be of the same general order. Wise[4] has shown that ferric chloride at high concentrations of the salt in selenium oxychloride forms a true molecular compound, $FeCl_3.SeOCl_2$. This may in part be responsible for its low molecular conductance in selenium oxychloride, and the low value for this constant indicates further the absence of any action corresponding to the hydrolysis in aqueous solution.

The writer wishes to express his appreciation to Professor Victor Lenher for his valuable suggestions and stimulating interest during the progress of this work.

Summary

1. The determination of the specific conductance of selenium oxychloride has been described.

2. The conductances of six chlorides in selenium oxychloride have been determined.

3. A method of analyzing selenium dioxide for its water content has been described, and a process given by which this material may be obtained in the anhydrous state.

Madison, Wisconsin

[Contribution from the Department of Chemistry of Yale University]

PREPARATION AND ANALYSIS OF CONSTANT MIXTURES OF AIR AND CARBON DIOXIDE[1]

By John Johnston and Albert C. Walker

Received October 27, 1924 Published July 3, 1925

In a re-determination of the equilibrium in the system, alkali carbonate—carbon dioxide—water, the method necessitated a continuous supply of a mixture of air and carbon dioxide, having a constant partial pressure of carbon dioxide. To establish equilibrium conditions in an experiment, two to five days were required, depending upon the concentration of carbonate in solution, and therefore a large volume of gas mixture of uniform composition was essential. A variation of 50 parts of carbon dioxide per million (0.000050 atmosphere of carbon dioxide) of the gas mixture caused a decided shift in the equilibrium in dilute solution, and consequently it was necessary to reduce the variations to 10 parts per million or less, and to have a method of analysis capable of detecting with certainty variations of this order of magnitude.

In this paper will be discussed, (I) the variations in the content of atmospheric air, and the consequent limitations of this gas mixture for use in studying the system: alkali carbonate—carbon dioxide—water, or

---

[1] From a part of the dissertation presented by Albert C. Walker to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1923.

similar cases; (II) the preparation of mixtures of air and carbon dioxide of any desired constant partial pressure of carbon dioxide, such mixtures to be supplied continuously over periods of several days; (III) a rapid method of determining the carbon dioxide content of gas mixtures, such as air, within five parts per million.

I. Atmospheric Air

The proportion of carbon dioxide in the atmosphere and the constancy of this proportion have been the subject of many investigations during the last hundred years. The general result is that the proportion is about 310 parts per million over the land, and slightly less over the ocean,[2] which acts as the regulator and reservoir. There has been some difference of opinion as to how much this proportion may vary, in any one locality, with wind conditions, seasons, etc. The results of Letts and Blake,[3] and of Benedict,[4] indicate that the fluctuations may be at least 10% of the total quantity. However, recent evidence presented by Kendall[5] led us to hope that outside air might be used as a sufficiently constant gas phase for the carbonate equilibrium study, so we endeavored to use it for this purpose, making more than 100 determinations of the carbon dioxide content of atmospheric air during a period of 15 months in 1921–1922.

The analyses were made during the course of a large number of individual equilibrium experiments, under a wide variety of weather conditions, during both rain and snow storms, on windy and on calm days, and some at night, thus giving a representative cross section of the variations to be expected during the course of a year in New Haven. It became evident that the carbon dioxide content might not vary more than 5 to 10 parts per million in the course of a day, or for several days, if the wind conditions were not variable; but with variable winds, the carbon dioxide content might change markedly in the course of only a few hours. For example, on June 7, 1922, three analyses made within eight hours showed a progressive decrease from 335 to 294 parts per million; this accords with the statement of Henriet and Bouyssy[6] that the variations in carbon dioxide content of the air are due to atmospheric currents. During the months of August and September, 1921, unusually long periods of relatively uniform weather prevailed, the winds then seeming to be less variable than at other seasons, and frequently over intervals of three to four days the partial pressure

[2] Except for the remarkable findings of Krogh in air over the sea about the island of Disko, near Greenland, where the proportion in July–August, 1903, ranged up to 700 parts per million [*Meddelelser om Gronland*, **26**, 409 (1904)].

