3. The oxide so prepared is shown to contain 10.87% of oxygen as compared with the calculated percentage, 10.85, of oxygen in auric oxide. Qualitative evidence is also adduced to show that the product is pure within the limits of experimental error.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A STUDY OF THE PROPERTIES OF THE SYSTEM LITHIUM CHLORATE-WATER. I. INTRODUCTION. II. PHASE RELATIONS

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I. Introduction

The present investigation was undertaken for the purpose of gaining some knowledge of the influence of small additions of water on the properties of a fused electrolyte. It was anticipated that if a salt of sufficiently low melting point could be found, the properties of its mixtures with water might be studied over the whole concentration range from pure salt to pure water. According to the literature, lithium chlorate melts at 127° and it was thought that this salt would prove to be completely miscible with water at and above its melting point. This proved to be the case.

With the exception of some electrochemical data due to Ostwald,[2] the literature relating to lithium chlorate is concerned chiefly with the nature of the solid phases that exist in equilibrium with its aqueous solutions. The salt appears to have been prepared first by Wächter,[3] who obtained what corresponds to a hemihydrate, $LiClO_3.{}^1/_2H_2O$. Troost,[4] who prepared the same compound a little later, agrees with Wächter regarding the hydrate, and states that it melts at 50° and decomposes at 100°. Potilitzin[5] placed the melting point of the anhydrous salt at 124° and reports a hemihydrate, $LiClO_3.{}^1/_2H_2O$, melting at 50° and losing water at 90°. Retgers,[6] who studied the crystalline form of the salt, and Mylius and Funk,[7] who determined its solubility in water, hold that no hydrate is formed. Brühl[8] investigated the salt by crystallographic methods and described three anhydrous modifications, as well as a hemihydrate, melting at 63–65°. The highest temperature modification melted at 125–127°.

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[1] Metcalf Fellow in Chemistry at Brown University, 1924–1925.

[2] Ostwald, *Z. physik. Chem.*, **1**, 83 (1887).

[3] Wächter, *J. prakt. Chem.*, **30**, 321 (1843).

[4] Troost, *Ann. chim. phys.*, [3] **51**, 136 (1857).

[5] Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **16**, 840 (1883).

[6] Retgers, *Z. physik. Chem.*, **5**, 449 (1890).

[7] Mylius and Funk, *Ber.*, **30**, 1716 (1887).

[8] Brühl, *Bull. soc. ind. minérale,* **35**, 155 (1912).

In view of the uncertain and often contradictory nature of the data, it seemed desirable to make a detailed investigation of the phase relations for the system lithium chlorate-water. This was followed by a determination of the density of highly concentrated solutions of lithium chlorate and water at various temperatures and finally by conductance (electrical) measurements with the pure fused salt as well as with its concentrated solutions in water at various temperatures.[9]

II. Phase Relations

Preparation of Lithium Chlorate.—The salt was prepared according to the method of Potilitzin,[5] in which barium chlorate is treated with lithium sulfate. Some other methods were tried but were found unsatisfactory. Because of the difficulty in removing any precipitated material from strong solutions of lithium chlorate (these solutions act on filter paper), it is necessary to carry out the preparation with strictly pure materials.

Barium chlorate from various sources was tested for purity. The purest samples were recrystallized from water several times, until the final product gave only a faint qualitative test for calcium or chloride ions It was dried at 130°.

For the preparation of lithium sulfate, lithium carbonate was purified by recrystallization from hot water, its solubility per 100 g. of water being 1.539 g. at 0° and 0.728 g. at 100°.

Lithium sulfate was prepared by treating the recrystallized carbonate with sulfuric acid, a 5 *N* solution of the acid being added little by little to the dry carbonate. A slight excess of acid was added to insure complete conversion of the carbonate. The solution was evaporated until about three-fourths of the salt had separated, when it was thrown on a filter and thoroughly washed with alcohol to remove traces of acid. It was then dried at 130°.

Lithium chlorate solutions were prepared by slowly adding a 5.5 *N* solution of barium chlorate to a 4.5 *N* solution of lithium sulfate, both solutions being near the boiling point. The precipitated barium sulfate was removed by repeated filtration. To insure equivalence of lithium and chlorate ions, the filtered solution was titrated with dilute solutions of barium chlorate and sulfate. A dilute solution of silver chlorate was added until no test for chloride ions could be obtained.

