Professor Derby has suggested (in conversation) the use of fused salts for electrolytically heated thermostats at much higher temperatures, and the same idea could be applied to calorimetry. In fact the use of such a calorimeter should open up a whole new field to accurate physical-chemical measurements.

Summary.

In conclusion it may be said that adiabatic calorimeters eliminate cooling corrections, thereby excluding errors from precision work and saving time in commerical work. They permit a slow and careful reading of a thermometer while the temperature is constant, and the taking of temperature before and after a determination becomes unnecessary.

Errors from evaporation are negligible in the Richards type of calorimeter or in the modification described in this article, as there is no colder matter in contact with the vapor; and heat can not be lost or gained from the room by conduction. For high temperatures, for slow reactions, or for large temperature differences, these calorimeters are absolutely necessary.

The description of an adiabatic calorimeter of new design is given and it has proved to be accurate and simple of operation.

The automatic control of this calorimeter by means of a selenium cell has been successful, and this very sensitive relay may find application in other work.

The calorimeter herein described is being used in this laboratory in the accurate determination of the specific heats of salt solutions and of organic liquids.

Worcester, Mass., April 29, 1916.

[Contribution from the Department of Chemistry of Columbia University, No. 269.]

THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.

By James Kendall.

Received May 20, 1916.

1. Introduction.

The evaluation of the specific conductivity of pure water in equilibrium with the carbon dioxide of the atmosphere is a problem which is of especial importance in connection with the water correction in conductivity determinations.[1]

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[1] This subject will be discussed fully in a forthcoming communication.

Carefully prepared conductivity water, when in contact with air, has been found by many observers[1] to possess a constant specific conductivity of $0.7–0.8 \times 10^{-6}$ reciprocal ohms at the ordinary temperature (usually 18°). Considering the different methods of preparation employed by different investigators in different laboratories, the numerous values recorded in the literature are remarkably uniform. Whatever method may have been followed and however small the specific conductivity of the water obtained may be when first prepared, its value rises rapidly, on standing, to the limits indicated above, and then remains practically constant.

The suggestion has frequently been made that the conducting impurity in such samples of water consists almost entirely of carbonic acid derived from the atmosphere.[2] It is of interest, therefore, to test whether the *directly-determined* experimental value for the specific conductivity of water in contact with air is in agreement with the value which may be calculated *indirectly* with the help of the following data:

(*a*) The ionization constant of carbonic acid.
(*b*) The mobility of the hydrogen carbonate ion, HCO_3^-.
(*c*) The carbon dioxide content of the atmosphere.
(*d*) The solubility of carbon dioxide in water.

Concordance between the observed and calculated values will obviously support strongly the validity of the above suggestion.

The figures at present available, however, for such a calculation are only approximate and incomplete. It is the purpose of this paper to establish exact values for all of the quantities tabulated above at 0°, 18° and 25°, the three temperatures most generally employed in conductivity investigations. It may also be mentioned that an accurate knowledge of these quantities is of some importance apart from the present problem, since their use is essential in many geological studies and in questions of interest in various other fields.[3]

2. Previous Work.

The problem has already been taken up, for the temperature of 18°, in the researches of Knox[4] on the conductivity of carbonic acid solutions

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[1] A complete list of references will be found in the succeeding article.

[2] See especially Kohlrausch and Holborn, "Leitvermögen der Electrolyte," p. 111 (Leipsic, 1898); Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900); and Arrhenius, *Meddelanden från K.-Vet. Akads. Nobelinstitut*, Band 2, No. 42 (1914).

[3] For example, see R. C. Wells, *J. Wash. Acad. Sci.*, **5**, 617 (1915); Johnston, THIS JOURNAL, **38**, 947 (1916); Walker and Kay, *J. Soc. Chem. Ind.*, **31**, 1013 (1912); Arrhenius, *Phil. Mag.*, **41**, 237 (1896).

[4] Knox, *Ann. der Physik.*, **54**, 44 (1895). The figures given in this and all succeeding references have (where necessary) been recalculated from Siemens' units to units of the reciprocal ohm.

and of Walker and Cormack[1] on the dissociation constants of very weak acids.

The conductivity measurements of Knox, as will be shown in a later section of this paper, are obviously considerably in error; the method employed by him for the calculation of the solubility of carbon dioxide in water under atmospheric conditions is also inaccurate. Consequently, his conclusion that the calculated value for the specific conductivity of water in equilibrium with the carbon dioxide of the atmosphere (0.60×10^{-6} reciprocal ohms at 18°) is substantially identical with the direct experimental value of Kohlrausch and Heydweiller[2] (0.64×10^{-6} reciprocal ohms at 18°) is not entirely convincing.

The results obtained by Walker and Cormack are of much greater value. It was found that carefully purified Dundee water (prepared by three successive distillations, namely from alkali, from phosphoric acid, and without the addition of any chemical) possessed a specific conductivity of 0.75×10^{-6} reciprocal ohms at 18°. The ionization constant of carbonic acid at this temperature was found to be 3.04×10^{-7} (a value differing by 20% from that obtained by Knox). The dilution of a solution saturated with carbon dioxide at a pressure of 760 mm. was taken as equal to 24 liters, according to Bunsen's absorption data.[3] Assuming the partial pressure of carbon dioxide in air to be 0.0003 atmosphere,[4] the specific conductivity of water in equilibrium with atmospheric carbon dioxide was calculated to be 0.70×10^{-6} reciprocal ohms at 18°. The agreement of this value with that directly determined is clearly close enough to support the assumption that the specific conductivity of water in contact with air is to be ascribed almost entirely to dissolved carbon dioxide. Further confirmation was found in the results obtained from the application of a correction made under this assumption to the conductivity values of aqueous solutions of phenol.[5] This will be more fully discussed in the following communication.

