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.

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[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

undertaken in 1920 for the purpose of obtaining results of somewhat better accuracy over a wider range of concentrations than were available at that time, and of checking and harmonizing the analytical data by means of appropriate potential measurements.

The first section of this paper describes the work on the analytical determination of the carbonate-bicarbonate equilibrium at 25° (and in part at 37°) in solutions of the carbonates of sodium, potassium and lithium, ranging in concentration from 0.01 to 2.5 *M*, and also in solutions of sodium and potassium carbonate containing the respective chloride at concentrations up to 2.5 *M*. The principle of the method is to equilibrate the solution with a gas phase containing a known partial pressure of carbon dioxide, and then to analyze the solution for total base and for bicarbonate; hence, by difference, for carbonate. The second section presents measurements of the potential of (*a*) a hydrogen electrode, (*b*) a silver–silver carbonate electrode immersed in a potassium carbonate-bicarbonate solution, against a silver–silver chloride electrode; and also of the solubility product constant of crystalline silver carbonate. This is followed by a discussion of the experimental results, in which the calculated activity coefficients of bicarbonate and of carbonate are shown to be in thorough agreement with the analytical results. The data as a whole may therefore be used with some confidence in the solution of other problems.

Let us now briefly recapitulate the theory underlying the interpretation of the results. The relation between the effective concentration, or activity, (H_2CO_3),[4] of carbonic acid in a solution, and the partial pressure (P, in terms of atmospheres) of carbon dioxide in the gas phase in equilibrium with the solution is

$$(H_2CO_3) = \gamma\lambda cP \qquad (1)$$

where c is the total molal concentration, at 1 atmosphere, of carbon dioxide in the solution,[5] and γ and λ are the activity coefficients of carbonic acid and of water in the solution. We have also

$$(H^+)\,(HCO_3^-)/(H_2CO_3) = K_1 \qquad (2)$$

$$(H^+)\,(CO_3^=)/(HCO_3^-) = K_2 \qquad (3)$$

where K_1 and K_2 are the first and second ionization constants of carbonic acid in terms of activities;[6] and hence by division and combination with

with a hydrogen electrode in sodium bicarbonate–sodium chloride solutions of ionic strength 0.01–0.18 *N*, and in sodium bicarbonate–sodium carbonate solutions of ionic strength 0.02–0.21, at 38°. (1) With respect to the discussion of the physiological significance of this equilibrium, particularly in blood, see, especially, recent volumes of *J. Biol. Chem.*

[4] Parentheses will be used to denote an activity, brackets to denote a concentration.

[5] $c = \alpha/22.4$, where α is the absorption coefficient [compare Johnston, THIS JOURNAL, **37**, 2002 (1915); Johnston and Williamson, *ibid.*, **38**, 975 (1916)].

[6] This mode of treatment, in terms of activity instead of concentration, obviates the necessity of taking into account the proportionate hydration of carbon dioxide in

Equation 1

$$(HCO_3^-)^2/(CO_3^=)P = \gamma\lambda c K_1/K_2 \qquad (4)$$

What we determined by analysis, however, is not (HCO_3^-) and $(CO_3^=)$ but total bicarbonate $[MHCO_3]$ and carbonate $[M_2CO_3]$; however, we may write $(HCO_3^-) = \alpha[MHCO_3]$ and $(CO_3^=) = \beta[M_2CO_3]$, where α and β are the respective ion-activity coefficients, and thus transform Equation 4 to

$$[MHCO_3]^2/[M_2CO_3]P = \gamma\lambda c \frac{K_1}{K_2}\frac{\beta}{\alpha^2} = \varphi \qquad (5)$$

Measurements in a series of equilibrated solutions of the quantities on the left side of Equation 5 enable us to calculate directly the corresponding value of the function φ. This function contains a factor K_1/K_2 independent of the total concentration of alkali metal [M], together with five coefficients that vary with [M]; as [M] and P approach zero, α and β approach unity. With respect to the other three coefficients, when [M] is zero, c_0 is the solubility of carbon dioxide in water when P is 1 atm., and if we denote the corresponding values of γ and λ by γ_0 and λ_0, we have $c_0\gamma_0\lambda_0 = c\gamma\lambda$. Thus a plot of the function φ, as derived directly from the measurements, against the molality [M], if extrapolated properly to zero concentration, would determine the ratio K_1/K_2, and hence yield information as to the quotient of the two activity coefficients, α and β.

