$$Q = \int_0^a 2\pi x\Theta dx = \int_0^a 2\pi x\Theta_1 dx - \int_0^a 2\pi x\cdot 2\Theta_1 \sum_{m=1}^{m=\infty} \frac{J_0\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)} e^{-\frac{kt}{a^2}(R_m)^2} dx$$

$$Q = 2\pi\Theta_1 \int_0^a x dx - 4\pi\Theta_1 \int_0^a x \sum_{m=1}^{m=\infty} \frac{J_0\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)} e^{-\frac{kt}{a^2}(R_m)^2} dx$$

$$Q = \pi a^2\Theta_1 - 4\pi\Theta_1 \Big[\sum_{m=1}^{m=\infty} \frac{\frac{a}{R_m} x J_1\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)} e^{-\frac{kt}{a^2}(R_m)^2} \Big]_0^a$$

$$Q = \pi a^2\Theta_1 - 4\pi\Theta_1 \sum_{m=1}^{m=\infty} \frac{\frac{1}{R_m} a^2\, J_1\,(R_m)}{R_m\, J_1\,(R_m)} e^{-\frac{kt}{a^2}(R_m)^2}$$

$$\frac{Q}{Q_1} = 1 - 4\left\{ \frac{1}{(R_1)^2} e^{-\frac{kt}{a^2}(R_1)^2} + \frac{1}{(R_2)^2} e^{-\frac{kt}{a^2}(R_2)^2} + \ldots. \right\}$$

$$\frac{Q}{Q_1} = 1 - 4\left\{ \frac{1}{5.78} e^{-\frac{kt}{a^2}\times 5.78} + \frac{1}{30.47} e^{-\frac{kt}{a^2}\times 30.472} + \frac{1}{74.895} e^{-\frac{kt}{a^2}\times 74.895} + \ldots. \right. \quad (6)$$

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE BUREAU OF STANDARDS OF THE UNITED STATES DEPARTMENT OF COMMERCE]

A METHOD FOR STUDYING THE RAPID ABSORPTION OF GASES BY LIQUIDS[1]

BY P. G. LEDIG AND E. R. WEAVER

RECEIVED DECEMBER 15, 1923

This paper is a report of experimental work carried out at the Bureau of Standards with the purpose of developing a method for the accurate study of the absorption of gases in liquids. The data given relate to the absorption rates of sodium hydroxide solutions for carbon dioxide, not because of any special interest in this particular reaction, but because it is a convenient reaction for use in developing the method. This study was made as the first part of a general investigation of the rates of solution of gases in liquids. A later complete report will include other methods of attack used in the study of absorption, but the apparatus and the results to be described here are of such interest that they are reported separately.

The method used is very simple in principle. A bubble of carbon dioxide is absorbed in a closed system, open to the air only through a capillary tube. The resulting contraction of the bubble produces motion in the thread of solution in the capillary tube and a photographic method is used to obtain a time record of this motion.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

Description

The apparatus, a section of which is represented diagrammatically in Fig. 1, consists of three parts: (1) the light-tight drum in which the photographic record is made; (2) the absorption apparatus; and (3) an arc light with condensing lenses to give parallel light.

The light-tight drum has in it, mounted on a steel shaft, a rotatable cylinder 15 cm. wide which holds the 1.5-meter strip of bromide paper used for making the record. A suitable opening is provided for introducing and removing the paper, and a narrow slit which has a shutter provides for making the exposure. A 54-cycle electrical tuning fork is mounted on one end of the slit and has a thin copper shutter on one prong which alternately opens and shuts the slit and produces a record of time intervals on one edge of the moving paper. The cylinder is driven by a shunt-wound direct current motor, which has a rheostat in the armature circuit used as an adjustable drop coil. This makes it possible to change the motor speed readily, which nevertheless remains satisfactorily constant when adjusted, in spite of variations in line voltage.

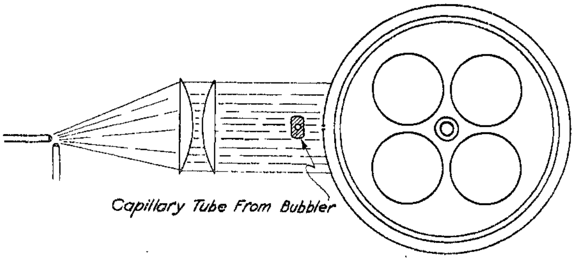
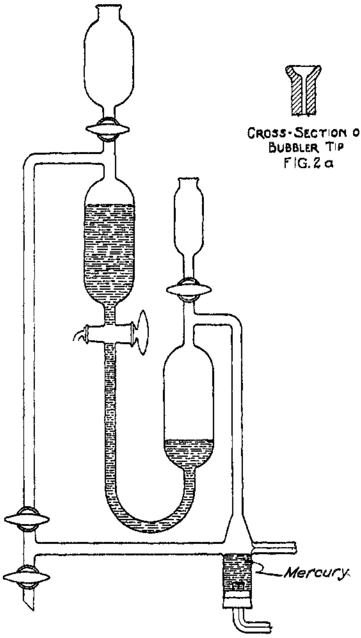


Fig. 1.—Diagrammatic sketch of the complete apparatus.



