nearly proportional to the weight concentration than to the elevations calculated by the Washburn general boiling-point law.

TABLE IV

RATIO OF Δt OBSERVED CALCULATED

	Ratio of weight concns.	Ratio of Δt	
Solvent		Observed	Calcd.
Alcohol	1:1.961	1:1.955	1:1.930
Acetone	1:2.06:3.075	1:2.06:3.06	1:2.045:3.02

Summary

1. An ebullioscopic apparatus capable of an accuracy of 1% has been constructed. One of its principal features is a simple pressure regulator capable of other applications in physics and chemistry.

2. The Lewis equation for change in boiling point of a binary mixture on addition of a non-volatile solute has been tested experimentally and found to have the same order of accuracy as other laws of dilute solutions.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE ELECTRICAL CONDUCTANCE OF SELENIUM OXYCHLORIDE SOLUTIONS[1]

BY A. P. JULIEN

RECEIVED JULY 21, 1924 PUBLISHED JULY 3, 1925

Introduction

This paper deals with the specific electrical conductance of selenium oxychloride and the molecular conductance of certain metallic chlorides in this solvent. The lack of quantitative experimental conductance data in non-aqueous solvents and the importance of such data in studying the laws of solution, render valuable any additional contributions in this field.

The literature contains but two references to earlier determinations of the electrical conductance of selenium oxychloride. Lenher[2] used carbon electrodes and found the specific conductance to be approximately 9.6×10^{-5} mhos. and Wildish[3] stated that in the determination of the dielectric constant of selenium oxychloride he used a product having a conductance of about one-tenth that of conductivity water. Since the values reported for the specific conductance of selenium oxychloride are in such wide variance, there is an obvious necessity for establishing a method for the preparation of that compound which will yield a product having a constant electrical conductance.

---

[1] This paper is an abstract of a thesis submitted by A. P. Julien in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Lenher, THIS JOURNAL, **43**, 29 (1921).

[3] Wildish, *ibid.*, **42**, 2607 (1920).

The active chemical nature of selenium oxychloride has been shown by Lenher[2] and for this reason the choice of solutes for a study of solutions includes but a few of the salts usually employed in such work. Wise[4] has found, however, that certain of the metallic chlorides are dissolved by selenium oxychloride without apparent chemical reaction and these salts were the ones used in the study of solutions.

Selenium Oxychloride.—This substance was prepared from very pure selenium and selenium dioxide by the method of Lenher[5] with special precautions to exclude moisture, particularly during the entire process of fractional distillation at reduced pressure.

Metallic Chlorides.—Since very small amounts of moisture produce such a marked effect on the conductance of selenium oxychloride, it is obvious that a study of this nature necessitates the use of anhydrous chlorides as well as anhydrous reagents. The sodium, potassium and barium chlorides were purified by two precipitations from aqueous solution with hydrogen chloride and then dried. The sodium and potassium chlorides were fused in platinum to insure freedom from moisture and the barium chloride was heated in a current of pure air at 500° for several hours. The ammonium and mercuric chlorides were purified by repeated sublimation. The ferric chloride used was Merck's C. P., resublimed and kept anhydrous by handling only in a dry atmosphere.

The Analysis of Selenium Dioxide for Water

The literature contains no mention of an accurate method for the determination of water in selenium dioxide. Other workers in this field have seen fit to avoid the direct determination of water and have used an arbitrary standard to establish the fact that the selenium dioxide used was free from moisture. Manchot and Ortner[6] have stated that selenous acid can be completely dehydrated to selenium dioxide by desiccation over phosphorus pentoxide. Their conclusions are based on the loss in weight of the material rather than on a direct determination of water. Meyer[7] claims to have prepared and used dry selenium dioxide, but mentions no method of analyzing the material for its water content.

