LABORATORY MANUAL

OF

COLLOID CHEMISTRY

BY

HARRY N. HOLMES

Professor of Chemistry in Oberlin College

PREFACE

THIS manual was written at the request of the Colloid Committee of the National Research Council.

Most of the experiments have been tested in the laboratory course given at Oberlin for the past six years, while others have been contributed by the leading colloid chemists of this country.

There has long been need of a suitable laboratory manual to advance the teaching of colloid chemistry, and for lack of such a book instruction has lagged. Lecture courses in plenty are given at various universities, but in very few institutions is there a real laboratory course in the subject. It is the laboratory method of instruction that has advanced science so wonderfully in the last half century; obviously, instruction in colloids must develop in the same way.

The general interest in the subject grows apace. Not only theoretical chemists but industrial men as well are expressing the belief that a great many of their problems are colloidal. Hundreds of able chemists would study colloid chemistry in their private laboratories if a self-teaching manual were available. To meet this demand this manual offers a large amount of text material in the way of comment and explanation. The carefully selected references for collateral reading will guide the experimenter and enable him to pursue his studies with a minimum of wasted effort. It is, as the author knows from personal experience, very difficult for the beginner in the subject to know what to read first, or what experiments are worth performing.

Twenty years ago, when colloid chemistry was still in its swaddling clothes, chemists concerned themselves too much with the mere preparation of new colloids, just as organic chemists once prided themselves too much on the mere preparation of new compounds. Now we are making genuine progress by a more intensive study of the properties of material in the colloid state,

by discovering general principles and by the use of quantitative methods.

In preparing this manual the author has been greatly helped by advice and criticism from Mr. Jerome Alexander of the Uniform Adhesive Co., Professor W. D. Bancroft of Cornell University, Dr. Martin H. Fischer of the Cincinnati General Hospital, Dr. Leon Parsons and Mr. Robert E. Wilson of Massachusetts Institute of Technology, Dr. Ellwood Spear of the Goodyear Rubber Co., Dr. S. E. Sheppard of the Eastman Kodak Co., Dr. J. A. Wilson of the Gallun Tanneries at Milwaukee, and Professor J. H. Mathews of the University of Wisconsin.

A number of detailed experiments were generously given by Mr. Alexander (on the ultramicroscope), by Professor Bancroft (on dyeing), by Dr. Spear (on rubber), by Dr. Sheppard (on silver nuclei), by Dr. J. A. Wilson (on tanning) and by Dr. Parsons (on varied topics).

Most of the chapter on Adsorption of Gases was used by permission of the Silica Gel Co. of Baltimore and represents the work of Dr. Patrick. Cuts were loaned by Dr. Martin H. Fischer, the Central Scientific Co. and the Telling-Belle Vernon Co.

HARRY N. HOLMES.

OBERLIN, OHIO, March, 1922.

SELECTIONS FOR SPECIAL COURSES

IT is not expected that any one student shall perform all the experiments in this manual. If he did he would probably spend two full days each week for a year in the colloid laboratory.

The teacher must use judgment in selecting representative experiments from each chapter to suit the time allowed for the course. There is a distinct gain in general interest if similar experiments are given to different students rather than to give all exactly the same drill.

Again we must admit that a single definite list of experiments does not meet equally well the needs of students interested in a general fundamental course, in medical work, in agriculture and ceramics, in geology and in industrial work. To meet these different demands the author suggests the following courses based on a time allowance of at least twelve clock-hours per week for one semester:

A General Course.—Experiments 1, 2, 5, 6, 7, 10, 12, 15, 17, 20, 25, 26, 29, 38, 40, 41, 42, 44, 47, 48, 49, 56, 59, 60, 62, 63, 65, 67, 68, 69, 71, 74, 76, 78, 84, 89, 91, 94, 95, 96, 98, 100, 101, 103, 104, 105, 107, 110, 111, 113, 115, 116, 125, 128, 129, 133, 138, 134, 135, 136, 138, 139, 140, 141, 144, 148, 150, 151, 153–159, 160, 161, 165–166, 167–174, 175, 176, 177, 181, 184,

A Course for Medical Students.—Experiments 1, 6, 8, 11, 12, 15, 17, 20, 25, 31, 39, 41, 44, 47, 48, 49, 52, 53, 54, 56, 57, 60, 62, 64, 65, 67, 68, 69, 71, 73, 74, 75, 80, 81, 82, 83, 84, 85, 86, 89, 91, 92, 93, 95, 96, 98, 99, 101, 104, 110, 112, 115, 119, 126, 133, 135, 144, 148, 150, 153–159, 182.

