LECTURE AND LABORATORY EXPERIMENTS
IN
PHYSICAL CHEMISTRY

Lecture and Laboratory Experiments

IN

PHYSICAL CHEMISTRY

BY

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To M. L. T.

"Quoniam menti humanae nulla corporum "vel qualitatum corporearum est innata "cognitio : omnia, quae ad corpora pertinent, observationibus, vel experimentis "addiscenda sunt."

—*PETRUS VAN MUSSCHENBROEK,*

Introductio ad Philosophiam
Naturalem, p. 4 (1742).

PREFACE TO SECOND EDITION

The need for a second edition has been most gratifying to the author and has given an opportunity to revise the text and make a number of additions.

The chapters on catalysis, electrochemistry and ionic theory, solubility, colloid chemistry and adsorption—have been enlarged —and two new chapters dealing with radio-activity and miscellaneous experiments added. About one hundred new experiments have been described.

Although originally planned only for classes in physical chemistry which, as a rule, do not comprise more than forty to fifty students, quite a number of elementary experiments useful to lecturers in general chemistry have been included. In giving these demonstrations before large audiences it may be advisable to perform them on a larger scale than outlined in the text. This may be safely left to the individual lecturer and a change of the text on this account has not been made.

Considering that a large number of the experiments described in the text are also well adapted to be performed by the student in the laboratory the title has been modified so as to indicate this possibility.

The author gratefully acknowledges his indebtedness for suggestions received from different quarters, especially from Drs. W. D. Bancroft, F. H. Getman, H. R. Kruyt, A. T. Lincoln, E. B. Millard, J. L. Rosenholz, A. Simek, G. Tammann and H. S. Taylor.

Suggestions and corrections from those who use the book will be greatly appreciated by the author.

H. S. VAN KLOOSTER.

WALKER LABORATORY, TROY, N. Y.,
September, 1924.

PREFACE

This volume of lecture demonstrations has been prepared with the idea that it would be of service to have a set of experiments at hand, suitable to be shown in the lecture for the illustration of our present conceptions on physical chemistry.

Arrhenius, in the introduction to his "Theory of Solutions" states "that there are very few doctrines in exact science, where so few lecture experiments are shown as in physical chemistry." This is, of course, partly due to the fact that *quantitative measurements* are needed on which the general laws must be based, while lecture experiments, as a rule, can only illustrate the principles involved in a *qualitative* way. It may be said, however, that quite a number of experiments well adapted to illustrate the different chapters of physical chemistry can be performed. Some of these are found in any of the well-known standard works of Heumann, Arendt, Newth and Benedikt, but little or no attention is paid in these text-books to physical chemistry as a separate branch of teaching, as the connecting link between chemistry and physics. In fact, the interesting topics of physical chemistry such as osmosis, diffusion, catalysis are treated in connection with some element or compound, the properties of which are under discussion, thereby unconsciously and perhaps unwillingly introducing the idea, that these phenomena are typical or especially characteristic of certain elements or compounds. To take a few instances out of many: absorption is a standing property of charcoal, colloids are discussed in connection with silicon, allotropy is taken up with oxygen and ozon, etc. The scope of this volume is diametrically opposed to this system in so far that relationships, rather than distinctions are emphasized, the general character of the different topics is stressed and the all-embracing grip of physical or—as it is frequently called—*general* chemistry underlined.

It is interesting to note as can be seen from the references, which have been given wherever available, that many experiments along this line originate from the great masters, which have given to the science of physical chemistry a place in the front ranks of exact sciences. The very fact, that chemists like Faraday, Graham, Ostwald, Fischer and others have spent part of their time in devising suitable demonstrative experiments is sufficient proof for the usefulness of lecture experiments, wherever practicable, even in the case of such a "theoretical" subject as physical chemistry. However important the theoretical part may be, the experimental side will remain our first and our final resort; to quote the words of an early Dutch physicist, cited on a preceding page in the original version: "Since the human mind has no innate knowledge of matter or its properties, everything pertaining to matter must be learned by observation and experiment."

It is hoped that this volume will be useful in the preparation of lecture experiments and stimulate the interest of the students in "practical" physical chemistry.

v. K.

WASHINGTON, D. C.,
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Note. All footnote references, not fully specified, refer to the text-books and journal articles mentioned above.

CHAPTER I

GENERAL PROPERTIES OF MATTER IN THE LIQUID AND SOLID STATE

Fundamental to the study of chemistry and physics is the differentiation of matter into the solid, liquid and gaseous states. A distinction between a liquid and a gas is easily made, since they can only merge into each other at the critical point, the constants of which (critical temperature and pressure) are readily defined. Solids are usually defined as having a definite form and a definite shape, while liquids have their own definite volume, but take on the shape of the vessel in which they are contained. These simple definitions do not hold, however, in the case of very viscous or plastic substances like glass, pitch, sealing wax, clay and similar materials. A sharp demarcation between a solid and a liquid is possible by defining a solid as a substance which requires a definite shearing force to produce a *permanent deformation*. A liquid on the other hand is permanently deformed by *any* shearing force, no matter how small.[1] This may be effectively demonstrated as follows:

1. A bar of pitch is made up 1 centimeter square and 10 centimeters long. A similar bar is made of modeling clay and both laid horizontally on two supports, 9 centimeters apart. After a time, which depends on the temperature, the clay bar remains perfectly straight, while the pitch bar has flowed, showing its essentially liquid condition.

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[1] **Bingham, An Investigation of the Laws of Plastic Flow, Bulletin Bureau of Standards, No. 278, p. 309, 1916.**

Starting again with two other bars of exactly the same dimensions a load of 100 grams is placed upon the pitch bar for a moment only. No perceptible sag is noted. On placing the same weight upon the bar of plastic clay, it gives way completely. The clay is, therefore, a soft (or plastic) *solid,* and the pitch a very viscous *liquid.*

Among the properties of chemical compounds in the liquid and solid state, which are most suitably illustrated by lecture demonstrations may be mentioned the phase transitions which are brought about by a change of temperature or pressure. Since 1884, when the importance of the phase rule as a guiding principle for the rational classification of heterogeneous equilibria was gradually recognized, a very considerable amount of work on phase transitions in general has been done by van 't Hoff, Bakhuis Roozeboom, Tammann, Bancroft and their coworkers. It is safe to say that their results could hardly ever have been successfully mastered without the aid of the law which was put forward by Willard Gibbs in 1874.

The following experiments on phase transitions deal with:

A. Polymorphic transformations of compounds.
B. Dissociation of solids.
C. Undercooled liquids.
D. Liquid crystals.
E. Allotropy.
F. Passivity.

A. Polymorphic Transformations of Compounds

Although it has been known for a long time, that certain compounds exist in two or more polymorphic modifications, the recognition of the general character of polymorphism dates from the recent investigations by Tammann and others on the polymorphism of a great many inorganic compounds (water and various salts). The greatly improved methods for the measurement of temperatures, due to the introduction of thermo-elements in physico-chemical work, bring us daily in contact with an ever-increasing number of polymorphic compounds. The transition of one solid phase into another is usually made evident by the heat effect at the transformation temperature; sometimes also by a marked change in color or a noticeable increase or decrease in volume.

2. The change in *color* is easily observed by inserting a test-tube with 5-10 grams of cuprous mercuric iodide in a beaker, containing water at about 80°. The color of the compound changes from red to black and is reversed by dipping the tube in water of 50°, or by allowing the tube to cool in the air. In preparing this double salt,[2] mercuric iodide is precipitated from a solution of 6.8 grams of mercuric chloride in 100 cc. of water by the addition of 50 cc. of a solution containing 8.3 grams of potassium iodide. The precipitate is washed out and dissolved in a solution of 8.3 grams of potassium iodide in 50 cc. of water. The filtered solution is mixed with a concentrated solution of 12 grams of copper sulphate in water and the mixture reduced with sulphur dioxide. The precipitate is thoroughly washed, dried at 90-100° and kept in a closed tube.

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[2] cf. H. and W. Biltz, Uebungsbeispiele aus der unorg. Experimental Chemie, Leipzig, p. 27, 1907.

In lecture courses mercuric iodide is usually taken; this substance, however, has the disadvantage, that the reverse change (on cooling) from yellow to red proceeds rather slowly, the transition temperature (126°) is frequently overshot by more than 100°, and it requires several hours, sometimes a day or more to complete the transformation. The *reversible,* enantiotropic character of most phase transitions is therefore more clearly demonstrated in the case of cuprous mercuric iodide than with the latter substance.

3. Antimony trisulphide is an example of a monotropic substance. In the laboratory it is always obtained in the form of a brick-red amorphous powder while it occurs in nature under the name of stibnite as needle-shaped black crystals with a metallic luster. Although the red modification is apparently stable and may be kept unchanged for months and years it can be readily transformed into the stable black form in the presence of dilute hydrochloric acid.[3] The action is due to the solution of the less stable red sulphide and the precipitation of the more stable less soluble black sulphide (the less stable form is always the more soluble[4]). The speed with which this *irreversible* monotropic transformation takes place depends to a large extent on the temperature as the following experiment clearly shows.

About 10 grams of the dry red powder, passed through a 40-mesh screen, are divided in three portions and placed in each of three small beakers containing dilute

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[3] Wilson and McCrosky, *Journ. Am. Chem. Soc.*, 43, p. 2178, 1921.

[4] Findlay, The Phase Rule, 3rd Ed., London, p. 144, 1911.

hydrochloric acid (50 cc. of the concentrated acid, specific gravity 1.19 diluted with 150 cc. of water). Boiling for a few minutes brings about the change in stibnite in a very short time. Keeping one beaker over a small flame at about 50° causes a slow change, visible after an hour or more while the third beaker kept at room temperature requires several days to show the conversion of the red into the black sulphide.

4. A considerable change in *volume* at the transformation from one modification into another occurs in the case of potassium tungstate. This salt is easily prepared by fusing dry potassium carbonate with (previously ignited) tungsten trioxide. It is exceedingly hygroscopic and must be kept in closed tubes. It melts at 921°,[5] and has one transition point at 388°, which temperature is far overshot on cooling, before the transformation starts with *increase* of volume. Four to five grams of this salt are fused on a square piece of platinum or nickel foil over a Bunsen flame. On solidifying it will be seen—keeping the foil inclined towards the audience—that the solid crust crumbles after a while and drops as a fine dust from the foil, owing to the expansion during the transformation.[6]

5. Another instance is potassium bichromate.[7] On fusing about 10 grams in a thin-walled test-tube, and allowing the molten salt to cool, it solidifies at 397°, forming triclinic crystals, which change at 236°,[8]—with hardly

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[5] van Klooster, *Zeitschr. f. anorg. Chem.*, 85, p. 49, 1914.

[6] Hüttner and Tammann, *ibidem*, 43, p. 215, 1905.

[7] Mitscherlich, *Pogg. Annalen*, 28, p. 120, 1833.

[8] Zemczuzny, *Zeitschr. f. anorg. Chem.*, 57, p. 267, 1908.

any perceptible heat evolution—into a powder, causing the tube to crack by the expansion.

B. Dissociation of Solids

6. The dissociation, which a number of solid compounds undergo on heating is easily exemplified in the case of ammonium chloride or ammonium carbamate. With the former substance the demonstration is conveniently carried out by placing a little ammonium chloride near the middle of a hard glass tube (about 40 centimeters long, inner bore 1 centimeter), held in a slightly inclined position by a clamp, fastened to a ring stand. A loose plug of asbestos wool is placed a little above the salt, and two strips of moist litmus paper inserted, a blue paper at the lower end and a red paper at the upper end. The salt is gently heated, and dissociates into a mixture of hydrogen chloride and ammonia gas. The latter, being the lighter gas of the two, diffuses more quickly than the hydrogen chloride, with the result that the blue paper is reddened by the excess of hydrogen chloride in the lower part of the tube and the red paper is turned blue by the ammonia, which diffuses faster than the hydrogen chloride. This experiment also serves as a demonstration of atmolysis. The very simple arrangement described above for demonstrating the heat-dissociation of ammonium chloride, is due to Fenton.[9] Other types of apparatus for the same purpose have been devised by Pebal[10] and Than.[11]

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[9] Outlines of Chemistry, Cambridge, p. 20, 1910.

[10] *Liebigs Annalen,* 123, p. 199, 1862.

[11] *Ibidem,* 131, p. 129, 1864.

C. Undercooled Liquids

7. The familiar phenomenon of an undercooled (also called: supercooled) liquid may be conveniently demonstrated with sodium thiosulphate ($Na_2S_2O_3 . 5H_2O$). About 100 grams of the salt are heated in a flat-bottomed bulb flask of 250 cc. The compound melts at 48° and the molten salt is allowed to cool to about 30°. By closing the flask with a loose plug of cotton wool—thus preventing the access of minute crystals or dust particles, which occasionally act as "germs" in breaking up the metastable condition, the supercooled liquid may be kept for an indefinite time. Crystallization can only be started by a crystal of the salt (which may be almost invisible). By introducing a glass rod, covered at its lower end with a thin crust of the solid salt, without *any* adhering *loose* powder, into the undercooled liquid, crystallization starts from the end of the glass rod (with simultaneous evolution of heat) and after a few seconds the rod is lifted out of the liquid, covered with a conglomerate of crystals; (Fig. 1) at the same time, however, no further solidification is observed in the liquid, due to the fact, that the solid phase has been completely removed.[12]

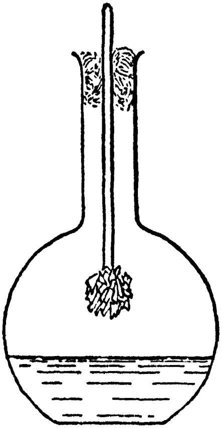

Fig. 1

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[12] Ostwald, Grundlinien der anorg. Chemie, 3e Aufl., p. 537, 1912.

According to Tammann,[13] who first investigated this phenomenon in detail, the amount of undercooling depends (for pure substances) on two factors: The rate of cooling and the crystallization power of the undercooled liquid. The latter is determined: first, by the capacity of the substance to form nuclei from which the crystallization starts and secondly, by the linear velocity of crystallization. In general there is a relation between the number of nuclei and the undercooling and also between the velocity of crystallization and the amount of undercooling as represented graphically in Figs. 2A and 2B. With suitable substances both of these relations can be experimentally demonstrated.

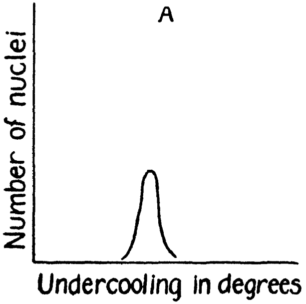

Fig. 2A

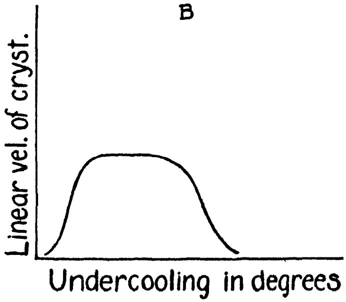

Fig. 2B

8. Benzophenone (melting point 48°) can be readily undercooled. The compound is fused in a thin-walled U-tube and the latter placed in a tall beaker containing water at 40°. The crystallization is started by dropping a tiny crystal into one limb of the U-tube and by means

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[13] Krystallisieren und Schmelzen, Leipzig, 1903.

of a stop-watch the time is measured required for the crystallization to proceed over a definite length, (10 centimeters). The operation is then repeated at lower temperatures (35°, 30°, etc.). The times decrease at first to a minimum value at about 25°, remain constant to about —20° and then increase rapidly. In a mixture of carbon dioxide and ether the velocity of crystallization is practically zero or in other words the time becomes infinite.

9. Betol (melting point 126°) is a suitable substance to show the formation of nuclei. The experiment is carried out in wide capillary tubes which are sealed after introducing the betol. The substance is fused in an oil bath at 150° and then quickly transferred to a bath of 60° (50°, etc.) in which it is kept for two minutes. During this time invisible nuclei are formed which do not grow because the velocity of crystallization is very small. On transferring the tube to a bath at 70° the nuclei develop so that they can be easily counted. The maximum number of nuclei will be formed in the neighborhood of 15°.

10. The effect of impurities on the velocity of crystallization of undercooled liquids can be seen in the following experiment adapted from a similar one by Walton and Krauskopf.[14]

Two narrow pieces of glass tubing (outer diameter 4 millimeters) 40 centimeters long, thoroughly cleaned and dried beforehand, are constricted at both ends by drawing the tubes out to capillaries over a distance of about 5 centimeters.

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[14] Laboratory Manual of General Chemistry, Menasha, p. 19, 1920.

A test-tube is then half-way filled with crystallized sodium acetate ($NaC_2H_3O_2 + 3H_2O$), a few drops of water are added and the whole liquified over a Bunsen burner. The hot liquid is quickly sucked into one of the tubes and the tube sealed at the constrictions.

To the remainder of the liquid in the test-tube a pinch of cane sugar is added and when dissolved to a homogeneous solution, the second tube is filled to the same height and then sealed at both ends. The tubes are allowed to cool to room temperature and placed with their lower ends in a shallow dish with powdered sodium acetate. The point is broken off and the time necessary for the crystallization to proceed over a given length noted. It will be found that the addition of sugar greatly increases the time *i. e.*, reduces the linear velocity of crystallization of the salt.

11. A case, analogous to the crystallization of an undercooled liquid is that of the devitrification of a (silicate) glass, as can be shown with sodium metasilicate (Na_2SiO_3). This salt melts at 1088°,[15] and solidifies, when *slowly* cooled, at temperatures, varying from 1080°-1000°. The salt is easily prepared by mixing sodium carbonate and silica (quartz) in equivalent quantities, heating the mixture for 1-2 hours at a temperature of 600°-800°, thereby effecting a partial combination. The sintered mass is pulverized and the above process repeated two or three times, in order to insure perfect homogeneity. Finally the powder is fused and on slowly cooling changes into a conglomerate of opaque crystals.

[15] Jaeger, *Journ. of the Wash. Ac. of Sc.*, 1, p. 53, 1911.

Ten grams of the salt are heated in a small platinum crucible and rapidly cooled by means of a stream of cold air,[16] whereupon a perfectly clear and transparent glass is formed. This glass is then slowly heated, either in the crucible or on a piece of platinum or nickel foil over a Bunsen flame. At a temperature where the glass just begins to soften (about 550°) the devitrification (crystallization) suddenly starts, often accompanied by a strong glowing, indicating an enormous increase of temperature.

D. Liquid Crystals

12. As an example of a group of organic compounds, which are characterized by two melting points, the case of para-azoxyanisol may be quoted. This substance, discovered by Gattermann, melts at 116° to a turbid bright yellow liquid, which on further heating, suddenly clears at 135°. The phenomenon is suitably projected on the screen by heating the substance in a small glass trough with parallel walls of rectangular cross-section. The first melting point (116°) represents the conversion of a crystalline solid into (anisotropic) *liquid* crystals, which change at 135° into an (isotropic) liquid.

E. Allotropy

The recent work of Cohen and his co-workers on this topic have clearly brought out the frequent occurrence of polymorphism among elements, especially heavy metals. Since in most cases the change from one solid phase into another at the transition point is accompanied by an ap-

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[16] Guertler, *Zeitschr. f. anorg. Chem.*, 40, p. 268, 1904.

preciable change in volume the method chiefly employed is that, which makes use of a dilatometer.

13. The following lecture experiment[17] gives a good idea of the enormous decrease in volume, resulting from the transformation of grey tin into white. At the temperature of transformation (18°) the specific gravities, as determined by Cohen,[18] are 5.79 and 7.28 respectively. The dilatometric apparatus (Fig. 3), consists of a glass cylinder (*A*), filled with 60-70 grams of grey tin, and a connecting U-shaped tube, containing mercury. The

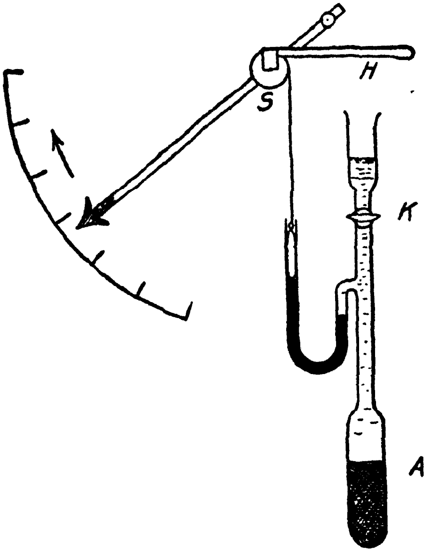

Fig. 3

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[17] Cohen, *Transactions of the Faraday Soc.*, 7, p. 6, 1911.

[18] *Zeitschr. f. phys. Chem.*, 30, p. 601, 1899.

space between mercury and tin is filled, as far as the stopcock *K*, with distilled water. On the mercury in the open limb of the U-tube floats a small cylindrical weight connected by means of a thin thread with the disk *S*, which turns around an axis, kept in its place by the beam *H*. A pointer fastened to the disk and moving along a graduated scale, follows the displacements of the mercury in the U-tube. The zero-position is reached by opening the stopcock and pouring water in the apparatus, until the pointer is adjusted. The stopcock is then closed and the cylinder *A* warmed up with water of about 80°. The mercury sinks in the open limb and a sudden upward move of the pointer over three or more scale divisions is observed.

It has been found, that the reverse change, from the white modification, in which tin is usually known, into the grey form goes fastest at a temperature of —45°, and also, that the transformation is accelerated in the presence of pink salt solution. In the absence of the grey modification white tin can be kept below 18° several months, or even years, without the slightest indication of any transformation. If, however, the white tin is "infected" with a trace of grey tin, the transformation goes on, until the "*tin pest*" has entirely affected the white modification.

14. The phenomenon of *dynamical allotropy* in the liquid state is shown by sulphur and was thoroughly investigated, first by A. Smith and his pupils, and afterwards by Kruyt and his co-workers. The peculiar behavior of molten sulphur in the neighborhood of 160°

and the formation of plastic and amorphic sulphur are usually demonstrated in first courses on inorganic chemistry and need no special description at this place. It may be remarked, that from a colloid-chemical standpoint this behavior is interesting, when sulphur is considered,—as Wo. Ostwald proposes[19]—as an "allo-colloid."

F. Passivity

15. The change in condition, which some heavy metals, especially iron and chromium undergo, when inserted in strong nitric acid (specific gravity 1.50), usually called "passivity,"[20] may be demonstrated in the following manner. A square piece of thin sheet iron, well cleaned, is attached to a platinum wire, and lowered in a beaker containing dilute nitric acid, in which the iron is immediately attacked. It is then transferred to another beaker with concentrated nitric acid (specific gravity 1.50); nothing happens. Having removed the adhering acid by inserting the iron in a beaker with distilled water, the now passive iron is brought in a fourth beaker containing a dilute solution of copper sulphate. No film of copper is formed on the iron, which remains grey as before. Care has to be taken, that the iron is not touched in some way or other, because hammering, bending or scratching immediately restores the active state as will be seen by the formation of a thin copper coating.

16. Iron can also be brought in the passive state by dissolving the metal electrolytically, using the iron as an

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[19] Ostwald-Fischer, Handbook of Colloid Chemistry, p. 104, 1915.

[20] Schönbein, *Pogg. Ann.*, 37, pp. 390, 590, 1836.

anode in electrolyzing an aqueous solution of sulphuric (or nitric) acid, or a solution of a nitrate or sulphate.

Passivity was discovered by Keir[21] and studied more in detail by Faraday (1836) and simultaneously by Schönbein. A good explanation for this peculiar phenomenon is still lacking. Some authors[22] ascribe the activity to the presence of hydrogen ions at the surface of the iron; by dipping the metal in concentrated nitric acid the hydrogen is oxidized and the metal becomes passive. Activity is restored by heating in hydrogen gas or inserting the metal as a cathode in a ferrous sulphate solution. Another explanation, first advanced by Faraday, traces the cause of passivity to the formation of a protecting skin of oxide. Recently Smits[23] has given an entirely new explanation, based on the assumption of different kinds of molecules or ions in the metal, which are in mobile equilibrium. Passivity, according to Smits, would be nothing but a disturbance of this internal equilibrium.

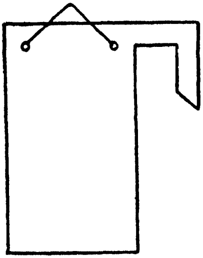

Fig. 4

17. The following experiment, taken from Smits' paper, shows that passivity can be overcome by bringing the iron in contact with solutions of chlorides, bromides, or iodides, a fact, which cannot well be reconciled with the oxide theory. A piece of sheet iron, provided with an elbow (Fig. 4), is first inserted in strong nitric acid,

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[21] *Phil. Transact.*, 80, p. 374, 1790.

[22] cf. Rathert, *Zeitschr. f. phys. Chem.*, 85, p. 567, 1914.

[23] *Chem. Weekblad*, 12, p. 676, 1915.

and then in a concentrated solution of copper sulphate. No copper is deposited, but on bringing the elbow-appendix in contact with a solution of potassium chloride, bromide, or iodide, activity is restored at once.

18. The experiment is next repeated using mercuric chloride. No effect, hence the activating action is exerted by the Cl', Br' and I'-ions respectively.

CHAPTER II

DIFFUSION

I. Diffusion in Gases

19. The process of diffusion of gases has been the subject of exhaustive researches by Graham (1832), to whom we owe the laws governing gaseous diffusion and the related phenomena of effusion and transfusion. As Graham has shown, the relative speeds of diffusion of gases are inversely proportional to the square roots of their relative densities. That hydrogen, being the lightest of all known gases, diffuses faster than air through the walls of a thin porous membrane, while air itself, being lighter than carbon dioxide travels faster through the membrane than does carbon dioxide, is readily

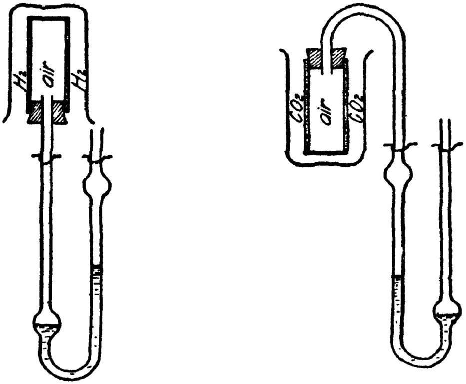

Fig. 5

shown by the use of unglazed, porous, porcelain cylinders, connected with a long narrow glass stem, as were first recommended for this purpose by Wöhler.[24] The whole arrangement may be seen from the figure (Fig. 5). Both cylinders contain air, under atmospheric pressure as indicated by the open manometers, with which the stems are connected. An inverted beaker filled with hydrogen is brought over one pot and another beaker filled with carbon dioxide over the second cylinder. The different speed of diffusion instantly causes, in one case, a (temporary) excess of pressure, and in the other a reduction of pressure, until, after a few minutes, equilibrium is reestablished. On removing the beakers the reverse takes place.

20. The different speed of diffusion can also be demonstrated in an elegant manner by the use of small glass bulbs (of about 1.5-2 centimeters in diameter) filled with liquid bromine, as used by Biltz.[25] These bulbs are made by drawing out a glass tube into capillary ends and blowing the intermediate piece of tubing into the required shape. Two of these bromine bulbs are placed in two glass cylinders (height 27 centimeters, width 6.5 centimeters) closed at both ends by well-fitting glass plates coated with a little grease, so as to insure gas-tight connections. The upper glass plates are perforated and closed by rubber or cork stoppers. One of the stoppers has one hole, which allows the passage of a long glass rod, bent at right angles at its end in the form of a

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[24] *Ber. d. chem. Ges.*, 4, p. 10, 1871.

[25] *Zeitschr. f. phys. Chem.*, 9, p. 152, 1892.

circle, in order to crush the bromine bulb at the proper moment. The other stopper has two holes, through which passes a glass tube (inner bore 0.4 centimeter) similar in shape to the glass rod in the first mentioned cylinder and serving for a like purpose, and another L-shaped tube, provided with a piece of rubber tubing and a pinchcock for the introduction of hydrogen gas (Fig. 6). The dry gas is passed through in a rapid stream, expelling at the same time the air through the "crushing" tube. After 2 minutes the cylinder is filled and both

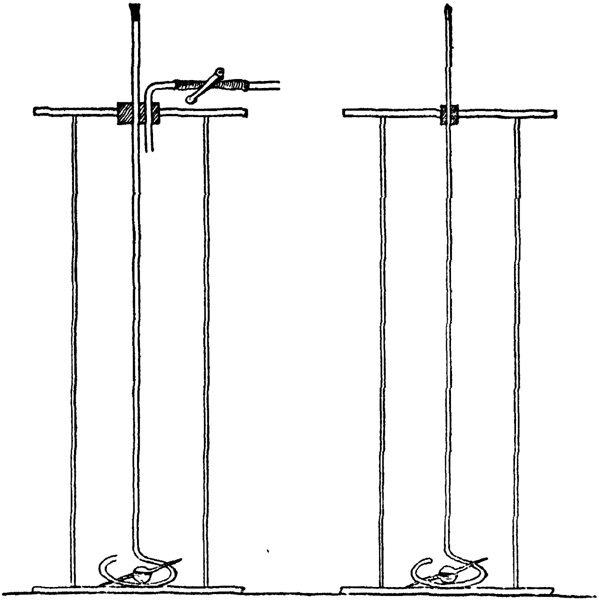

Fig. 6

tubes closed by the pinchcock and a cork stopper respectively. The two bromine bulbs are crushed simultaneously and the difference in behavior of the air-bromine and hydrogen-bromine mixture becomes visible in the course of 3-5 minutes. Using white screens to make the colors visible at a distance, it will be seen that in the hydrogen cylinder the bromine fills the space half way up, while in the air cylinder the bromine has moved only one-fourth upward.

21. On the different speed of diffusion through a porous septum is based a method first applied by Graham, called atmolysis to separate one gas from another. Ostwald[26] has given the following arrangement to show the separation of detonating gas into hydrogen and oxygen by this method.

The gas is generated in a wide-mouth bottle (Fig. 7), filled with a rather strong solution of caustic soda, which is electrolyzed by the current from two storage cells. Two cylindrical iron or nickel sheets are used as electrodes. The gas is dried by a U-tube filled with granu-

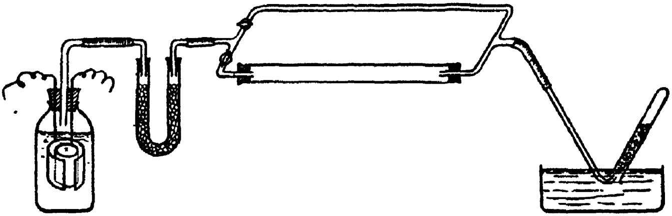

Fig. 7

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[26] Ostwald-McGowan, The Scientific Foundations of Anal. Chem., 3rd ed., p. 232, 1908.

lated calcium chloride and enters first the left (glass) arm of a branched tube, the one stopcock being turned on and the other turned off; the gas collected in a test-tube over water explodes with a lighted match. When however the gas is made to pass through the right tube of unglazed porcelain, it will be seen that, under proper conditions the hydrogen diffuses out almost completely with the result that the collected gas rekindles a glowing splint, thereby showing that it is oxygen that is left.

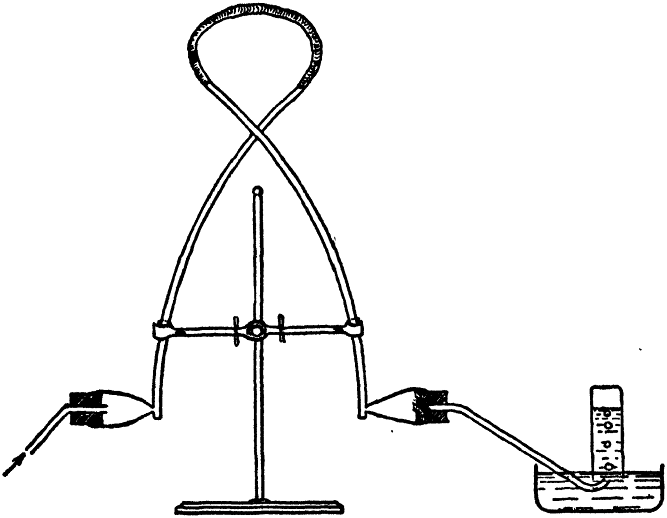

Fig. 8

22. The same effect is obtained by passing the electrolytic gas through two crossed "churchwarden" clay pipes, connected by a piece of thick-walled rubber tubing

(Fig. 8). Both in this and in the preceding experiment the proper rate at which the gas mixture travels has to be found out beforehand. If the gas stream is too *rapid,* the hydrogen has no time to diffuse out; on the other hand, if the rate is too *slow,* air will diffuse into the tube so that a glowing splint will not burst into flame.

23. That the law of diffusion also holds good for effusion, *i. e.,* the passage of a gas through a fine orifice, was also found by Graham (1832); and may be shown for hydrogen and oxygen with an apparatus devised by Freer[27] (Fig. 9), consisting of a U-tube, connected on one side with a two-hole stopcock (*A*) and on the other side with a barometer tube. The left limb of *A* (*a*) contains a piece of glass rod and is drawn out into an extremely narrow tip, while the right outlet tube (*b*) is left unchanged. After the bend of the U-tube has been covered with mercury, so as to separate the air space on both sides, dry hydrogen gas is passed through the tube, escaping through *b* (*a* being closed). After a few minutes *A* is turned off, and mercury poured in the long limb of the

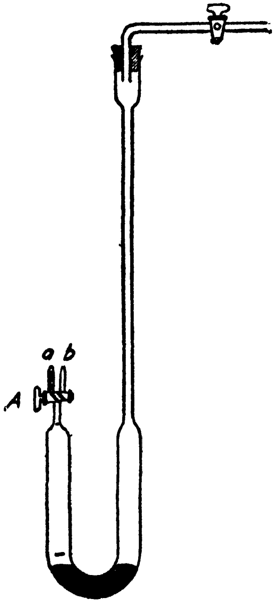

Fig. 9

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[27] *Zeitschr. f. phys. Chem.,* 9, p. 669, 1892.

U-tube up to a certain height, the hydrogen in the short limb occupying a volume of about 80 cc., marked off by a strip of paper. The gas is then allowed to escape through the tip *a*, a metronome being used to note the time necessary to drive the gas out to a mark just below the stopcock. This ought to require about 7 seconds. The experiment is then repeated replacing the hydrogen by oxygen. If proper care is taken in filling the tube with an equal volume of pure oxygen, the time of effusion will be four times as long as before.

24. The same results are obtained by using Schilling's apparatus[28] (Fig. 9A) which is widely used for determining the specific gravity of gases. The effusion tube is first filled with oxygen (stopcock A closed, B open) then, with stop-watch in hand, B is closed, A opened and the time noted for the water to pass from the mark on the lower constriction to that on the upper constriction on the tube. The tube is next filled with hydrogen and the time of effusion in this

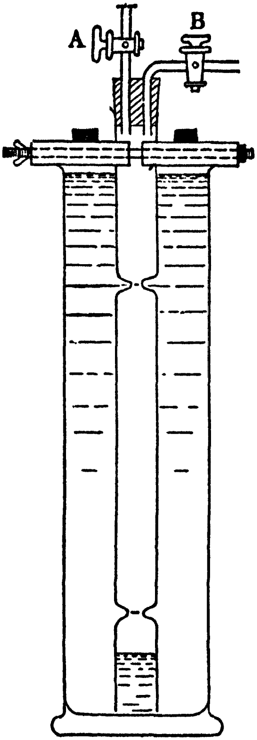

Fig. 9A

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[28] Davison and van Klooster, Laboratory Manual of Physical Chemistry, New York, p. 14, 1922.

case likewise recorded. The times of effusion will be approximately in ratio of four to one.

II. Diffusion in Liquids

25. Diffusion in liquid state, (and taking as a typical instance that of salt solutions in water), first carefully studied by Graham (1850-51) requires such a considerable time to show a visible result that the effect of diffusion can only be seen after half a day or longer. The experiment may be carried out,—following Graham's directions—by filling a bottle with a concentrated solution of the salt, (copper nitrate or chloride) and placing this bottle in a cylindrical vessel which is then filled to the top with distilled water (Fig. 10).

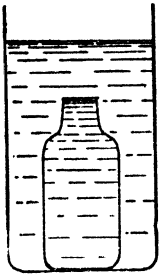

Fig. 10

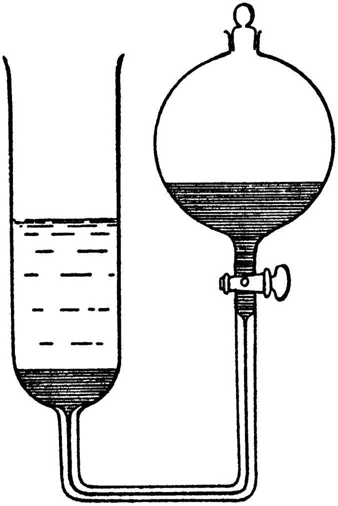

Fig. 11

A sharp boundary surface between the water and the solution may also be obtained by connecting the cylinder containing the water through a bent capillary glass tubing with a separatory funnel (Fig.

11), and allowing the heavy salt solution to slowly push the aqueous layer upward without any perceptible mixing. Still another scheme is to cover the salt solution, filling a cylindrical jar halfway, with a thin cork disk and to allow the water to drop slowly on the disk. The original sharp demarcation line between the two layers disappears as the diffusion progresses.

III. Diffusion in Solids

Diffusion of solids into each other, requires months and years to show a noticeable result, as has been demonstrated by the work of Robert-Austen[29] on the diffusion of gold in lead at 20°, 100° and 250°. An experiment, that takes a few weeks and illustrates to a certain extent the diffusion in solids, is the following:

26. A 5 per cent solution of gelatine in water (150 cc.) is made and divided in three equal volumes. One part is left uncolored, the other two portions are dyed with congo-red and methyl violet, or any other organic dyes. The solutions are poured in three crystallizing dishes of 10-centimeter diameter, and when coagulated, taken out in the form of thick plates, which are placed in a large glass jar, one on top of the other, the uncolored plate being put in the middle. The jar is covered by a cork stopper and set aside in a suitable place, where the result of the diffusion of the colors can be observed at any time.

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[29] *Transactions of the Royal Soc.*, 187, p. 383, 1896.

CHAPTER III

OSMOSIS

I. Osmotic Experiments with Gases

The property of palladium, especially when heated, of dissolving hydrogen readily, but not nitrogen has been used by Ramsay[30] to carry out osmotic experiments with a nitrogen-hydrogen mixture. Since it is necessary to work at high temperatures, in order to obtain satisfactory results, it is more convenient to carry out a similar experiment at the ordinary temperature with air and ammonia, replacing the palladium by animal membrane moistened with water. Ammonia is extremely soluble in water, while hydrogen, oxygen and nitrogen are difficultly soluble in this solvent. The thin film of water on the membrane acts in this way as a semipermeable membrane.

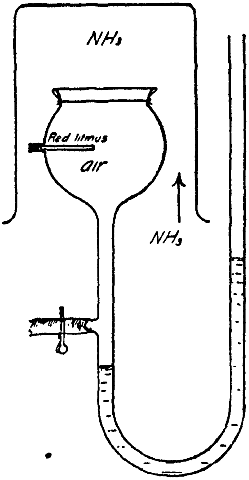

Fig. 12

27. A thistle tube covered with the moist membrane, is bent in the form of a U, and contains air, under atmospheric pressure as indicated by the height of some colored oil in both limbs of the U-bend (Fig. 12).[31] If now a beaker is

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[30] *Phil. Mag.*, 38, p. 206, 1894.

[31] Stieglitz, Elements of Qualitative Chemical Analysis, Vol. I, New York, p. 22, 1916, also: Alex. Smith, Introduction to Inorg. Chemistry, 3rd ed., New York, p. 329, 1917.

inverted over the head of the thistle tube and hydrogen admitted, no increase of pressure inside the thistle tube is observed. On substituting an atmosphere of ammonia for the hydrogen, the gas dissolves quickly in the water on the membrane until saturation, and then enters the inside of the tube producing an increase in pressure. A piece of red litmus paper changes color at the same time.

II. Osmotic Experiments with Liquids

28. A very simple osmotic experiment, which forms a modification of the original experiment, performed by the discoverer of osmosis, the abbé Nollet[32] was described by Lüpke[33] as follows:

A 100 cc. glass jar is filled with a nearly saturated solution of cane sugar and closed with bladder. On submerging the jar in water the volume increases considerably in the course of 2 or 3 hours and the membrane swells up to such an extent, that on piercing the latter with a thin needle a stream of liquid, about 20 centimeters high, is thrown up.

29. The rôle of osmosis in plant life may be illustrated by cutting away the lower end of a large potato, peeling off the skin for about one-half of its length and boring by means of a large cork borer a deep hole to within one centimeter from the bottom. The cavity is filled with a sugar solution colored with a little indigotine and closed air-tight with a perforated stopper carrying a long narrow bore glass tube. The potato is then placed in a crys-

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[32] *Mémoires de l'Ac. Royale des Sc.*, p. 57, 1748.

[33] Grundzüge der Electrochemie, 5e Aufl., p. 91, 1907.

tallizing dish filled with water and the initial height of the liquid in the tube marked by a strip of paper. After a few hours a considerable rise of the level of the liquid in the tube will be noticed provided no leaks are present.

30. Instead of a potato a large carrot free from worm holes or other defects may be used. The top is cut off, the skin scraped from the outer surface and a cylindrical hole about 2 inches deep bored in the top. The cavity is filled with sugar solution and the osmosis shown as in the preceding experiment.[34]

31. The realization of practically semipermeable membranes rests on the discovery by M. Traube of the copper ferrocyanide precipitation membrane, the formation of which may be shown in a way suitable for projection, in a small trough with parallel walls (Fig. 13), filled with a half-saturated solution of copper sulphate.[35] From a pipette, containing a nearly saturated solution of potassium ferrocyanide, one drop is allowed to fall on the copper sulphate solution. An exceedingly tenuous membrane of the brown copper ferrocyanide is formed, through which water passes into the solution, enclosed by the precipitate. The result is, that the solution, surrounding the drop becomes more concentrated and sinks in thread-like streaks to the bottom. These streaks are easily seen, owing to the different refractive

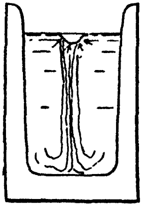

Fig. 13

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[34] Walton and Krauskopf, Laboratory Manual of General Chemistry, Menasha, p. 77, 1920.

[35] c.f. Nernst, Theoretische Chemie, 6e Aufl., p. 133, 1909. Thiel, *Zeitschr. f. Electrochemie*, 12, p. 229, 1906.

indices of solutions of different densities. Tammann[36] has used this method of "streaks" in an ingenious way to detect isosmotic (isotonic) solutions.

32. Precipitation membranes, like the above mentioned, are obtained in a similar manner, by pouring a moderately concentrated sodium silicate solution (specific gravity 1, 1) into a number of lecture jars containing a few crystals of copper-, iron-, manganese-, nickel- and cobalt salts respectively. After standing over night in a quiet place, peculiar, coralline shoots (so-called "chemical gardens") are formed, of different shape and color, characteristic of the salts used. The mode of formation is the same as in the case of the copper ferrocyanide.

33. Instead of silicate solutions one may use a 3-6 per cent gelatine solution which has lost its property of gelatinizing on cooling by boiling on a water bath for two hours or longer. On adding this solution drop by drop to a 5 per cent solution of tannin in water white or colorless little bags are formed which on standing become dark and unelastic.[37]

34. The precipitation of efficient copper ferrocyanide membranes in the pores of unglazed porcelain cells (after Pfeffer) is connected with considerable experimental difficulties, as was clearly brought out by Morse and his collaborators.[38] It is, therefore, preferable to use for lecture experiments, demonstrating osmotic pressure, parchment thimbles (as may be obtained from Schleicher and

[36] *Wiedeman's Annalen*, 34, p. 299, 1888.

[37] Ostwald-Wolski, Practikum der Kolloidchemie, 3e Aufl., Leipzig, p. 96, 1922.

[38] *Am. Chem. Journ.*, 29, p. 173; 34, p. 1; 36, p. 39, 1903-'06.

Schüll, in the dimensions of 100 by 16 millimeters, No. 579), tightly fastened to a long narrow tube[39] (Fig. 14). The cell is filled by pouring through the funnel a colored, concentrated solution of cane sugar. The stopcock is then closed and the cell placed in a beaker of distilled water. Although the parchment is not quite impermeable to sugar, it will be seen that the water passes very easily through the parchment membrane causing a rapid rise of the solution in the narrow tube. The initial height of the liquid is marked by a strip of paper. The rise amounts to several centimeters in the course of an hour.

