting the indicator on the dial to read zero when the beam is suspended in a horizontal position and then loading small weights on the ring and determining the pull (reading on the dial) necessary to again bring the beam to its original (zero) position. Repeat several times to cover the range of the scale. The length of the wire may be 4. or 6. cm and is usually marked on the container. Using the above equation, calculate the dynes per cm for each dial reading. From this a proportionality factor for all dial settings may be obtained. On some instruments, the length of the beam can be adjusted to make the dial read directly in dynes/cm.

The force to lift the ring through the surface of the liquid may also be measured by means of an analytical balance.

The test consists of determining the surface tension of various solutions. Scrupulous cleanliness is of utmost importance. The ring and containers must be kept very clean. The ring is carefully washed in warm chromic acid solution, several times in distilled water, and then heated to dull redness momentarily in a Bunsen flame. Suspend the ring from the beam and adjust to zero balance. Place the liquid in its container on the platform below the ring and raise the platform until contact with the ring is made. Slowly lower the platform and simultaneously increase the torsion of the wire so that the beam remains suspended. Continue this movement slowly. The reading of the dial at the moment the ring detaches from the liquid is used to calculate the surface tension of the liquid. Repeat this process several times for each liquid to be tested. The ring is cleaned between change of solutions only.

Temperature has an important effect on the surface tension of a liquid. Test all liquids at constant temperature, preferable at 25°C. Determine the effect of increasing or decreasing the temperature on surface tension, for one solution concentration.

Report: The report should include graphs showing the relationship between the surface tension and the concentration of the solvents. If possible express the concentration in mol percent.

Question:

- 1) How does the surface tension of a solution affect its wetting properties?
- 2) Why is the absolute surface tension not obtained by the above procedure?

Experiment 27

DISTILLATION OF BINARY MIXTURES

Reading: Daniels, Matthews and Williams, pp. 44-50, 78-82, 316-319.

Purpose: To determine the liquid-vapor equilibrium composition of a binary mixture, and to use the Abbe' Refractometer.

Equipment: Special distilling flask, thermometer, condenser, immersion heating coil, adjusta-volt transformer, liquids, refractometer.

Procedure: In order to make rapid determination of the composition of the condensed vapor and liquid samples, the Abbe refractometer is used. It is necessary to know the relationship between the refractive index and the composition of the solutions. When this information is not available, it must be ascertained by making several solutions of known composition and measuring the refractive index of these solutions. Values of refractive index at 25 degrees C for the benzene-methanol system and benzene-butanol system are given below at several concentrations. These values should be plotted and this curve used during the test in the analysis of the solutions used and the distillation samples.

Benzene Mol.%	Refractive Index at 25°C	
	Benzene-Methanol	Benzene-Butanol
100	1.498	1.498
85	1.487	1.482
70	1.472	1.466
50	1.446	1.446
30	1.411	1.426
15	1.375	1.412
0	1.328	1.398

Several different solutions of benzene and methanol or benzene and butanol are prepared to give the desired range in composition. Each of these solutions is to be distilled in turn. A sample of condensed vapor and residue (at equilibrium) is to be taken for analysis for each of these solutions distilled. The boiling point of each mixture is also to be observed.

Set up the apparatus. **BE SURE THAT THE TRANSFORMER SWITCH IS IN THE "OFF" POSITION, THAT THE VOLTAGE IS SET AT ZERO, AND THE SCALE SWITCH IS SET FOR "LOW"!** CAUTION: The heating coil must be covered with liquid at all times when heating.

Pour 100 to 150 ml. of pure benzene (enough to cover the heating coil completely) into the distilling flask. Turn the transformer switch to "ON", and gradually increase the voltage from ZERO to not over TEN VOLTS. The liquid should begin to boil rather vigorously after two or three minutes of heating. It may be necessary to increase the voltage a little. Do this cautiously until boiling occurs. Allow the solution to boil for 5 minutes to reach equilibrium. Read and record the boiling temperature.

Take a sample of the condensed vapor by lowering the sampling tube through the top of the condenser and determine its refractive index at 25°C. The sampling tube is 5 mm glass tubing with a piece of rubber tubing on one end and a fine tip on the other. The rubber tubing is closed off with a clamp. A sample is taken by immersing the tip in

the trapped condensate, squeezing the rubber tubing as if it were the bulb of a medicine dropper, and extracting about 1/2 cc of sample. Leave the heater on while sampling the condensed vapor.

Snap off the current to the heater. After boiling ceases, take a sample of the residue and read its refractive index. Clean the refractometer and the sampling tube.

CAUTION: The prisms of the refractometer are of soft glass and easily scratched. Never allow the prisms to be touched by glass (as from the sampling tube), cloth, or anything but the liquid sample and the soft cleaning paper provided.

Repeat for the next solution, and continue until all solutions have been tested. It is not necessary to dry the flask thoroughly between each solution. However, it is necessary to dry the flask before distilling a pure liquid, such as benzene, methanol, or butanol.

Results: Plot the boiling temperature versus equilibrium liquid-vapor composition for the system studied.

Report the temperature and composition of the minimum boiling mixture.

Questions:

- 1) What is an ideal solution?
- 2) What is a non-ideal solution?
- 3) Which solution does the system studied represent?

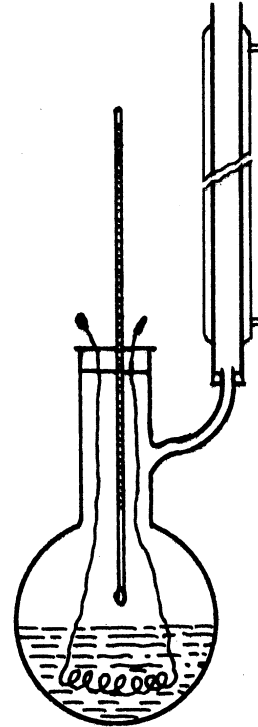


Fig. 16. Distillation Apparatus

Experiment 28

STEAM DISTILLATION

Reference: Daniels, Matthews, and Williams, pp. 91-94, 452.

Purpose: To illustrate the principle of steam distillation and to show that the molecular weight of the less volatile constituent can be calculated from the partial pressures of the distilling vapors and the weights of the respective liquids obtained in the distillate.

Theory: The principle of steam distillation obtains only when the liquid to be distilled is immiscible with water. If the two liquids were miscible, then their separation would depend on a distillation process known as rectification. Two immiscible liquids in contact will obey Dalton's law of partial pressures in a fashion similar to that of a mixture of gases. For miscible liquids the vapor pressure of the mixture is not the sum of the partial pressures of the components in general, but for immiscible liquids, the total pressure is the sum of the partial pressures.

By referring to Fig. 10, this principle may be easily seen. Suppose curve A represents the vapor pressure curve for water and curve B the vapor pressure curve for the immiscible liquid. The boiling points at atmospheric pressure are represented by t_A and t_B . For a given binary system, there is only one temperature possible (at equilibrium) for distillation. That temperature is determined by the vapor pressures. If the distillation is carried out at atmospheric pressure, then the total pressure must be equal to P_A plus P_B , the vapor pressures of A and B respectively at t_{AB} . Thus, the following relationship holds:

$$\frac{WtA}{WtB} = \frac{\text{Vapor pressure A} \times \text{M.W.A.}}{\text{Vapor pressure B} \times \text{M.W.B.}}$$

Steam distillation is of considerable importance in industrial practice. Fats, vegetable oils, and many other substances are purified in this manner. Why?

Procedure: The laboratory apparatus is set up according to Fig. 26, (D.M. and W.). Do not put too much water in the steam generator, else it will boil over when heated. Before starting the distillation it is necessary to make a meniscus correction as described on page 93 of the above reference. It should be understood that precise work would necessitate the calibration of the graduates used to measure the volume of the distillate. For the purposes of this experiment, it may be assumed that the graduates read correctly and thus the calibration may be omitted.

Pass live steam through the flask to correct for the exposed stem and errors in the thermometer. Place 300 to 350 ml. of the unknown liquid in the distillation flask. Be sure that cooling water is passing through the condenser. Distillation is maintained at constant rate by passing live steam through the samples in the flask.

CAUTION: Keep the inflammable organic liquid away from the flames of the Bunsen burner.

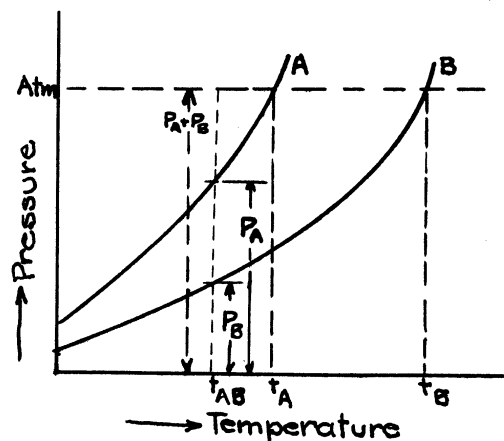


Fig. 17. Vapor Pressure-Temperature Curve

Discard the first 10 to 20 ml of distillate. Read temperatures and volumes of distillate collected at one-minute intervals until three 100 ml samples of distillate are obtained. Distill slowly, not over 7 ml per minute. Why?

Record the barometric pressure and room temperature at the beginning and end of the experiment.

Disconnect the steam generator first, and then turn out the fire. Why?

Read the volumes of water and organic liquid as carefully as possible and record. Take the temperature of the distillate. The density of the water at this temperature may be determined from the literature. The density of the organic liquid must be found by using the Westphal balance.

DO NOT DISCARD the organic liquid: Decant most of the water and put the organic liquid distillate in the bottle provided.

Calculations and Results:

Consider each 100 ml sample of distillate as a separate test. Calculate the molecular weights of the unknown liquid.

Questions:

- 1) Enumerate the sources of error in this equipment.
- 2) What limits the application of this method of distillation?
- 3) What are the advantages gained by this method?
- 4) Why must the thermometer bulb be in the same position during the steam run and the steam distillation?

Experiment 29

SOLUTIONS - PARTIAL MISCIBILITY

Reference: Daniels, Matthews, and Williams pp. 89-91.

Reading: McKelvey and Simpson J.A.C.S., 44, 105 (1922)

Object: To study the effect of temperature on partly miscible liquids, and to determine their critical solution temperature.

Equipment: Thermometer, stirrer, test tubes, jackets, water bath.

Theory: When two partly miscible liquids of different densities are well stirred and allowed to settle, two phases will separate out through some range of temperature. Solubility usually increases with temperature so that a similar composition in both phases is approached as temperature is increased and the two phases form a homogeneous liquid. Cooling separates the liquids into two phases again, the transition being marked by a sudden turbidity which clears up on standing. By varying the initial amounts of the two liquids, the complete solubility curve can be obtained.

Procedure: Weigh carefully about 10 gms of one of the liquids into the apparatus.

Add a small amount of the second liquid (to give a 5 to 10 weight per cent mixture). Stir thoroughly. If the mixture appears as a homogeneous liquid the mixture is above the temperature of mutual solubility. Cool or warm the mixture with stirring until the turbidity appears and the mixture clears again. Observe this temperature. Cool (or warm) the mixture very slowly and record the temperature at which the first turbidity appears. The experiment is repeated once or twice and the mean of the temperatures at which turbidity appears and disappears is taken as the temperature at which the liquids, in the particular proportions taken, become completely miscible.

Add small increments of the second liquid and continue the experiment until sufficient data have been obtained to make a good temperature-composition curve for the mixture over the entire composition range.

Report:

- 1) Plot the transition temperature as ordinate versus the percentage amount of one liquid. Use both weight and mol percent.
- 2) Define the "critical solution" temperature and "consolute" temperature and report these values for your experiment.
- 3) Discuss the degrees of freedom of the system at two widely separated temperatures.

Experiment 30

FREEZING POINT CURVE OF A BINARY MIXTURE

Reference: Daniels, Matthews, and Williams, pp. 151-154.

Purpose: To determine and plot the equilibrium diagram of a binary mixture by observing the freezing temperature of definite mixtures covering the entire range of composition. From the intersection of the curves, the eutectic compositions and temperatures are determined.

Equipment: Water baths, test tubes (1" x 8"), stirrers, thermometer.

Theory: The phase diagram of a binary system may be experimentally determined by varying the composition and finding the transition temperature between phases. The pressure must remain constant.

Procedure: Determine the freezing point of the two pure components. Weigh 7-8 grams of the pure constituent into a test tube fitted with a cork. After weighing, replace the solid cork with one fitted with a thermometer and stirrer. Melt the constituent in a bath. Cool with stirring and observe the approximate freezing point. Remelt and cool again. This time remove the test tube from the cooling bath when the temperature is within 0.5°C of its freezing point. Dry the tube and place it in a larger test tube as a jacket to retard the rate of cooling. Continue the stirring at a regular rate until the true freezing point is observed. Supercooling below the freezing temperature should be restricted to 0.2 to 0.4 degree by stirring, or by touching the edge of the freezing tube with ice, or by the introduction of a minute crystal of the constituent crystallizing out.

CAUTION: BOTH PHENOL AND PARA-TOLUIDINE ARE CORROSIVE TO HUMAN FLESH AS WELL AS TO BALANCE PANS. Furthermore, phenol is very hygroscopic, so weigh it in a stoppered test tube in which the test is to be conducted.

The freezing points of definite mixtures are then determined in a similar manner until sufficient data are obtained to plot the equilibrium diagram for the system.

The Report: Tabulate the freezing temperature for each composition, expressed as mol per cent. Plot the freezing temperature, or transition temperature, as ordinate versus composition in mole percent. Join the points by smooth curves, locating the eutectic compositions and temperatures. Draw horizontal lines corresponding to the experimentally determined eutectic temperatures. Draw lines on the diagram dividing it into characteristic regions and label each area with the names of the phases represented there.

Experiment 31

HEAT OF SOLUTION

Reference: Daniels, Matthews, and Williams, pp. 107-111, 350-352.

Purpose: To measure the heat effect produced by dissolving chemical compounds in solvents. Theoretically, the heat of solution may also be correlated with the heat of dilution and temperature coefficient of solubility.

Equipment: Thermometer, vacuum bottle, heating coil, voltmeter, rheostat, stop watch, storage battery, stirring rod.

Discussion: From the first law of thermodynamics the following equation is derived for a batch or non-flow reaction proceeding at constant pressure.

$$\Delta H = q$$

Where $H = U + PV =$ enthalpy
and $U =$ internal energy
 $P =$ absolute pressure
 $V =$ volume
 $+q =$ the heat absorbed by the system
from its surroundings

The increase in enthalpy resulting from the isothermal solution of a solute in a solvent is called its heat of solution. This heat effect may include ionization, hydration or solvation effects. If the heat of solution is endothermic, q is positive and heat is absorbed from the surroundings in the isothermal formation of the solution or the temperature of the solution drops for the adiabatic solution of the solute.

Chemical literature sometimes uses the term, Q_s , the heat of solution defined as the heat liberated by one gram mol of dissolved solute. Thus: $-Q_s = q = \Delta H$.

If the adiabatic ($q = 0$) solution of a pure solute in a pure solvent to form a given concentration results in a decrease in temperature of the solution, the heat evolved by the solvent (or the heat absorbed by the reaction) is called the endothermic integral heat of solution and is equal to $-q$. This heat may be measured in an insulated Dewar flask by adding sufficient heat from a thermally insulated electrical heater to return the solution to its original temperature.