[3] Letts and Blake, *Proc. Roy. Soc. Dublin*, **9**, 173 (1900).

[4] F. G. Benedict, "The Composition of the Atmosphere," *Carnegie Inst. Pub.*, No. 166 (1912).

[5] Kendall, THIS JOURNAL, **38**, 1492 (1916).

[6] Henriet and Bouyssy, *Compt. rend.*, **146**, 977 (1908).

of carbon dioxide changed very little. In Table I representative values (on a moisture-free basis) are given[7] to show the character of the fluctuations.

TABLE I

VARIATIONS IN THE CARBON DIOXIDE CONTENT OF ATMOSPHERIC AIR AT NEW HAVEN

Date: Aug., 1921	1	2	3	8	9	10	11	12	13	18	19	20	21	26	27	29	30
Parts per million	306	321	351	320	380	386	344	353	359	334	329	371	346	331	322	342	384
	306	312		322			344	348	362	331							

Date: Sept., 1921	2	4	5	6	12	13	19	24
Parts per million	327	364	330	331	332	332	353	392

The mean value for the carbon dioxide content of the atmosphere, from all of the 104 determinations made in this work was 345 parts per million; the minimum was 294, the maximum 407 and the maximum deviation from the mean 18%. All of these results were corrected for the moisture in the air, and the error in the method of analysis is, we believe, not greater than 1.5%.

The experimental work was performed in the Kent Chemical Laboratory of Yale University, situated near the center of the city of New Haven, but this fact does not necessarily account for the high concentration of carbon dioxide as compared with previous data on outside air, nor for the large variations in carbon dioxide content recorded. The sampling line by means of which air was drawn from without the building, was not located near chimneys or other sources of combustion, and it should be noted that during the month of August, 1921, when it was unlikely that neighboring sources of combustion gases could have a marked influence on the results, they ranged from 306 to 386 parts per million, corresponding to a deviation of at least 11% from the mean. The variation from day to day was normally much less than the maximum of 18%, and was frequently, for several days at a time, small enough to enable us to utilize atmospheric air in the carbonate equilibrium experiments. Previous observers have stated that the carbon dioxide content of atmospheric air in the cities is somewhat higher in winter than in summer, owing to the increased combustion of fuel; a general plot of all the determinations, made in an effort to test this point, indicated that the data conform to the requirements for a random distribution.

From these determinations we draw the following conclusions: (1) marked changes in the direction or velocity of the wind may be accompanied by variations in the carbon dioxide content of the air, but the magnitude or direction of these changes cannot now be predicted from a study of wind conditions; (2) the average carbon dioxide content of the atmosphere in New Haven in 1921 was about 345 parts per million; any trend towards higher values during the colder months is so small as to

---

[7] The method of analysis is described on a later page.

be negligible in comparison with the apparently fortuitous deviations from the mean, which occur at all seasons and may amount to as much as 18%.

It is clear, therefore, that atmospheric air cannot itself be used as an assured source of a constant partial pressure of carbon dioxide, for equilibrium experiments extending over several days, except during periods when wind conditions change little; accordingly, a method was sought which should at any time yield a mixture of substantially constant composition, over a range of partial pressures of carbon dioxide.