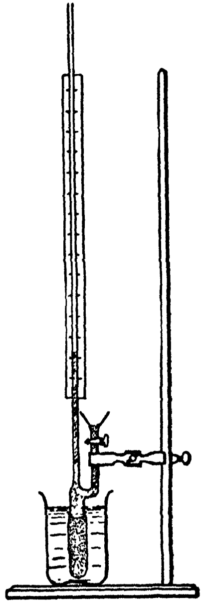
Fig. 14

35. Nernst[40] has constructed an osmotic cell based on selective solubility, similar to the osmotic gas cell, described above, consisting of an inverted thistle tube (7 centimeters wide), to which a piece of pig bladder, thoroughly soaked in water of 40° is tightly fastened by means of a string. The cell, filled with ether in which benzene has been dissolved, is pressed against a wire gauze, suspended in a 400 cc. beaker, and is held in its place by a clamp from a ringstand (Fig. 15). The beaker contains ethyl ether, saturated with water, and is

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[39] Alex Smith, *l. c.*, p. 328.

[40] *Zeitschr. f. phys. Chem.*, 6, p. 37, 1890.

covered by a one-hole stopper (allowing the passage of the stem) in order to limit the loss of ether by evaporation. The wire gauze serves to prevent the bladder from distending as a result of the passage of ether through the bladder into the thistle tube. The water contained in the bladder, dissolves the ether, but not the benzene and acts in this manner as a semipermeable membrane. A rise of 10-20 centimeters in the course of an hour will be observed, provided the stem of the thistle tube is not too wide.

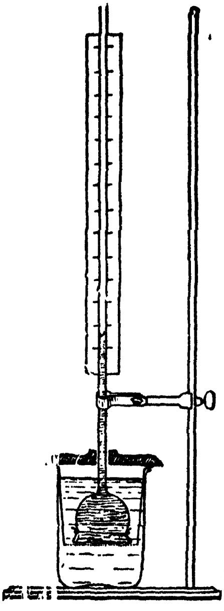
Fig. 15

36. In a very striking manner Crum Brown[41] has illustrated the rôle of a perfectly semipermeable membrane. A strong solution of calcium nitrate is shaken with a little phenol, until saturation is reached and the mixture poured into a high and narrow cylindrical jar. The phenol, left undissolved, floats as a thin layer, (which should not be more than a few millimeters thick) on top of the calcium nitrate solution, saturated with phenol. The phenol-layer is then cautiously covered with a saturated solution of phenol in distilled water. The calcium nitrate being insoluble in phenol, the latter acts as a semipermeable membrane dissolving the water and allowing its passage from the upper

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[41] *Proc. of the Royal Soc. of Edinburgh,* 22, p. 439, 1898.

layer into the lower, and the result is,—as a daily observation and demarcation of the height of the thin phenol layer by means of strips of paper shows,—that the phenol is gradually displaced upward until finally only two layers are left: a dilute, calcium nitrate solution, surmounted by a thin layer of phenol.

The experiments with three liquid layers, of which the middle acts,—to a certain extent—as an osmotic membrane, were first carried out by a French scientist, Lhermite.[42] As liquids he used an aqueous solution of alcohol (35 per cent), castor oil (or turpentine) and water; also ethyl ether, water and oil of bitter almonds (or carbon disulphide).

37. A modification of one of Lhermite's three liquid combinations, was introduced by Kahlenberg,[43] who fixes the middle layer (in this case water) in its position, in order to be able to demonstrate the osmotic pressure, resulting from the difference in solubility of ether in water and carbon disulphide. A glass apparatus (Fig. 16), contains at the bottom and in the communicating narrow side tube, mercury. The latter is covered by a layer of carbon disulphide (*C*), then fol-

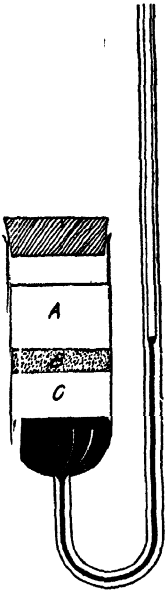

Fig. 16

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[42] *Ann. de Chim. et. Phys.*, (3) 43, p. 420, 1855.

[43] Outlines of Chemistry, Revised ed., New York, p. 443, 1916. *Journ. of phys. Chem.*, 10, p. 141, 1906.

lows a tightly pressed cork-disk (*B*), soaked with water, and finally a layer of (aqueous) ethyl ether (*A*). The apparatus is closed by a loosely fitting cork to avoid evaporation of the ether. The initial position of the mercury in the narrow gauge tube is marked by a strip of paper. The gradual rising of the mercury may be still better observed by pouring some colored water on to the mercury in the side tube.

CHAPTER IV

VAPOR PRESSURE AND DETERMINATION OF MOLECULAR WEIGHTS

A. Vapor Pressure

Of the two methods for measuring vapor pressures, the static and the dynamic, the former is easily carried out as follows:[44]

38. In three out of four barometer tubes, all inverted over mercury, are inserted,—by means of pipettes, with their ends curved upward—small quantities of water, ethyl alcohol and ethyl ether respectively. The fourth is kept as a standard showing the atmospheric pressure. The fall of the mercury in the three tubes as compared with the height of the mercury pile in the fourth tube is a direct measure of the vapor pressure of the liquids at room temperature. Expressed in centimeters of mercury at 20°, these pressures are:

for water	1.74
for alcohol	4.40
for ether	44.24

By mounting the tubes within a jacket, connected with a distilling flask containing a suitable distilling liquid, the vapor pressure can be demonstrated for any desired temperature.

The dynamic method, which consists in a slow but continuous diminution of pressure while keeping the liquid constantly at ebullition, allows the pressure and tempera-

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[44] Bigelow, Theor. and General Chemistry, New York, p. 274, 1914.

ture to be read at the same time; but, owing to the fact that only the decrease in pressure can be made visible to a large audience, this method is less fit for a lecture demonstration.

39. The vapor pressure of solutions is shown in the same way as for pure liquids, *viz.*, by the use of four barometer tubes over mercury, of which one is kept as standard of comparison. Into the vacuum of the first tube is introduced a little ethyl ether, in the second is placed a few drops of a solution of 12.2 grams benzoic acid in 100 cc. ether (molecular weight of benzoic acid = 122) and in the third tube an ethereous solution of benzoic acid of double this strength (22.4 grams in 100 cc. ether).[45] After a while the difference in mercury level between tube one and two is about half as much as that between tube one and three showing that the lowering of the vapor pressure is proportional to the concentration of the solute. (Fig. 17).

Fig. 17

40. The depression of the vapor pressure at the boiling point (under atmospheric pressure) of the solvent, is directly connected with the ebullioscopic methods for the determination of molecular weights and is conveniently carried out with the aid of an apparatus as

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[45] Lüpke-Bose, Grundzüge der Electrochemie, 5e Aufl., p. 106.

sketched in Fig. 18,[46] consisting of an outer jacket and an inner "test"-tube (to which a narrow gauge tube has been sealed), held by a two-holed cork stopper, provided with a second tube for the escape of the vapor of the solvent. Pure solvent is poured in the outer jacket and also in the test-tube, to a height of 7 centimeters above the bend. In order to make any difference in level better visible, a trace of some *aniline* dye is added. On gently heating the solvent in the outer jacket, the vapor condenses along the walls and finally escapes in the open through the outlet tube. The latter is then closed by a cork stopper and the vapor is forced through the narrow gauge tube, expelling the remaining air, and condensing above the constricted part of the test-tube. After the vapor has bubbled through for a few minutes, the cork stopper above the constriction is pushed down, and at the same time the stopper removed from the outlet tube, thus allowing the vapor to escape directly in the open as before. It will be found that the level is practically the same in the test-tube and the gauge tube. A weighed quantity of a solid, easily soluble in the chosen solvent (about 0.3 gram) is introduced in the inner tube, and the operation is repeated. When equilibrium is reached, the liquid stands lower in the gauge tube (2 centimeters or more)

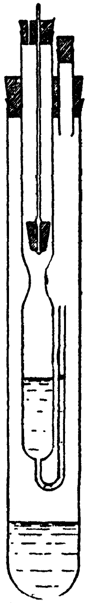
Fig. 18

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[46] *Journ. Am. Chem. Soc.*, 40, p. 193, 1918.

than in the test-tube, thus clearly showing that the pure solvent has a higher vapor pressure than the solution at the same temperature. On adding the same quantity of solute once more, the fall in level in the gauge tube will be, after equilibrium is reestablished, approximately twice as much as before. A suitable solvent for a lecture demonstation is carbon tetrachloride, on account of its low boiling point (76°), its non-inflammability, and its low surface tension (the capillary ascension being negligible). As solute naphthalene or any other organic compound, which dissolves readily in this solvent may be used.

B. Determination of Molecular Weights

41. The above described method of heating the solution by means of the vapor of the solvent has been used by several investigators for the determination of molecular weights. In cases where it is only necessary to decide what multiple of the empirical formula represents the molecular weight, the use of a modified Landsberger apparatus as the one devised by Eykman[47] (Fig. 19), or a similar one, by McCoy,[48] allows a molecular weight determination to be carried out with an accuracy of 5-10 per cent in the course of a

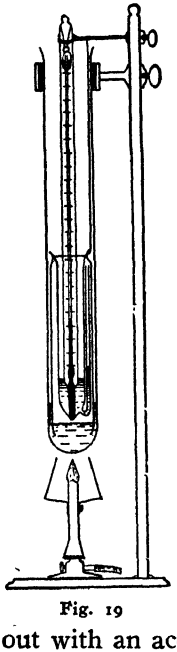

Fig. 19

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[47] *Journ. de Chimie Physique.*, 2, p. 47, 1903.

[48] *Am. Chem. Journ.*, 23, p. 353, 1900; obtainable from Eimer and Amend, New York.

few minutes. For a lecture demonstration a weighed quantity of naphthalene preferably in the form of a tablet (0.3 gram) is introduced into the inner tube of the Landsberger apparatus containing 12-16 cc. of benzene. The outer jacket is filled with about 50 cc. of the solvent. The thermometer, on which the boiling point is read, need not be a "Beckmann;" one graduated in tenths of a degree is quite sufficient for this purpose. As a matter of course, the reading of the boiling point and the volume of the solution can only be made by the lecturer or his assistant.

42. The vapor density method, due to Victor Meyer, is applied for substances which can be readily evaporated. A description can be found in any text-book on organic chemistry. Care has to be taken, that all connections are gas-tight (thick-walled India rubber tubing should be employed) and that the water in the graduated glass tube is saturated with air. Using aniline (boiling point 184°) in the outer jacket, and xylene (ortho, meta or para, boiling point 140°) in the glass-stoppered weighing bottle, about 20 cc. of air will be collected from a weight of about 0.1 gram of liquid.

Instead of glass-stoppered weighing bottles it is more convenient to use small glass bulbs with a sealed capillary stem, bent at the end, so that by a short pull of the copper wire from which the bulb is suspended the stem breaks off and the

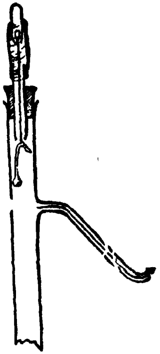
Fig. 20

bulb falls in the cylinder below. The arrangement is readily understood from Fig. 20. A side tube for the passage of a glass rod as the Meyer-apparatus usually contains, is then unnecessary.

43. The cryoscopic method is conveniently carried out with the Eykman depressimeter (Fig. 21). This simple apparatus[49] consists of a short thermometer, divided into twentieths of a degree and fitted at the end in the neck of a small flask (contents about 20 cc.), fastened inside a glass cylinder by means of a cork stopper at the top and a plug of cotton at the bottom. The thermometer, a modified "Beckmann" has to be "set" before use. A weighed quantity of the solvent, say water (10 grams) is poured in the flask and the freezing point is read. A quantity of solute of known weight is then added and the freezing point again determined. Taking for example 0.2 gram of sodium chloride, the depression will be found to be about 1.30°, instead of a calculated value (for undissociated molecules) of 0.65°.

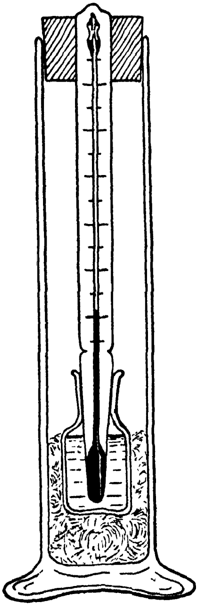

Fig. 21

44. Whenever it is desired to make the readings visible to the audience, the use of a large air thermometer is unavoidable. Ciamician has proposed the follow-

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[49] *Zeitschr. f. phys. Chem.*, 2, 964, 1888.

ing arrangement.[50] A cylindrical glass reservoir (Fig. 22) is sealed to a glass tube (inner cross-section 1.5 millimeters), twice bent at right angles and provided with two bulbs at a distance of 50-60 centimeters. The lower part of the glass tube is inserted in an alcoholic solution of fuchsine, serving as a confining liquid. Around the glass cylinder a copper stirrer moves in a large test-tube (20 by 3 centimeters). This test-tube is filled successively with equimolecular solutions of cane sugar (34.2 grams in 100 cc. of water), mannite (10.2 grams in 100 cc.) and acetic acid (16 grams in 100 cc.) and after inserting the tube each time in a freezing mixture of salt and ice the freezing point is determined. In all three experiments the confining liquid rises to about the same height.

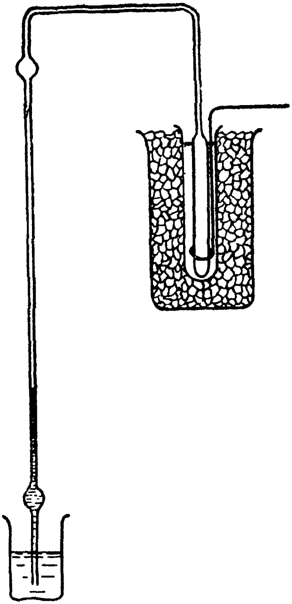

Fig. 22

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[50] *Ber. d. chem. Ges.*, 22, p. 31, 1889.

CHAPTER V

CHEMICAL EQUILIBRIUM AND THE LAW OF MASS ACTION

Since the publication of van 't Hoff's epochmaking "Études de dynamique chimique" (1884) chemical equilibrium and the law of mass action have become the nucleus of modern physical chemistry. The frequent and manifold applications of these fundamental principles, in analytical chemistry and elsewhere make it desirable, to take up the discussion of this subject, directly after the properties of gases, liquids and solids have been expounded. It goes without saying, that lecture experiments in this field especially, can only illustrate the general laws in a qualitative way; nevertheless they may be considered of great use, in clearly demonstrating the effect of concentration, temperature and pressure on the course of chemical reactions. Taking up first of all, the question of reversibility, a few typical reversible reactions are mentioned, then the concentration of the reacting substances is considered more in detail, followed by a demonstration of the change of equilibrium by varying temperature or pressure. In connection herewith, the effect of the factors, which influence the velocity of chemical reactions is illustrated. Finally some space is devoted to the rule of successive reactions.

Thus the chapter may be subdivided under the following headings:

I. Reversible reactions.
II. The law of mass action.
III. Displacement of equilibrium.
IV. Time reactions.
V. Velocity of chemical reactions.
VI. The rule of successive reactions.

I. Reversible Reactions

In spite of the tendency prevailing in analytical chemistry, of carrying out reactions along "irreversible" lines, it has been recognized in the past decades, that in principle every reaction is reversible, and that it is only a question of choosing the proper conditions in order to reverse the course of a reaction. Out of the great many cases at our disposal, the following examples, easily performed, may be quoted:

45. $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$

To a small quantity of bismuth trichloride in a conical lecture jar a few cubic centimeters of 5N hydrochloric acid are added, until a clear solution is obtained. When water is added, hydrolysis occurs and a white precipitate is formed, which redissolves on the addition of concentrated hydrochloric acid.

46. $Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S.$

Concentrated hydrochloric acid in a separatory funnel is allowed to drop slowly on red antimony sulphide in a fractionating flask, and the escaping gas passed into a solution of antimony chloride, forming a precipitate of red antimony trisulphide.

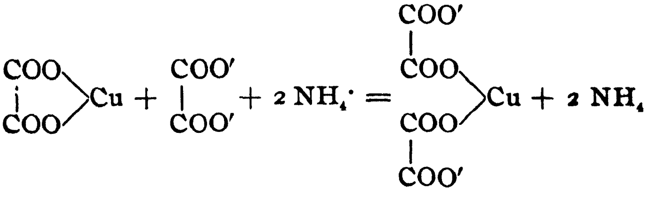
47. $$2CuI_2 \rightleftharpoons 2CuI + I_2.$$

Addition of a solution of potassium iodide to a copper sulphate solution results in the precipitation of cuprous iodide and the separation of iodine. By taking out the iodine by means of sodium thiosulphate the reaction goes to completion in the direction from left to right (→). In this form the reaction is used in quantitative analysis as a method for determining copper.

Inversely by taking out the copper in the bivalent state the reaction is completely reversed.[51] By adding a solution of ammonium oxalate to the mixture of cuprous iodide and iodine formed by the interaction of potassium iodide and copper sulphate the precipitate and the color of the iodine disappear:

$$2CuI + I_2 + 4(NH_4)_2C_2O_4 = 4NH_4I + 2(NH_4)_2Cu(C_2O_4)_2.$$

The liquid takes on a deep blue color owing to the formation of a complex anion as expressed by the following equation:



$$\left.\begin{array}{c}\mathrm{COO}\\|\\\mathrm{COO}\end{array}\right\rangle \mathrm{Cu} + \begin{array}{c}\mathrm{COO'}\\|\\\mathrm{COO'}\end{array} + 2\,\mathrm{NH_4^{\cdot}} = \left.\begin{array}{c}\mathrm{COO'}\\|\\\mathrm{COO}\\ \\\mathrm{COO}\\|\\\mathrm{COO'}\end{array}\right\rangle \mathrm{Cu} + 2\,\mathrm{NH_4}$$

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[51] Elbs, *Zeitschr. f. Electrochemie*, 23, p. 147, 1917.

48. H_2S disp$\overset{\rightarrow}{\underset{\leftarrow}{\text{la}}}$ces CO_2 from its salts.

That hydrogen sulphide can displace carbon dioxide from its salts, just as well as the latter can liberate hydrogen sulphide from its salts, was shown by Emil Fischer[52] as follows: A strong current of hydrogen sulphide is passed into a solution of sodium bicarbonate thereby liberating carbon dioxide. The gas mixture, bubbling through a barium hydroxide solution precipitates barium carbonate. The reverse takes place by passing carbon dioxide into a solution of sodium hydrosulphide; the hydrogen sulphide evolved, precipitates lead sulphide from a solution of lead acetate.

49. CH_3COOH disp$\overset{\rightarrow}{\underset{\leftarrow}{\text{la}}}$ces CO_2 from its salts.

In the same way acetic acid (dilute) displaces carbon dioxide from a solution of potassium carbonate, while on the other hand carbon dioxide passed into a solution of potassium acetate in absolute alcohol, produces a precipitate of potassium carbonate, the acetic acid, set free, remaining in solution.[53]

50. $2H_2O \rightleftharpoons 2H_2 + O_2$.

The decomposition of water and its re-formation from the resulting 2 : 1 mixture of hydrogen and oxygen can easily be shown,[54] by fastening a coil of platinum wire (0.6 millimeter in diameter) to stout copper wires, passing air-tight through small thick-walled glass-tubes

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[52] Heumann-Kühling, Anleitung zum Experimentieren, 3e Aufl., p. 95, 1904.

[53] Le Chatelier, Lecons sur le carbone, p. 210, 1908.

[54] Hofmann, *Ber. d. chem. Ges.*, 23, p. 3303, 1890, also Lash Miller and Kenrick, *Journ. Am. Chem. Soc.*, 22, p. 296, 1900.

(Fig. 23) held by a cork, which closes the neck of a fractionating flask. Water is boiled in the flask, until the vapor escapes free from air; the platinum wire is cautiously heated electrically to white heat, by connecting the copper wires with a strong current cable provided with ampere meter and a rheostat (for currents up to 20 amperes). The arrangement resembles Deville's cold-hot tube in bringing about a dissociation of the water vapor. The gas mixture, formed in the reaction is collected over water in a eudiometer and then,—after passing the spark—recombined to water.

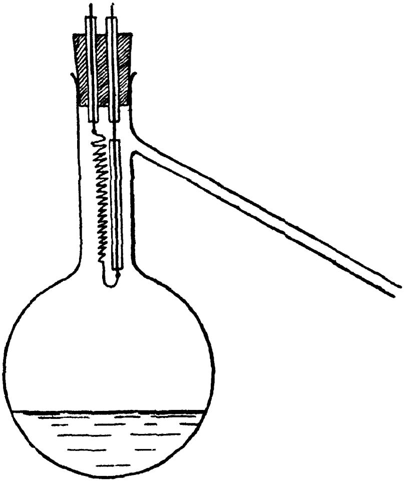

Fig. 23

II. The Law of Mass Action

As illustrations of the law of mass action several instructive lecture experiments have been devised. Those given below have been found to be most convenient.

51. $FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$.

This reaction, which was first systematically investigated by Gladstone,[55] may be carried out—following the directions of Lash Miller and Kenrick[56]—as follows: Approximately equivalent solutions of ferric chloride and ammonium thiocyanate are prepared, the first, containing 6 grams of commercial ferric chloride, 25 cc. of concentrated hydrochloric acid (specific gravity, 1.175) and water to make up 200 cc.; the second solution contains 7.5 grams of ammonium thiocyanate dissolved in 200 cc. of water. Five cc. of each solution are mixed and 2 liters of (tap) water added. The orange-colored mixture is equally divided between four beakers of 600 cc. each. From the color of the four solutions it is evident that the equilibrium is considerably displaced to the left, ferric thiocyanate [$Fe(CNS)_3$] being dark red in solution; ferric chloride is more or less yellow, while ammonium salts are colorless. Therefore, the amount of ferric thiocyanate, present in solution, can be fairly well judged from the depth of color of the solution.

On adding to the first beaker 5 cc. ammonium thiocyanate solution and to the second 5 cc. ferric chloride solution the color becomes in both cases *dark red*, showing an equilibrium displacement from left to right (→).

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[55] *Phil. Trans. Royal Soc.*, p. 179, 1855.

[56] *Journ. Am. Chem. Soc.*, 22, p. 292, 1900.

An addition of 50 cc. of a saturated solution of ammonium chloride to the third beaker makes this solution almost colorless, thereby showing, in accordance with the law of mass action, that the equilibrium is now displaced from right to left (←). The fourth beaker is kept for comparison.

52. $\mathrm{Ag}^{\cdot} + \mathrm{Fe}^{\cdot\cdot} \rightleftharpoons \mathrm{Ag} + \mathrm{Fe}^{\cdot\cdot\cdot}$.

This reaction was recently studied in detail by A. A. Noyes and Brann[57] and its equilibrium conditions (at 25°) determined carefully. As a lecture experiment this reaction may be performed in the following manner:[58]

Pure powdered ferrous sulphate ($FeSO_4 7H_2O$) is dissolved in cold water (previously boiled, to drive out the air), to which a few drops of sulphuric acid have been added. The liquid is then quickly filtered and kept in an Erlenmeyer flask with a coil of thin, rust-free iron wire.

A second solution is made by adding a solution of sulphuric acid (specific gravity 1.25) to a nearly saturated solution of ferric ammonium alum [$Fe(NH_4)(SO_4)_2 12H_2O$] until the solution is almost colorless, or slightly yellow. The addition of sulphuric acid serves to hinder hydrolysis.[59] Five to ten cc. of a dilute silver nitrate solution are then poured into a conical lecture jar and mixed with enough ferrous sulphate solution to form a precipitate of silver. The latter is redissolved after the

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[57] *Journ. Am. Chem. Soc.*, 34, p. 1016, 1912.

[58] Luther, Die chemischen Vorgänge in der Photographie, Halle, p. 35, 1899.

[59] Ostwald, Grundlinien der anorg. Chem., 2e Aufl., p. 594, 1904.

subsequent addition of enough ferric alum solution (about four to six times the quantity of the ferrous sulphate solution, required for precipitating the silver).

In connection with this experiment it is interesting to point out the mechanical conceptions by which Luther[60] and later on van 't Hoff[61] and Baur[62] have tried to illustrate the chemical equilibrium in this reversible reaction. The former imagines a balance beam (Fig. 24) kept in its position by wire coils $\mathrm{Fe}^{\cdot\cdot}$ and Ag combining their efforts at opposite ends in one sense, while Ag and $\mathrm{Fe}^{\cdot\cdot\cdot}$ coils act in the reverse. More appealing to the mind is the idea of van 't Hoff and Baur, as represented in Fig. 25. By plotting the percentage composition as abscissa against the energy of the system as ordinate, we see that like a rolling ball, reaching from whatever side of a curved line it comes down, the lowest level, the energy

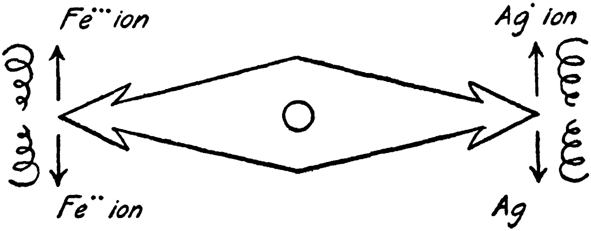

Fig. 24

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[60] Luther, *l. c.*, p. 35.

[61] Van 't Hoff, Physical Chemistry in the Service of the Sciences, p. 88, Chicago, 1903.

[62] Baur, Themen der physik. Chemie, Leipzig, p. 6, 1910.

of the system reaches a minimum value. Similar views have been expressed by Leveing[63] in 1885.

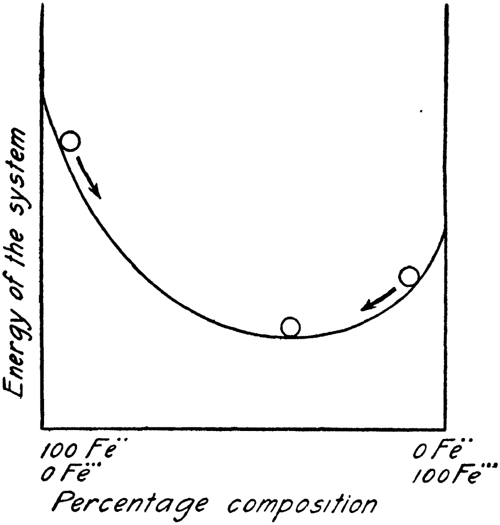

Fig. 25

53. $HgCl + OH' \rightleftharpoons HgOH + Cl'$.

Von Dieterich and Wöhler[64] propose the reversible reaction, expressed in the above equation as another suitable illustration of mass action. Phenolphthalein being used as indicator, a N/100 solution of potassium hydroxide shaken with calomel remains red; this means an

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[63] Leveing, Chemical Equilibrium, Cambridge, p. 35, 1885.
[64] *Zeitschr. f. anorg. Chem.*, 34, p. 194, 1901.

incomplete consumption of hydroxyl ions; if instead of a N/100 solution a N/1,000 solution is used, the color of the solution changes from red to grey on shaking with calomel; an addition of a few drops of potassium chloride restores the original red color.

III. Displacement of Equilibrium

54. The change of equilibrium by lowering or raising the temperature, can be easily shown, in dealing with gaseous mixtures, *e. g.*, nitrogen tetroxide, partly dissociated in nitrogen dioxide:

$$N_2O_4 \rightleftharpoons 2NO_2.$$

The thermal equilibrium displacement can be made visible in this case first by the accompanying change in color, and secondly by the abnormal change in pressure at constant volume.

Taking first two glass tubes (size 10 by 1.5 inches) filled with the carefully dried gas mixture (prepared by heating lead nitrate) and closed at both ends by rounding off the ends in the blast flame, one is lowered into a cooling mixture of alcohol and carbon dioxide, while the other tube is carefully heated—with proper precautions, by moving the flame of a Bunsen burner along the tube. The result is then shown by placing both tubes simultaneously against a white background.

55. For the second experiment, two round-bottom flasks of exactly the same size (contents 600-800 cc.) with air-tight fitting ground glass stoppers, to which U-shaped open manometer tubes (inner bore 2 millimeters) have been sealed, are filled, 1 or 2 hours in advance, with carbon dioxide and nitrogen tetroxide respectively. Care has to be taken that the stoppers, carrying the manometer tubes, are well attached to the necks of the flasks, so as to hold an excess pressure (Fig. 26). At the outset both manometers show the same pressure, the gases being under atmospheric pressure. On inserting the flasks held by clamps, to the same depth in a large water bath of 50°, the manometer of the nitrogen tetraoxide flask indicates a much higher pressure than the second manometer, due to an equilibrium displacement from left to right (→). When taken out of the bath, the difference in pressure gradually decreases, until finally the initial state is reached.

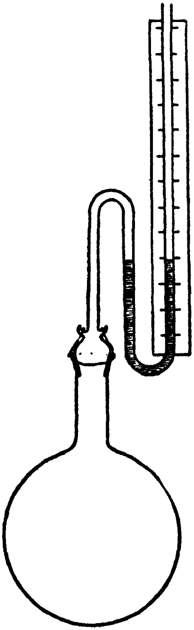
Fig. 26

56. The effect of heating on gaseous dissociation can also be demonstrated in the reaction:

$$PBr_3 + Br_2 \rightleftharpoons PBr_5.$$

Here, too, the progress of dissociation is direcly visible by a more intense color, since on raising the temperature, the equilibrium is displaced from right to left (←). By using equimolecular quantities in one tube and an excess of phosphorus tribromide in another tube, the same experiment also illustrates the mass action law in a very satisfactory way. Following the directions, given by Stieglitz,[65] two small sealed bulbs, blown at the end of glass capillaries, containing 0.029 gram bromine and 0.058 gram phosphorus tribromide (a little more than 1 mole) respectively, are placed in a piece of thick-walled glass tubing, closed at one end and drawn out at the other end into a capillary. The length of the tube is about 10 centimeters and its capacity 40 cc. The air is exhausted to 20-30 millimeters mercury pressure, the capillary end sealed off and bent into a loop. By vigorous shaking the bulbs are broken. A second tube of the same size is filled in the same way with a mixture of 0.029 gram bromine (1 mole) and 0.45 gram tribromide (9 moles).

The tubes are suspended by means of the glass loops at the upper ends in a tall beaker of water and a glazed white porcelain tile or a piece of white cardboard placed behind the beaker, to make comparison of colors easier. On heating the first tube is slightly colored at 50°, the second not at all. At about 85° the most favorable stage for comparison, the first tube appears reddish brown and opaque, while the latter is reddish yellow, through which the white of the tile or cardboard can still be seen. A similar experiment with greater differences in color may be carried out, using phosphorus trichlordibromide *with* and *without* an excess of the trichloride.

IV. Time Reactions

57. The fact, that certain reactions require a perceptible time, until separation of one of the reaction prod-

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[65] *Am. Chem. Journal*, 23, p. 404, 1901.

ucts starts, is illustrated by an experiment, performed by Landolt,[66] demonstrating the reduction of iodic acid by sulphurous acid in a dilute acid solution, according to the equation:

$$5H_2SO_3 + 2HIO_3 = 5H_2SO_4 + H_2O + I_2.$$

Two solutions are made up, one of 1.8 grams iodic acid in 1 liter water and the other composed of 0.9 gram sodium sulphite ($Na_2SO_37H_2O$), 5 grams dilute sulphuric acid (1 : 10) and 9.5 grams soluble starch (rubbed to a thin paste by adding a little water) in 1 liter water.[67] These stock solutions serve to make up solutions of one-half and one-quarter of the two original concentrations. On mixing rapidly 100 cc. of the original and of the more dilute solutions, different times will be found before noticeable separation of iodine sets in. Sodium sulphite, being easily decomposed in contact with air, it will be found that on repeating the experiment, for the same concentration, not necessarily the same time as before is registered.

58. More reproducible values can be obtained in performing another time reaction, also studied in detail by Landolt:[68] the decomposition of thiosulphates by acids:

$$H^{\cdot} + S_2O_3'' = HSO_3' + S.$$

The experiment may be carried out as follows:

To three beakers (of 200 cc. each) containing respectively 0.1, 0.2 and 0.3 gram sodium thiosulphate

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[66] *Ber. d. chem. Ges.*, 19, p. 1317, 1886; 20, p. 745, 1887. See also: Eggert, *Zeitschr. f. Electrochemie*, 23, p. 8, 1917.

[67] H. u. W. Biltz, *l. c.*, p. 111.

[68] *Ber. d. chem. Ges.*, 16, p. 2958, 1883.

($Na_2S_2O_35H_2O$) 100 cc. distilled water is added and after complete solution of the salt, in each beaker is poured, at the same time, a solution of 1 cc. concentrated hydrochloric acid in 20 cc. distilled water (ready at hand in three test-tubes). After 14, 6½ and 4 minutes respectively a milky suspension of finely divided sulphur becomes visible. In a fourth beaker, containing 0.2 gram thiosulphate dissolved in 100 cc. distilled water and kept at 50° is poured, simultaneously 1 cc. concentrated hydrochloric acid; the result, in this case is a visible sulphur separation after 1¼ minutes.

It is interesting to notice, that the different investigators,[69] who studied this reaction carefully, all agree in admitting an *immediate* formation of sulphur on mixing the salt and acid solutions. The sulphur is supposed to remain in solution, until a definite concentration is reached or a certain change has set in, which causes the appearance of visible sulphur drops.

59. Another useful clock reaction is that between arsenious acid and sodium thiosulphate,[70] resulting in the separation of arsenious sulphide. The reaction is rather complicated and different equations are given. The induction periods are extremely sharp and their duration depends largely on the temperature, the acid used and the concentration of the thiosulphate. For the purpose of a lecture experiment two solutions are made up: one con-

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[69] Holleman, *Rec. d. Trav. Chim. des Pays-Bas,* 14, p. 71, 1895.
v. Oettingen, *Zeitschr. f. phys. Chem.,* 33, p. 1, 1900.
Ostwald, Grundlinien der anorg. Chemie, 3e Aufl., p. 337, 1912.

[70] Forbes, Estill and Walker, *Journ. Am. Chem. Soc.,* 44, p. 97, 1922.
Meyer, *Ibidem,* 44, p. 1498, 1922.

taining a tenth molar solution of sodium arsenite acidified with an excess of hydrochloric acid (17 grams of arsenite, dissolved in about 500 cc. of water, acidified with 30 cc. of concentrated hydrochloric acid of specific gravity 1.19, made up to 1 liter) and the other a molal thiosulphate solution (248 grams per liter).

Mixing 100 cc. of each solution results in the separation of arsenious sulphide after about 15 seconds. A half molar solution of thiosulphate (50 cc. of solution + 50 cc. of water) increases the induction period to about 45 seconds, while a quarter normal solution (25 cc. of solution + 75 cc. of water) extends the induction period to almost 3 minutes.

V. Velocity of Chemical Reactions

60. That the rate, at which a chemical reaction takes place, is proportional to the *concentration* of the reacting substances, is shown by the following experiment of A. A. Noyes and Blanchard,[71] referring to the reaction, expressed by the equation:

$$HBrO_3 + 6HI = 3H_2O + 3I_2 + HBr.$$

Four 500 cc. glass-stoppered bottles, 8 centimeters in diameter, are filled with 400 cc. dilute hydrochloric acid, made up by mixing 1600 cc. distilled water and 50 cc. N/2 hydrochloric acid, to which is added 40 cc. of a starch solution (obtained by rubbing 1 gram potato starch with 5 cc. cold water and pouring 150 cc. boiling water over it).

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[71] *Journ. Am. Chem. Soc.*, 22, p. 739, 1900.

From four 10 cc. graduates, in front of these bottles, are added respectively 5, 10, 5 and 10 cc. of a N/2 solution of potassium bromate, and then, simultaneously—as far as possible,—from another set of four 10 cc. graduates, 5, 5, 10 and 10 cc. respectively of a N/2 solution of potassium iodide. The glass stoppers are quickly inserted and the bottles vigorously shaken. The first mixture will become of the same shade of blue as a standard starch-iodine solution[72] in about 120 seconds, the second and the third will both require half that time, (about 60 seconds) while the fourth takes on the color of the standard solution after the lapse of only 30 seconds.

61. After Nernst and Handa[73] the velocity of chemical reaction can clearly be demonstrated by saponifying methyl formate, the progress of the decomposition of the ester being shown by the change in color of different indicators. For this purpose a set of five 100 cc. flasks are filled with 50 cc. (previously boiled) water, brought to the titer of N/1000 with barium hydroxide. The following indicators, a few drops in each case, are added: phenolphthalein, litmus, ganin, p-nitrophenol, and methyl orange, respectively. From five small test-tubes, all attached to the same strip of wood,—in order to insure a simultaneous action,—and each containing 1 cc. of methyl formate, the ester is poured into the five flasks. Besides these, another set of five flasks *without* addition

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[72] The standard solution kept in a 500 cc. glass-stoppered bottle is made by adding to 400 cc. water 10 cc. of the starch solution and 1 cc. of a solution of 1 gram iodine and 2 grams potassium iodide in 500 cc. water.

[73] *Ber. d. chem. Ges.*, 42, p. 3178, 1909.

of ester and a third similar set of five flasks, to which some acid has been added, are kept for comparison, both sets containing the indicators in the above-mentioned order. The times required for changing the color of the indicators will be about 0, 1, 15, 30 and 120 minutes respectively, and give an idea of the sensibility of the indicators towards OH′-ions.

62. The influence of *temperature* on velocities of chemical reactions is preponderant and may be shown by cooling concentrated hydrochloric acid and a piece of marble separately, in test-tubes to —80° in a mixture of carbon dioxide and alcohol, and then bringing both together by dropping the marble on the acid. No perceptible gas evolution is seen.

63. Even comparatively small temperature differences bring about considerable changes in velocities of reaction. An instance was given on page 53 in connection with the decomposition of sodium thiosulphate by acids. A more detailed experiment, illustrating the general rule, that equal increments of temperature cause an equal multiplication of the velocity of any chemical reaction (roughly speaking: every increase of temperature by about 10° doubles the velocity of the reaction), was given by Noyes and Blanchard.[74]

The reaction, carried out, was the same as given on page 55:

$$HBrO_3 + 6HI = 3H_2O + 3I_2 + HBr.$$

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[74] Noyes and Blanchard, *l. c.*, p. 741.

A solution of 100 cc. N/2 hydrochloric acid and 30 cc. starch solution in 1100 cc. water is made and 400 cc. of this solution poured into each of three 500 cc. glass-stoppered bottles and kept in three water baths at 4°, 16°, and 28°[75] respectively. The temperature is indicated by a large-size thermometer, inserted in succession in each of the bottles. Another solution is made up by mixing 10 cc. N/2 potassium bromate, 10 cc. N/2 potassium iodide and 25 cc. water. Ten cubic centimeters of this mixture is placed into each of three 10 cc. graduates. In a fourth bottle is prepared a blue iodine starch solution, in order to serve as a standard. At a definite moment, when the clock (or stop-watch) shows a full minute, the three bromate solutions are poured in the three bottles and then after being stoppered, vigorously shaken. All four bottles are placed against a white background and the times noted, at which the three solutions show in succession the standard blue color. If properly carried out, it will be seen, that these times are approximately 32, 58 and 105 seconds. Thus a rise in temperature of 12° and 24° multiplies the velocity of the reaction by 1.8 (58/32) and $(1.8)^2$.

64. The influence of *pressure* on the velocity of chemical reactions is usually of no great importance. One well-known instance, however, where pressure has a marked effect, may be quoted, an exception also to the adage of the ancients, that substances do not react, ex-

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[75] The temperature of the third solution must not be above 30°, because the depth of color of the blue solution is lessened on raising the temperature, however, not perceptibly below 30°.

cept when dissolved, *viz.*, the formation of mercuric iodide:

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

A mixture of powdered potassium iodide and corrosive sublimate, in equivalent quantities, shaken in a wide-mouth bottle, is only slightly colored yellow, due to the slow formation of mercuric iodide, but on rubbing the mixture with a pestle in a glass mortar, the color changes to red, owing to a more rapid formation of the red iodide of mercury.

65. The presence of *protective colloids* (see exp. 240, 241 and 242, Chapter IX) has a retarding effect on the velocity of such reactions as involve a change of state in one or more of the components. This may be illustrated for the reaction given in the preceding experiment.

A 2 per cent solution of mercuric chloride added to a 2 per cent solution of potassium iodide gives an unstable yellow precipitate of mercuric iodide which rapidly turns to orange then red. However, in a KI-solution containing 1 per cent of gelatin the liquid first turns momentarily yellow because of the formation of colloidal mercuric iodide, then becomes turbid and develops a beautiful canary yellow color which remains unchanged for about half an hour or more before changing slowly to red.[76]

66. An increase of the speed of a chemical change is usually brought about by so-called *catalysts*.

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[76] J. N. Friend, *Nature,* 109, p. 341, 1922.

A familiar example is the following: Some potassium chlorate is fused in a hard-glass test-tube when it will be seen that very little oxygen is given off by the fused salt. A small quantity of manganese dioxide dropped from the tip of a knife blade causes the whole mass to effervesce as a result of the enormous acceleration of the decomposition of the salt.

A number of catalytic reactions are described in detail in the next chapter.

VI. The Rule of Successive Reactions

That many reactions take place with the temporary formation of less stable intermediate compounds, was first observed by Gay-Lussac and as a result of many observations the "law" of successive reactions was introduced by Ostwald[77] and simultaneously by Bancroft. The validity of this "law" taken in the categorical sense in which it was pronounced by these two investigators has been questioned by Nernst, Bakhuis Roozeboom, Mellor and others. More acceptable is the formulation of this principle (avoiding the much abused term "law"), proposed by Alexander Smith,[78] stating, that "transformations, which proceed spontaneously and with evolution of heat, *may* go forward by steps, when there are intermediate substances or allotropic forms capable of existence."

67. The following well-known example is easily carried out. On adding a solution of stannous chloride to

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[77] *Zeitschr. f. phys. Chem.*, 22, p. 306, 1897.

[78] *l. c.*, p. 545.

a solution of mercuric chloride first a white precipitate of calomel is observed, which changes after a while (and rapidly on heating) into metallic mercury.

68. In the same way it will be noticed that on adding a solution of sodium thiosulphate to a solution of silver nitrate first a white precipitate of silver thiosulphate is formed which on standing (quickly when heated) blackens, due to the formation of silver sulphide.

CHAPTER VI

CATALYSIS

The term catalysis was introduced in chemistry in 1836 by Berzelius. The importance of catalytic processes, not only in the laboratory but also for industrial purposes has since then been generally recognized.[79] The search for suitable adsorbents in gas masks has greatly stimulated the interest in catalytic reactions and led to a number of important investigations under the auspices of the Chemical Warfare Service.[80]

Ostwald has defined catalysis as a change (either increase or decrease) of velocity of chemical reaction, by the addition of substances, which do not appear in the final products of the reaction. Although in most cases the catalyst accelerates a reaction there are a few instances known where reactions are retarded by the presence of other substances. This is called *negative catalysis.* Thus by adding a little alcohol to chloroform the decomposition of the latter by air and light is retarded. The oxidation of sodium sulphite by air is greatly retarded by the addition of small quantities of mannite, benzaldehyde, glycerol, phenol and other substances.

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[79] Woker, Die Katalyse, Vol. I, 1910, Vol. II, 1915.
Sabatier, La Catalyse en Chimie organique, 1913.
Jobling, Catalysis and its Industrial Applications, 1916.
Henderson, Catalysis in Industrial Chemistry, 1919.
Rideal and Taylor, Catalysis in Theory and Practice, 1919.

[80] Publications by Lamb, Frazer and others, *Journ. Ind. and Eng. Chem. and Journ. Am. Chem. Soc.,* 1920 and 1921.

69. The following experiment is a beautiful illustration of the retarding effect of acids on the formation of the cobalt compound of nitroso R-salt.[81] Fifty cc. of a slightly colored cobalt solution (about 0.01 molar) is placed in each of four beakers. To the second, third and fourth beaker different amounts of hydrochloric acid (specific gravity 1.19), say 0.5, 3 and 10 cc. are added. About 10 cc. of nitroso R-salt solution (0.5 gram in 100 cc.) are poured into each of the four beakers. A red color is produced at once in the first beaker while the reaction in the other beakers is not completed until after several minutes or hours depending on the acidity of these solutions. Addition of acid to the beaker in which the color appeared first does not destroy the red color, while addition of a sufficient amount of sodium acetate either in the form of a powder or as a solution in water immediately produces the red color in any of the other beakers.

70. An interesting example of a negative catalyst was recently discovered by Taylor in lead tetra-ethyl, the "anti-knock" compound of Midgley. This has a pronounced retarding effect on the oxidation of benzaldehyde by oxygen. The experiment is suitably carried out[82] in a 75-cc. cylindrical tube, preferably vacuum-jacketed to minimize thermal variations in handling which is connected by means of a rubber tube to an open water manometer. If 5 cc. of freshly distilled benzaldehyde is introduced in the tube and the latter shaken by

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[81] van Klooster, *Journ. Am. Chem. Soc.*, 43, p. 748, 1921.
[82] Private communication of Dr. Taylor.

hand for about 3 minutes a 5- to 6-centimeter diminution in water pressure becomes noticeable. On removing the benzaldehyde from the tube and introducing a fresh 5 cc. containing 2 drops of lead tetra-ethyl taking care to replace the rubber tube by another piece of tubing no change of pressure is observed in 5 minutes time.

