A COURSE OF
LABORATORY EXPERIMENTS
ON
PHYSICO-CHEMICAL PRINCIPLES

BY

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NEW YORK
THE MACMILLAN COMPANY
1923

PRINTED IN THE UNITED STATES OF AMERICA

Set up and electrotyped. Published May, 1923

Press of J. J. Little & Ives Co.
New York

PREFACE

THIS book presents a group of laboratory experiments which have been developed during a period of many years at the Massachusetts Institute of Technology as part of the general course of instruction in Chemical Principles given to junior and senior students in Chemistry and Chemical Engineering. Although especially designed to supplement Noyes and Sherrill's "Chemical Principles," published by The Macmillan Company, the experiments are presented in a form suited to accompany any text-book of physical chemistry.

The main purpose of this laboratory course is to illustrate and to emphasize the principles that are being simultaneously considered in the class-room, by giving the student a more concrete acquaintance with the underlying phenomena. It serves also to illustrate some of the common methods of physico-chemical measurement. It differs, however, from most previous laboratory manuals of physical chemistry in the respect that this is an incidental, not a primary feature; emphasis being here placed on illustrating fundamental principles in close coördination with the general class-room course on the subject.

The laboratory course in which these experiments have been used has been taken by large classes having a very limited time to devote to it. The author ventures to outline the policy pursued in overcoming the difficulties which are bound to be met with under such conditions. The class is divided into small sections of ten to twenty students, depending on the duplication of apparatus and number of assistants available. Each section is scheduled for laboratory work for a three-hour period at regular intervals,—for example, once every week or every other week. At a given exercise all students perform the same kind of experiment, though it is advantageous to vary somewhat the substances or reactions which they are studying. In order that the experiment may be completed within two and a half or three hours, all the apparatus required is dispensed individually to the students at the beginning of the exercise; as far as possible all complicated or fragile apparatus being avoided. And all the solu-

tions needed are ready in the laboratory. Thus bottles containing standardized solutions for titrations are permanently set up with an attached buret which can be quickly filled by means of a pressure bulb. Attempt is thus made to save time for the student by avoiding the delays of getting together the apparatus and by diminishing the work of preparing and analyzing solutions, already familiar to the student from his course in quantitative analysis, without sacrificing the thought and initiative involved in setting up the apparatus and making the measurements.

The student is expected to obtain a good knowledge of the essential features of each experiment before he reports at the laboratory. To assist in this, each experiment is systematically described in the book under several sections. An *Outline* devoid of all detail is given first, together with a summary of the *Principles Involved*, for which reference should be made to the general text-book employed. The apparatus is then described and illustrated by diagrams when it seems desirable. The student should be prepared to recite on these sections on coming into the laboratory. These sections are followed by a *Procedure* describing the important details of manipulation which are essential for successful results. In a later paragraph, entitled *Discussion*, the broader aspects of the experiment and the sources of error are considered. Under *Treatment of Results* the student is told specifically what calculations are to be made from the experimental data. At the end of the first and fifteenth experiments are given data sheets which are typical of the final form in which the observed data and the results calculated from them should be tabulated and presented in the report. For the other experiments a corresponding blank form of data sheet should be prepared by the student before the experiment is started.

A short informal conference is held in the laboratory with each section at the beginning of the experiment. The instructor emphasizes the salient features of the experiment, and the students are questioned and given opportunity to ask questions for themselves. The purpose of the conference is to make sure that the student can carry out the experiment expeditiously and intelligently without routine following of directions.

The simplification of procedure which is necessary to enable an experiment to be completed in so short a time must frequently result in a lesser accuracy than is attainable by the method. This must not.

however, be allowed to be made an excuse by the student for careless work. Thus, a volume measured in a graduate should be read as carefully as if measured in a buret, even though the result is necessarily less accurate. If time and circumstances permit, the instructor can increase the interest of the course by suggesting and encouraging changes that will increase the accuracy; thus more exact measurements of freezing-point lowering can be made by substituting a Beckmann thermometer for the one graduated to 0.1° suggested in the experiment.

The author desires to acknowledge with gratitude the coöperation of Professor A. A. Noyes in the development of this laboratory course and his advice in preparing the book for publication. He desires also to express his appreciation of the assistance of Professor E. B. Millard, especially in simplifying the experiments and standardizing the equipment and procedure of the laboratory.

Cambridge, April, 1923.