Cross-Section of Bubbler Tip
Fig. 2a

Fig. 2.—The absorption apparatus.

In the absorption apparatus shown in Fig. 2, the method of introducing a single bubble of known volume into the liquid is new. This is done by using a bubbler tip of the form shown in Fig. 2a, immersed in mercury. Careful testing showed that a clean tip immersed in clean mercury gives accurately reproducible bubbles, the size of which can be determined by counting and measuring the total volume of a large number of single bubbles. Most of the results given in this report were obtained by the use of a tip which produced bubbles 0.036 cc. in volume. The bubble rises to the surface of the mercury and if conditions are right it will remain as a mercury bubble for one to three seconds. This gives plenty of time to open the shutter on the drum and close the gas flow to the tip before the bubble breaks through the mercury surface and absorption begins. A flow of solution down through the conical absorber tube keeps the bubble suspended free from the walls and gives a method of absorbing from a rising bubble at constant pressure. Two mercury bulbs are so connected that as mercury flows from the upper one to the lower one, the solution is made to flow as described above. Suitable stopcocks and bulbs provide flow control and access for filling, emptying and cleaning the apparatus. The capillary tube opens from one side of the absorber cone, and is ground and polished plane-parallel on two opposite sides so that the light passing through it is not refracted around the capillary tube into the slit of the drum.

The arc light is a small compact one, designed at the Bureau for oscillograph work, and the light from it is made parallel by two 15cm. condenser lenses.

To use the apparatus, the drum is first loaded with bromide paper in the dark room, and the motor and tuning fork are started and adjusted. Then the arc is started and the absorption apparatus so placed between the drum and the light that the capillary bore of the tube entirely shuts off light from the slit of the drum. The flow of solution down through the absorber cone is started and adjusted to the proper rate and then a single bubble of carbon dioxide is passed into the mercury in the lower end of the absorber tube. Before this bubble breaks through the mercury surface, the flow of carbon dioxide is shut off and the shutter in the drum is opened. It is closed when the absorption is completed.

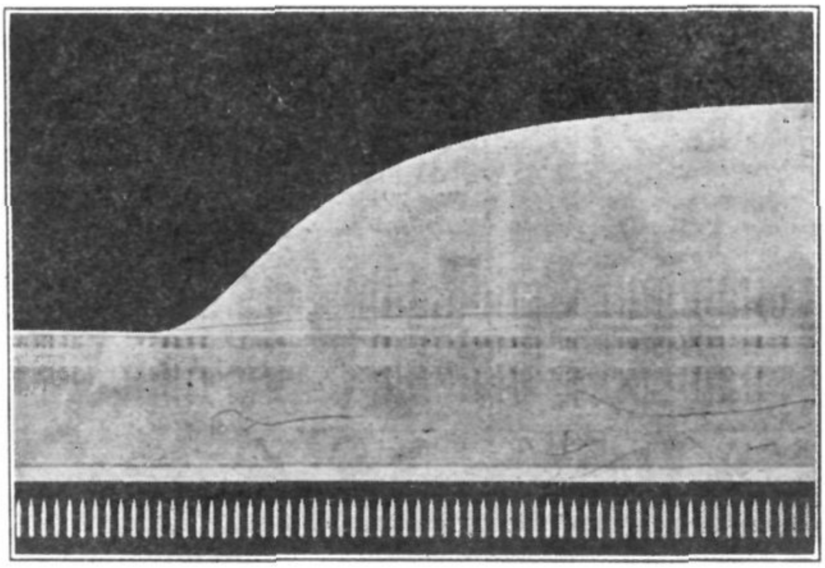


Fig. 3.—A photographic record produced by this method.

A record produced by this method is shown in Fig. 3. Data for rate calculations are taken from this curve by means of a curve-drawing instrument designed at the Bureau. Since the motion of the solution in the capillary is proportional to the volume absorbed, a measurement of displacement is made at convenient time intervals (recorded on the edge of the sheet by the tuning fork) and after determining the average volume and area of the bubble during each interval of time, the rate is calculated by means of the formula, $V/(A \times T) = a$, where a is the rate of absorption in cc. per min. per sq. cm. of surface, V is the volume absorbed, A is the average area and T is the time of absorption (time of interval taken on record).