The author has developed a method of analysis for small amounts of water in selenium dioxide based on the principle that when selenium dioxide is volatilized through heated potassium chromate, the selenium dioxide combines with the chromate to form stable compounds and the water may be collected and weighed. Manipulating the boats, weighing bottles, etc., inside a box desiccator, a 1g. sample is covered with 4 to 5 times its weight of potassium chromate. The boat and contents are then transferred to a combustion tube heated to 600° in an electric furnace. Dry oxygen is used to sweep the gases out of the tube and the moisture from the sample is collected in a weighed U-tube filled with phosphorus pentoxide. A blank determination is made to compensate for opening

---

[4] Wise, This Journal, **45**, 1233 (1923).

[5] Lenher, *ibid.*, **44**, 1664 (1922).

[6] Manchot and Ortner, *Z. anorg. Chem.*, **120**, 300 (1922).

[7] Meyer, *ibid.*, **83**, 51 (1913); *Ber.*, **55**, 2082 (1922).

the combustion tube and for any moisture in the potassium chromate. The results of many analyses by this method showed that freshly sublimed selenium dioxide as well as material which had been desiccated over phosphorus pentoxide for as long as 12 months always contained from 0.045 to 0.088% of water. It was found, however, that samples of selenium dioxide which had been heated for three to four hours at 150° in a current of dry air contained no water.

Apparatus

Conductances were measured by the familiar Kohlrausch arrangement. A Leeds and Northrup combination bridge and resistance was found to be sufficiently accurate for this work. The source of alternating current was an audio oscillator made by the General Radio Company. The water-bath was regulated at 25° ± 0.02°. Practically all the modern refinements in bridge assembly were available for this work, but they afforded no advantage, since the experimental error from other causes was several times that of the measuring apparatus proper.

One of the cells used was a modified Washburn type which could be sealed to different designs of distilling apparatus. This cell had electrodes of polished platinum of 25mm. diameter and a cell constant of 0.18002. All cell constants were based on the assumption that the specific conductance of 0.02 N potassium chloride solution (volume method) at 25°, is 0.002768 reciprocal ohms.

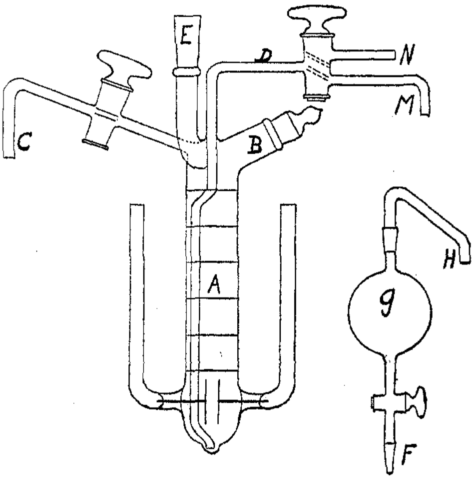

Fig. 1.—Conductivity cell and reservoir.

The type of cell used in studying solutions is shown in Fig. 1.

The body of the cell, A, had a capacity of 30 cc. and was carefully calibrated after the cell was complete. The reservoir for pure solvent, G, joined the cell at the ground joint EF. Openings C, H and N were all protected with phosphorus pentoxide drying tubes. No stopcock grease of any sort could be used because of the active chemical nature of selenium oxychloride. For this reason all stopcocks were ground to a smooth surface with rouge and selenium oxychloride was used as a lubricant.

Just previous to use, the cell and reservoir were connected and while they were held at 135° in an air-bath, dry oxygen was passed at a rapid rate through the whole apparatus for a period of not less than one hour. The whole was allowed to come to room temperature, while the current of dry gas was continued. Selenium oxychloride was transferred from the receiver of the distillation apparatus to the reservoir G by means of an L-shaped glass tube which allowed an exchange of contents between the two containers without opportunity for moisture contamination from the atmosphere.

To empty the cell, a source of dry oxygen under a pressure of 3 cm. of mercury was attached to C and the stopcock in D turned so as to give exit at M. For the introduction of solutes which were hygroscopic, the neck B was projected through a rubber valve opening in the side of a box desiccator. With a steady flow of dry gas entering through C, B could be opened and a solute introduced without danger of atmospheric contamination.