It must be admitted, however, that the greater part of the data employed by Walker and Cormack in the above calculation is only approximate. In fact, the only exact figure utilized is that for the ionization constant of carbonic acid, and even that differs considerably from the value found by Knox.

In the present paper, therefore, the conductivity measurements of Walker and Cormack for the temperature of 18° have been repeated, and results have also been obtained for two other temperatures—0° and

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[1] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894).

[3] These results may be in error by several per cent., as may be seen by reference to the original paper, *Ann.*, **93**, 1 (1855).

[4] Obviously only a very rough approximation.

[5] Walker and Cormack, *J. Chem. Soc.*, **77**, 18 (1900).

25°. Exact determinations have been made regarding the carbon dioxide content of the atmosphere, and more recent and accurate data for the solubility of carbon dioxide in water have been employed in the final calculations. The different steps necessary for the exact solution of the problem are taken up in order below. The summarized results will be found in Section 8.

3. The Ionization Constant of Carbonic Acid.

A solution of carbon dioxide in water possesses considerable electrical conductivity, due to the fact that the gas does not exist in solution merely as carbon dioxide, but also combines with the solvent to give the acid H_2CO_3, which ionizes into H^+ and HCO_3^-. The complete equilibrium to be considered[1] is

$$CO_2 \text{ (gas)} \rightleftarrows CO_2 \text{ (dissolved)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-.$$

(The secondary dissociation of HCO_3^- into H^+ and $CO_3^=$ is so minute[2] that it need not be taken into consideration here.)

The conductivity of carbonic acid solutions was first investigated by Pfeiffer[3] at temperatures of 0° and 12.5°. Ionization constants were unknown quantities when these measurements were published, and since the results of Pfeiffer, recalculated according to the dissociation theory, have not previously been tabulated, they are summarized in the following table. The first column indicates the dilution of the solution in liters (V); the second the equivalent conductivity[4] (Λ); the third the dissociation constant k, multiplied by 10^7 to avoid an excess of zeros. Subsequent tables are arranged according to the same scheme.

TABLE I.—CARBONIC ACID (PFEIFFER).

Temperature, 0°.			Temperature, 12.5°.		
V.	Λ.	$k \times 10^7$.	V.	Λ.	$k \times 10^7$.
2.37	0.167	1.68	2.79	0.304	3.18
3.07	0.188	1.65	3.29	0.334	3.25
3.85	0.213	1.69	5.27	0.421	3.23
4.39	0.235	1.81	6.59	0.450	(2.95)?
13.38	0.458	(2.26)?	13.38	0.661	3.14
∞	264.0	..	∞	323.0	..
Whence $k = 1.7 \times 10^{-7}$			Whence $k = 3.2 \times 10^{-7}$		

The constancy of the values in the last column is by no means all that could be desired at either temperature, and the dissociation constants given are, at best, only approximate values. This is probably due to the poor quality of water (specific conductivity $= 3.2 \times 10^{-6}$ reciprocal ohms) employed in the investigation; the conducting impurities present

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[1] The discussion of this equilibrium is deferred to a later section; see page 1493.

[2] McCoy, *Am. Chem. J.*, **29**, 437 (1903); Johnston, THIS JOURNAL, **37**, 2001 (1915).

[3] Pfeiffer, *Ann. Phys.*, **23**, 625 (1884).

[4] The determination of the equivalent conductivity at infinite dilution (Λ_∞), which is necessary for the evaluation of k, is described in a following section.

might suffice to account for a considerable portion of the measured conductivities.

The measurements of Knox[1] may also be used to calculate the ionization constant of carbonic acid at temperatures of 12.5° and 18°. Knox did not attempt to carry out these calculations himself, in an abstract[2] an erroneous value is given, and Walker and Cormack[3] have given one series of results under the old Siemens units. The complete results of Knox have, therefore, been calculated to modern units and are summarized in Table II, below.

TABLE II.—CARBONIC ACID (KNOX).

Temperature, 12.5°.			Temperature, 18°.		
V.	Λ.	$k \times 10^7$.	V.	Λ.	$k \times 10^7$.
10.48	0.603	3.32	12.61	0.778	3.76
12.24	0.652	3.32	14.54	0.838	3.79
15.43	0.735	3.34	24.9	1.090	3.75
20.79	0.853	3.36	53.2	1.581	3.70
29.77	1.019	3.35	125.0	2.445	3.77
∞	323.0	....	∞	354.0	....
Whence $k = 3.34 \times 10^{-7}$			Whence $k = 3.75 \times 10^{-7}$		

The constancy of the values obtained by Knox appears to be quite satisfactory; the dissociation constant at 12.5° is also in good agreement with that given by the measurements of Pfeiffer. Nevertheless the later results of Walker and Cormack indicate that Knox's measurements also are considerably in error. The cause is again, most probably, the poor grade of water (specific conductivity as high as 2.8×10^{-6} reciprocal ohms) used in the determinations. Thus, at dilution 125 in Table II, the conductivity of the water amounted to 12% of the total conductivity of the solution. For dilutions higher than 125, k is no longer a constant.

The careful measurements of Walker and Cormack at 18° are recalculated to modern units and given in Table III, below. A column indicating the ratio of the ionized to the total solute, $[\alpha]$, is added.