The complete dehydration of lithium chlorate is accomplished with some difficulty. The method finally adopted is described below.

The solution, as prepared, was concentrated in an apparatus of the type outlined in Fig. 1. Two chambers, *A* and *B*, each having a capacity of 100 cc. of solution, are connected by means of tubes having a diameter of 15 mm. The solution was introduced

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[9] Burgess, *Dissertation*, Brown University, **1925**.

into *A* and, after exhausting through the stopcock *D*, *A* was placed in a bath of boiling water and *B* in ice water. By this means, the solution was concentrated until it contained approximately 85% of salt. The tube was then opened at *C*, the water was withdrawn from *B* and phosphorus pentoxide introduced. It was then sealed and evacuated and the chamber *A* again placed in warm water. Care should be exercised not to allow the solution to come in contact with phosphorus pentoxide, as otherwise explosive pressures may result.

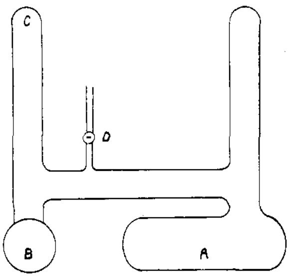

Fig. 1.—Apparatus for drying lithium chlorate.

When the solution reaches a concentration of 12% of water, it decomposes at higher temperatures. In the neighborhood of 100°, it turns yellow and yellow vapors are evolved. After a time the color disappears and thereafter no indications of further decomposition are observed. When the temperature was kept below 70°, no signs of decomposition were noted.

When the solution reached a concentration where decomposition was liable to set in, the temperature was reduced to 50° and the process of dehydration continued until the major portion of the salt could be crystallized out. Because of the marked tendency of the solution to supercool, it was necessary to cool it strongly in order to induce crystallization.

To eliminate the last traces of water, the salt was removed from the tube and, after pulverizing, was placed in a desiccator over phosphorus pentoxide under a high vacuum. Under these conditions complete dehydration was effected at the end of several months.

The dry salt absorbs water from the atmosphere about as rapidly as does phosphorus pentoxide. In order to weigh it out without absorption of moisture it is necessary to work in a strictly dry atmosphere. For this purpose a "dry box" was constructed into which a desiccator containing the salt or other apparatus was introduced. The interior of the box was dried with phosphorus pentoxide. It was provided with a pair of rubber sleeves with attached gloves and a window. With this apparatus it was found possible to transfer lithium chlorate without change of weight. The salt was weighed in a weighing bottle which in turn was placed in a second bottle, the cover of which was lubricated to guard against moisture. The bottles were ordinarily kept in a desiccator over phosphorus pentoxide. Transfer from the bottles was carried out in the "dry box."

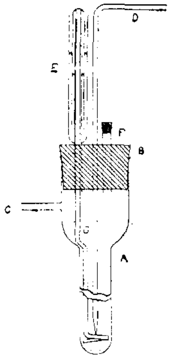

Fig. 2.—Apparatus used in solubility determination.

Method and Apparatus.—Because of the marked tendency of solutions of lithium chlorate to supercool, the method of thermal analysis was not generally applicable. Certain of the fixed temperatures, however, were checked by this method, both cooling and heating curves being obtained. To determine the solubility, the temperature was observed at which the last crystals of solid phase disappeared in the melt. In order to obtain reliable results careful control of temperature and vigorous stirring were found necessary.

The apparatus employed in making the solubility measurements is outlined in Fig. 2. A weighed quantity of salt (12 to 28 g.) was introduced into Tube *A* in the dry box. This tube was provided at the top with a closely fitting rubber stopper *B* and the interior of the tube throughout the experiments was placed under a slight excess pressure of dry nitrogen. The temperature was read by means of a copper-constantan thermocouple *D*, one element of which was centrally located on the axis of the tube under the surface of the solution while the other was placed in melting ice. The solution was stirred by means of a stirrer *G* which was provided with a mercury seal *E*. The water to be introduced into the salt was weighed out in a special pycnometer provided with a long delivery tube. This tube was introduced through *F* until the end was only a few centimeters above the liquid in *A*. By this means the splashing of liquid on the walls of the cell was avoided. While introducing water, a strong stream of nitrogen was kept passing through the upper part of the apparatus. Tube *A* was provided with an air jacket and placed in an oil or water thermostat whose temperature was carefully controlled by means of an automatic regulating device. The thermocouple was calibrated against the melting point of carbon tetrachloride, a known temperature of 25.00° and boiling water. A satisfactory deviation curve resulted when compared with the values given by Adams.[10]

The melting point of the anhydrous salt was determined by means of heating curves. The first series gave the most reliable value because of the greater dryness of the salt used. After having determined the melting point of the pure salt, successive known quantities of water were introduced and the point of disappearance of the solid phase was observed. To obtain a solid phase, the liquid was cooled in water, ice water or liquid ammonia, depending upon the concentration of the solution and the nature of the phase desired.