Rate of absorption is plotted against the average volume of the bubble for each run. Figs. 5 and 6 indicate the general appearance of such curves.

Results

The study of rates of absorption by the use of this apparatus has given a more complete conception of the course of absorption of gas from a spherical bubble by liquid reagents than it has hitherto been possible to obtain.

Contrary to some earlier assumptions, the rate is not constant during the whole period of absorption from a bubble (at constant pressure), but follows a three-stage cycle. This can best be seen in the absorption curves for very dilute solutions (see Fig. 4), and the higher concentrations undoubtedly follow the same course, though this is not entirely evident if a curve is studied by itself. The cycle is begun by a very high absorption rate at the newly formed liquid-gas surface, but as absorption goes on it falls again very quickly to a rate where an equilibrium condition exists, the rate being controlled by the diffusion of the reagent to the surface and of the reaction product away from the surface. The third stage in the cycle begins when the diluting gas[2] starts to slow up diffusion of the gas to the surface. This latter stage is undoubtedly affected by the diminished buoyancy or rate of rising as the bubble becomes smaller and there is a decrease in the stirring action which renews the absorbing liquid at the surface.

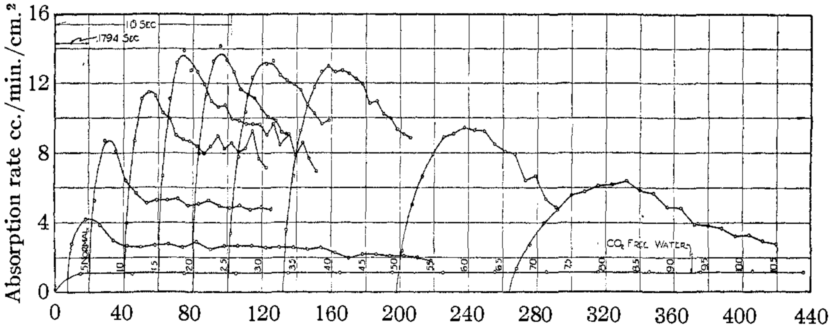


Fig. 4.—The effect of concentration of the sodium hydroxide solution.

The curves shown in Fig. 4 are rates of absorption plotted against time, though the initial points of the curves themselves are arranged to show the concentration relations of the solutions used. The curves were all made under the same conditions of apparatus control, bubble volume, temperature and pressure, and the capillary tube in each case was filled with the

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[2] Even in case the carbon dioxide introduced into the solution is absolutely pure, some other gas (such as dissolved air) will diffuse into the bubble while it is still large and will become apparent when the size is greatly reduced. In other cases an insoluble gas was purposely introduced.

solution being studied. The average rate of absorption a during the period of absorption is shown in Table I.

TABLE I

AVERAGE RATE OF ABSORPTION

Normality	0.0	0.2	0.5	1.0	1.5	2.0	2.5	3.3	4.95	6.6
a	1.0	2.8	5.6	9.0	10.5	11.0	11.5	11.0	8.0	5.0

The fact that the rate does not rise instantaneously to the maximum can be attributed in part to three things: (1) the bubble breaks out of the mercury during a measurable period of time rather than instantaneously, as might be supposed; (2) the inertia of the liquid in the capillary tube and surface tension at the free meniscus require a definite pressure difference caused by absorption to produce motion; and (3) the viscosity of the solution itself produces a lag in this rise to the maximum, as will be shown later. These factors seem sufficient to account for the time (about 0.1 second) required to reach a maximum rate in the case of the dilute solutions; but the concentrated solutions in which as much as 0.75 second is required to attain the maximum rate must involve some additional factor which has not been fully explained. Judging from the rather meager conductivity data available it appears probable that the maximum concentration of ions in a sodium hydroxide solution occurs at a concentration of the alkali not far from that at which the rate of solution of carbon dioxide is a maximum. The concentration of the active reagent may, therefore, actually increase with neutralization of the stronger solutions, and the delayed maximum may be caused partly by the effect of mass action.