A Course for Students of Agriculture or Ceramics.—Experiments 1, 4, 6, 10, 12, 13, 17, 21, 25, 31, 39, 40, 44, 46, 47, 48, 49, 50, 56, 57, 58, 59, 63, 65, 67, 68, 69, 72, 80, 84, 91, 94, 95, 96, 98, 100, 101, 104, 105, 112, 115, 122, 123, 133, 134, 144, 147, 148, 153–159, 162, 163, 164, 182, 184.

A Course for Students of Geology.—Experiments 1, 3, 4, 10, 12, 13, 17, 21, 25, 31, 40, 43, 44, 46, 47, 48, 49, 50, 56, 57, 58, 59, 63, 65, 67, 68, 69, 71, 72, 84, 91, 95, 100, 106, 115, 122, 123, 125, 127, 128, 133, 134, 144–152, 159–164, 182, 184.

A Course for Students of Industrial Chemistry.—Experiments 1, 2, 3, 10, 12, 13, 16, 21, 25, 31, 41, 42, 46, 47, 48, 50, 55, 56, 57, 58, 59, 65, 67, 68, 69, 70, 72, 79, 81, 84, 85, 86, 90, 91, 94, 95, 96, 102, 104, 105, 108, 109, 112, 115, 116, 125, 127, 133, 134, 135, 136, 137, 138, 139, 140, 141, 144, 148, 153-159, 160, 161, 165, 166, 167–174, 177, 178, 180, 185, 186.

Quantitative experiments for a course in Physical Chemistry are scattered throughout the book and may readily be selected.

TABLE OF CONTENTS

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER X

CHAPTER XI

CHAPTER XII

CHAPTER XVI

COLLOID LABORATORY MANUAL

CHAPTER I

SUSPENSIONS—COARSE AND FINE

Exp. 1.—With three sieves, of 50-mesh, 100-mesh and 200-mesh, sift any suitable powder, such as quartz flour, clay or starches, into three grades of particles. Suspend about 1 g. of each in test tubes of distilled water and note the time of settling. Make observations on the portions that settle rapidly. In each case a very small fraction is slow to settle.

What has mere size of particle to do with time of settling?

Exp. 2.—Precipitate barium sulfate cold and attempt to filter it. Now precipitate the salt by mixing the proper hot solutions and keeping hot an hour. Will a filter paper retain the precipitate?

The solubility of small particles, slight though it may be, is greater than that of larger particles (greater surface). This solubility is increased by rise in temperature, so the smaller particles dissolve and the dissolved salt deposits on the larger particles which are in contact with their own saturated solution.

Exp. 3. Surface and Solubility.—Kenrick (Jour. Phys. Chem., **16,** 515, 1912) outlines a convincing demonstration of the difference between the solubility of small particles and that of larger particles:

Make a normally saturated solution of calcium sulfate by stirring gently, for some hours, 30 g. of coarsely powdered gypsum in 300 cc. of distilled water. The finer particles must previously have been rinsed away with water. This saturated solution may well be kept in contact with the crystals. Now grind some gypsum to an impalpable powder in an agate mortar. To one of two beakers containing about 50 cc. of the previously made " normally saturated " gypsum add about 0.5 g. of the gypsum powder. Shake a moment and filter twice if not clear. With the greater surface more gypsum dissolves, although the solution was saturated with the larger particles.

A duplicate of the "normally saturated" solution is filtered at the same time (both portions handled rapidly). To 20 cc. of each filtrate is added 10 cc. of a solution prepared as follows: 100 g. $Na_2HPO_4 \cdot 12H_2O$ and 2.5 g. NaOH made up to 1000 cc. and 29 cc. (exact amount to be found by titration) of this are colored a deep pink with phenolphthalein and diluted to 100 cc.

The liquid shaken with the finer powder turns colorless, but the other remains pink. An actual titration would show a difference of 10 per cent in

the concentration of calcium sulfate. If the difference in color is not sharp with addition of 10 cc. try 10.5 cc.