Equation 5 expresses the relation which at equilibrium must subsist between the partial pressure of carbon dioxide and the concentration of carbonate and bicarbonate for a given total base concentration, and thus determines the extent of the reaction $2\,HCO_3^- = CO_3^= + H_2O + CO_2$. It shows that the ratio of bicarbonate to carbonate is significant only when the partial pressure is specified and controlled; neglect in this particular detracts seriously from the usefulness of much previous work which otherwise was done very painstakingly. The rate at which the equilibrium finally adjusts itself after a change in carbon dioxide pressure apparently depends largely upon the rate of diffusion of carbon dioxide into or out of the solution, the other processes involved being presumably relatively rapid.[3j,7]

I. Analytical Determination of the Equilibrium[8]

A stream of air containing a definite constant proportion of carbon dioxide was passed, usually at a rate of about 8 liters hourly, through the solution until equilibrium was attained, this requiring four or five days,

the solution—so as to set a value of the concentration $[H_2CO_3]$—and the change of this fraction with change in salt concentration. With respect to estimates of the proportion hydrated, based upon measurements of the rate of neutralization by alkali of carbon dioxide in solution, see Thiel and Strohecker, *Ber.*, **47**, 945, 1061 (1914). Faurholt, *Z. anorg. Chem.*, **120**, 85 (1921).

[7] Compare Johnston, THIS JOURNAL, **38**, 947 (1916).

[8] Experimental work mainly by A. C. Walker.

unless the solution initially was close to the equilibrium distribution; samples of the solution were then withdrawn and analyzed. In the earlier experiments cleaned outside air was used directly, but it proved in general not to be sufficiently constant for the purpose, and so in the later work we used a special method of preparation of constant mixtures of air and carbon dioxide. This and the method of analysis have already been described in detail.[9]

The dry gas stream from the gas machine passed through a bead tower filled with water (so that it would be substantially saturated and hence not abstract water from the equilibrium solution) and a glass trap (to catch spray) into an intake manifold A which connected through the mercury seals B with the three reaction flasks C in parallel; the gas bubbled up through the solution[10] in the flask and was sucked away through an exhaust manifold D, to which was attached a manometer. The flow of gas to each flask was regulated by an inlet stopcock E and due correction was made for the small difference in pressure. To prevent condensation, the bead tower, intake manifold and flasks were all completely immersed in the thermostat; in all of the later experiments this was an air thermostat[11] which, on direct test, proved to be as satisfactory as, and more convenient than, the usual water thermostat when, as in this case, the system must remain for days at one temperature.

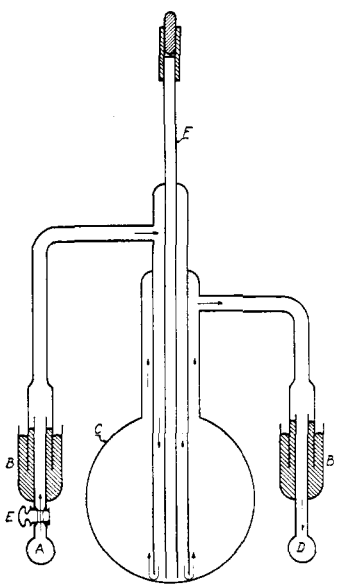

Fig. 1.—Equilibration vessel.

The flasks finally used were of the type sketched in Fig. 1; the gas enters one side-arm, passes down through the annular space surrounding the central sampling tube, bubbles through the liquid and leaves by the other arm. The sampling tube F, normally closed by a plug, extends almost to the bottom of the flask; the sample was withdrawn by means of a pipet after the gas stream had been momentarily stopped. These flasks, of Pyrex to minimize attack, were usually of 100 cc. capacity; the experiment was started with about 90 cc. of solution, which made possible four complete analyses. The use of an all-glass apparatus connected together by mercury seals instead of by the usual rubber tubing (as used in the earlier experiments

[9] Johnston and Walker, THIS JOURNAL, **47**, 1807 (1925).

[10] Usually different solutions, in some cases of different bases.

[11] A wooden box (100 × 110 × 80 cm.) with a hinged door partly of glass, heated by a carbon lamp controlled by a mercury regulator of large surface, the air being kept in circulation by a small electric fan.

in the water thermostat) was found to be, apart from its convenience, highly advantageous in that leaks were eliminated entirely and that, in case of accident to another part of the apparatus, the seals break before water is sucked through the gas line into the solution in the flask.