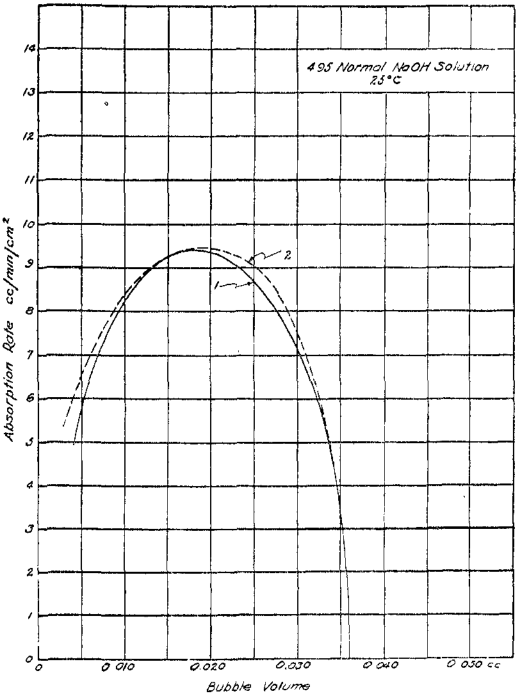

Fig. 5.—The effect of the viscosity of the solution (in capillary tube only).

There is some evidence that viscosity is a factor (a similar delay is shown by Curve 2 of Fig. 6) but the reason why viscosity should have this effect is not evident. The viscosity of the solution in the capillary tube itself seems to produce only a very slight effect, if any, upon the shape of the rate curve. This is shown very clearly in Fig. 5, where the rate curves from two runs on 4.95 *N* sodium hydroxide solution are compared. Run 1 was made with the capillary filled with the solution itself, but in Run 2 it was filled with heptane, which has only half the viscosity of water. That the viscosity of the solution does affect the absorption and changes the form of the curve is shown in Fig. 6. Curve 1 was made by running a 2.5 *N* sodium hydroxide solution in the apparatus in the usual way, but Curve 2 was made with a solution of 2.5 *N* sodium hydroxide containing also 100 g. of cane sugar per liter, which practically doubled the viscosity of the solution. In every other respect the runs were identical, and since it has been shown that the viscosity of the solution in the capillary has no effect upon the shape of the rate curve, the change is undoubtedly caused in part by the decreased rate of rise of the bubble and by the increased thickness of the unstirred film around the bubble.

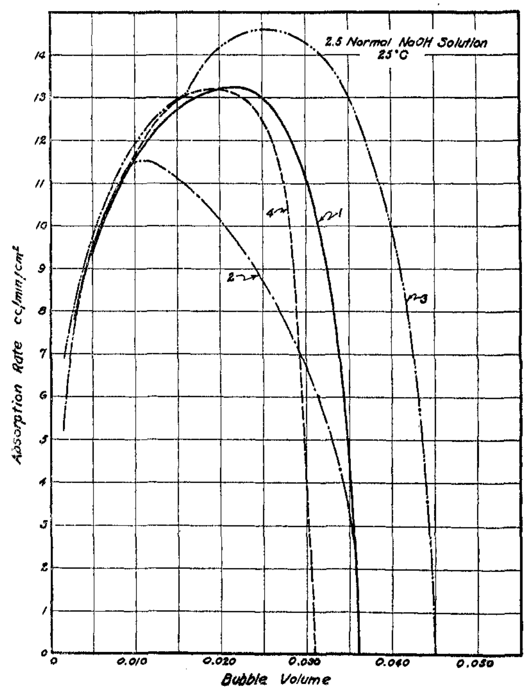

Fig. 6.—The effect of the viscosity of the solution (Curves 1 and 2) and of original bubble volume (Curves 1, 3 and 4).

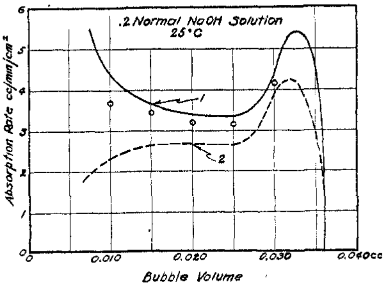

Fig. 7.—The effect of adding an inert gas to the carbon dioxide.

In the same figure (Fig. 6) are shown two other curves, 3 and 4. These were made with 2.5 *N* sodium hydroxide solution in the apparatus at standard conditions (25°, 750 mm.) but with carbon dioxide bubbles of different volume than the standard 0.036cc. bubbles. The stage of rapid rise and fall is different from that in the standard case, but when the point of constant rate seems indicated, all three curves follow the same course.

In Curve 1 of Fig. 7 is shown the effect of substituting a mixture of air and carbon dioxide (83.6%) for the pure carbon dioxide used in all the other experimental work cited. All other conditions were standard. The values of a were calculated in the usual way with the additional operation of dividing by the partial pressure of the carbon dioxide. The rate of absorption seems to vary inversely as the square root of the gas pressure and the small circles near the curve are values of a calculated from the normal rate curve (using pure carbon dioxide) for 0.2 N sodium hydroxide solution (Curve 2) by the use of the relation $a = a_1 \frac{\sqrt{p_1}}{\sqrt{p}}$.