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LABORATORY EXPERIMENTS ON PHYSICO-CHEMICAL PRINCIPLES

GENERAL DIRECTIONS FOR THE LABORATORY WORK

General Directions in Regard to Laboratory Work. — The following experiments are designed for a series of laboratory exercises of three hours' duration. The apparatus * and the stock solutions will be found ready at the beginning of each exercise. The experiments are usually of such length that they can be completed in the allotted time only by students who have studied the experiment carefully and planned the work to be done before coming to the laboratory.

By way of preparation the student must plan a blank form (on a letter-size sheet) suitable for recording the experimental data, the results of the calculations, and the calculations themselves. Examples of a satisfactory form of data sheet are given in the first and fifteenth experiments. It will be noted that blank spaces are left for recording both the observations made during the Procedure, and the quantities specifically called for under the Treatment of Results. Space is left also or the calculations.

No work in the laboratory should be started until a data sheet, approved by the instructor, has been prepared. During the experiment all data obtained by the student should be directly recorded in ink (or hard pencil) on this sheet. At the close of the exercise the experimental results should be shown to the instructor. If the work is satisfactory, the data will be stamped and returned to the student for the completion of the report.

* A desk outfit suitable for the course is listed in the Appendix.

The data sheet, when properly filled out, constitutes the finished report. The method by which the calculations are made from the data should be clearly indicated, without showing the arithmetical detail involved. This can usually be done by formulating a general equation and by substituting in it the numerical quantities. A slide rule should be used for the calculations when it is sufficiently accurate for the purpose. Diagrams or curves should be drawn neatly in ink or hard pencil. If an extra sheet of paper is necessary, it should be firmly bound to the original data sheet (not merely attached by paper clips).

The finished report should be handed in within one week from the date of performing the experiment. Untidy reports with roughly sketched in curves are not acceptable, even if the data are satisfactory. All reports will be promptly examined and returned to the student. When a report is returned for corrections, the corrections specified must be made and returned with the original data before a fixed date which is stamped on the report.

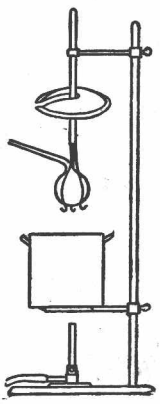
I. MOLECULAR WEIGHT FROM VAPOR-DENSITY

EXPERIMENT 1. THE DENSITY AND MOLECULAR WEIGHT OF VAPORS DETERMINED BY THE DUMAS METHOD

Principles Involved. — Perfect-gas laws, including Dalton's law. Definition and determination of molecular weight. See *Chem. Prin.*, Arts. 8–14.

Outline. — Liquid carbon tetrachloride is introduced into a glass bulb of known weight and volume. The bulb, except for its protruding stem, is then submerged in a vessel of boiling water. The carbon tetrachloride in vaporizing expels the air and fills the bulb with its vapor. The bulb is sealed under these conditions, and is then cooled and weighed with its carbon tetrachloride content. The weight of carbon tetrachloride is thus determined which in the form of vapor completely fills the bulb at the barometric pressure and at the temperature of boiling water.

Apparatus. — A "Dumas" bulb of about 200 ccm. capacity. A three-pronged wire holder for the bulb. A covered 4-liter enamel pot serving as a water-bath. A slot is cut in the cover to fit the rod of the wire holder. A gas burner to heat the bath. The bulb is held in position in the bath by clamping the holder to a ring-stand as shown in the figure. An extra gas burner. A pair of cutting pliers. Pure carbon tetrachloride.



Procedure. — Weigh with an accuracy of one milligram a clean thoroughly dry Dumas bulb whose stem has been drawn to a capillary tip. Introduce into it about 10 ccm. of pure carbon tetrachloride by heating the bulb slightly and then letting it cool with its tip beneath the liquid. Heat the water-bath to

about 75°, and immerse the bulb in it with about 2 cm. of the stem protruding. Support the bulb in this position by clamping the wire holder to a ring-stand. Cover the bath, heat the water to boiling, and boil it steadily until vapor of carbon tetrachloride no longer escapes, as shown by its failure to extinguish a lighted match applied to the tip. Keep the bath boiling steadily with one burner; and by means of a second burner heat the exposed stem of the bulb gently to vaporize any liquid carbon tetrachloride that may have condensed in it; then seal quickly the tip. Remove the bulb and set the water-bath aside at the sink to cool. Dry the sealed bulb; and weigh it accurately, after it has come to the temperature of the balance case. Read the barometer, its temperature, and the temperature of the balance case.