Methods of Analysis[7]

(a) **For Total Base.**—A sample of the equilibrium solution is pipetted into a weighed amount of standard (0.1 *M*) hydrochloric acid, containing one drop of a methyl orange solution, until the color change begins; the titration flask and contents are then weighed again, and the titration[12] continued with standard (0.025 *M*) barium hydroxide solution until the color matches that of a standard made by saturating with carbon dioxide a similar volume of water to which one drop of the methyl orange solution had been added. The salt error of the indicator in the more concentrated solutions was corrected for by means of special experiments; it proved to be small in all cases. The results are accurate, we believe, within $\pm 0.05\%$, except in the most dilute solutions.

(b) **For Bicarbonate.**—A sample is added rapidly to a weighed amount of standard barium hydroxide solution containing barium chloride, and the excess of base is then titrated with standard hydrochloric acid (0.02 *M*), with phenolphthalein as indicator. The barium hydroxide solution is kept from contact with laboratory air by previously washing the flask with air free from carbon dioxide, and the solution is introduced rapidly so as to obviate a shift in its equilibrium. The precipitated barium carbonate tends to obscure the final end-point, particularly in the more concentrated solutions, but this difficulty is minimized by making the titrations in constant illumination, as noted above. The salt error was again studied and allowed for; the correction was again very small. The results are probably correct to within $\pm 0.15\%$.

It should be added that since the carbonate concentration is derived by subtracting the bicarbonate from the total base, the accuracy with respect to carbonate will be highest—other things being equal—when the ratio of carbonate to bicarbonate is one half; consequently, we endeavored to achieve this, particularly in the less concentrated carbonate solutions, by appropriate regulation of the partial pressure of carbon dioxide.

(c) **For Partial Pressure of Carbon Dioxide.**—This, which has already been referred to, is in general the least precise of the analytical procedures; the uncertainty is, we believe, about 5 parts per million, corresponding to $\pm 0.8\%$ on the smallest partial pressures used.

(d) **For Neutral Salt.**—In two of the series of experiments neutral

[12] All titrations were made by weight, inside a wooden box, open on one side, lined with filter paper, illuminated by a daylight lamp; with this procedure the uncertainty in end-point is brought within one drop (0.03 g.) of the titrating solution.

salt (sodium or potassium chloride) was added to increase the total ion concentration; the chloride was determined gravimetrically when its concentration was less than 0.2 M, at higher concentrations by the silver nitrate-thiocyanate titration in the presence of a nitric acid solution of ferric alum to aid in coagulating the silver chloride precipitate. In any case the error from this source is negligible.

All salts used were purified by repeated crystallization, the bicarbonates from a cooling solution through which carbon dioxide was bubbled. The standard solutions were kept in Resistenz bottles, previously steamed and fitted with a siphon tube; they were well protected from the atmosphere and calibrated repeatedly. Concentrations are expressed throughout in terms of moles per 1000 g. of water, with due regard, where necessary, to the added salt. All analyses were made in duplicate, at least; the mean values only are tabulated. The uncertainty in φ proved to be about $\pm 1.5\%$, in accordance with the expectation as to the accuracy of the several analytical methods.

Experimental Results

Experiments were made in series of carbonate-bicarbonate solutions of sodium, potassium and lithium at 25 and 37°, and of sodium and potassium containing the respective chloride at 25°. In some cases equilibrium was approached from the bicarbonate side, in others from the carbonate side. The analyses recorded in Tables I–VII were made only after equilibrium had been established for a day; each represents a distinct solution, some apparent duplicates being months apart, and each is the average of at least two concordant determinations. Col. 1 gives the partial pressure of

TABLE I

ANALYSES OF EQUILIBRATED SOLUTIONS OF SODIUM CARBONATE-BICARBONATE AT 25°

$P \times 10^6$	$[NaHCO_3] \times 10^3$	$[Na_2CO_3] \times 10^3$	$\mu \times 10^3$	φ
360	7.86	0.69	10	249
342	8.69	.93	11	238
346	8.77	.95	12	234
378	8.99	.86	12	249
311	9.25	1.08	13	254
360	9.51	1.02	13	246
360	10.80	1.33	15	243
312	16.29	3.72	28	229
343	23.55	7.51	46	215
325	28.29	12.17	65	203
325	28.46	12.12	65	205
320	40.08	28.77	126	174
350	42.25	29.45	131	173
380	43.38	29.05	131	170
332	42.05	30.98	135	172
332	42.47	30.98	135	175
332	43.93	34.11	146	171