TABLE III.—CARBONIC ACID (WALKER AND CORMACK), 18°.

V.	Λ.	α.	$k \times 10^7$.
27.5	1.033	0.00289	3.05
55.0	1.454	0.00407	3.03
82.5	1.784	0.00500	3.04
110.0	2.052	0.00575	3.02
∞	354.0	...	..

Whence $k = 3.04 \times 10^{-7}$

The value of the ionization constant is about 20% less than the value calculated from Knox's figures, corresponding to an actual difference in the conductivity of 10%. The better quality of the water used (specific

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[1] Knox, *Loc. cit.*

[2] *Z. physik. Chem.*, **17**, 186 (1896).

[3] Walker and Cormack, *J. Chem. Soc.*, **77**, 9 (1900).

conductivity = 0.75×10^{-6} reciprocal ohms) and the fact that a more exact method was employed for measuring the concentration of the solutions[1] cause the investigators to conclude that their own numbers are probably the more accurate.

This conclusion is confirmed by the present author's measurements, which are given in Table IV, below. The experimental method adopted for the conductivity determinations was precisely that followed and described in previous investigations.[2] A Cantor cell[3] (with large electrodes only a small distance apart) was employed, this type possessing the advantage that successive dilutions can be made rapidly and accurately *within* the cell. A rotating commutator and a galvanometer were used in place of the more general induction coil and telephone, and gave satisfactory results throughout. The bridge employed was a three-meter platinum wire with one thousand divisions; readings could be obtained and duplicated to one-tenth of a division at all dilutions, the galvanometer being used as a zero instrument. The cells were immersed when in use in a large electrically-controlled thermostat, the greatest variations in temperature during the observation period being 0.005°.

The solutions of carbonic acid were prepared by passing pure carbon dioxide (obtained by the action of tartaric acid[4] on sodium carbonate) first through several wash-bottles containing conductivity water, and finally through the water (60 cc. in volume) contained in the Cantor cell. The water employed possessed a specific conductivity of 0.60×10^{-6} reciprocal ohms at 0°, 0.75×10^{-6} reciprocal ohms at 18°, and 0.85×10^{-6} reciprocal ohms at 25°. The method of its preparation will be described fully in the following paper.

The concentration of carbonic acid in each solution was determined *immediately after* the conductivity measurements had been completed, by running out half of the volume (30 cc.) from the cell and estimating its carbon dioxide content by a suitable modification of the Walker-Pettenkofer method.[5] The results obtained from duplicate experiments were in agreement within 0.2%.

An examination of the last column of Table IV will show that the ionization constants obtained at each temperature are *true* constants

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[1] A modification of Pettenkofer's method; see Walker, *J. Chem. Soc.*, **77**, 1110 (1900).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

[3] Cantor, *Z. Elektrochem.*, **9**, 922 (1903).

[4] If the carbon dioxide is prepared by the action of hydrochloric acid on marble in the usual manner, a trace of hydrochloric acid is invariably carried over into the conductivity cell, in spite of the several intervening wash-bulbs.

[5] Walker, *Loc. cit.* The solution was run directly into a bottle containing air free from CO_2, excess of baryta solution of known concentration added, and the normal procedure then followed.

throughout the whole range of dilutions. The value obtained at 0° is much higher than that given by the measurements of Pfeiffer; the value at 18° is in good agreement with that of Walker and Cormack.

Table IV.—Carbonic Acid (Kendall).

V.	Λ.	α.	$k \times 10^7$.
	T. 0°.		
25.4	0.631	0.00239	2.25
38.3	0.770	0.00292	2.23
50.0	0.888	0.00336	2.27
76.3	1.081	0.00409	2.21
99.8	1.242	0.00471	2.23
152.6	1.548	0.00586	2.27
∞	264.0	...	..
	Whence $k = 2.24 \times 10^{-7}$		
	T. 18°.		
30.9	1.100	0.00311	3.13
42.0	1.281	0.00362	3.12
61.2	1.550	0.00438	3.14
83.4	1.792	0.00506	3.09
∞	354.0	...	..
	Whence $k = 3.12 \times 10^{-7}$		
	T. 25°.		
36.4	1.403	0.00357	3.51
51.3	1.659	0.00422	3.48
72.8	1.977	0.00503	3.49
102.4	2.341	0.00595	3.48
145.5	2.820	0.00717	3.55
∞	393.4	...	..
	Whence $k = 3.50 \times 10^{-7}$		

4. The Heat of Ionization of Carbonic Acid.

The accuracy of the values for the ionization constant of carbonic acid given in Tables I–IV may be tested by calculating, from the figures for two different temperatures, the heat of ionization, Q, according to the van't Hoff formula

$$\log k_1 - \log k_2 = (Q/2.303\ R)\ (1/T_1 - 1/T_2)$$

(where k_1 and k_2 are the dissociation constants at absolute temperatures T_1 and T_2, respectively) and comparing the calculated value with that obtained by direct thermal measurements. The heat of the reaction: $\mathbf{H_2CO_3}$(aq.) = $\mathbf{H^+ + HCO_3^-}$ is the heat of mixture of one mol H_2CO_3 and one mol NaOH, less the heat of neutralization of one equivalent of a strong acid. From the measurements of Thomsen[1] it is equal to —2800 cals.

The values for Q as calculated from the results tabulated above are as follows:

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[1] Thomsen, "Thermochemische Untersuchungen," Leipzic (1882).