Negative catalysis should be clearly distinguished from the paralyzing effect which certain substances exert upon positive (or accelerating) catalysts. These substances when present in the catalyst even in small quantities (0.1-0.01 per cent) have a poisoning or deadening influence on the activity of the catalyzing agent and are called *poisons* or *anti-catalysts.* Although these poisons are not the same for all catalysts it is known that most catalysts are poisoned by arsenic, hydrocyanic acid and its salts, mercuric chloride, iodine and sulphur. The poisoning effect of potassium cyanide on the catalytic action of colloidal platinum is shown in exp. 89.

An increase in the activity of the catalyst is sometimes observed by the addition of minute quantities of certain substances called *promoters.* Thus a trace of potash increased to a noticeable extent the activity of the iron used as a catalytic agent in the manufacture of ammonia according to Haber's process. No example showing the effect of a promoter in a lecture demonstration can be given.

The rôle of a catalyst has often been compared to the action of a lubricant in an engine. A mechanical analogy between a (positive) catalyst and a siphon developed by Nelson and Northrop[83] is of some interest when considering the energy of affinity relationships. A beaker A (Fig. 26A) is filled to the level C with water. A

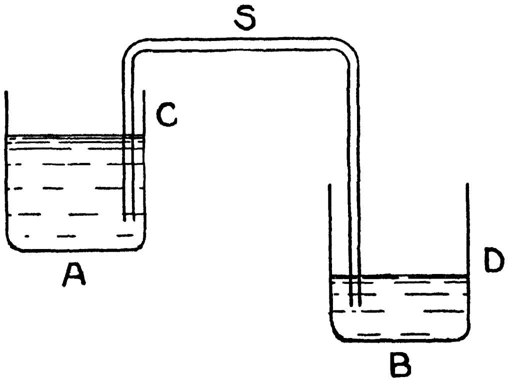

Fig. 26A

siphon S filled with water, dips into this water and also into the water in another beaker B filled to the level D. If the initial substances are represented by the water in A and the final reaction products by the water in B the difference in free energy contents is shown by the difference in level CD. The change takes place through the siphon and the rate of change depends mainly on the bore. The equilibrium is the same whatever the bore may be, even if the latter were infinitesimal and the speed of reaction consequently extremely small. Furthermore the catalytic properties of the siphon remain after the reaction the same as before.

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[83] Falk, Chemical Reactions, p. 70, 1920.

Ostwald's definition of catalysis covers a great many different types of reactions, which are all labelled as "catalytic" and which may be distinguished following the classification of A. A. Noyes and Sammet[84] in seven types:

1. Reactions, catalyzed by carriers,
2. Reactions, catalyzed by adsorbent contact agents,
3. Reactions, catalyzed by electrolytic contact agents,
4. Reactions, catalyzed by water,
5. Reactions, catalyzed by dissolved electrolytes,
6. Reactions, catalyzed by enzymes,
7. Reactions, catalyzed by inorganic colloids:

   to which might be added three other types:
8. Autocatalytic reactions, and closely related with this type,
9. Reactions with intermediate formation of catalytic agents, and
10. Reactions, catalyzed by "germs."

The experiments described in this chapter, are arranged according to these ten different types. Particulars concerning most experiments described below, were taken from the interesting article by Noyes and Sammet, which gives complete details for making the performance as easy as possible.

1. REACTIONS, CATALYZED BY CARRIERS

Carriers are catalysts which are known to accelerate reactions through the formation of addition compounds with one of the reacting substances.

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[84] *Journ. Am. Chem. Soc.*, 24, p. 498, 1902.

71. Reaction catalyzed:

$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$

Catalyst: ferric bromide ($FeBr_3$).

A 250 cc. distilling flask[85] is supported upon a ring stand and its side arm connected with the stem of a funnel, the mouth of which dips just below the surface of a potassium hydroxide solution. In the flask is brought 4 cc. of bromine and then 30 cc. of benzene are poured through a long-necked funnel, nearly reaching the bottom of the flask. No reaction occurs. On adding 0.5 cc. of powdered iron and after blowing some gas into the neck of the flask from a small wash bottle, containing strong ammonia, a tight-fitting cork stopper being finally inserted,—great clouds of white fumes are seen, escaping through the side arm, and being absorbed in the caustic potash solution.

72. Reaction catalyzed:

$$3C_6H_6 + CHCl_3 = CH(C_6H_5)_3 + 3HCl.$$

Catalyst: aluminium chloride ($AlCl_3$).

This is the type of reaction, known in organic chemistry as the synthesis of Friedel and Crafts. The experiment is carried out by pouring in a test-tube 5-10 cc. of benzene, to which a few drops of chloroform are added. No reaction takes place, not even on gently heating over a small flame. As soon as a small quantity of anhydrous aluminium chloride, contained in a small tightly stoppered tube is added, a copious evolution of dense white fumes becomes visible and at the same time

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[85] **Noyes and Sammet, *l. c.*, p. 501.**

the contents of the test-tube turns dark brown, due to the formation of triphenylmethane. The reaction has to be carried out under a glass hood. Its success depends entirely on the quality of the aluminium chloride used for the experiment. Good results are obtained by using the granulated, absolutely dry product, of which small samples are to be kept in *well-corked* small tubes, ready for use. Noyes and Sammet (*l. c.*) recommend a similar reaction, *viz.*, the formation of acetophenone from benzene and acetyl chloride, requiring a more complicated apparatus. The arrangement chosen above is just as efficient and far more simple, since only a test-tube is needed. Other reactions of this type may be looked up in the original paper.[86]

2. REACTIONS, CATALYZED BY ADSORBENT CONTACT AGENTS

Adsorbent contact agents may be defined as solid substances that accelerate reactions by adsorbing one or more of the reacting substances on their surfaces. A striking characteristic of these solid contact catalysts is that they are readily made inactive (poisoned) by such substances as arsenic, sulphur and cyanides. Among the numerous reactions catalyzed by contact catalysts are several of great technical importance like the contact sulphuric acid process, Haber's ammonia process, Ostwald's nitric acid process, Bone's surface combustion process and Sabatier's hydrogenation process.[87] The following reactions are chosen to illustrate this type of reactions.

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[86] Noyes and Sammet, *l. c.*, pp. 499-502.

[87] For a critical discussion see: Bancroft, Applied Colloid Chemistry, pp. 40-64, 1921.

73. Reaction catalyzed:

$$2H_2 + O_2 = 2H_2O.$$

Catalyst: finely divided platinum.

A mixture of hydrogen and oxygen, in the proportion to form water (about 10-15 cc.) is collected over mercury in a eudiometer tube. By introducing a few lumps of platinized, granulated pumice stone (prepared by soaking the pumice in a 10 per cent solution of chloroplatinic acid and prolonged heating in a Bunsen flame, until the platinum is left in a finely divided state) to the mixture, combination takes place, demonstrated by a decrease in volume and the formation of a water nebula.

74. Another instance of this type is the decomposition of hydrogen peroxide by the catalytic action of platinum black and bone black.[88]

$$2H_2O_2 = 2H_2O + O_2.$$

In each of two lecture test-tubes is placed a solution of commercial, concentrated hydrogen peroxide (about 25 cc.), which has been made slightly alkaline by the addition of ammonia. To the first tube is added 1 cc. of bone black, to the second a small portion of platinum black. In both tubes a violent development of oxygen gas takes place and a glowing wood splinter inserted in each tube rekindles. The required platinum black is prepared by soaking two 9 centimeter filter papers in a 10 per cent solution of chloroplatinic acid and igniting them in a large porcelain crucible, until the carbon is burned off.

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[88] Noyes and Sammet, *l. c.*, p. 504.

75. Bone has shown[89] that all incandescent substances are capable of accelerating gaseous combustion. An example is the following: A platinum crucible is placed on a triangle and brought to a bright glow over a Bunsen burner. The gas is turned out and after a few seconds turned on again and allowed to strike the hot crucible. The latter becomes red hot but the gas does not catch fire (at least not immediately) due to the so-called "flameless combustion" which takes place (see also exp. 265). According to Curtman the platinum metals can be readily detected by this property: Thin asbestos paper is soaked in the aqua regia solution of the unknown metals and then heated to a red hot glow. By transferring the hot paper to the cold gas stream of a Bunsen burner (with open air-influx) the paper begins to glow when either platinum, palladium, iridium or rhodium is present in quantities of no less than 0.005 milligram.

3. REACTIONS, CATALYZED BY ELECTROLYTIC CONTACT AGENTS

Electrolytic contact agents are substances which accelerate reactions involving metals through the formation of a voltaic couple.

76. A well-known case is the increase of reaction velocity by the addition of one drop of a solution of chloroplatinic acid to a dilute solution of pure sulphuric acid, in which a sheet of pure zinc is inserted.

77. A similar reaction[90] is the following, also catalyzed by platinum:

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[89] *Journ. Franklin Inst.*, 173, p. 101, 1912.

[90] Noyes and Sammet, *l. c.*, p. 505.

$$Sn + 2HCl = SnCl_2 + H_2.$$

In a 300 cc. Erlenmeyer flask, provided with a two-hole rubber stopper, through which passes a thistle tube and a delivery tube (ending in a beaker of water) is placed a layer of pure feathered tin, covering the bottom of the flask to a depth of 2 centimeters. On pouring through the thistle tube enough hydrochloric acid (specific gravity 1.12) to entirely cover the tin, only a slight action occurs. As soon as a little chloroplatinic acid (or copper sulphate solution) from a medicine dropper is added, a rapid gas evolution occurs.

78. Still another reaction (suitable for projection on the screen) belonging to this type is the displacement of hydrogen from a copper solution to which an excess of potassium cyanide has been added. No appreciable reaction takes place on inserting a copper rod in this solution but a brisk evolution of hydrogen starts when the rod is wrapped in a spiral of platinum wire. This particular type of catalysis was noticed as early as 1830 by De la Rive.

4. REACTIONS, CATALYZED BY WATER

Water is one of the most important and certainly the most common of all catalysts. Its action may consist either in a hydration or a dissociation of the reacting substances. The following reactions may be performed:

79. Reaction catalyzed:

$$Zn + I_2 = ZnI_2.$$

Four cubic centimeters of powdered iodine are placed into a test-tube and 2 cc. of zinc dust in a 25 cc. wide-mouthed glass-stoppered bottle. The iodine is poured into the bottle and the mixture vigorously shaken. Nothing visible happens. The mixture is then brought into a 4-liter glass balloon, supported on a suitable ring and a fine stream of water from a wash bottle directed on the dry powder. A violent action, attended by a whizzing noise and a copious evolution of iodine vapors takes place.[91]

80. Reaction catalyzed:

$$Al + 3I = AlI_3.$$

Instead of zinc powdered aluminium may be used.[92] Equal measures (10 cc.) of dry powdered iodine and powdered aluminium are thoroughly mixed and poured into a conical pile on a piece of asbestos placed in the fume cupboard. A few drops of water will set the whole mass ablaze.

81. Reaction catalyzed:

$$2H_2S + SO_2 = 2H_2O + 3S.$$[93]

A thoroughly dry flat-bottomed flask of about 2-liter content is fitted with a cork stopper carrying four holes through which pass two long dry delivery tubes reaching down to the bottom, and a short delivery tube terminating below the stopper while the fourth hole is closed

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[91] Noyes and Sammet, *l. c.*, p. 508.

[92] Davison, *General Science Quarterly*, 6, p. 300, 1921.

[93] An interesting application of this reaction is Peachy's process of rapid vulcanization of rubber without the aid of heat.

by a piece of glass rod. All three tubes are bent at right angles above the cork. (Fig. 26B). One of the long tubes is connected with a drying tower containing calcium chloride, which is connected with a gas wash bottle containing dilute (1 : 3) sulphuric acid and this in turn with a hydrogen sulphide generator. The other delivery tube leading to the bottom of the flask is connected through two gas wash bottles containing concentrated sulphuric acid with a distilling flask in which sulphur dioxide can be made by dropping concentrated sulphuric acid from a separatory funnel into a strong solution of acid sodium sulphite. The short delivery tube

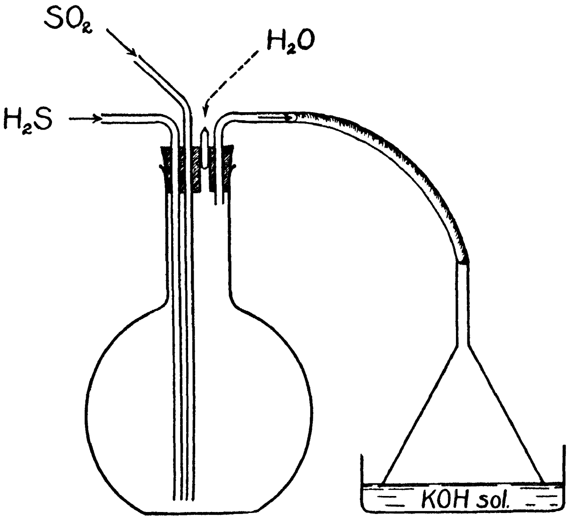

Fig. 26B

is connected with a large 6-inch glass funnel the mouth of which dips just a little below the surface of a strong soda or potash solution. While the two gases are passed into the flask (the hydrogen sulphide twice as fast as the sulphur dioxide), a flat-bottomed flask filled one-third full of water is heated to boiling over a wire gauze. The flask is fitted with a stopper provided with delivery tube which can be readily inserted in the fourth hole of the 2-liter flask. It will be seen that the dry gases do not combine. After admitting steam through the fourth hole sulphur begins to deposit on the walls of the flask and after a little while completely covers them.[94]

5. REACTIONS, CATALYZED BY DISSOLVED ELECTROLYTES

A great number of reactions are known in which electrolytes act as catalysts. One of the most important reactions, of great technical value, is the hydrolysis of starch by acids in virtue of their hydrogen ions. Noyes and Sammet suggest that the hydrogen ions are hydrated and that water carried as hydrate is more active than ordinary water. If this suggestion is accepted this reaction belongs to the first type, mentioned above, *viz.*, that of carriers, the hydrogen ions acting as water carriers.

82. The hydrolysis of starch, catalyzed by sulphuric acid:

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6,$$

is carried out as follows:[95]

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[94] Noyes and Sammet, *l. c.*, p. 506.

[95] Noyes and Sammet, *l. c.*, p. 510.

In each of two large size test-tubes is brought an equal weight (1 gram) of starch. To one of the tubes is added 25 cc. of water, to the other 25 cc. of a 5 per cent sulphuric acid solution. Both solutions are boiled for about half a minute. The acid solution is neutralized with 9 cc. of a 50 per cent caustic potash solution. The contents of both tubes are then boiled and after adding 5 cc. of Fehling's solution to each tube, both are boiled again. A red precipitate of cuprous oxide is formed only in the tube to which acid had been added.

83. Ferrous sulphate, a salt which is easily oxidized accelerates the oxidizing action of such oxidantia as hydrogen peroxide. A few drops of dilute (1 per cent) hydrogen peroxide solution are added to a dilute potassium iodide starch solution. At first no reaction is observed. On adding a little ferrous sulphate the liquid at once turns blue.

6. REACTIONS, CATALYZED BY ENZYMES

Enzymes are the catalysts produced in living organisms. They are of a complex colloidal nature with powerful catalytic activity. They play an important rôle in the chemical and physical changes taking place in living matter, known as metabolism (constructive metabolism or anabolism and destructive metabolism or catabolism) and find extensive use in the industries and biological laboratories. They are highly specific in their action so that Fischer has compared the combination of enzyme and substance acted upon (called substrate) to key and lock. Armstrong likens the specificity and the combination of enzyme and substrate to the fitting of a glove upon a hand. The temperature range of activity is limited: they are usually destroyed at temperatures above 65°, have a maximum activity around 37° and exhibit little or no activity at 0°. They are sensitive to the presence of acids, alkalies and most salts although many poisonous substances like fluorides, potassium cyanide, chloroform or toluene are not so prejudicial and in fact are often used to prevent bacterial activity. The reactions in which enzymes participate are mainly hydrolysis reactions, oxidations and reductions, and clotting reactions. Experiments are described below in which some of the properties described above are illustrated.

84. Reaction catalyzed:

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6.$$

Catalyst: ptyalin. Ptyalin is the enzyme present in saliva which converts starch into dextrin and maltose from which eventually dextrose is formed.

In a test-tube is placed a small quantity of starch, about the volume of a split pea. Ten cc. of water is added and after heating to boiling 10 cc. more of cold water is added and then 2 or 3 drops of a 1 per cent iodine solution. The liquid turns deep blue, which color disappears immediately on addition of 25 cc. of fresh saliva. Even when a second portion of iodine solution is added, the color is not restored.[96]

85. The specificity of enzyme action can be shown as follows: Ptyalin hydrolyses starch but not cane sugar.

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[96] Noyes and Sammet, *l. c.*, p. 512.

About half a gram of starch is placed in a large 100 cc. test-tube, 15 cc. of water is added and after heating to boiling 15 cc. more cold water added. Half of the starch solution is placed in another test-tube labelled 2. In a third test-tube 15 cc. of a 1 per cent cane sugar solution is put. Ten cc. of fresh saliva are added to the second and to the third tube; all three tubes are then kept for 5 minutes in a large beaker containing water having a temperature around 40°. Meanwhile 10 cc. of Fehling's alkaline tartrate solution are mixed with 10 cc. of Fehling's copper solution, the mixture diluted with 100 cc. of water, and the resulting dilute solution poured (in three equal volumes) into three small Erlenmeyer flasks. The flasks are heated simultaneously to a gentle boil and the contents of the three test-tubes poured into the flasks. The heating is continued for a few minutes when it will be seen that the first solution remains blue (starch does not reduce Fehling's solution), the second solution turns red and cuprous oxide separates out while the third solution also retains its blue color showing that neither sucrose, nor saliva reduce Fehling's solution.

86. In the same way it can be demonstrated that invertase hydrolyses sucrose but not starch. The invertase can be obtained from yeast by grinding 60 grams of yeast in a mortar with 3 grams of powdered calcite ($CaCO_3$) and a little water into a thick paste which is then placed in a wide-mouthed bottle. About 3 cc. of chloroform are added and the stoppered bottle kept for 3-4 days in a warm room. The solution is filtered and the filtrate treated with an equal volume of alcohol (95 per cent).

The precipitate is washed with alcohol and ether and then dried (if possible in vacuo) over sulphuric acid.[97] The dry powder (0.2-0.5 gram) retains its activity for many months. Using a 0.1 to 0.5 per cent solution of invertase the following three solutions placed in large test-tubes are kept at 40° for about 5 minutes:

A. Fifteen cc. of a 1 per cent cane sugar solution.

B. The same + 15 cc. of invertase solution.

C. Fifteen cc. of a dilute starch solution (see exp. 85) + 15 cc. of invertase solution.

On pouring the three solutions in the boiling hot Fehling solutions it will be noticed that only solution B is reduced by the alkaline copper solution.

87. That the activity of enzymes is destroyed by boiling is demonstrated by boiling 15 cc. of the invertase solution used in the previous experiment and then adding the same to 15 cc. of the cane sugar solution. No reduction of Fehling's solutions occurs on subsequent boiling. In the same way it can be shown that the starch-hydrolyzing activity of saliva is destroyed by boiling.

88. The activity of enzymes near the freezing point is zero or very slight. Two Einhorn tubes as used for glucose determinations in hospitals are filled with the same dilute (5 per cent) glucose solution to which some fresh yeast has been added. One tube is kept at room temperature while the second is placed in a refrigerator. After several hours standing the number of cc. of gas collected in each tube is compared.

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[97] Plimmer, Practical Organic and Bio-chemistry, revised ed., p. 401, 1918.

7. REACTIONS, CATALYZED BY INORGANIC COLLOIDS

89. Inorganic colloids possess strong catalytic power. Colloid platinum for instance greatly accelerates the decomposition of hydrogen peroxide.

$$2H_2O_2 = 2H_2O + O_2.$$

A colloid platinum solution, prepared according to Bredig's directions (Chapter IX, exp. 206) is used. Placing 25 cc. of hydrogen peroxide (commercial, concentrated) in each of two lecture test-tubes, made slightly alkaline with ammonium hydroxide, 10 cc. of the colloid platinum solution is added to each. To the first, however, has previously been added 5 drops of a saturated potassium cyanide solution. The difference in gas evolution in both tubes is striking. A vigorous effervescence starts in the solution, which contains no cyanide, while in the other solution hardly any gas evolution occurs, thus proving, that potassium cyanide acts as a poison in retarding or entirely hindering the reaction.

8. AUTOCATALYTIC REACTIONS

Reactions which are catalyzed by one or more reaction products are said to be autocatalyzed.

90. A case of autocatalysis is the action of nitric acid on metals.[98] A sheet of pure copper or silver is inserted in a lecture jar, filled with pure nitric acid (about 20 per cent solution). The reaction proceeds very slowly until after a while a vigorous gas evolution takes place. If on the other hand, instead of pure nitric acid, fuming

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[98] Ostwald, Grundrisz der allgem. Chemie, 4e Aufl., Leipzig, p. 336, 1909.

nitric acid, containing several oxides of nitrogen, is taken, an immediate solution of the metal will be seen The same happens on addition of a small amount of sodium or potassium nitrite to the pure acid.

Reactions of this "autocatalytic" type are called by Baur[99] "fever reactions," owing to the strong resemblance which they show with the fever process in the human body. A period of scarcely perceptible reaction (incubation stage) is followed by one of ever increasing velocity (induction stage) and finally by a decrease in activity, generally more rapid than the foregoing increase (period of extinction), as is graphically represented in Fig. 27, where the velocity of the reaction is plotted against the time as abscissa.

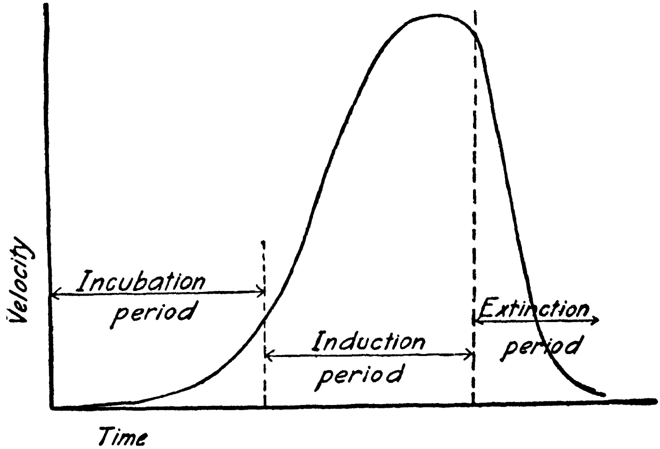

Fig. 27

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[99] Baur, *l. c.*, p. 66.

91. That the acceleration of the velocity of reaction is wholly due to the formation of lower oxides of nitrogen *during* the reaction is clearly shown by an interesting experiment of Quartaroli.[100]

The reaction, studied by him is expressed by the equation:

$$2KNO_3 + 6HCOOH = N_2O_3 + 4CO_2 + 5H_2O + 2HCOOK.$$

Taking 5 cc. of absolute formic acid, heated in a test-tube at 40°, to which is added 0.3 gram of potassium nitrate, the reaction sets in slowly, but after 2 minutes a violent gas evolution occurs, which is finished after 5 minutes.

The same experiment is performed simultaneously in another test-tube, to which 1 milligram of potassium chlorate has been added. A slight retardation is perceptible.

On adding 3 milligrams of the chlorate to a third tube, containing as before 5 cc. of formic acid and 0.3 gram of the nitrate, a visible gas evolution takes place after about 10 minutes.

To a fourth tube, is added 5 milligrams of chlorate; no reaction at all, not even after half an hour.

9. REACTIONS WITH INTERMEDIATE FORMATION OF CATALYTIC AGENTS

A behavior similar to autocatalysis is shown by reactions, in which the catalyzing agent acts *temporarily*, being formed and destroyed again during the reaction.

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[100] *Gazz. chim. ital.*, 41, (II), p. 64, 1911.

The same periods of incubation, induction and extinction can be distinguished, as, for instance, in the reduction of potassium permanganate by oxalic acid.[101]

92. The reaction takes place in three stages:

I $Mn^{VII} + {}^5/_2\, C_2O_4^{II} \longrightarrow Mn^{II} + 5CO_2$ (incubation).
II $Mn^{VII} + 4\, Mn^{II} \longrightarrow 5Mn^{III}$ (induction).
III $Mn^{III} + {}^1/_2\, C_2O_4^{II} \longrightarrow Mn^{III} + CO_2$.

The experiment is carried out in four 200 cc. beakers, the first of which contains a solution of 10 cc. N/10 potassium permanganate in 110 cc. of water, serving as a standard. In the second is placed a mixture of 10 cc. N/10 potassium permanganate solution, 10 cc. saturated oxalic acid solution and 10 cc. of water. The third beaker and the fourth have the same contents as the second, with the addition of one drop of manganous chloride (or sulphate) solution to the third and of an excess of the same reagent to the fourth beaker. A temporary brown coloration becomes visible in all three solutions, but with largely different velocity.

93. A reaction belonging to the same type is the catalysis of hydrogen peroxide by chromic acid, studied by Spitalsky.[102]

The reaction is performed by carefully heating in a test-tube at 40-50° 20 cc. of a 20 per cent solution of hydrogen peroxide, to which has been added 5 cc. of a N/100 solution of chromic acid. The reaction starts slowly, the solution becoming blue; after about 10 min-

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[101] Baur, *l. c.*, p. 68.

[102] *Zeitschr. f. anorg. Chem.*, 56, p. 72, 1908.

utes a violent reaction takes place, the color of the solution changing into red-violet (induction period). Finally the reaction slackens and comes to a stop, and the original color of the chromic acid is restored.

10. REACTIONS, CATALYZED BY "GERMS"

94. The part played by so-called "germs" in catalysis is illustrated by an experiment, due to Luther,[103] and described by him as follows:

Some word is written, with an alum crystal, on a clean glass plate. Invisible minute crystals remains, where the crystal has been passed. On pouring a supersaturated alum solution over the glass, crystallization starts at the "germs" and the word becomes visible.

95. As a final experiment on catalysis a case may be quoted, studied by Bredig and Wilke,[104] which shows the periodic character of some catalytic reactions. In a test-tube is brought a mixture of 3.3 cc. of hydrogen peroxide (the authors use Merck's "perhydrol"), 6.7 cc. of water and 33 cc. of concentrated sodium acetate solution. A rather small drop of pure mercury is added, and after a while a periodic gas evolution becomes visible, due to the alternate formation and decomposition of a bronze-colored peroxide coat on the mercury drop.

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[103] *l. c.*, p. 24.

[104] *Verh. des Naturhist, med. Vereins Heidelb*, N. F. 8, p. 165, 1905.

CHAPTER VII

ELECTROCHEMISTRY AND IONIC THEORY

Arrhenius' theory of electrolytic dissociation (1887) has such an important bearing on the science of electrochemistry that a joint consideration of both is nowadays a matter of course, the one being inseparably connected with the other. Numerous instructive lecture demonstrations illustrating the present conceptions on this subject have been devised by various physico-chemists. In the selection, chosen below, a review of the material at hand is made under the following headings:

I. Electrolysis.
II. Migration of ions.
III. Electromotive chemistry.
IV. Conductivity and degree of ionization.
V. The common ion effect.
Va. The salt effect.
VI. Hydrolysis.
VII. Ionization and chemical activity.
VIII. Ionization and color of solutions.

I. Electrolysis

96. Experiments on electrolysis of salt solutions and fused salts are so well known, that a special description at this place seems superfluous. Familiar demonstrations in elementary chemistry courses are: the electrolysis of copper sulphate solutions between platinum and between copper electrodes, also of sulphuric acid, usually carried out in a Hofmann apparatus, formerly frequently called "apparatus for electrolysis of *water,*" and of potassium sulphate solutions. The electrolysis of stannous chloride and of lead acetate is interesting on account of the formation of tin and lead "trees" and is for projection purposes conveniently performed in small glass troughs with parallel walls, using small metal rods, running through a cork, as electrodes.

97. In order to obtain the easily decomposable alkali metals in the form of amalgams Nernst[105] has devised the following arrangement:

A large test-tube (12 by 1.5 centimeters) connected with a capillary outlet tube (Fig. 28), contains mercury, covered by a layer, about 3 centimeters thick, of chloroform and another layer of concentrated potassium chloride solution. The tube is closed by a three-hole cork stopper, allowing the passage of (*a*) a glass tube for the escape of gases during the electrolysis, (*b*) a strong platinum wire with spiral windings and (*c*) a funnel of about 25 cc. capacity, drawn out into a capil-

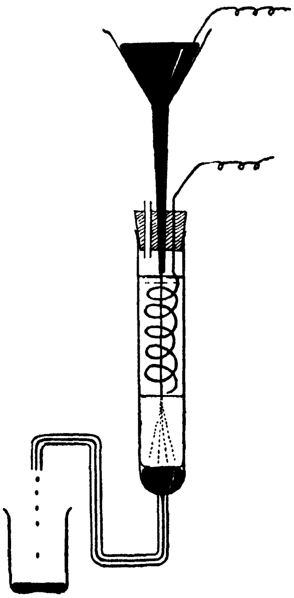

Fig. 28

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[105] *Zeitschr. f. Electrochemie,* 3, p. 308, 1897.

lary tip, and filled with mercury. A platinum wire is inserted in the mercury and both wire electrodes connected with a battery of three lead accumulators. The mercury, dropping into the solution forms potassium amalgam, protected from the decomposing action of water by the chloroform layer and collects in the beaker placed under the outlet. On pouring water, containing a few drops of phenolphthalein into the beaker, the liquid instantly turns red and evolution of hydrogen becomes visible.

98. That fused salts are excellent electric conductors may be exemplified by connecting a platinum dish, containing potassium nitrate, and a platinum cathode dipping in the salt with the lighting circuit and an electric lamp. The dry salt does not conduct the current and is not perceptibly ionized. When fused over a Bunsen burner the lamp begins to light due to the ionization of the salt.[106]

99. Two platinum wires are fused into the ends of a short glass rod to a distance of 1-2 centimeters and connected with the lighting circuit and a sensitive large-scale galvanometer. On heating the glass gradually over the flame of a Bunsen burner, the glass begins to soften and a current is found to pass through (Fig. 28A).[107]

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[106] Stieglitz, *l. c.*, p. 75.

[107] *Ibidem*, p. 76; Hopkins, Experimental Electrochemistry, New York, p. 94, 1905.

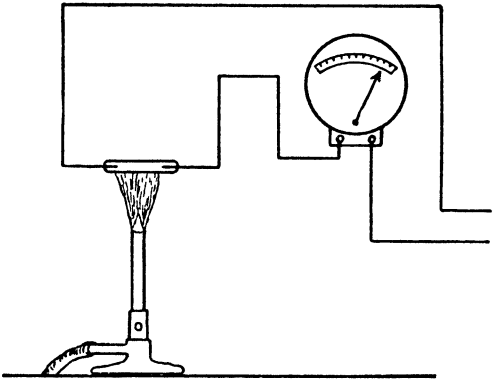

Fig. 28A

The effect of electrolysis may often be observed in incandescent lamps and the cracking of the glass along the weld seal lines exhibited.

II. Migration of Ions

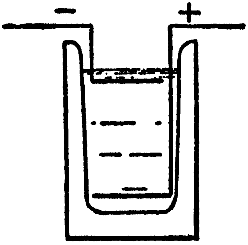

Fig. 29

100. As introductory to lecture experiments, showing migration of ions, the change in concentration near the electrodes may be demonstrated.

A small glass trough (Fig. 29), with parallel walls, as used for projection purposes, is filled with a dilute copper sulphate solution acidified with some sulphuric acid. Two L-shaped copper wires are inserted and connected with the poles of a storage cell. After a while it will be seen on the screen that the blue color at the cathode brightens, whereas a more concentrated solution collects near the anode.[108]

101. A similar experiment was devised by Palmaer.[109] A U-shaped glass tube, about 70 centimeters high, with an inner bore of 1.5 millimeters, filled with a 4N solution of hydrochloric acid is used. A silver wire is used as anode, while a platinum wire serves as cathode; both are inserted as far as the middle of the limbs (Fig. 30). The electrodes are connected with a 100-volt circuit. The current is about 0.02 ampere at the start, but sinks in the course of the electrolysis to about 0.015 ampere, the silver wire being gradually covered with a thin layer of silver chloride. The difference in level amounts to 4 millimeters after 5 minutes, and increases on further passing the current through the solution.

A silver anode is employed in order to avoid an increase of specific gravity by dissolved chlorine. The wire must have been used several times since the gas is not easily taken up by a polished, uncorroded surface.

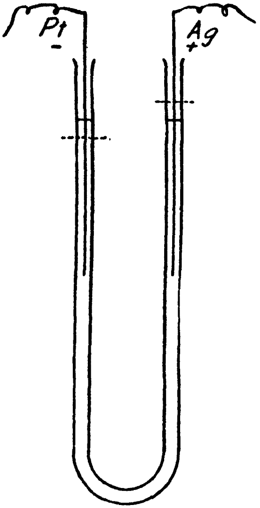

Fig. 30

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[108] Coehn in Müller-Pouilet's Handbook IV, p. 493, 1909.

[109] *Zeitschr. f. Electrochemie*; 12, p. 513, 1906.

102. Lodge[110] first introduced the use of gelatin jellies for the direct measurement of ionic velocities. These jellies may be safely used instead of pure aqueous solutions provided the percentage of gelatin does not exceed 4-5 per cent since careful investigations have brought out the fact that dissolved salts diffuse through gelatin jellies at about the same rate as through pure water. The method of Lodge is as follows:

A graduated glass tube, 40 centimeters long and 8 millimeters wide, is twice bent at right angles and the end slightly curved upward, as shown in Fig. 31. The tube is filled with a solution of sodium chloride in gelatin, made up by dissolving 10 grams of gelatin in 140 cc. of hot water, and adding 7 grams of salt and a few drops of a slightly alkaline solution of phenolphthalein. This mixture readily gelatinizes upon cooling. Both ends of the tube are then inserted in two beakers, containing dilute sulphuric acid. On passing a current through the

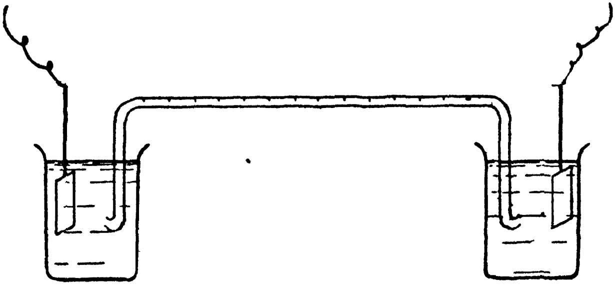

Fig. 31

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[110] Brit. Ass. Report, p. 393, 1886; p. 389, 1887.

solutions and the jelly,—applying a storage battery of ten cells (about twenty volts) as electromotive force,—a gradual decoloration of the jelly will be observed. It will be seen that the boundary surface moves at the rate of 1.5 centimeters in 1 hour.

103. In the particular case that colored ions are considered, the migration is easily shown by means of a simple apparatus, originally devised by Nernst[111] and slightly modified, as described below:

A U-shaped glass tube, 1.2 centimeters in diameter and 10 centimeters high, is connected in the lower part of the bend with a piece of capillary glass tubing (length 20 centimeters, inner bore 2 millimeters) bent upward, to which is sealed a separatory funnel of 100 cc. contents. The solution used for this experiment is made up by dissolving 0.5 gram of potassium permanganate in 100 cc. of distilled water, the specific gravity of which has been increased by the addition of 5 grams of urea. In order to fill the capillary tube, some of the solution is poured in the bend and sucked up into the funnel, until the liquid has risen above the stopcock which is then turned off. The liquid remaining in the bend, is rinsed out with distilled water and the latter removed by turning the U-tube upside down. The funnel is then filled with the rest of the permanganate solution. In the now empty U-tube, is poured by means of a 10 cc. pipette, a solution of 0.5 gram of potassium nitrate in 1 liter of water. Both limbs are closed with two-hole rubber stoppers, allowing the passage of two platinum wires, pro-

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[111] *Zeitschr. f. Electrochemie*, 3, p. 308, 1897.

vided with perforated platinum electrodes, and of two small glass tubes for the escape of the gases evolved during the electrolysis. On carefully opening the stopcock the permanganate solution drives the colorless nitrate solution with sharp boundary surfaces into the limbs of the U-tube to a certain height, marked by a white and a black strip of paper respectively (Fig. 32).

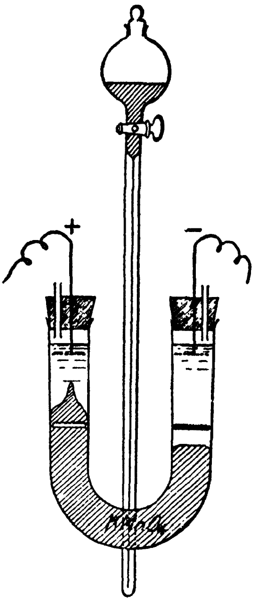

Fig. 32

When a current,—not exceeding 0.2-0.3 ampere—is passed through the tube, the violet boundary surface is gradually displaced in the direction of the anode, distinctly visible after about 5 minutes. The current is turned off as soon as the boundary surface on the anodic side becomes irregular owing to convection currents. In the right (cathodic) limb, the boundary surface remains extremely sharp and, as Nernst has pointed out,[112] the migration velocity of the MnO_4'-ion can be approximately calculated from the lowering of the boundary surface.

104. Küster,[113] with the aid of two U-tubes, as described in the foregoing experiment, shows how copper in a copper sulphate solution moves towards the cathode and in Fehling's solution in the opposite direction.

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[112] Nernst, *l. c.*, p. 309.

[113] *Zeitschr. f. Electrochemie*, 4, p. 112, 1898.

The bend of the left U-tube is filled with a light blue (dilute) solution of copper sulphate, separated by a sharp boundary surface from a dilute sodium sulphate solution in both limbs. The second U-tube is filled in an exactly similar way with a dark blue Fehling's solution covered in both limbs by a dilute alkaline solution of Rochelle (Seignette) salt. After inserting the platinum electrodes, joined in parallel, an electric current, derived from a storage battery of 15-20 accumulators, is passed through both tubes. After 5-10 minutes the copper sulphate boundary has moved several millimeters towards the cathode, while in the other tube a movement in opposite direction has taken place, a sure indication that in this case the copper forms part of a complex anion.

105. Instead of an apparatus as used by Nernst, a simple U-tube (suitable dimensions: height 16 centimeters, inner bore 2 centimeters) will serve the requirements, when in place of *aqueous* solutions, agar-agar *jellies* are employed,[114] thus returning to Lodge's original device.

A solution of agar-agar is first made by cutting 25 grams of this substance in small pieces and treating with 500 cc. of distilled water. The mixture is then heated until a clear solution is formed, which is, while still hot, strained through a piece of cloth. To 50 cc. of this hot solution is added about 10 cc. of a saturated copper sulphate solution and this mixture poured into the U-tube to about 4 centimeters above the bend (Fig. 33). The jelly is allowed to harden and a little bone

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[114] A. Smith. *l. c.*, p. 346.

black sprinkled on the surface to mark the boundary. In order to fix the bone black in its place a solution of potassium nitrate, saturated at 0°, containing agar-agar is poured in each limb of the tube, and after hardening,

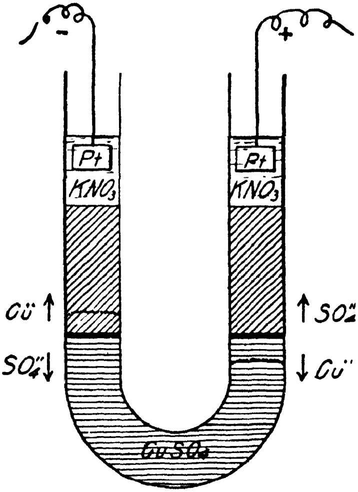

Fig. 33

the tube on both sides filled up with potassium nitrate solution. The U-tube is placed in a large beaker with ice water, to preserve the jellies from melting on electrolyzing the copper sulphate. Electrodes of platinum wire are inserted in the potassium nitrate solution and connected with a 16 candlepower lamp in series, with the terminals of a 110-volt lighting circuit. On passing the current through the tube for 5-10 minutes, the effect of the displacement of the blue boundary surface towards the cathode becomes apparent. The movement of the colorless SO_4''-ions can be demonstrated by interposing, on the positive side a thin layer of jelly containing some barium salt, in which case a cloudy layer of barium sulphate jelly is formed.

106. A similar experiment with a jelly containing a solution of copper chromate enables the demonstration of the simultaneous movement of the blue copper ion and the yellow chromate ion in opposite directions.[115] Using the same U-tube as in the previous experiment and a 2 per cent agar-agar jelly, 8 cc. of saturated copper chloride solution, a few drops of acetic acid and 6 cc. of saturated potassium bichromate solution are dissolved in 35 cc. of remelted agar-agar. This is poured into the U-tube to fill it 3-4 centimeters above the bend, and allowed to harden. Some bone black is sprinkled on top of it, to mark the boundary and a few drops of a solution made by dissolving 4 cc. of saturated potassium chloride solution in 15 cc. of the agar-agar stock added to fix the bone black in its place. After a few minutes enough more of this jelly is added to form a layer a few centimeters high in each limb. As soon as this has hardened a few cc. of a saturated potassium chloride solution are added in both arms and the electrodes of platinum wire inserted. The U-tube is placed in a beaker of water containing a large quantity of ice. A current is then passed through by connecting the electrodes with a 32-candlepower, 110-volt lamp and the terminals of a 110-volt direct-current circuit. After passing the current for 10-30 minutes (stopping temporarily if the jelly

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[115] Noyes and Blanchard, *l. c.*, p. 729.

shows signs of melting) a blue zone appears above the bone black in one arm and a yellow zone (due to the chromate ions) above the bone black in the other arm. The zones immediately below the bone black also acquire a blue and yellow color while the central portion beneath remains unchanged in color.

107. The relative velocity of migration of different ions can be demonstrated in an instructive experiment given by Noyes and Blanchard.[116] Careful determinations have established that at room temperature the ionic mobilities per hour, in dilute aqueous solutions for a potential difference at the electrodes of 1 volt amounts to 2.05, 2.12, 10.8, 5.6, and 1.6 centimeters for the ions $K^{\cdot}$, Cl', $H^{\cdot}$, OH' and $Cu^{\cdot\cdot}$ respectively. Broadly speaking, $K^{\cdot}$ and Cl'-ions move at the same speed, $H^{\cdot}$-ions move about five times as fast, double as fast as $OH^{\cdot}$-ions and eight times as fast as $Cu^{\cdot\cdot}$-ions. Therefore, it is advisable to use a potassium chloride solution in which these different ions are all present, $Cu^{\cdot\cdot}$-ions being visible by their color, $H^{\cdot}$-ions being recognized by decoloration of phenolphthalein and OH'-ions by coloring this indicator.

The bend of a U-tube, as described above, and the right limb (Fig. 34), up to a point 5 centimeters from the top, is filled with a jelly made by mixing 32 cc. of saturated potassium chloride solution, 1 cc. of a 1 per cent solution of phenolphthalein in alcohol, 100 cc. of a 2 per cent agar-agar solution and 8 drops of a normal solution of potassium hydroxide. The other limb, up to 5 centimeters from the top, is filled with the same mix-

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[116] *l. c.*, p. 731.

ture, to which has been added twice the amount of hydrochloric acid, necessary for decolorizing the liquid. The boundaries in both limbs are fixed by sprinkling a little bone black on the surfaces and covering the bone black with a thin layer of the underlying jelly in order to keep the black demarcation surface intact. The platinum wire electrodes are placed at the top of the limbs of the U-tube and connected through a 32 candlepower electric lamp with the terminals of a 110-volt direct-current circuit. Just before starting the experiment the left limb is filled up with a mixture of 2 cc. of a 10 per cent potassium hydroxide solution and 20 cc. of a saturated potassium chloride solution; the other arm of the tube is then filled up with a mixture of 0.5 cc. of hydrochloric acid (specific gravity 1.12), 6 cc. of a saturated copper chloride solution and 20 cc. of water. The U-

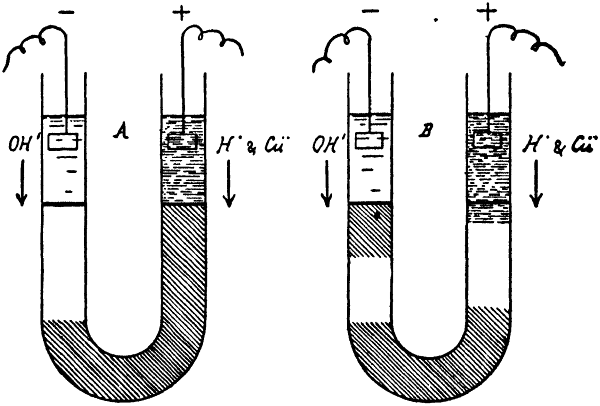

Fig. 34 (A and B)

tube is placed in ice water, to prevent the melting of the jelly by the heat generated during the electrolysis. On closing the switch and allowing the current to pass for about 15 minutes, it will be observed, that a colorless zone (due to the $H^{\cdot}$-ions) descends into the pink jelly in the right limb to a depth of about 5-6 centimeters, followed by a blue zone (accounting for the $Cu^{\cdot\cdot}$-ions) of about 1 centimeter deep. (See Fig. 34B). In the other arm a pink zone (due to the OH'-ions) descends into the colorless jelly to a depth of about 2.5 centimeters.