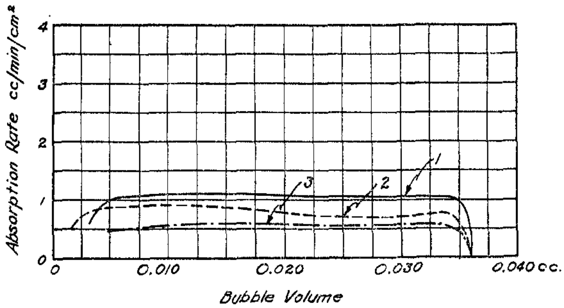

Fig. 8.—Rate curves for carbon dioxide-free water, sodium carbonate solution and carbon dioxide-free sugar solution.

A determination of the rate curve for water free from carbon dioxide and for 2.5 N sodium carbonate solution brought to light the interesting fact that the carbonate solution absorbs carbon dioxide at less than half the rate at which it is absorbed by pure water. Fig. 8 shows the results obtained; Curve 1 is that for pure carbon dioxide-free water and Curve 3 that for sodium carbonate solution.

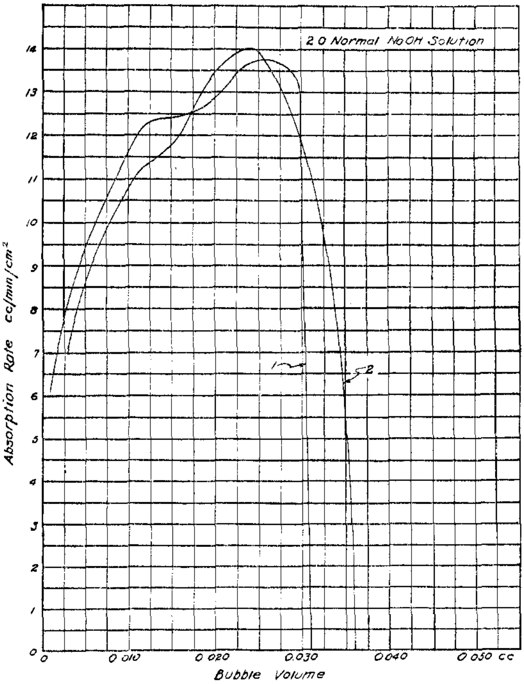

Fig. 9.—Comparison of rate curves from two forms of apparatus.

It was thought that the viscosity of the carbonate solution might be great enough to account for this difference and so a third determination (Curve 2) was made with a cane sugar solution having the same viscosity as the carbonate solution, which was freed from carbon dioxide by boiling under a vacuum. This gave a rate considerably lower than that for water, but not as low as the sodium carbonate solution. The remaining difference is probably due to the mass-action effect of the carbonate and bicarbonate ions in solution.

An independent means of making a check on the general accuracy of form and values of a rate curve is provided by some preliminary work done with a motion picture method for determining the rate of absorption, which used a similar absorber tube and a bubbler tip of the same form but which produced smaller bubbles. Curve 1 of Fig. 9 was made from data obtained with the motion picture apparatus using 2.0 N sodium hydroxide solution at 27°, and Curve 2 was made with the same solution at 25° using the present apparatus. In spite of the difference in bubble volume and the increase in temperature, which always raises the values of a, the curves show a very satisfactory general agreement as to shape and height.

Summary

An apparatus has been described which makes possible a detailed study of absorption from small bubbles. The rate of absorption from a bubble of pure carbon dioxide is not a constant but goes through three stages, finally diminishing to zero at the end. The effect of concentration and other variables has been studied with the particular purpose of determining the reproducibility and accuracy of the method.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM.[1] VII. THE HYDRIDES OF GERMANIUM

BY L. M. DENNIS, ROBERT B. COREY AND ROY W. MOORE

RECEIVED DECEMBER 17, 1923

Introduction

When this investigation was begun in 1921, the only statement in the literature concerning germanium hydride was one by Voegelen,[2] who had found that a volatile hydride of germanium was formed when the chloride was reduced by nascent hydrogen (zinc and sulfuric acid), that the gas reduced a solution of silver nitrate, and that it yielded a "germanium mirror" when passed through a heated glass tube. The amount of ger-

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[1] This article is based upon the theses presented to the Faculty of the Graduate School of Cornell University by Robert B. Corey and Roy W. Moore in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Voegelen, *Z. anorg. Chem.*, **30**, 325 (1902).