II. Artificial Mixtures of Air and Carbon Dioxide

The information to be gained from the literature on the subject of the preparation of mixtures, in large amounts, of two or more gases in any desired, constant proportions is meager. Höber[8] realized the necessity of maintaining a constant pressure of carbon dioxide in the gaseous hydrogen employed in making hydrogen-electrode measurements on blood solutions, and used an elementary method of preparing mixtures of hydrogen and carbon dioxide having any desired carbon dioxide tension. Schloesing[9] utilized a unique method of preparing any concentration of carbon dioxide in air, in large amounts, and his data on the equilibrium in solutions of calcium and magnesium carbonates indicate that he was successful in preparing mixtures of quite constant composition. G. B. and H. S. Taylor[10] recently described a method of mixing a gas with a liquid in constant proportions. In the present work, some experiments were conducted with a modification of their apparatus in an attempt to mix air and carbon dioxide in constant proportions, but the experiments were discontinued when another type of apparatus was developed which is simpler than either Schloesing's or the Taylors', and possesses the decided advantage of having no moving parts. With this new apparatus, continuously flowing mixtures of air and carbon dioxide may be prepared having any given concentration of the components from values as low as 50 parts per million up to one atmosphere of the pure gases, with a variation not exceeding 10 parts per million over a period of several days. For example, a mixture of air and carbon dioxide was maintained for a week within the limits 932 and 941 parts of carbon dioxide per million (as determined each day by analysis of a sample) and there is no reason to doubt that this degree of constancy could be maintained indefinitely.

The principle of this apparatus is to have air, under a constant pressure head, stream past one surface of a thin rubber diaphragm, and to have carbon dioxide, likewise under a constant head, stream past the other surface of the diaphragm. As has long been known, carbon dioxide diffuses through rubber several times as fast as air and, accordingly, a

---

[8] Höber, *Pfluger's Arch.*, **99**, 572, 593 (1903).

[9] Schloesing, *Compt. rend.*, **74**, 1552 (1872).

[10] G. B. and H. S. Taylor, *J. Ind. Eng. Chem.*, **14**, 1008 (1922).

thin sheet of rubber serves to regulate the mixing of the two gases, the composition of the resulting mixture depending—other things being equal—upon the effective area of the rubber diaphragm. Reasonable variation in pressure, hence of rate of flow, of the carbon dioxide, was without effect upon its concentration in the resulting mixture, provided that the rate of flow of air was constant.

Air from the low-pressure supply line[11] passed through the towers A, B, C and the flowmeter D to one side of the mixing device H (Fig. 1); carbon dioxide, from a cylinder, passed through a reducing valve, the tower E, reservoir F and flowmeter G to the other side of H, and diffused through the rubber membrane (a sheet about 0.15 mm. thick, such as is used by dentists) to the left side. The mixed gases then passed through the tower I, filled with glass beads, to insure thorough admixture, to the large reservoir J, whence the mixture was drawn off through the flowmeter K. The air pressure on either side of the flowmeter D was determined by the hydrostatic head in the overflow tubes M and P; similarly the pressure drop of the carbon dioxide through G was controlled by N and O. All four of these overflow tubes were immersed in water contained in a vessel L; this water level need not be maintained exactly constant, since the rates of flow depend, not upon the total hydrostatic head, but only upon the differential heads fixed by the relative positions of the four adjustable overflow tubes. To secure the necessary constancy of head, the overflow tube P, on the mixture side, it is to be noted, is