Crush the capillary tip of the bulb with a pair of cutting pliers beneath the surface of the water in the bath which was set aside to cool. (Since this water was previously boiled, and allowed to cool for only a short time, it will still be warm and will contain practically no dissolved air.) Keeping the capillary tip submerged, cool the bulb with tap water until no more water is sucked in. Weigh the bulb with its water content on a platform balance to 0.5 gram. (In case there are more than 3 ccm. of air in the bulb, determine the volume of this air, and in the subsequent calculations correct for it.) After finishing the weighing, empty the bulb, but do not attempt to dry it.

Prepare a form like that shown at the end of the experiment, and record upon it the original observations and the results calculated from them. In reporting all subsequent experiments prepare a similar form for tabulating the data and calculated results.

Treatment of Results. — By reference to the tables given in the Appendix, reduce the barometer reading to 0°, and find the boiling-point of water at this barometric pressure. Derive the general equation by which the correction for the barometer reading given in the table was made. Calculate the correction for air-buoyancy that must be applied in evaluating the weight of carbon tetrachloride in the sealed bulb.

Calculate from these experimental data the density of carbon tetrachloride vapor, and the corresponding molecular weight of carbon tetrachloride. Find the percentage deviation of this molecular weight from that corresponding to the formula CCl_4, and state whether this deviation may be reasonably due to deviation of the vapor from the laws of perfect gases.

Discussion. — The bulb containing the liquid carbon tetrachloride is immersed in the water-bath at 75°, a temperature below the boiling-point of carbon tetrachloride, in order that its vaporization may take place at its surface, and not throughout the liquid as in boiling. There is thus formed at the surface a layer of vapor which, being heavier than air, acts as a piston and expels the air continuously without mixing with it. The bulb should be placed in such a position that the air may be readily expelled without becoming trapped.

After complete expulsion of the air and equalization of the pressure of the vapor of the carbon tetrachloride with the external pressure, continuous boiling of the bath must be maintained until the capillary is sealed; for momentary cooling will obviously cause air to be sucked into the bulb.

It is very important to remove the last trace of liquid carbon tetrachloride condensed in the exposed stem of the bulb before sealing the capillary. (Estimate the percentage error in the vapor-density caused by leaving in the stem of a 200 ccm. bulb 0.01 g. of liquid carbon tetrachloride at the time of sealing.)

EXPERIMENT 1. VAPOR-DENSITY AND MOLECULAR WEIGHT OF CARBON TETRACHLORIDE

Performed by **Date:**

ORIGINAL DATA

Weight of bulb (empty but open to air)	g.
Weight of bulb plus CCl_4 (sealed)	g.
Temperature of balance case	°
Barometer reading at °	mm.
Barometer reading (corrected to o°)	mm.
Weight of bulb plus water	g.
Volume of bulb	ccm.
Boiling-point of water at barometric pressure	°
Correction for air-buoyancy	g.
Weight of CCl_4 (in the sealed bulb)	g.

TABULATION OF RESULTS

Wgt. CCl_4 *m*	Volume *v*	Pressure *p*	Temp. *t*	Density *d*	Mol. Wgt. *M*	Percent deviation

CALCULATIONS

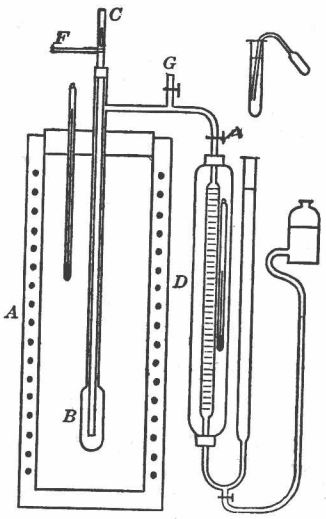
Correction for air-buoyancy =
Molecular weight =

EXPERIMENT 2. THE DENSITY AND MOLECULAR WEIGHT OF VAPORS DETERMINED BY THE AIR-DISPLACEMENT METHOD OF VICTOR MEYER

Principles Involved. — Perfect-gas laws. Pressure-volume relations of wet and dry gases. Definition and determination of molecular weight. See *Chem. Prin.*, Arts. 8–14; 31.