Four independent series of experiments were carried out. In the earlier experiments of the first series (Table I), a proper stirring device had not been developed and the data obtained are less reliable than subsequent ones. These earlier determinations (Nos. 2–19, Series I) have been omitted from the figure. In the more dilute solutions the results of the first series are in good agreement with later determinations.

Experimental Results.—The experimental data are given in Table I. The Roman numerals indicate the series of the experiment, and the Arabic numerals the sequence of observations in the series. Temperatures which are underscored indicate that the solid phase present is a metastable one.

The solubility relations are shown graphically in Fig. 3, where the solubilities in percentages of water are plotted as abscissas, from right to left, and temperatures are plotted as ordinates. The broken lines indicate solubility curves in the metastable regions.

Discussion.—As may be seen from Fig. 3, lithium chlorate forms two

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[10] Adams, THIS JOURNAL, **36**, 68 (1914).

TABLE I

SOLUBILITY OF LITHIUM CHLORATE IN WATER

A. Solid phase, α-$LiClO_3$

No. I	1	2	3	4	5	6	7	8
H_2O, %	0	0.83	1.53	2.67	3.14	3.98	4.30	5.40
Temp., °C.	127.6	126.7	121.3	115.1	114.1	108.0	107.3	102.5

No. II	1	2	3	4	5	6
H_2O, %	0.0	1.44	2.46	3.68	4.44	4.91
Temp., °C.	127.0	120.3	115.3	107.7	103.4	100.2

B. Solid phase, β-$LiClO_3$

No. I	9	10	12	12	13	14
H_2O, %	6.23	7.06	7.85	9.98	11.81	13.67
Temp., °C.	95.7	90.7	86.4	72.6	61.6	48.1

No. II	7	8	9	10	11	12	13
H_2O, %	5.65	6.32	7.46	8.61	9.72	12.83	13.73
Temp., °C.	95.7	92.3	85.8	78.9	71.3	48.3	36.9

No. III	1
H_2O, %	7.4
Temp., °C.	86.6

No. IV	1	2	3
H_2O, %	6.55	10.57	12.51
Temp., °C.	90.0	67.2	49.8

C. Solid phase, γ-$LiClO_3$

No. I	15	16	17	18	19
H_2O, %	15.48	17.20	18.33	20.32	21.67
Temp., °C.	36.2	32.0	27.6	16.4	8.4

No. II	12	13	14	15	16	17
H_2O, %	12.83	13.73	14.64	16.09	17.33	18.32
Temp., °C.	43.9	39.6	36.8	32.0	27.2	22.1

No. IV	4	5	6	7
H_2O, %	16.42	20.74	22.41	23.41
Temp., °C.	32.8	12.8	2.9	−3.2

D. Solid phase, $LiClO_3.H_2O$

No. I	20	21	22	23	24	25
H_2O, %	23.79	24.55	25.37	26.26	27.20	28.11
Temp., °C.	14.6	13.4	11.2	9.1	6.8	3.8

No. II	18	19	20	21	22
H_2O, %	19.73	21.46	22.75	25.03	27.61
Temp., °C.	20.5	18.9	16.7	12.0	5.1

No. IV	7
H_2O, %	23.41
Temp., °C.	14.1

TABLE I (*Concluded*)

E. Solid phase, $LiClO_3.3H_2O$

No. I	21	22	23	24	25	26	27	28
H_2O, %	24.55	25.37	26.26	27.20	28.11	28.82	30.26	31.61
Temp., °C.	−7.8	−5.8	−3.6	−1.6	0.0	0.9	3.4	4.5

No. I	29	30	31
H_2O, %	32.82	33.89	35.12
Temp., °C.	6.0	6.8	7.4

No. I	32	33	34	35	36	37	38	39
H_2O, %	36.56	38.49	39.85	41.84	43.34	45.43	46.73	48.05
Temp., °C.	7.9	7.85	7.3	6.1	4.8	2.2	0.5	−1.8