The dilution of solutions within the cell was accomplished by adding through B a weighed amount of solute, or a concentrated solution containing a known amount of solute, and then adding sufficient selenium oxychloride to bring the contents of the cell to any desired volume. The contents of the cell were stirred by applying the oxygen pressure at N and slowly bubbling the gas through the solution. This gave a very efficient agitation, and did not affect the conductance of the solution. After the apparatus had come to constant temperature the resistance was measured. A fraction, usually one-half of the solution, was then forced from the cell and an equal quantity of pure solvent added from the reservoir. The calibration of the cell had taken account of the volume of solution which would remain in the tube D between the stopcock and the bottom of the cell. After the fresh portion of solvent had been added, oxygen was passed in at N, thus forcing the concentrated solution out of the tube D to become intimately mixed with the solute and solvent in A. By this process the dilution of the solution could be carried to any desired point.

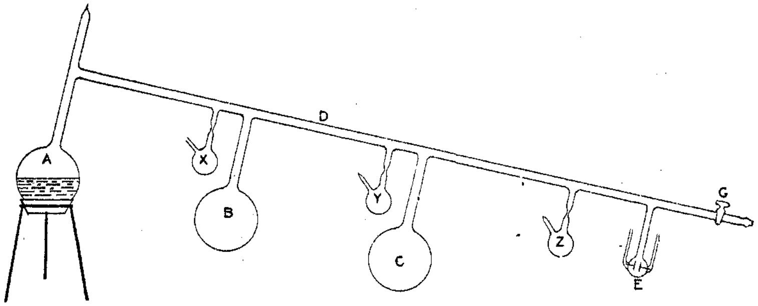

Fig. 2.—Fractional distillation apparatus.

The Specific Conductance of Selenium Oxychloride

Preliminary work had shown that moisture was among the chief disturbing factors in the preparation of pure selenium oxychloride. Hence, to secure the reagent in a high state of purity necessitates either the use of only anhydrous materials in its preparation or the removal of impurities after the preparation is complete. The latter scheme proved more successful. Fractional distillation was found to be the best method of purification, and the all-glass closed apparatus shown in Fig. 2 was used for this purpose.

As illustrated, D is a continuous piece of soft glass tubing about 2 cm. in diameter to which are attached the distilling bulbs A, B and C, the fraction bulbs X, Y and Z and the conductivity cell E. Bulbs A, B and C are about 10 cm. in diameter and have necks made into Vigreux columns to prevent the mechanical carrying over of non-volatile material. The fraction bulbs are attached to D with slightly constricted necks to facilitate sealing off with a flame.

Before being used the whole apparatus was cleaned with chromic-sulfuric acid mixture, washed out with distilled water, and then rinsed with impure portions of selenium oxychloride to remove any material from the glass which might be soluble in this strong reagent. The apparatus was finally cleaned with distilled water, and dried by heating at 150° in an air-bath and alternately exhausting and filling with pure, dry air.

Fractional distillation of selenium oxychloride in this apparatus gave a final product which had been thrice distilled and completely protected from contamination by atmospheric moisture. The volatile water, chlorine, selenium tetrachloride and the less volatile selenium monochloride had been progressively removed. The even less volatile selenium dioxide remained behind in the distillation flasks, and ample opportunity had been given for the dissociation of all but the most stable molecules of selenium oxychloride. Five distillations were made with separate samples of selenium oxychloride. The original portions contained such impurities as the excess of selenium dioxide, free chlorine and water, and had specific conductances ranging from 2.33×10^{-5} to 8.30×10^{-5} mhos. The final products of the five distillations had the following specific conductances: 2.59×10^{-5}, 2.33×10^{-5}, 2.14×10^{-5}, 2.33×10^{-5} and 2.33×10^{-5} mhos.

The fact that the values for samples of selenium oxychloride, carefully prepared and protected from contamination, agree within the limits of experimental error with the value found for the specific conductance using the closed apparatus and starting with material having various degrees and amounts of contamination, establishes this constant as $2.0\ (\pm\ 0.3) \times 10^{-5}$ mhos.