Outline. — A cylindrical bulb provided with a long stem and delivery tube, as shown in the figure, is heated in an electric furnace at a constant temperature of about 200°. A weighed quantity of benzene is dropped into this bulb, which is filled with air at barometric pressure. The benzene rapidly vaporizes, occupying a definite volume at this temperature and pressure, and expels an equal volume of air. The air displaced is collected and measured over water, and its weight is calculated from the known molal weight of air 29.0 by the perfect-gas equation. The ratio of the weight of benzene taken to this weight of air is equal to the ratio of the densities of the two gases at the temperature of the furnace and at barometric pressure.

Apparatus. — An electric furnace *A* with a thermometer; and an external resistance for regulating the current and thus adjusting the temperature. A cylindrical bulb *B* of about 125 ccm. capacity with a long stem having a side-arm which is connected by capillary tubing with a 25 ccm. water-jacketed eudiometer *D*. The eudiometer is provided with a thermometer and a leveling bottle. A tube inserted in the stem of the cylindrical bulb to within 3 cm. of the bottom, and having a side-arm *F* carrying through rubber tubing a movable glass rod which serves to support and release a small glass bulb containing the



benzene. The manner of assembling these parts is shown in the figure. The three stop-cocks are employed for convenience of manipulation. The accessory apparatus is as follows: A small glass bulb of about 0.05 ccm. capacity which has a capillary stem 6 cm. long bent 2 cm. above the bulb so as to make an angle of about 60°. A test-tube 7 cm. long. A sulfuric acid drying bottle. A suction pump.

Procedure. — Draw through the bulb a moderate current of hot air, previously dried by passing it through sulfuric acid, so as to expel the moist air, or the benzene which may be left in it from a previous experiment.

Weigh accurately the small bulb with the capillary stem. Charge it with benzene by dipping the capillary tip into some benzene in a small test-tube, as shown in the figure, and alternately heating the bulb and letting it cool until it is nearly filled with benzene. Remove the bulb and drive out with a flame any benzene that has collected in the capillary. Again weigh the bulb accurately. Break the stem off at the bend, taking care to avoid loss of any benzene in the operation. Drop the bulb on to the support at *F*, and close the tube at *C*.

In order to test the furnace for constancy of temperature, bring the water in the arms of the eudiometer to the same level, and close *G*. No change in level should occur within three or four minutes. Test the apparatus for leaks by producing a difference of level of about 10 cm. in the eudiometer-arms, and noting whether the level changes. Finally bring the water in the two arms to the same level near the top, and record the eudiometer reading as the initial volume of the air.

Close *G*, and drop the little bulb containing the benzene into the heated part of the apparatus. While the air is being driven over into the eudiometer, keep the levels in the two arms nearly the same by letting the water flow slowly into the leveling bottle. Read the volume of the air, always at the barometric pressure, once a minute for five minutes, when the volume should have become constant. Read the temperature of the eudiometer, that of the furnace, and also the height of the

barometer and its temperature. Reduce the barometer reading to 0° and record the corrected value.

Treatment of Results. — Calculate from the experimental data the weight of the air displaced by the benzene. Take into account the fact that the measured air is saturated with water-vapor. Calculate the ratio of the density of the benzene vapor to that of air, and the corresponding molecular weight of benzene at the temperature of the furnace and the barometric pressure. Find the percentage deviation of the observed molecular weight from that corresponding to the molecular formula C_6H_6.

Discussion. — Rapid vaporization of the benzene into a vaporization chamber of large capacity is essential in order to minimize the chances for diffusion and condensation of benzene vapor in the cooler upper parts of the apparatus. A gradual decrease of the volume of the displaced air at the end is an indication of such condensation. The maximum volume observed should accordingly be recorded as the final value.

The volume of the moist displaced air is calculated over to a dry basis regarding its humidity to be one hundred percent. This correction for moisture is justifiable only in case the vaporization chamber is filled at the start with dry air. The dry air drawn into the vaporization chamber should be preheated by passing it through glass tubing warmed by a gas flame.

The constant high temperature of the vaporization chamber is usually attained in the Victor Meyer method by immersing the bulb in a vapor-bath above a suitable boiling liquid and regulating the conditions so that condensation of the vapor takes place along the upper part of the long stem. The constant temperature electric furnace here employed has the advantage that it can readily be made large enough to accommodate four bulbs at once.