TABLE II

ANALYSES OF EQUILIBRATED SOLUTIONS OF SODIUM CARBONATE-BICARBONATE CONTAINING SODIUM CHLORIDE AT 25°

$P \times 10^{6}$	$[NaHCO_3] \times 10^{3}$	$[Na_2CO_3] \times 10^{3}$	[NaCl]	$\mu \times 10^{3}$	φ
268	26.40	12.87	0	65	202
268	25.16	12.65	0.0484	111	186
268	23.67	13.17	.0993	163	159
289	23.91	14.60	.201	269	136
289	22.48	13.88	.278	342	126
289	22.29	15.28	.461	529	113
346	22.46	14.97	.727	794	98
346	22.57	16.43	.883	955	90
346	21.59	15.67	.972	1041	86
320	21.11	17.89	1.225	1300	78
365	19.86	15.95	1.740	1808	68
364	19.86	16.61	1.750	1820	65
326	20.25	18.98	1.794	1871	66
326	18.99	17.79	1.894	1967	62
364	19.74	16.47	1.956	2023	65
365	19.14	16.69	2.158	2227	60
362	17.25	15.75	2.439	2503	52
362	16.40	16.58	3.076	3142	45

TABLE III

ANALYSES OF EQUILIBRATED SOLUTIONS OF SODIUM CARBONATE-BICARBONATE AT 37°

$P \times 10^{6}$	$[NaHCO_3] \times 10^{3}$	$[Na_2CO_3] \times 10^{3}$	$\mu \times 10^{3}$	φ
311	4.49	0.40	6	162
362	7.60	1.00	11	160
321	7.49	1.11	11	158
372	12.91	2.94	21	152
323	12.34	3.25	22	145
326	18.39	7.45	41	139
311	22.95	13.70	64	124
333	32.71	27.13	114	118
314	31.44	29.83	121	106
314	31.68	30.58	123	105
314	31.80	31.62	127	102
312	33.66	33.34	134	109
312	33.67	33.60	134	108
312	33.82	33.59	135	109
348	34.61	33.07	134	104
348	35.18	32.96	134	108
309	33.65	33.58	134	109
360	36.59	32.73	135	114
321	34.01	35.12	139	103
382	37.33	33.83	139	108
314	34.48	37.13	146	102
357	42.30	56.85	213	88
357	43.05	56.56	213	92
357	42.50	56.85	213	89

carbon dioxide, P, in atmospheres (the values as given representing parts per million): Cols. 2 and 3 give the molality (that is, moles per 1000 g.

TABLE IV

ANALYSES OF EQUILIBRATED SOLUTIONS OF POTASSIUM CARBONATE-BICARBONATE AT 25°

$P \times 10^6$	$[KHCO_3] \times 10^3$	$[K_2CO_3] \times 10^3$	$\mu \times 10^3$	φ
378	8.81	0.85	11	243
346	8.70	0.91	11	242
311	9.11	1.05	12	254
342	10.09	1.22	14	244
330	19.33	5.09	35	222
334	19.23	5.15	35	215
324	19.41	5.20	35	224
316	19.74	5.43	36	227
314	19.68	5.54	36	223
343	22.89	6.85	43	223
325	27.56	10.85	60	215
337	31.30	14.22	74	205
329	30.38	14.64	74	192
334	30.48	14.67	74	190
329	30.50	14.88	75	191
350	41.03	25.69	118	187
320	41.57	29.50	130	183
329	46.16	35.43	152	183
334	45.77	35.72	153	176
301	46.64	37.27	158	194
298	44.64	38.34	160	174
301	75.52	117.80	429	159
298	73.59	120.45	434	151

TABLE V

ANALYSES OF EQUILIBRATED SOLUTIONS OF POTASSIUM CARBONATE-BICARBONATE CONTAINING POTASSIUM CHLORIDE AT 25°

$P \times 10^6$	$[KHCO_3] \times 10^3$	$[K_2CO_3] \times 10^3$	$[KCl]$	$\mu \times 10^3$	φ
334	18.87	5.57	0.0811	117	191
334	18.67	5.70	.1259	162	182
316	18.51	6.27	.1692	207	173
325	17.61	5.93	.2290	264	161
310	17.89	6.38	.2289	266	162
320	18.26	6.39	.2346	272	163
320	39.90	30.46	.2051	336	163
325	16.96	5.98	.4113	446	148
310	17.46	6.69	.4258	463	147
325	17.02	5.95	.4393	474	150
310	16.97	6.57	.6392	676	141
320	36.80	30.63	.5888	717	138
314	17.01	6.76	.8300	867	136
324	16.06	6.85	1.290	1327	116
324	16.28	6.70	1.970	2006	122
314	16.07	6.47	2.149	2184	127
330	16.00	6.51	1.994	2249	119

of water) of bicarbonate and of carbonate, respectively, the latter being half the difference between the total alkalinity [M] and [$MHCO_3$]; Col. 4 gives the molality of added chloride; Col. 5 the ionic strength μ ($=[MHCO_3] + 3[M_2CO_3] + [MCl]$) to the nearest millimole and Col. 6 the function φ ($=[MHCO_3]^2/[M_2CO_3]P$), to the nearest unit. In each case the experiments are ranged in order of increasing ionic strength.