Procedure: In carrying out the experiment, the resistance of the heating coil is first determined by means of the resistance test set. A constant resistance wire is used which makes corrections for changes in resistance at higher temperatures unnecessary.

Connect the circuit as shown in the diagram (Fig. 18).

A small sample of the solute is weighed in a glass tube having a thin-walled bulb blown on one end. This sample tube is placed in the vacuum bottle together with a thermometer (marked to 0.2 deg. C), the stirring rod, and the resistance coil. Add enough distilled water (carefully measured) to cover the thermometer bulb and sample bulb. This may require 175 to 200 ml. Use as little as possible, but no less than 150 ml. The slide-wire rheostat is adjusted to give a current of 0.3 ampere. The temperature is set approximately at room temperature.

CAUTION: The solute is weighed out accurately in the thin-walled glass tube. Record the temperature of the water. Carefully break the bottom of the sample tube

(avoid damaging the vacuum bottle), by tapping the push rod gently. Stir. Close the switch to the heating circuit and start the stop watch simultaneously. Time the flow of current with the watch until the original temperature is restored.

Two or three successive determinations may be made by adding small increments of solute to the existing solution resulting from the addition of the previous samples.

Calculations: Calculate the heat supplied to the calorimeter in calories for each increment of solute. Determine the total number of moles of solute per 1000 grams of water after each addition of salt and the corresponding cumulative heat losses. Draw a graph showing these heat effects as a function of the concentration of solute per 100 grams of water.

Draw tangents to this curve and determine the slope at two different concentrations and at infinite dilution. These slopes give the differential heat of solution at the different concentrations and are equal to

$$\partial q / \partial n$$

where "q" is the total heat effect, and "n" is the number of moles of solute.

Questions:

- 1) Define (a) the differential heat of solution.
(b) the integral heat of solution.
- 2) Compare the experimental results at several different concentrations with those in the literature.
- 3) How would the heat of solution of an exothermic salt be determined experimentally?

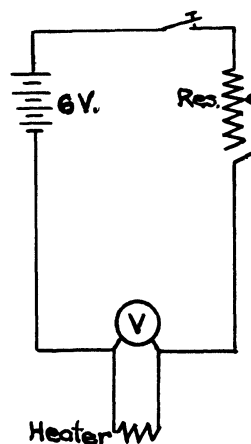


Fig. 18. Heater Wiring Diagram

Experiment 32

DISTRIBUTION OF SOLUTE BETWEEN IMMISCIBLE SOLVENTS

Reading: Daniels, Matthews, and Williams, pp. 143-146.

Apparatus: Three 100 ml separatory funnels; three 100 ml erlenmeyer flasks; 100 ml volumetric flask; 1 N acetic acid; 0.5 N NaOH; CO₂ free water; burette; phenolphthalein; solvents; thermostat.

Discussion: If a solute is added to two immiscible or nearly immiscible liquids at constant temperature and pressure, the solute will distribute itself between the two liquid phases in a definite manner so that the following relationship is satisfied:

$$(1) K = \frac{C_1}{C_2}$$

Where K = a constant at fixed temperature and pressure

C₁ = Concentration of the solute in phase 1

C₂ = Concentration of the solute in phase 2

The rule that the chemical potentials of any substance must be equal in two phases in equilibrium can be used to derive the above law. This proof is limited by the assumptions of dilute solutions and ideal behavior and the assumption that the solute does not affect the solubility relationship of the two immiscible liquids.

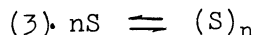
In the case of either ionization or association of the solute in one or both of the two liquid phases, the distribution law must be modified to apply only to each individual species or unchanged molecule.

$$(2) K = \frac{(1 - F_1) C_1}{(1 - F_2) C_2}$$

Where (1-F₁) and (1-F₂) = The total fraction of the total amount of solute which dissociated or associated in phases 1 and 2 respectively.

F₁ and F₂ = The fraction of unchanged molecules in phases 1 and 2 respectively.

In the simple case of association of a solute S in solvent 2 to give a complex molecule (S)_n and no change in solvent 1, there will be an equilibrium attained in phase 2 between the simple and associated molecules:



If (1 - F₂) represents the fraction of unassociated or simple molecules, the law of mass action gives:

$$(4) k_S = \frac{\left(\frac{F_2 C_2}{n}\right)}{[(1 - F_2) C_2]^n}$$

or:

$$(4a) (1 - F_2)(C_2) = \left(\frac{F_2 C_2}{n k_S}\right)^{1/n}$$

where k_s = the association equilibrium constant

$(1-F_2)C_2$ = concentration of simple molecules in phase 2

$\left(\frac{F_2 C_2}{n}\right)$ = concentration of complex molecules in phase 2

n = Degree of association or complexity of the complex molecule

Now assuming the distribution law to apply only to simple molecules and substituting equation (4a) in equation (2), since F_1 is zero in this case:

$$(5) \frac{C_1}{(1-F_2)C_2} = \frac{C_1}{\frac{n \sqrt{F_2 C_2}}{n k_s}} = K$$

If the molecules are almost completely in the associated form, F_2 is nearly equal to unity and

$$(6) \frac{C_1}{\sqrt{C_2}} = K' \quad (\text{a constant, since } n, k_s, \text{ and } K \text{ are constants})$$

Procedure: Make solutions of .5 N acetic acid and .25 N acetic acid from the stock solution. Use CO_2 free water in preparing these solutions.

Measure 25 ml of each 1 N, 0.5 N, 0.25 N concentration of acid into separatory funnels and add 25 ml of the organic solvent. Mix well and let settle for 20 minutes at 25°C .

When the solutions have come to equilibrium, draw off 10 ml samples of both the top and bottom layers and titrate with the standard NaOH solution, using phenolphthalein as an indicator. Make check titrations in each case. (Titrations must be rapid to avoid absorption of CO_2 from the air.)

.5 N NaOH is suitable for titration of the water layer from the extraction of 1.0 N acid.

0.1 NaOH should be used for the titration of the other water layers, and for the organic solvent samples from all concentrations if the solvent is ether.

0.01 N NaOH should be used for the titration of the organic solvent layer when CCl_4 is used.

Make a study of the effect of successive extraction by shaking 50 ml of 1.0 N acetic acid with 25 ml of the organic solvent at 25°C until equilibrium is reached. 10 cc portions of the solvent layer are titrated. The remaining water layer is again extracted with 25 ml of solvent and portions of both layers are titrated.

Results:

(1) Report the values of K obtained for each extraction. Express K as the ratio of mols of solute per liter in the organic solvent to mols per liter in water.

(2) Calculate the value of n .

(3) Calculate the concentration of acetic acid in water after each of the two successive extractions of 1.0N acetic acid with equal volumes of solvent.

Experiment 33

ADSORPTION

Reference: Daniels, Matthews, and Williams, pp. 112-119, 353-363.

Purpose: To demonstrate some of the properties of highly activated surfaces.

Equipment: Six 250 ml erlenmeyer flasks, 1.0 Normal acetic acid solution, 0.1 N. sodium hydroxide solution, Norite charcoal, burettes, volumetric flasks, balance, constant temperature bath, and centrifuge.

Theory: Some materials in the solid state possess the property of holding molecules on their surface. The nature of the attracting force is still debatable. The amount of adsorption depends upon the temperature, the nature of the adsorbent, the nature of the material being adsorbed, and its concentration. Freundlich put forth an equation to express the relation between the quantity adsorbed and the amount of adsorbent. The equation is referred to as the "isotherm of Freundlich" and is given below:

$$\frac{x}{m} = kc^n$$

where x is the number of grams of material adsorbed by m grams of adsorbent. c is the equilibrium concentration of the material being adsorbed from a solution and both k and n are constants.

Procedure: Prepare six acetic acid solutions of 100 ml each in the following concentrations: 1.0 M, 0.5 M, 0.25 M, 0.1 M, 0.025 M, and 0.01 M. Mix in 1.0 gram of Norite charcoal in each solution and shake vigorously at frequent intervals for about thirty minutes. (Cooling to 25°C after each period of agitation.) The Norite is separated from the solution by centrifuging. Draw off a suitable volume of the clear solution and titrate with 0.1 N. sodium hydroxide. For the two weakest solutions, use 0.01 N sodium hydroxide.

Calculations: Calculate the amount of adsorbed acid in each sample. Test the validity of Freundlich's isotherm by plotting x/m versus equilibrium concentration. A parabolic curve should result.

Plot a second graph of logarithm x/m versus logarithm c. Draw the best straight line through the experimental points and calculate the constants k and n.

Experiment 35

MOLECULAR WEIGHT BY FREEZING POINT DEPRESSION METHOD (Beckman)

References: Daniels, Matthews, and Williams, pp. 72-78, 422-432.

Discussion: The lowering of the freezing point, and lowering of the vapor pressure of a solvent due to the presence of a solute is, under certain conditions, directly proportional to the molal concentration of the solute in question, and may be employed for the purpose of obtaining the value of the molecular weight and for studying the changes in the molecular state of substances in solution.

If w grams of a substance when dissolved in W gms of a solvent lower the freezing point of the latter by $d^{\circ}\text{C}$, the molecular weight of the solute is obtained by means of the expression:

$$m = K \frac{w}{dW}$$

where K is a constant depending only on the solvent. This expression is applicable only when (1) the solute does not form a solid solution with the solvent, i.e., only the solvent crystallizes out pure, (2) the solute concentration is small, (3) the solute does not react in solution either with the solvent or with itself (to form associated molecules).

Freezing Point of Constants

Solvent	K
Acetic Acid	3900
C_6H_6	5120
Water	1858
Nitrobenzene	6995

In order to apply equation (1) under conditions for which it is valid, it is necessary to measure with accuracy small values of d . The instrument most often used is the Beckmann thermometer, a mercury thermometer having an adjustable range and a short scale ($5\text{-}6^{\circ}\text{C}$) graduated in 0.01°C and permitting estimation to 0.001°C .

The freezing point depression d is measured by noting successively the readings on the Beckmann thermometer when immersed in the freezing solvent and in the freezing solution of known weight concentration. The liquid is immersed in a suitable cooling mixture. The approach to freezing is indicated by a sudden rise of temperature which occurs when crystals start to separate from the super-cooled solution. Following this rise, the temperature should stay nearly constant for several minutes, the constant temperature being taken as the freezing point.

Actually, the constant temperature observed may differ quite appreciably from the true freezing point of the system investigated. The method is at best a semi-empirical one, depending for its success on the balancing of the systematic errors of the experiment which may be reduced to practically the reading error of the thermometer with proper care. Since depression of the freezing point only is being observed over a small temperature range, effects such as thermometer lag, heat exchange by radiation and conduction, heat effects from stirring, etc., may be controlled, and, being practically identical in all readings, will cancel out. Precautionary measures then are:

1. Control rate of heat removal in the cooling bath. Uniformity of temperature, and temperature difference between solvent and bath.
2. Control of gain of heat due to stirring. Stirring must be uniform, 2-3 strokes per second.
3. Control of addition of heat due to crystallization of the solvent. The same degree of supercooling for each test is essential.
4. Change of concentration due to separation of the solid solvent may be in part corrected by using dilute solutions. "Apparent" molecular weights at increasing concentrations may be determined, and molecular weight (at zero concentration) determined by means of a graph or by proportion.

Procedure: Assemble the apparatus to see that it operates freely. The Beckmann Thermometer should be so set to permit readings to about 3° or 4° below the freezing point of benzene.

Weigh into the freezing point tube enough benzene to cover the thermometer bulb. Determine the approximate freezing point reading by immersing the tube in ice water, stirring and observing reading at 1/2 minute intervals. Dry the tube, warm slightly (by holding in the hand until crystals just melt) and place the tube in the cooling jacket immersed in the freezing mixture. Stir uniformly, add a seed crystal to the solvent when the reading is about 0.1° below the previously observed freezing point and observe the apparent freezing point reading. Record time-temperature readings for each test. Warm till crystals melt, return to jacket, repeating the observations until freezing point reading is accurately established.

Add a weighed amount of the solute sufficient to give a freezing point depression of about $.2^{\circ}\text{C}$. Warm the solvent, stir to dissolve the solute and repeat the above process until the freezing point of the mixture is determined accurately.

Repeat, using additional weighed amounts of solute, obtaining at least three points.

Results: Determine the apparent molecular weight at each concentration. Plot the resulting molecular weights against concentration of solute in solvent and determine the true molecular weight of the solute.

Experiment 40

ELECTROMOTIVE FORCE AND THE HYDROGEN ELECTRODE

Reference: Daniels, Matthews, and Williams, pp. 187-188, 192-197, 373-375.

Purpose: To demonstrate the principles and practical usefulness of the hydrogen electrode.

Equipment: Student potentiometer, standard cell, resistance box, key, double-pole-double-throw switch, two dry cells, galvanometer, galvanometer shunt, platinized-platinum electrode, saturated KCl, calomel reference electrode, H₂ purification train, H₂ cylinder, 50 ml burette, solutions, glassware.

Procedure: Wiring connections for the student potentiometer are made as in Experiment 54. Write the reactions that take place in each half-cell to determine the polarity of the electrolytic cell.

In this experiment 0.5 M/L Na₂CO₃ is to be titrated with HCl according to the directions given on p. 196 of the reference book. Instead of using 25 ml as suggested in the text, use 35 ml in a 100 ml beaker. Notify the instructor if the initial voltage of the Na₂CO₃ solution with respect to saturated calomel is not correct. (approx. 0.9 volt with sat'd calomel).

Add approximately 5 ml of HCl solution. Record this volume and the e.m.f. of the solution. Repeat for additions of 5 ml to within 10 cc of end point (approx.), then take readings of e.m.f. at more frequent intervals. When the phenolphthalein indicator shows that the end-point is near, take e.m.f. readings for 0.1 or 0.2 ml additions.

Record the e.m.f. corresponding to the color change of the phenolphthalein. Add methyl orange.

Continue the titration to about 5 ml past the methyl orange end point. Record the e.m.f. corresponding to color change of M.O.

Rinse the platinum electrode thoroughly with distilled water and leave it immersed in distilled water to protect the platinized electrodes.

Flush out the calomel bridge by withdrawing 2 or 3 ml of sat'd KCl from the tip. Leave the tip immersed in distilled water. (Note: if the calomel reference electrode is of the L and N type, only rinse the outer surface with distilled water, then immerse the electrode in a test tube of sat'd KCl).

The Report:

1. A graph is plotted of e.m.f. in volts as ordinate versus ml HCl added as abscissa. The e.m.f. corresponding to color change of both indicators is shown on the graph.

2. Compute the pH corresponding to the color changes of the indicators. Compare them with values found in the literature.

3. Which of the following gases might be used in obtaining titrations: N₂, Air, O₂? Explain.

Questions:

1. Sketch and label the parts of the calomel and hydrogen half cells.
2. Write the balanced reactions for the hydrogen and calomel half cells.
3. What are the advantages of an e.m.f. titration compared to the use of indicators?

Experiment 41

pH MEASUREMENTS WITH THE QUINHYDRONE AND THE GLASS ELECTRODE

Reference: Daniels, Matthews, and Williams, pp. 197-200, 205-206.

Purpose: To measure the pH of various solutions and to demonstrate the operation of commercial instruments commonly employed in the measurement of pH.