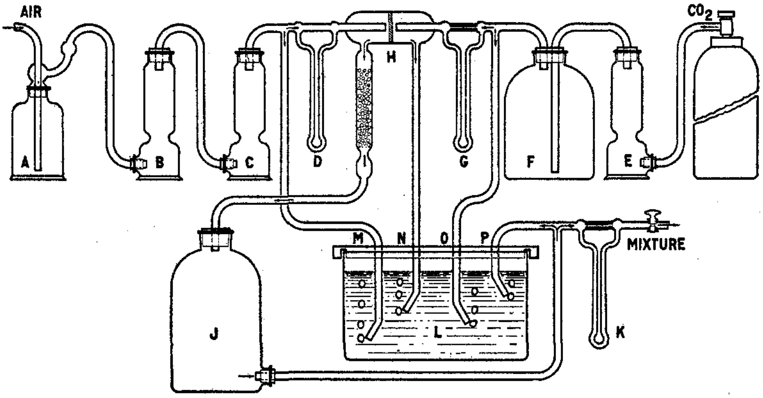

Fig. 1.—Apparatus yielding a constant mixture, in any desired proportion, of air and carbon dioxide. *A*, *B* and *C* contain, respectively, H_2SO_4, soda-lime and $CaCl_2$, to purify and dry the air-stream; *E* contains $CaCl_2$, to dry the CO_2 supply. *D*, *G*, *K* are flowmeters; *F*, *J* are reservoirs. The mixing device *H* consists of a thin rubber diaphragm cemented between the open ends of the two bell-shaped tubes; the stream of each gas being directed against this diaphragm to promote uniformity in the rate of diffusion of the CO_2 through the rubber into the air. *I* is a tower filled with glass beads, to ensure thorough mixing. *M*, *N*, *O*, *P* are constant head overflow tubes immersed in water in *L*; their relative positions, which are adjustable, control the pressure differences through the apparatus.

---

[11] This line was subject to marked fluctuations of pressure owing to the intermittent use of air elsewhere, but the apparatus took care of this.

essential; without it, the composition of the mixture will vary somewhat with variation in the amount used, which affects slightly the pressure at the exit side of the flowmeter K. We found it advisable to arrange for a constant flow through K continuously, by means of a stopcock which, when no equilibrium experiment was in progress, was adjusted so as to maintain the same pressure drop through K.

With this mode of controlling the several gas streams, satisfactory constancy of composition can be obtained with a simple T-tube (in which case the overflow tube N is unnecessary) in place of the diffusion device H; but for concentrations lower than about 1000 parts per million, and especially for the lowest concentrations, the use of the rubber diaphragm is distinctly advantageous. In order to secure a series of constant mixtures, it is necessary to have a number of diaphragms of different effective areas. In the experimental work for which this apparatus was primarily designed, a mixture of exactly predetermined composition was not required; what was important was to insure that when once a mixture in approximately the desired ratio had been obtained, its composition should remain unchanged for the duration of the experiment. In our work, the mixing device H consisted of two bell-shaped glass tubes, of diameter appropriate[12] to the composition desired, between which the rubber diaphragm was stretched and cemented; in some cases it would be preferable to use a single mixing chamber of metal, so constructed that a diaphragm of any effective area could readily be inserted between its two halves.

The samples for analysis were taken in an evacuated sampling bottle and analyzed, as described later. The evacuated bottle, with stopcock closed, was quickly connected to the exit line, thus momentarily shutting off the flow through K and directing the excess to P; the stopcock was opened until the manometer of K returned to its former steady reading and was continuously adjusted to maintain this. When the bottle was filled, as shown by a vanishing head on K, it was quickly disconnected and the normal flow through the apparatus recommenced.

The effectiveness of this general type of apparatus, even with a T-tube in place of the diffusion device, may be gaged from the following data,[13] representative of some of the many series of analyses carried out on separate settings. The results of one series of ten determinations follow.

Feb. 22		23		24		26	27	28	Mar. 1
A.M.	P.M.	A.M.	P.M.	A.M.	P.M.				
935	938	941	932	940	936	938	933	932	935

---

[12] With a rubber diaphragm of 40mm. diameter, the mixture contained about 350 parts of carbon dioxide per million; with 150mm. diameter, 1800 parts. The fact that these concentrations are not proportional to the total area of the diaphragm probably implies that the air stream did not sweep over the whole surface of the larger diaphragm.

[13] Furnished by Dr. W. D. Kline, who used this form in re-investigating the equilibrium of calcium carbonate and of magnesium carbonate in solution.

In another series the range in five days was between 375 and 384 parts per million; and, with concentrations greater than 2000, the variations were always within the error of analysis, estimated to be about 5 parts per million.

With the rubber diaphragm, the variations from day-to-day in mixtures of concentration less than 2000 were likewise negligible. However, in a continuous run, extending over sixteen days, with a single rubber diaphragm, the analyses made show a steady drift, as follows.