III. Electromotive Chemistry

A large number of reactions involving ionogens are known, in which chemical changes are accompanied by the liberation of electrical energy. Since all these arrangements for obtaining electric currents are in reality nothing but voltaic cells, this special branch of chemistry may very appropriately be designated as electromotive chemistry.[117] The essential feature about the combinations for the production of electric currents consists in preventing the active substances from coming in contact with each other and connecting these places by means of metal wire so as to complete the circuit and make a flow of electricity (transfer of electrons) possible. Ostwald in an interesting and much quoted article on "Chemical Action at a Distance"[118] was the first to emphasize and explain these points.

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[117] A. Smith, *l. c.*, p. 786.

[118] *Zeitschr. f. phys. Chem.*, 9, p. 540, 1892; see also *ibidem*, 15, p. 409, 1894, or *Phil. Mag.*, [5] 32, p. 45, 1891.

108. One very illuminating experiment illustrating this chemical action at a distance is as follows: Two beakers containing a dilute (5 per cent) solution of potassium sulphate are joined together by a siphon containing the same solution. In the left hand beaker a rod of pure zinc is inserted while a piece of platinum wire is placed in the second beaker. Both electrodes are connected with a sensitive current indicator. If a little sulphuric acid is introduced into the solution around the zinc rod the effect is hardly noticeable. On the other hand if a few drops of sulphuric acid are poured into the right beaker around the platinum wire a copious evolution of hydrogen takes place from the wire and a positive current[119] flows in the direction indicated by the arrow (Fig. 34C). At the same time zinc goes into solution as can be demonstrated by any of the known zinc reactions.

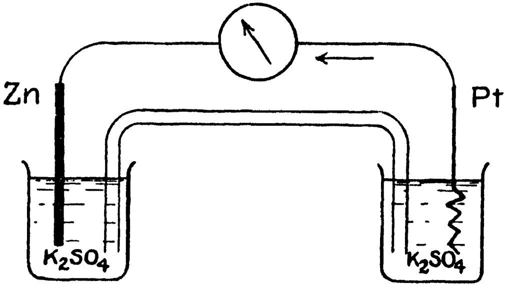

Fig. 34C

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[119] We still speak of "positive current," although we mean by that, in the language of the Electron theory, a flow of electrons, (which are always negative) in the opposite direction.

There are several reactions which can be used in such a way that an electrical current is produced instead of heat. These may be classified under four headings:

A. Displacement cells.
B. Oxidation-reduction cells.
C. Combination cells.
D. Concentration cells.

109. The first type of cell to be considered is the "*displacement cell.*" Iron, displacing copper from its solution according to the equation:

$$Cu^{\cdot\cdot} + Fe \rightleftarrows Cu + Fe^{\cdot\cdot},$$

produces a current in the connecting wire, running from the copper to the iron, as indicated by the arrow. As a current indicator for this and the following demonstrations a sensitive lecture galvanoscope or a suitable milliammeter may be used. A Weston station voltmeter, in which the series resistance coil has been short-circuited, will also serve the purpose. A full scale deflection is obtained with a current of about 0.01 ampere. The experiment is carried out as follows:[120]

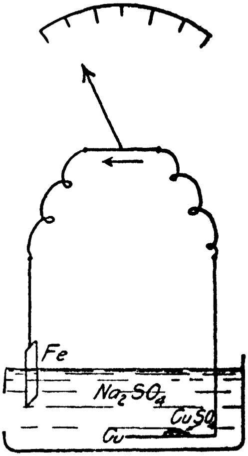

Fig. 35

A disk-shaped copper electrode and a polished iron rod electrode are inserted in a large crystallization dish filled with a solution of

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[120] Küster, *Zeitschr. f. Electrochemie*, 4, p. 107, 1897.

sodium sulphate (Fig. 35). On connecting both electrodes with the current indicator, no current, or at least no *lasting* current, is noticed. As soon as some solid copper sulphate is placed on the copper disk, thereby surrounding the electrode with $Cu^{\cdot\cdot}$-ions a strong current results.

110. Another ionic reaction, already mentioned in a preceding chapter, *viz.*:

$$Fe^{\cdot\cdot} + Ag^{\cdot} = Fe^{\cdot\cdot\cdot} + Ag,$$

can be adapted to give a current of electricity in the manner described by Lermontoff.[121] The experiment is well fitted for projection on the screen by dividing a glass cell with parallel sides into two partitions by means of a piece of brown paper cemented in a vertical position, water-tight to each side and to the bottom. The cell is then filled on one side with a 2 per cent solution of silver nitrate and on the other with a cold saturated solution of ferrous sulphate. On connecting both solutions through a bent silver wire, dipping in each partition half way to the bottom, a crystalline growth of silver on the wire can be observed on the side which contains the silver nitrate.

111. Another way of producing an electric current is by discharging a cation and at the same time giving another cation a higher charge:

$$Sn^{\cdot\cdot} + Hg^{\cdot\cdot} \rightleftarrows Sn^{\cdot\cdot\cdot\cdot} + Hg.$$

An apparatus, as devised by Lüpke[122] may be used, consisting of two beakers, one of which contains an acidu-

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[121] Meldola; the Chemistry of Photography, London, p. 179, 1891.

[122] Lüpke-Bose, *l. c.*, p. 164.

lated solution of stannous chloride, (112 grams in 1 liter), while the other is filled with an acidulated normal sodium chloride solution. The beakers are connected by a wide siphon, filled with the same solution of sodium chloride. Platinum electrodes, bent at right angles, are inserted in the beakers, and attached to copper wires, leading to a galvanoscope. No current is observed. On placing a few crystals of corrosive sublimate on the right electrode, a current flows through the wire circuit from right to left, as shown by the galvanoscope. (Fig. 36).

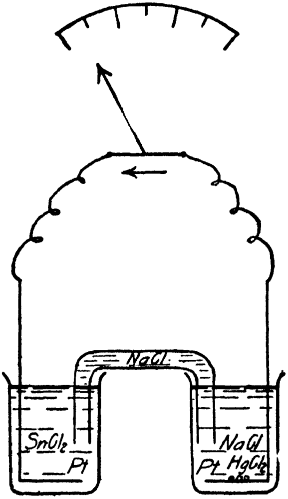

Fig. 36

As will be noticed from the foregoing examples all these cells are analogous, the metal higher up in the electrochemical series of metals going into solution and producing a current (outside the solution) from the less chemically active metal to the more chemically active metal.

112. Instead of cations, anions, may be used to furnish electricity as in the reaction:

$$I' + Br \rightleftharpoons Br' + I.$$

In a H-shaped vessel (Fig. 37) two circular platinum foils are sealed in near the bottom, and the connecting copper wires attached to a galvanoscope. A 10 per cent potassium chloride solution is poured into the vessel and the platinum disk in the left limb covered with a few drops of bromine. No current is observed, but on placing a crystal of potassium iodide on the electrode in the right limb, the pointer indicates a current in the wire circuit from left to right. At the same time the solution on the left side is colored brown by the separation of iodine.[123]

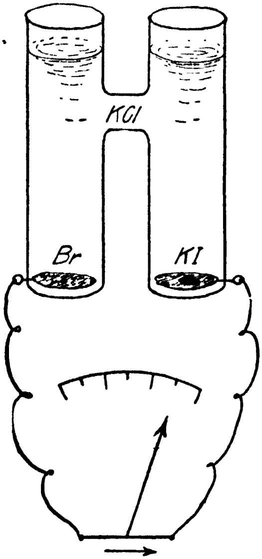

Fig. 37

The next following reactions deal with the type of galvanic cells called *oxidation-reduction* or briefly: *oxidation cells.* Viewed in the light of the Electron theory there is no sharp distinction between displacement and oxidation cells as oxidation is defined as a loss of electrons by ions or atoms, whereas the reverse process consisting in a gain of electrons is termed reduction.

113. The reaction:

$$2\ Fe^{\cdot\cdot\cdot} + Fe \rightleftharpoons 3\ Fe^{\cdot\cdot}$$

will give an electric current, in the direction of the arrow. The same apparatus is used as in experiment 109, re-

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[123] Küster, *l. c.*, p. 109.

placing the sodium sulphate solution by a solution of sodium chloride and the copper electrode by a platinum disk.[124] No perceptible current is observed, but on bringing some solid ferric chloride on the platinum disk, which is thus surrounded by $Fe^{\cdot\cdot\cdot}$-ions, a current in the direction of the arrow results (Fig. 38). The process that takes place consists in discharging the trivalent iron ion and the simultaneous loading of the uncharged iron.

114. The reversible ionic reaction:

$$Fe^{\cdot\cdot} + I^0 \rightleftharpoons Fe^{\cdot\cdot\cdot} + I',$$

in which both cations and anions take part, can also produce an electric current.

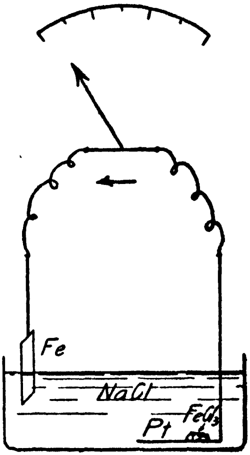

Fig. 38

Following again Küster's directions,[125] a large size crystallization dish, (Fig. 39), filled with moderately diluted hydrochloric acid, is used. Two small dishes are placed inside, so that the liquid covers both. Platinum foils, bent at right angles, are inserted in each dish to serve as electrodes. The platinum foil, on the left is covered with some iodine crystals, the other by a few pure ferrous sulphate crystals (eventually 2 or 3 drops of a freshly prepared ferrous chloride solution). The

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[124] Küster, *l. c.*, p. 107.
[125] Id., *l. c.*, p. 108.

galvanoscope showes a current flowing through the wire from left to right.

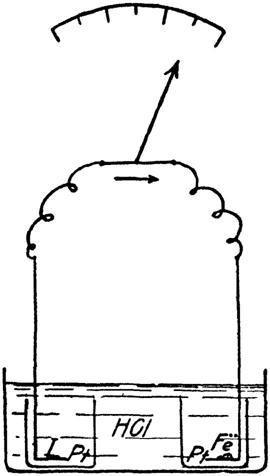

Fig. 39

115. An analogous oxidation and reduction experiment[126] may be carried out with the aid of the arrangement sketched in Fig. 36 by filling both beakers and the intermediate "salt bridge" with a dilute sodium chloride solution. On introducing by means of a pipette some concentrated ferric chloride solution on the platinum electrode in the right beaker only a slight momentary deflection of the needle is observed. If now some hydrogen sulphide water is pipetted on to the electrode in the left beaker a deflection of the needle is observed showing a positive current (outside the solution) from the ferric chloride solution to the hydrogen sulphide solution, in accordance with the reaction:

$$2\mathrm{Fe}^{\cdots} + \mathrm{S}'' = 2\mathrm{Fe}^{\cdot\cdot} + \mathrm{S}.$$

The reaction described in exp. 115 is just the reverse of what was demonstrated in exp. 114. In the latter case the ferrous iron is oxidized and the current flows from left to right, while in the former the ferric iron is reduced with the current flowing from right to left. Without

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[126] Ostwald, *Zeitschr. f. phys. Chem.*, 9, p. 540, 1892, see also Stieglitz, *l. c.*, p. 254.

entering into a discussion of the theory of electromotive force it may be well to show the effect of ionic concentrations on the strength of the current and to demonstrate the possibility of reversal of the direction of the current in these oxidation cells.

116. After the oxidation of the ferrous iron (see exp. 114) has been going on for a while and enough ferric ions have been formed the current can be reversed by adding potassium iodide crystals to the platinum electrode on the left.

117. In the reaction mentioned in exp. 115 the concentration of the S''-ions can be greatly increased by adding a solution of an alkali to the beaker containing the hydrogen sulphide and a decided increase in the strength of the current will be observed. On the other hand the addition of a solution of ammonium or potassium fluoride leads to the formation of complex FeF'''-ions[127] thereby greatly reducing the number of $Fe^{\cdots}$-ions with the result that the current is instantly greatly reduced. At the same time a change in color from brown to pale yellow (color of FeF'''-ion) takes place in the right beaker.

What has been said here about oxidation cells applies, mutatis mutandis, also to displacement cells. Since there are, when a metal is placed in a solution of its salt (to use Nernst's nomenclature) two opposing forces, the constant solution tension and the opposing osmotic pressure of the metal ion which can be varied at will, it is evident that by changing the ratio of the ionic concentrations in

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[127] Peters, *Zeitschr. f. phys. Chem.*, 26, p. 229, 1898.

cells of the Daniell type the current can be reduced in strength and finally reversed.

118. In setting up a cell of the Daniell type for demonstration purposes the copper electrode may be placed in a wide tube the lower end of which is closed with parchment. The tube, filled with copper sulphate solution, is supported in a beaker containing zinc sulphate solution and a zinc electrode.[128] Another arrangement consists of a H-shaped tube with the electrodes passing through one-hole rubber stoppers.[129] Perhaps the most satisfactory way of keeping the zinc and the copper solution apart is the use of two beakers and an intermediate salt bridge (Fig. 34C), the latter containing a solidified 5 per cent agar-agar jelly in which potassium chloride has been dissolved. Using any one of these three types the deviation of the needle of the current indicator is first noted and then a solution of sodium hydroxide added, little by little. The current is reduced noticeably. If sodium sulphide solution is added to the cuprous hydroxide the current is still further reduced owing to the conversion of the hydroxide in the almost insoluble copper sulphide. Finally on practically completely suppressing the copper ions by adding enough potassium cyanide solution to dissolve the sulphide, the current is reversed and zinc precipitated while copper goes into solution.

[128] Ostwald, Wiss. Grundlagen der anal. Chem., 5e Aufl., p. 231, 1910.

[129] Lüpke-Bose, *l. c.*, p. 156; Küster, *l. c.*, p. 503.

One example will be given of a *combination cell.*

119. A combination cell may be set up for instance by taking a glass vessel, divided in two partitions by a porous diaphragm (of unglazed porcelain) and filled on one side with a sodium chloride solution, in which a zinc rod is dipped, and on the other side with the same solution to which some bromine has been added. A platinum wire or a rod of carbon is inserted in this solution and both poles connected with copper wires to a galvanoscope.[130] A current flows through the wire circuit from the platinum (or carbon) to the zinc and the reaction, that takes place in the solutions on both sides of the septum is the following:

$$Zn^0 + 2Br^0 = Zn^{\cdot\cdot} + 2Br'.$$

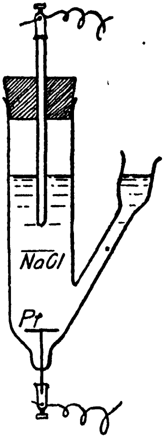

Fig. 40

120. The different types of galvanic types discussed so far may be divided in two groups: *inconstant* and *constant* cells. Thus the combination Fe-NaCl-Pt (page 102) *e. g.,* is an inconstant cell. The ferric chloride added to the platinum electrode, acts as a "depolarizer." Lüpke[131] has modified the apparatus, as sketched in the figure (Fig. 40), the ferric salt being poured on the platinum disk through the side tube.

121. The "polarization" current can be easily demonstrated by electrolyzing dilute sulphuric acid (1 : 10) in an

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[130] A. Smith, *l. c.,* p. 790.

[131] Rüdorff-Lüpke, Grundrisz der Chemie, 12e Aufl., p. 306, 1902.

H-shaped vessel (Fig. 41), communicating with a large crystallization dish, filled to two-thirds of its height with the same acid. The electrodes are platinized platinum foils, the cathode being inserted twice as deep into the acid as the anode. The acid is electrolyzed with one storage cell and the electrolysis continued until the lower end of the platinum foils just touches the liquid in both limbs. The current is then turned off and connection is made with a galvanoscope, which indicates a current in the connecting wire, flowing in the opposite direction.

The electrodes are platinized by placing the platinum foils, previously cleaned by means of chromic acid, in a solution of 3 grams of platinum chloride and 0.02-0.03 gram of lead acetate in 100 cc. water, and connecting the electrodes with a battery of two lead accumulators. The current is passed for 10-15 minutes, reversing its direction through a commutator every half minute.[132]

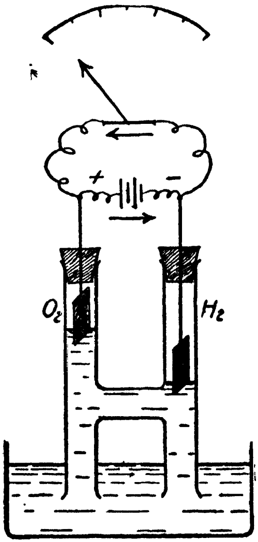

Fig. 41

122. During the electrolysis of dilute acids *both* platinum electrodes are polarized. On adding oxidizing agents to the cathode, the evolution of hydrogen is stopped and cathodic polarization prevented.

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[132] Findlay, Practical Physical Chemistry, p. 171, 1915.

This is clearly shown in the following experiment, devised by Lüpke:[133]

Three U-shaped tubes with sealed platinum foil electrodes (Fig. 42), are connected in series with a battery of eight lead accumulators. The first tube is filled with a 19 per cent nitric acid solution, the second with a 52 per cent nitric acid solution and the third with a chromic trioxide solution. As soon as the current is turned on, it will be noticed that oxygen is evolved at all three anodes; hydrogen is only set free in the first tube, while in the second vapors of nitrogen oxide escape. In

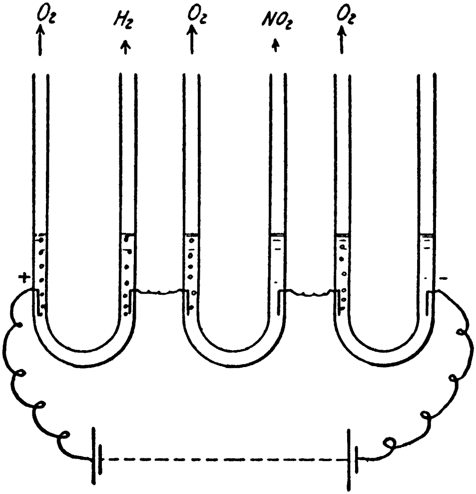

Fig. 42

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[133] Rüdorff-Lüpke, *l. c.*, p. 305.

the third tube the color of the liquid turns gradually to a darker shade.

123. A well-known inconstant cell is the combination Zn-H_2SO_4-Cu. By eliminating polarization a constant cell results, as is proved by the following lecture experiment.[134] The funnel *A* (Fig. 43), about two-thirds filled with dilute sulphuric acid (1 : 10) is connected by means of rubber tubing with a second, leveling funnel (provided with stopcock) containing a copper sulphate solution. A conical sheet of zinc, which is amalgamated with mer-

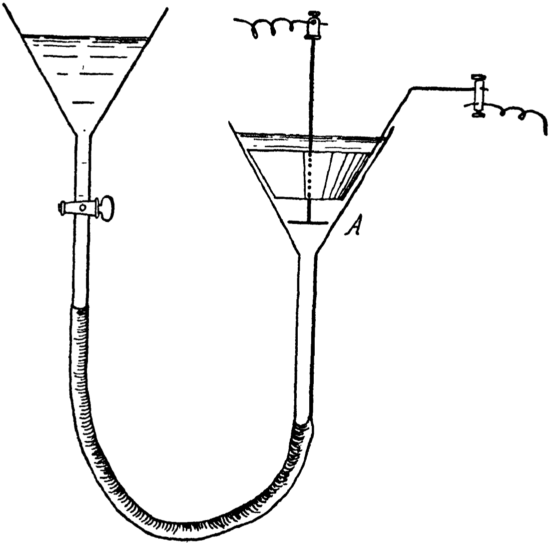

Fig. 43

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[134] Bräuer, Lehrbuch der anorg. Chemie, 2e Aufl., p. 188, 1913.

cury in order to minimize the direct action of the zinc on the acid acts as anode, while a copper disk, farther down to the bottom serves as cathode. On connecting the electrodes with a low resistance ammeter, the latter indicates right at the start a current of about 1.5 amperes, rapidly decreasing, however, to 0.2-0.3 ampere. When the copper sulphate is allowed to flow into the cell, covering the cathode and forming a "Daniell" or "gravity" cell, the current increases in strength and becomes constant.

124. Very simple in construction is the apparatus, described by Lüpke,[185] which enables the use of several depolarizers in succession.

The electrolyte, dilute sulphuric acid. (1 : 25) is contained in a narrow-mouthed bottomless bottle held upside down by a clamp fastened to a ring stand (Fig. 44). The cathode is a large copper disk soldered to a copper rod, passing through the cork stopper. The anode, a platinum disk, is separated from the cathode by a crystallization dish. On connecting the electrodes with a galvanoscope, no appreciable current is indicated, but on pressing crystals of potassium permanganate, corrosive sublimate, silver nitrate, small cubes of manganese dioxide or red lead on the platinum disk, the pointer immediately deviates.

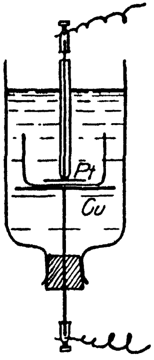

Fig. 44

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[185] Rüdorff-Lüpke, *l. c.*, p. 307.

125. *Concentration cells* are cells in which two different concentrations of the same salt are used. Such a cell is readily set up by half-filling with a concentrated solution of copper chloride (20 grams $CuCl_2$ in 40 cc. water), a wide glass tube (15 by 2.5 centimeters) closed at its lower end by a one-hole cork stopper, through which passes a copper rod. On top of this is poured a dilute solution of the same salt (20 grams in 1 liter water), taking care that a sharp boundary surface is maintained. The tube is closed by another perforated stopper carrying a copper rod dipping in the dilute solution (Fig. 45). When connection is made with a galvanoscope, the pointer indicates a current, flowing—outside the tube,—from the lower rod to the upper.[136] Similar concentration cells may be constructed with Ag-$AgNO_3$- and Zn-$ZnSO_4$-solutions.

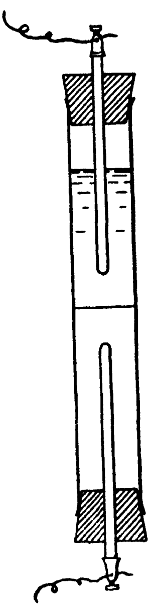

Fig. 45

126. With a slight modification "short-circuited," concentration cells are formed, first described by Bucholz in 1804.[137]

A lecture jar (15-20 centimeters high) is filled to one-half of its contents with a concentrated solution of stannous chloride, obtained by dissolving 15 grams of tin in dilute hydrochloric acid and evaporating to 40 cc.,

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[136] Lüpke, Grundzüge der Electrochemie, 5e Aufl., p. 144.

[137] Coehn, *l. c.*, p. 555.

and this solution is covered with a very dilute solution of the same salt. A tin rod, inserted in the jar, so that it passes through both layers, is partly corroded by dissolving in the dilute solution, and below the boundary surface covered with a "tin tree." (Fig. 46).

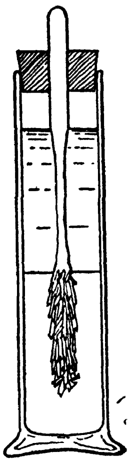

Fig. 46

127. An experiment, showing that short-circuited galvanic cells, are possible, which are entirely built up of liquids, has been devised by Krüger and Dolezalek.[138]

An O-shaped glass vessel (Fig. 47), with a bore of 6 centimeters, is half-way filled with a 35 per cent solution of sulphuric acid, colored with litmus. On the left side a layer of sodium acetate solution (30 per cent), 2 centimeters high, is placed. In order to obtain a sharp boundary, the solution is cautiously dropped from a pipette on a thin cork disk, floating on the acid. The ring is then filled up, in the same way, with a 20 per cent lithium chloride solution, containing a few drops of ammonia, colored with litmus. The ring is brought around a small magnet system, so that the latter occupies the center of the ring. The system consists of several small magnets, suspended from a wire, 3 centimeters long, and enclosed in a thick-walled copper box (5 centimeters high and 2 centimeters wide) provided with a small glass window. A mirror is fixed on the magnet system which allows to throw the image of an illuminated arrow on a graduated

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[138] *Zeitschr. f. Electrochemie*, 12, p. 669, 1906.

screen at 2-3 meters distance. A curved, astatic bar magnet, the distance of which from the magnet system can be regulated, is placed underneath the ring, in order to increase the sensibility of the measuring instrument, which indicates a slight current flowing through the ring. By turning the ring through 180°, the arrow moves in the opposite direction, over the same number of scale divisions on the other side of the zero-point. Upon shaking the ring the liquids become mixed and the arrow returns to its initial position. The experiment may be taken as proof that Volta's law does not hold for solutions.

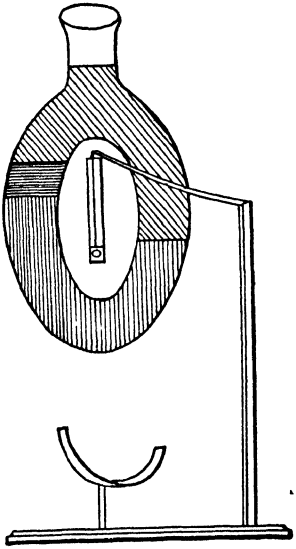

Fig. 47

IV. Conductivity and Degree of Ionization

128. Pure water does not conduct an electric current perceptibly. A current of appreciable strength is only noticed by dissolving salts, acids and bases in water. This is shown by filling a beaker of 200 cc. with distilled water and inserting two platinum foils (3 by 4 centimeters) parallel to each other, at a distance of 1-2 centimeters. On connecting the electrodes with a galvanoscope and a battery of three lead accumulators, no current is indicated; but on allowing concentrated hydrochloric acid to drop from a pipette into the water, the instrument shows a constantly increasing deviation from the zero point.

129. That, on the other hand, it is not the acid alone which is responsible for the conductivity, can be proved by passing dry hydrochloric acid gas into carefully prepared toluene, from which all traces of water have been removed. On inserting two platinum electrodes, connected with a galvanoscope and a battery of seventy volts, into the solution, no current is indicated. A few drops of water, however, immediately have the effect of producing a current of noticeable strength.[139]

130. The following experiment, due to Scriba,[140] illustrates the same fact for sodium chloride. Solid rock salt, like pure water, does not perceptibly conduct electricity, but when it is dissolved in water, the solution shows itself a good conductor. A glass tube, 20 centi-

[139] Küster, *l. c.*, p. 109.

[140] *Zeitschr. f. phys. u. chem. Unterricht*, 28, p. 94, 1915.

meters long and with a diameter of 2.5 centimeters, closed at one end and provided with two platinum wires sealed in the glass at the lower end of the tube, is half filled with distilled water. A cubical piece of solid rock salt (if necessary, dried with absolute alcohol) is fixed between two brass clamps (Fig. 48). Connection is made with the terminals of a 110-volt direct circuit, a switch and a 32-candlepower lamp being interposed, so that the salt and water are in parallel in the circuit. On closing the circuit, no electrolysis is observed and the lamp does not glow, but on dropping a small piece of the rock salt in the water the lamp gradually shines with a bright yellow light and electrolysis takes place in the solution of rock salt. The experiment may be repeated, replacing the rock salt by a large crystal of cane sugar. The result in this case is negative.

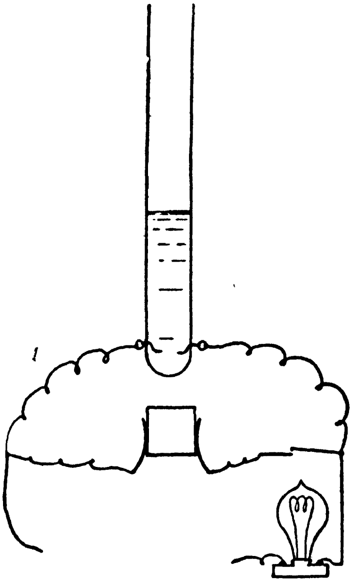

Fig. 48

131. That the conductivity becomes practically zero when insoluble products are formed in a reaction is shown in the following experiment.[141] A 600 cc. beaker

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[141] Watts, *Journ. Am. Chem. Soc.*, 46, 1210, 1924.

contains a 5 per cent solution of barium hydroxide to which a drop of phenolphthalein is added. Two platinum electrodes are connected in series with an electric light bulb and an alternating-current source. While the solution is stirred, dilute sulphuric acid is added from a burette little by little. When enough acid has been added to neutralize all of the base the light goes out entirely and the red color of the solution disappears. On adding an excess of acid the current begins to pass again and the filament glows with increasing brightness as more acid is added.

132. That the conductivity of a given weight of electrolyte increases with increasing dilution is readily demonstrated by the following experiment of Stieglitz,[142] adapted from a similar one by Noyes and Blanchard.[143]

A rectangular glass trough, of about 1 liter capacity, 4.6 centimeters wide 11.5 centimeters long and 20 centimeters high is fitted with copper electrodes, 4.6 centimeters broad and 21 centimeters high (Fig. 49) connected with a lead accumulator and an ammeter. On bringing 20 cc. of a 4N hydrochloric acid solution in the trough, the current registered by the ammeter will be after a few seconds, 0.17 ampere. On adding successively 20, 40, 80, 160 and 320 cc. of distilled water, the mixture being well stirred after each addition, the

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[142] Qualitative Analysis, Vol. I, p. 49, 1916.

[143] *l. c.*, p. 726; similar experiments have been described by Lüpke and by Ostwald. See also: Lash Miller and Kenrick, *Journ. of phys. Chem.*, 4, pp. 599-618, 1900.

current is increased to 0.22, 0.26, 0.30, 0.31, and 0.32 ampere respectively, thus showing that the increase in strength grows smaller, the greater the dilution.

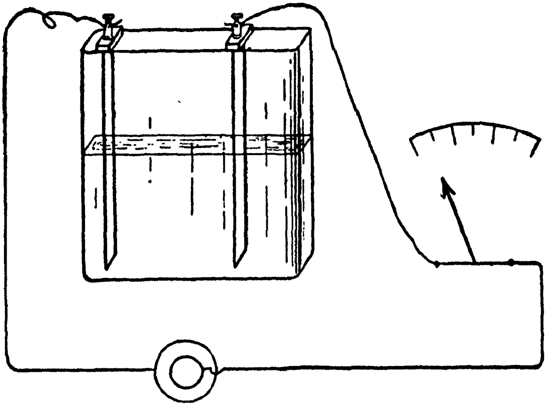

Fig. 49

133. Different acids of the same molecular concentration exhibit marked differences in conductivity and hence in degree of dissociation. This may be shown in a simple way[144] by means of three U-shaped capillary tubes of exactly the same size (18 centimeters long, inner bore 3 millimeters) filled with normal solutions of hydrochloric, sulphuric and acetic acid respectively. The limbs in each tube are widened up, so as to allow the passage of disk-like platinum electrodes of the same diameter, placed at the same height in the solutions (Fig. 50). Each tube

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[144] Rüdorff-Lüpke, *l. c.*, p. 136; Ostwald, Grundlinien, 3e Aufl., p. 282, 1912.

is connected in its turn with the aid of a switch to a battery of twenty accumulators and a galvanoscope or milliammeter. It will be seen that the deviation from the zero-point is greatest for hydrochloric acid, somewhat less for sulphuric acid and exceedingly small for acetic acid.

Fig. 50

134. The same principle can be demonstrated in a very elegant manner with a more complicated apparatus, devised by Whitney and described by Noyes and Blanchard.[145]

Four glass tubes, as nearly alike as possible (internal diameter 3 centimeters; length 20 centimeters), are closed at their lower ends with a one-holed rubber stopper, in which has been inserted a thick-walled capillary glass tube containing a stout copper wire to which a thin platinum disk, covering the small end of the stopper has been soldered, and attached to it by means of sealing wax. The tubes are set up in a vertical position and held in place by a suitable wooden frame. In the upper

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[145] *l. c.*, p. 736.

end of each tube, a one-holed rubber stopper is inserted carrying a moveable thick-walled glass tube (22 centimeters long) containing a stout copper wire, to the lower end of which is soldered a thin platinum disk (diameter about 2.8 centimeters) reinforced by a conical layer of sealing wax. Each lower electrode is connected with a 32-candle 110-volt lamp, and all other connections made as shown in Fig. 51. The upper electrodes are connected through an open switch with one terminal and the lamps

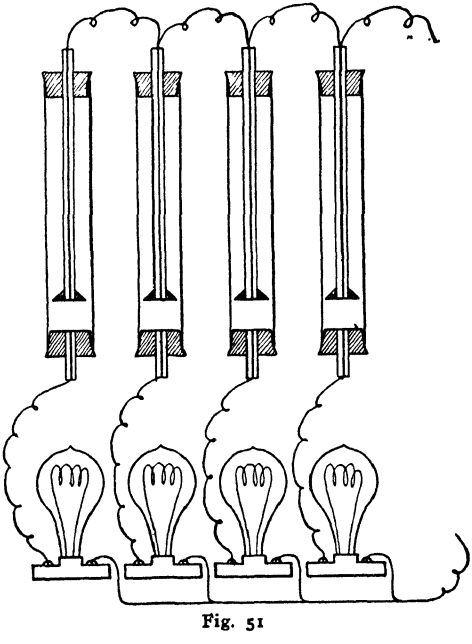

Fig. 51

with the other terminal of an alternating 110-volt circuit. (In case no alternating current is available, the upper electrodes are suitably shaped conically in order to allow the gases, evolved during the electrolysis, to escape. For the same reason the upper rubber stoppers must be provided with a second hole, and the circuit be closed for as short a time as is necessary). After placing 120 cc. of distilled water in the tubes, they are filled with 5 cc. of half-normal solutions of hydrochloric acid, sulphuric acid, monochlor-acetic acid (freshly prepared) and acetic acid respectively and the mixtures thoroughly stirred. The upper electrodes are reinserted at the same height, (one-third of the distance from the bottom), the lecture room is somewhat darkened and the circuit closed. The lamp beneath the hydrochloric acid solution is found to glow brightest, the resistance in this case being least; the other lamps follow in brightness in the order given above, the fourth lamp not glowing perceptibly.

The electrodes are next adjusted so that the lamps are equally bright, when it is seen, on readmitting light to the room, that if the upper electrode in the hydrochloric acid is at the top, in the second solution (H_2SO_4) it is about one-quarter of the distance down, in the third ($CH_2ClCOOH$), three-quarters of the distance down, while in the acetic acid tube both electrodes are almost in contact. Finally, in order to show, that the alkali salts of these acids all have nearly the same conductivity and degree of dissociation, the solutions are neutralized (about the same amount of potassium hydroxide being required in each case) and then the equal brilliancy reestablished. It will be found this time that the upper electrodes stand approximately at the same height. The same apparatus may be used for the demonstration of the so-called Ostwald's dilution law and for the illustration of the conductivity and dissociation of other substances.[146]

135. That the "strength" of acids does not bear any relation to the "potential" amount of hydrogen ions, as found by titration (see foregoing experiment), but is intimately connected with the "actual" amount of H·-ions in solution, may be further illustrated by the different speed of reaction of normal solutions of different acids on equal-sized pieces of metal (zinc or magnesium). On bringing the dilute acids

$$(\mathrm{N\ HCl,\ N\ H_2SO_4,\ N\ CH_3COOH})$$

with the metal in small Erlenmeyer flasks, connected through rubber tubing with gas collecting tubes of the same size and diameter, the volumes of gas, collected over water in the same time (5-10 minutes), are different. The solutions are most suitably treated beforehand with equal amounts of a dilute copper sulphate solution and the gases allowed to escape for some time, before the experiment is started.[147]

136. What has been said about the strength of acids also applies to bases. Decinormal solutions of sodium- and ammonium hydroxide solutions differ considerably in their concentration of hydroxyl ions as found by con-

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[146] Noyes and Blanchard, *l. c.*, p. 739.

[147] Ostwald, Grundlinien, p. 281; Rüdorff-Lüpke, Grundrisz, p. 136.

ductivity measurements (ratio 97:2). The same proportionality is exhibited by their action on esters, showing that the "strength" of bases (measured by the rate of saponification of esters) depends on the actual amount of OH′-ions in solution.

This may be roughly shown by decomposing methyl acetate by tenth normal solutions of sodium- and ammonium hydroxide.[148] To 100 cc. of cold (recently boiled) water in each of two beakers is added a little phenolphthalein and then in the first 20 cc. of tenth normal sodium hydroxide and in the second an equal amount of tenth normal ammonium hydroxide. Five cubic centimeters of methyl acetate are introduced simultaneously into both solutions and the mixtures stirred for a moment. The solution in the first beaker becomes pale in a few minutes and colorless afterwards while the second mixture remains deep red even after half an hour.

V. The Common Ion Effect

The effect of a common ion represents a special case of the mass action principle, of which several instances were given in Chapter V. Other examples will be discussed in the chapter on solubility. Some further applications, in which the dissociation of either H·-ions or OH′-ions is driven back by the addition of salts with common anions or cations, may be considered here.

137. *H·-ions.* A typical case is the following, given by Crum Brown.[149] A dilute solution of ferrous sulphate

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[148] Stieglitz, *l. c.*, p. 80.

[149] Proc. Royal Soc. of Edinburgh, 21, p. 57, 1896.

or ferrous ammonium sulphate (Mohr's salt) is acidified with such an amount of acetic acid solution, that on addition of hydrogen sulphide gas no ferrous sulphide is precipitated. On throwing a few particles of solid sodium acetate in the solution, each crystal forms the starting point of a long streak of iron sulphide. The experiment fits admirably well for projection on the screen.

138. The same result is obtained by the use of an indicator,[150] *viz.* methyl orange, which colors a dilute acetic acid solution pink. On adding a large volume (about six to eight times the amount of acid) of a 10 per cent solution of sodium acetate, which, to prevent the suspicion of alkalinity, has been made very slightly acid, the color turns to a bright yellow. If, instead of methyl orange, congo red is used as an indicator, the observed change in color is from blue to violet red.

139. Ostwald[151] has shown the effect of salt addition on acids with common anion in the following manner:

In two small conical flasks are placed two equal-sized pieces of zinc, covered by dilute acetic acid. The escaping gases are collected after some time over water or glycerine in eudiometer tubes. The distance between the gas bubbles in both tubes is observed. A concentrated sodium acetate solution is poured into the flask, from which the bubbles are coming forth somewhat faster than in the other. The gas evolution instantly slackens and consequently the distance between the rising gas bubbles is considerably increased.

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[150] Küster, *l. c.*, p. 109.

[151] Ostwald, Wiss. Grundlagen der Anal. Chem., 5e Aufl., p. 225, 1910.

140. Another good illustration is given by Treadwell.[152] On adding dilute acetic acid to a solution containing potassium iodide and potassium nitrite, the solution turns yellow or brown, owing to the separation of iodine, in accordance with the equation:

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

If, however, before adding the acid, the solution is mixed with a concentrated potassium (or sodium) acetate solution, the addition of dilute acetic acid causes no separation of iodine, although enough $H^{\cdot}$-ions are present in solution to turn blue litmus paper red. This proves that the amount of $H^{\cdot}$-ions is not sufficient to reduce the nitrous acid. Addition of a few drops of a strong mineral acid causes the immediate liberation of iodine.

141. *OH'-ions.* The forcing back of the concentration of hydroxyl-ions is easily carried out as follows: A concentrated ammonium chloride solution is made very slightly alkaline with ammonia, so as to make sure that it contains no free acid (hydrolysis is likely to cause a slight acidity). It is then poured into an aqueous solution of ammonia, colored by phenolphthalein. The red color fades to a scarcely perceptible pink.

Va. The Salt Effect

Under this heading a number of experiments will be described illustrating the effect of addition of salts *without common ion* on the ionization of acids, bases and salts.

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[152] Analytische Chemie, 5e Aufl., p. 311, 1911.

142. One of the most common cases which is frequently met in organic and in analytical chemistry is the addition of a salt of a weak acid such as sodium acetate to a strong mineral acid like hydrochloric acid:

$$Na^+ + CH_3COO^- + H^+ + Cl^- = CH_3COOH + Na^+ + Cl^-.$$

The acetic acid is only slightly ionized and by regulating the addition of sodium acetate the acidity can be varied within wide limits.

Half a gram of crystal violet dissolved in 120 cc. of approximately normal hydrochloric acid (10 cc. of concentrated acid, specific gravity 1.19, diluted with 110 cc. of water) does not precipitate on the addition of 80 cc. of saturated salt solution. The liquid retains a yellowish green hue and does not leave any precipitate on a filter. On adding several spoonfuls of powdered sodium acetate (15-20 grams) the color changes to violet and the dye precipitates. It is retained on the filter while a slightly violet colored solution runs through the filter.

143. In the same way it can be shown that on passing hydrogen sulphide into an acid solution of a zinc salt no zinc sulphide precipitates. On adding a sufficient amount of a concentrated sodium acetate solution the sulphide separates out.

The addition of a salt of a weak base like ammonium chloride to a base also finds frequent application in analytical chemistry and is taken up in the next chapter (see exp. 185).

144. An interesting case is the combination: mercuric chloride + hydrocyanic acid. Taking a dilute solution of the latter and adding a drop of methyl orange indicator the color indicates the merest trace of acidity, the acid being only very slightly ionized. However on pouring some mercuric chloride solution (this salt is also only slightly ionized) on the acid solution the color becomes decidedly pink. This is due to the fact that mercury cyanide is formed which is scarcely ionized with the concomitant accumulation of enough hydrogen ions to produce the pink color.[153]

145. Salts derived from weak acids and those derived from weak bases are considerably affected by the addition of other salts. For instance the addition of a spoonful of sodium acetate to an approximately normal solution of copper sulphate changes the color to a darker shade of blue. The change is due to the formation of the less ionized (partly hydrolyzed) copper acetate. To another portion of the same solution of copper sulphate are added several grams of sodium chloride when a green solution results. The color is due to the slightly ionized copper chloride formed by metathesis. A third cylinder with the original copper sulphate solution is kept for comparison.

146. A similar experiment may be performed by adding to a dilute, pale yellow solution of ferric chloride some solid sodium acetate when a reddish brown liquid results.

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[153] Stieglitz, *l. c.*, p. 117. See also Arrhenius, *Zeitschr. f. phys. Chem.*, 31, p. 197, 1899; Szyszkowski, *Ibidem*, 58, p. 420, 1907.

VI. Hydrolysis

The slight ionization of water (according to Kohlrausch and Heydweiller[154] the degree of dissociation for H· and OH′-ions, expressed in gram-equivalents per liter is 1.05 times 10^{-7} at 25°) accounts for the hydrolysis of salts, *viz.*, the decomposing effect of water on dissolved salts. The salts of a strong base and a strong acid are not appreciably hydrolyzed; the solutions show a neutral reaction. However, under exceptional conditions, water is able to decompose for example sodium chloride, according to the equation:

$$NaCl + HOH = NaOH + HCl.$$

147. The following experiment demonstrates this decomposition.[155]

A platinum crucible is heated in a blast-lamp or over a Méker burner to a bright yellow heat (1100°) and a small quantity of sodium chloride (melting point 884°) fused in the crucible. One cubic centimeter of water is dropped from a pipette drop by drop on the fused salt. When half of the water has been evaporated, which takes about 30 seconds, the remaining aqueous solution is poured off into a beaker containing a blue litmus solution which turns red. After the crucible has cooled down the residual salt is dissolved in water, and the solution poured into a solution of red litmus which changes into blue.

148. Salts of weak acids with strong bases, show an *alkaline* reaction, readily detected by litmus, *viz*: Aque-

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[154] *Zeitschr. f. phys. Chem.*, 14, p. 317, 1894.

[155] Emich, *Ber. d. chem. Ges.*, 40, p. 1482, 1907.

ous solutions of alkali salts of hydrocyanic acid, carbonic acid, boric acid, hydrosulphuric acid. Addition of a little alkali hydroxide will stop hydrolysis as can be proved in the case of potassium cyanide solution when the characteristic odor of hydrocyanic acid disappears.

149. Salts of strong acids with weak bases react *acidic* as for instance solutions of copper sulphate, zinc sulphate, ferric and aluminium chloride, bismuth and antimony chloride. Addition of acid in this case prevents or at least forces back hydrolysis and is always applied in case oxysalts should be formed. Thus the brownish red color of aqueous ferric sulphate disappears on the addition of sulphuric acid.