Theory: The Hydrogen electrode is capable of accuracy to 0.001 pH unit and is used as the fundamental measuring device for pH. Nevertheless, large errors will occur if the solution under test contains any oxidizing or reducing substances, or traces of poisons. Further disadvantages of the Hydrogen electrode are: cumbersome equipment, time, patience, experience, and technical skill. The two methods used in this experiment overcome these disadvantages to a large degree.

A. Quinhydrone Electrode

The ratio between the amount of quinone and hydroquinone present and the quinhydrone depends on the pH of the solution in which it is dissolved. Quinhydrone may not be used to measure the pH of solutions containing oxidizing and reducing substances since they also affect the ratio of quinone to hydroquinone. The electrode is also susceptible to poisons. Apart from these limitations, the quinhydrone electrode is reasonably exact from one to 7pH and may be used as high as 8.5 pH for approximations.

B. Glass Electrode

The ordinary glass electrode consists of a bulb made of pH sensitive glass. Glass electrodes are filled with a variety of solutions, depending on the manufacturer. The Coleman electrode is filled with a solution of a stable chloride in which is immersed a stabilized silver - silver chloride electrode. This is hermetically sealed at the factory to prevent evaporation and contamination.

Glass has the peculiar property of acquiring a surface potential with respect to any solution in contact with it. This potential is fixed by the pH of the solution, and to this extent it follows the same law as the hydrogen electrode. The glass membrane of the bulb is an integral part of the electrical circuit and is of very high resistance. This means the current to the galvanometer is very low. In order to make this current measurable, it must be amplified by vacuum tube amplifiers. (Study the wiring diagram on p. 14 of the Leeds and Northrup bulletin number 7662 - A1).

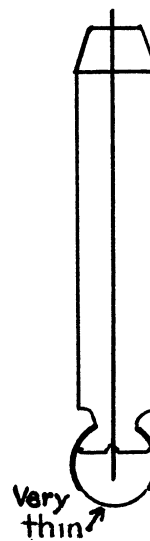


Fig. 19. Glass Electrode

Since the bulb resistance is very high, both bulb and stem may act as electrode surface. This is eliminated by making the bulb only of pH glass. The stem is made of glass having a far greater resistance, so that the pH action is confined to the bulb and thereby the stem error is avoided.

There are three potentials developed by a glass electrode. Two of these are at the two surfaces of liquid contact, and the third (developed internally) is called "assymetry potential." This potential is not fixed, but varies with time in an unpredictable manner. This potential is compensated for by means of an AP dial and calibration against a standard buffer solution.

Procedure: There are several solutions available for pH measurement. The pH of each solution is first to be determined by the Glass electrode, then a check determination is to be made by the Quinhydrone electrode wherever this is possible. Measure the pH of the following solutions:

1. Distilled water
2. Cold tap water
3. Hot tap water (cooled to room temperature)
4. 0.05 Normal Acetic acid
5. Other solutions as assigned by the instructor

A. Glass Electrode

Follow the instructions in top of instrument box.

B. Quinhydrone Electrode

Follow the instructions on page 199 of the reference text. It is not necessary to do the titration.

The Report: Present the results in tabular form, showing pH determinations for each solution by both methods.

Question:

- 1) Write the reactions for the quinhydrone and calomel electrode.
- 2) Write the reactions for the glass electrode showing how the final result gives pH as a function of the measured e.m.f.

Experiment 42

CONDUCTOMETRIC TITRATIONS

Reading: Daniels, Matthews, and Williams, pp. 174-181, 184-187.

Purpose: To demonstrate methods of measuring resistance of water solutions of electrolytes and the application of three methods to chemical analysis.

Theory: It is significant to remember that the electrical conductivity of water solutions is of an entirely different magnitude than metals. The best conducting solutions show less than one reciprocal ohm per centimeter, molten salts about five times this much, and copper 6×10^6 reciprocal ohms per centimeter. Water usually considered conductive, has a specific conductance of as low as 0.043×10^{-6} ohms⁻¹ cm⁻¹ when relatively pure.

Fundamentally, electrolytic conductivity might be measured in the same way as the conductivity of solids: namely, by the Wheatstone bridge. However, if direct current is used, electrolysis takes place and a counter-e.m.f. is set up. This phenomenon is known as polarization. In order to avoid polarization, alternating current must be used and the electrodes must be of platinized platinum. Such electrodes increase the surface exposed and decrease the polarization.

Since ordinary d.c. galvanometers cannot be used for a.c. current, then some other means of detecting the balance point on the bridge must be found. A very common way is to use telephone receivers and observe the minimum tone which coincides with the balance point.

The specific conductance, L , of a solution is defined as the reciprocal of its resistance when measured between electrodes 1 sq. cm. in area and 1 cm. apart:

$$(1) L = \frac{1}{\rho} = \frac{l}{aR} \quad \text{Where } \rho = \text{resistivity of the solution in ohms cm.}$$

l = distance between electrodes, cm.
 a = electrode area, cm.
 L = specific conductance in cm⁻¹ ohm⁻¹

Often in chemical literature the specific conductance is labeled reciprocal ohms and the cm⁻¹ label is omitted.

The conductance, C , of a solution is the reciprocal of its resistance:

$$(2) C = \frac{1}{R} = \frac{a}{lR} = \frac{La}{l}$$

Where C is conductance in reciprocal ohms or mhos.

Inasmuch as it would be difficult to make a cell having electrodes of 1 sq. cm. area and spaced at 1 cm distance the actual cell must be tested with a solution of known specific conductance to determine K , the cell constant:

$$(3) K = LR \quad \text{where } K = \text{the cell constant in Cm}^{-1}$$

L = specific conductance in Cm⁻¹ohm
 R = measured resistance of solution

The conductivity cell can be used to obtain the specific conductance of unknown solutions once its constant has been determined accurately.

The equivalent conductance (Λ) is the conductance in sq. cm/ohm - gram - equivalent of solution when placed between electrodes of indefinite height placed one centimeter apart. This quantity is calculated from the relation

$$(4) \Lambda = LV$$

where V is the volume of the solution in cubic centimeters which contains the gram equivalent of solute.

The degree of ionization for a weak electrolyte may be calculated from the equation

$$(5) \alpha = \frac{\Lambda}{\Lambda_0}$$

where Λ is the equivalent conductance at dilution V and Λ_0 is the equivalent conductance at infinite dilution. This assumes the validity of the Arrhenius theory.

The dissociation constant K_D for weak electrolytes may be found from the relation

$$(6) \frac{\alpha^2 C}{1-\alpha} = K_D$$

where C is the concentration in moles per liter

Equipment: 1000 cycle hummer, 6 volt storage battery, resistance boxes, conductivity cells, various solutions and glassware.

Procedure: (1) Determine the cell constant in cm^{-1} of your conductivity cell by means of 0.1 N KCl solution. The wiring diagram for the circuit is shown below.

(2) Measure the resistance of three different acetic acid solutions, using 1.0 normal, 0.1 normal, and 0.01 normal.

(3) Place 25 ml of 0.1 N hydrochloric acid solution in the special conductivity titration flask. Add two drops of phenolphthalein indicator. Titrate the acid with 0.1 normal sodium hydroxide solution. The resistance of the pure acid is first determined. Then record the resistance of the mixture at frequent intervals while the titration is in progress. Observe the minimum point of conductance and compare this end point with that shown by the indicator. Estimate, if necessary by a separate test, the smallest amount of base which will produce a measurable change in conductance and compare it with the smallest amount necessary to produce a color change in the indicator.

The Report:

1. Compute the degree of ionization, α , and the dissociation constant K_D for the three acetic acid solutions. Λ_0 for acetic acid is 390 at 25°C.
2. Report the cell constant.
3. Plot a graph of the conductometric titration, using specific conductance as the ordinate and ml of sodium hydroxide added as abscissa.

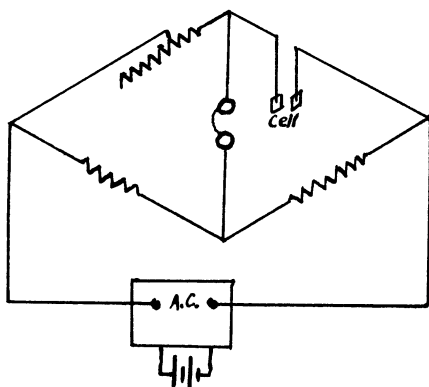


Fig. 20. Conductivity Circuit

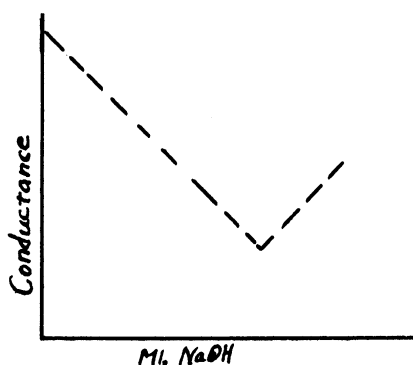


Fig. 21. Conductance Conc. Curve

Experiment 43

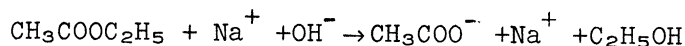
SAPONIFICATION OF ETHYL ACETATE (USING CONDUCTIVITY CELL.)

Reference: Daniels, Matthews, and Williams, pp. 157-158, 167-170.

Purpose: To evaluate the rate of a bimolecular chemical reaction.

Equipment: CO₂-free water, glassware, Fisher Conductivity Bridge Model RC-1B, thermostatic bath, electric chronometer, carbonate-free NaOH.

Theory and Calculations: The saponification reaction may be written:



The sodium ion appears on both sides of the equation, and hence the reaction may be considered to be between the ester and the hydroxyl ion. If at the start of the reaction an equal number of moles of these materials were present and if the conductivity of reaction mixture were measured as the reaction progressed, the conductivity would be found to decrease due to the disappearance of OH⁻ ion. The OH⁻ ion is very mobile compared to the acetate ion, and hence carries most of the current.

The rate, dx/dt, of a second-order reaction is proportional to the concentration of the two reacting materials. It may be expressed by the equation:

$$\frac{dx}{dt} = k (a-x) (b-x) \quad (1)$$

where

x = the number of moles of each component which have reacted in time t (minutes)

a = initial concentration of one reacting material in mols/liter

b = initial concentration of the other reactant in mols/liter

k = "Specific reaction rate"

Since in this experiment a = b equation (1) becomes

$$\frac{dx}{dt} = k(a-x)^2 \quad (2)$$

$$\frac{dx}{(a-x)^2} = kdt \quad (3)$$

Equation (3) may be integrated to yield

$$kt = \frac{1}{(a-x)} - \frac{1}{a} \quad (4)$$

or

$$\frac{1}{a-x} = kt + \frac{1}{a} \quad (5)$$

Eqn. (5) represents a straight line of slope k and intercept $\frac{1}{a}$.

The solutions used in this experiment are 0.01 M, hence when equal volumes are mixed together, a = 0.005M. In order to plot equation (5), it is necessary to know the value of x at a given time, t. If we designate the specific conductances of the reacting mixture as follows:

L_0 = specific conductance in $\text{cm}^{-1} \text{ohm}^{-1}$ at time = 0

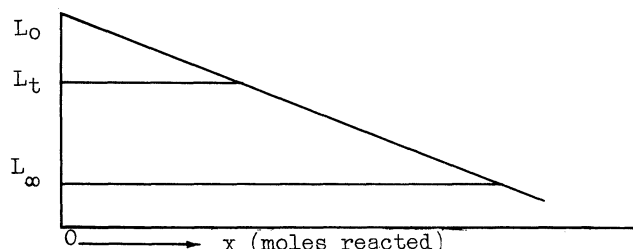
L_t = specific conductance in $\text{cm}^{-1} \text{ohm}^{-1}$ at time = t

L_∞ = specific conductance in $\text{cm}^{-1} \text{ohm}^{-1}$ at infinite time,

Then

$$x = a \left[\frac{L_0 - L_t}{L_0 - L_\infty} \right] \quad (6)$$

Equation (6) may be better understood by referring to the graph below:



Experimental Procedure: At the outset, it should be clearly understood that good results can be obtained only by strict adherence to the following:

CAUTION: 1) DO NOT ALLOW ELECTRODES TO BECOME DRY.

2) KEEP ALL SOLUTIONS STOPPERED TO KEEP OUT CO_2 FROM THE AIR.

In a very short time the CO_2 absorbed from the air can change the conductivity of the solutions enough to cause an error of 100% in the results.

Determine the cell constant. This is done at the temperature of the thermostatic bath (Either 20°C or 25°C). It is necessary to measure the resistance of a standard potassium chloride solution with the conductance cell which will be used. The potassium chloride may be put into a 150 ml test tube. The cell constant, Kc, may then be found from the equation:

$$Kc = L \times R$$

where R is the resistance in ohms and L is the "specific conductance" (or "conductivity") in $\text{ohm}^{-1} \text{Cm}^{-1}$. Values of L for potassium chloride solution are as follows:

	1.0M	0.1M	0.01M
20°C	0.10209	0.01167	0.001278
25°C	0.11180	0.01289	0.001413
30°C		0.01412	

Precool the Reactants: The reactants must be precooled to bath temperature before mixing. Pipette 100 ml of 0.01 N ethyl acetate into the wide-mouth test tube which will be used for the reaction vessel. Stopper it and place in the bath. Allow 10-15 minutes for coming to temperature. Pipette 100 ml. of 0.01 N sodium hydroxide into a test tube and stopper. Place in the bath and allow to cool.

Determine the value of L_0 . While the reactants are cooling, clean the conductance cell by rinsing carefully with distilled water to remove all KCl from the cell walls and electrodes. Prepare 100 ml of 0.005 N sodium hydroxide by diluting 50 ml of 0.01 N sodium hydroxide with 50 ml of CO_2 -free distilled water.

CAUTION: KEEP NaOH SOLUTION STOPPERED TO KEEP OUT CO_2 :

Put the 0.005 N NaOH a 150 ml test tube and stopper carefully. Allow to come to bath temperature, measure the resistance, and compute L_0 .

Technique of mixing the reactants

Check the electric chronometer to see that it is working properly. Set the hands at zero. When the reactants are at bath temperature, pour the hydroxide into the acetate rapidly without spilling. Start the watch just before the last 1/3 of the solutions have been mixed. Stir the reactants gently but thoroughly. Then set the conductance cell in position BEING CAREFUL NOT TO BREAK THE CONDUCTANCE CELL.

Readings of the conductance must be made frequently during the early period of the reaction. After mixing take conductance readings at 1, 2, 3, 5, 8, 12, 18, 20, 30, 45, and 60 minutes and at frequent intervals thereafter if time permits. Do not move or stir the solution while conductance is being measured. Stir the solution gently for 30 seconds before each reading. Record the time in minutes.

The value of L_{∞} given below has been calculated from more complete data extending over a longer time interval and will not have to be determined.

The Report

- (1) Plot a curve of $1/(a-x)$ versus t (minutes).
- (2) Determine the specific reaction rate, k . Give proper units.
- (3) In the calculations, use $L_{\infty} = 0.000484 \text{ cm}^{-1}, \text{ ohm}^{-1}$ at 25°C .

Experiment 45

PHOTOELECTRIC COLORIMETER

Reference: Daniels, Matthews, and Williams, pp. 55-63, 394-397.

Purpose: To demonstrate a few of the applications of colorimetry. Various types of colorimeters are finding a very wide field of application in colorimetric analysis, or chemical colorimetry. Such a colorimetric analysis implies the determination of the concentration of a colored solute by measurement of the relative transmission of light by the solution. If there is a definite functional relationships between the intensity, or "depth," of color of a solution and its concentration, colorimetry can be used for analytical and plant control purposes.