TABLE VI

ANALYSES OF EQUILIBRATED SOLUTIONS OF POTASSIUM CARBONATE-BICARBONATE AT 37°

$P \times 10^6$	$[KHCO_3] \times 10^3$	$[K_2CO_3] \times 10^3$	[KCl]	$\mu \times 10^3$	φ
311	4.40	0.34		5	183
321	7.45	1.08		11	161
362	7.60	0.96		10	167
323	12.81	3.64		24	140
372	13.47	3.32		23	147
326	19.16	8.01		43	141
311	22.22	12.68		60	126
377	24.81	12.86		62	127
333	30.59	22.57		98	125
314	34.44	35.61		141	106
338	37.14	37.50		150	109
338	37.16	37.80		150	108
377	23.73	12.92	0.0999	162	116
377	24.15	13.90	.1517	218	111
305	34.53	31.70	.1492	279	123
305	33.26	31.43	.1942	322	115

TABLE VII

ANALYSES OF EQUILIBRATED SOLUTIONS OF LITHIUM CARBONATE-BICARBONATE AT 25°

$P \times 10^6$	$[LiHCO_3] \times 10^3$	$[Li_2CO_3] \times 10^3$	$\mu \times 10^3$	φ
342	8.55	0.91	11	236
382	9.35	0.91	12	254
346	9.12	1.02	12	236
311	10.86	1.54	15	247
312	17.66	4.50	31	225
343	23.99	8.45	49	199
325	27.83	12.18	64	195
325	27.64	12.33	64	191
320	39.24	30.10	130	160
350	41.09	30.14	131	160

TABLE VIII

ANALYSES OF EQUILIBRATED SOLUTIONS OF LITHIUM CARBONATE-BICARBONATE AT 37°

$P \times 10^6$	$[LiHCO_3] \times 10^3$	$[Li_2CO_3] \times 10^3$	$\mu \times 10^3$	φ
311	4.66	0.44	6	161
321	7.42	1.15	11	149
362	7.58	1.07	11	149
323	13.37	4.14	26	134
372	14.03	3.84	26	138
326	19.19	8.68	45	130

TABLE VIII (*Concluded*)

$P \times 10^6$	$[LiHCO_3] \times 10^3$	$[Li_2CO_3] \times 10^3$	$\mu \times 10^3$	φ
315	22.84	14.38	66	115
333	31.10	27.70	114	104
321	30.63	30.11	121	97
360	34.04	30.62	126	105
301	32.51	34.77	137	101
382	36.20	35.98	144	95
314	36.17	46.84	177	89
331	55.64	130.55	447	72
296	54.90	134.31	458	76
287	55.40	135.22	461	79
296	59.10	171.3	573	68

Discussion of Results

It is best to consider first the variation with change of total concentration—or rather, of ionic strength—of the activity function φ, the value of which, it may be recalled, involves no assumption other than that the analytical methods are trustworthy. A number of modes of plotting were tried, all of which yielded substantially identical results in so far as *interpolation* is concerned. When concentration is expressed in terms of ionic strength, the points for the solutions with added chloride lie on the same curve, within the accuracy of the measurements, as those for the solutions containing only carbonate-bicarbonate. The method finally adopted was to plot $\log \varphi$ against $\mu^{1/2}$, the square root of the ionic strength, as this yielded lines of slight curvature and, at the same time, seemed to be the least arbitrary way of extrapolating to zero concentration.

For, in accordance with Equation 5, we may write $\log \varphi = \log K_1/K_2 + \log c\lambda\gamma + \log \beta - 2 \log \alpha$. Of these terms, the first and second are constant, so that the initial variation of φ with concentration depends upon the way in which the activity coefficients α and β change. Now, according to the Debye-Hückel theory, the limiting slope at zero concentration of the curve of $\log \alpha$ (for HCO_3^-) against $\mu^{1/2}$ is $d \log \alpha/d\mu^{1/2} = -0.5$; similarly, of $\log \beta$ (for $CO_3^=$), $d \log \beta/d\mu^{1/2} = -0.5 \times 4 = -2.0$. Hence, $d \log \varphi/d\mu^{1/2} = -1$; that is, the initial slope of our curve should be —1, or the curve should meet the axis at 45°. Moreover, the curves for the several alkalies must all meet the axis at the same point, for at zero concentration all of the activity coefficients become unity and, therefore, $\varphi_0 = c_0\lambda_0\gamma_0K_1/K_2$, c_0 being the solubility of carbon dioxide at 1 atm. pressure in pure water, and λ_0 and γ_0 the corresponding activity coefficients of water and of carbonic acid.