Exp. 4.—Problem in analysis: To titrate any unused $Ca(OH)_2$ when carbon dioxide is run into clear limewater. Hydrochloric acid neutralizes unused $Ca(OH)_2$ and then attacks the precipitated $CaCO_3$.

First try heating this limewater, with its suspended $CaCO_3$, for fifteen minutes at about 60°. The $CaCO_3$ particles grow in size, probably becoming crystalline and compact, offering far less surface to attack the acid. In fact they settle out rapidly. They now dissolve so slowly in dilute acid that the end point with phenolphthalein can be secured before the $CaCO_3$ is attacked noticeably.

Exp. 5.—Project a powerful beam of light from some source into a small jar or flask containing an As_2S_3 sol (or any colloid at hand) and note whether the path of the beam becomes strongly luminous. Luminosity of the path of the beam is known as the Tyndall effect and indicates the presence of suspended particles, provided that this luminosity is not due to fluorescence.

Insert a Nicol prism between the light source and the colloidal suspension and rotate the prism. Note whether there is any change in the intensity of the luminosity as the Nicol is rotated. Such a change in luminosity is to be expected if the luminosity is due to the Tyndall effect, because the light is polarized by reflection from the surfaces of the suspended particles, but it will not be observed if the luminosity is due to fluorescence. (J. H. Matthews.)

Compare the Tyndall cone in ordinary water and the same water from which a gelatinous precipitate of $Al(OH)_3$ has settled. Square bottles or small, flat battery jars are suitable for this experiment. What is " optically clear " water?

Exp. 6.—Pour 2 cc. of a 10% alcoholic solution of rosin or mastic into 100 cc. of water and get a suspension of minute solid particles of mastic in water. Pour an acetone solution of any liquid fat into water and get a suspension of minute liquid particles of fat in water. It is a general principle that if A is soluble in B but is insoluble in C, A will be thrown into suspension, frequently colloidal, when a solution of A in B is added to an excess of C (if B and C are miscible).

The color change is explained by the reaction:

$$3CaSO_4 + 2Na_2HPO_4 \rightarrow Ca_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4$$
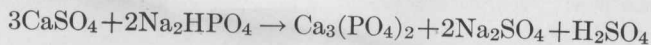
The more calcium sulfate there is in solution, the more sulfuric acid is set free to react with the small amount of base present. Of course, the exact amount of base must be carefully adjusted to show the difference expected.

Hulett (Zeit. phys. Chem., **37**, 385, 1901) found that a coarsely crystalline calcium sulfate (1.8μ) was soluble 2.29 mg. per liter at 25°, while the solubility of the same gypsum ground in an

agate mortar to 0.1μ rose to 4.5 mg. per liter. Red mercuric oxide becomes yellow on grinding, and its solubility increases threefold.

Surface increases enormously with subdivision, and all surface phenomena become greatly magnified. A cube, 1 cm. on edge, when subdivided into cubes $10\mu\mu$ on edge, would possess a total surface of 600 square meters, and the number of particles would be 10^{18}.

Interesting experiments may be devised for the use of the Kober nephelometer in determining the amount of suspended material. Read the excellent discussion of nephelometry by Kober and Graves (Jour. Ind. Eng. Chem., **7**, 843, 1915).

Exp. 7.—Add a saturated solution of mercuric chloride to colloidal silver which the instructor has previously prepared. The dark color disappears, and a milkiness, due to the precipitation of white mercurous chloride and silver chloride, appears.

$$Ag + HgCl_2 \rightarrow AgCl + HgCl$$
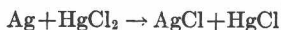
This reaction becomes apparent when silver in colloidal form, with enormous surface, is used although, of course, some reduction must occur when silver foil is used.

THE COLLOID CHEMISTRY OF FEHLING'S TESTS [1]

Exp. 8.—When Fehling's solution is treated with a reducing substance it is generally expected that a bright-red precipitate will be obtained. Frequently, however, an orange or yellow precipitate is obtained, and in certain instances nothing but a yellowish-green discoloration results.