TABLE V.—HEAT OF IONIZATION OF CARBONIC ACID.

Temperature interval.	Observer.	Heat of ionization.
0°–12.5°	Pfeiffer	—7850 cals.
12.5°–18°	Knox	—3480 cals.
0°–25°	Kendall	—2890 cals.
0°–18°	Kendall	—2910 cals.
18°–25°	Kendall	—2830 cals.

The agreement of the values of the present paper with that directly determined is very satisfactory, the results of Pfeiffer and of Knox, on the other hand, give figures which are far too high.

A careful consideration of the complete equilibrium in carbonic acid solutions, however, introduces a disconcerting factor into the above calculation. The "ionization constants" and "heats of ionization" given in the tables preceding have not the exact signification that is usually attached to those quantities. The equilibrium equation

$$CO_2 \text{ (gas)} \rightleftarrows CO_2 \text{ (dissolved)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

shows that the nonionized portion of the solute exists partly as H_2CO_3 and partly as CO_2 in the solution. The *true* ionization constant: (conc. H^+)(conc. HCO_3^-)/(conc. H_2CO_3) will therefore be different from (and greater in value than) that calculated in Tables I–IV according to the formula: (conc. H^+) (conc. HCO_3^-)/(conc. H_2CO_3 + conc. CO_2). Similarly the *true* heat of ionization will differ from that calculated above, in which the heat of the reaction $\mathbf{CO_2}$ **(dissolved)** + $\mathbf{H_2O}$ = $\mathbf{H_2CO_3}$ is also included.

Owing to the fact that the ratio: (conc. CO_2)/(conc. H_2CO_3) in the solution will not vary with the dilution (providing only dilute solutions are investigated,[1] the "ionization constants" obtained in the above tables still show a constant value, although they are not the *true* ionization constants. The true values could be found from them if the ratio (conc. CO_2)/(conc. H_2CO_3) at each temperature were known. Unfortunately there does not appear to be any simple way of evaluating this ratio; the conclusion of Walker and Cormack[2] (recently re-expressed by Johnston)[3] that it is less than unity at ordinary temperature is quite devoid of experimental support.[4] In a following section, however, it will be shown that for the purpose of the present investigation the value of the ratio is quite immaterial, since it does not enter into any of the calculations involved.

Only with regard to the heat of ionization does our lack of knowledge concerning the ratio (conc. CO_2)/(conc. H_2CO_3) cause any confusion here. For if the value of this ratio changes to any great extent within the temperature interval 0–25°, then the heat of hydration:—$\mathbf{CO_2}$ **(dissolved)** + $\mathbf{H_2O}$ = $\mathbf{H_2CO_3}$ must be considerable (either positive or negative according

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[1] See page 1493.

[2] Walker and Cormack, *J. Chem. Soc.*, 77, 13 (1900).

[3] Johnston, THIS JOURNAL, 37, 2003 (1915).

[4] Walker, *J. Chem. Soc.*, 83, 182 (1903).

as the ratio increases or decreases). Heat produced (or absorbed) by this reaction is included in the "heat of ionization" given by the measurements of Thomsen, consequently the *true* heat of ionization may differ considerably from the value of 2800 cals. found by him. Any change in the ratio (conc. CO_2)/(conc. H_2CO_3) within the temperature interval 0–25° also introduces considerable errors into the calculation of the (apparent) "heat of ionization" by means of the van't Hoff equation, as given in Table V. Nevertheless, the fact that these calculated values show satisfactory agreement *for different temperature intervals* with the experimental value of Thomsen indicates that any disturbing factors are only small—*i. e.*, that the heat of hydration is negligible and that the degree of hydration varies but slightly with temperature.

5. Velocity of the Hydrogen Carbonate Ion.

In order to obtain the values for Λ_∞ (the equivalent conductivity at infinite dilution) for carbonic acid given in Tables I–IV above, we require to know the velocities of the ions H^+ and HCO_3^- at the temperatures studied.

The velocity of the hydrogen ion at 25° has recently been determined by the present author[1] and found to have the value 347.2 ± 0.4. With the aid of the temperature coefficient given by Kohlrausch[2] and the tables of Johnston[3] the probable values for the remaining temperatures may be found: at 18°, 313.9; at 12.5°, 288; and at 0°, 239. The accuracy of these values naturally decreases as the extrapolation interval increases, the last value may be in error by 1%.

The velocity of the hydrogen carbonate ion is not so accurately known. From conductivity measurements of sodium hydrogen carbonate solutions, Walker and Cormack[4] deduced the value 40.4 at 18°. Since, however, the highest dilution investigated was 512 liters, the error of extrapolation to infinite dilution might be appreciable.

Conductivity measurements with more dilute solutions of both sodium and calcium bicarbonates at 25° have been described by the author[5] in a previous investigation. The values for HCO_3^- obtained from the two series were 46.0 and 46.5, respectively. These figures are rendered only approximate by reason of the grade of the conductivity water employed in the dilutions (specific conductivity $= 1.10 \times 10^{-6}$ reciprocal ohms at 25°), which exercised a disturbing influence upon the values obtained at high dilutions and necessitated an uncertain correction. The measurements have, therefore, been repeated with a better sample of

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[1] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

[2] Kohlrausch, *Z. Elektrochem.*, 8, 290 (1902).

[3] Johnston, THIS JOURNAL, 31, 1010 (1909).