150. Salts of weak acids and weak bases are largely hydrolyzed and react either alkaline or acidic, according to the nature of the base and acid. In case both are equally weak, the solution is neutral: ammonium acetate for instance. If the acid is stronger the solution is acidic, if the base is stronger the solution is basic. Thus ammonium carbonate reacts alkaline, while ferric acetate is acid.

In most cases hydrolysis increases with the dilution. Arrhenius[156] first derived formulae establishing the relation between the two, namely:

$$K_h = \frac{K_w}{K_a} = \frac{x^2}{(1 - x) \cdot v}$$

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[156] *Zeitschr. f. phys. Chem.*, 5, p. 14, 1890.

in the case of a salt consisting of a weak acid and a strong base. Similarly

$$K_h = \frac{K_w}{K_b} = \frac{x^2}{(1 - x) \cdot v}$$

in the case of a salt consisting of a weak base and a strong acid. In these expressions K_h represents the hydrolytic constant, K_w the dissociation constant of water, K_a that of the weak acid, K_b that of the weak base while x represents the fraction of a mole of the salt which is hydrolyzed and v the dilution. From these two equations it follows in agreement with the facts that increase of volume involves an increase of hydrolysis. Goodwin[157] found for instance in the case of ferric chloride at 25° that at concentrations of 0.45, 0.225, 0.09, 0.045, 0.0225, 0.009 and 0.0045 N the degree of hydrolysis in per cent is 2, 11, 37, 53, 67, 84 and 91 per cent respectively.

151. The effect of dilution may be shown by adding water to a slightly acid solution of bismuth chloride:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

152. In the same way it can be shown that on pouring water on a concentrated solution of stannous chloride ($SnCl_2 + 2H_2O$) a milky liquid result from which finally stannous oxychloride separates out:

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl.$$

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[157] *Zeitschr. f. phys. Chem.*, 21, p. 1, 1896.

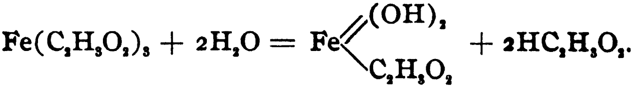
Considering now the case of a salt containing both a weak acid and a weak base the theory shows that

$$K_h = \frac{K_w}{K_a\,K_b} = \frac{x^2}{(1 - x)^2},$$

which indicates that the extent of the hydrolysis must be independent of the dilution. In the case of aniline acetate this formula has been verified.[158] Tizard found that at dilutions of 12.5 and 800 liters aniline acetate is hydrolyzed to an extent of 45.4 and 43.1 per cent respectively. The slight deviation is due to the fact that the assumptions made in deriving the formula are not quite correct.

153. On adding a few drops of a concentrated aniline acetate solution to neutral methyl orange indicator solution placed in a tall glass cylinder a rise in color is noticed. The same color is found on pouring a large volume of the aniline acetate solution into a second cylinder containing the same indicator solution.

154. The effect of boiling is demonstrated by heating a ferric acetate solution (prepared by treating freshly precipitated ferric hydroxide with dilute acetic acid) when a voluminous precipitate of basic ferric acetate will be formed:



$$Fe(C_2H_3O_2)_3 + 2H_2O = Fe\begin{cases}(OH)_2 \\ C_2H_3O_2\end{cases} + 2HC_2H_3O_2.$$

That boiling favors hydrolysis is due to the fact that the water is dissociated to a greater extent at its boiling

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[158] Tizard, *Trans. Chem. Soc.*, 97, p. 2477, 1910.

temperature, than when cold. From Fig. 51A it will be seen that the dissociation at 50° is about three times that at 18° and at the boiling point about ten times as great.

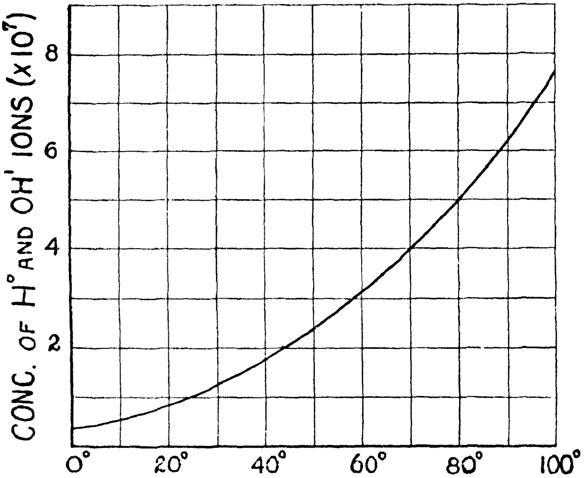

Fig. 51A

155. Schoorl[159] recommends the *change* in color of aqueous indicator solutions on boiling as an easy way for demonstrating the increasing dissociation of water with the rise of temperature.

To 600 cc. of pure, distilled water is added 3-5 cc. of the indicator solution, and then a few drops of a base or an acid, in order to bring the color to its neutral point. The solution is divided into three equal parts and each portion is poured into a 500 cc. flat-bottomed flask of Jena

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[159] *Chem. Weekblad,* 3, p. 771, 1906.

or Pyrex glass, previously steamed out. Two of the solutions are made slightly alkaline and acid respectively and kept for comparison. The third flask, closed by a plug of cotton wool is heated on a wire gauze. A change in color is visible, even before the boiling point is reached. By placing the flask in cold water, the original color returns. Indicators sensitive to bases, cause a change in color towards the alkaline color. Thus methyl orange turns yellow, congo red changes from violet to red, lacmoid from violet to blue. Semi-sensitive or neutral indicators (litmus), remain unchanged, while indicators, sensitive to acids show a change in color towards the acid color, *e. g.*, phenolphthalein turns from pink to colorless.

The following table gives the approximate concentration of H· and OH′-ions at 25° expressed in gram-equivalents per liter, at which a marked change in color is perceptible.

Indicator	H· 1×10^{-3} OH′ 1×10^{-11}	H· 1×10^{-4} OH′ 1×10^{-10}	H· 1×10^{-5} OH′ 1×10^{-9}	H· 1×10^{-6} OH′ 1×10^{-8}
Methyl orange	red orange	orange	yellow	
Congo red....	blue	violet	red	
Litmus.......				red
Phenolphthalein				

Indicator	$H^{\cdot}$ 1×10^{-7} OH' 1×10^{-7}	$H^{\cdot}$ 1×10^{-8} OH' 1×10^{-6}	$H^{\cdot}$ 1×10^{-9} OH' 1×10^{-5}	$H^{\cdot}$ 1×10^{-10} OH' 1×10^{-4}
Methyl orange				
Congo red....				
Litmus.......	violet	blue		
Phenol-phthalein		colorless	pink	red

It should be remarked that experiment 155 is not quite satisfactory since it is tacitly assumed that a change in temperature does not affect the dissociation of the indicator. Now an indicator is either a weak base or a weak acid whose dissociation is certainly affected by a change in temperature and it all depends on whether its dissociation changes little in comparison with that of water or not.

VII. Ionization and Chemical Activity

156. Ionization easily explains the immediate interaction of chemical compounds in aqueous solution, and the inactivity or slow reaction in non-aqueous (non-ionized) solutions. A comparison of the properties of hydrochloric acid dissolved in water and in toluene may be taken as an illustration.

An aqueous solution of hydrochloric acid dissolves marble rapidly while a solution in toluene, a non-conductor of electricity, has little or no effect on calcium carbonate.

157. Another experiment of the same kind is the following:[160] One hundred cc. of nearly saturated aqueous solutions of potassium bromide and zinc bromide and equal volumes of 5 per cent *alcoholic* solutions of isopropyl bromide, ethyl bromide and phenyl bromide are prepared and placed in five lecture jars. A nearly saturated alcoholic solution of silver nitrate (2.5 grams in 100 cc.) is then prepared and 20 cc. of this solution added to each of the five jars after which the mixtures are thoroughly stirred. An immediate precipitate is formed in the first two cases in which the reactions are ionic. An incomplete reaction, although immediate turbidity is visible, is shown in the case of isopropyl bromide. A slow reaction takes place in the ethyl bromide solution, while apparently no reaction is going on in the solution containing phenyl bromide. Care must be taken that the organic bromides are free from hydrobromic acid and bromine, from which they may be freed by washing first with a dilute sodium carbonate solution and then with water.

158. As has been pointed out by Kahlenberg,[161] this difference in behavior need not necessarily be a consequence of electrolytic dissociation. In fact, it has been proved that copper oleate dissolved in benzene or toluene gives an immediate precipitate of copper chloride with hydrochloric acid, phosphorous trichloride, tin tetrachloride, antimony trichloride, etc., dissolved in these same hydrocarbons, notwithstanding the fact that all these

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[160] Noyes and Blanchard, *l. c.*, p. 728.

[161] Outlines of Chemistry, revised ed., New York, p. 453, 1916; *Journ. of phys. Chem.*, 6, p. 1, 1902.

solutions are non-electrolytes. In the same way, as may be shown in the lecture, sodium alcoholate and ferric chloride (sublimed) both dissolved in absolute ethyl alcohol, react with the formation of ferric alcoholate and the direct precipitation of sodium chloride. Recent investigations by Cady and his co-workers,[162] however, lead to the conclusion that these "exceptional" cases are in agreement with the dissociation theory.

VIII. Ionization and Color of Solutions

All salts of a metal, whose ion is colored, show the same color in dilute aqueous solutions, independent of the anion, present in the solution (provided the latter is colorless), whatever the colors of the undissociated salts may be.

Thus dilute aqueous solutions of copper sulphate, acetate, chloride, and nitrate all show the same blue color due to the $Cu^{\cdot\cdot}$-ion. On the other hand, the same salt, when dissolved in a small amount of water or dissolved in solvents other than water, very often shows a different color:

159. Twenty-seven grams of anhydrous copper chloride, dissolved in 100 cc. of absolute alcohol give a dark green solution; about the same color is exhibited by a concentrated aqueous solution. On diluting with water, both show the same shade of blue.

160. Characteristic changes in color occur with cobalt solutions. Alcoholic solutions of cobalt chloride and ni-

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[162] *Journ. Am. Chem. Soc.*, 35, p. 1434, 1913; *Ibidem*, 43, p. 646, 1921.

trate are deep violet-blue and purplish-red respectively. The solutions are made up[163] by dissolving 60 grams of $CoCl_2 6H_2O$ and 73 grams of $Co(NO_3)_2.6H_2O$ in 100 cc. of ethyl alcohol (96 per cent). On adding water to the solutions, they both turn pink. The reverse change: pink $\longrightarrow$ blue is observed when a concentrated hydrochloric acid solution is added to a pink-colored aqueous solution of cobalt chloride.

The original idea of Ostwald, that the change in color in this case is *solely* due to a change in dissociation, according to the equation:

$$CoCl_2 \rightleftharpoons Co^{\cdot\cdot} + 2Cl',$$

must be abandoned in the light of recent investigations.[164] It is highly probable that in this and similar other cases the change in color is mainly caused by hydration of the salts, dissociation being of minor importance.

161. A few more interesting examples may be presented here. Picric acid gives an almost colorless solution in benzene and a straw-colored solution in water, a fact which has been explained by saying that the "dissociative power" of water is far greater than that of such solvents as benzene. About 0.5 gram of dry picric acid is dissolved in 20 cc. of dry benzene. The resulting solution is nearly colorless. On shaking the solution with 20 cc. of water the aqueous bottom layer strongly shows the yellow color of the anion, which becomes even more

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[163] Noyes and Blanchard, *l. c.*, p. 727.

[164] cf. Böttger, Qualitative Analyse, 3e Aufl., p. 223, 1913. Hantzsch, *Zeitschr. f. anorg. Chem.*, 73, p. 309, 1912.

pronounced when a little alkali is added, the alkali picrate being far more dissociated than the acid itself.

162. A small quantity of eosin $(C_{20}H_6O_5Br_4)K_2$ is placed in a test-tube containing about 20 cc. of anhydrous ether + 1-2 cc. of absolute alcohol. After thorough shaking the mixture is filtered through two layers of filter paper. The filtrate is colorless or at most slightly yellow. A portion of the filtrate is transferred to another test-tube containing water. On shaking the aqueous bottom layer shows in transmitted light the red color and in reflected light the beautiful green fluorescence color characteristic for eosin solutions.[165]

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[165] Luepke-Bose, *l. c.*, p. 78.

CHAPTER VIII

SOLUBILITY AND ITS CHANGES

In this chapter, which needs no special description of apparatus, most experiments being conveniently carried out in large test-tubes, only a few suitable combinations of gases, liquids and solids are given, in order to illustrate the more common cases of solubility. These may be divided in four groups, demonstrating:

I A. Solubility of gases in liquids.
I B. Solubility of liquids in liquids.
II. Solubility in a ternary system of two solvents and one solute.
III. Solubility of solids in liquids.

I A. Solubility of Gases in Liquids

163. A very simple arrangement for demonstrating the volume of gases dissolved in water is represented in Fig. 51B. A cylindrical vessel of 25 cc. contents is filled with water, previously saturated with carbon dioxide (at room temperature *i. e.*, 15°). It is connected by means of rubber tubing to a K-piece attached to a graduated test-tube, held in position by a clamp. A rubber tube attached to the side arm of the K-piece dips into a large jar filled with colored water.[166] When all air has been expelled so that the whole apparatus is completely filled with water the cylinder is placed in a large beaker of

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[166] In order to prevent the flow of the colored water into the cylindrical vessel, the K-piece is narrowed down to 15 mm. internal diameter at two places, and the colored water brought to about 40-45°.

water and the latter heated over a Bunsen burner to about 95° when the flame is removed. About 25 cc. of gas will be collected.

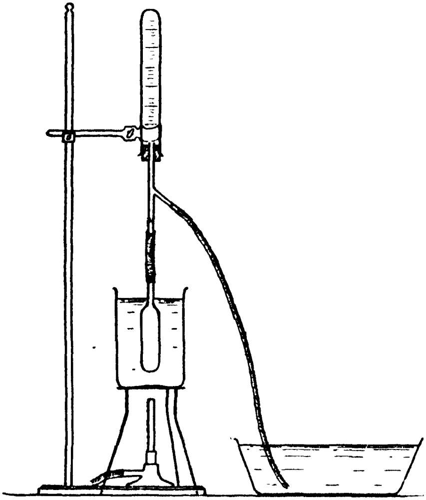

Fig. 51 B

164. The solubility of gases in water is considerably diminished by dissolved solids or liquids. This is readily seen by placing a second cylinder (with the same attachments) containing a sugar solution or preferably a saturated solution of sodium chloride, previously saturated with carbon dioxide, in the same bath and heating both vessels simultaneously. The difference in the volumes of gas collected is very striking. The most plausible explanation is that the diminution of solubility is caused by the hydration of the solute.[167]

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[167] Philip, *Transactions of the Faraday Soc.*, 3, p. 140, 1907.

165. It is also feasible to collect carbon dioxide in a graduated test-tube over distilled water and in another tube over saturated sodium chloride solution. After standing for one or more days it will be noticed that the water level has moved upward over a considerable distance in the first tube while the volume of the gas has only slightly decreased in the second tube.

I B. Solubility of Liquids in Liquids

166. A case of miscibility in all proportions is that of alcohol and water (consolute liquids).

167. Another case is that of ethyl alcohol and carbon bisulphide. However when this consolute mixture is cooled in a freezing mixture of ice and salt, the liquid becomes cloudy since below —14.4° only limited miscibility exists. There is therefore no essential difference between consolute and partially miscible liquids (experiments 168-172).

168. Partially miscible at room temperature are water and butyl alcohol. Equal volumes of both liquids are shaken in a test-tube and equilibrium established at 25°. On inserting the tube in a beaker of hot water (about 40°) without any further shaking, the lower layer, being an aqueous solution of butyl alcohol, becomes turbid. On putting the tube in a beaker of cold water (about 10°) the reverse happens: the lower layer clears up and the supernatant liquid turns milky by the separation of water drops.[168]

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[168] Müller and Abegg, *Zeitschr. f. Electrochemie*, 11, p. 3, 1905.

169. The couple ether and water is another well-known example. At room temperature (20°) water dissolves about 7 per cent ether and ether about 1 per cent water. Twenty-five cc. of water are placed in a eudiometer tube and the surface of the water marked by a strip of paper. An equal volume of ether slightly colored with butter yellow (an aniline dye insoluble in water) is carefully poured on top of the water layer and the surface of the ether layer likewise marked. The tube is closed and the liquids mixed by shaking. Finally the tube is placed vertical and the liquids allowed to settle. While the total volume has not noticeably changed it will be seen that the water boundary has moved upward showing that ether has dissolved in the water. That the upper layer contains some water is demonstrated as follows: By means of a pipette 10 cc. of the ethereal layer are placed in a test-tube and an equal volume of carbon bisulphide is added. On shaking the mixture becomes cloudy (*pure* ether and carbon bisulphide are miscible in all proportions).

The lower layer contains ether which fact is demonstrated by pouring some of the liquid in a small flask, provided with a glass tube, 30 centimeters long. On heating the flask, ether is driven off and ignited with a lighted match.

170. A mixture of 36 per cent phenol and 64 per cent water forms a two-layer system, but on raising the temperature the mutual solubility increases, so that at 68.8,°

where the "upper" critical temperature of solution is reached, a homogeneous liquid forms.[169]

171. A "lower" critical temperature of solution is exhibited at 18.6°, by a mixture of 52 per cent tri-ethyl amine and 48 per cent water.[170] On account of the sharp odor of the amine the mixture should be kept in a sealed tube. Newth[171] recommends this couple as an extremely sharp indicator for slight changes in temperature, a rise of the temperature above 18.6° being immediately shown by a milky appearance, followed by the formation of two layers from the homogeneous liquid.

172. Nicotine and water is a most interesting combination because it is characterized by the occurrence of an upper and lower critical temperature of solubility at 210° and 61° respectively for a mixture of 32 per cent nicotine and 68 per cent water.[172] This may be shown by heating the mixture in a small, strong, well-sealed glass tube (inner bore 0.5 centimeter, length 10 centimeters) taking proper precautions in case the tube should crack. If the experiment is to be shown to a large audience, a projection apparatus may be used.

173. Three liquids may be consolute or they can form two or three liquid layers. One instance is given here of a ternary liquid system, composed of two pairs of consolute and one pair of partially miscible liquids, namely water, alcohol and chloroform. Ethyl alcohol and

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[169] Rothmund, *Zeitschr. f. phys. Chem.*, 26, p. 452, 1898.

[170] Rothmund, *Ibidem*, p. 459.

[171] Chemical lecture experiments, London, p. 69, 1899.

[172] Hudson, *Zeitschr. f. phys. Chem.*, 47, p. 113, 1904.

water are consolute and also alcohol and chloroform, while water and chloroform are only slightly soluble in each other. By means of a pipette 25 cc. of water are placed in a large test-tube and from a burette 25 cc. of alcohol are added. From another burette, filled to the zero mark, chloroform is added gradually (shaking after each addition) until the mixture becomes cloudy. The number of cc. of chloroform is noted. This simple experiment gives an idea how one may establish the boundary of the region of unmixing in this ternary system. Lincoln,[173], Schoorl[174] and others have shown how an exact knowledge of the boundary line can be applied to the determination of the water contents of a mixture of water and alcohol.

II. Solubility in a Ternary System of Two Solvents and One Solute

174. The relative decrease in solubility of one solvent in a second by the addition of a solid easily soluble in one of the solvents only may be demonstrated by the couple water and ethyl ether on adding naphthalene. For this experiment a flask with a long calibrated bulb-neck, as devised by Tolloczko,[175] is used (Fig. 52). The flask is filled to the mark (*a*) with water saturated with ether, and then enough ether saturated with water is added to fill the neck up to the mark (*b*). In order to get a visible boundary line, the ether is slightly colored

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[173] A Text-book of Physical Chemistry, Revised ed., p. 162, 1920.

[174] *Rec. trav. chim.*, 41, p. 1, 1922.

[175] *Zeitschr. f. phys. Chem.*, 20, p. 389, 1896.
Ber. d. chem. Ges., 28, p. 804, 1895.

with a dye, insoluble in water (*e. g.*, butter yellow). On pouring successively equal weights (0.25 gram) of naphthalene into the flask, it will be found, that each time—after vigorous shaking—, the boundary is displaced downward for about the same number of scale divisions, showing that the addition of naphthalene causes a decrease of the solubility of ether in water proportional to the weight of the dissolved solid. This principle of the lowering of solubility, discovered by Nernst[176] has been worked out into a procedure for the determination of molecular weights.

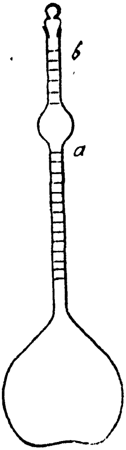

Fig. 52

175. The solubility of a solid may be decreased by the addition of another solvent which is consolute with the first, like water and ethyl alcohol. On adding alcohol to a saturated solution of cane sugar in water, part of the sugar is precipitated.

176. A homogeneous mixture of two, wholly or partially, miscible liquids may be separated into two layers by the addition of a salt. Thus, on adding some solid potassium sulphate to an aqueous solution of phenol, the latter separates in the form of a milky emulsion which changes into a liquid layer after a while. This is the process, well-known in organic chemistry, of "salting out." It is by this method, that compounds like alcohol, acetone, etc., which are very soluble in water, are easily separated out.

[176] *Zeitschr. f. phys. Chem.*, 6, p. 16, 1890.

177. As an exception to the rule that the solubility of a non-electrolyte in water, diminishes by the addition of a salt, the case of iodine and water may be noted. To a saturated solution of iodine in water, with an excess of iodine at the bottom of the test-tube, some crystals of potassium iodide are added. On vigorously shaking the mixture, the iodine goes in solution, forming as is well known a dark brown solution with the salt. The increase in solubility is accounted for by the formation of complex ions.[177]

III. Solubility of Solids in Liquids

178. Before considering the more important cases of salts dissolved in water it may not be out of place to mention the brown, yellowish-brown and violet solutions that iodine forms when dissolved in ether, water and carbon bisulphide. A few small crystals of iodine, dropped into a tall cylinder containing three layers: of carbon bisulphide, water and ether, will form a violet solution with the first, a yellow with the second (middle layer) and a brown solution with the top layer (of ether). Free iodine is assumed to be present in the violet solution while in the other cases a compound of iodine with the solvent is formed.[178] (See also exp. 159-162).

179. The solubility of potassium nitrate increases very rapidly as the temperature rises, while that of sodium chloride is nearly independent of the temperature; a

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[177] Leblanc and Noyes, *Zeitschr. f. phys. Chem.*, 6, p. 401, 1890.
[178] Mellor, *l. c.*, p. 266.

decrease of solubility on raising the temperature occurs in the case of lithium sulphate. The heat absorption and the resulting fall in temperature on dissolving the potassium nitrate and conversely the rise in temperature, due to heat evolution, when lithium sulphate is dissolved (at room temperature) may be demonstrated with the aid of a large air or liquid thermometer, as used for lecture experiments.

180. Most salts on dissolving in water absorb heat. This heat absorption is very considerable in the case of ammonium rhodanide as the following experiment shows. Some water is poured on a block of wood and a beaker containing about 200 cc. of water placed on the wet spot. A spoonful of powdered ammonium rhodanide dropped into the beaker will cause the water underneath to freeze and on lifting the beaker the block of wood sticks solidly to the glass.

181. A *decrease* in the solubility of salts is generally observed on addition of salts with common ions.

Thus addition of concentrated hydrochloric acid to saturated solutions of sodium chloride, potassium chloride, barium chloride, etc., causes an immediate precipitation of the salt in question.[179]

In the same way lead chloride is precipitated from its saturated solution by the addition of concentrated sodium chloride solution.[180]

Nernst was the first who showed that an excess of either the anion or the cation of the salt in solution

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[179] Engel, *Ann. de chim. et phys.*, (6) 13, p. 132, 1888.

[180] Küster, *l. c.*, p. 111.

causes precipitation from its saturated solution. He found that an addition of concentrated potassium hydroxide solution or potassium chloride solution to 10 cc. of a saturated solution of potassium chlorate gave in the former case directly, in the latter after a few minutes, an abundant precipitate of potassium chlorate. The same result was obtained by the addition of a very concentrated solution of sodium chlorate.[181]

182. The precipitation of silver acetate from its saturated solution by the addition of either silver nitrate or sodium acetate solution is another instance, described in detail by A. A. Noyes and Blanchard.[182]

Five hundred cubic centimeters of a saturated solution of silver acetate is prepared by shaking an excess of the salt with warm water, cooling and filtering. In each of two lecture jars is placed 200 cc. of this solution and then 5 cc. of a 4N solution of sodium acetate added to one jar and 5 cc. of a 4N solution of silver nitrate to the second. On vigorously stirring for a few moments, in *both* jars a feathery, crystalline precipitate is produced.

183. However convincing these experiments may be as viewed from the theory given by Nernst, more recent investigations by A. A. Noyes and his pupils have proved that the principle of the constancy of the solubility-product and of the concentration of the non-ionized salt in the saturated solution as derived from the law of mass-action, cannot be universally applied. To cite one example: the solubility of thallous sulphate (Tl_2SO_4) is

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[181] Nernst, *Zeitschr. f. phys. Chem.*, 4, p. 372, 1887.

[182] *l. c.*, p. 750.

increased by the addition of solutions of sodium sulphate, sodium hydrosulphate and even more of sulphuric acid.[183]

184. Some exceptions find a suitable explanation in the formation of complex ions. Thus by adding powdered copper oxalate, which is practically insoluble in water to a saturated solution of ammonium oxalate a deep blue solution results owing to the formation of a complex copper anion (see exp. 47, p. 43). The solutions contains very few $Cu^{\cdot\cdot}$-ions since potassium iodide does not produce any cuprous iodide and free iodine. Hydrogen sulphide, however, still gives a black precipitate. The presence of the complex anion is further substantiated by the fact that the electrical conductivity of the ammonium oxalate solution is not increased by the addition of the copper oxalate. Another example is the addition of silver cyanide freshly precipitated to potassium cyanide when a complex silver anion is formed.

185. An *increase* in solubility of salts, hydroxides and oxides, that are slightly soluble, is usually observed, in accordance with a rule, formulated by A. A. Noyes,[184] on the addition of salts *without* a common ion, and especially when there is an opportunity for forming non- (or slightly) ionized salts by double decomposition.

Thus mercuric oxide, which is hardly soluble in water, goes into solution by shaking vigorously with an alkali chloride solution and, still better, on applying a solution

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[183] Harkins, *Journ. Am. Chem. Soc.*, 33, p. 1836, 1911.

[184] *Zeitschr. f. phys. Chem.*, 6, p. 262, 1890.

of potassium cyanide, mercuric cyanide being scarcely ionized.[185]

The case, well-known in analytical chemistry, of magnesium hydroxide, dissolving on the addition of ammonium salts is another example belonging to this class.[186]

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[185] Bersch, *Ibidem,* 8, p. 383, 1891.

[186] Lovén, *Zeitschr. f. anorg. Chem.,* 11, p. 404, 1896.

CHAPTER IX

COLLOIDS AND ADSORPTION

The importance of colloid chemistry need not be emphasized, since it has been recognized that in the organic world colloids play an important rôle. Since the time when Thomas Graham, the father of colloid chemistry, made his famous discovery which led to the now obsolete distinction of crystalloids and colloids (1861), this subject has been invariably dealt with in almost every text-book of inorganic chemistry in the chapter on silicon, as if the colloid state was primarily characteristic of this substance. During the past twenty-five years, however, it has been realized that colloid properties are not connected with some definite chemical composition, but that all materials may occur in the colloid state.

186. In order to illustrate this point clearly sodium chloride is exhibited in different degrees of subdivision as follows: a large crystal of rock salt, finely powdered table salt, Karczag's sodium chloride gel[187] (preparation see below) and an aqueous solution of sodium chloride.

The sodium chloride gel is prepared in advance by placing 20 grams of thionyl chloride ($SOCl_2$) in a wide-mouthed, glass-stoppered bottle and adding, without shaking the vessel, about 18 grams of previously dried sodium salicylate. The bottle is loosely closed and left standing for 24 hours under a good draft hood. A beautiful reddish-green gel, which under suitable pre-

[187] *Biochem. Zeitschr.*, 56, p. 117, 1913.

cautions remains stable for a couple of weeks, is produced.[188]

187. Instead of sodium chloride sulphur may be shown in various stages of subdivision:

1. Large crystals of rhombic sulphur.
2. Roll sulphur (micro-crystallinic).
3. Flowers of sulphur (microscopic sulphur globules).
4. Colloid sulphur sol (see exp. 195 and 205).
5. Solution of sulphur in carbon bisulphide.[189]

Colloid chemistry deals with matter in a sufficiently finely divided state or, as Bancroft[190] has so aptly said: "It is the chemistry of bubbles, drops, grains, filaments and films." The chief characteristic of a colloid substance lies in its *specific surface* (expressed by the quotient of absolute surface by the total volume of the disperse phase, according to Wo. Ostwald). It is therefore readily understood that ad-(ab) sorption is intimately connected with colloids and for this reason is included in this chapter. Speaking of colloids in general, colloid solutions are usually meant, as distinguished from colloid precipitates or gels. In the following experiments colloid solutions will be considered first, and chiefly those in which *water* is the dispersion medium, while the finely subdivided discontinuous phase,—the disperse phase—is either a *solid* or a *liquid* (perhaps of complex nature). The whole system is conveniently called: *dispersoid.*

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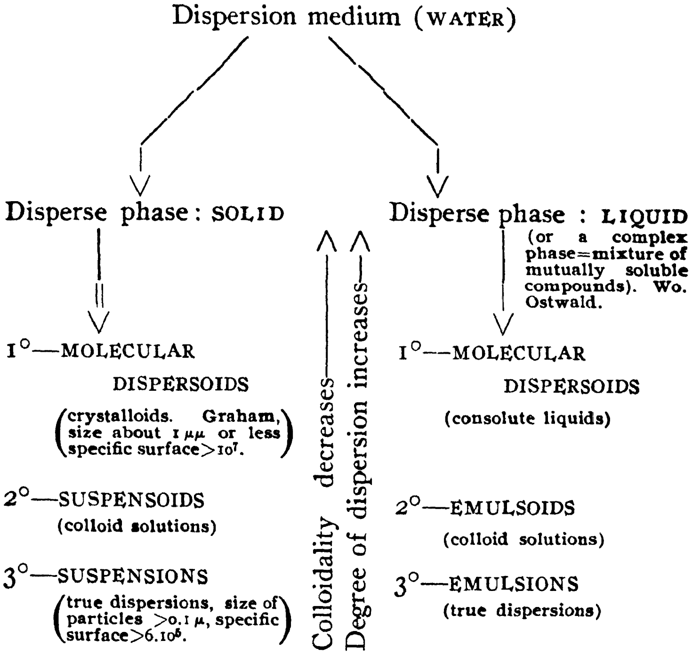
[188] Ostwald-Wolski, *l. c.*, p. 9.

[189] *Ibidem, l. c.*, p. 154.

[190] Applied Colloid Chemistry, New York, p. 2, 1921.

This leads to the following rough classification: (Wo. Ostwald).[191]



As will be seen from this table colloid solutions (suspensoids and emulsoids) occupy an intermediate position, although in reality no sharp boundary line can be drawn between colloid solutions and "real" solutions on one side or between colloid solutions and suspensions or emul-

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[191] Handbook of Colloid Chemistry, American edition, by M. Fischer. p. 33, 1915.

sions on the other side. There is, however, a rather wide gap between typical emulsoids and typical suspensoids, although it must be admitted that transitions between these two groups have been observed in a number of cases.[192] It has been found for instance that some chemical substances like soaps, many dyes, etc., form emulsoids in water and suspensoids (or molecularly dispersed solutions) in alcohol. Likewise some hydroxides, especially those of iron behave like suspensoids in dilute aqueous solutions and like emulsoids in concentrated solutions.

The experiments, described below, are subdivided for the sake of convenience into the following nine groups:

A. Preparation of suspensoids.
B. Preparation of emulsoids.
C. Mechanical properties of dispersoids.
D. Optical properties of dispersoids.
E. Electrical properties of dispersoids.
F. Factors affecting the stability of dispersoids.
G. Suspensions and emulsions.
H. Gels and reactions in gels.
I. Adsorption.

A. Preparation of Suspensoids

According to the appearance of the materials used and the manner in which the colloid solutions are obtained we can divide the methods for preparing suspensoids in two classes:

I. Condensation methods and
II. Dispersion methods.[193]

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[192] Ostwald-Fischer, *l. c.*, pp. 44, 45, 55, 56, 136, 147.

[193] Svedberg, Nova Acta, Upsala (4), 2, No. 1, p. 3, 1907.

I. Condensation Methods

Condensations are processes in which matter is brought together within a smaller boundary surface. There is decrease in surface with the concomitant loss (liberation) of energy and for this reason condensation methods are more numerous and more common than dispersion methods. In order to condense matter in a liquid medium it is in the first place necessary to produce a state of *supersaturation.*

188. The simplest way to accomplish this is cooling. On cooling a large test-tube containing a boiling hot solution of benzene in water, in crushed ice, the water becomes supersaturated with benzene and the latter separates out in minute particles giving the liquid a milky appearance. The solution is unstable.

189. In some cases heating accomplishes the same result. A mixture of 15 cc. of pyridine, 100 cc. of water and 10 grams of anhydrous potassium carbonate gives a clear liquid which on heating above 20° becomes turbid. This sol is well adapted for the demonstration of the Tyndall phenomenon (see p. 173).

It may be remarked that the above mixture is a beautiful illustration of a liquid with a lower and an upper critical solubility temperature. Heating above 92° results again in a clear liquid. (See Chapter VIII, exp. 172).

190. Supersaturation is also achieved by means of the dilution process which consists in pouring a few drops of a non-aqueous solution of the substance to be dispersed in a large excess of water. Thus colloid solutions of sulphur and selenium of great stability are formed by dissolving pulverized sulphur and selenium (either the red amorphous or the greyish crystalline modification) in a few cubic centimeters of hydrazine hydrate and pouring two or three drops of the dark viscous liquid in several liters of water. In this way an intensely red colloid solution of selenium and a yellowish white colloid solution of sulphur are obtained.[194]

Finally supersaturation can be produced by means of chemical reactions which furnish the disperse phase in a concentration high with respect to its solubility. For a successful reaction it is necessary that the solubility of the colloid material in the dispersion medium is low, the ion concentration not too high and the temperature (as a rule) low. The chemical reactions can be subdivided as follows:

a. Reductions.
b. Oxidations.
c. Dissociations.
d. Double decompositions.
e. Hydrolyses (special case of d).

Ia. Reductions.

Reduction methods are chiefly confined to the noble metals and have been applied for a great many years. Gold hydrosols were prepared already in the eighteenth century by the reduction of gold chloride solutions with urine or ethereal oils and were known to the alchemists under the name of aurum potabile. Since Faraday's

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[194] Meyer, *Ber. d. chem. Ges.*, 46, p. 3089, 1913.

classical researches on colloid gold (1856) an enormous amount of work has been done on the preparation of colloid metals by the reduction process. Zsigmondy (1898) employed formaldehyde, Gutbier (1902) hydrazine and hydroxylamine, Donau (1905) carbon monoxide, Vanino (1906) hydrogen and Amberger (1912) lanolin. Numerous other, mostly organic, reducing agents have been successfully used. The following preparations are easily made by the reduction method.

191. A few drops of a 1 per cent solution of gold chloride, neutralized towards litmus with sodium carbonate, are added to 100 cc. of distilled water (sometimes even tap water will do) placed in a small Erlenmeyer flask. A few drops of a freshly prepared solution of tannin (1 gram in 1000 cc.) are then added and the whole heated over a Bunsen burner with constant shaking. A pure wine-red sol is obtained.[195] The color deepens by adding alternately, little by little, more gold chloride and more tannin. This sol is rather stable owing to the fact that the tannin acts, in part at least, as a protective colloid. For this reason this sol should not be used for subsequent experiments. (The same remark applies to the silver sol prepared in experiment 194).

192. A blue gold sol is obtained by using phenylhydrazine chlorhydrate as reducing agent. Using again 100 cc. of a 0.01 per cent solution of neutralized gold chloride, it will be seen that on adding a very dilute

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[195] Ostwald-Wolski, Kleines Prakticum der Kolloid Chemie, Third Ed., p. 2, 1922.

solution of $C_6H_5NH.NH_2.HCl$ (a small crystal dissolved in 20 cc. of water) a blue gold sol is produced at once.[196] Too little of the reagent gives a violet color, a too strong solution produces a bluish-black liquid from which the gold precipitates after a while.

193. A beautiful, finely dispersed, red gold sol is produced by passing carbon monoxide (prepared by dropping sulphuric acid from a separatory funnel, fitted in a small distilling flask containing formic acid, in the acid, gently warmed over a small flame) into a very dilute (0.01 per cent) neutralized gold chloride solution.[197]

194. Silver-hydrosols are less stable. A useful preparation, however, is obtained in the following manner.[198] To 5 cc. of a 1 per cent solution of silver nitrate is added, drop by drop, a dilute ammonia solution, until the first formed precipitate exactly disappears, and then diluted with distilled water to a 100 cc. By mixing equal volumes of this solution and a 2 per cent tannin solution a clear and transparent, brown silver-hydrosol results, which sometimes shows a green color in reflected light.

Ib. Oxidations.

There is only one oxidation process that deserves mention: the oxidation of hydrogen sulphide to sulphur, according to the equation: $2H_2S + SO_2 = 3S + 2H_2O$. Thio-acids are also formed:

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[196] Ostwald-Wolski, Kleines Practicum der Kolloid Chemie, Third Ed., p. 3, 1922.

[197] Donau, *Monatshefte der Chemie,* 26, p. 525, 1905.

[198] Hatschek, Physics and Chemistry of Colloids, London, p. 8, 1913.

$$5H_2S + 10H_2SO_3 = 3H_2S_5O_6 + 12H_2O.$$
$$5H_2S + 10SO_2 = 3H_2S_5O_6 + 2H_2O.$$

195. On passing hydrogen sulphide into solutions of sulphur dioxide of different strengths a number of sols of varying degree of dispersion (depending on the concentration) are obtained. The maximum amount of colloid sulphur is formed at a strength of 0.9N, very little at 0.45N and only a trace at 0.225N.[199]

Ic. Dissociations.

Only a few cases of dissociations are known. One of them is the dissociation of nickel carbonyl:

$$Ni(CO)_4 = Ni + 4CO.$$

196. A colorless, dilute solution of nickel carbonyl (made by passing CO at 50° C. over Ni-wire, previously oxidized and then reduced by H_2) in benzene, when boiled (care) gives a violet bluish-gray nickel benzosol which can be kept for 1-2 days.[200]

Id. Double Decompositions.

Among these reactions which are quite numerous may be mentioned the formation of salt sols and sulphide sols. As a rule double decompositions have to be carried out in the absence of electrolytes, the latter having the tendency to precipitate the suspension colloids. Therefore only very dilute solutions can be used, so that the small quantity of electrolyte, if formed in the reaction, will not do any harm; on the contrary it is well-

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[199] Svedberg, the Formation of Colloids, London, p. 85, 1921.

[200] Wa. Ostwald, *Kolloid Zeitschr.*, 15, p. 204, 1914.

known that traces of electrolytes increase the stability of suspensoids.

For lecture experiments the following preparations of this type may be performed.

197. By mixing equal volumes of N/50 ferric chloride solution and N/50 potassium ferrocyanide solution a colloid solution of prussian blue is obtained,[201] which is so dense in color, that it is only transparent in thin layers.

198. Wo. Ostwald[202] prepares this solution in a different manner: One hundred cc. of a saturated ferric chloride solution are added with stirring to 50 cc. of a saturated solution of potassium ferrocyanide. A thick blue paste results which does not flow on turning the cylinder containing the mixture upside down. On stirring a little of this paste in a large volume of distilled water a clear fairly stable colloid solution of ferri-ferrocyanide results which runs through a folded filter.

199. Two hundred cubic centimeters of a 1 per cent solution of arsenious oxide (As_2O_3), (prepared by boiling water, containing 12 grams of the oxide, cooling and filtering the solution) are mixed with 200 cc. of a saturated solution of hydrogen sulphide. A turbid yellow solution is formed, which can be filtered through a folded filter.[203]

200. Two hundred cubic centimeters of a one-eighth molar solution of mercuric cyanide and an equal volume of a saturated hydrogen sulphide solution are simultane-

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[201] A. A. Noyes, *Journ. Am. Chem. Soc.*, 27, 85—104, p. 93, 1905.

[202] Wo. Ostwald, die Welt der vernachl. Dimensionen, 3rd ed., p. 22.

[203] Noyes, *l. c.*, p. 93.

ously poured in a beaker. The resulting black liquid passes almost completely through a folded filter.[204]

201. Two grams of tartar emetic are dissolved in 100 cc. of water and mixed with an equal volume of the common strong ammonium sulphide solution diluted to one-twenty-fifth of its strength. The color changes gradually into orange-yellow by the formation of an antimony sulphide sol.[205]

202. A black silver sulphide sol is obtained by bubbling hydrogen sulphide through 0.002N silver nitrate.[206]

Ie. Hydrolyses.

203. Hydrolysis of salts affords another means for preparing suspensoids. Thus a dilute iron hydroxide sol,—which behaves like a suspensoid—, of great stability, is obtained by heating 500 cc. of water to boiling in a large Erlenmeyer flask or a 800 cc. beaker, and adding to the boiling water 1 cc of a 33 per cent solution of ferric chloride freshly prepared by dissolving anhydrous ferric chloride in water. A clear sol of a beautiful reddish-brown color is formed. The same amount of solution added to 500 cc. of cold water (for comparison) produces a faint yellow solution.[207]

204. By pouring a dark red solution of ferric ethylate (see exp. 158) into a large volume of water a dilute iron hydroxide sol is also obtained.[208]

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[204] Noyes, *l. c.*, p. 93.

[205] Hatschek, *l. c.*, p. 8.

[206] Friedrich and von Hahn, *Kolloid Zeitschr.*, 29, p. 139, 1921.

[207] Ebler and Fellner, *Ber. d. chem. Ges.*, 44, p. 1915, 1911.

[208] Grimaux, *Comptes rendus*, 98, p. 105, 1884.

II. Dispersion Methods

There are comparatively few dispersion methods. According to Svedberg[209] only two groups exist: (a) partial dissolution, (b) grinding. Wedekind and Kuzel's methods of colloidation are not quite understood but are probably a real dispersion combined with peptization. Kuzel's colloids are at present of great industrial importance. When coagulated and pressed through fine holes thin wires result, which on sintering harden and can then be used for incandescent lamps. By the simple process of grinding secondary aggregates are often formed which prevent an effective colloidation. Pihlblad[210] has succeeded in making colloid sulphur with the aid of an indifferent solid as the following experiment shows.

205. Five grams of sulphur rolls are ground for a few minutes in an agate mortar. A small quantity (0.5 gram) is then added to 5 grams of urea and the whole well ground. Half a gram of this mixture is then ground after mixing with 5 grams of urea. Finally 0.5 gram of this second mixture is ground with another 5 grams of urea. These four powders are placed in four cylinders each containing 100 cc. of distilled water. After shaking it will be seen that only the second and the third cylinder contain colloid sulphur sols while the fourth shows a mere trace of turbidity.

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[209] *l. c.*, p. 107.

[210] Diss. Upsala, p. 46, 1918.

Electrical disintegration processes as carried out by Bredig,[211] Svedberg[212] and others are in reality a vaporization and condensation of the vapor in the liquid surrounding the arc.[213] Most text-books still classify these methods as dispersion methods and for this reason they are described under this heading.

206. Following Bredig's directions, two short wires of the metal to be dispersed (usually platinum, gold or silver), 1-3 millimeters in cross-section, are attached to stout copper wires. Each wire is insulated by slipping small capillary glass tubes over it, leaving a free end of 1 centimeter. Both are connected with the terminals of a 110-volt direct-lighting circuit, having a suitable resistance (a 20-ohm rheostat or a 32-candlepower lamp) in series, in order to secure a current of 4-5 amperes.

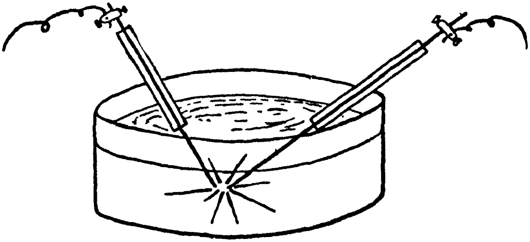

Fig. 53

Pure distilled water (to which in the case of Au a little 0.001N NaOH is added) is then placed in a crystallizing dish, 10 centimeters in diameter, cooled by ice water in

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[211] Anorganische Fermente, Leipzig, 1901.

[212] *Ber. d. chem. Ges.*, 38, p. 3616, 1905; p. 1705, 1906.