Equipment: Fisher Electrophotometer No. 819, filters, sample tubes, solutions, glassware.

Theory: If we consider monochromatic light of intensity I_0 penetrating a solution of thickness t having a concentration c and emerging with an intensity I , then we have

$$I = I_0 10^{-Kct} \quad (1)$$

or

$$\log_{10} I_0/I = Kct \quad (2)$$

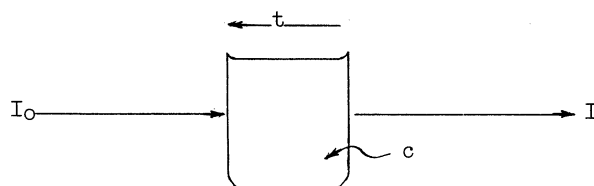


Fig. 22. Absorption of Light

If the thickness of the solution is constant, then the equation (2) becomes

$$\log_{10} \frac{I_0}{I} = Kc \quad (3)$$

This is the equation of a straight line of slope K , and is a mathematical statement of Beer's law. Equation (2) is a mathematical statement of the Beer-Lambert law. The colorimeter employs glass absorption cells of constant thickness, hence it can be used to determine whether or not a given solute follows Beer's law. However, it should be recognized that colorimetric analysis is not prevented by failure of a solute to follow Beer's law. In such cases it is necessary to calibrate the solution at several concentrations to determine the actual shape of the curve. The ratio I/I_0 is called the "transmission" of the solution, and is customarily expressed in percent. The above equations cannot be expected to be strictly valid unless monochromatic light is used. In the old style visual colorimeters, white light was used and the equations were approximately applicable.

The best instrument available for colorimetric analysis is a spectrophotometer. With such an instrument, truly monochromatic light is obtainable. They are, however, quite expensive, and hence there have been developed "abridged spectrophotometers" or electrophotometers such as the Fisher instrument. True monochromatic light is not employed, but light of "Narrow band wavelength" is used. The human eye is sensitive to light of wave lengths from about 400 to 700 millimicrons (or 4000 to 7000 Angstrom units) Fig. 23).

A blue filter will absorb white light of most all wavelengths except those lying in the range of 400 to 500 millimicrons. The peak transmission for a blue filter will be somewhere near 450 millimicrons. A red solution appears red to the eye because the solute has absorbed light of all wavelengths except those in the range of 575 to 700, approximately. If blue light, such as that transmitted by a blue filter, should be allowed to fall on a red solution, it is readily seen that the solute would tend to absorb it and very little would be transmitted. The amount absorbed would depend on the concentration of the solute. We may say that this solution is "selectively" absorbing blue light since it transmits red light. This is the way the proper filter may be chosen for photometric purposes.

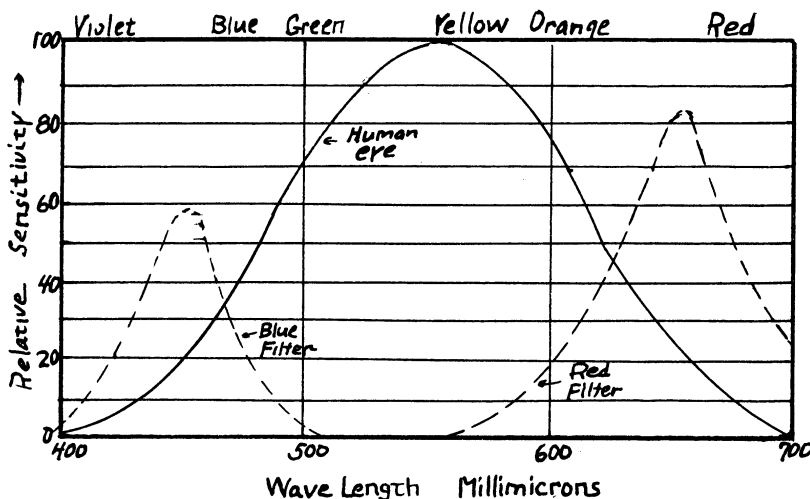


Fig. 23. Spectral Sensitivity

The electrophotometer used in the laboratory contains two photoelectric cells in a Wheatstone bridge circuit. (Fig. 24). These photocells are of the "barrier layer" type or "photovoltaic" type. In these cells, light causes a transfer of electrons across the rectifying boundary between two dissimilar materials, such as copper and copper oxide, or selenium and another metal. The current is sent through the external circuit entirely by the voltage generated within the cell, and no battery is required.

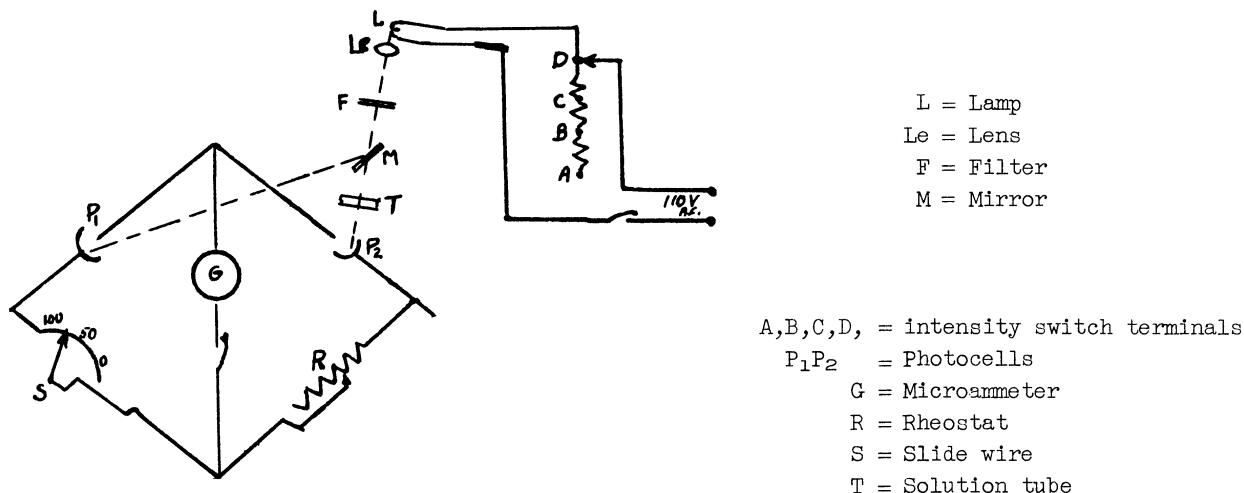


Fig. 24. Electrophotometer

The construction of the Photometer may be seen by referring to Fig. 24. A tungsten lamp is arranged so that its intensity may be varied as shown. Light from the Lamp passes through the lens and the filter. Half of the light falls on the mirror and

is reflected into photocell P_1 . The remainder of the light passes directly through the solution into photocell P_2 .

The operation of the photometer is simple. The pure solvent used in making the solution is placed at T and the slide wire is set at 100. This slide wire is marked in % transmission, and naturally the solvent should correspond to 100% transmission. The light into P_2 is slightly less intense than that into P_1 due to absorption by the glass and by the solvent. In order to make the bridge indicate equal light on both photocells, it is necessary to adjust the rheostat R until the microammeter needle shows no deflection. The solution whose transmission is to be measured is placed at T in place of the solvent. The slide wire pointer is adjusted until the microammeter needle is again at zero, and the % transmission read off directly.

Procedure: Study the effects of concentration and wave length on the transmission of light through the assigned solutions. A stock solution of known concentration is examined in the electrophotometer, using each of the filters. Dilute the stock solution with distilled water and repeat, until concentrations over the entire operating range have been examined with each filter.

Study the effect of pH by diluting the stock solution with tap water and determining the percentage transmission for several concentrations, using one filter.

Note: If cylindrical sample tubes are used, extreme care must be used to properly center the tube in the colorimeter.

Report: Plot \log_{10} percent transmission versus solute concentration in micrograms per milliliter.

Discuss whether the solute did or did not obey Beer's law.

Experiment 51

THE WHEATSTONE BRIDGE

Reference: Smith, pp. 84-92.

Purpose: To acquaint the student with this fundamental method of measuring resistance.

Equipment: Slidewire bridge, dry cell, galvanometer, key, standard resistances, micrometer, unknown resistances.

Theory: The apparatus is assembled according to the theoretical Fig. 25. Instead of being separate resistances, A and B are usually combined into a slidewire resistance.

In this case, if X represents the unknown resistance and R represents the known or standard resistance,

$$X/R = \frac{a}{1000 - a} \quad (1)$$

where a is the distance in millimeters along the 1000 mm bridge. These equations hold for a single measurement. For the double method (refer to Smith, p. 88), the equation (2) becomes

$$X/R = \frac{1000 + d}{1000 - d} \quad (2)$$

where d is the difference in the balance point when X and R are interchanged.

In selecting the proper standard R to use in measuring X, it should be remembered that both X and R ought to be of the same magnitude. (Study Fig. 56, page 91 in Smith for the reason). Consult the table given below to find the proper standard.

Resistivity is defined as follows:

$$\rho = R A/L \quad (3)$$

where R is the resistance of the wire. A is its cross-sectional area, and L is its length in consistent units. For English units, R is in ohms, A is in circular mils, and L is in feet. In this case, ρ is usually referred to as "ohms per circular mil - foot." For metric units, R is in micro-ohms (10^{-6} ohm), A is in square centimeters, and L is in centimeters. In this case, ρ is said to be in "micro-ohms per cubic centimeter."

Attention is called to the fact that the resistivities expressed as above are not dimensionally correct. Actually, for English units, ρ is in "ohms-circular mils per foot." For metric units, ρ is "micro-ohms centimeters." Nevertheless, the handbooks and the Int. Critical Tables all refer to resistivities as mentioned in the preceding paragraph, and consequently the reports are to indicate the resistivities of the unknown coils in those terms.

One mil is a measure of the diameter of a wire and is equivalent to 0.001 inch. Thus, a wire having a diameter of 0.015 inch has a diameter of 15 mils. The area of the wire in circular mils is equal to the square of its diameter in mils.

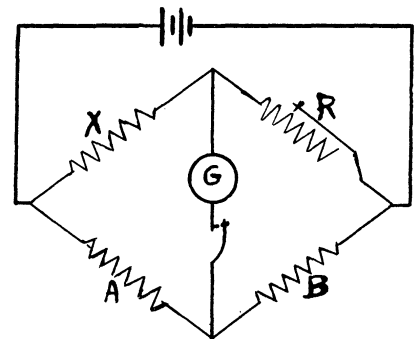


Fig. 25. Theoretical Wheatstone Bridge

Procedure: The resistance of three unknown coils of wire are to be measured, namely, U_2 , U_4 , and U_7 . The lengths are marked on each coil.

1. Select a standard resistance from the Table below and hook up the wiring according to Fig. 25.

<u>Unknown</u>	<u>Standard</u>
U_2	Ammeter shunt (notice that leads are included)
U_4	S_4 or S_5
U_7	One ohm standard resistor

2. Determine the balance point on the slidewire and from this find "a".
3. Exchange the position of the battery and the galvanometer and again find the balance point.
4. Put the galvanometer and battery back in the original positions.
5. Exchange X and R and find the new balance point. From this double method measurement, determine "a".
6. Measure the other two unknown resistances by both the single and double methods. It is only necessary to exchange the battery and the galvanometer once during the entire experiment.
7. Measure the three diameters of the unknown coils of wire by means of the micrometer. Record the lengths as well as the diameters of the unknowns. Look up the B and S (Brown and Sharpe) gauge numbers of each coil.

The Report:

- (1) Tabulate the results in the form given below.

Un-known No.	Length		Diameter			B & S Gauge No.	Resist-ance in chms	Area		Resistivity	
	Feet	Cms.	In.	Cms.	Mils			Cir. Mils	Cm. ²	Ohms per Cir-mil ft.	micro-ohms per cm. ³
U_2											
U_4											
U_7											

- (2) What reason is there for operation 3?
- (3) Discuss what factors may have influenced the difference between the values obtained by the single method and those obtained by the double method.
- (4) Which other electric quantities may be measured with a bridge set-up similar in principle to the Wheatstone?

Experiment 52

FINDING FAULTS IN A CABLE WITH A RESISTANCE TESTING SET

Reference: Smith, 84-104.

Purpose: To gain experience in the use of a testing set and applying it to a practical case.

Equipment: Testing Set, lead wires, dry cell, voltmeter, micrometer, simulated cable in box.

Theory: The testing set is built on the principles of the Wheatstone bridge, but instead of having an infinite variation of the ratio of the resistance in the two parts, P and Q, of the bridge, only a few coils are used which give a certain definite ratio, usually 1000, 100, 10, 1, 0.1, 0.01. and 0.001. The resistance, R, can be varied in steps of one ohm. The unknown resistance, X, is $R(P/Q)$. See (Smith, p. 84, Fig. 53).

When an unknown resistance is to be determined, it should be "bracketed;" that is, its approximate value determined by taking two extreme settings, and gradually narrowing the value down by repeated new settings. While getting approximate values, the least sensitive setting of the galvanometer is used.

A fault in an electric line of any kind is any trouble which impairs the insulation of the line, or which interferes with the proper working of the line.

The principle kinds of faults are:

- (1) A ground is an electrical connection more or less completed between the line and the ground.
- (2) A cross is an electrical connection between two wires.
- (3) An open is a break in the line.

In testing for a fault it is first necessary to determine in which of the classes the trouble belongs. A testing circuit is arranged by connecting a battery in series with a voltmeter or other current indicating device.

Test for Grounds. The battery side of the testing circuit is connected to the ground, and the lead wire from the voltmeter side is brought into contact successively with each wire to be examined, as in Fig. 26. The circuit is completed when the wire is grounded.

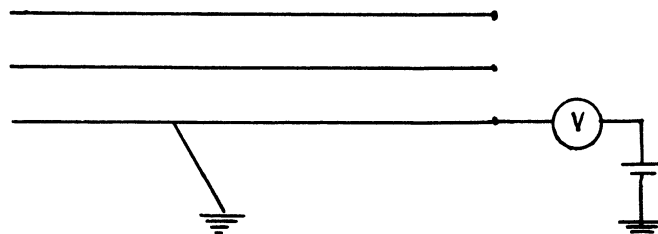


Fig. 26

Test for Opens. The distant end of the wire to be tested is connected to the ground. The voltmeter, in series with the battery and grounded as in Fig. 27, is connected to the near end of the same wire. An open is indicated if there is no deflection on the voltmeter.

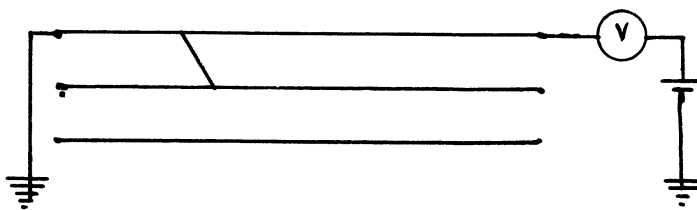


Fig. 27

Test for Crosses. Select a wire to test for a cross, and connect its distant end with a wire suspected of being crossed with it, through the voltmeter and battery in series as per Fig. 28. (Note: the near ends can be used just as well.) If these two wires are crossed, there will be a deflection on the voltmeter. This same wire is connected with the other wires in turn until it has been checked with all the others. Take a second wire and proceed in the same way after all possible crosses have been identified for the first wire under test.