[4] Walker and Cormack, *Loc. cit.*

[5] Kendall, *Phil. Mag.*, 23, 974 (1912).

water, the experimental procedure (preparation of the solutions, estimation of their concentration, etc.) being exactly as described in the previous communication. The results are given in the following table:

Table VI.—Sodium and Calcium Hydrogen Carbonates. 25°.

$NaHCO_3$		$^1/_2[Ca(HCO_3)_2]$	
V.	Λ.	V.	Λ.
12.1	77.3	64	83.3
24.2	81.7	128	88.8
48.4	85.3	256	93.4
96.8	88.2	512	96.7
193.6	90.6	1024	99.6
387.2	92.4	2048	102.0
774.4	93.8	∞	107.7
1548.8	94.8		
3097.6	95.5		
∞	97.1		

The water employed in the dilutions possessed a specific conductivity of 0.80×10^{-6} reciprocal ohms at 25°. No correction has been made in the above values for the water conductivity. That this procedure leads to accurate values for bicarbonate solutions will be seen in the following paper, where it is also shown that the extent and influence of hydrolysis is inappreciable throughout the range of dilutions investigated.

The values for the equivalent conductivity at infinite dilution are derived by graphical extrapolation, according to the method of Bates.[1] Subtracting the figures for the cation of each series ($Na^+ = 51.0$ and $^1/_2Ca^+ = 61.4$), we obtain the values 46.1 and 46.3, respectively, for the velocity of the hydrogen carbonate ion at 25°. The mean value, 46.2, identical with that previously determined, is employed for the calculation of the velocities for the remaining temperatures, an average temperature coefficient[2] for the ion being assumed. The results obtained are: at 18°, 40.1; at 12.5°, 35; and at 0°, 25. The accuracy of these values is in each case commensurate with that given for the hydrogen ion at the same temperature.

The final values derived for the equivalent conductivity of carbonic acid at infinite dilution are therefore:

At 25°, 393.4; at 18°, 354.0; at 12.5°, 323; at 0°, 264. These are the figures which have been employed in Tables I–IV above.

The ionization data for carbonic acid solutions having now been established, we require to know the concentration of that solution which is in equilibrium with the carbon dioxide of the atmosphere. For this purpose it is necessary to determine two quantities—the carbon dioxide content of the atmosphere and the solubility of carbon dioxide in water.

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[1] Bates, This Journal, **35**, 519 (1913).

[2] Kohlrausch, *Z. Electrochem.*, **14**, 129 (1908).

6. The Carbon Dioxide Content of the Atmosphere.

A general impression exists that the carbon dioxide content of the atmosphere is a quantity which, although always very small, varies widely according to the conditions. Among the factors that have been mentioned as producing variations are the following:

(*a*) *Location.*—Land or sea, country or city, height above the ground, height above sea-level, latitude.

(*b*) *Time.*—Day or night, season of year, long-periodic changes.

(*c*) *Weather.*—Rain or fine, foggy or clear, sun or cloud, windy or calm, hot or cold.

(*d*) *Chance.*—Volcanic eruptions, forest fires, factory fumes, etc.

The actual effect of most of these influences is still uncertain.[1]

If large variations do constantly occur, then obviously it will be impossible to calculate standard values for the specific conductivity of pure water in contact with air, since the concentration of the saturated solution will vary considerably with the conditions. Nevertheless the fact that the experimentally-obtained values of different investigators in different laboratories check so remarkably closely suggests that, even in a laboratory atmosphere, any variations are in general only of minor importance.

The question of the difference between a normal out-door atmosphere and a laboratory atmosphere may first be considered. In this connection, the extensive researches of Benedict[2] on the oxygen content of the atmosphere afford some interesting evidence. The normal carbon dioxide content of outdoor air was found by him to be 3.1 parts in 10,000 by volume (mean of 212 analyses). Even in the Grand Central subway station of New York City, during a rush hour, the value is only doubled—6.1 parts in 10,000. Observations on the air of a crowded business street in Boston showed only the slightest trace of an increase. Hence in a well-ventilated laboratory the divergence from the normal out-door value should obviously not be excessive.

With regard to the influence of location, etc., the following quotation from a memoir by Letts and Blake[3] is, in view of the exhaustive nature of their tabulations, quite decisive: "It must be granted that the *average amount* of atmospheric carbonic anhydride is much the same under the most diverse conditions of weather, locality, season, etc. But on the other hand, there can be no doubt that variations in the amount do occur. These variations, if small in actual amount, are *relatively* large, and correspond with fluctuations of at least 10% of the total quantity."

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[1] Letts and Blake, *Proc. Roy. Soc. Dublin*, **9**, 107–270, 436–453 (1900).

[2] Benedict, "The Composition of the Atmosphere," *Publ. Carnegie Inst. Wash.*, 1912.

[3] Letts and Blake, *Loc. cit.*, pp. 173–4.

The present author is fortunate in being able to give direct experimental results on this important part of the problem from four laboratories situated in widely-separated localities: Edinburgh, Petrograd, Stockholm and New York City. The figures obtained are in entire agreement with the conclusions of Letts and Blake, the extreme variation in any one laboratory being ± 5% and for the whole range of observations being ± 10%. Conditions were kept as nearly constant as possible by working in large, well-ventilated rooms which contained no gas flames and were not employed for any other chemical work at the same time. The experimenter was the only person in the room and carefully abstained from smoking until determinations were completed.