[213] Svedberg, *l. c.*, p. 23.

a larger surrounding dish. (Fig. 53) The ends of both wires are then dipped in the water, brought in contact and immediately separated 1-2 millimeters, so as to form an electric arc in the water. One of the wires is suitably fastened to a clamp stand; the glass-insulated part of the other is grasped in the hand. The arc is maintained for about 10 minutes, taking care, each time that the arc disappears, to unite and separate the ends of the wires, or in case of fusing together, to re-form the required distance. The solution, thus obtained is filtered and kept in a stoppered bottle. Its color is greenish-brown for silver, red for gold and black for platinum. The gold sol contains about 150 milligrams of gold, the platinum sol about 200 milligrams of platinum per liter.

207. The electrical dispersion can sometimes take place without arc formation. Muller and Lucas[214] place a small rod of pure tellurium as cathode opposite a platinum wire at a distance of about 5 centimeters in a beaker filled with distilled water. On applying a potential difference of 220 volts (or less) brown clouds are formed and a colloid solution of tellurium is obtained. In the case of the non-conducting metalloids selenium and sulphur a small quantity of these elements is fused on to a platinum foil, placed as cathode in pure water, opposite a platinum wire at some distance. Red selenium- and milk-white sulphur sols are obtained.

Washing out- and peptization processes, also frequently classed as dispersion methods will be taken up later (see p. 187).

[214] *Zeitschr. f. Electrochemie,* 11, p. 521, 1905.

B. Preparation of Emulsoids

Examples of this class of colloids are the proteins (like egg-albumen), gelatin, agar-agar, starch dextrin, many gums, silicic acid, stannic acid, many hydroxides in concentrated solution (iron for instance) dye-stuffs (like night-blue, benzo-purpurin, azo-blue, etc.). The preparation of these colloids does not require any special description.

208. As characteristic lecture demonstration types, besides the classical silicic acid usually gelatin or agar-agar solutions (containing 1-5 grams in 100 cc. of water) are selected.

209. Mercury sols although according to Wo. Ostwald's definition emulsoids are, as far as their prop-

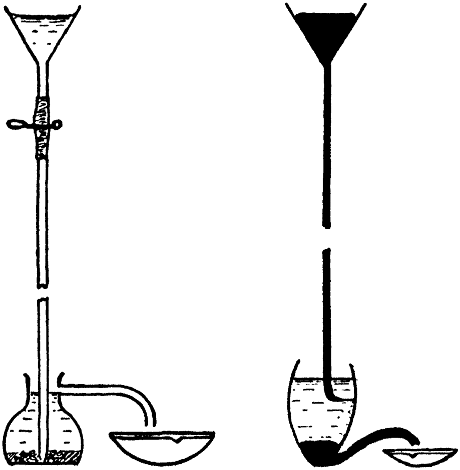

Fig. 53A and B

erties are concerned, on a level with suspensoids. Nordlund[215] gives two interesting methods for making mercury sols (Fig. 53A and B). In the first one (Fig. 53B) mercury is ejected through a fine horizontal point against a glass wall under water containing a trace of potassium citrate (0.0025N solution). The mercury drops are crushed against the glass and a slight coarsely dispersed sol results. On the other hand the formation and breaking up of lamellae (dispersion and subsequent condensation) gives a highly disperse hydrosol in the same solution of citrate (Fig. 53A).

C. Mechanical Properties of Dispersoids

Among these will be described:

I. Diffusion.
II. Dialysis and Ultrafiltration.
III. Viscosity.
IV. Surface Tension.

I. DIFFUSION EXPERIMENTS

210. An easy method for distinguishing between true solutions and colloid solutions is based on diffusion. Wo. Ostwald[215*] uses 5 per cent gelatin solutions which, while hot, are poured in test-tubes, until these are halfway filled and then allowed to congeal. Care must be taken that the gelatine is thoroughly washed and purified. To this end a hot 25 per cent solution is filtered through a porcelain funnel, the filtrate allowed to solidify, cut in small cubes and the latter placed in distilled water in

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[215] Svedberg, *l. c.*, p. 111.

[215*] Ostwald, Fischer, *l. c.*, p. 9.

which electrolytes diffuse. The wash water is decanted and fresh water added from time to time. The pure product which contains about 20 per cent gelatine can be kept for months under water to which a little chloroform is added.[216] The solid layers in the two test-tubes are covered with As_2S_3-sol and K_2CrO_4-solution respectively (same color). The result of the diffusion is clearly visible after 24 hours. The yellow sol, being a colloid, has not perceptibly spread into the jelly while the chromate which forms a true solution has passed into it for a considerable distance so that the originally sharp boundary surface is hardly visible.

211. In a similar way Noyes[217] showes this difference in speed of diffusion between crystalloid and colloid solutions. Two cylindrical sticks of agar-jelly, 5 centimeters in diameter and 15 centimeters in height are prepared by pouring a hot 4 per cent solution of agar-agar into large glass tubes, corked at one end. When cold, the solid sticks are pushed out and placed in two lecture jars of which one is half-way filled with a nearly saturated solution of copper sulphate, treated with enough ammonium hydroxide to redissolve the precipitate first formed, while the other contains a colloid solution of prussian blue, made by mixing equal volumes of N/50 solutions of ferric chloride and potassium ferrocyanide. After the diffusion has been in progress for two days, the result is shown to the audience by removing the sticks and cutting them in two. The blue copper solution has pene-

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[216] Svedberg in Stähler's Handbuch, IV, (1), p. 186, 1916.

[217] Noyes, *l. c.*, p. 90.

trated the stick uniformly to the very center, while the prussian blue has not entered into the stick over any perceptible distance, thus proving, that colloid solutions practically do not diffuse at all. Accurate measurements by Voigtländer[218] have brought out that the diffusion of crystalloids is not appreciably influenced by jellies, provided these are not present in greater percentage than 3-5 per cent.

II. Dialysis and Ultrafiltration

The fact established by the foregoing experiments, that one colloid (the solid jellies being nothing else but gelatinized emulsoids) is practically impermeable by another, leads to their recognition as dialyzing membranes. Dialysis therefore, is intimately connected with diffusion. Every substance, which does not diffuse appreciably, but allows itself the passage of crystalloids may be used as a dialyzer, and inversely we might say "that any membrane, which permits the passage of a crystalloid and hinders the passage of a colloid, is itself a colloid."[219]

Such membranes are parchment, (first used by Graham in 1861) fish-bladder, urinary bladder, egg-membrane, parchment paper and collodion film (in sheet or tube form) as introduced by Malfitano (1904).

The process of dialysis requires too much time to show marked results in the course of one lecture hour. Besides the classical Graham dialyzer some modern types of dialyzer in tube form (made of parchment paper or

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[218] *Zeitschr. f. phys. Chem.*, 3, p. 316, 1889.

[219] Bigelow, *l. c.*, p. 246.

collodion) and the new "star-dialyzer," devised by Zsigmondy and Heyer[220] may be demonstrated.

212. To show the extreme facility, with which crystalloids pass through a parchment membrane, a solution of potassium thiocyanate (KCNS) is put inside a flat Graham dialyzer, which is then left floating in distilled water for 1 or 2 minutes. On adding ferric chloride to the outside water a red color appears, demonstrating that the inside crystalloid passes readily through the membrane.[221] Placing a colloid solution of prussian blue into a second parchment dialyzer, no perceptible trace of a blue coloration is seen in the outside water, not even after several hours.

213. The difference in efficiency in using different membranes may be conveniently illustrated[222] by pouring a moderately concentrated solution of fluoresceïn into a parchment paper tube and into a similar collodion tube. Both tubes are inserted in large lecture jars, filled with tap water. The dye-stuff diffuses after a short time through the collodion membrane, as is shown by the rapid appearance of green fluorescent bands in the outside water, while it takes a considerable time to pass through the parchment membrane.

214. The collodion tubes, as used by many colloid-workers (Malfitano, Henry, Duclaux, Biltz, Bigelow and others) are made—as is easily demonstrated in the lecture—by sticking large well-cleaned bulb test-tubes

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[220] *Zeitschr. f. anorg. Chem.*, 68, p. 169, 1910.

[221] Bigelow, *l. c.*, p. 244.

[222] Zsigmondy, Kolloidchemie, Leipzig, p. 33, 1912.

(Fig. 54) into solutions of collodion in ether, ether and alcohol, or acetic acid and water, allowing the layer to harden in the air and repeating the process two or three times if necessary, finally hardening the whole by washing in water. The collodion coating is then cut off in the middle of the bulb and carefully stripped off. Details may be looked up in Bigelow and Gemberling's article[223] on "collodion membranes."

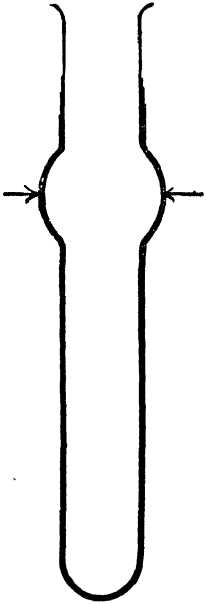

Fig. 54

215. With the aid of these collodion thimbles the principle of ultrafiltration which serves to (partially or completely) separate the disperse phase from the dispersion medium can be demonstrated. Using a collodion sack connected airtight to a funnel, the latter fitted in a suction flask, it will be seen that, on carefully applying suction by means of the water pump, a colorless filtrate is obtained from a sol placed in the thimble (gold-, silver- or other sol) (Fig. 54A).

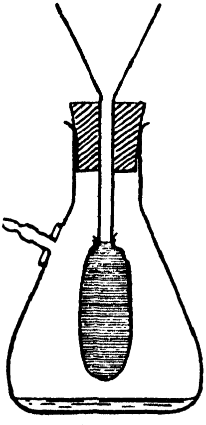

Fig. 54A

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[223] *Journ. Am. Chem. Soc.*, 29, pp. 1576-89, 1907.

III. Viscosity Experiments

216. The viscosity of suspensoids does not perceptibly differ from that of pure water; the viscosity of emulsoids on the other hand, even at small concentration is much greater than that of water and increases rapidly on cooling, while suspensoids do not assume an oily or even a gelatinous appearance on lowering the temperature. This is most readily shown[224] by allowing 10 cc. of a 2 per cent gelatin solution (an emulsoid) and 10 cc. of colloid arsenious sulphide (a suspensoid) to flow simultaneously from two 10 cc. pipettes with capillary tips which are as nearly alike as possible. The time of outflow, which is —roughly speaking—directly proportional to the fluidity or inversely proportional to the viscosity, is much longer for the emulsoid solution. Test-tubes with both solutions, cooled in ice water, show a marked difference; the gelatin solution changes into a thick jelly; the suspensoid does not gelatinize at all.

217. On standing many (solvated) emulsoids change their viscosity to a marked extent as can be seen by comparing the flow of freshly prepared solutions with those that have stood for some time. Gelatine sols increase their viscosity while starch sols decrease their viscosity.

218. Finally the effect of additions of salts and of non-electrolytes on the viscosity of emulsoids is readily demonstrated.[225] A pure gelatine sol of about 2 per cent

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[224] Ostwald-Fischer, *l. c.*, p. 13.

[225] Wo. Ostwald, die Welt der vernachl. Dimensionen, Third Edition, p. 70.

solidifies to a gel which can be broken up by shaking the test-tube containing the gel. The same sol treated with a little solid magnesium sulphate gives a much more rigid sol. In a third tube some crystals of potassium iodide added to the same sol prevent solidification: the sol remains liquid. A non-electrolyte like urea likewise lowers the viscosity: some urea added to a fourth tube containing the sol keeps the sol in a liquid state.

IV. SURFACE TENSION

219. From careful measurements it has been deduced, that coarse suspensions and suspensoids hardly alter the surface tension (against air) of the dispersion medium (water); emulsions and emulsoids on the other hand decrease the surface tension of their dispersion medium. This difference, therefore, can be used for discriminating between both classes of colloids.[226] The decrease of surface tension is manifested by the more or less easy formation of foam. Thus by shaking two glass-stoppered bottles, containing arsenious sulphide sol and a dilute solution of venetian soap (or egg albumen) respectively, only in the latter case an abundant foam formation is observed. Instead of shaking the liquids, an indifferent gas, like nitrogen or air may be bubbled through.

D. Optical Properties of Dispersoids

220. Differences between true solutions and dispersoids become visible by exposing the liquids to be examined to the light of a powerful incandescent lamp (arc-light), or

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[226] Ostwald-Fischer, *l. c.*, p. 183.

still better, to a beam of sunlight entering the darkened lecture room through a hole in the window shutter. Usually a condenser with diaphragm is used to concentrate the light on the liquid, contained in a beaker or a Dewar tube (in case hot or very cold liquids are tested). The heterogeneity of colloid solutions is then easily recognized by a more or less opaque cone of light, caused by the diffuse reflection of light from the discrete particles present in the liquid. This is the so-called "Tyndall phenomenon." Suitable demonstration liquids are: a ferric chloride solution, a dilute ferric hydroxide sol (preparation, see p. 161), having the same color, a gold sol (preparation, see p. 157) and an arsenious sulphide sol. In the case of the ferric chloride solution the cone is hardly visible, in the other cases Tyndall cones of slightly different turbidity are observed. Experiments by Wolski[227] show that the optical inhomogeneity of solutions of hydrolyzed salt like ferric- and aluminium chloride can be removed by traces of acid. The faint turbidity often observed in the case of concentrated crystalloid solutions like citric acid, sucrose and saccharin is to be attributed to the presence of foreign substances (dust particles). Ultrafiltration of these solutions gives liquids which are optically empty.

221. That the diffuse light of a Tyndall cone is polarized and thereby distinguishable from fluorescence can be shown to a large audience by throwing the light of an arc lamp through a lens and a nicol (mounted in a collar and the latter fastened in the side wall of a small box

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[227] *Kolloidchem. Beihefte,* 13, p. 137, 1920.

blackened on the inside) on the colloid solution contained in a square glass cell with parallel sides (Fig. 55). The cone is colored and by turning the nicol through 90° or 270° the complementary color appears (change from red to light green). The phenomenon is very pronounced with mastix or rosin suspensions[228] (preparation, see exp. 243).

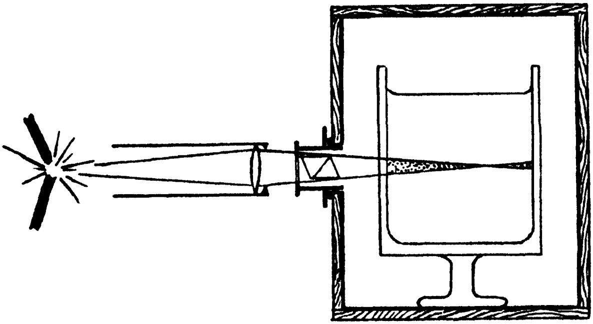

Fig. 55

A somewhat better arrangement which allows the phenomenon to be observed anywhere is to let the polarized light fall vertically by means of a reflecting mirror in a tall cylinder containing the colloid solution.[229]

E. Electrical Properties of Dispersoids

The most striking reactions shown by colloid solutions are those connected with their electric behavior. The fact that many substances in colloid solution assume an

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[228] Hatschek, Laboratory Manual, p. 77.

[229] This arrangement was suggested to the author by Dr. Kruyt.

electric charge towards the dispersion medium may be illustrated by migration experiments. Taking as examples two typical suspensoids of opposite character such as silver sol and ferric hydroxide sol suitably dialyzed before use the following migration experiment may be performed.[230]

222. A U-shaped tube (length of limbs about 10 centimeters; diameter 1-1.5 centimeters) is half-filled with silver sol and covered in both limbs by a 0.01 per cent sodium hydroxide solution, in order to increase the stability of the sol. A second tube is filled with ferric hydroxide sol covered by a 0.01 per cent sodium acetate solution. For these and similar experiments U-tubes with two stop-cocks, having the same bore as the inner cross-section of the tube, as devised by Coehn[231] (Fig. 56), are very useful. These tubes are half-filled with the solutions to be used, the stop-cocks are then closed, the excess of the liquid poured out, the upper parts of both limbs rinsed with distilled water and filled to the same height with the required solution. Platinum electrodes are then inserted, the stop-cocks opened and the current passed through. In the above mentioned experiment both U-tubes are connected in series with the

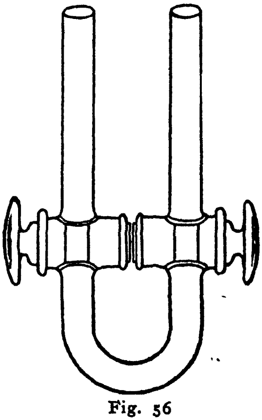

Fig. 56

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[230] Forster, *die chemische Industrie*, 28, p. 733, 1905.

[231] *Zeitschr. f. Electrochemie*, 15, p. 653, 1909.

terminals of the 220-volt direct-current lighting circuit. After 20-30 minutes it will be seen, that the silver sol has moved towards the anode, the iron hydroxide sol towards the cathode. No actual separation on the electrodes occurs, the visible effect being limited to a more or less dense cloud, collecting in the neighborhood of the electrodes. Disturbing effects like convection currents often affect the phenomenon.

223. A more elaborate arrangement, insuring very good results, for the demonstration of colloid migration in an electric field—sometimes called "electrophoresis" or "cataphoresis,"—was given by Noyes.[232]

The suspensoids used for this purpose were arsenious sulphide sol and ferric hydroxide sol. The latter had been prepared by adding to a *molal* ferric chloride solution a *molal* ammonium carbonate solution until the precipitate on each addition would barely dissolve. Both sols had been dialyzed for a week, first against distilled water and finally against the purest water obtainable (conductivity water), This was done to remove electrolytes as completely as possible, in order to avoid convection by the heat, produced by the current, causing disturbance of the moving surface. Two U-tubes, 15 centimeters in total height with a 3-centimeter bore covered at both ends with goldbeaters' skin, are completely filled by pouring the sols through a hole at the bottom of the bend, 1 centimeter in diameter, closed by slipping a rubber band over it. The limbs of each tube are surrounded by glass tubes of a slightly greater diameter

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[232] Noyes, *l. c.*, p. 97.

and fitted tightly by means of rubber bands, connecting both glass walls. These tubes extend about 5 centimeters above the goldbeaters' skin and are filled with conductivity water (Fig. 57). After inserting platinum wire electrodes, the tubes are connected in parallel with the terminals of a 110-volt (if available 220-volt) direct-current lighting circuit with a copper coulomb-meter in series to indicate the direction of the current. After 5-10 minutes the ferric hydroxide sol is seen moving downward with a sharp boundary surface, leaving clear water

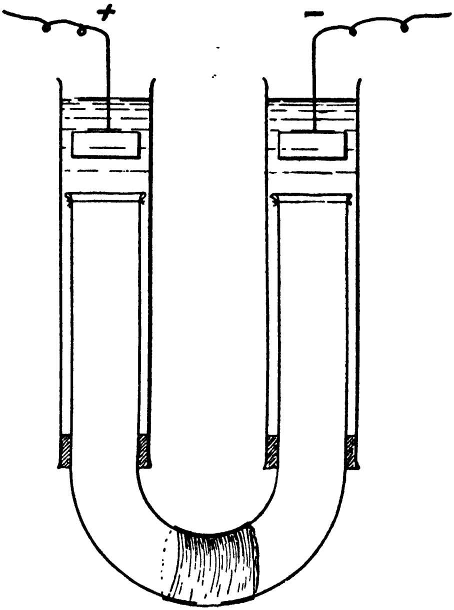

Fig. 57

above, towards the cathode, while the arsenious sulphide moves downward towards the anode, thus proving that the former possesses a positive charge, while the latter is negatively charged.

It should be remembered, that this phenomenon is not limited to suspensoids (and some emulsoids like egg-albumen) but is also observed in the case of suspensions like kaolin, quartz and lamp black. The reverse of this motion is called electrical "endosmosis," and was discovered by Reusz (1807). For the sake of completeness two experiments demonstrating this electro-osmosis may be cited.

224. A plug of cotton is tightly pressed into the constricted part of the tube, sketched in Fig. 57A. Platinum electrodes are inserted and the tube filled by pouring enough distilled water into the funnel on the left until no more water escapes through the capillary outlet on the

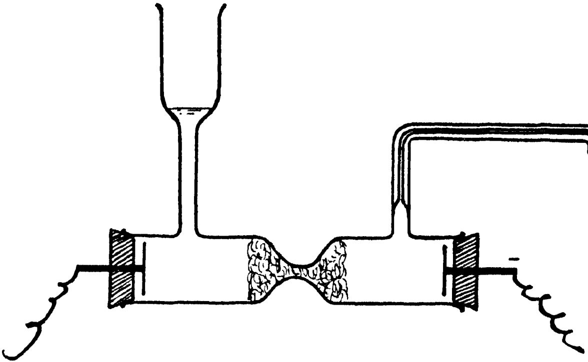

Fig. 57A

right. On connecting the electrodes with the terminals of the direct-current lighting circuit the water is seen moving towards the cathode as shown by the water droplets falling from the capillary tip.[233]

225. An interesting modification of the foregoing experiment is the following: An unglazed porcelain plate, covered with distilled water is supported on an iron ring, connected with the negative pole of the lighting circuit (220-volt, direct current), while the positive pole is formed by a lead disk, dipping in the water. (Fig. 58). As soon as the current is turned on, the water is seen dropping from the plate, a flow, which comes to a standstill on disrupting the connection.

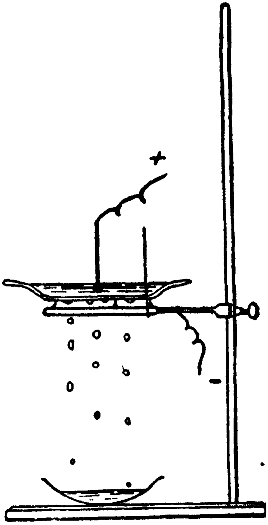

Fig. 58

On account of the different behavior in an electric field we distinguish between *negative* and *positive* colloids.

Examples of the first are, besides arsenious sulphide: antimony sulphide, gold, silver, sulphur, selenium, prussian blue, etc. Positive colloids are metallic oxides (iron, aluminium, etc.).

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[233] This shape of apparatus was suggested by Dr. Kruyt.

226. A simple method to discriminate between these two types of colloids without electrophoresis is based on capillary analysis, the use of which was introduced about fifty years ago by a Swiss chemist Goppelsroeder, and recently extensively applied in colloid chemistry by Fichter and Sahlbohm.

The experiment consists in dipping strips of filter paper into colloid solutions of (1) ferric hydroxide and (2) prussian blue. In the latter case the colloid ascends along with the water up the strip of paper over some 10-20 centimeters, depending on the kind of blotting paper used, while the ferric hydroxide shows a marked lag in rising. The dispersion medium (water) rises as high as in the case of the prussian blue sol, but the colloid phase (ferric hydroxide) rises only slightly above the level of the liquid, concentrates then and finally coagulates.[234]

A third method to determine the charge of an unknown colloid in solution is to test with two solutions of known character, such as ferric hydroxide sol (+) and arsenious sulphide sol (—).

This is based on the fact, that colloid solutions of opposite charge precipitate each other. If the unknown solution is precipitated by arsenious sulphide, it is positive, and in case ferric hydroxide sol is an effective precipitant, the unknown sol is negatively charged.

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[234] Ostwald-Fischer, *l. c.*, p. 15. This method has been criticized and condemned as being "fallacious" by Thomas and Garard, (*Journ. Am. Chem. Soc.*, 40, p. 101, 1918). It is therefore advisable to check the results of the "capillary analysis" by at least one other method.

227. In the lecture the formation of a precipitate, in bringing together these two typical sols ($Fe(OH)_3$ and As_2S_3) may be carried out.

About 150 cc. of dialyzed ferric hydroxide sol and 200 cc. of dialyzed arsenious sulphide-sol, prepared according to the foregoing directions (see p. 160 and 161) are simultaneously poured into a lecture jar; a flocculent precipitate is formed, leaving a clear solution above.[235]

228. In order to show the application on a large scale of mutual precipitation of colloid solutions of opposite electric charge, it is interesting to test for this purpose the waste water of some industrial plant, which usually forms a negative colloid solution.[236] The solution is filtered to separate particles suspended in the liquid. On addition of the required quantity of a dialyzed colloid solution of ferric hydroxide of known strength, a precipitate is formed, which settles after a few minutes, leaving a clear solution easily separated by filtration from the precipitate. The quantity of ferric hydroxide sol must correspond with the so-called *optimum* of precipitation,[237] and has to be found out by trial experiments before the lecture. Taking three different portions of the test solution, the second of which represents about the required amount, the effect of too much or too little ferric hydroxide sol can also be demonstrated.

229. Two colloid solutions of the same electric charge do not give a precipitate on mixing. Thus by bringing

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[235] Noyes, *l. c.*, p. 101.

[236] Baur, *l. c.*, p. 104.

[237] Biltz, *Ber. d. chem. Ges.*, 37, 1095, 1904.

together 200 cc. of an arsenious sulphide sol and 200 cc. of a gold-sol no precipitate is formed. The gold-sol is previously made by dialyzing a colloid gold solution, obtained by pouring an ethereal solution of dry gold chloride into an aqueous solution of acetylene.[238]

Precipitation of colloid solutions is easily brought about by the addition of electrolytes. Schulze and later on Linder and Picton found that the precipitating action of a salt is determined by the ion carrying a charge opposite to that of the colloid particle.

230. This is demonstrated in an elegant manner in the case of arsenious sulphide sol (negative) using new fuchsine as precipitating electrolyte. With different concentrations it is found that for a certain strength (on shaking the sol and the salt solutions in equal volumes) which is called the limiting value, the sulphide is completely thrown out and the supernatant liquid becomes colorless. The cation of the dye is then completely adsorbed (compare exp. 275). The limiting values vary widely for different cations. On the basis of a value of 58 for LiCl, HCl has a value of 31, aniline chloride a value of 2.5 and new fuchsine a value of only 0.11.

In a number of cases, especially when the discharging ion is very powerful certain irregularities are observed: for small electrolyte concentrations there is no precipitation; when the limiting value is reached complete precipitation occurs, for a somewhat higher concentration

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[238] Noyes, *l. c.*, p. 101.

no precipitation and for still higher concentration again flocculation. This is represented graphically in Fig. 58A

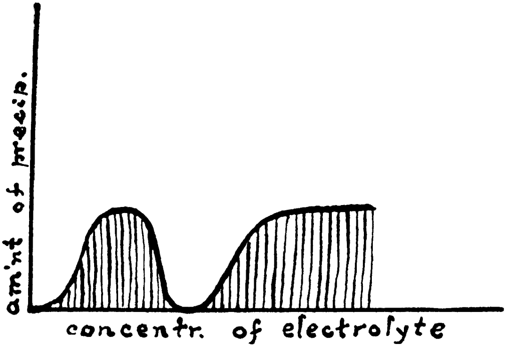

Fig. 58A

where the amount of precipitate is plotted against the concentration of electrolyte as abscissa.

231. The following experiment with mastix sol and aluminium chloride as precipitant illustrates this irregular series.[239]

A mastix sol is prepared by pouring 10 cc. of a 5 per cent solution of mastix in alcohol into 90 cc. of water. This concentrated sol is diluted to one-tenth of its strength and then filtered. In a series of thoroughly cleaned test-tubes 10 cc. of the sol are placed. Starting with a molar solution of aluminium chloride (No. 1) from which are obtained a number of dilute solutions each one of half the strength of the previous solutions 10 cc. of electrolyte is shaken with 10 cc. of sol. The result

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[239] Ostwald-Wolski, *l. c.*, p. 123.

is: complete flocculation for the numbers 1-5, no flocculation for 9-12, complete flocculation for 15 and 16, no flocculation for concentrations lower than 17.

Other examples may be found in the literature.[240]

The influence of the valence of the precipitating ion, as proved by experiments of Freundlich and others, is very pronounced and was demonstrated by Noyes[241] in the following manner:

232. A colloid solution of (negative) arsenious sulphide is made by mixing equal volumes of a 1 per cent solution of arsenious oxide and a saturated hydrogen sulphide solution and filtering the resulting liquid.

Fifty cubic centimeters of this sol are poured into each of seven conical lecture jars, containing 200 cc. of the following solutions, having in 1 liter dissolved:

(1) 0.6 milli-equivalent of $AlCl_3$.*
(2) 1.5 milli-equivalents of $MgCl_2$.
(3) 20.0 milli-equivalents of $MgCl_2$.*
(4) 60.0 milli-equivalents of NaCl.
(5) 400.0 milli-equivalents of NaCl.*
(6) 60.0 milli-equivalents of Na_2SO_4.
(7) 400.0 milli-equivalents of Na_2SO_4.*

Coagulation depends here on the cation, the $Al^{\cdot\cdot\cdot}$-ion having the strongest effect and the monovalent $Na^{\cdot}$-ion the least. The $Mg^{\cdot\cdot}$-ion occupies an intermediate position. Precipitation only occurs in the cases marked with an asterisk.

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[240] Kruyt and van der Spek, *Kolloid Zietschrift*, 25, p. 1, 1919.

[241] Noyes, *l. c.*, p. 102.

233. Taking a positive colloid like ferric hydroxide sol, it is the anion, that causes precipitation, trivalent anions having the greatest effect, monovalent anions the smallest, insofar that then the *greatest* quantity of salt is required to bring about precipitation.

To eight conical lecture jars, containing respectively 200 cc. of solutions having in 1 liter:

(1) 0.02 milli-equivalent of $K_3(FeCy_6)$.
(2) 0.10 milli-equivalent of $K_3(FeCy_6)$.*
(3) 0.10 milli-equivalent of Na_2SO_4.
(4) 1.60 milli-equivalents of Na_2SO_4.*
(5) 5.00 milli-equivalents of NaCl.
(6) 50.00 milli-equivalents of NaCl.*
(7) 5.00 milli-equivalents of $MgCl_2$.
(8) 50.00 milli-equivalents of $MgCl_2$.*

is added 50 cc. of the ferric hydroxide sol, whereupon precipitation is observed in the cases, marked by an asterisk.

While suspensoids are most readily precipitated by small quantities of electrolytes, emulsoids are not precipitated by the addition of salts unless in excessive amounts. The reason for this difference in behavior according to Kruyt[241*] is that emulsoids are hydrated suspensoids. They possess instead of one, two stability factors: electric charge and hydration. If only the charge is removed a hydrophilic sol remains while if dehydration alone occurs, a suspensoid results. This is

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[241*] *Inleiding tot de physische Chemie,* Amsterdam, p. 143, 1924.

expressed schematically in Fig. 58B and may be illustrated by the following experiment:

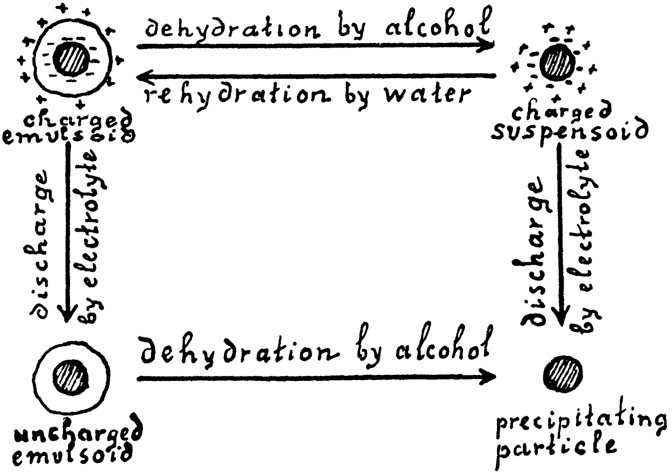

Fig. 58B

234. To a dilute agar sol (one-fifth per cent or less), free from electrolytes, is added a sufficient amount of 95 per cent alcohol. The sol loses its emulsoid character, the viscosity becomes that of the dispersion medium and the sol acquires the bluish appearance of mastix and sulphur sols. A small quantity of electrolyte solution is now sufficient to precipitate the sol.

Salting out combines discharge and dehydration. The effect is different for metal sulphates in the following "lyotropic" order: Li, Na, K, Rb, Cs, Mg.

235. Taking a number of test-tubes each filled with 5 cc. of a 2 per cent gelatine solution the effect of addition of 20 cc. of magnesium sulphate of 4 normal, 3 normal, 2 normal, normal and half normal strength is observed. A precipitate occurs only in the first tube.

236. The experiment is repeated using sodium sulphate solutions of corresponding strength. A precipitate is formed in both the first and the second tube, showing that sodium has a stronger effect than magnesium.

F. Factors Affecting the Stability of Dispersoids

The stability of dispersoids is largely dependent on the presence of protective agents. In certain cases as Svedberg has found non-electrolytes have a stabilizing effect. More frequently electrolytes stabilize colloid solutions but the most effective agents are organic colloids like gelatine, agar-agar and proteins which are spoken of as protective colloids. Experiments demonstrating the stabilizing action of electrolytes are given below.

I. PROTECTIVE ELECTROLYTES

As has been shown previously electrolytes precipitate suspensoids readily and only when the concentration is low they have a beneficial effect on the stability of the sol. Two ways are open therefore: to reduce the ion concentration to a suitable point (washing-out process) or to increase the ion concentration sufficiently in case there are not enough stabilizing ions (peptization process).

237. To a solution of silver nitrate (about tenth normal) is added in small portions a solution of potassium chloride (about tenth normal) taking care not to add an excess nor even an equivalent quantity of salt. The contents of the flask are shaken for a few minutes and then the bulk of the silver chloride precipitate transferred to a filter. The rest is washed out with small quantities of distilled water and the wash water poured on the filter. The first portions of the filtrate run through clear but after a while the filtrate becomes cloudy. The colloid silver chloride thus formed is collected separately. Finally on replacing the water by a dilute solution of ammonium nitrate the filtrate becomes clear again. The same phenomenon can be observed by adding a solution of mercurous nitrate to a neutral solution of potassium bichromate.[242]

The process of peptization is also a reversible coagulation and was first described by Berzelius (1833). Graham (1861) to whom the introduction of the term peptization is due, and Spring (1883) have carried out several investigations on the peptization of colloid hydroxides and sulphides. Cadmium sulphide sol may be prepared as follows:

238. The sulphide is precipitated by hydrogen sulphide from an ammoniacal solution of cadmium sulphate, the precipitate thoroughly washed and suspended in distilled water. Thus far the experiment may be completed before demonstrating the change from a suspension into a suspensoid. By passing hydrogen sulphide through the suspension, the latter becomes milky and turbid, until

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[242] Böttger, Qualitative Analyse, Third Edition, Leipzig, p. 121, 1913.

finally it changes into a clear, transparent suspensoid of a beautiful gold color.[243]

239. Instead of cadmium sulphide mercuric sulphide can be peptized in an analogous manner as was first done by Winssinger.[244]

II. PROTECTIVE COLLOIDS

The protective action of organic emulsoids like gelatine and egg albumen was first discovered by Lobry de Bruyn[245] and studied in detail by Zsigmondy.[246] The latter expresses the protective action of different colloids by means of their gold number *i. e.*, the number of milligrams of colloid which is just unable to prevent the precipitation of a standard gold sol by 1 cc. of a 10 per cent solution of sodium chloride.

240. The use of emulsoids in preventing the precipitation of dispersoids is demonstrated as follows:[247] Adding first 200 cc. of a N/50 sodium chloride solution to 200 cc. of a N/50 silver nitrate solution, containing 5 cc. of strong nitric acid (specific gravity 1.42), a white flocculous precipitate immediately forms.

The experiment is then repeated with equally strong solutions of both salts, containing 1 per cent of gelatin dissolved. The mixture becomes opalescent, and the

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[243] Prost, *Bull. de l'Ac. des sc. de Brux.*, (3), 14, p. 312, 1887.

[244] *Ibidem*, 15, p. 390, 1888.

[245] *Zeitschr. f. phys. Chem.*, 29, p. 562, 1899.

[246] Zur Erkenntnis der Kolloide, Jena, p. 67, 1905.

[247] Noyes, *l. c.*, p. 91.

turbidity increases after a while, without forming a precipitate.

241. Another experiment of the same type is the following: Half a gram of crystallized barium chloride is dissolved in 50 cc. of water and then 0.25 gram of ammonium sulphate in an equal volume of water. Five cc. of the first solution added to 5 cc. of the second produces a precipitate that settles in a few minutes.

The sulphate solution is warmed to 30°, 5 cc. of a 15 per cent gelatine solution added and after thorough mixing the chloride solution added with continuous stirring. No precipitate is formed and the liquid passes through a filter without leaving a residue.[248]

242. Instead of adding the emulsoid to one component of a reaction which produces a precipitate, the emulsoid can be added to an existing sol thus protecting the latter from electrolytes. Nine cc. of a gold sol (exp. 193) turn blue in a few seconds on adding 1 cc. of a normal sodium chloride solution. On adding to 9 cc. of the same sol 1 cc. of a dilute gelatine solution and thorough shaking, no change is noticed on the addition of one cc. of the sodium chloride solution.[249]

G. Suspensions and Emulsions

I. SUSPENSIONS

243. Suspensions of mastix, gutta-percha, etc., as were used by Perrin, Henri and others in their study of the Brownian movement may be obtained by pouring a few

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[248] Hatschek, Laboratory Manual, p. 96.

[249] Hatschek, *Ibidem,* p. 97.

drops of an alcoholic solution into an excess of water.

In about the same manner as suspensoids suspensions can be stabilized by suitable peptizing ions or by protective colloids as the following experiments demonstrate.[250]

244. Ordinary China clay is stirred up in water, so as to form a suspension, which settles out rather quickly, leaving a clear liquid above and sharply defined sediment below. If, however, a little alkali, or a salt with alkaline reaction is added, it will be observed that the settling takes place much more slowly, the smallest particles not settling out at all, or if so only very gradually. Instead of clay, fine suspensions of blood coal, lampblack, natural or artificial graphite or amorphous silica may be used. A maximum of stability was found for an alkali concentration of 0.008N.[251]

245. The mobility of a clay suspension containing a little acid is very much less than that of the same suspension with a trace of alkali as may be shown by allowing the suspensions (which must be rather concentrated) to flow down an inclined glass plate.

246. The protective action of soap solutions was first studied by Spring[252] as follows: A suspension of finely powdered rouge (or carbon black) is poured on a filter. All the solid material is retained and the filtrate is colorless. The same suspension is now treated with a little of a soap solution and after thorough shaking again thrown on the filter. A cloudy red filtrate is now obtained.

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[250] Whitney and Straw, *Journ. Am. Chem Soc.*, 29, p. 325, 1907.

[251] Whitney and Straw, *l. c.*

[252] *Zeitschr. f. Kolloidchemie*, 4, p. 161, 1909; 6, pp. 11, 109, 164, 1909.

After adding a little acid the soap is destroyed and the filtrate is again colorless.

247. Acheson has studied the protective action of tannin in detail.[253] Placing in three large test-tubes some finely powdered kaolin, and pouring in the first pure water, in the second and third an aqueous solution of tannin (2 per cent) to which a trace of ammonia is added, all three tubes are thoroughly shaken and then set aside. After a while the kaolin in the first tube settles while that in the other tubes remains suspended. Addition of electrolytes (NaCl or HCl) causes settling of the kaolin in the third tube. Protected suspensions of graphite (and colloidal graphite or aquadag) are likewise precipitated by electrolytes. Acheson[254] has coined a new word for the protective action of these colloids and speaks of "deflocculation."

II. EMULSIONS

IIa. OIL-IN-WATER EMULSIONS

248. An oil-in-water emulsion is readily obtained by injecting a fine stream of oil into water or by pouring an alcoholic solution of oil into water. This emulsion is unstable.

249. It can be shown that by lowering the surface tension of two immiscible liquids against each other, a stable emulsion is readily obtained.[255] In a beaker with

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[253] *Journ. Ind. and Eng. Chemistry,* 4, p. 62, 1912.

[254] Seventeen Years of Experimental Research and Development, p. 12.

[255] Donnan, *Zeitschr. f. phys. Chem.,* 31, p. 42, 1899.

water a thin layer of olive oil is poured. By stirring the mixture, an emulsion forms, which disappears rapidly. If, however, a few drops of potassium or sodium hydroxide are added, a milky emulsion is formed on stirring, which does not noticeably change, even after several hours.

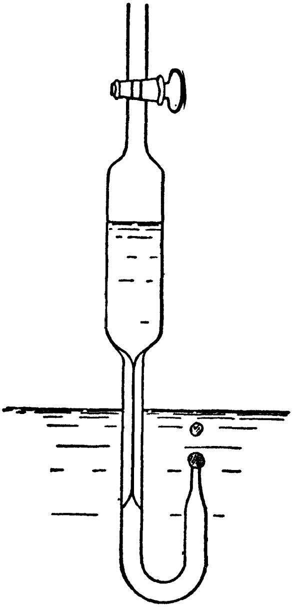

Fig. 58C

250. This decrease in surface, (or better, boundary-) tension can be followed on a measuring scale with the aid of Donnan's pipette and is most suitably made visible to a large audience by projection on the screen.[256]

The pipette, used for this purpose (Fig. 58C), is provided with a stopcock and a capillary outflow, bent upward. It is filled with olive oil (containing free fatty acid) or paraffin oil, to which a small amount of fatty acid (palmitic or steoric acid) has been added. By carefully opening the stop-cock the oil is allowed to slowly escape in water with the formation of well-shaped spherical drops which rise to the surface (10-20 drops in a minute). If now the

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[256] Donnan, *l. c.*, p. 42, cf. Hatschek, *l. c.*, p. 38; and Kruyt, *Chem. Weekbl.*, 10, p. 530, 1913.

water is replaced by a solution containing a few drops of a base (sodium or potassium hydroxide), the number of oil drops, formed in one minute is more than doubled or even changes into a continuous stream of small droplets, the rapid succession not allowing the number of drops to be counted.

Both phenomena may be explained on the basis of Willard Gibbs' theorem, stating that substances, which lower the surface tension of the dispersion medium, tend to collect in its surface. We must, therefore, assume, that the emulsification is caused by the strong superficial adhesion of the soap formed by the oil.

251. That the so-called "emulsifying agent" in the previous experiments is an alkali soap may be demonstrated as follows: In five test-tubes, marked 1, 2, 3, 4 and 5 are placed 10 cc. of water and 2 cc. of neutral olive oil. Neutral olive oil is obtained by dissolving the commercial oil in ether, shaking with dilute sodium carbonate solution, washing with water until free from alkali and distilling the ether. To the second tube is added 1 drop of sodium hydroxide solution (10 per cent), to the third 2 drops of oleic acid, to the fourth the same and 1 drop of NaOH solution and to the fifth 2 cc. of ordinary commercial olive oil + 1 drop of alkali. All tubes are thoroughly shaken. A *permanent* emulsion is formed only in tubes 4 and 5.

252. In the same way a permanent emulsion is obtained when oil or kerosene is shaken with egg-albumen. A layer of coagulated protein is formed around each oil particle. As Bancroft[257] has pointed out emulsifying agents are not necessarily emulsoids (gelatinous colloids) but may be anything that will go into the dineric interface and make it sufficiently viscous (fine powders).

253. Of great industrial importance is the "breaking up" of emulsions.[258] Anything which destroyes the protecting film will destroy the emulsion. Addition of mineral acid to the emulsions stabilized by soap destroys the same. To the emulsions obtained in exp. 249 and 250 hydrochloric acid is added when the emulsion is separated on standing in two layers.

IIb. WATER-IN-OIL EMULSIONS

The emulsions of this type although quite common in pharmaceutical practice have long escaped the attention of chemists. As emulsifying agents are used polyvalent soaps, oil-soluble colloids and certain solid powders which are wetted by oil.

254. A pasty "water-in-oil" emulsion of water in benzene is obtained by mixing together in a mortar (in small quantities at a time and in a pharmaceutical way) benzene and water in the presence of magnesium- or calcium oleate.[259]

255. In order to distinguish between both types of emulsions Briggs' drop method[260] may be applied. It

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[257] Bancroft, Applied Colloid Chemistry, p. 260, 1920.

[258] Parsons and Wilson, *Journ. Ind. and Eng. Chem.*, p. 1116, 1921.

[259] Newman, *Journ, of phys. Chem.*, 18, p. 34, 1914.

[260] *Ibidem.*

can be shown to the audience by projection on a screen. A drop of the emulsion is brought on a glass plate. If water is the external phase a drop of water will mix freely with the emulsion, if not, the emulsion is of the water-in-oil type.

256. A beautiful demonstration of a chromatic emulsion was recently given by Holmes and Cameron[261] by using a mixture of carbon bisulphide and a 50-50 glycerol-amyl acetate solution, the amyl acetate containing 2-4 per cent cellulose nitrate (Dupont's nitrocellulose, with 11 per cent nitrogen is most suitable) as emulsifying agent. The liquids are taken in the ratio of eight volumes of glycerol-amyl acetate to three to six volumes of carbon bisulphide until the chromatic emulsion appears. To view the emulsion it is best to use a 125 cc. oil specimen bottle as container and hold it some distance from the source of light.

H. Gels and Reactions in Gels

257. Gels are formed by cooling emulsoid sols like gelatine or agar-agar sols.

258. Chemical reactions afford another means of producing gels. One instance was given in exp. 198. Another example easily carried out is the following: About eighty-five volumes of 90 per cent alcohol are quickly mixed with fifteen volumes of a saturated solution of calcium acetate in water. The mixture sets instantaneously to a solid jelly and can be used as "solid alcohol fuel."