Aug. 2	3	9	11	16	17
361	362	365	364	369	370

Two months later, this identical diaphragm was again set up, under the same conditions as before, and now yielded 425 parts per million, a concentration which, according to the analyses, remained constant during the two weeks its use was continued. This secular change of permeability of rubber to gases is well known, as in the case of balloon fabrics to hydrogen; if it were of consequence in any case, it could probably be minimized by preventing access of light or oxygen to the rubber.

III. Method of Determining the Carbon Dioxide Content of Mixtures of Air and Carbon Dioxide

Some changes in manipulation and arrangement of Walker's[14] modification of the Pettenkofer method for determining atmospheric carbon dioxide were made, so that it was possible to analyze outside air for the carbon dioxide content rapidly, with an error less than 5 parts per million, as compared with the precision in the original method, of 10 parts per million. This corresponds, however, to a percentage error of about 1%, because of the very small quantity of carbon dioxide present in the atmosphere; but further improvements in the precision of the method would be attended with difficulties. Methods of the type used by Reiset[15] and others, while more precise, are slow and complicated. The form of apparatus is obvious from Fig. 2.

Manipulation.—Bottle A, after being cleaned and dried, was closed with the rubber stopper carrying the stopcock C, and evacuated to a pressure of 1 to 2 mm. of mercury; C was then closed, the bottle disconnected from the vacuum pump and the samples taken as described previously.

For atmospheric air, 50 to 60 g. of 0.03 *N* standard barium hydroxide solution was weighed[16] in a 75cc. glass-stoppered Erlenmeyer flask which

---

[14] Walker, *J. Chem. Soc.*, **77**, 110 (1900).

[15] Reiset, *Ann. chim.*, [5] **26**, 148 (1882). This type of method involves the determination of the gain in weight of an absorption tube after the passage of a measured, large volume of air. Reiset used at least 600 liters of air in an analysis.

[16] The normalities of the standard solutions were expressed in equivalents per 1000 g. of water and the titrations were made on a weight basis.

had previously been "washed out" with air free from carbon dioxide; this alkali was then transferred to A as rapidly as possible by removing the stoppers, pouring the solution into A, and quickly replacing the stoppers. The empty Erlenmeyer flask was again weighed and the exact weight of barium hydroxide solution added to A thus ascertained. The bottle A was shaken vigorously, with C closed, to facilitate the absorption of carbon dioxide, which was found to be complete in two minutes.[17] Meanwhile standard 0.1 N hydrochloric acid in quantity somewhat more than equivalent to the barium hydroxide solution to be filtered from A to B, was weighed into a flask B, closed with a glass stopper. The apparatus was then connected as shown in Fig. 2 and suction applied at S. C was opened and as much of the solution in A as would run out was filtered through the Munroe

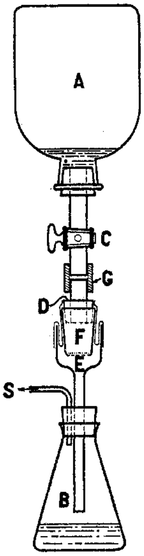

Fig. 2.—A is a bottle (2700 cc.), in which the sample was taken, connected through the stopcock C and the piece of heavy rubber tubing G with the tube passing through the rubber stopper D. D fits into the platinum Munroe filtering crucible F, which has a layer of spongy platinum, connected through the funnel E with the glass-stoppered Erlenmeyer flask B, which contains an excess of standard hydrochloric acid. S is a suction line to facilitate filtration.