In fact, it was found that the three curves (for M = K, Na, Li, respectively) converge as the concentration decreases, and that when plotted in terms of $\log \varphi$ against $\mu^{1/2}$, the points for any one base can be represented fairly by an unforced curve whose slope is initially 45°, and

decreases gradually as the concentration rises. As an aid in fixing the position of these "best" curves, use was made of another relation which became apparent when the data for the two temperatures 25 and 37° were compared. For, since at any given concentration the several activity coefficients are not affected appreciably by small temperature change, the ratio $\varphi_{25}/\varphi_{37}$ should vary only slightly with concentration, and this variation should be substantially the same for each of the three similar bases; this again was readily secured without forcing the curves, which indeed corroborate one another. From curves drawn in this way, on a large scale, were derived the values of log φ for a series of values of ionic strength, given in Table IX.

TABLE IX

VALUES OF LOG φ INTERPOLATED AT A SERIES OF IONIC STRENGTHS

	25° Base			37° Base			
μ	K	Na	Li	K	Na	Li	$\varphi_{25}/\varphi_{37}$
0.00	2.491	2.491	2.491	2.296	2.296	2.296	1.57
.01	.403	.400	.396	.205	.204	.200	1.57
.02	.376	.371	.362	.177	.174	.165	1.58
.04	.342	.334	.318	.142	.135	.118	1.59
.06	.319	.308	.286	.118	.106	.084	1.59
.08	.300	.286	.260	.096	.082	.055	1.60
.10	.286	.267	.238	.079	.060	031	1.61
.20	.236	.194	.160	.015	1.980	1.952	1.64[a]
.40	.186	.100				.871	
.60	.158	.034				.828	
.80	.139	1.982					
1.0	.122	.939					
1.5	.098	.860					
2.0	.085	.802					
2.5	.074	.753					

[a] The average of 1.66, 1.64 and 1.63 for potassium, sodium and lithium, respectively.

The interpolated *experimental* data are presented in this form so that they may be applied directly to actual cases of solutions containing one or other of these alkali metals, without the necessity of any assumption as to extent of ionization of the solubility of carbon dioxide in the particular solution. In previous treatments of this problem such assumptions have been made and the deductions are subject, therefore, to a corresponding error. The only uncertainty in the application of Table IX appears to be in the width of the range of P over which φ may, for a given ionic strength, be regarded as constant. Thus, since $\varphi = [MHCO_3]^2/[M_2CO_3]P$, this table enables one to calculate the concentration of bicarbonate and of carbonate in any solution in equilibrium with the partial pressure P (atm.) of carbon dioxide, provided the total alkali associated with both car-

bonate and bicarbonate is known;[13] or, conversely, to compute the equilibrium pressure.

The fact may be noted that φ diminishes least rapidly in the case of potassium, more rapidly in presence of sodium, and most with lithium; at an ionic strength about unity it is for potassium about one-half, for sodium only one-third, of its value at an ionic strength of 0.01, even though the difference in ionic strength is due entirely to chloride. Obviously, therefore, the use of a constant or nearly constant presumed value of K_1/K_2, expressed in terms of concentration, as has been usual, must have caused appreciable errors in some of the calculations in which it has entered, for the variation of φ with concentration is considerably greater than would be compensated for by the usual assumptions as to extent of ionization.

The value of φ_0, as derived by extrapolation to zero concentration in the way described above, is 310 at 25° and 198 at 37°. Now, from Equation 5, $K_1/K_2 = \varphi_0/c_0\lambda_0\gamma_0$, K_1 and K_2, it may be recalled, being defined in terms of activities. The first ionization constant of carbonic acid, as determined heretofore by measurement of the conductance of water saturated with carbon dioxide at a pressure ranging from 0.25 to 1 atm., is, however, K_1', which may be shown to equal, in our notation, $K_1\lambda_0\gamma_0$. Therefore, $K_1'/K_2 = \varphi_0/c_0$, c_0 being 0.0341 at 25° and 0.0256 at 37°,[14] whence K_1'/K_2 is 9100 at 25° and 7750 at 37°.[5]