Several methods were attempted for the estimation of carbon dioxide but the only simple procedure to afford rapid and consistent results was the Walker modification of the Pettenkofer method.[1] This gave values for the carbon dioxide content of the atmosphere which, as checked by duplicate measurements and by blank experiments, were found to be accurate to less than 0.1 part in 10,000 of the total volume. For a description of the experimental procedure and for the method of calculating the results the original paper of Walker should be consulted.

The results obtained are summarized in the following table. The values are expressed as parts of carbon dioxide in 10,000 parts by volume of air, without correction for moisture. They consequently represent partial pressures of carbon dioxide, in atmospheres multiplied by 10^{-4}.

TABLE VII.—CARBON DIOXIDE CONTENT OF THE ATMOSPHERE.

Laboratory.	Time.	Number of determinations	Carbon dioxide. Vols. per 10,000. High.	Low.	Average.
University of Edinburgh..........	March, 1911	18	3.88	3.56	3.69
Technological Institute, Petrograd...	Jan., 1913	10	3.80	3.51	3.65
Nobel Institute, near Stockholm....	June, 1913	8	3.56	3.21	3.29
Columbia University..............	July, 1915	24	3.52	3.26	3.39
		60	3.88	3.21	3.53

From an inspection of the above figures it will be evident that the variations are within the limits indicated by Letts and Blake, the greatest divergence from the final mean value—out of a total of sixty determinations—being a little less than ± 10%. If the results for any one laboratory only are considered, the maximum variation is in the region of ± 5%.

Such fluctuations are, in fact, only what may be looked for under the circumstances. The experimental method is accurate to less than 0.1 part in 10,000 of the total volume, but this represents an error of ± 3% in the carbon dioxide content. The tension of the water vapor in the atmosphere at the ordinary temperature of 20° may vary between 0 mm.

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[1] Walker, *J. Chem. Soc.*, **77**, 1110 (1900); see also Letts and Blake, *Loc. cit.*, pp. 219–229.

and 17.5 mm., *i. e.*, about 2% of the total atmospheric pressure, and since the results in Table VII are not corrected for moisture,[1] this involves a corresponding variation of 2% in the carbon dioxide content. The variations in the results for any one laboratory are thus practically accounted for. The larger variations in the mean value for different laboratories are in all probability due rather to small locality influences than to differences of ventilation. Thus the higher values at Edinburgh and Petrograd may be explained by the fact that the university buildings are situated in each instance near the center of the city. The Nobel Institute, on the other hand, lies out in the country several miles from Stockholm and the laboratories at Columbia are exposed to the fresh breezes across the Hudson[2] even in July.

As legitimately-comparable values of another observer, the results of Letts and Blake for the carbon dioxide content of "air collected in a large unused room in Queen's College, Belfast, with open windows and free circulation" may be quoted.[3] A total of twenty-three determinations shows the following values (expressed in parts per 10,000 by volume and not corrected for moisture): high, 3.73; low, 3.28; mean, 3.49; maximum variation, ±7%.

It is evident, therefore, that the carbon dioxide content of the atmosphere of a well-ventilated laboratory, unused for other chemical work, is in all normal cases near to the average value of 3.53 parts in 10,000 by volume given in Table VII above. The deviations *may* amount to ±10%. The fact may be pointed out at once, however, that such deviations will in no way vitiate the conclusions drawn in the following sections of this paper. A variation of 10% in the partial pressure of carbon dioxide involves, indeed, a variation of only 5% in the specific conductivity of the solution in equilibrium with the gas.[4] Variations of this magnitude are found in the observed values, as will be seen later.

In view of the relatively large errors that have been mentioned, it would be difficult to obtain a "standard value" for the carbon dioxide content of the atmosphere to a much higher degree of accuracy than the above, even if that content were (as it certainly is not) a true constant. The fact that exceedingly large variations (as much as 700%) have been recorded by numerous observers is probably due to the faulty methods of estimation that have been generally employed. The most careful and

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[1] In order that the values shown may represent actual partial pressures of carbon dioxide.

[2] Also, at times, to the acid fumes from the New Jersey factories. When these were present in quantity, it was necessary to defer experimental work until the wind changed to another quarter.

[3] Letts and Blake, *Loc. cit.*, pp. 136–138.

[4] The specific conductivity varies as the square root of the partial pressure; see the following section.

recent analyses of pure out-door air indicate relatively constant values. Unfortunately most of the observations on record have been obtained in connection with nonchemical investigations, and these frequently betray the fact that at least a little knowledge of chemistry would have been of great assistance to the experimenter, both in the choice of a method and in the execution of the necessary manipulations.

7. The Solubility of Carbon Dioxide in Water.

The old and approximate absorption data of Bunsen[1] may be discarded in favor of the more recent and accurate determinations of Bohr and Bock[2] and of Just.[3] Bohr and Bock obtained the following solubility values for the temperatures considered in this paper:

	Absorption coefficient.	Solubility in g. mols per liter.
0°	1.713	0.0764
18°	0.928	0.0414
25°	0.759	0.0338

The second column indicates the number of volumes of carbon dioxide (reduced to 0° and 760 mm.) absorbed by one volume of water at the given temperature when the partial pressure of the gas is one atmosphere (760 mm. Hg). In the third column the concentration of the saturated solution under the same conditions is shown. The values of Just are in close agreement with these.