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[261] *Journ. Am. Chem. Soc.*, 44, p. 74, 1922.

259. The effect of salt additions on the viscosity of gels has already been emphasized in exp. 218.

260. Gels on standing show the phenomenon of synaeresis, *i. e.*, a separation in a dilute sol and a more concentrated gel, sometimes distinguished as serum and cake. In order to show that the liquid separating from a gelatine gel is not pure water but a sol a few drops of dilute hydrochloric acid and some tannin solution is added to some of the serum. A white turbidity demonstrates the presence of gelatine.

261. Most gels exposed to air dry up but on being placed in water take up water again, *i. e.*, they swell up. A piece of solid glue is cut in two equal halves and one part dipped in water. After a while its size is compared with the dry half. Instead of glue a piece of unvulcanized rubber may be taken and part of it submerged in benzene.

262. Of the interesting phenomena taking place in test-tubes or on plates by placing certain solutions on gels containing chemicals forming a precipitate with the supernatant solution some typical instances may be exhibited. These not yet completely understood Liesegang rings need no further description at this place.

I. Adsorption

Adsorption includes a number of closely related phenomena, sometimes distinguished as (1) adsorption, (2) absorption, occlusion or solution and (3) formation of absorption compounds. A sharp demarcation between these groups is impossible. In some cases, *e. g.*, that of palladium, taking up hydrogen, it is likely that all three phenomena occur. In order to avoid these cumbrous distinctions some authors speak of "sorption." The following mostly well-known experiments on sorption or, —using the more familiar term adsorption as a general designation—on adsorption refer to the condensation of (*a*) gases, (*b*) liquids, and (*c*) dissolved substances on different solids.

263. *Gases.*—Twenty to thirty cubic centimeters of dry ammonia gas are collected over mercury in a eudiometer tube. A small piece of charcoal,—preferably cocoanut charcoal,—previously heated over a Bunsen flame to expel adsorbed gases, on coming in contact with the gas, immediately takes up several cubic centimeters, thereby causing a considerable rise of the mercury column.

264. The usefulness of charcoal as a deodorant is demonstrated by passing a slow stream of hydrogen sulphide, washed with distilled water and dried over granulated calcium chloride, through a tube (length 50-100 centimeters, diameter 2 centimeters) filled with previously ignited wood charcoal. The tube is connected by means of an ┐ -shaped delivery tube with a lecture jar containing a lead acetate solution. No blackening is seen.

265. The fact that adsorption is accompanied by heat evolution, accounts (partly) for the following phenomenon. A piece of platinum foil, heated over a Bunsen flame, is allowed to cool by turning off the gas, until the foil is no longer red hot. The gas is then turned on again, causing the platinum to glow stronger and stronger, until finally the gas is relighted. Adsorption and combination heat accumulate here in raising the temperature to the ignition point.

If adsorption involves heat evolution, lowering of the temperature must increase the quantity of absorbed gas. Numerous experiments by Dewar and others have corroborated this conclusion and an ingenious method of creating a high vacuum was based hereon. (See Chapter XII).

266. *Liquids.*—The adsorption of water by charcoal, powdered clay, kaolin, silica and other finely divided materials is illustrated by heating 5-10 grams of the substance in a test-tube. Water will be seen to condense against the upper walls of the tube.

267. *Dissolved Substances.*—The adsorptive power of amorphous carbon in the form of wood charcoal, bone black, blood charcoal, etc., has been so universally recognized, that only quite recently other equally effective and cheaper substances have come into use. In the sugar industry animal charcoal has been replaced by mixtures of wood meal and fuller's earth; in the oil industries the last named substance has been lately introduced for decolorizing oils; in purifying potable waters use is made of the flocculent precipitates formed by aluminium and iron salts, etc. The difference in absorptive power of various adsorbentia may be exemplified by adding to five 200 cc. Erlenmeyer flasks, each containing 100 cc. of a dilute congo-red solution (0.1 gram in 1 liter water): 1

gram of talcum powder, 1 gram of fuller's earth, 1 gram of finely divided bone black, 10 cc. of alumina cream and 10 cc. of ferric hydroxide cream respectively. The aluminium and iron hydroxide paste are made by precipitating dilute solutions of aluminium and ferric chloride with an excess of ammonia, decanting the supernatant liquid and frequent washing of the flocculent precipitates with distilled water. The pastes should contain in 10 cc. about 0.6-0.8 gram of the anhydrous oxides. On heating the flasks over a Bunsen flame until the liquids boil and subsequent filtering, it will be seen that the five filtered solutions show different degrees of decoloration, compared with the original solution. The talcum is only slightly colored, and the shade of color of the liquid is only little lighter than that of the original solution; fuller's earth shows a better result, while the solution, treated with bone black retains a faint red color. The fourth and the fifth solution, however, are completely decolorized, and the alumina cream precipitate on the filter shows the color of the congo-red very distinctly. Similar results may be obtained by using other organic dye-stuff solutions (*e. g.* litmus, indigo, etc.).

268. Two or three milligrams of methyl violet are dissolved in 100 cc. of water. The solution is shaken with 2 grams of charcoal powder. The whole is poured on a filter. The filtrate is colorless. If now water is poured over the coal the filtrate remains colorless. Addition of alcohol or acetone gives a violet filtrate showing that the equilibrium in the organic solvent is much higher than in water or in other words the amount adsorbed from it is smaller.[262]

269. The rapidity with which dissolved dyes are adsorbed by glass walls and the tenacity with which the adsorbed film of dye adheres to the glass,—a fact well-known to all organic chemists—, is strikingly illustrated by pouring a quantity of an aqueous solution of malachite green or methylene blue into a tall clean beaker. The solution is then poured out and the beaker rinsed with cold tap water until the wash water is colorless. A sample of the water is placed in a test-tube.

The beaker is then rinsed with about 10 cc. of glacial acetic acid and the acid transferred to another test-tube. A colored solution of the dye is formed.[263]

270. With filter paper the two following interesting adsorption experiments can be performed. A few drops of a barium hydroxide solution are allowed to fall on one spot of a piece of filter paper. At 2-3 centimeters distance from this spot, outside the wet ring is put 0.2-0.5 cc. of a 1 per cent alcoholic phenolphthalein solution. The red color does not appear until the wet rings have overlapped each other over some distance, thus clearly showing that the dissolved substances are absorbed by the paper.[264] Therefore, the first 5-10 cc. of a filtrate should be rejected, when solutions of a definite strength are required.

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[262] Hatschek, Laboratory Manual, p. 110.

[263] Tanner, *Journ. Am. Chem. Soc.*, 45, p. 437, 1923.

[264] Bigelow, *l. c.*, p. 241.

271. Differences in the degree of adsorption are shown by allowing solutions of hydrochloric acid and barium hydroxide of the same strength to creep along strips of filter paper, dipped with their lower end into the solutions. After the liquids have been sucked up as high as 5-10 centimeters, the wet portions of both strips are tested by touching at different heights with glass rods, moistened with methyl orange and phenolphthalein respectively. It will be seen, that the base has travelled only one-third as far into the paper as the acid which has gone up almost as far as the water itself.[265]

272. The process of dyeing is largely one of adsorption by the animal or vegetable fiber. On bringing 150 grams of woolen yarn into a large beaker, containing 30 milligrams of crystal violet in two liters of distilled water, the solution is practically decolorized, the dye-stuff having been completely adsorbed by the wool.

273. A piece of cotton fabric, dipped in a dilute solution of purified congo-red, which is a direct dyeing cotton dye-stuff, no mordant being required for "fixing" the color, takes on a fairly light shade of red color. On adding sodium chloride, or still better Glauber's salt to the solution, and dipping another piece of cotton into the liquid, the fabric takes on a much deeper tinge of red, thus showing the marked effect of salt in driving the color, uniformly distributed (German: "egalisiert") on to the fabric. The dye, being a sodium salt of a complex organic acid ($Na_2C_{32}H_{22}N_6S_2O_6$), is of colloid nature, and "salted out" within the fibers of the fabric by the in-

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[265] Ostwald-McGowan, *l. c.*, p. *229*.

organic salt, thus materially assisting in the process of adsorption by the cotton.

On bringing the fabric in a beaker with hot water, part of the color is lost; the cotton "bleeds."

274. An interesting phenomenon is the "selective adsorption" of fine powders, suspensions and suspensoids. It has been found for instance that, if a solution of potassium chloride is shaken with clay and poured on a filter, part of the potassium is missing in the filtrate, while all the chlorine passes through the filter.[266]

Van Bemmelen's well-known experiment, showing the strong selective absorption power, which Fremy's voluminous manganese peroxide exerts on potassium sulphate is a typical instance.[267]

The manganese peroxide is made, according to Fremy's directions[268] by adding a cold mixture of 150 grams of water and 500 grams of concentrated sulphuric acid to 100 grams of potassium permanganate. The resulting acid is slowly decomposed, in the course of 2-3 days, with evolution of oxygen. After frequent shaking with fresh quantities of distilled water, a powder results, which when dried in air has the average composition of MnO_22H_2O, and does not impart an acid reaction to water. Twenty grams of the powder are suspended in 100 cc. of water and the suspension, mixed with 100 cc. of a normal solution of potassium sulphate (neutral towards litmus), shaken for some time. The manga-

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[266] H. W. Wiley, Agricultural Analysis, Vol. I, p. 127, 1906.

[267] *Journ. f. prakt. Chemie,* N. F. 23, p. 342, 1881.

[268] *Comptes rendus,* 82, p. 1232, 1876.

nese peroxide is allowed to settle and the supernatant liquid filtered and tested with methyl orange. The solution shows a distinct acid reaction.

275. An analogous result is obtained, when a suspensoid like colloid arsenious sulphide is precipitated by a potassium chloride solution, as was first observed by Whitney and Ober.[269]

On adding a sufficient amount of potassium chloride (20 cc. of a normal solution) to 100 cc. of dialyzed arsenious sulphide sol (with no appreciable acid reaction, the sol is precipitated, absorbing the cation, and the supernatant liquid becomes acid.

276. The selective absorption power of soil is conveniently demonstrated with the aid of an apparatus, devised by Müller.[270] A vertical glass cylinder (Fig. 59), 75 centimeters long, with an internal diameter of 4.5 centimeters is closed at each end by a perforated rubber stopper, provided with L-shaped glass tubes for the passage of the solution to be used. The lower part of the cylinder is filled with broken glass

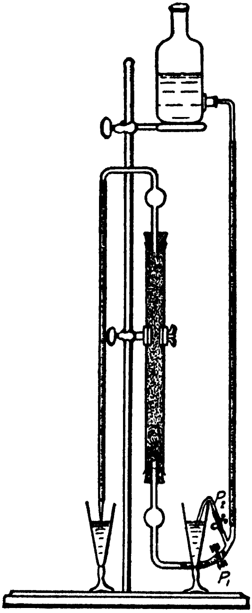

Fig. 59

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[269] *Journ. Am. Chem. Soc.*, 23, p. 852, 1901.

[270] *Zeitschr. f. angew. Chem.*, 13, p. 501, 1880.

or glass beads, covered by a layer of glass wool, about 1 centimeter thick. The cylinder is then filled up with soil, carefully sampled, air-dry and previously passed through a sieve. The soil is covered with glass wool. The standard solution of N/10 potassium carbonate, contained in a 2-liter bottle, is allowed to rise slowly in the soil and is gradually deprived from its potassium, the latter being absorbed by the soil. The solution, finally collected in the lecture jar is compared with a sample of the original solution, collected in another jar by opening a pinchcock (P_2) in a connecting T-piece. The flow of the solution through the soil is regulated by a screw pinchcock (P_1). If the experiment is properly carried out, nearly all the potassium is adsorbed, so that the final solution is neutral towards red litmus, while the original solution is distinctly alkaline.

As this test is not quite satisfactory for showing the loss of potassium, a solution of picric acid, saturated at room temperature (not exceeding 17°) may be used as indicator. Taking N/5, N/10, and N/20 solutions of potassium salts (K_2CO_3, K_2SO_4, KCl), it will be seen that on shaking 10 cc. of the solution with 10 cc. of the picric acid solution, a heavy precipitate is formed with the N/5 solution, a slight precipitate with the N/10 solution, and no precipitate at all with the N/20 solution. A N/5 solution of a potassium salt may be suitably used, since more than half of the potassium will be adsorbed.

The following data, obtained by Huston,[271] may be included, to show the selective action of the soil: Two

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[271] Experim. Station, Purdue Univ., Bull. 33, p. 50.

hundred and fifty cubic centimeters of N/10 solutions of sodium phosphate, potassium chloride, potassium sulphate, ammonium sulphate and sodium nitrate, when treated for 48 hours with 100 grams of soil lost by adsorption respectively: 0.259 gram P_2O_5, 0.316 gram K_2O, 0.332 gram K_2O, 0.096 gram N and 0.000 gram N.

277. Finally one out of many cases of reciprocal adsorption of colloids may be mentioned. Mutual adsorption of two suspensoids has as yet not been observed; on the other hand a number of cases, in which either one or both colloids are emulsoids have been studied. The action of protective colloids is probably nothing but an adsorption of the emulsoid by the suspensoid. As an example of reciprocal adsorption compounds Cassius' gold purple, may be prepared. This substance, long considered as a chemical compound of tin oxide and aurous oxide is really a mixture of (suspensoid) colloid gold and (emulsoid) colloid stannic acid, as has been proved by the investigations of Zsigmondy[272] and his pupils.

It is usually obtained, as is easily shown in a lecture demonstration, by adding a solution of stannic and stannous chloride to a very dilute solution of gold chloride. The gold purple can, however, also be prepared by *mixing* colloid solutions of gold and stannic acid. These solutions have to be made up beforehand and are obtained as follows: The gold solution is made according to Zsigmondy's directions,[273] by starting with 100 cc. of pure water, (redistilled from a quartz or pyrex flask, using a

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[272] *Lieb. Ann.*, 301, p. 361, 1898.

[273] *Ibidem*, 301, p. 30, 1898.

silver or tin condenser) to which are added 25 cc. of a solution containing 0.6 gram auric acid. The latter is obtained by evaporating a solution of gold in aqua regia. The mixture is then treated with 3 cc. of a N/5 solution of potassium carbonate and boiled. Four cubic centimeters of a solution, containing one part of freshly distilled formaldehyde in one hundred parts of water is poured gradually and with frequent stirring in the boiling liquid. In this manner a deep red or purple red gold solution of great stability is obtained. The colloid stannic acid is easily prepared by dissolving 2 grams of anhydrous stannic chloride in 3 liters of distilled water. On mixing both solutions, no change in color is observed, not even after the addition of a few drops of dilute nitric or sulphuric acid, but on boiling the same gold purple is obtained as in the usual procedure of reducing gold chloride with stannous chloride.

CHAPTER X

ACTINO-CHEMISTRY

Although a great many reactions are known, which are influenced by light, our knowledge of radiant energy as such is still very limited. No theory connecting a multitude of observations and forecasting unknown phenomena, thereby stimulating further researches in this important branch of physical chemistry has been put forward. In spite of persistent investigations, especially in organic chemistry, where "light" reactions are most obvious, the work of Ciamician and Silber, Benrath, Plotnikov and others has not led to any far-reaching generalization.

278. The most typical case of photo-synthesis, which has formed the subject of exhaustive researches by some of the most famous chemists of the nineteenth century (Berthollet, Draper, Bunsen and Roscoe), is the combination of hydrogen and chlorine. The reaction takes place with explosive rapidity under the influence of bright sunlight or the light of burning magnesium ribbon. The experiment, shown in first courses in chemistry, may be safely carried out by filling,—in diffuse light,— small thick-walled medicine bottles of 100 cc. contents over brine with the mixture of the gases in equal volumes, keeping the bottles corked in the dark until needed. Using glass screens of various color (yellow and red), the absorption of the actinic rays may be shown in addition.

279. A reversal of the photochemical union of chlorine and hydrogen is the decomposition of hydrochloric acid under the influence of light. Coehn and Wassiljewa[274] perform this experiment by passing the gas (prepared from fused sodium chloride and sulphuric acid), free from air, through a quartz tube 20 centimeters long and 0.5 centimeter in diameter, illuminated by a Heraeus' mercury quartz lamp at a distance of about 2 centimeters, into a narrow glass tube, blackened on the outside, which is inserted in a flask with potassium iodide solution. The hydrogen gas, not absorbed in the solution, is collected in an explosion eudiometer and exploded with oxygen in the usual way. The operator in the immediate neighborhood of the quartz lamp should not forget to protect the eyes with blue glasses.

280. As a common type of actinometer, Eder's mercuric oxalate actinometer may be mentioned. The light activity is measured here by the chemical transformation, which mercuric oxalate undergoes when exposed to light.

A solution of 4 grams of crystallized ammonium oxalate in 100 cc. of distilled water is added to an equal volume of a 5 per cent mercuric chloride solution and the clear liquid is then exposed to arc light.[275] The separation of white crystals of calomel soon becomes visible; at the same time carbon dioxide is liberated:

$$2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2.$$

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[274] *Berichte d. chem. Ges.*, 42, p. 3183, 1909.

[275] Meldola, the Chemistry of Photography, London, p. 32, 1891.

By measuring the gas volume or by weighing the precipitate the light intensity may be quantitatively determined.

281. The same solution may be used for illustrating photochemical extinction. This phenomenon, also called, —after its discoverer,—the law of Draper (1841), serves to demonstrate, that photochemical decomposition implies absorption of the chemically active rays. For demonstration purposes,[276] two glass troughs are taken, with parallel sides, at least 1 inch apart, each divided by a vertical septum, and strapped together by means of rubber bands. A mixture of mercuric chloride and ammonium oxalate solutions, made up as above mentioned is poured in three of the four cells, the second: *B* (Fig. 60), being filled with distilled water. The whole system is then exposed to the arc light, *A*-*B* being nearest to the light. As soon as the contents of *A* becomes opalescent, the cells are disconnected and on exhibiting the results it will be observed, that while *D* has become opalescent *C* has not appreciably been affected, no opalescence being visible.

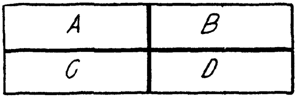

Fig. 60

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[276] Meldola, *l. c.*, p. 327.

282. An electro-chemical actinometer is described by Coehn,[277] adapted for a demonstration from experiments by Gouy and Rigollot.[278] Into a U-tube, filled with a 1 per cent sodium chloride solution, two strips of copper foil, 1 centimeter wide, previously heated over a Bunsen flame until the clean surface has taken on a uniform brown color, are inserted, and connected by means of a copper wire with a lecture galvanometer and a contact key. Both limbs are covered by black cardboard caps. On closing the circuit no deviation of the pointer is visible, but on removing one of the caps a deviation is observed. On lowering the cap the pointer moves back again. Raising of the other cap reverts the current.

283. The chemistry of photography covers a large field of highly interesting phenomena, offering a number of unsolved scientific problems. One of the most important reactions, which has been and is, up to the present time, a matter of controversy among chemists, is the well-known photo-decomposition of silver chloride and the accompanying change in color. This may be illustrated by placing some moist silver chloride, freshly prepared, on the bottom of a cylindrical vessel, closed by a rubber stopper, through which passes a glass rod, carrying a strip of starch iodide paper.[279] The chloride is exposed for about 10 minutes to the electric light. (Fig. 61). It

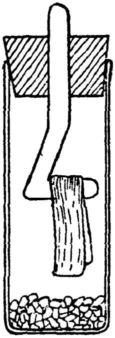

Fig. 61

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[277] Müller-Pouillet's Handbook of Physics, p. 598.

[278] *Journal de Physique,* (3) 6, p. 520, 1897.

[279] Meldola, *l. c.,* p. 66.

will be seen that the chloride rapidly darkens, while at the same time the paper becomes intensely blue.

284. The retarding effect of mercuric chloride may be shown at the same time by exposing, in another vessel, freshly prepared and washed silver chloride, to which a few drops of mercuric chloride have been added. Exposure to the light produces no visible change in the salt.[280]

285. Other inorganic salts, which are readily affected by light, are cuprous and thallous chloride. The following experiment with cuprous chloride, due to Priwoznick,[281] is easily performed. A sheet of polished copper with a perfectly clean surface, is immersed in a photographic dish, filled with a concentrated copper chloride solution (made by boiling hydrochloric acid with an excess of cupric oxide), until it is uniformly covered with a thin grey film. After 5 minutes the plate is removed, washed, drained on blotting paper, and when still moist, exposed under a design, cut in black paper, for about 10 minutes or longer, to the electric light. The design appears photographed on the plate, the exposed portions being much darker than the protected parts.

286. The action of light on sulphur is shown in the following experiment. A saturated solution of sulphur in carbon disulphide is prepared and placed in three test-tubes, loosely corked. The first tube is exposed to the direct sunlight, the second is put in a beaker containing

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[280] Meldola, *l. c.*, p. 67.

[281] *Dingler's Pol. Journ.*, 221, p. 38, 1877.

a solution of potassium bichromate and the third in a beaker with copper sulphate solution. After standing for a while in the light only the first and the third tube show a separation of amorphous sulphur, indicating that the violet light is mainly responsible for the action taking place. As Rankin has demonstrated[282] the action is reversed in the dark.

287. Apart from the preëminent value of the silver haloids for reproduction purposes, two other processes deserve to be mentioned: the "blue print" and the "pigment" process. The former may be carried out in the following manner: A sheet of drawing paper is coated with a 10 per cent ferric ammonium citrate solution by floating on the liquid for a few minutes and dried in the dark. It is then covered with a piece of black paper in which a design has been cut out and exposed to direct sunlight or to arc light, concentrated by means of a lens, for 5 or 10 minutes. Under the influence of the light the ferric salt is reduced by the organic material of the paper and a faint image becomes visible. By brushing a solution of potassium ferric cyanide over the exposed surface, the pattern is developed in Turnbull's blue. Finally the non-exposed ferric salt is washed out with tap water.

288. The pigment process depends on the fact, that gelatin, containing some potassium bichromate, is sensitive to light, when dry, but hardly sensitive when wet. The process may be illustrated by exposing a sheet of

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[282] *Journ. of phys. Chem.*, 11, p. 1, 1907.

drawing paper, previously coated with a mixture of gelatin and potassium bichromate together with finely divided carbon (or any other pigment used in oil painting) and dried in the dark, under a negative to direct sunlight or to arc light for several minutes. On the exposed parts, the gelatin is rendered almost insoluble. Consequently, on washing the paper in warm water, a picture appears in the pigment, held by the undissolved gelatin.[283]

Actino-chemistry does not only treat of reactions, in which light causes chemical changes, but also includes the converse processes of chemical reactions, producing radiant energy. Here we are with regard to a deeper understanding of these transformations almost completely ignorant, since apart from the phenomena and the names customarily given to them, little or nothing is known about the fundamental principles governing these different cases of so-called luminescence.

A number of subdivisions have been made, distinguished as: electro-luminescence, tribo-luminescence, crystallo-luminescence, fluorescence and phosphorescence. Electro-luminescence deals in the first place with the light emitted by rarified gases under the influence of a rapidly alternating high-potential current as furnished by an induction coil. The cold light obtained by electrolysis of salt solutions with a mercury anode also comes under this heading. The following example of an "electrolytic flame" given by Bancroft and Weiser[284] is well worth performing:

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[283] Bigelow, *l. c.*, p. 515.

[284] *Transactions Am. Electrochem. Soc.*, 25, p. 121, 1914. See also Lifschitz' article on Volta-luminescence, *Versl. kon. Akl. Amsterdam*, 32, p. 642, 1923.

289. A crystallizing dish (diameter about 10 centimeters is placed in finely crushed ice. A layer of mercury of approximately 1 centimeter thickness is connected with copper wire through an insulating glass tube to the positive pole of a battery of twelve to fifteen lead accumulators. A platinum foil dipping in a 25 per cent solution of potassium bromide, which covers the mercury forms the cathode. The current is so regulated that about 1.5 amperes pass through the solution. The mercury becomes coated with a film of bromide and glows for at least 10 minutes with a brilliant orange light. The phenomenon is best shown in a darkened room with a mirror put behind the cell so as to throw the light forward into the audience.

290. Tribo-luminescence may be observed, when a bottle, containing uranium nitrate crystals, is shaken vigorously in the dark.

291. Another substance showing a marked tribo-luminescence is salophen (acetyl para-amidophenyl salicylate or $C_6H_4OHCOOC_6H_4NHCOCH_3$). For a demonstration in the lecture room two test-tubes of slightly different diameter are used, so that the one with smaller bore can be pushed into the larger tube (Fig. 62). If about 1 gram powdered salophen is placed in the annular space between the tubes and

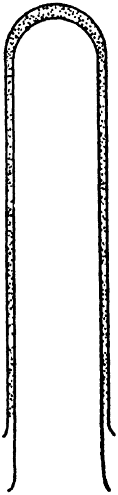
Fig. 62

crushed by rotating one tube within the other, an intense glow is observed in the dark.[285] For individual observation a number of these tubes, filled with salophen are circulated among the audience.

292. Crystallo-luminescence is more difficult to observe. It is usually shown, by shaking in the darkened lecture room a supersaturated solution of arsenious acid or sodium fluoride. As soon as crystallization sets in flashes are seen, but the light being very faint, the phenomenon is difficult to observe from a distance.

293. The crystallo-luminescence of the alkali halides has been studied in detail by Bandrowski[286] and Weiser.[287] The best results are obtained by mixing a solution of potassium or sodium chloride saturated at 25° with an equal volume of hydrochloric acid of specific gravity 1.12. In order to insure rapid uniform mixing Weiser uses two concentric glass tubes with a common stopper at the bottom and places one liquid in the inner tube and the other in the annular space between the tubes. By pulling the inner tube up the liquids are mixed almost instantaneously.

294. Fluorescence, first discovered with fluorspar, from which mineral the phenomenon derives its name, is characteristic of several mineral oils and is exceedingly marked with dilute solutions of fluorescein or cosin.

295. It may also be seen, by exposing a card, moistened with a quinine sulphate solution in the violet and ultra-

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[285] Plotnikov, Photochemische Versuchstechnik, Leipzig, p. 235, 1912, which contains a large number of lecture experiments on the subject of actino-chemistry (pp. 190–279).

[286] *Zeitschr. f. phys. Chem.*, 15, p. 323, 1894.

[287] *Journ. of phys. Chem.*, 22, p. 480, 1918.

violet region of the arc-light spectrum obtained with a quartz or flint-glass prism.

296. Phosphorescence derives its name from the glow which phosphorus emits in contact with oxygen. As is well known, no glowing is seen, when the element is exposed to pure oxygen, under atmospheric or higher pressure. On reducing the pressure below a certain limit, the glow becomes visible. This is particularly well shown by using the arrangement, given by Newth,[288] consisting of a glass tube (length 30-50 centimeters; diameter 2.5 centimeters), bent upward at both ends and provided with two stopcocks (Fig. 63). A solution of yellow phosphorus is made by gently warming a few pieces, the size of a pea, in a conical flask with olive oil. The bottom of the tube is then covered with a layer of this solution, and after expelling the air, filled with oxygen. No glowing is seen, but on reducing the pressure with the water-suction pump, the tube becomes luminous over its entire length. The experiment requires darkening of the lecture room.

Fig. 63

297. The glowing of phosphorus can be observed even in diffuse daylight, by following the directions, given by Marino and Porlezza.[289] The authors pass carbon dioxide

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[288] Newth, *l. c.*, p. 241.

[289] *Gazz. chim. ital.*, 41, (II), p. 420, 1911.

through a saturated sodium bicarbonate solution, dry it in a calcium chloride tower and then introduce it in a hard glass tube (2 centimeters diameter), in which red phosphorus is heated over three wing-top Bunsen burners (Fig. 64). When starting the experiment the phosphorus is heated very gradually, while at the same time the gas current passes over the phosphorus very slowly, until all traces of moisture have been expelled. An L-shaped delivery tube is then connected with the open end of the tube, leading down to the bottom of a large 2-liter Florence flask. The combustion tube is then heated up, until the phosphorus condenses in yellow droplets in the delivery tube. The gas stream, which has been kept

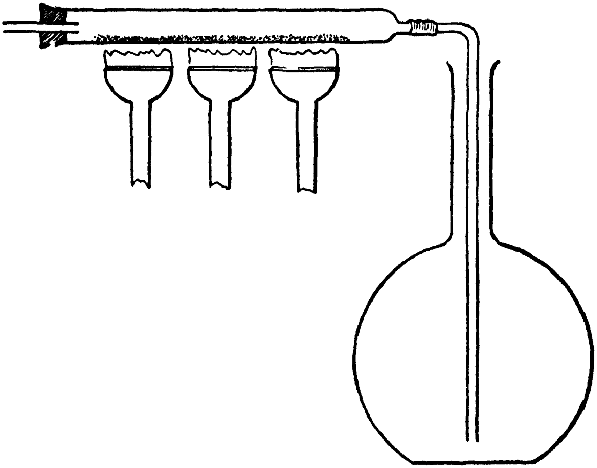

Fig. 64

slow for a while, is then suddenly increased. Immediately a beautiful greenish flame appears, while the flask itself shows, in its lower part a splendid phosphorescence.

298. What is sometimes called "chemiluminescence" may be seen in certain chemical reactions, where luminescence accompanies the reaction. Thus, on adding rapidly 50 cc. of a 30 per cent hydrogen peroxide solution to a mixture of 35 cc. of a 50 per cent potassium carbonate solution, 35 cc. of a 10 per cent pyrogallol solution, and 35 cc. of a 35 per cent formaldehyde solution,[290] vigorous foaming accompanied by a reddish glow, results.

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[290] Trautz, *Zeitschr. f. Electrochemie,* 10, p. 593, 1904; *Zeitschr. f. phys. Chem.,* 53, p. 1, 1905.

CHAPTER XI

FLAME, COMBUSTION AND EXPLOSION

From the time when the phlogiston hypothesis was universally accepted by Priestley, Scheele, Bergmann and other prominent chemists of the eighteenth century, up to the recent flame gas investigations by Haber, Bone and their co-workers, many attempts have been made to arrive at a clear insight into the nature of flames and the causes of their luminosity. Numerous experiments are known,—the more important are given in almost any text-book of elementary inorganic chemistry,—but up to the present time a general explanation, covering all the research work, that has been done by Davy, Frankland, Heumann, Smithells, Lewes, Bone and others cannot be given.

In the following a number of experiments will be mentioned and briefly described, illustrating:

I. Combustion of gases in general.
II. The structure and chemical reactions of flames.
III. Luminosity in the presence of solid particles.
IV. The separation of solids from flames.
V. Luminosity without solid particles.
VI. Changes in luminosity.
VII. Explosion and its prevention.

I. Combustion of Gases in General

299. A flame, defined as a mass of glowing gas, requires a medium in which it can "burn," that is the combustion must be supported by another gas, in order to produce a combination of the two gases with evolution of heat and light. The term "combustible" and "supporter of combustion" are interchangeable, however, as shown by the experiment of the "reversed flame."[291]

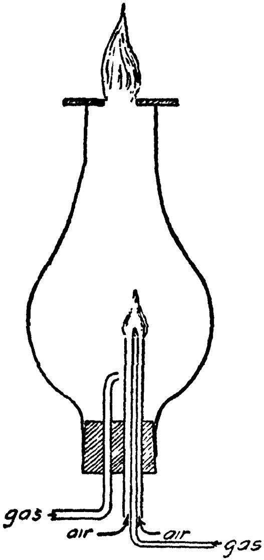

Fig. 65

A lamp-glass (Fig. 65) is closed at its lower end by a cork stopper, carrying a central tube of metal or glass, 1 centimeter in diameter and a smaller side tube (inner bore 2-3 millimeters), through which coal gas is admitted. The lamp chimney is closed at the top by a perforated asbestos disk, and the hole in this cover closed until the lamp is filled with gas. After 2-3 minutes the gas is ignited at the bottom of the central tube and the hole in the asbestos disk slowly opened. The flame is drawn up into the tube and the reversed flame appears in an atmosphere of coal gas. The gas, issuing from the hole at the top is ignited and represents the ordinary coal gas flame. By introduc-

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[291] Wartha, *Ber. d. chem. Ges.*, 4, p. 91, 1871.

ing a small tube, from which coal gas is burned, into the central tube, both flames are close together, the one enveloping the other.

300. The same inference is reached by passing a jet of oxygen into an inverted glass cylinder, filled with hydrogen and ignited at the lower end. The ordinary oxy-hydrogen flame is obtained by lowering a jet of burning hydrogen into a glass cylinder filled with oxygen.

301. Substances, that give off oxygen readily, may be used to burn oxygen in a coal gas atmosphere. In the flame of coal gas, burning from a lamp-glass, covered by an asbestos disk with a hole in the middle, dry chlorates of potassium, barium and strontium are fused successively on a deflagrating spoon until oxygen is given off. The spoon is then lowered and the liberated oxygen burns with a brilliantly colored light.

302. That oxygen may be replaced, either as a "supporter of combustion" or as a "combustible" by another gas, chlorine for instance is illustrated by introducing a jet of burning hydrogen into a glass jar, filled with chlorine. In a similar way chlorine can be made to burn in an atmosphere of hydrogen by the use of the apparatus for the "reversed" flame. Replacing the short central tube by a long tube, which reaches the hole in the asbestos disk, from which hydrogen burns, the chlorine is introduced through this central tube in a slow stream and ignites on issuing from the opening. The tube is then drawn down carefully. It will be seen that the chlorine continues to burn with a copious evolution of hydrogen chloride vapor.

II. The Structure and Chemical Reactions of Flames

Taking the flame of illuminating gas, obtained with a Bunsen or Teclu burner as an instance, it will be noticed, that the non-luminous flame represents an inner and an outer cone. The inner cone burns with a bright green color, which must be ascribed to luminescence since the temperature of this cone, under a strong draught, according to Haber and Richardt[291*] is only about 1550°. The mixture of gas and air burns in the inner cone to carbon monoxide, carbon dioxide, hydrogen and water vapor, mixed with uncombined nitrogen and is, therefore, nothing but "a water gas, diluted with nitrogen" (Haber).

In the outer cone (temperature *ca* 1800°) the carbon monoxide and hydrogen form carbon dioxide and water vapor. The gas mixture between the two cones does not contain any oxygen, consequently it is inferred, that "nothing burns in the flame." Inside the inner cone we have the unburned gas mixture; the flame, therefore, is *hollow*. From the experiments, devised to prove this, the following may be quoted:

303. Well glazed writing paper, dusted on the upper side with mercuric iodide, asbestos paper or thin copper foil, when depressed for a short time upon the flame, at various angles, show the well-known flame figures. (Fig. 66).

304. A glass tube, about 10-15 centimeters long, with an inner bore of 5 millimeters, cut off at an angle of 45°

[291*] Haber-Lamb, Thermodynamics of Technical Gas Reactions, p. 301, 1908.

at its lower end, is held in the flame, as indicated in the figure (Fig. 67), and the unburned gas lighted at the upper end.

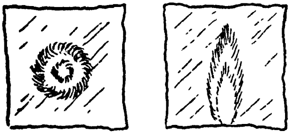

Fig. 66

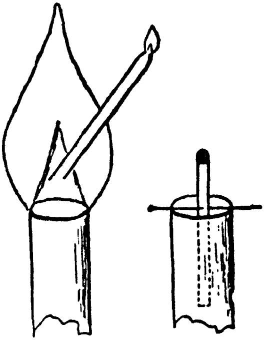

Fig. 67

305. A pin is pushed at right angles through a match, about 1 or 2 centimeters from its head and the latter thus supported vertically on the jet of the burner.[292] On lighting the gas, the match-head does not catch fire. The experiment can be repeated by thrusting a match quickly into the center of the flame; only the middle part burns off directly.

306. A modification of the foregoing experiment is obtained by connecting the gas supply with the stem of a small funnel (5-7 centimeters in diameter) covered with a piece of fine copper wire gauze. Right in the center of the gauze a number of match-heads or a small

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[292] Hofmann, *Ber. d. chem. Ges.*, 2, p. 254, 1869.

heap of gunpowder may be placed. On turning on the gas and igniting the latter with a burning taper, held over the gauze, the inflammable material in the center remains unconsumed.

307. The device which made it possible to investigate the chemical composition of the interconal gas in the Bunsen flame is the flame- or cone-separator, found by Smithells and Ingle[293] and simultaneously by Teclu.[294]

The apparatus (Fig. 68) consists of a glass tube, 40 centimeters long and 15 millimeters wide, fitted at its lower end either with a T-piece for the inlet of gas and air, the supply of each being regulated by stop-cocks (or screw clips) or with a one-hole rubber stopper, through which passes the mouth of a Bunsen or Teclu burner. This glass tube is surrounded by a second glass tube, 20 centimeters long and 3 centimeters wide, fitted with a rubber union and one (or two) asbestos or cork rings, to permit the outer tube to be easily slid up and down. The inner tube is held by a clamp in a vertical position. The upper ends of both tubes are provided with metal ends (preferably platinum, but aluminium or copper foil will do just as well). In order to make both cones visible to a large

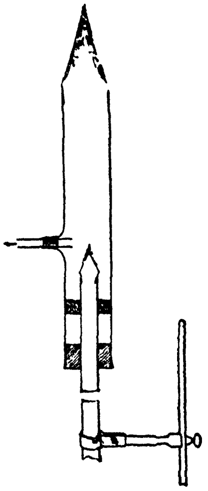

Fig. 68

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[293] *Journ. Chem. Soc.*, 61, p. 204, 1892; Brit. Ass. Rep., Leicester, 1907, p. 469.

[294] *Journ. f. prakt. Chemie*, 44, p. 246, 1891.

audience, the metal ends are moistened with a sodium chloride solution. The outer tube may be provided with a small side tube (closed by a cork stopper) to show how in practice the interconal gas can be drawn off for analysis (Smithells, Haber and others). At the beginning of the experiment both tubes are adjusted to the same level. The gas is turned on, the air being completely shut off; the air is then gradually admitted and the luminous flame changed into the ordinary non-luminous flame. The outer tube is then raised and the flame split in two cones, the outer cone ascending with the wide tube, the inner cone continuing to burn at the opening of the narrow tube. By increasing or decreasing the supply of air the inner cone can be made to "strike back" or to ascend to the mouth of the outer tube, in which case the original Bunsen flame is restored.

308. The presence of carbon in the luminous flame of illuminating gas is indicated also by Soret's optical test. The flame placed between a screen and a strong light causes a shadow to be formed on the screen. No shadow is formed by the flames of carbon disulphide and burning phosphorus.

309. The view of a preferential combustion of hydrogen, liberating carbon, which should cause the luminosity in luminous flames of hydrocarbons has been given up in favor of the conception of a gradual dissociation, preceding combustion. In fact, intermediate formation of acetylene can be shown in certain cases, for instance by drawing off the gases formed, when a Bunsen burner strikes back and passing the gas mixture through an ammoniacal solution of cuprous chloride (Fig. 69).

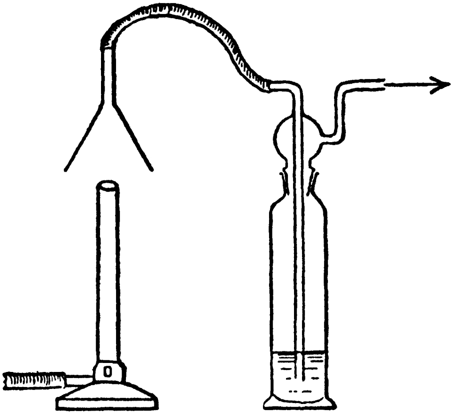

Fig. 69

Another case is that of air burning in an excess of illuminating gas; here again acetylene is formed and the formation of this gas shown in the same way as before.

III. Luminosity in the Presence of Solid Particles

310. That non-luminous flames become luminous in the presence of solids is well-known. The easiest illustration is holding a thin platinum wire in the colorless flame of hydrogen, burning from a platinum jet. Other instances are "Drummond's lime-light" being an oxy-hydrogen flame, directed on a piece of quicklime, and the Welsbach lamp, which is an ordinary Bunsen burner, giving a non-luminous flame, made luminous by the incandescent mantle of thorium oxide (ThO_2) mixed with about 1 per cent of its weight cerium oxide (CeO_2).

311. The flame of burning alcohol which is almost invisible, can be made luminous by passing a jet of chlorine into an Erlenmeyer flask, in which alcohol is boiled. The flame, burning from the neck becomes luminous by the separation of carbon, formed by the decomposition of the alcohol by the chlorine.

312. A number of experiments have been devised showing the "carburetion" of non-luminous flames by the introduction of carbon in the flame. This is usually done by mixing the gas with unsaturated hydrocarbons, rich in carbon, as benzene or acetylene. The hydrogen from a Kipp generator is passed through a calcium chloride tower, connected with a U-tube, both legs of which are provided with fish tail tips (Fig. 70). A plug of cotton soaked with benzene is inserted in the left limb, and after having expelled the air completely, both tips are lighted. The luminous flame appears on the left side, while the right flame is almost colorless.

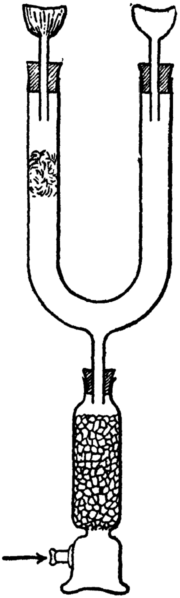

Fig. 70

313. The enrichment of illuminating gas with acetylene makes the colorless flame of the Bunsen burner quite luminous and is conveniently carried out by passing the gas into a wide-mouthed bottle, introduced between the gas outlet and the Bunsen burner, and half-way filled with water. A piece of calcium carbide is held by a copper wire, as shown in the figure (Fig. 71).[295] After shaking off the carbide into the water, the luminosity of the flame will be considerably increased for several minutes.

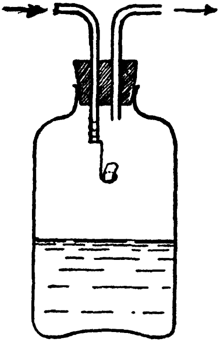

Fig. 71

IV. The Separation of Solids from Flames

An interesting way of separating solid particles from a flame, is by the formation of vortices, of which two instances are given by Newth.[296]

314. Coal gas is passed through a T-shaped tube, connected with two glass tubes (6-8 millimeters bore) drawn out in capillary jets, held by clamps and inclined at such an angle, that by carefully regulating the gas stream in each

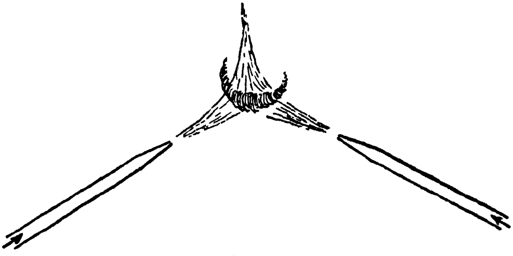

Fig. 72

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[295] Baker, *Journ. Am. Chem. Soc.*, 39, p. 646, 1917.

[296] Newth, *l. c.*, p. 216.

tube, two horn-shaped wings of carbon vortices are formed (Fig. 72). Draught must be avoided, as the phenomenon is affected by the slightest air currents.

315. Much easier to set up is another arrangement, in which an Argand burner and a blowpipe are used. The chimney of the burner (about 4 inches high) is covered with a piece of twenty-five-mesh wire gauze and the jet of a blowpipe pressed against the gauze (Fig. 73). The burner is lighted and the flame turned down as far as possible. Coal gas is then admitted through the blowpipe, and a beautiful vortex ring of sparkling carbon particles will be formed.

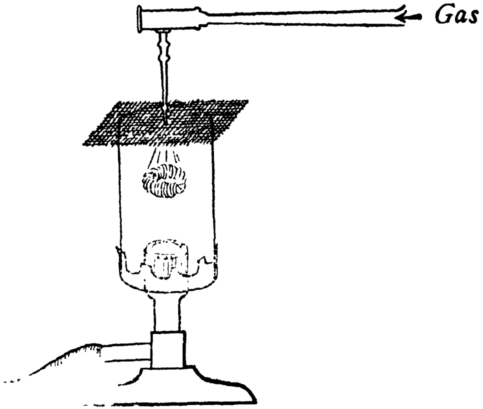

Fig. 73

316. In many cases the substance, to which the luminosity is due can be separated by cooling the flame with a cold object. Thus by holding a porcelain dish over the flame of illuminating gas, arsine, stibine and nickel carbonyl respectively, the separation of carbon, arsenic, antimony and nickel will be observed.

317. In the experiment given below the separation of heavy metals from the flames may be demonstrated, by following the example given by Ste. Claire Deville[297] in his cold-warm tube. The arrangement, as proposed by Bancroft and Weiser[298] consists of a Bunsen burner, provided with an asbestos chimney (Fig. 74). The latter has a hole, through which passes a platinum wire, bent in a loop, covered with a piece of asbestos soaked in a concentrated solution of an easily volatilized metal salt (like cadmium chloride, bismuth nitrate, lead nitrate). After introducing the salt in the hottest part of the flame, a porcelain tube of about 1 centimeter outer diameter, cooled by a rapid stream of cold tap water, is held for a few minutes in the upper part of the flame. The result is a separation of the metal,—very often in the form of an extremely lustrous mirror.