[13] For instance, at 25°, if $P = 300 \times 10^{-6}$ (about the proportion in the atmosphere) and $[KHCO_3] + 2[K_2CO_3] = 0.04$, we may as a first approximation put $\mu = 0.05$, corresponding to which $\varphi = 214$, whence $[KHCO_3] = 0.0232$ and $[K_2CO_3] = 0.0084$, corresponding to $\mu = 0.0484$ and $\varphi = 215$ which, in turn, yields the same values of the concentrations. If in addition we have present potassium chloride at 0.05 M, μ would be about 0.1 and φ 193, whence, in such a solution, $[KHCO_3] = 0.0225$ and $[K_2CO_3] = 0.0087$, numbers again left unchanged by a second approximation. If the potassium chloride were 1.0 M, μ would be about 1 and $\varphi = 132$, whence $[KHCO_3] = 0.0199$ and $[K_2CO_3] = 0.010$. Thus, for a constant value of P and a constant concentration (0.04) of base associated with bicarbonate-carbonate, the ratio $[KHCO_3]/[K_2CO_3]$ changes from 2.75 to 2.58 in the presence of 0.05 M potassium chloride, decreasing to 1.97 when the solution is 1 M with respect to potassium chloride.

[14] The solubility of carbon dioxide in sodium chloride solutions, recalculated from data of Bohr and Bock, and of Bohr [*Ann. Physik*, **44**, 318 (1891); **68**, 500 (1899)] in terms of moles of carbon dioxide per kilogram of water in the solution in equilibrium with a partial pressure of 1 atm. of carbon dioxide, and interpolated at 25 and 37° for round molalities (by plotting log c against $1/T$ and then against M, both sets of lines being very nearly straight and parallel) is as follows.

Molality of NaCl	0.0	0.1	0.2	0.5	1.0	2.0	3.0
c_{25}	0.0341	0.0333	0.0326	0.0305	0.0276	0.0228	0.0191
c_{37}	.0256	.0250	.0244	.0229	.0207	.0174	.0148
c_{25}/c_{37}	1.33	1.33	1.33	1.33	1.33	1.31	1.29
c_0/c (25)	1.000	1.024	1.047	1.118	1.237	1.493	1.783
c_0/c (37)	1.000	1.023	1.047	1.118	1.236	1.473	1.724
λ/λ_0 (25)	1.000	0.9970	0.9937	0.9841	0.9676	0.9321	0.8934
γ/γ_0 (25)	1.000	1.027	1.054	1.136	1.278	1.602	1.996

This value at 25° is considerably higher than that usually ascribed to this ratio (about 6000), and is, we believe, more nearly correct. Combining these with values of K_1' from Kendall's measurements,[15] namely, 3.50×10^{-7} at 25° and 4.23×10^{-7} at 37°, we find $K_2 = 3.85 \times 10^{-11}$ at 25°[16] and 5.46×10^{-11} at 37°, whence the heat change of the reaction $HCO_3^- = H^+ + CO_3^=$ is 5360 cal.

The ratio $\varphi_{25}/\varphi_{37}$ changes gradually from about 1.57 at zero concentration to 1.64 when μ is 0.2, this variation having been made the same for all three cases in drawing the curves. Now of the factors of φ, the K's are all constant, as is the ratio c_{25}/c_{37};[14] $\lambda_{25}/\lambda_{37}$ is unity, because the relative lowering of vapor pressure of water by a given concentration of salt is independent of such a temperature difference, and therefore γ_{25}/γ_{37} is likewise unity; thus it would appear that this gradual rise is to be ascribed to relative changes in the coefficients α and β. From the definition of φ (Equation 5), and of φ_0 it follows that

$$\varphi/\varphi_0 = \beta/\alpha^2 \qquad (6)$$

Thus we can calculate β if we know α, or conversely; generally, this relation may be used as a check upon values of the ion-activity coefficients α and β, as derived from measurements of potential, the left-hand member of Equation 6 having already been determined.[17]

II. Measurements of Potential on Solutions of Potassium Carbonate-Bicarbonate[18]

We now proceed to discuss measurements in solutions, over a range of ionic strength from 0.01 to 0.25 N, made (a) with a hydrogen electrode, (b) with a silver-silver carbonate electrode; together with a direct redetermination of the solubility product of crystalline silver carbonate. From the results, values of the separate ion-activity coefficients α and β may be derived.