From the above figures the concentration of the saturated solution under atmospheric conditions (carbon dioxide 3.53 parts in 10,000 by volume) can be calculated. It may be noted that variations in the atmospheric pressure—which may amount to about 3% of the total pressure, affecting the partial pressure of carbon dioxide in the same ratio—may be neglected in this calculation, owing to the greater uncertainty in the "standard value" of 3.53 parts in 10,000 for the carbon dioxide content of the atmosphere. The deviations of carbon dioxide from Boyle's law for pressures below atmospheric[4] may also be left out of consideration for the same reason. The partial pressure of carbon dioxide in the air may therefore be taken as equal to $760 \times 3.53 \times 10^{-4}$ mm. Hg.

Henry's law in its simple form cannot be employed in our calculations, since at the high dilutions involved the degree of ionization of carbonic acid becomes considerable. It is here that Knox[5] and others have gone astray in estimating the concentration of the solution in equilibrium with the atmosphere. The complete equilibrium series:

$$CO_2 \text{ (in air)} \rightleftarrows CO_2 \text{ (dissolved)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

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[1] Bunsen, *Ann.*, **93**, 1 (1855).

[2] Bohr and Bock, *Ann. Physik*, **44**, 318 (1891).

[3] Just, *Z. physik. Chem.*, **37**, 342 (1901).

[4] See Washburn, "Principles of Physical Chemistry," pp. 30–31 (1915).

[5] Compare Walker and Cormack, *J. Chem. Soc.*, **77**, 12 (1900).

leads for dilute solutions[1] to the equations

$$\text{conc. } CO_2 \text{ (in air)} = k_1 \text{ conc. } CO_2 \text{ (dissolved)} = k_2 \text{ conc. } H_2CO_3 = k_3 \text{ conc. } H^+ \text{.conc. } HCO_3^-,$$

in which k_1, k_2 and k_3 are constants for any given temperature. The fact that the nonionized solute exists partly as CO_2 and partly as H_2CO_3 does not complicate our calculations at all, since, as will be seen from the above equations, the ratio: (conc. CO_2)/(conc. H_2CO_3) in dilute solutions will be a constant, k_2/k_1. The series of equilibria therefore simplifies to the following relationships:

(1) p/C_u = constant; where p is the partial pressure of CO_2, C_u the concentration of the *total* nonionized solute.

(2) C_i^2/C_u = constant; where C_i is the concentration of the ionized solute.

These may be further condensed into the simple equation: C_i^2/p = constant, whence it follows that *the specific conductivity of a solution of carbonic acid is proportional to the square root of the partial pressure of carbon dioxide under which it exists.* The specific conductivities of the solutions in equilibrium with the air, in which the partial pressure of CO_2 is 3.53×10^{-4} atmospheres, can therefore readily be obtained for the three temperatures of 0°, 18° and 25° by combination of the results of Table IV with those of the present section.

For purposes of comparison, the complete solubility and ionization values for these temperatures, under partial pressures of CO_2 of 1 atmosphere and 3.53×10^{-4} atmospheres, respectively, are given in Tables VIII and IX below. All concentrations are expressed in mols per liter.

TABLE VIII.—SOLUBILITY OF CO_2 IN WATER (p = 1 ATM.).

T.	Conc. "total nonionized" solute.	Conc. ionized solute.	Total concentration.	% ionization.
0°	7.63×10^{-2}	1.3×10^{-4}	7.64×10^{-2}	0.16
18°	4.13×10^{-2}	1.1×10^{-4}	4.14×10^{-2}	0.26
25°	3.37×10^{-2}	1.1×10^{-4}	3.38×10^{-2}	0.33

TABLE IX.—SOLUBILITY OF CO_2 IN WATER ($p = 3.53 \times 10^{-4}$ ATM.).

T.	Conc. "total nonionized" solute.	Conc. ionized solute.	Total concentration.	% ionization.
0°	2.69×10^{-5}	2.46×10^{-6}	2.94×10^{-5}	8.4
18°	1.46×10^{-5}	2.13×10^{-6}	1.67×10^{-5}	12.8
25°	1.19×10^{-5}	2.05×10^{-6}	1.40×10^{-5}	14.7

It will be seen that the concentration of the nonionized portion of the solute decreases rapidly as the temperature rises. In the case of the ionized portion, however, the decrease is but slight, the diminution in the

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[1] Where the partial pressure of carbon dioxide is small and the concentration of the water in the solution has not been changed appreciably by the addition of the solute.

solubility being almost counterbalanced by the increase in the ionization constant. The last column shows that the degree of ionization of the saturated solution under atmospheric conditions is considerable.

8. The Specific Conductivity of the Saturated Solution.

The specific conductivity of pure water in equilibrium with atmospheric carbon dioxide at the temperatures of 0°, 18° and 25° can be calculated directly from the above tables. It may be noted that the specific conductivity of the water itself under these conditions becomes quite negligible in view of the relatively large hydrogen-ion concentration of the solute.

TABLE X.—CALCULATED CONDUCTIVITY OF WATER IN EQUILIBRIUM WITH CO_2 OF AIR.

T.	Dilution of saturated soln.	Concentration of ionized solute.	Λ_∞ H_2CO_3.	Specific conductivity.
0°	34000 liters	2.46×10^{-6}	264.0	0.65×10^{-6}
18°	60000 liters	2.13×10^{-6}	354.0	0.75×10^{-6}
25°	71400 liters	2.05×10^{-6}	393.4	0.80×10^{-6}

It will be seen that, while the concentration of the ionized solute decreases slowly with rise of temperature, the ionic mobilities increase at a greater rate, hence the specific conductivity of the saturated solution, as shown in the last column of the table, *increases* with the temperature. The degree of accuracy of these values, taking into account the errors inherent in the standard value for the CO_2 content of the atmosphere, may be stated as $\pm 5\%$.