[17] Freund, *Z. Hygiene*, **91**, 219 (1920). Freund investigated the determination of carbon dioxide in air by three different modifications of Pettenkofer's method. In one of these he absorbed carbon dioxide from a sample of air in a solution of sodium hydroxide and barium chloride, and states that absorption was complete after 20 minutes of shaking or rolling the sample bottle on a rolling table. There seems to be no reason to doubt that the reaction was completed in much less time than he reported necessary. He also endeavored to absorb carbon dioxide from a sample of air in neutral distilled water, but found absorption still incomplete after a full hour of shaking. Apparently he failed to realize that a condition of equilibrium exists between the carbon dioxide content of water and a gas phase in contact with it, which would render it quite impossible to absorb all of the carbon dioxide in this way. He cited 5% as being the accuracy of the Pettenkofer method and added: "one can perhaps assert that none of these rapid methods ever give the accuracy claimed." It is evident that his conclusions were drawn without considering the equilibrium conditions or difficulties which, by proper manipulation, may be overcome.

crucible[18] F into B; but instead of washing out the residual solution in A, as recommended by Walker, we preferred to determine what weight of solution reached B and to apply the appropriate correction. The apparatus was disconnected by closing C, opening S and taking off Flask B, which was closed with its glass stopper and weighed again. The excess of hydrochloric acid was then titrated with 0.03 *N* barium hydroxide solution, with phenolphthalein as indicator, to a faint pink color which was finally established by a single drop (0.03 g.) of the barium hydroxide solution provided that Flask B had been washed out with air free from carbon dioxide prior to the introduction of the acid.

The method of calculation may best be illustrated by an example: 54.350 g. of barium hydroxide solution (0.02950 *N*) was weighed into A, which initially contained 2725 cc. of the sample; 51.800 g. filtered into 16.600 g. of hydrochloric acid (0.08897 *N*)[19] contained in B, and 0.793 g. of the barium hydroxide (=0.0234 milliequivalent) was required to complete the neutralization of the acid. The total acid was 1.4769 milliequivalents, whence there were 1.4535 milliequivalents of alkali in the 51.800 g. of solution which reached B, and $1.4535 \times (54.35/51.80) = 1.5251$ milliequivalents of alkali in A after absorption of the carbon dioxide, as compared with 1.6033 initially. Therefore there was 0.0782 milliequivalent, or 0.0391 millimole of carbon dioxide, in $2725 - 54 = 2671$ cc. of sample, corresponding to a partial pressure of carbon dioxide of 0.000357 atmospheres or a concentration of 357 parts per million.

When air free from carbon dioxide[20] was taken, and the identical procedure followed, the results were always as if the sample had contained 25–30 parts of carbon dioxide per million. The fact that a large number of such determinations made over a period of two years gave a result consistently between 0.0027 and 0.0032 millimole of carbon dioxide (corresponding to 25 to 30 parts per million) is presumptive evidence that this is a constant of the apparatus used, in which case the results of actual analyses should be corrected by subtraction of this amount. This "blank" was not due to leakage of air into the sample

---

[18] The filter of platinum sponge completely removed the precipitate of barium carbonate in a few moments under a slight suction head; there was therefore no appreciable loss of water by evaporation, and no error in the weight of the solutions from this source. The filter was prepared according to the directions of Snelling, THIS JOURNAL, **31**, 456 (1909).

[19] Standardized (a) by precipitation as silver chloride (b) by titration with carefully purified sodium carbonate, with very concordant results. The barium hydroxide solution was standardized against this acid.

[20] Made by passing air slowly through a tube, two meters long, containing moist soda lime, and tested by the total absence of a precipitate in an hour when it was bubbled slowly through a solution of barium hydroxide and barium chloride contained in an efficient absorption apparatus. Air actually containing 25 p.p.m. would have given, under these conditions, a definite precipitate in a few minutes.