No. I	40	41	42
H_2O, %	49.51	51.04	52.06
Temp., °C.	−4.8	−7.3	−8.8

No. I	43	44	45	46
H_2O, %	54.65	60.95	61.9	62.58
Temp., °C.	−15.7	−33.9	−37.1	−39.0

No. II	20	21	22	23
H_2O, %	22.75	25.03	27.61	30.56
Temp., °C.	−13.6	− 7.3	− 1.8	4.0

F. Solid phase, Ice

No. I	47	48	49	50	51	52	53	54
H_2O, %	63.27	64.62	67.29	69.67	71.32	73.30	75.56	77.37
Temp., °C.	−39.1	−36.6	−30.5	−26.2	−23.3	−19.9	−17.4	−15.2
	55	56						
	79.27	84.24						
	−13.2	− 8.7						

hydrates, $LiClO_3.3H_2O$ and $LiClO_3.H_2O$, the former of which has a congruent melting point at 8°. The monohydrate has a transition point to anhydrous salt and solution at 21.0°. The anhydrous salt appears in three solid forms. The alpha form melts at 127.6° and has a transition point to the beta form at 99°. The beta form has a transition point to the alpha form at 41.5°, and the latter has a transition point to the monohydrate at 21.0°, as already stated.

The melting point of 127.6° (Series I) was obtained with a sample of salt that had been dried for months over phosphorus pentoxide. In another determination (Series II), a value of 127.0° was obtained with a sample of salt that had been less rigidly dried. According to the solubility curve this difference of temperature corresponds to a water content of only 0.1%.

The solutions of lithium chlorate have a tendency to supercool, yielding equilibria in which metastable solid phases are present. The different forms of the anhydrous salt likewise have a marked tendency to appear as metastable phases, at higher as well as at lower temperatures.

In Table II are given the nine monovariant equilibria which have been observed with this salt, together with the concentration of the solutions in per cent. of water, the temperature, and the nature of the transformation occurring.

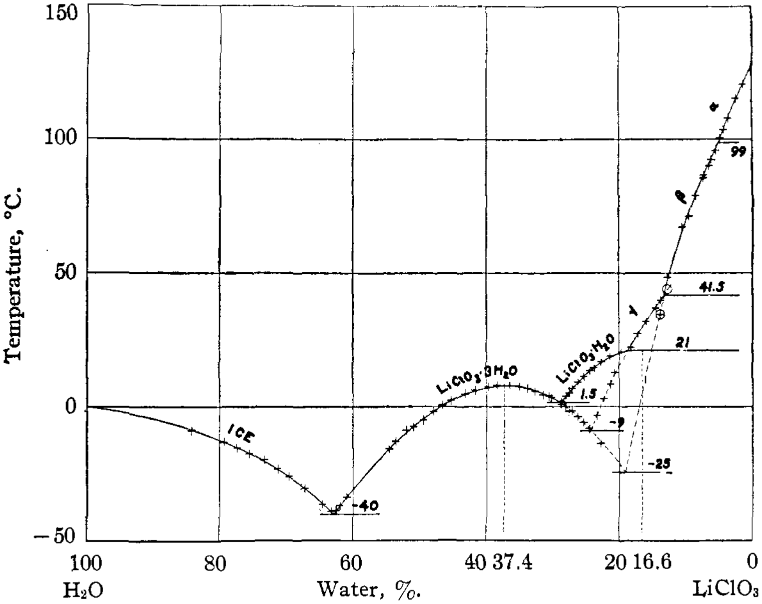

Fig. 3.—Phase diagram of the system lithium chlorate-water.

TABLE II

MONOVARIANT EQUILIBRIA

Phases	H_2O, %	Temp., °C.	Transformation
α-$LiClO_3$—Melt	0	127.6	fusion
β-$LiClO_3$—α-$LiClO_3$	5.1	99	transition
γ-$LiClO_3$—β-$LiClO_3$	13.4	41.5	transition
γ-$LiClO_3$—$LiClO_3 \cdot H_2O$	18.8	21.0	transition
β-$LiClO_3$—$LiClO_3 \cdot 3H_2O$	19	−25	*eutectic*
γ-$LiClO_3$—$LiClO_3 \cdot 3H_2O$	24.3	− 9	*eutectic*
$LiClO_3 \cdot 3H_2O$—$LiClO_3 \cdot H_2O$	28.9	1.5	eutectic
$LiClO_3 \cdot 3H_2O$—Melt	37.4	8	fusion
$LiClO_3 \cdot 3H_2O$—Ice	63.0	−40	eutectic

These fixed points are clearly indicated on the phase diagram and they have been checked by means of the thermal effects accompanying the transformations in question.