The above three tests are somewhat modified from that given in Smith's "Electrical Measurements" to fit the actual laboratory apparatus. It should be understood that the usual commercial job would better be done by following the procedure in Smith.

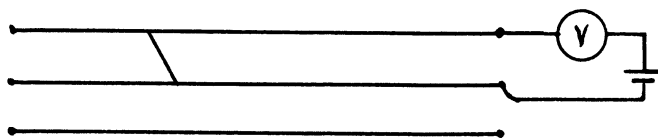


Fig. 28

The usual methods for locating faults in a telephone line or a cable are based on the simple slidewire bridge. They are called "loop tests" because the wire being tested is joined to a good wire, thus forming a long loop out one wire and back the other. In case the line is open so it cannot be used as one arm of a resistance Wheatstone bridge, the position of the break can be located by comparing the capacitance of the line out to the break with the capacitance of a similar line whose length is known.

The Murray and the Varley Loop tests are used for finding the distance to a cross on a wire, and the distance to a ground. The diagrams and formulae are found in the inside top cover of the test set used.

1. Test for the temperature of the cable box by the resistance test set, using the leads from the nickel coil which are found at the top of the box of wires. The temperature is found from the equation $R \text{ (ohms)} = 0.00342 t \text{ (}^\circ\text{C)} + 0.673$. (Eqn. 1)
2. Determine, qualitatively, the types of faults that may be present to each wire by the methods previously described, (refer to Figs. 26, 27, and 28).
3. Determine the lengths of the wires that are not open, using the formula

$$L = (AR)/\rho \quad (2)$$

R is the resistance in ohms, L is the length in feet, A is the area in circular mils, and ρ is the resistivity in ohms per circular mil foot. The diameters of the wires are found with the micrometer. Numbers 1 through 8 are the same size, and a sample is found at No. 8 terminal. One mil in diameter is 0.001 inch. The area in circular mils is found by squaring the diameter in mils. See page 66.

4. Determine the resistance of each lead wire used in step 3.
5. Determine the distances to the faults by instructions in the top of the test set cover. Note: In case of crossed wires, the distances to the cross are unequal. Therefore the distances to crosses must be found for each wire that is crossed. It should be realized that the most common experience commercially is to find that crosses

occur at the same distance from the near end of two crossed wires. This laboratory apparatus gives the general case.

6. Find the distance to the fault on wire No. 9, which requires the use of a good wire. Two settings are necessary.

Experiment 53

CALIBRATION OF A RESISTANCE THERMOMETER

Reference: Wood and Cork, pp. 88-101.

Purpose: To acquaint the student with the use of resistance thermometers.

Equipment: Oil bath, mercury-in-glass thermometer, L and N test set and resistance thermometer (nickel coil).

Theory: The resistance of all pure metals and practically all alloys increases with the temperature, but not linearly. There is a close relationships between the decrease of electrical conductivity and the decrease of thermal conductivity with increasing temperature. The variation of resistance with temperature may be expressed by a second degree equation:

$$R_t = R_0 (1 + \alpha T + \beta T^2)$$

If high accuracy over a wide temperature range is desired, a third order term is added to the equation.

The metals commonly used for making resistance thermometers are platinum, copper and nickel. Platinum is relatively immune to contamination, but the cost is high. Due to the fact that platinum does not oxidize, it can be used up to 1000°C when enclosed in a quartz container. Nickel is cheaper but can be used only from -100° to +150°C.

The advantage of resistance thermometers is the high accuracy obtainable. For example, for a platinum thermometer up to 100°C, an accuracy of 0.01°C can be obtained, up to 500°C an accuracy of 0.7°, and up to 1,000°C, an accuracy of 2.5°. If differences in temperature are required only, a difference of 0.0002°C can be detected. Resistance thermometers also have the advantage over thermocouples in that they can be used conveniently around room temperature and do not require a cold junction.

Note that resistance thermometer leads must be compensated as described on page 96 in Wood and Cork.

Procedure: It is necessary to identify the lead wires. Use the resistance test set for this purpose. After determining the number of the leads, set up the apparatus as shown in Fig. 29.

Both thermometers are first immersed in melting ice so as to determine the value of R_0 . After this, dry the thermometer bulbs well and immerse them in the oil bath. Be careful not to allow either bulb to touch the sides or the bottom of the container. Immerse the resistance thermometer bulb completely with the above precaution in mind. If the mercury thermometer is calibrated for total immersion, make corrections for this.

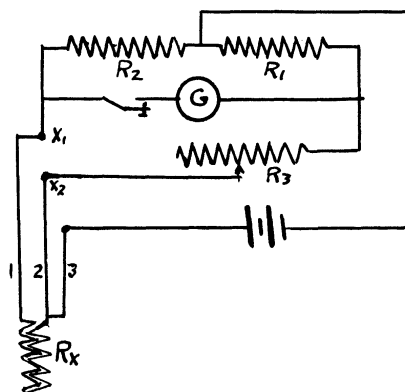


Fig. 29. Resistance Thermometer Circuit

Take temperature readings at room temperature and continue up in temperature but do not go above 125 degrees C. Remember that the nickel coil is electrically insulated from the brass sheath, and hence there will be a time lag between the coil and sheath for attaining the bath temperature. Allow 5-7 minutes for this, and plan your readings accordingly. Stir vigorously before taking readings.

The Report:

1. Determine the coefficients of the second degree equation.
Use degree centigrade.
2. Estimate your accuracy both in reading the temperature and resistance.
3. Plot a graph of resistance as ordinate versus temperature as abscissa.
4. Prove analytically that the resistance as read by the test set is not affected by variation of resistance of the lead wires when using the three-wire method of compensation.
5. Explain how temperatures could be read directly with this set-up using a less sensitive galvanometer.

Experiment 54

THE STUDENT POTENTIOMETER

Reading: Wood and Cork, pp. 66-68. Smith, pp. 137-142.

Object: To acquaint the student with the potentiometer principle and its utilization in measuring unknown sources of e.m.f.

Equipment: Student potentiometer, a standard cell, a slidewire rheostat with high resistance, one key, one double pole - double throw switch, two dry cells, galvanometer, galvanometer shunt, and several unknown sources of e.m.f.

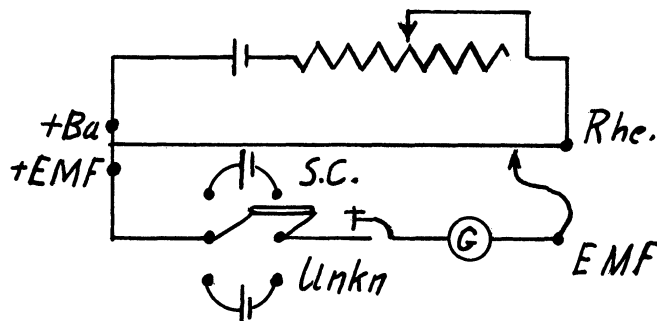


Fig. 30. Potentiometer (Theoretical)

Directions: The wiring diagram is shown in Fig. 30. See also appended wiring diagrams of the L and N portable potentiometer, mainly intended for reading of e.m.f. of thermocouples. It is very important that the standard cell does not deliver more current than 0.1 milliamp, and that only for a moment. The galvanometer shunt protects the sensitive galvanometer.

After the apparatus is wired, have it checked by the instructor. The sliding contact of the potentiometer slidewire is set in such a way as to indicate the e.m.f. of the standard cell. With this cell placed in the measuring circuit, the slidewire rheostat is adjusted until the galvanometer reads zero. This means that the working circuit current is now at the proper value so that the potentiometer reads directly in volts. The potentiometer is then said to be standardized. This means that the potential drop in the working circuit at this particular setting equals the potential of the standard cell. Since the scale markings of the potentiometer are linear, we can read off an unknown e.m.f. or a voltage drop on the scale after throwing the double pole switch to place the unknown cell in the measuring circuit.

- Measurements:
- (1) Find the e.m.f. of an unknown standard cell, a storage battery, and a dry cell.
 - (2) Connect the same dry cell as used in part (1) to a 100 - ohm resistor and measure the voltage drop over the resistor.

- Compute:
- (a) The current flowing in the potentiometer working circuit. For this computation, utilize the resistance of the potentiometer.
 - (b) Assuming that the galvanometer is not able to respond to less than 10^{-7} ampere, what percentage is this of the current flowing?
 - (c) Since the same percentage of insensitivity will show up on the measurement of e.m.f., how accurately should the standard cell be calibrated?

- (d) Compute the current in the 100 - ohm resistor. If the current is known, and the potential drop is known, the value of the resistance can be found. This is an important way of measuring resistance.
- (e) Compute the internal resistance of the battery used.

WIRING DIAGRAM OF THE PORTABLE POTENTIOMETER

The circuit diagram of Fig. 31 is only a slight modification to that of Fig. 30. This arrangement is designed for measuring the e.m.f. of thermocouples without the necessity of having a cold junction. If the unknown e.m.f. is not a thermocouple, then the sliding contact D must be set at A. In order to standardize the working circuit current, key K is set to put the standard cell (SC) in series with the galvanometer and the slidewire ADPB, and also the fixed resistance BF. The resistance of ADBF is such that when the working circuit current is correct, the resulting IR drop through it is exactly equal to the voltage of the standard cell. It should be observed that the position of P is immaterial in the current standardization operation. However, the position of D must be at A when this operation is done. In practice, the maximum variation of D is from 0 to 5 mv. The value of the SC voltage is 1.018 volts. Consequently the maximum error caused by neglecting the position of D is about 5 parts per 1000. As a matter of fact, the position of D is neglected in the usual commercial portable potentiometer when standardizing the working circuit current.

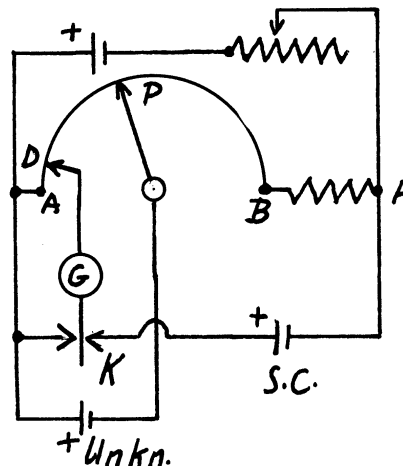


Fig. 31. Simplified Potentiometer Circuit

The net e.m.f. generated by a thermocouple depends upon the temperature of both the hot and cold junctions. This e.m.f. varies directly as the temperature difference between these junctions. If we consider the hot junction temperature of the thermocouple to remain constant, then the e.m.f. of the thermocouple will decrease as the cold junction temperature increases. To balance this decreased e.m.f., slider D is moved closer to P (Fig. 31). The new position of D is set to indicate the temperature of the cold junction in millivolts. The correct temperature of the hot junction will then be obtained by moving slider P on out to the position of no galvanometer deflection.

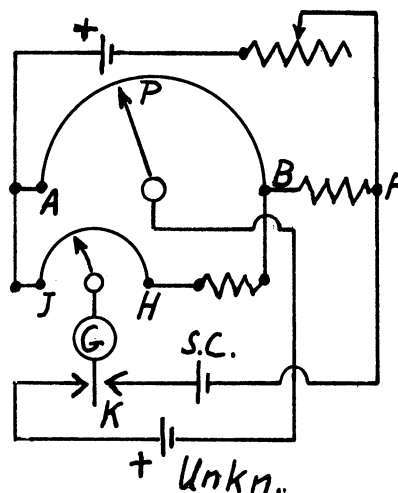


Fig. 32. Potentiometer Circuit with Cold Junction Compensation

Whenever the portable potentiometer is used to measure an e.m.f. other than that produced by thermocouples, the slider D must be set at zero millivolts.

Experiment 55

DETERMINATION OF THE e.m.f. - TEMPERATURE RELATIONSHIP OF AN UNCALIBRATED COUPLE

Reading: Wood and Cork, pp. 1-15, 52-58, p. 84., Daniels, Matthews, and Williams, pp. 424-426.

Object: To acquaint the student with a common method of calibration of thermocouples using a chromel-alumel couple or a platinum platinum-rhodium couple as a standard. Several kinds of thermocouples may be calibrated: Chromel-alumel, chromel-constantan, constantan-copper or constantan-iron. The student should acquaint himself thoroughly with the circuit and operation of the potentiometer used.

Equipment: Portable potentiometer, electric furnace with or without automatic regulation, ammeter for furnace circuit, standard thermocouple wire, unknown pair of wires, ice, test tubes, double pole, double throw switch.

Theory: The international temperature scale conforms with the thermodynamic scale as closely as possible with the present knowledge. It is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values have been assigned. A calibration of an instrument according to the specified procedures is quite elaborate and time consuming.

Recourse is therefore taken to calibration by means of secondary standards. For higher temperatures, such a secondary standard may be a Pt-PtRh thermocouple calibrated by the Bureau of Standards.

For convenience sake the standard couple used in this experiment is a chromel-alumel couple. It should be remembered, however, that for important work, a Pt-PtRh-couple treated with great care should be used.

If only one or two points of calibration is desired a furnace may be regulated to attain the desired temperature and the unknown and the standard couple are placed closely together and the two e.m.f.'s read.

In this experiment, a continuous curve is desired.

Procedure:

1. Permit the temperature of the furnace to rise continuously without interruption using the set-up shown in Fig. 33.
2. For each point to be determined upon the calibration curve, take a series of five potentiometer readings at equal intervals of time. Make each time interval about one minute, the shorter the better.
3. Take readings alternately upon the standard and the unknown thermocouple. Then the 1st, 3rd, and 5th readings will be upon the standard. The 2nd and 4th readings will be upon the unknown.
4. A straight-line relationship is assumed between time and temperature over those short ranges. The readings for the standard thermocouple are then interpolated to find what the e.m.f. of the standard would have been at the moment when the e.m.f. of the unknown was measured. The temperature of the unknown couple at any given time is the same as the temperature of the standard couple at the same time.
5. This procedure is repeated as many times as there are points desired upon the calibration curve. For instance, if ten points are desired upon the calibration curve, ten series of five readings each would be taken.

Results: From your measurements plot the corrected temperature-e.m.f. curve.

Answer the following questions:

1. How can you distinguish between the positive and the negative wires?
2. Why is the cold junction kept at 0°C ?
3. Is it enough to keep the cold junction in ice water? Why?
4. What is a "straight line" thermocouple?

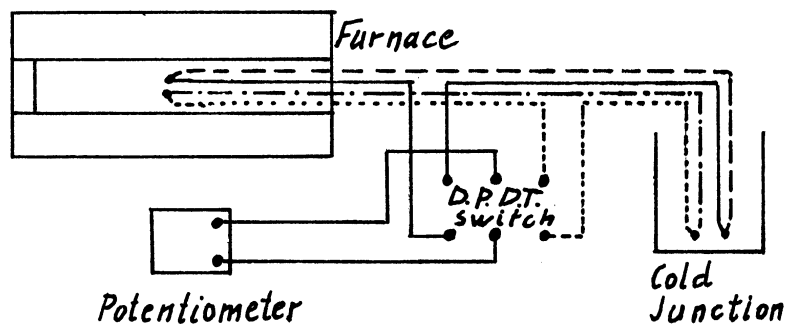


Fig. 33. Thermocouple Calibration

Experiment 56

CALIBRATION OF A MILLIVOLTMETER BY A POTENTIOMETER

Reading: Wood and Cork, pp. 62-69.