Temperature Coefficient.—Knowing the specific conductance at 25°, the conductance of selenium oxychloride may be calculated for any other temperature by means of the following equation.

$$K_t = K_{25^\circ} + 0.0392t - 0.943 - 0.0002\,(t - 12)^2$$

Observed and calculated values agree within 0.1% for temperatures of 11.8°, 25.0°, 36.7°, 46.0° and 64.0°.

Effect of Some Common Impurities on the Conductance of the Reagent

Many quantitative data were obtained which may be briefly summarized as follows. Water and hydrogen chloride increase the conductance quite markedly; chlorine gas and selenium tetrachloride produce a similar effect, but to a much smaller degree; selenium mono-chloride in very small amounts causes a very slight decrease in the conductance; selenium dioxide, although but slightly soluble in the reagent, decreases the conductance in a very marked manner. This latter fact was at once unique and interesting. Further, it was found that an excess of selenium dioxide acted, in a selenium oxychloride solution, very much like a dehydrating agent. In order to determine whether or not selenium dioxide had the power to lessen the effect on one or more of the other constituents which increased the conductance, a solution of selenium oxychloride containing an excess of the compound under question was treated with an excess of selenium dioxide. It was learned that solutions containing chlorine and selenium monochloride were but little affected by the excess of selenium dioxide, whereas those containing water, hydrogen chloride and selenium tetrachloride had their conductances lowered. In the case of the tetrachloride the results were anticipated, since selenium tetrachloride and selenium dioxide unite to form more pure reagent.

As might be expected from the nature of the products formed, there seems to be a very definite relation between water and hydrogen chloride in their effect on the conductance of selenium oxychloride. The action of each on selenium oxychloride is according to the equations: $SeOCl_2 + H_2O = SeO_2.2HCl$; $2SeOCl_2 + 2HCl = SeO_2.2HCl + SeCl_4$. Selenium tetrachloride has but little effect on the conductance of selenium oxychloride, so in both cases the active agent in increasing the conductance must be the compound $SeO_2.2HCl$. Furthermore, since the $SeOCl_2$ required in the equation is always present in large excess in the experimental work, it may be concluded that one mole of hydrogen chloride forms but one-half as much of the compound responsible for the increased conductance as does one mole of water. This ratio is confirmed by the molecular conductances of hydrogen chloride and water in selenium oxychloride, that for hydrogen chloride being 2.51 and for water 4.78, both at dilutions of one mole per 136 liters of solvent. This established the fact that $SeO_2.2HCl$ has a relatively low molecular conductance, and in whatever way it may be considered that this compound ionizes in selenium oxychloride solution, it is certain that selenium dioxide will have the mass-law effect and repress this ionization. This accounts for the apparent dehydration effect of selenium dioxide, and for the decrease in conductance caused by this substance when added to selenium oxychloride containing water or hydrogen chloride.

The decrease in the conductance of the pure solvent when selenium dioxide is added is attributed to the fact that the equilibrium, $2SeOCl_2 \rightleftharpoons SeO_2 + SeCl_4$, is shifted in the direction of decreasing the dissociation of the selenium oxychloride.

Molecular Conductance of Metallic Chlorides in Selenium Oxychloride

Chloride solutions of known concentration were prepared in one of two ways. Ferric chloride, mercuric chloride and sodium chloride dissolve in the reagent to give clear solutions, and since their solubilities were known, weighed quantities of these were added to weighed portions of the solvent. Both potassium and ammonium chlorides form an insoluble addition compound with the solvent and barium chloride dissolves quite slowly, so that solutions of these salts were made by adding an excess of solute, allowing the mixture to come to equilibrium at 25°, filtering out of contact with the air, and then analyzing the filtered solution for its content of solute. Dilution in the cell was carried out as previously described.