These color changes are coincident with differences in size of particles of the cuprous oxide formed. The smallest particles are yellowish green; as they grow in size they become yellow, then orange, and when very coarse they are red. When the bright-blue Fehling's solution is mixed with a little dextrose solution, or some diabetic urine, and the mixture is not boiled as ordinarily, but is allowed to stand several hours at room temperature, this series of color changes, beginning with bluish green and ending with red, is observed. Drops of these suspensions examined under the microscope show the corresponding growth in size of particle.

Mix cold 1.5 cc. of Fehling's solution and 20 cc. of 2 per cent dextrose. In 30 minutes the colors change from green to yellow to orange and in 7 hours to red.

[1] Adapted from Martin H. Fischer, Science, **45**, 505, 1917. See also Journal of Laboratory and Clinical Medicine, **3**, 368, (1918).

In the action of the alkali of Fehling's solution upon dextrose, for example, there are produced, from a chemical point of view, not only the various degradation products which are responsible for the reduction of the copper salt, but from a colloid point of view, certain hydrophilic colloids which tend to inhibit a precipitation of the cuprous oxide in coarse form.

To allow adequate time for the growth of the cuprous oxide particles to the red form, it is better to make reductions at low temperatures than at higher ones.

With much sugar present the number of points at which the copper salt is attacked and reduced will evidently be much larger than when less sugar is added. All the available copper salt for further growth of the particles will, therefore, have been exhausted when the copper oxide particles are still small. Therefore too much reducing sugar is likely to yield only the greenish discoloration. In such cases dilution or reduction and long standing at room temperature may help.

It might be well, before testing for sugar, to boil and filter urine in order to remove any albumin present. Albumin is a protective colloid.

An interesting presentation of **von Weimarn's** law is found in Ostwald's " Theoretical and Applied Colloid Chemistry " and in Washburn's " Principles of Physical Chemistry," 432, 1921, pages 24–33. As demonstrated with Prussian blue and with barium sulfate the size of precipitated particles is greatest when medium concentrations of the two reacting solutions are used. With very low or very high concentrations the precipitated particles are smaller.

Exp. 9.—To 10 cc. of M/200 $FeCl_3$ add 10 cc. of M/200 $K_4Fe(CN)_6$ solution; dilute to about 100 cc. and note whether the solution is clear. Repeat the experiment, using M/10 solutions and explain the difference in the phenomena observed.

Add 5 cc. of a practically saturated solution of $FeCl_3$ to 10 cc. of a practically saturated solution of $K_4Fe(CN)_6$. Take a small quantity of the gel and stir up in water. Prove by filtering that the resulting suspension is colloidal.

CHAPTER II

DIALYSIS AND DIFFUSION

GRAHAM distinguished between " colloids " and "crystalloids" by diffusion and dialysis tests. Colloids he classed as substances with a much lower rate of diffusion than crystalloids. Furthermore he observed that some substances diffused through various animal and plant membranes while others did not. Thus with bladder or parchment separating pure water from water containing both colloids and crystalloids he was able to dialyze or purify the colloid suspension, in other words, free it from the so-called crystalloids. For such a process, dialysis, we now use goldbeater's skins (the peritoneal membranes of cattle), collodion membranes, parchment paper and fish bladder. For ultrafiltration read page 115.

Exp. 10.—With a narrow flame or a hot wire cut off the bottom from widemouthed bottles. Tie membranes (parchment paper, bladder, gold-beater's skin, collodion, etc.) tightly over the mouth, invert the bottle, add liquid; if no drops form on the lower side, the dialyzer is free from leaks. Use 2-inch dialyzing tubes made by Central Scientific Co., Chicago, and Scientific Materials Co., Pittsburgh, or flanged test tubes open at both ends, or make parchment-paper cups of any size, as described by Holmes, Jour. Am. Chem. Soc., **38**, 1203 (1916).

A quotation from this reference follows:

" The cheapest and most easily made dialyzer I have used is a sheet of parchment paper shaped like a beaker. In other words, it is all membrane and has a much greater dialyzing surface than the usual forms. These beakers or cups can be shaped easily by any student. A sheet of parchment, free from pin-holes, is soaked in water a few minutes to soften it and then folded over a bottle of the desired size and shape. The folds should be triangular and narrow, and should cover each other much as do the folds of an umbrella. It is best to crease them moderately. A cord is tied around the paper and bottle about 1 centimeter from the upper edge, and the whole set aside to dry. When dry, the bottle is

5