bottle after evacuation, as was proved both directly and indirectly. Moreover, when a sample bottle twice as large was used, the rest of the apparatus remaining the same, the "blank" remained the same, corresponding then, however, to half the apparent proportion observed before, or about 15 parts per million. All of this indicates that the blank is due to the presence of carbon dioxide in the air in that part of the apparatus—namely, the Munroe crucible and the funnel—which was not washed out, before each analysis, with air free from carbon dioxide; and a calculation based on the relative volume of this part and on the proportions of carbon dioxide present in the room shows that the greater part of the blank is in fact thus accounted for.[21] The remainder doubtless entered Flask B during the manipulation; this amount, however, was always the same, both in the blank and the actual determinations. The fact that the "blank" varied so little—for one drop (0.03 g.) of the barium hydroxide solution corresponds to 0.0004 millimole of carbon dioxide—encouraged us to apply it as a proper correction to the results. Consequently, we subtracted 0.0030 millimole from the amount of carbon dioxide found; thus, in the example given above, the net amount of carbon dioxide is $0.0391 - 0.0030 = 0.0361$ millimole, corresponding to 330 parts per million. We venture to believe that the final result is in error by less than 5 parts per million, and that the relative precision is appreciably better than this. Greater accuracy could doubtless have been secured by a method in which a large volume of the air was slowly bubbled through a barium hydroxide solution; but such a method seemed less well adapted to our primary purpose.

This method was planned, and used mainly, for mixtures of carbon dioxide content not very different from that of the atmosphere. For mixtures containing more than 2000 parts per million (0.2%) some modifications would be advisable; for instance, more concentrated standard solutions would be used, but the difficulty in securing accurate results occurs, not in the case of such mixtures, but in those which contain only a few hundred parts per million.

Summary

1. It was found that outside air in New Haven was a convenient source of a constant proportion of carbon dioxide for work on equilibrium in carbonate solutions, during periods of settled weather, but was not satisfactory when the wind was changeable.

---

[21] In later work, Mr. U. B. Bray has reduced to a minimum the volume of this part of the apparatus, with a corresponding reduction in the "blank;" the net result is the same. Mr. W. D. Kline, working with somewhat higher concentrations of carbon dioxide, found it necessary to modify the manipulation by introducing the barium hydroxide solution into A through a second glass tube inserted in the stopper from a weight buret having a tip about 10 cm. long.

2. A form of apparatus is described which has proved altogether satisfactory as a means of securing mixtures of air and carbon dioxide in fixed proportions. It could be used with equal success in other cases in which the composition of a gas phase must be maintained within narrow limits; for instance, to furnish constant mixtures of hydrogen with carbon dioxide, so as to enable one to apply the hydrogen electrode to carbonate solutions.

3. A modification of the Pettenkofer method of analysis is described, which yields more accurate results, particularly when the proportion of carbon dioxide is very small.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. I. THE EFFECT OF VARIOUS CONCENTRATIONS OF WATER VAPOR ON THE REACTION BETWEEN CHLORINE AND POTASSIUM IODIDE AND CHLORINE AND POTASSIUM BROMIDE[1]

BY L. B. PARSONS

RECEIVED OCTOBER 27, 1924 PUBLISHED JULY 3, 1925

Although both solid potassium iodide and solid potassium bromide react immediately with moist chlorine to liberate the corresponding halogens, there is no appreciable reaction if the various substances are dry. The effect of different concentrations of water vapor upon these reactions constitutes the subject of this investigation. The method of attack consisted in passing chlorine containing a known concentration of water vapor over the potassium halides and subsequently determining the quantity of the halide converted to the chloride.

Method.—The extent of the reaction between the chlorine and the salts was measured by obtaining the loss in weight of the well-dried halide after the halogen set free by the chlorine had been removed by evacuating and heating to 200–250° in a current of dry air. Suitable precautions were taken to insure that at the initial and final weighings the walls of the reaction chamber were in the same state and that the material was dry. Since in most cases the loss in weight amounted to 0.003–0.1 g. this method gave sufficiently accurate results.

The partial pressure of the water vapor in the chlorine for amounts up to 15 mm. was controlled by bubbling the gas through saturators containing various concentrations of sulfuric acid at suitable temperatures; for partial pressures of water vapor greater than that indicated above, the gas was passed through water. The vapor pressures of the sulfuric acid solutions were interpolated from Sorel's data.[2] The saturators, leads

---

[1] The work included in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[2] Sorel, *Z. angew. Chem.*, 3, 272 (1889).