Object: To acquaint the student with the millivoltmeter for measuring e.m.f. and to bring out the precautions that must be taken when this instrument is used. The experiment also provides another illustration of the potentiometer principle which is utilized to such an extent nowadays in instruments of all kinds.

Equipment: Portable or semiprecision potentiometer, millivoltmeter, several slidewire resistances of at least 1000 ohms, one dry cell.

Procedure: Build a circuit in such a way that small e.m.f.'s can be taken out over the range of the millivoltmeter. This can be achieved by letting the voltage from the battery drop through the whole winding of the slide wire rheostat, and take out part of it as shown in the sketch: (Potential divider). It is desirable to repeat the process a second time to get finer steps.

This current is left on all the time through the voltmeter. The binding posts of the voltmeter are also connected to the potentiometer in such a way that the two e.m.f.'s will oppose each other. Regulate the current flowing through the millivoltmeter in steps of 5 millivolts and read the corresponding e.m.f. at the binding posts on the potentiometer.

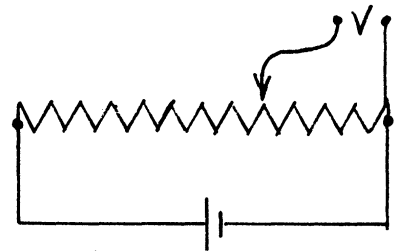


Fig. 34. Potential Divider

Results:

1. Record a number of readings in this way and construct a curve showing the relation of the reading of the potentiometer and the millivoltmeter.
2. Add a known resistance to that of the millivoltmeter, for instance 10%, repeat the readings, and record them. Connect as shown below.
3. Such a change of the resistance in the outer circuit of a thermocouple could easily be made either accidentally or on purpose. Calculate the per cent error in the voltmeter scale readings when 10% resistance is added. Compare it to the observed measurements.

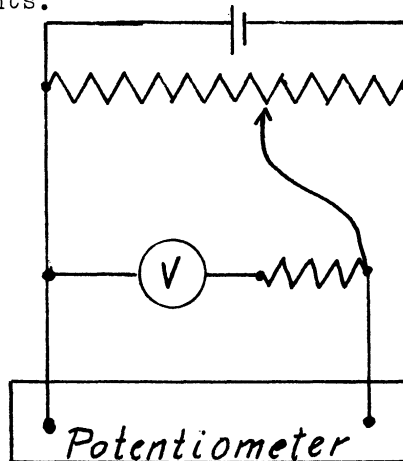


Fig. 35. Potentiometer Millivoltmeter Connection

Experiment 57A

OPTICAL PYROMETRY

Reference: Wood and Cork, pp. 103-116, 119-121, 123-128, 133-134, 138-140.

Purpose: To demonstrate the principle of operation and to calibrate two optical pyrometers.

Equipment: L and N Optical No. 341175 (standard), L and N Optical No. 237265, Pyro Optical No. 1950, standard test lamp, constant voltage transformer (5 volts and resistance equipment).

Theory: The theory of optical pyrometry is rather extensive and cannot be treated here. The reference listed above MUST BE READ by the student before attempting to perform this experiment.

There are three optical pyrometers available in the laboratory, and each one has a unique operating mechanism. Study the diagrams in the reference book and on the walls of the laboratory. All optical pyrometers must be focused on the surface whose temperature is being measured.

Procedure: 1. Study the wiring diagram (p. 115 in reference) and the operation of the L and N No. 341175 pyrometer. This pyrometer has a potentiometric indicator and is to be used as a standard to determine the temperature of the standard test lamp, which is simply a means of providing constant temperature.

2. Connect the standard lamp circuit as shown in Fig. 36. Place the contact C at setting "2700." Focus the eye-piece on the heated wire inside the pyrometer. Next focus the objective on the standard lamp filament when the pyrometer is placed about 3 feet from it. Record the temperature as read.

3. Change the objective setting so that the lamp is badly out of focus. Now take a new reading. The purpose of this is to show the importance of focusing the objective on the surface to be measured. This step need not be done for any other reading during this experiment.

4. Set the contact C at the 2500 and take a reading. Do the same for the 2000 setting.

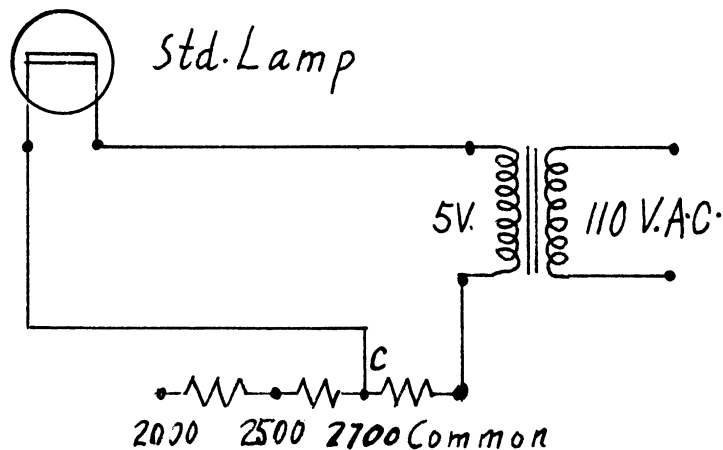


Fig. 36. Standard Lamp Circuit

5. Now read the temperature corresponding to these three lamp settings with the other pyrometers, being careful to focus the lamp filament.

The Report: 1. Compute the true temperature of the 3 standard lamp settings by means of the following equation:

$$\frac{1}{T} - \frac{1}{T_a} = \frac{\log_{10} E_\lambda}{9880}$$

where T = true temperature in degree Kelvin, T_a = the apparent or observed temperature in degrees Kelvin, and $E_\lambda = 0.46$.

2. Present a table of data as follows:

Apparent Temperature, °F as read with			True T, °F from No. 341175
No. 341175	No. 237265 (milliamps)	No. 1950	

3. Draw a correction curve for pyrometer No. 1950, plotting the correction in degrees F as ordinate versus reading in degrees F as abscissa.
4. Define what is meant by a "black body." (P. 104, reference).
5. Explain how the color of a radiating body changes with temperature.

Experiment 57B

TOTAL RADIATION PYROMETRY

Reference: Wood and Cork, pp. 149, 155 - 162.

Purpose: To demonstrate the principle of operation and to calibrate a total radiation pyrometer.

Equipment: L and N Rayotube No. 407214, Pyro Perfect No. 4463, portable potentiometer, thermocouple, and furnace.

Theory: The theory of radiation pyrometry is adequately treated in the above reference. This must be read before attempting to carry out this experiment.

In contrast with optical pyrometers, the total radiation pyrometers need not be focused manually on the source of radiation. However, their correct operation depends upon the distance from the source. In all cases the opening of the pyrometer must be completely filled with the radiation emanating from the source.

Procedure: 1. Study the L and N booklet on the Rayotube.

2. Compute the distance that the tip of the Rayotube must be placed from the heated source for correct readings by the formula:

$$D = A \times \frac{(N + E)}{N}$$

where D = diameter of the heated surface in inches

A = a constant, depending on the instrument (0.35 for Rayotube 407214)

N = a constant, depending on the instrument (2.7 for Rayotube 407214)

E = distance in inches from the front end of the sighting tube to the radiating surface

3. Clamp the Rayotube in place, allowing for the distance from the mouth of the furnace to the radiating surface
Start the furnace. The resistance for regulating the furnace is mounted under it and should be in the "9" position similar to the dial on a clock. Decrease the resistance when the furnace is red hot by moving the pointer counterclockwise, but not further than to the 6 position.
4. Check the temperature of the furnace with the thermocouple. Start the readings at 1700°F.
5. Read the Rayotube indicator in millivolts. Keep the temperature as constant as possible during readings. The temperature-millivolt table for this instrument is found on the indicator plate.
6. Read the Pyro Perfect Temperature (degrees F). About 30 seconds are required for the needle to come to its final position.
7. Check the furnace temperature at once.
8. Take further readings with the Rayotube and the Pyro Perfect at about 1900 and 2100°F.

The Report:

1. Present a table of data similar to that used in experiment 57A.
2. Draw correction curves for the Rayotube and the Pyro Perfect pyrometers. Plot correction in degrees F as ordinate versus instrument reading in degrees F as abscissa.
3. Define "Emissivity"
4. Explain briefly the principle of operation of the Rayotube.
5. If the distance E were not known exactly, would one commit a greater error by moving the Rayotube away too far from the furnace than having it too close within reasonable limits?

Experiment 58

CALIBRATION OF POTENTIOMETRIC RECORDERS

Reference: Pyrometry, pp. 169-202.

Purpose: To demonstrate principles of operation and to calibrate a potentiometric recorder.

Equipment: L and N Potentiometric Recorder, portable potentiometer, dry cell.

Theory: The recording potentiometer is widely used to obtain automatically a graphic representation of variations in the temperature of plant processes. This may be done almost simultaneously in as many as twelve different places with the same instrument.

Potentiometers have a much wider range of use than just temperature recording. With slight changes of standard models, they may be made to record pH of solutions, composition of gases, and density of smoke in smoke stacks. New applications are frequently reported. The reason is that many processes will progress under such conditions that an e.m.f. can be generated which will vary depending on degree of progress made in the process. (Neutralization of acids and bases can be made to produce an e.m.f. by formation of concentration cell.) Or, conditions under which a process works may be made to change the electrical resistance of some device and the potential drop may be recorded. An example of this is the measurement of the composition of the atmosphere in a heat treating furnace. This composition may be recorded by following the change in resistance of a wire surrounded by gases in the furnace.

With recording, there often follows manual control. However, it is more sensible to make the instruments themselves take over the controls. If the conditions can be recorded, they generally can also be controlled by much the same type of mechanism. For these reasons it is of considerable interest to study recording potentiometers. High speed recorders use the electronically amplified e.m.f. to drive the recorder motor.

Procedure: 1. Observe the instruments in operation until the purpose and relations of all parts are clear. Take notes.

2. Draw a sketch of the central balancing mechanism. This includes the galvanometer needle, cams, slide-wire wheel, clutch, pen and pulleys, etc. Do not include the motor or gears and other accessory parts.

In calibrating one potentiometer against another, it is unnecessary to employ an external source of e.m.f., such as in Exp. 56. However, a potentiometer always needs a dry cell or similar device in the working circuit.

3. Standardize the working circuit current in the recording potentiometer. Make sure the recorder galvanometer is not shorted out before this.

4. Short-circuit the galvanometer on the recorder and turn the balancing mechanism to such a position that the clutch is released. This allows the main shaft to be rotated freely to any position.

5. By thus rotating the shaft, set the pen indicator at various points on the high scale, and check the reading with the portable potentiometer.

6. Calibrate the low scale in the same manner.

The Report:

1. Prepare a correction curve for each scale. Plot correction (in millivolts) as ordinate versus instrument reading as abscissa.
2. Why is it unnecessary to employ an external source of e.m.f. when calibrating one potentiometer against another?

Experiment 59

DETERMINATION OF PHASE CHANGES

Reference: Wood and Cork, pp. 201-213, Thermal Analysis of Steel, A.S.T.M. Designation E 14-33. A.S.T.M. Standards 1946, Part I-A, pp. 284-288.

Purpose: To acquaint the student with a method of studying transformation in solids by means of the thermal effects occurring.

Equipment: Furnace, thermocouple fastened to specimen, potentiometer, two stop watches, ammeter and variable transformer. It is desirable to use a high vacuum oil pump with manometer for evacuation of the furnace tube to protect the specimen from oxidation.

Theory: Whenever there is a change in the structural arrangement of the atoms in a crystalline solid, including the liquid-solid transformation itself, a heat effect will be observed. Such an effect can occur at a very definite temperature such as at the freezing point of pure metals. This definite temperature can be used for calibration of temperature measuring devices. The heat effect may also be extended over an interval of temperature. This happens on solidification of a solid solution, or on breaking up of a solid solution to form the eutectoid and a new phase. This latter case is very important in steels.

The study of cooling curves is the most convenient method for establishing the equilibrium phase diagram for two or more substances. Cooling curves can also be used for observing transition points in pure elements or in compounds.

Cooling curves may be recorded either as plain time-temperature curves, as differential curves or as inverse rate curves. The latter two show up the heat effects more strikingly than the first.

The iron-carbon equilibrium diagram to be studied is very important, and even pure iron is most interesting since it has two phase changes and one magnetic transformation.

Procedure: The specimen is mounted in the furnace tube in the middle of the furnace, supported by the thermocouple. If a vacuum pump is used, all connections must be tight. This can be tested with the manometer. Suitable current is used to raise the sample temperature 2-4°C per half minute intervals. If it is necessary to increase the rate during a run, care should be taken to do it at a time when no heat effects are apparent. A cooling curve may also be taken in the same way, but the current in the furnace is not entirely shut off, since this would make the cooling rate excessive.

The results are recorded in the form of differential curves. By this method the time for a certain definite rise or fall in the temperature of the specimen is recorded. This is most easily done by starting one stop watch at the beginning of a temperature interval and stopping it at the end, simultaneously starting the second stop watch for the next temperature interval.

It is easier and less confusing to read temperatures in terms of millivolts. The important readings may then be changed into degrees later.

In the case of steel it is only desired to investigate the region including the three lowest critical points. Thus readings need not be started till about 700°C on heating and stopped at 930°C.

The Report:

This should include:

- (a) A brief discussion of the set-up, including the size of the specimen and the thermocouple wires.
- (b) A plot of the results with the temperature expressed either in degrees or millivolts.
- (c) The temperatures at which the beginnings and ends of the inflections can be definitely recognized.
- (d) The carbon content on the basis of the curves, as compared to the iron-carbon equilibrium diagram, a drawing of which should be appended.

QUESTIONS

1. What is the mathematical connection between an ordinary time-temperature cooling curve and an inverse rate curve?
2. What points on the time-temperature curve correspond to the points asked for under (c)?

Experiment 60

CHARACTERISTICS OF A TRIODE RADIO TUBE

Reference: Müller, Garman and Droz, pp. 25-35; Daniels, Mathews and Williams, pp. 429-31.

Purpose: To determine the characteristics of a triode radio tube.

Equipment: Triode tube, galvanometer, voltmeters, adjustable grid and plate voltage supply milliammeter, resistance box.

Tube	Filament Voltage
76	6.3
56	2.5
27	2.5

Theory: A three-electrode electron tube is called a triode. It contains three elements: the anode or plate, the cathode which is often the filament, and a grid of wire mesh placed between the plate and filament.

When the cathode filament is heated, electrons will be liberated but will remain around the filament giving rise to a space charge. If the plate is made positive relative to the filament, the electrons will flow to the plate and the tube becomes a conductor. However this flow of electrons can be regulated and almost completely stopped by adjusting the potential of the grid. If the grid is made slightly negative with respect to the cathode, the electrons will be repelled to a degree, but a considerable current will flow. However, if the grid is made more and more negative, less and less current will flow. The grid potential can thus be made to control the plate current so that the grid potential acts as a valve with practically no inertia for the grid current.

From this property arise many of the characteristics of the radio tube. By impressing the potential produced by a feeble current on the grid, the tube can be made to act as an amplifier. If we vary the grid potential periodically, oscillations will be set up in the plate circuit, and the tube acts as an oscillator.