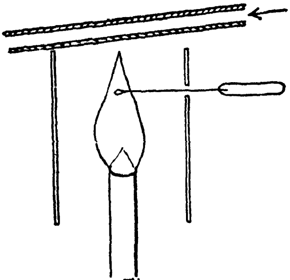

Fig. 74

V. Luminosity without Solid Particles

318. Vapor of carbon bisulphide, burning in nitric oxide, produces an intense blue light, although no solid par-

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[297] Lecons sur la dissociation, Paris, pp. 45-63, 1864.

[298] *Journ. of phys. Chem.*, 18, p. 213, 1914.

ticles are present. In a jar, filled with nitric oxide (over water), a few drops of carbon disulphide are introduced from a dropping funnel, and after thorough shaking, the mixture is ignited.

319. On burning phosphine in pure oxygen (Fig. 75), the gas burns with a dazzling white flame.

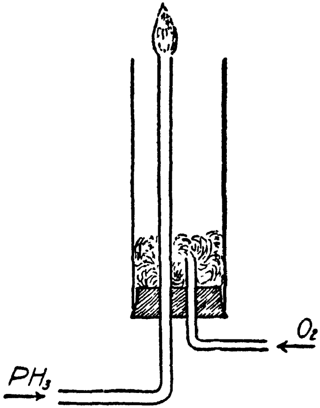

Fig. 75

VI. Changes in Luminosity

The luminosity of flames can be changed either by increasing or decreasing the pressure or by raising or lowering the temperature. The following set of experiments illustrates this point:

320. Cooling of the flame diminishes the luminosity: the luminous flame of a Bunsen or a fish-tail burner becomes practically colorless by holding a platinum disk or a sheet of nickel or iron plate against the flame. The luminosity can be restored by heating the disk or sheet by means of a blast lamp on the opposite side.

321. Lüpke[299] illustrates the effect of a cooling in the following manner. A 10 per cent solution of ether in water is poured in a test-tube and the tube closed with a cork stopper, through which a needle is run down to the bottom. The solution is solidified in a freezing mix-

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[299] Rüdorff-Lüpke, *l. c.*, p. 372.

ture, the test-tube stripped off and the frozen cylinder fixed upside down in a candlestick. The ether, when lit with a match burns with an almost colorless flame.

322. The chilling of the flame can also be brought about by diluting the gas with an inert gas like nitrogen or carbon dioxide. Thus by introducing, through a T-tube, dry carbon dioxide in coal gas, the luminous flame of a Bunsen burner becomes colorless.

323. The difference in luminosity of phosphorus and sulphur, burning in oxygen and in air also demonstrates strikingly the effect of temperature change.

324. Diminished pressure reduces the luminosity of flames. Thus the light of a candle, burning in the receiver of an air pump, will become almost invisible on quickly reducing the air pressure. The carbon dioxide, formed in the combustion is conveniently removed by placing a dish with quicklime in the receiver.

325. Detonating gas ("Knall-gas") when exploded in an eudiometer or in an explosion pipette forms water with a luminous flash, owing to the enormously increased pressure, while in case the gas mixture is bubbled through a soap solution and a taper held near the froth hardly any flash is visible.

326. A change in luminosity through absorption of rays is noticed in the so-called *reversal of the sodium flame* which has an important bearing on the explanation of the dark lines in the solar spectrum. The arrangement as given by K. A. Hofmann[300] is very simple and easily

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[300] Lehrbuch der anorg. Chemie, Berlin, Third Edition, p. 423, 1920.

put in operation (Fig. 75A). In the three-necked Woulfe-bottle is placed granulated zinc and some sodium chloride. Through the funnel on the left dilute hydrochloric acid is added during the experiment while illuminating gas is introduced through the middle neck. The gas escapes through an iron tube and burns from the wing top with a large yellow flame. By bringing close to the luminous part of the flame a micro-burner burning with a bright yellow flame by means of a platinum wire with a soda bead in the loop it will be observed that the

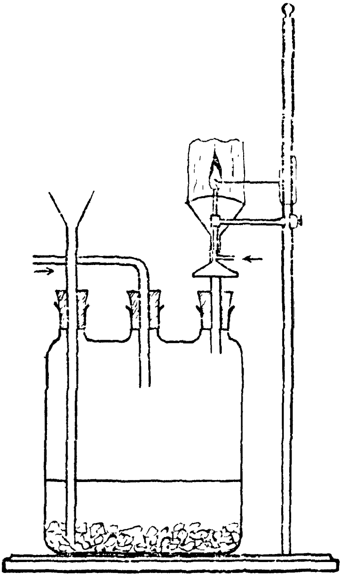

Fig. 75A

small flame appears, against the bright background of the large flame, surrounded by a black sooty fringe. This is due to the fact that on the edge of the small flame cooler vapors of sodium exist which absorb the rays which they emit themselves at higher temperature, thus obscuring the bright background. The experiment is best performed in a darkened lecture room.

VII. Explosion and Its Prevention

The question of explosion and the means of preventing gas mixtures from exploding may be treated in connection with the familiar phenomenon of the "striking back" of the Bunsen flame. The principle on which this burner, invented by Bunsen in 1855, is built, is as follows: The illuminating gas, escaping from a narrow jet in the base of the burner, creates a partial vacuum around the jet and consequently air is drawn through the air holes in the burner tube. By turning the air regulator, fitted with two opposite holes, corresponding to the draught holes in the tube, the air supply can be varied at will.

327. The reduction of the pressure can be made visible by closing one air-hole and connecting the other with a small manometer (Fig. 76), containing an indigo solution. As soon as the gas is turned on, the liquid in the gauge tube moves towards the burner, and moves back again on turning the gas off. If necessary, the movement of the liquid can be projected on the screen.

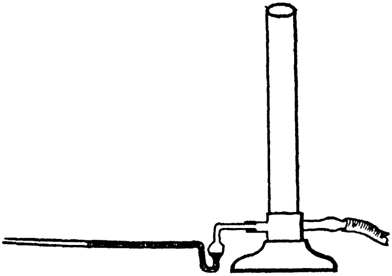

Fig. 76

328. On fully opening the air holes, it will be seen, that the inner cone, distinguished by its green color, burns with a loud noise and moves constantly up and down. This is due to cross-currents and incomplete mixing of the gases, as can be proved by lengthening the tube with another piece of copper tubing, 20-30 centimeters long, after which the inner cone burns quietly and becomes stationary. It represents a state of dynamic equilibrium, which is only disturbed by decreased gas supply. On gradually turning off the gas, the flame first begins to flicker and finally strikes back.

329. More striking and directly visible to a large audience, is the following modification of the preceding experiment:[301]

A glass tube, 4 to 6 feet long and 1 to 1½ inches wide, is clamped vertically over a Bunsen or Teclu burner and the space between burner and tube closed by a plug of cotton wool. The top of the tube is fitted with

[301] Mellor, *l. c.*, p. 758; Newth, *l. c.*, p. 230.

a piece of platinum or nickel foil to prevent the glass from cracking. The gas is lighted as it issues from the top and burns with a luminous flame when the air supply at the base of the burner is shut off. The cotton plug is then gradually removed and the blue Bunsen flame is obtained. On admitting more air by opening the air holes gradually, or by reducing the gas supply the blue cone will recede down the tube. By careful adjustment it can be made to travel up and down slowly at will. From this it may be concluded that the flame of the Bunsen burner represents a "stationary" explosion, in which the speed of the combustion wave is just held in equilibrium by the speed of the gas mixture moving upward.

330. In order to show the propagation of the combustion wave, Le Chatelier[302] passes a mixture of nitric oxide and carbon bisulphide, [made by allowing nitric oxide (from nitric acid, specific gravity 1.2 and copper turnings and dried by concentrated sulphuric acid) to move over the surface of a layer of carbon disulphide, contained in a small flask] through a glass tube, 3-4 meters long and 3 centimeters wide, slightly inclined under an angle of 5-10°, until the tube becomes colorless again, thereby indicating that the nitrogen peroxide, first formed, has been completely expelled. The gas generator is then put aside and the mixture lit at the upper end of the tube. The route of the dazzling white flame can be followed for about 1-2 meters, until a sudden report indicates the transition of the combustion wave into the ex-

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[302] *l. c.*, p. 273.

plosion wave. The latter travels at a speed of several (two or more) kilometers per second.

331. H. Erdmann[303] uses a three-necked Woulfe-bottle of 1-1.5 liters contents, to show that not every gas mixture is explosive. The middle neck is provided with a one-hole rubber or cork stopper, through which passes a glass tube, about 1 meter long and 10-15 millimeters wide. Through the ┐-shaped delivery tube on the left (Fig. 77), illuminating gas is passed into the bottle, until all air has been removed, the third neck being closed by a stopper. The gas is lit at the mouth of the outlet tube and a luminous flame results. On removing the stopper, the flame becomes non-luminous, blue, and although the gas is now mixed with air, there is no explosion. On gradually turning off the gas supply the blue flame cone flattens and recedes with a concave surface first slowly, then with increased speed, until after a few seconds a loud report is heard, resulting from the explosion of the gas-air mixture in the bottle. A possible collapse of the bottle may be counteracted by wrap-

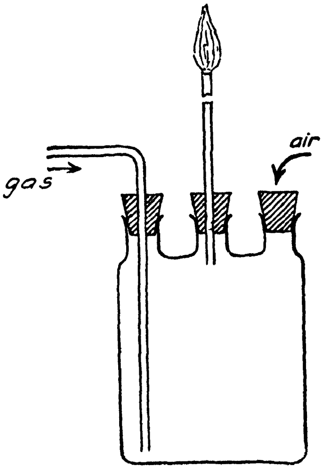

Fig. 77

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[303] Lehrbuch der anorg. Chemie, 5e Aufl., p. 435, 1910.

ping the bottle in strong copper wire gauze, although this may seem to many chemists an unnecessary precautionary measure.

332. An analogous experiment is the following,[304] performed with a glass tube, 60 centimeters long and 3 centimeters wide, held in a clamp at an angle of about 30°. The upper end is fitted with a one-hole cork stopper, through which passes a copper tube 6 millimeters in diameter and 30 centimeters long; the lower end is closed by a perforated stopper, carrying the delivery tube, connected with the gas supply. The gas is turned on and lighted at the orifice of the copper tube. On cutting off the gas and removing the stopper at the lower end, air enters the tube, forming an explosive mixture; the flame retreats down the copper tube and explodes the mixture in the glass tube. The experiment is then repeated, replacing the copper tube by another copper tube, with a 3-millimeter bore. If properly adjusted, the flame is extinguished, before reaching the explosive mixture in the glass tube, which is then lit at the lower end by applying a match.

333. The following lecture experiment, due to Dixon[305] illustrates the contrast between the quiet burning of carbon monoxide and oxygen in a short tube, where no explosion wave can be set up and the violent explosion which takes place when a wave is formed. First a thin-walled test-tube filled with the gaseous mixture is ignited by a taper. The quiet passage down the tube of the blue

[304] Mellor, *l. c.*, p. 743.

[305] Mellor, Chemical Statics and Dynamics, London, p. 485, 1909.

flame of the burning mixture can be followed by the eye. The tube is then refilled and fastened to the end of a piece of lead tubing a few feet long, filled with the mixture. The test-tube is inclosed in copper gauze and surrounded by a thick glass cylinder. When a flame is applied at the open end of the pipe, a loud report is heard and the test-tube is shattered to pieces.

334. The cooling effect of metallic surfaces in keeping the temperature below the ignition point, may be further illustrated by suddenly depressing a piece of copper wire gauze on a Bunsen flame. The flame remains for a while entirely below the gauze. As the latter becomes heated, the gas above the wire catches fire after a few moments.

335. The Davy safety lamp, the best known practical application of the metal wire gauze as a means of preventing explosion, may be demonstrated and its usefulness illustrated by lowering it into a highly explosive mixture of ethyl ether and air, contained in a 2-liter beaker. The flame inside the lamp is extinguished after a few moments, but no explosion results.

336. The same principle, slightly modified, is also applied in the construction of the burner, invented by Méker. On taking the burner apart, it will be seen that the air holes (four or five, instead of two) are unusually large, so that really an explosive mixture of gas and air is formed. No striking back is observed, however, on lighting the gas, since a deep nickel grid, closing the enlarged outlet of the burner tube, exerts its cooling effect, thereby preventing the flame from striking back.

CHAPTER XII

LIQUID AIR EXPERIMENTS

The experiments which can be carried out with the aid of liquid air are among the most striking that can be performed in chemistry courses. Since liquid air is on the market nowadays at reasonable prices, there is no obstacle in the way of performing a number of interesting low-temperature experiments which can all be shown in a 1- or 2-hour period.

Liquid air can be stored for quite a while when kept in the double-walled vessels with an evacuated space between, first introduced by d'Arsonval in 1887. Recently Weinhold has devised vessels with four walls, having three air-free layers between the liquid air and the outside atmosphere (Fig. 78). A further improvement for the conservation of liquid air has been made by Dewar in 1893 by silvering the inner walls in order to keep off radiant heat. In this way, it has been made possible to store quantities of 1-2 liters of liquid air for about 8-14 days, the daily loss being about 100 cc. Liquid air should never be *poured* from one vessel into another since it very often happens that the vessel from which the air is

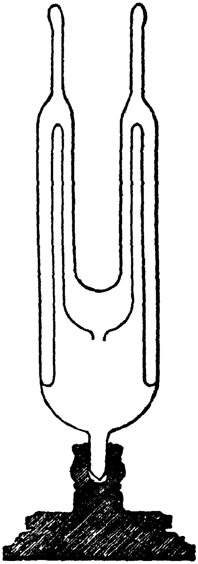

Fig. 78

taken cracks at the junction of both walls. For this reason it is necessary to transfer the liquid air by blowing it from one vessel into another by means of a rubber ball with valve, as shown in Fig. 79. Care should be taken,

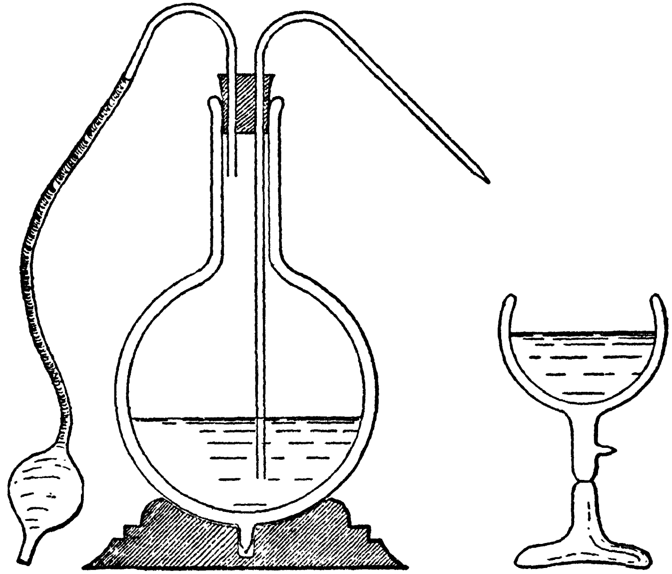

Fig. 79

that the two-hole stopper, carrying the glass tubes, is not pressed too tightly into the neck of the flask or jar, containing the air.

The stopper (preferably of rubber) should be taken away after each withdrawal of liquid air to keep it from freezing and loosing its tightness. The tube reaching in the liquid should be one or two centimeters from the bottom to avoid the possibility of striking the thin-walled bottom when the stopper is inserted.

Vessels containing liquid air should always be open to air. When received from the factory and especially after long standing liquid air is opalescent and shows a milky appearance due to the presence of minute crystals of ice and carbon dioxide. It can be freed from these impurities by filtering through a fluted filter.

The experiments to be performed are conveniently divided in two sets: First—those illustrating purely physical properties of matter at very low temperature (liquid air boils at about —193°) and in the second place—those illustrating chemical reactions at extreme temperatures, depending on the fact that liquid air is a source of oxygen. Liquid air when freshly prepared contains about 30 per cent of oxygen, but on standing it gradually becomes richer in oxygen (up to 55 per cent) due to the fact, that nitrogen having a lower boiling point (—196°) evaporates more rapidly than oxygen (boiling point —183°).

I. Physical properties of matter at—193°

337. Most of the familiar gases change into almost colorless solids when cooled to the temperature of liquid air. Two 500 cc. glass balloons, with hollow bottoms, (Fig. 80), containing dry chlorine and dry bromine gas respectively, are sealed and then held upside down by clamps between two thick-walled glass plates placed parallel to each other, so that in the event of an explosion the lecturer and his auditory are sufficiently protected. Liquid air is cautiously poured into the cavities of the bottoms, with the result that both gases instantly solidify (freezing point of chlororine: —102°, of bromine —7°). An almost perfect vacuum is created, no gas being left in the balloons which appear absolutely colorless.

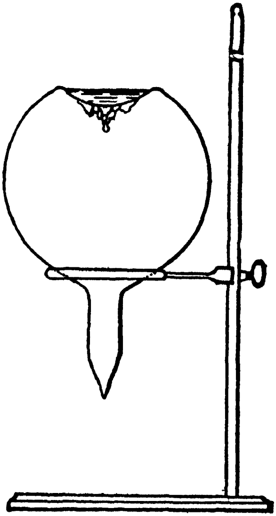

Fig. 80

338. That a high vacuum can be effected in this way is clearly shown by solidifying carefully dried carbon dioxide gas in a T-shaped tube (length of horizontal limb 20 centimeters, of vertical limb 22 centimeters, diameter 3 centimeters). The tube is provided with two platinum electrodes to which are soldered two short aluminium wires 2 centimeters long and 3 millimeters thick, (Fig. 81). The electrodes are connected with the secondary poles of an induction coil. The distance between the aluminium wires (about 15 centimeters) is too large to allow the passage of sparks but on slowly lowering the vertical limb of the tube into a Dewar vessel, half filled with liquid air (a preliminary cooling is effected by the escaping air vapor, before the tube is lowered in the liquid air) the gas immediately changes into a white snow, deposited against the walls of the vertical limb. At the

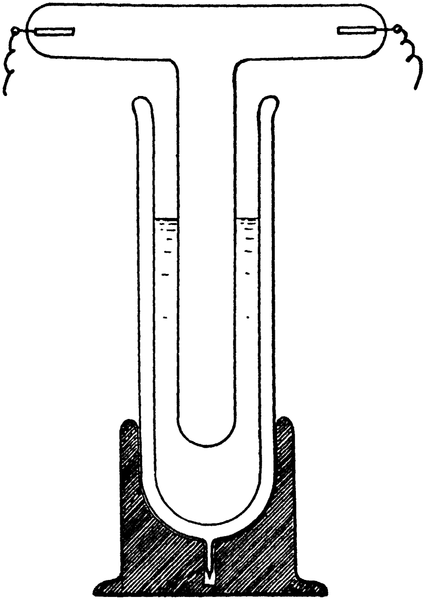

Fig. 81

same time a brilliant yellowish green spark light becomes visible, increasing in intensity the more the tube cools. Darkening of the lecture room helps to demonstrate this striking phenomenon in all its splendor.

339. The freezing of water by its own evaporation is brought about instantly in liquid air. Two glass bulbs, about 4 centimeters in diameter are connected by a glass tube, 30 centimeters long and 0.8 centimeter wide, twice bent at right angles (Fig. 82). One of them is partly filled with water. The air is completely driven out, so that the whole apparatus contains nothing but water and water vapor. On plunging the vapor-bulb in liquid air, the water in the second bulb freezes at once. It may be remarked that this apparatus, Wollaston's "cryophorus,[306] gives good results even at much higher temperatures (—20°) although not as readily as in liquid air.

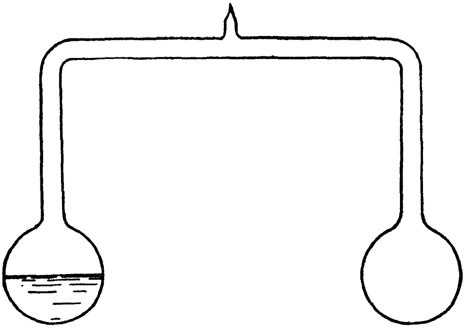

Fig. 82

340. The freezing of liquids, like ether and alcohol, may be next shown. An alcoholic solution of iodine is transformed into a viscid glass-like material which contracts on solidifying. At the same time it becomes yellowish-orange in color while in the liquid state the solution is distinctly brown.

341. Many solid substances change color when cooled in liquid air, proving that the power of absorbing light is considerably modified at low temperature.[307] Crystals

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[306] Graham, Elements of Chemistry, ed. Watts and Bridges, p. 75, 1866.

[307] Kreuz, *Phil. Mag.*, (5) 39, p. 209, 1895.

of sulphur, potassium bichromate and cinnabar may be used as examples.

342. Rubber, when brought to the temperature of liquid air becomes as brittle as glass and may be ground in a mortar. The same is true for grapes, meat, lard, etc. On allowing the temperature to rise, all these substances regain their original properties. Flowers cooled in liquid air fall to dust on shaking. Thin sheet iron becomes so brittle that it can be readily broken up by a blow with a hammer.

343. Metals become stronger towards a steady pull. A coil of lead wire, 3 millimeters in diameter, when cooled in liquid air is able to hold a weight of 300 grams without considerable stretching. Rise of temperature causes the wire to stretch and finally to become almost straight on returning to room temperature.

344. The magnetic properties of liquid air due to the oxygen it contains are easily made visible to a large audience by suspending a thin-walled test-tube filled with liquid air from a long thread (about 1.5-2 meters long) and approaching the same with a powerful electromagnet. The tube is attracted but falls back immediately on cutting off the current.[308]

345. The electric resistance of metals is enormously reduced at the temperature of liquid air as the following experiment strikingly demonstrates (Fig. 82A). The current from a few storage batteries is passed through

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[308] Claude-Cottrell, Liquid Air, Oxygen and Nitrogen, Philadelphia, p. 244, 1913.

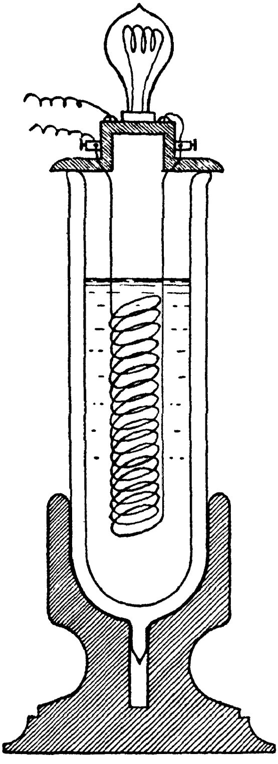

Fig. 82A

the filament of an incandescent lamp and through a long coil of copper wire of sufficient length to cause a barely visible glow of the electric bulb. On plunging the coil into liquid air the lamp shines with a bright white light.[309] Quantitative experiments have shown that the resistance

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[309] Claude-Cottrell, *l. c.*, p. 271.

of copper at —193° is only one-fiftieth of the value at room temperature.

346. On striking a small lead disk (or bell) cooled to —180° with a wooden hammer a clear metallic sound is heard.

347. Liquid air, when kept for several hours in a Dewar vessel is heavier than water. This is due to the fact that it contains then about 40-50 per cent oxygen, with a specific gravity of 1,135 (at —182°) against 60-50 per cent nitrogen with a specific gravity of 0.885 (at —195°). On pouring 20-30 cc. of liquid air in a beaker of water, a few drops of air are seen floating on the water, separated by a layer of gaseous air (phenomenon of Leidenfrost), but occasionally some drops sink down and rise again by the continuous formation of gas.

This Leidenfrost phenomenon also explains why liquid air can be poured (at least for a few seconds) on the back of the hand without injury to the operator. Direct contact with metallic articles dipping in liquid air should be avoided as there is, in this case, no intervening gaseous layer.

348. The usefulness of liquid air for the creation of high vacua is due to the fact that the power of charcoal to absorb gases is greatly increased at low temperatures. Thus Dewar found,[310] that 1 cc. of charcoal at 0° takes up 4 cc. of hydrogen or 18 cc. of oxygen, at —185° it takes up 135 cc. of hydrogen or 239 cc. of oxygen. The charcoal obtained from the shells of the cocoanut is es-

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[310] *Proc. Royal Soc.*, 74, p. 126, 1904; *Chem. News*, 94, p. 173, 1906.

pecially adapted for this purpose. A tube, filled with this charcoal (previously heated to drive off absorbed gases and moisture), is sealed to another tube (dimensions 20 by 3.5 centimeters) containing dry nitrogen, and provided at both ends with platinum wires to which are soldered short aluminium electrodes. When connection is made with the secondary poles of an induction coil (Fig. 83), nothing except an occasional flash is observed, showing that absorption of nitrogen has not taken place to any marked extent. On slowly lowering the limb containing the charcoal into a Dewar vessel filled with liquid air, forked brush-like reddish sparks begin to leap from electrode to electrode. As the gas absorption proceeds there appears a luminous band breaking up (at a pressure of 3 millimeters) into a number of striae, while at the same

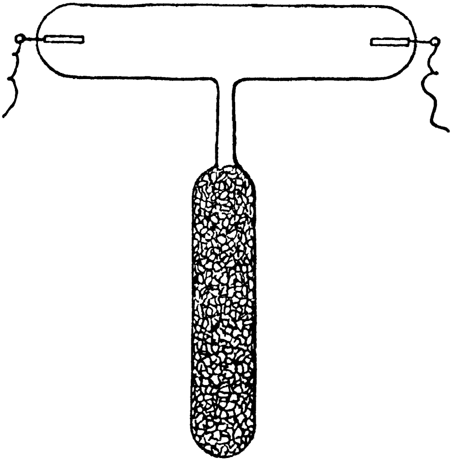

Fig. 83

time a dark space, Faraday's dark space, forms around the cathode. After about 10 minutes, when the pressure has sunk to about 0.03 millimeter of mercury the striae disappear, and a dark space, starting from the cathode, "Crookes' dark space," expands and fills the tube. A green fluorescent light is emitted from the walls around the cathode which, on reversing the primary current, switches over to the other end of the tube. If the exhaustion is still further continued the intensity of the fluorescence decreases, the tube "hardens," and finally the light is extinguished, the pressure being reduced to less than one ten-millionth of an atmosphere.

349. By using the device mentioned in the previous experiment Dewar[311] showed in a very ingenious experiment the selective absorption of charcoal. A number of spectroscopic tubes are connected in series with a large U-tube containing charcoal. The tubes are exhausted by cooling the charcoal until the electric discharge barely passes through the tubes. The U-tube is then placed in liquid air and a slow current of air allowed to enter the system passing first through the charcoal tube which takes out oxygen, nitrogen and argon which are readily absorbed, while helium, neon and hydrogen pass through. When the pressure in the first tube has sufficiently risen it begins to glow with the characteristic orange hue of neon. After a while the other tubes begin to glow showing the colors of neon and helium.

[311] Dewar, *Proc. Royal Inst.*, 18, p. 444, 1906.

II. Chemical properties of matter at—193°

350. Chemical action at —193° is hardly perceptible; the molecules are, according to Dewar, near to the "death of matter." When a small piece of sodium and a few cubic centimeters of strong hydrochloric acid are cooled separately in two test-tubes in liquid air and then brought in contact with each other, no reaction takes place.[312]

351. On the other hand a small piece of burning sulphur dropped into liquid air placed in a cavity in a block of ice continues to burn with a bluish light of remarkable brilliancy.

352. Liquid air, on standing, becomes rich in oxygen. This accounts for the fact that a burning taper, when plunged into some liquid air, contained in a beaker, is not extinguished, but burns vigorously notwithstanding the extremely low temperature in the beaker. In performing this experiment, proper precautions must be taken, the beaker in most cases being reduced to pieces.

353. A plug of cotton is treated with powdered charcoal so that the latter becomes finely divided in the cotton. The preparation held in the loop of platinum wire, is then dipped into liquid air for a few minutes. On igniting the cotton-charcoal in a flame the mixture burns like gun cotton,[313] with an intensely bright flame.

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[312] Pictet, *Comptes rendus*, 115, p. 814, 1892. It should be noted however that solid fluorine and liquid hydrogen combine at a much lower temperature, at —250°.

[313] Erdmann, *l. c.*, p. 243.

CHAPTER XIII

RADIOACTIVITY

A new branch of chemistry, described in all modern text-books under the heading "radioactivity" has grown up in the last twenty-five years. On account of its unique and unparalleled features it has occupied the attention of the foremost chemists and physicists. A few experiments, however simple, may be of some use in presenting the subjects to students taking up the study of radioactivity for the first time.

354. A comparison of the radioactivity of different substances can be made with the aid of an electroscope. This instrument in the form suggested by H. N. Schmidt may be constructed with simple materials and gives satisfactory results. It consists of a single strip of gold or aluminium leaf which is attached to a brass rod A (Fig. 84) by moistening the surface of the brass and tightly pressing the leaf against it. The whole system is fixed by means of a ball of sulphur into another rod R. The latter is held by a cork which closes a hole in the center of a metal container. Through the cork passes a second metal rod with handle of sealing wax which can

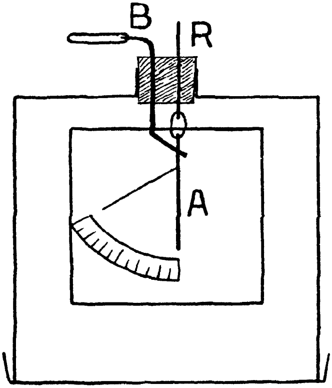

Fig. 84

be rotated so as to touch the brass rod A and charge the system. On opposite sides glass windows are inserted through which the movement of the metal leaf can be observed. The bottom of the container should be made removable.

In operating the electroscope the natural leakage is first shown. B is brought in contact with A and by means of a charged rod of sealing wax a charge is transferred to the system. B is then revolved and grounded, together with R and the container itself. The charged leaf is repelled through a considerable angle but falls back slowly. The time to pass through five or more scale divisions is noted. The average of several determinations is taken. The empty glass dish placed on the bottom of the container is then filled with the radio-active substance (pitchblende or other material) and the rate of fall of the leaf determined. It will be seen that the leaf falls rapidly.

355. One of the characteristics of radioactive disintegration is that the rate of change at any time is proportional to the number of atoms present at that time, *viz.*, we have to deal with a reaction of the first order (mono-molecular, or rather mon-atomic reaction). Reactions of this type are expressed by the equation:

$\lambda \,.\, t = \log \frac{a}{a - x}$, in which a is the initial concentration, x the amount changed after the time t and λ is a constant which in this case is called the disintegration constant. In order to represent the rate of decomposition in an easily reproducible manner, the so-called period of half change has been introduced, *viz.*, the time necessary to reduce the initial amount of substance to one-half of its value. By substituting ½ a for x in the above equation, we obtain: $\lambda . t = \log(\text{nat})\ 2 = 0.693$. It is customary to give for each radioactive substance either its disintegration constant or its period of half change $t = \frac{0.693}{\lambda}$. Thus we have for the series of transformations, starting from radium, the following disintegration products with their respective periods of half change:

Ra 2000 years → Niton 3.85 days →
Ra A 3 min. → Ra B 26.7 min. → Ra C 19.6 min. →
Ra D 16.5 years → Ra E 5 days →
Ra F 136 days → Pb ∞.

Assuming that at the time O only Ra A is present, it may be asked how do the relative quantities of Ra B, Ra C and Ra D change with the time? Plotting the number of atoms as ordinates against the time as abscissa, the result obtained is as given in Fig. 85. The curve for Ra A decreases rapidly in accordance with the exponential law, the curve for Ra B shows a sharp, that for Ra C a flat maximum while the curve for Ra D advances asymptotically towards a maximum.

By using a mechanical analogon, *viz.*, the flow of water (or an aqueous solution) through glass tubes with small holes blown in the bottom,[314] a fairly close resemblance to the radioactive disintegration of Ra A into Ra B, Ra C and Ra D can be obtained. Four glass tubes (inner diameter about 3 centimeters, length 20 centimeters) are

[314] P. Ludewig, *Radioactivität, Leipzig*, p. 29, 1921.

clamped on an iron stand, one above the other. The upper one, labelled Ra A has a small hole (time of outflow for 100 cc. of sugar solution of 30 per cent about 2 minutes), the next Ra B a very small hole (time 5½ minutes) the third Ra C a hole intermediate between the two (time 4½ minutes) while the bottom of the lower (fourth) tube is not perforated. While closing the hole in the first tube with the finger, 100 cc. of colored water (or preferably a colored sugar solution, to increase the viscosity and thereby the time of outflow) is poured in and at the desired moment the liquid allowed to flow. The results as given in Fig. 86 and 87 show the close qualitative agreement with the curves of Fig. 85.

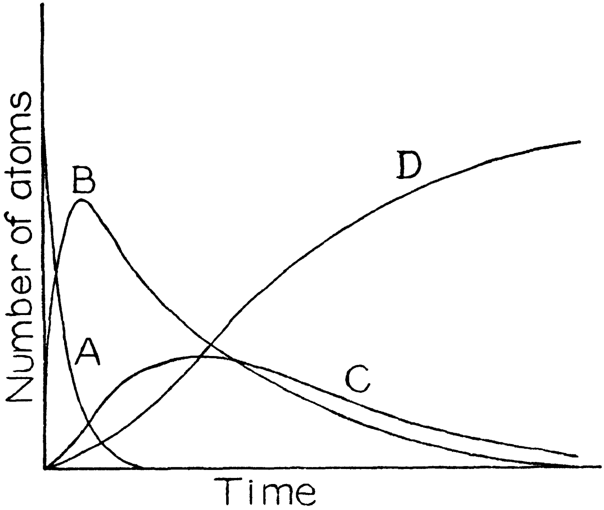

Fig. 85

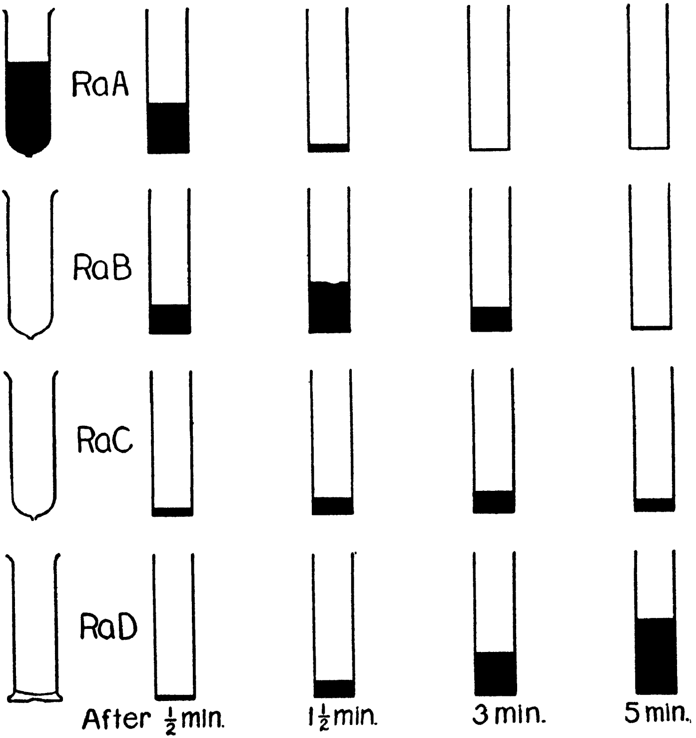

Fig. 86

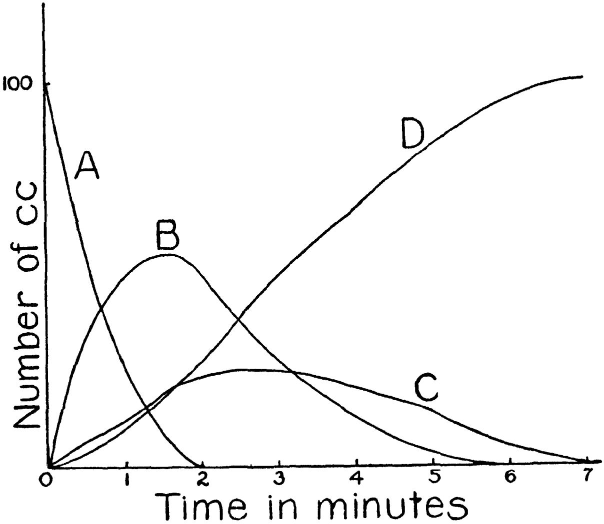

Fig. 87

356. Although it is not possible to give an idea of the radioactive equilibrium for the long series of products leading from radium to lead, some mental picture of the quantity relations in the state of dynamic equilibrium between a few members of this series may be obtained if we confine ourselves to the five elements: Niton, Ra A, Ra B, Ra C and Ra D. Niton (or radium emanation, a gas) has, compared with the next three radioactive elements a rather long period of half change (3.85 days) while Ra D has an extremely long period of half change (16.5 years). A large bottle (Fig. 88) provided with a stop-cock at the bottom, containing several liters of col-

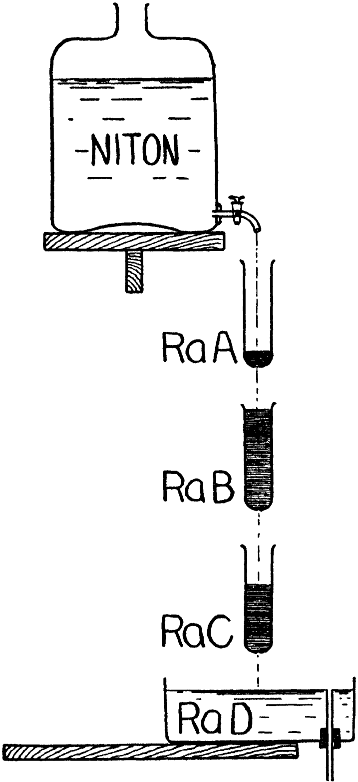

Fig. 88

ored water (or a solution) represents a quantity of niton. The same three tubes Ra A, Ra B and Ra C are used as in the previous experiment. The fourth tube is replaced by a large constant level basin to represent Ra D.[315] The flow from the bottle is so regulated that after a little while the levels in all three tubes remain practically stationary. The level in the bottle is kept about the same by adding some liquid from time to time. The result as indicated in Fig. 88 is: very little liquid in tube Ra A, a large column of liquid in Ra B and a column of medium length in Ra C.

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[315] Ludewig, *l. c.*, p. 30.

CHAPTER XIV

MISCELLANEOUS EXPERIMENTS

DULONG AND PETIT'S LAW

357. The law, discovered by Dulong and Petit in 1819, stating that the heat capacity of atoms is approximately the same for all solid elements, is very striking as is readily seen from the following table which contains a number of elements (metals) selected at random from a list of more than fifty elements arranged in the order of increasing atomic weight:

Element	Atomic weight	Specific heat	Specific gravity	Atomic volume	Atomic heat
Aluminium....	27.1	0.217	2.7	10.4	5.9
Zinc...........	65.4	0.094	7.1	9.2	6.1
Tin.............	118.7	0.055	7.3	16.3	6.5
Lead..........	207.2	0.031	11.3	18.2	6.4

The importance of this law is frequently not realized to its full extent, especially in elementary courses of inorganic chemistry because of the lack of a suitable lecture demonstration. This is, however, a very simple matter, since it is merely necessary to take amounts of two elements in ratio of their atomic weights, heat them to 100° and then plunge them in equal volumes of water at room temperature. The rise in temperature is approximately the same as can be readily seen at a distance by using two large air thermometers of equal size.

The apparatus[316] consists of a lead weight of 4144 grams (20 gram atoms) and a zinc weight of 1308 grams

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[316] Obtainable from Eimer and Amend, New York.

(20 gram atoms)of the same cross-section (10 centimeters square) as shown in Fig. 89. From the table given above, it is seen that the atomic volume of lead (18.2) is twice that of zinc so that the volume of the lead weight as judged from its height must be double that of the zinc weight. Both weights, provided with brass handles for ease of manipulation are heated in a pail (or dish) containing boiling water, simultaneously removed and plunged into two glass jars of equal size

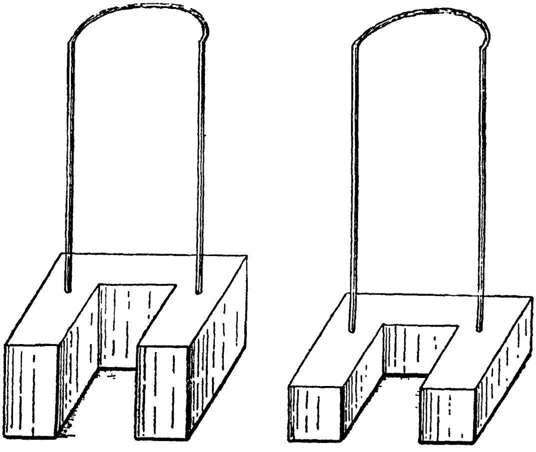

Fig. 89

(diameter 16 centimeters, height 9 centimeters) filled with 500 cc. of water at room temperature. In the center of the jars are placed two air thermometers filled with a colored liquid and carefully adjusted, so that both show the same rise of liquid in the stem for equal increments of temperature. The initial position of the liquid in the stem is marked by means of a clip. The rise of liquid will be found to be several centimeters (dependent upon the bore of the thermometer stem) but the same for both thermometers.

If desired, the experiment may be repeated using *equal* weights of lead and zinc in which case the rise of temperature will be more than three times greater for the zinc than for the lead.

VALENCE

358. The concept of valence or "habit" of an element for combination (Mellor) is illustrated in an instructive manner by means of the following experiment of W. A. Noyes.[317]

A quantity of 23 milligrams of sodium, freshly cut, is placed in a small gelatine capsule and introduced under an

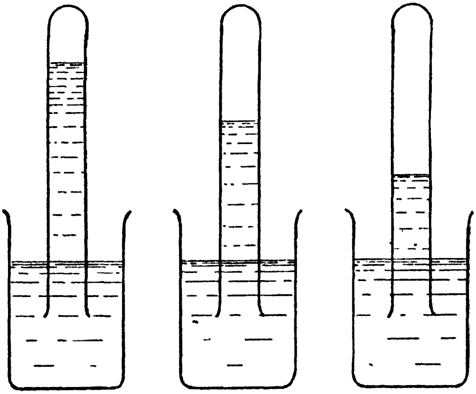

Fig. 90

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[317] Holmes, General Chemistry, New York, p. 60, 1921.

inverted test-tube (large size) filled with dilute hydrochloric acid.

In the same way 24 milligrams of magnesium ribbon (previously cleaned with sand-paper) and 27 milligrams of aluminium (etched beforehand with dilute base) are placed under two other tubes inverted in the same dilute acid (Fig. 90). It will be seen that the volumes of hydrogen collected in the three tubes are approximately in the ratio of 1 : 2 : 3 for the given quantities of metal, which are proportional to their atomic weights.

CRYSTAL GROWTH

359. The theory of the growth of large particles at the expense of small ones finds a very striking analogon in the following very pretty experiment of Boys.[318]

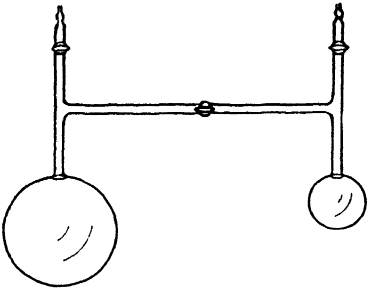

Fig. 91

A fairly wide double T-tube provided with stop-cocks (Fig. 91) is clamped on a ring stand and two soap bubbles of different size are blown on the open ends

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[318] Ostwald, die Wissenschaftlichen Grundlagen der Analytischen Chemie, Fifth Edition, p. 217.

(middle stop-cock closed, end ones open). On closing the stop-cocks to the left and right and opening the middle one, it will be noticed that the larger of the two bubbles grows at the expense of the smaller. The middle stop-cock is then closed and one side stop-cock opened so that the larger soap bubble becomes smaller in size than the other. On repeating the experiment it will now be seen that the second bubble becomes larger in size which is the reverse of what took place before.

The necessary soap solution is best made by dissolving 10 grams of oleic acid in the required amount of concentrated sodium hydroxide solution, adding 25 grams of glycerol + a trace of eosin and making up to a volume of 100 cc. with water.

SURFACE TENSION OF MERCURY

360. To show that the surface tension of mercury is decreased when it is covered with some electrolytes the following experiment may be carried out:[319]

Six to eight cc. of mercury are placed in a small evaporating dish and covered with dilute sulphuric acid (1 : 10) containing enough potassium bichromate to give the liquid a light lemon-yellow color. The mercury flattens out, showing that its surface tension is decreased. When touched with an iron wire it suddenly contracts. The wire is fixed in such a way that the contraction breaks the contact. The mercury again flattens, touches the wire, shrinks again and so on. A rhythmic pulsation of the mercury is thus brought about.

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[319] Bigelow, *l. c.*, p. 470.

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