TABLE I

CONDUCTANCE MEASUREMENTS

SODIUM CHLORIDE

Specific conductance, L, $\times 10^{-5}$ mhos.	78.00	43.12	23.06	11.69	5.70		
Liters containing 1 mole of solute, V_m	19.348	38.69	77.39	154.8	309.6		
Mol. conductance, μ	15.09	16.69	17.85	18.09	17.65		
Specific conductance, L, $\times 10^{-5}$ mhos.	209.3	121.6	67.43	37.14	19.33	9.801	4.849
Liters containing 1 mole of solute, V_m	5.835	11.67	23.34	46.68	93.36	186.7	373.4
Mol. conductance, μ	12.20	14.20	15.72	17.32	18.05	18.30	18.10

POTASSIUM CHLORIDE

Specific conductance, L, $\times 10^{-5}$ mhos.	387.21	26.30	161.8	93.04		
Liters containing 1 mole of solute, V_m	2.428	4.856	9.712	19.42		
Mol. conductance, μ	9.40	12.77	15.71	18.07		
Specific conductance, L, $\times 10^{-5}$ mhos.	52.59	28.19	15.09	7.766	3.806	
Liters containing 1 mole of solute, V_m	38.84	77.68	155.3	310.6	621.0	
Mol. conductance, μ	20.42	21.90	23.43	24.12	23.63	
Specific conductance, L, $\times 10^{-5}$ mhos.	413.0	268.7	157.6	93.66	50.85	26.82
Liters containing 1 mole of solute, V_m	2.428	4.856	9.712	19.42	38.84	77.68
Mol. conductance, μ	10.03	13.05	15.31	18.19	19.75	20.84
Specific conductance, L, $\times 10^{-5}$ mhos.	13.78	7.147	3.646	1.857	0.966	
Liters containing 1 mole of solute, V_m	155.3	310.6	621.0	1242	2484	
Mol. conductance, μ	21.40	22.20	22.64	23.07	24.00	

AMMONIUM CHLORIDE

Specific conductance, L, $\times 10^{-5}$ mhos.	477.1	327.5	192.7	112.2	62.96	34.90
Liters containing 1 mole of solute, V_m	1.984	3.968	7.936	15.87	31.74	63.48
Mol. conductance, μ	9.47	13.00	15.28	17.80	19.97	22.12
Specific conductance, L, $\times 10^{-5}$ mhos.	18.31	9.44	4.84	2.348	1.187	0.603
Liters containing 1 mole of solute, V_m	126.96	253.9	507.8	1015	2030	4060
Mol. conductance, μ	23.25	23.93	24.60	23.85	24.10	24.50
Specific conductance, L, $\times 10^{-5}$ mhos.	477.4	309.3	186.7	112.2	63.57	35.12
Liters containing 1 mole of solute, V_m	2.062	4.124	8.248	16.496	32.99	65.98
Mol. conductance, μ	9.84	12.77	15.40	18.50	20.95	23.15
Specific conductance, L, $\times 10^{-5}$ mhos.	18.34	9.67	4.77	2.32	1.14	0.582
Liters containing 1 mole of solute, V_m	131.9	263.8	527.6	1055	2110	4220
Mol. conductance, μ	24.20	25.50	25.15	24.50	24.08	24.55

MERCURIC CHLORIDE

Specific conductance, L, $\times 10^{-5}$ mhos.	0.608	0.278	0.114	0.042	0.025	0.016
Liters containing 1 mole of solute, V_m	30.0	60.0	120.0	240.0	480.0	960.0
Mol. conductance, μ	0.182	0.167	0.137	0.101	0.120	0.154
Specific conductance, L, $\times 10^{-5}$ mhos.	0.957	0.444	0.168	0.084	0.049	
Liters containing 1 mole of solute, V_m	20.35	40.7	95.0	190.0	380.0	
Mol. conductance, μ	0.195	0.181	0.160	0.160	0.186	

FERRIC CHLORIDE

Specific conductance, L, $\times 10^{-5}$ mhos.	230.6	149.7	85.55	49.30	
Liters containing 1 mole of solute, V_m	1.372	2.744	5.488	10.97	
Mol. conductance, μ	3.164	4.11	4.69	5.41	
Specific conductance, L, $\times 10^{-5}$ mhos.	28.66	16.90	10.54	6.787	3.387
Liters containing 1 mole of solute, V_m	43.9	43.9	87.8	175.6	351.2
Mol. conductance, μ	7.42	7.42	9.25	11.92	11.90