The present experiment is designed to demonstrate the variations in four quantities: grid current (i_g), grid voltage, (e_g), plate current (i_p), and plate voltage (e_p).

The wiring diagram is given in Fig. 37.

Since changes in current corresponding to changes in other variables are more important than the static values, the A.C. or dynamic resistances or conductances are usually measured and evaluated at various operating points. Thus, the equation

$$r_p = \left(\frac{\partial e_p}{\partial i_p} \right)_{e_g}$$

defines the dynamic plate resistance r_p for a small change in plate voltage resulting in a small change in plate current i_p at a fixed grid potential e_g . The reciprocal of this formula represents the conductance expressed in reciprocal ohms as the resistance is expressed in ohms.

The effect of the grid voltage on the plate current is expressed in conductance units:

$$g_m = \left(\frac{\partial i_p}{\partial e_g} \right)_{e_p}$$

where g_m is grid-plate-transconductance and the other terms have the usual significance.

Another constant which is often used expresses the ratio between the effects of the plate voltage and the grid voltage on the plate current.

$$\mu = \frac{\left(\frac{\partial i_p}{\partial e_g}\right) e_p}{\left(\frac{\partial i_p}{\partial e_p}\right) e_g}$$

μ is called the amplification factor of the tube. The numerator is the grid-plate transconductance, and the denominator is the reciprocal of the plate resistance.

When common terms are cleared from the equations the expression reduces to:

$$\mu = - \left(\frac{\partial e_p}{\partial e_g}\right) i_p$$

Procedure:

1. Connect the triode as shown in Fig. 37.
2. Record plate current vs. plate voltage at constant grid voltages of 0, -1, -2, -4 and -6v. The galvanometer should be shorted which the grid voltage is zero. When the grid voltage is different from zero, also read the grid current through the galvanometer. As these curves are generally non-linear at low plate currents, it is advisable to take more data in this region than elsewhere. Start the measurements with a plate voltage of 40 - 50 v.
3. Increase the plate voltage by steps of 30 volts up to 160 v. taking measurements as above for each setting. Do not exceed a plate current of 10 ma.
4. Plot a family of curves as shown in Fig. 38.
5. For a specific plate voltage, for instance 80 v. determine the value of r_p at several points by drawing a tangent to the curve at the desired point, thereby obtaining the slope $\frac{\Delta e_p}{\Delta i_p}$. Tabulate these values and specify grid and plate voltages at which these values of r_p were found.
6. Replot the data of Fig. 38 by treating i_p as a function of e_g for constant plate voltage. This gives a family of curves shown in Fig. 39. Draw tangents to the curves in various points and determine the transconductance

$$g_m = \left(\frac{\partial i_p}{\partial e_g}\right) e_p$$

This quantity is usually expressed as micromhos that is the reciprocal resistance times 10^6 .

7: Plot values of r_p , g_m and μ as a function of negative grid voltage as shown. Note that μ is almost a constant, but that g_m and r_p change rapidly at high grid voltages, but in opposite direction. This plot must be made for a definite plate voltage.

8. Plot grid current as a function of grid voltage for various plate voltages. Note that if the galvanometer sensitivity is too low, the lower part of the grid current curve of Fig. 39 may not be measurable.

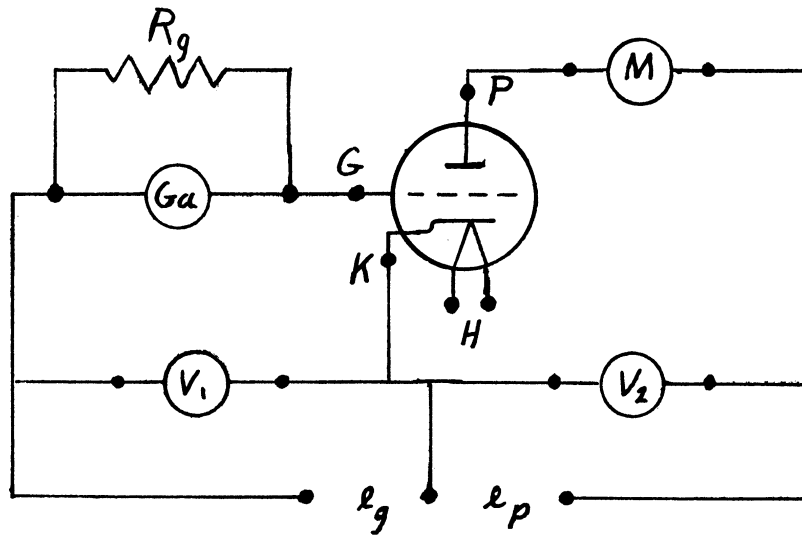


Fig. 37. Triode Wiring Diagram

G_a = galvanometer, L and N No. 476746, for measuring grid current
 Coil resistance is 329 ohms,
 sensitivity is 0.031 microamperes per millimeter
 R_g = damping resistance across galvanometer (1700 ohms)
 M = milliammeter for reading plate current
 V_1 = voltmeter for reading grid voltage
 V_2 = voltmeter for reading plate voltage
 H = heater connections to power pack
 e_p = plate voltage supply
 e_g = grid voltage supply

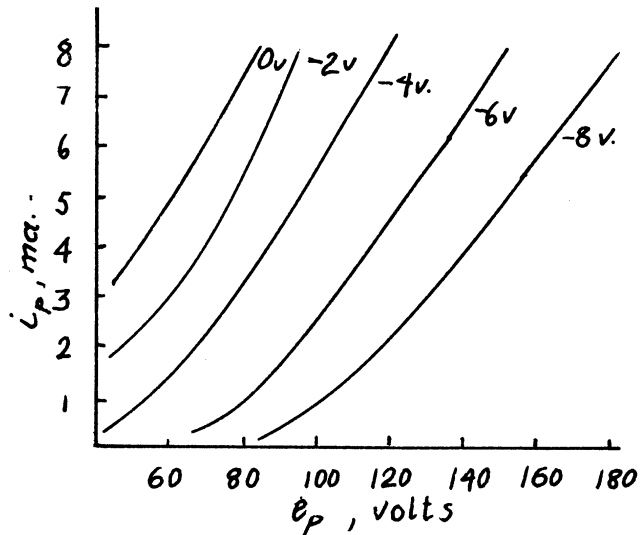


Fig. 38. Plate Voltage Versus Plate Current Curves

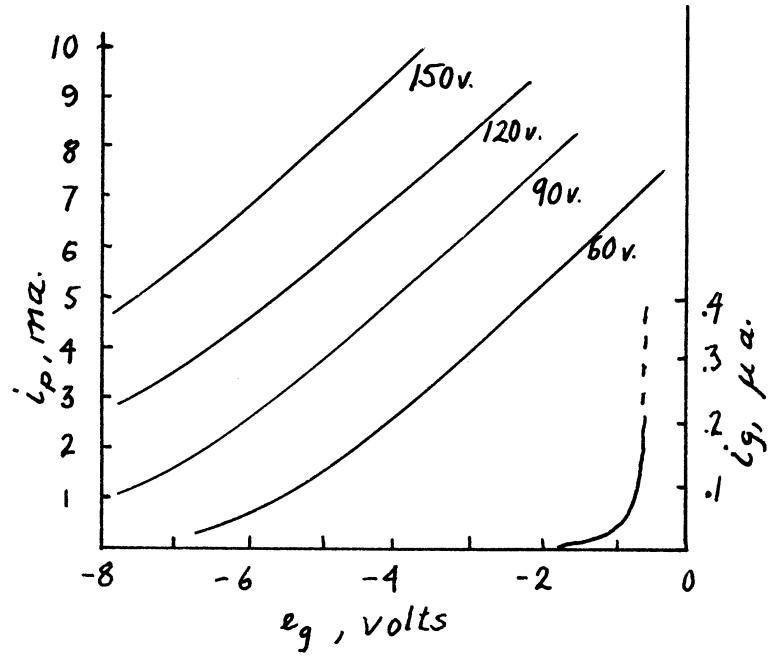


Fig. 39. Grid Voltage Versus Plate and Grid Current Curves

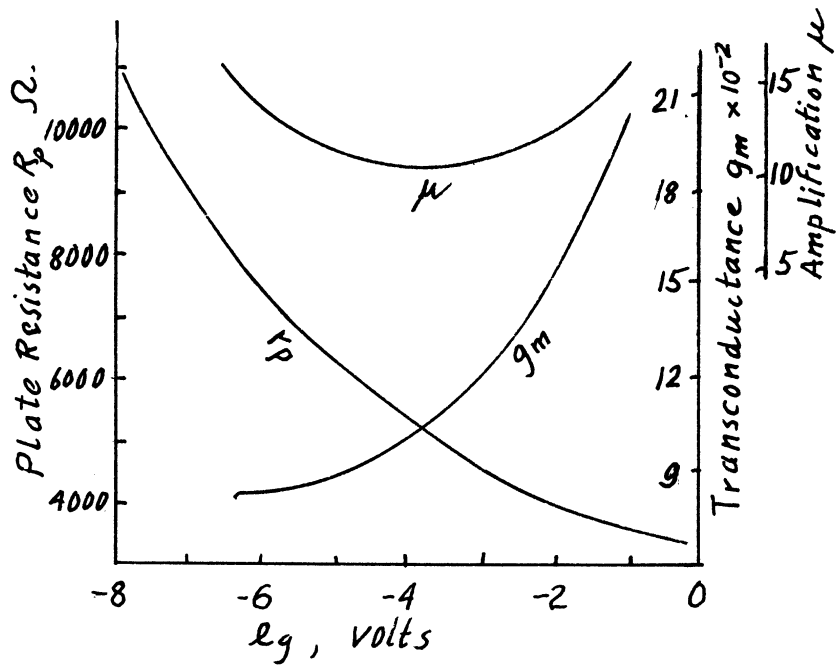


Fig. 40. Plate Resistance, Transconductance and Amplification Versus Grid Voltage

ERRORS OF MEASUREMENTS AND THEIR CORRECTION

Errors entering into the measurement of physical quantities may be divided into determinate errors and indeterminate errors. The first kind may be due to:

1. Instrumental errors resulting from poor construction or faulty graduation of an instrument. Cheap celluloid centimeter scales frequently are faulty.
2. Personal errors due to characteristic peculiarities of the individual observer, such as the tendency always to record the occurrence of an event too soon or too late.
3. Errors of method or theoretical errors. These may arise from using an instrument under conditions for which it is not suited, at least not without calibration. A certain scale may be calibrated for, say 20°C., and can therefore not be used for measuring anything at 0°C without an appropriate correction. Accurate measurements of length on an exposed photographic film is senseless unless the shrinkage of the film during the developing process can be corrected. Likewise, humidity, barometric pressure and numerous other conditions may be different from those under which the apparatus was calibrated, or these conditions may even change during an experiment.

The above errors may also be classified as constant or systematic errors.

After the known errors have been corrected there remains the residual errors. It is a common observation that repeated measurements usually differ by small amounts even if they seemingly have been carried out under identical conditions. These fluctuations are due to causes over which the observer had no control, such as sudden temperature fluctuations, mechanical jarring, etc. Most important are physiological causes arising from imperfections or fatigue of the ear or eye of the observer. They may, therefore, also be classified as observational errors. These errors have also been called random errors because the magnitude and sign of such accidental errors can be shown in many cases to follow the law of chance or a normal frequency distribution. The following actual experiment serves as an illustration of the way the law works. A skilled marksman fires 1000 shots against a target ruled in horizontal sections by lines 1 ft. apart, the center line (corresponding to the bull's eye) being in the middle of one of the spaces. The results shown in the graph Fig. 41 were obtained. By increasing the number of shots and smoothing the line, the curve of Fig. 41 would be obtained. This is the so-called curve of error whose equation was derived by Gauss. It is now commonly written

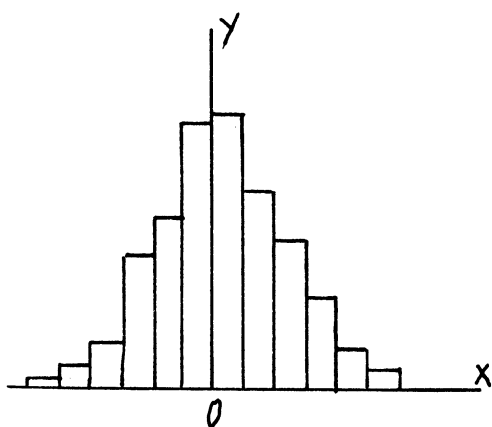


Fig. 41. Experimental Distribution Curve

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2 x^2}$$

Here y is the frequency of the occurrence of an error of magnitude x , and h is a constant which measures the precision of the marksman. If the shots concentrate around the bull's eye, we say that both accuracy and precision are high, and we get a narrow symmetrical distribution curve. In this case h is high.

Another case may happen, namely that the shots concentrate around some other point which is not the bull's eye. Here, the precision is high but the accuracy is poor.

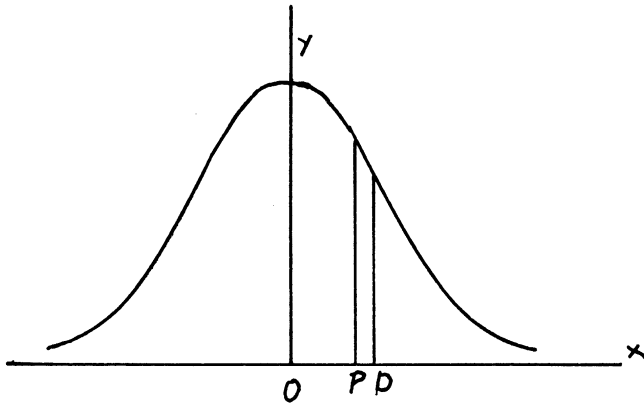


Fig. 42. Gauss Error Curve

In this case, there is probably an unsuspected constant error in the aiming of the gun, like not taking the wind into consideration, or simply faulty sights. If the shots are scattered over the whole target, both accuracy and the precision are low.

Taking of physical measurements will in many cases be analogous to shooting at a target. The bull's eye is the true value, and our measurements will be scattered around the unknown true value if there is no constant error.

the center of gravity of the half area.

In Fig. 42, the distance OD is the abscissa of the ordinate passing through

The Arithmetical Mean

The mean value m of a series of observations, a_1, a_2, \dots, a_n with equal probability is expressed as

$$m = \frac{\sum a}{n}$$

This mean value is not the true value of the desired quantity, especially if residual errors are present. In order to evaluate the quality of our observations we want to find the probable deviation of our measurements from the mean. If the probable deviation is high, our measurements are poor.

The average deviation is defined as

$$a.d = \frac{\sum d}{n}$$

where the individual deviations d_1, d_2, \dots, d_n have been summed, disregarding sign.

If we assign weights to the individual observations, the mean M becomes:

$$M = \frac{p_1 a_1 + p_2 a_2 \dots + p_n a_n}{p_1 + p_2 \dots + p_n} = \frac{\sum p a}{\sum p}$$

where $p_1, p_2 \dots p_n$ are the weights assigned to the various observations due to their degree of reliability.

Deviation of the Mean: Fractional and Percentages Deviations

The deviation of a single measurement, $a.d.$, is not so valuable as the deviation of the mean, denoted $A.D.$ It can be shown that

$$A.D. = \frac{a.d.}{\sqrt{n}} \text{ where } n \text{ is the number of measurements.}$$

In words, the arithmetical mean of n equally probable observations is n times as reliable as any single observations.

