Lecture Demonstrations

IN

PHYSICAL CHEMISTRY

BY

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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 a. s. o. 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.

Any remarks or suggestions as to changes or additions will be gladly welcomed.

The author takes pleasure in stating his indebtedness to Prof. Bingham, of Lafayette College, for the help received in correcting the manuscript and giving valuable additions (Nos. 1, 14, 170, 171, 172 on pp. 1, 12-14, 138 and 139). Acknowledgment is also expressed to Prof. Hart and Dr. Hunt Wilson, both of Lafayette College, and to Dr. van Rossen, of Bryn Mawr College, for a number of suggestions. In the reading of the proof sheets the writer was assisted by Miss M. S. Cline, of the Moravian College for Women, and by Mr. Ch. F. Fryling and in the preparation of the cuts by Mr. R. Resnikoff, to whom full credit for their painstaking labor is hereby given.

v. K.

WASHINGTON, D. C.,
August, 1918.

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

—*Petrus van Musschenbroek,*
Introductio ad Philosophiam
Naturalem, p. 4 (1742).

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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 co-workers. 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.

The chapter is concluded with a demonstration of the relation which apparently subsists between the specific heat and the atomic weight of elementary solids (Dulong and Petit's law).

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 of about 80°. The color of the compound changes from red to black. The color 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,[1] 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

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[1] cf. H. und W. Biltz, Uebungsbeispiele aus der unorg. Experimental-Chemie, Leipzig, p. 27, (1907).

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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.

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. 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°,[1] 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.[1]

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[1] Van Klooster, Zeitschr. f. anorg. Chem., **85**, p. 49, (1914).

4. Another instance is potassium bichromate.[2] 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°,[3]—with hardly any perceptible heat evolution—into a powder, causing the tube to crack by the expansion.

B. Dissociation of Solids.

5. 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.[1] Other types of apparatus for the same purpose have been devised by Pebal[2] and Than.[3]

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[1] Hüttner and Tammann, ibidem, **43**, p. 215, (1905).

[2] Mitscherlich, Pogg. Annalen, **28**, p. 120, (1833).

[3] Zemczuzny, Zeitschr f. anorg. Chem., **57**, p. 267, (1908).

C. Undercooled Liquids.

6. 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,

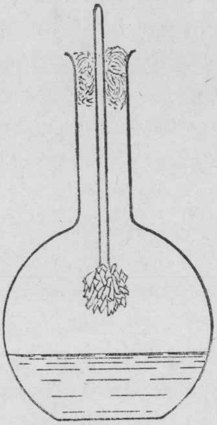

Fig. 1.

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[1] cf. Mellor, Modern Inorganic Chemistry p. 542, (1916).

[2] Liebigs Annalen **123**, p. 199, (1862).

[3] Ibidem, **131**, p. 129, (1864).

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.[1]

7. 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°,[2] 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. Ten grams of the salt are heated in a small platinum crucible and rapidly cooled by means of a stream of cold air,[3] 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 (crystal-

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[1] Ostwald, Grundlinien der anorg. Chemie, 3e Aufl, p. 537, (1912).
[2] Jaeger, Journ. of the Wash. Ac. of Sc., 1, p. 53, (1911).
[3] Guertler, Zeitschr. f. anorg. Chem., 40, p. 268, (1904).

lization) suddenly starts, often accompanied by a strong glowing, indicating an enormous increase of temperature.

D. Liquid Crystals.

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

9. The following lecture experiment[1] 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,[2] are 5.79 and 7.28 respectively. The dilatometric apparatus (Fig. 2), consists of a glass cylinder (*A*), filled with 60-70 grams of grey tin, and a connecting U-shaped tube, containing mercury. The space

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[1] Cohen, Transactions of the Faraday Soc., **7**, p. 6, (1911).

[2] Zeitschr. f. phys. Chem., **30**, p. 601, (1899).

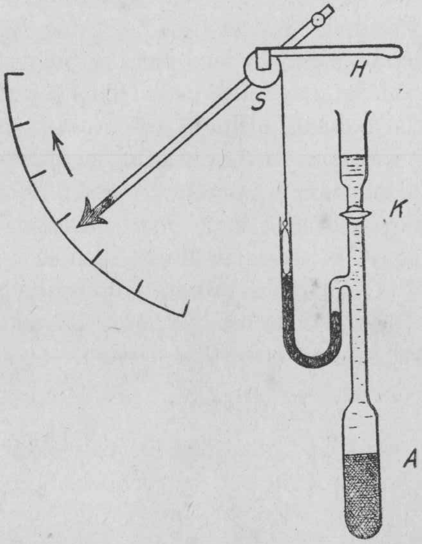

Fig. 2.

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

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