TABLE I (*Concluded*)

Specific conductance, L, $\times 10^{-5}$ mhos.	228.6	146.3	85.80	49.05	28.43	
Liters containing 1 mole of solute, V_m	1.574	3.148	6.296	12.59	25.18	
Mol. conductance, μ	3.61	4.60	5.40	6.18	7.15	
Specific conductance, L, $\times 10^{-5}$ mhos.	16.50	10.03	6.13	3.244	1.412	
Liters containing 1 mole of solute, V_m	50.36	100.72	201.4	402.8	805.6	
Mol. conductance, μ	8.31	10.10	12.35	13.07	11.38	
BARIUM CHLORIDE						
Specific conductance, L, $\times 10^{-5}$ mhos.	126.6	112.7	85.27	58.62	37.70	
Liters containing 1 mole of solute, V_m	2.714	4.428	10.856	21.71	43.42	
Mol. conductance, μ	3.44	6.12	9.26	12.73	16.37	
Specific conductance, L, $\times 10^{-5}$ mhos.	23.26	13.70	7.81	4.22	2.19	1.13
Liters containing 1 mole of solute, V_m	86.84	173.7	347.4	694.8	1389	2778
Mol. conductance, μ	20.20	23.80	27.13	29.30	30.40	31.40
Specific conductance, L, $\times 10^{-5}$ mhos.	127.57	107.1	75.57	50.77	32.86	20.28
Liters containing 1 mole of solute, V_m	3.256	6.512	13.024	26.05	52.1	104.2
Mol. conductance, μ	4.15	6.98	9.85	13.22	17.12	21.18
Specific conductance, L, $\times 10^{-5}$ mhos.	12.02	6.74	3.563	1.848	0.928	0.441
Liters containing 1 mole of solute, V_m	208.4	416.8	833.6	1667	3334	6668
Mol. conductance, μ	25.08	28.08	29.70	30.78	30.95	29.40

The results of conductance measurements are given in Table I and shown graphically in Fig. 3. With the exception of ferric chloride, the chlorides studied were found to have a conductance in selenium oxychloride which is approximately one-seventh that in aqueous solution, and to

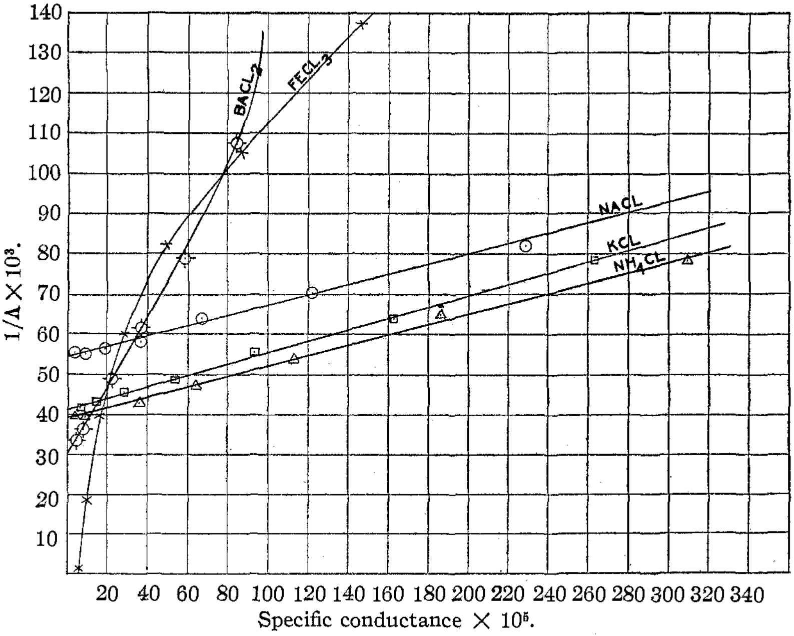

Fig. 3.—$1/\Lambda - L$ plot for metallic chlorides in selenium oxychloride. The $FeCl_3$ curve is displaced 80 on the axis of ordinates.

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.