We may now proceed to the final step of the investigation—the comparison of the calculated values with those obtained by direct conductivity measurements. In the following table the figures for the specific conductivities of samples of carefully purified water in equilibrium with a normal laboratory atmosphere are collected. Measurements were carried out in each of the four laboratories already mentioned, at the three temperatures of 0°, 18° and 25°. The method of preparation of the conductivity water was the same in all cases—a single distillation from ordinary tap water to which a few cubic centimeters of Nessler's solution had been added.[1] The water so obtained was allowed to stand exposed to the ordinary laboratory atmosphere, and, after it had rapidly come to equilibrium with this, was found to give readings which were practically independent of the time. The conditions in each laboratory during the measurements were kept as nearly as possible the same as in the determination of the carbon dioxide content of the atmosphere. The conductivity work was carried out in small cells of the Arrhenius type in the usual manner.

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[1] The preparation of conductivity water will be found fully described in the following paper.

TABLE XI.—MEASURED CONDUCTIVITY OF WATER IN EQUILIBRIUM WITH CO_2 OF AIR.

Laboratory.	Specific conductivity. (Reciprocal ohms × 10^{-6}.) T. = 0°.	T. = 18°.	T. = 25°.
University of Edinburgh	.....	0.75–0.80	0.85–0.90
Technological Institute, Petrograd	0.60–0.70	0.80–0.85	0.85–0.90
Nobel Institute, near Stockholm	.....	.....	0.75–0.80
Columbia University, New York City	0.60–0.65	0.70–0.80	0.75–0.85

The variations in the measured values are such as would be expected from the variations in the carbon dioxide content of the different laboratories.[1] The concordance of the values with those calculated is extremely satisfactory, as may be seen by comparison with the figures shown in the last column of Table X. The agreement obtained is, indeed, so striking as to warrant an emphatic repetition of the conclusion drawn by Walker and Cormack from their investigations,[2] that "*we may assume with confidence that carbon dioxide is the only substance in the atmosphere which confers conductivity on water.*"

Supplementary evidence in confirmation of the above assertion will be found in the succeeding paper, where the conductivity measurements of other observers on carefully purified water are collected and discussed. It will also be shown that solubility and electromotive force data support the assumption that *the purest distilled water of the laboratory is, in point of fact, a saturated solution of carbonic acid under the existing atmospheric conditions.* The significance of this in the interpretation of conductivity determinations at very high dilutions will then be examined in detail for electrolytes of different types.

9. Summary.

Exact values have been obtained, for temperatures of 0°, 18°, and 25°, for the following quantities necessary in the calculation of the specific conductivity of pure water in equilibrium with atmospheric carbon dioxide: (*a*) the ionization constant of carbonic acid; (*b*) the mobility of the hydrogen carbonate ion; (*c*) the carbon dioxide content of the atmosphere; (*d*) the solubility of carbon dioxide in water under atmospheric conditions.

The specific conductivity of a solution of carbonic acid at any given temperature is shown to be proportional to the square root of the partial pressure of carbon dioxide under which it exists.

The values for the specific conductivity of pure water in contact with air, derived with the use of the above data, are, for each temperature considered, practically identical with the directly-measured conductivity values.

The conclusion is drawn that carefully purified conductivity water really

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[1] Compare Table VII.

[2] Walker and Cormack, *J. Chem. Soc.*, 77, 12 (1900).

consists of a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable quantity.

In a following paper some practical applications of this result in the correction of conductivity determinations at high dilutions will be developed, and further evidence of its validity will be brought forward.

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THE RARE EARTH COBALTICYANIDE.

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The first rare earth cobalticyanide was prepared by Cleve and Hoeglund.[1] In 1915 the cobalticyanides were examined during a search for a method to separate yttrium from erbium,[2] and owing to the facts that the separation of yttrium from erbium was rapid, and that neodymium collected in the most soluble fractions, further investigations were carried out with the following results:

Neodymium Cobalticyanide, $Nd_2(CoC_6N_6)_2.9H_2O$.—This compound was easily precipitated from a boiling solution of neodymium chloride by adding potassium cobalticyanide. Neodymium chloride was kept in excess. The salt, which possessed a pale lilac color, formed a heavy crystalline powder. Microscopic examination showed that the crystals belong to the hexagonal system. They were almost insoluble in water, very slightly soluble in concentrated hydrochloric acid, and rapidly decomposed by boiling sodium hydroxide.

In order to determine the percentage of neodymium, some of the material was boiled with sodium hydroxide to decompose it. The hydroxide, after filtering and washing well, was dissolved in dilute hydrochloric acid and precipitated as the oxalate. This was ignited and weighed. The average for the neodymium amounted to 32.80 per cent., which seemed to indicate that the formula should be $Nd_2(CoC_6N_6)_2.9H_2O$. The cobalt was determined by electrolysis after breaking up the salt by fusion with bisulfate and rendering the solution alkaline by ammonium hydroxide. The results were a little below the theoretical.

When the compound was heated it gave off water and gradually turned blue. At higher temperatures it underwent rapid decomposition with the evolution of sparks.

Yttrium Cobalticyanide, $Y_2(CoC_6N_6)_2.9H_2O$.—This salt was prepared by precipitating a boiling solution of yttrium nitrate with a hot solution of potassium cobalticyanide.

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[1] *Bull. soc. chim.*, — 193–201 (1873).

[2] This Journal, 37, 2642 (1915).