The transition between the alpha and beta forms has been realized with the anhydrous salt with rising as well as with falling temperature. This transformation is usually a suspended one and has been observed at temperatures as low as 58° and as high as 106.4°. It was definitely shown to lie below 100° and above 93°, and doubtless lies near the latter temperature. The solubility curves show a slight break at 99°. The transformation between the beta and gamma forms was readily obtained in the presence of a few per cent. of water, but only from the gamma to the beta form. The reverse transformation could not be realized nor could the transformation be realized in either direction with the pure salt. At concentrations in the neighborhood of 6% of water and above, the transformation $\gamma \longrightarrow \beta$ was readily obtained, the temperature varying between 44.1 and 49°. To obtain the gamma form, particularly in very concentrated solutions, it is necessary to undercool below —25°, the eutectic temperature of the beta form of the salt with the trihydrate. This eutectic soon passes over to the monohydrate and, at temperatures above the transition point of the monohydrate (21.0°), the gamma form is always found to be present. The formation of the eutectic of β-$LiClO_3$ and the trihydrate is accompanied by a marked heat effect. The temperature of this eutectic was fixed by this means.

The monohydrate occurs only as a stable phase. This hydrate does not separate readily. On cooling solutions containing between 14 and 23% of water, not too strongly, the gamma form usually appears and then the eutectic with the trihydrate at —9°. This eutectic then goes over to the monohydrate. By exercising precautions against the presence of the gamma form (by heating to higher temperatures) the trihydrate appears on cooling to the necessary temperature. This metastable trihydrate is fairly permanent and the solubility curve could be followed into the metastable regions to —13.6° and a concentration of 22.75% of water. On vigorously stirring the undercooled solution, the monohydrate appears and the solution solidifies completely. With solutions containing from 10 to 18% of water, it is possible to realize the transition between the monohydrate and the gamma form with falling as well as with rising temperatures.

That the solid phase here described as monohydrate actually contains one molecule of water is indicated by the form of the solubility curve of this phase and is shown conclusively by the fact that all mixtures containing less than 16.6% of water are completely solid at temperatures below 21.0°. If this phase contained less than one molecule of water, mixtures containing approximately 16.6% of water would be partly liquid down to 1.5°, the eutectic point with the trihydrate.

The solubility curve of the trihydrate requires no particular comment. For compositions in the neighborhood of the melting point, the thermal effects are marked. So, also, the thermal effect is marked at the eutectic between the trihydrate and ice. From the thermal effect, the eutectic temperature was found to be —40.7°, while the intersection of the two solubility curves gives —40.3°. This is within the limit of error of the solubility determinations.

Wächter,[3] Troost,[4] Potilitzin[5] and Brühl[8] describe a hydrated lithium chlorate to which they assign the formula $LiClO_3.{}^1/_2H_2O$, while recently Berg[11] describes a hydrate to which he assigns the formula $LiClO_3.{}^1/_3H_2O$. None of these investigators have examined the phase relations, and their conclusions are based on the analysis of what they believed to be a pure compound but which may well have been wet crystals of the anhydrous salt; or, conceivably, they may have been mixtures of anhydrous crystals with the monohydrate at temperatures below 21.0°

If a hydrate containing less water than the monohydrate actually exists, it would have to be identified with what we have described as the gamma form of the anhydrous salt. Otherwise, and this is a rather remote possibility, it must have escaped our observation altogether. That the gamma form is not a hydrate was shown conclusively with mixtures containing 6.55 and 7.4% of water, respectively. These mixtures definitely showed the presence of solution at temperatures above 21.0° and below 41.5°. At lower temperatures they were completely solid, indicating the presence of monohydrate, while at higher temperatures the transition $\gamma \longrightarrow \beta$ was observed. We thus have conclusive evidence that in the temperature interval between 21.0 and 41.5°, the gamma form exists in equilibrium with solution for mixtures containing as low as 6.55% of water. A hydrate, $LiClO_3.{}^1/_3H_2O$, would contain 6.19% of water, and the difference between this and 6.55% would not supply enough solution to be observable.