In order to express the reliability of a quantity, the fractional and the percentage deviations are used.

The fractional deviation of a single observation = $\frac{a.d.}{a}$

The percentage deviation of a single observation = $100 \frac{a.d.}{a}$

The fractional deviation of the mean observation = $\frac{A.D.}{m}$

The percentage deviation of the mean observation = $100 \frac{A.D.}{m}$

The above expressions are derived on the assumption that the errors involved are accidental; in other words they fall with equal probability on both sides of the true value. We may, however, have constant errors that influence the result so as to make the shots concentrate in another spot outside of the bull's eye.

The Probable Error

In the error curve and its equation the term "probable error" is frequently used. The probable error of an observation is of such a magnitude that the probability of making an error greater than it is just equal to the probability of making one less than it, both probabilities being one-half.

In the graph Fig. 42., p.e. is denoted as O P.

From probability tables: p.e. = $\frac{0.477}{h}$

The probable error of a single and that of the mean observation are given by the expression

$$p.e. = 0.67 \sqrt{\frac{\sum d^2}{n-1}} \quad \text{and} \quad P.E. = 0.67 \sqrt{\frac{\sum d^2}{n(n-1)}}$$

These expressions can be rewritten:

$$p.e. = 0.85 \frac{\sum(+d)}{\sqrt{n(n-1)}} \quad \text{and} \quad P.E. = 0.85 \frac{\sum(+d)}{n\sqrt{n-1}}$$

For many purposes, the average deviation is simpler to handle and will be used here.

Rejection of Observations

Before measurements are discarded as unreliable, they should be carefully scrutinized. If the observations in question are read on a wrong scale, recorded by wrong numbers, etc., they must be rejected. If no mistake is apparent, they should never be rejected without the most scrupulous unbiased judgment on the part of the observer or the application of some mathematical criterion for the rejection of doubtful observations.

In most physical work the number of observations is not very great, and one value widely discordant from the others has undue weight on the value of the mean. A good criterion to follow in such cases is the following:

Compute the mean and the average deviation a.d. omitting the doubtful observation. Compute also the deviation d of the doubtful observation from this mean. If $d = 4$ a.d., reject the observation since it can be shown that the probability of the occurrence of an observation whose deviation is equal to four times the average deviation, is only one in a thousand.

Computation Rules and Significant Figures

Half of the time spent on computations is probably wasted owing to the retention of more figures than the precision of the data warrant. At the outset of each stage of a computation, all figures should be rejected which have no influence on the final results.

In the following, a short discussion of rules of computations is given.

A Digit is any one of the ten characters 1,2,3,4,5,6,7,8,9,0.

A Significant Figure is any digit to denote or signify the amount of the quantity in the place in which it stands. Thus zero may be a significant figure when it is written, not merely to locate the decimal point, but to indicate that the quantity in the place in which it stands is known to be nearer to zero than to any other digit.

For example, if a distance has been measured to the nearest fiftieth of an inch and found to be 205.46 inches, all five digits are significant. If the measurement had shown the distance to be nearer to 205.40 than to 205.41 or 205.39, the final zero would be significant, and should be retained. If the quantity had been written 205.4 instead of 205.40, the inference would be drawn either that the measurement had not been carried out with an accuracy which warranted the use of the last zero, in this case, that the measurements were not carried out to 1/50 or 1/100 of an inch, or that the person who wrote the number was ignorant or careless of the proper numerical usage.

The following rules are deduced subject to the condition that the accumulated errors in a computation shall not affect the second unreliable place of figures in the final result by more than one unit, even though as many as sixteen rejections of figures are made in the course of the computation.

RULE I: In rejecting superfluous figures, increase by 1 the last figure retained, if the following rejected figure is five or over.

RULE II: In all deviation and precision measures, retain only two significant figures.

The reason for this rule is as follows: Suppose a length m is measured to be 122.48 cm. with an A.D. of 0.12 cm. The significance of the A.D. is that the place of figures in m occupied by the four is uncertain by 1 unit, and the next place is uncertain by 12 units, while the third unit would be uncertain by at least 120 units, which of course renders it worthless.

In general, the place of figures corresponding to the first significant figure in the deviation measure is somewhat uncertain from 1 to 9 units, while the place corresponding to the second significant figure is uncertain by ten times this amount, or exactly 10 to 99 units. Beyond this the significance of additional figures is practically nil. Hence as precision and deviation measures are at best only estimates of the reliability of a result, it is useless to compute them to places of figures which have no real significance in the result to which they refer.

If the first significant figures in the precision measure is as great as 8 or 9, in which place the figures in the data corresponding to the second place in the precision measure is unreliable to 80 or 90 units, it is usually sufficient to retain only one significant figure in the precision measurement.

RULE III: Retain as many places of figures in a mean result and in data in general as correspond to the second place of significant figures in the deviation or precision measure.

RULE IV: In adding or subtracting a number of quantities, find the average deviation of each, and then retain in each quantity significant figures in the largest deviation.

The reason is that the sum or difference of two or more quantities cannot be more precise numerically than the quantity having the largest average deviation.

RULE V: In computations involving multiplication or division, the number of significant figures to be retained is determined by Rule III in the factor which has the largest percentage deviation. The reason is that the percentage precision cannot be greater in the product or quotient than the percentage precision in the least precise factor entering into the computation.

Computations involving a precision not greater than 1/5 per cent should be made on a slide rule. For greater precision logarithmic tables should be used. If multiplication and division must be resorted to, the "shortest method" of rejecting all superfluous figures at each stage of the operation should be used.

RULE VI: In carrying out the operations of multiplication and division by logarithms, retain as many figures in the mantissa of the logarithm of each factor as are properly retained in the factors themselves under Rule V.

Precision Discussion of Indirect Measurements

Indirect measurements are those in which the final result is a more or less complicated function of one or more directly measured quantities.

There are two distinct classes of problems:

1. The precision measures of the directly measured components are known, and it is desired to find the precision measure of the final result.
2. The desired precision of the final result is stipulated at the outset, and the problem is to ascertain what precision is necessary in the components, in order that the accumulated effect of the errors in these components on the final result shall not exceed the prescribed limit.

The importance of these problems cannot be overestimated. In the first case, a final result, whether it is the result of a chemical analysis, the value of a physical constant, the algebraic expression of a law, or an efficiency test of an engine, is practically worthless unless a numerical estimate of its reliability can be stated. It may even be worse than worthless if recorded to indicate a higher precision than the data warrant. The second case is of equal importance. If an investigator makes a preliminary precision discussion of his method and apparatus before beginning work, he will know, at least approximately, how precisely each quantity entering into the final result should be measured. In this way he might avoid wasting time and labor on measuring some components more precisely than necessary, while others may be measured to a degree of precision which will make it impossible to attain the desired precision in the final result.

The following notations will be used:

M = the final computed result of any indirectly measured quantity

Δ = numerical precision measure of M

m_1, m_2, \dots = direct measured quantities which may be either mean results or single observations

$\delta_1, \delta_2, \dots$ = numerical precision measures of m_1, m_2, \dots respectively.

The values of δ might be expressed as average deviations, probable errors or mean errors. In discussion of any problem, the same kind of precision measure must be used throughout. In this discussion we shall express δ as deviations.

$\Delta_1, \Delta_2, \dots$ will be used to denote the deviations produced in M by deviations $\delta_1, \delta_2, \dots$ in the components m_1, m_2, \dots respectively.

From this notation we have:

$\frac{\Delta}{M}$ = fractional precision of the final result

$100 \frac{\Delta}{M}$ = percentage precision of the final result

$\frac{\delta_1}{m_1}, \frac{\delta_2}{m_2}, \dots$ = fractional precision of the components, respectively.

$100 \frac{\delta_2}{m_1}$, $100 \frac{\delta_2}{m_2}$... = percentage precision of the components, respectively.

In general: $M = f (m_1, m_2 \dots)$ which may be written $f ()$.

The first class of problems may be stated as follows:

CASE I: THE DIRECT PROBLEM:

Given the precision measures $\delta_1, \delta_2 \dots$ of the components compute the precision measure Δ of the result M .

The solution is found by obtaining the effect of the deviation of each combining the separate effects to get the resultant effect.

Separate Effects:

The effect of a deviation δ_k in any component m_k will be to produce a deviation Δ_k in M of an amount:

$$\begin{aligned} \Delta_k &= \frac{\partial M}{\partial m_k} \delta_k \\ &= \frac{\partial}{\partial m_k} f () \delta_k \end{aligned}$$

Example 1: Find the deviation in the volume of a sphere whose diameter is 10.013 cm., if the average deviation in the measurement is A.D. = 0.012 cm.

$$V = 1/6 \pi D^3 = M$$

$$m = D = 10.013 \text{ cm, A.D.} = 0.012 \text{ cm}$$

$$V = 525.64 \text{ cm.}$$

$$\Delta = \frac{d}{dD} (1/6 \pi D^3) \delta = 1/6 \times \pi \times 3D^2 \times \delta = 1.9 \text{ cm}^3$$

This means that the volume 525.6 is uncertain by 1.9 cm³ or by 19 parts in 5300.

Otherwise expressed: a deviation of $100 \frac{\delta}{D} = 100 \frac{0.012}{10} = 0.12\%$ in the diameter produces a deviation of $100 \frac{\Delta}{V} = 100 \frac{1.9}{530} = 0.36\%$ in the volume, i.e., a percentage deviation three times as great. In this case V is a function of only one single variable, hence the resultant deviation in V is found at once.

Example 2: In the experiments of effusion of gases, $\frac{m_1}{m_2} = \frac{t_1^2}{t_2^2}$ where m_1 and t_1 are molecular weight and time of effusion for one gas, for instance air, and m_2 and t_2 the same quantities for another gas, for instance oxygen. If we use oxygen, $m_2 = 32.00$, and want to find m for air, we have:

$$m_1 = M = m_2 \frac{t_1^2}{t_2^2}$$

Our measurements have given us the following results: $t_1 = 40.1$ sec. with an A.D. of 0.5 sec., $t_2 = 42.5$ sec. with an A.D. also of 0.5 sec.

$$M = 32 \frac{40.1^2}{42.5^2} = 28.9$$

$$\Delta_1 = \frac{\partial M}{\partial m} \delta_1 = \frac{\partial \left(m_2 \frac{t_1^2}{t_2^2} \right)}{\partial t_1} \delta_1 = m_2 \times 2 \frac{t_1}{t_2^2} \delta_1$$

$$\Delta_1 = 32 \times 2 \frac{40.1}{42.5^2} \times 0.5 = 0.71 = \sim 0.7$$

In the same way,

$$\Delta_2 = -m_2 \times 2 \frac{t_1^2}{t_2^2} \delta_2 = -0.68 = -0.7$$

The negative sign indicates that a positive deviation in t_2 produces a negative deviation in M_1 and vice versa.

Resultant Effect. If it is desired to find the maximum effect of the several deviations, it is assumed that they occur simultaneously with the same sign:

$$\Delta = \Delta_1 + \Delta_2 \dots \Delta_n$$

This case is of importance only if an estimate of the extreme limit of error is desired.

The important case to consider is when the values of $\Delta_1, \Delta_2, \dots$ are equally likely to be plus or minus, and of a magnitude determined by the general law of deviations. If we compute Δ_k according to the above formula, we have that the most probable resulting deviation Δ is obtained by the formula:

$$\Delta^2 = \Delta_1^2 + \Delta_2^2 + \dots + \Delta_n^2$$

$$\text{or } \Delta = \sqrt{\Delta_1^2 + \Delta_2^2 \dots + \Delta_n^2}$$

This is not an exact solution of the problem but is better than any other in combining the values of Δ_k . The effect of the various signs is of course eliminated. The resultant deviation must of course be regarded as equally likely, plus or minus.

Example 2 (cont.)

The resultant precision in the effusion experiment would be:

$$\Delta = \sqrt{\Delta_1^2 + \Delta_2^2} = \sqrt{0.49 + 0.49} = \sqrt{1} = 1$$

A deviation in the time of 0.5 sec. will make the value of the molecular weight of air uncertain by 1 unit or $100 \frac{\Delta}{M} = 100 \frac{1}{28.8} = 3.5\%$

Criterion for Negligibility of Deviations in Components

It is frequently important to determine whether the deviation arising from one or more components may be neglected in computing Δ of the final result.

A safe criterion to adopt is that a certain Δ_k can be neglected, if $\Delta_k \ll 0.33 \Delta$

Likewise, if $\sqrt{\Delta_1^2 + \Delta_2^2 + \dots + \Delta_n^2} \ll 0.33 \Delta$, then the figures under the root sign may be neglected.

CASE II: THE CONVERSE PROBLEM:

Given a prescribed precision Δ to be attained in the final result M , to find the allowable deviations $\delta_1, \delta_2 \dots$ in the components $m_1, m_2 \dots$ respectively such that their combined effect on M shall not exceed the value of Δ .

We have: $\Delta^2 = \Delta_1^2 + \Delta_2^2 \dots + \Delta_m^2$

where $\Delta_k = \frac{\partial}{\partial m_k} f () \delta_k$ or

$$\delta_k = \frac{\Delta_k}{\frac{\partial}{\partial m_k} f ()}$$

If the value of Δ is given, and no further condition is imposed, there are evidently an indefinite number of values that can be found for $\Delta_1, \Delta_2 \dots$ which will satisfy the equation. The most advantageous distribution of errors among the components will evidently be one by which the desired precision is obtained with a minimum expenditure of time and labor on the part of the experimenter. Since this will vary greatly with each problem, no mathematical criterion can be formulated which will embrace all cases. It is best, therefore, at least for a preliminary distribution of errors among the components to so adjust them that the errors inherent in each variable or component shall produce the same effect on the final result. This is spoken of as the solution of the problem for "equal effects."

Example 3: It is proposed that the presence of natural gas in air might be detected by the effusion experiment referred to in Exp. 22. If the method should be of any worth, it must detect at least 3/10 per cent by volume. If the times of effusion could be measured with an A.D. of 0.1 sec. in 60 sec., would the method work?

Assuming the molecular weight of air 28.80, the mixture containing 3/10% CH_4 would have an av. m. w. of $99.7 \times 28.80 + 0.003 \times 16 = 28.71 + 0.05 = 28.76$ and the average deviation Δ is 0.04. In our case,

$$\Delta = \sqrt{\Delta_1^2 + \Delta_2^2} \quad \text{and} \quad \Delta_1 = \Delta_2. \quad \text{Hence}$$

$$\Delta = \Delta_1 \sqrt{2} = \Delta_2 \sqrt{2}$$

$$\Delta_1 = \Delta_2 = 1/2 \sqrt{2} \Delta = 0.028$$

$$\delta_1 = \frac{\Delta_1}{\frac{\partial}{\partial t_1} \left(m_2 \frac{t_1^2}{t_2^2} \right)} = \frac{0.028}{28.8 \frac{120}{3600}} = 0.03 \text{ sec.}$$

The result shows that the proposed precision of 1/10 sec. is not at all sufficient to detect the presence of natural gas in the specified concentration.

It is also possible to solve questions of precision of measurements by various short cuts such as indicated in Daniels, Matthews and Williams on p. 449. However, the above derivations are quite general and will always give solutions.

The above material is mainly taken from H. M. Goodwin, "Precision of Measurements," McGraw-Hill, 1920.

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