Values for the solubility (g. of salt per 100 g. of water) of lithium chlorate in water at 18° are given in Table III. These were read off from the graph reproduced as Fig. 3.

TABLE III

SOLUBILITY OF $LiClO_3$ IN WATER AT 18°, G. OF SALT PER 100 G. OF WATER

Phase	$LiClO_3.H_2O$	γ Form	β Form
Solubility	397.5	441.1	548.5

These values are much higher than those of Mylius and Funk,[7] who found 313.2 g. per 100 g. of water. These authors believe that the salt was present in anhydrous form. If that was the case, it must have been either the gamma or the beta form. The discrepancy is probably due to lack of equilibrium conditions.

Summary

The phase relations in the system lithium chlorate-water have been investigated for the complete series of mixtures between the two components.

Lithium chlorate melts at 127.6°. It exists in three anhydrous forms having transition points at 99 and 41.5°. It forms a monohydrate which

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[11] Berg, *Z. anorg. allgem. Chem.*, **155**, 311 (1926).

has a transition point with the lowest temperature formed at 21.5° and a trihydrate which has a congruent melting point at 8°.

Nothing was found indicating the existence of a hydrate lower than the monohydrate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

EQUILIBRIUM IN SOLUTIONS OF ALKALI CARBONATES

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Precise information on the equilibrium in aqueous solutions over a wide range of concentrations between carbonate, bicarbonate and hydrogen ion, in relation to the prevailing partial pressure of carbon dioxide in the gas phase in contact with the solution, is highly desirable; in the first place, for its own sake, and because it affords an independent measure of the effective concentration of certain ions; in the second place, because it may be applied towards a better understanding of apparently diverse problems, such as the respiratory equilibrium in the blood, the deposition of carbonates from natural water, either under geological conditions or in steam boilers, the behavior of certain soils and some phenomena of corrosion of metals. Various aspects of this equilibrium have been investigated,[3] especially in recent years; the present investigation was

[1] Constructed from the dissertations presented to the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, by Albert C. Walker in 1923, and Ulric B. Bray in 1925.

[2] Fellow on the Charles A. Coffin Foundation, **1924–1925**.

[3] (a) McCoy, *Am. Chem. J.*, **29**, 437 (1903); analyses of sodium bicarbonate-sodium carbonate solutions, 0.1 *N* at 25°, with determinations of the carbon dioxide in the gas phase. (b) Auerbach and Pick, *Arb. kais. Gesundh.*, **38**, 243 (1911); measurements with a hydrogen electrode, and indicator comparisons, in sodium carbonate solutions, 0.05–0.2 *N* at 18°. (c) Michaelis and Rona, *Biochem. Z.*, **67**, 182 (1914); hydrogen electrode in sodium carbonate–sodium bicarbonate–sodium chloride solutions 0.5 *N* in total sodium. (d) Frary and Nietz, THIS JOURNAL, **37**, 2271 (1915); measurements with a hydrogen electrode in sodium carbonate solutions, 0.005–2 *N*, at 25°. (e) Hasselbalch, *Biochem. Z.*, **78**, 119 (1916); measurements with a hydrogen electrode in bicarbonate solutions, 0.005–0.05 *N*, at 25°. (f) Seyler and Lloyd, *J. Chem. Soc.*, **111**, 138 (1917); analyses of sodium bicarbonate–sodium carbonate solutions (0.0125, 0.1, 1.0 *N*) at 25°, interpreted with the aid of McCoy's data. (g) Wilke, *Z. anorg. Chem.*, **119**, 365 (1921); acidity of carbonic acid from measurements with palladium capillary and hydrogen at 20 atm. pressure. (h) Menzel, *Z. physik. Chem.*, **100**, 276 (1922); extension of the work of Auerbach and Pick to solutions, 0.005–0.2 *N*. (i) Warburg, *Biochem. J.*, **16**, 153 (1922); measurements with a hydrogen electrode in sodium bicarbonate and potassium bicarbonate solutions, 0.01–0.1 *N*, at 25°. (j) Sieverts and Fritzsche, *Z. anorg. allgem. Chem.*, **133**, 1 (1924); analyses of potassium carbonate-potassium bicarbonate solutions (about 1 or 2 *N*), and of the gas phase, at 30, 40, 50, 60, 70, 80 and 97°. (k) Hastings and Sendroy, *J. Biol. Chem.*, **65**, 445 (1925); measurements