(A) Hydrogen Electrode Measurements in Carbonate-Bicarbonate Solutions.—From the equilibrium equations it is obvious that the hydro-

From these have been calculated the ratio c_0/c, which is obviously identical, up to a 1 M sodium chloride solution, at the two temperatures. The ratio of solubility c_{25}/c_{37} at the two temperatures is likewise constant up to 1 M, and varies but little even at the higher salt concentrations. We have also calculated the ratio λ/λ_0 of the activities of water from the relative measured vapor-pressure lowering of water in sodium chloride solutions at 25°, whence, since $\gamma/\gamma_0 = (c_0/c)/(\lambda/\lambda_0)$, we have derived the values of this ratio as given. It may be observed that this ratio is exactly proportional to M up to 1 M.

[15] Kendall, THIS JOURNAL, **38,** 1480 (1916). The value at 37° is by extrapolation on a log K against $1/T$ plot.

[16] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923,** p. 578.

[17] Perhaps the fact should be mentioned that the value of φ_0 was fixed before any of the calculations which follow were undertaken.

[18] Experimental work by U. B. Bray.

gen-ion activity of a carbonate solution has no definite significance unless the partial pressure of carbon dioxide is controlled and specified, although this condition has not always been attended to. We first attempted to meet this requirement by the use of a pump with a mercury plunger and mercury valves which circulated an atmosphere of hydrogen and carbon dioxide until equilibrium was reached, but were unable to secure constant or reproducible results, this being due presumably either to the presence of mercury vapor or to a little residual oxygen in the circulating system.

We therefore had recourse to a form of shaking electrode, illustrated in Fig. 2, which proved to be satisfactory. The electrodes were of very thin platinum foil, made rigid by melting glass around them; before each experiment they were replatinized and saturated with hydrogen, as recommended by Clark.[19] The hydrogen, made electrolytically, was passed over palladium asbestos at 250° and through a calcium chloride tower. In setting up an experiment, which was carried out entirely in an air thermostat, the electrode vessel was filled with the solution, which was then displaced with hydrogen until the electrodes were half immersed; a rapid stream of hydrogen was passed to remove residual air, the stopcocks were shut, and a small piece of rubber tubing closed with a glass bead was fitted over the built-in manometer. The vessel was now shaken vigorously for five minutes, and a reading made, and this process was repeated several times; it was found that after the second repetition the potential checked to 0.05 millivolt and then remained constant for several hours. The solution was then analyzed for bicarbonate and carbonate, as described on page 1239, this being in effect equivalent to a determination of the partial pressure of carbon dioxide in the cell atmosphere. The reservoir at the left of the figure holds a supply of the solution so that the liquid junction may be made without disturbing the equilibrated solution in the electrode vessel.

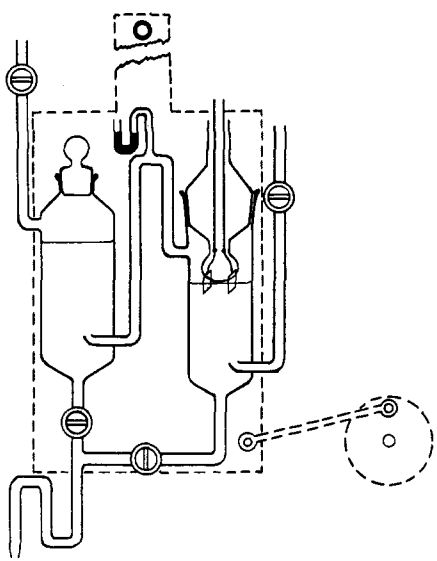

Fig. 2.—The hydrogen-electrode vessel.

The reference electrodes finally used were silver-silver chloride, made up in precisely the same way as the carbonate electrodes described later; they were immersed in the identical solution surrounding the hydrogen

[19] Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, p. 178.

electrode except for the addition of a quantity of potassium chloride sufficient to make the solution about 0.01 M with respect to chloride. Under these circumstances the junction potential is due to (a) the diffusion of 0.01 M potassium chloride across the boundary, which would presumably correspond to not more than 0.1–0.2 millivolt; (b) to the slight difference in activity of hydrogen ion on the two sides.

The average experimental results are listed in the first five columns of Table X, the value of E_1 for the combination being that observed, corrected only for the small amount (in no case greater than 0.4 millivolt) to make it refer to 1 atm. of hydrogen. The values of P (the partial pressure of carbon dioxide) were calculated from the interpolated value of φ and the measured concentrations [$KHCO_3$] and [K_2CO_3], this being in effect a direct determination of P but, under the circumstances, more convenient than analysis of the gas phase.

Now if the contact potential is negligible, $E_1 = -E^\circ_{Cl^-} - 0.05915 \log (H^+)(Cl^-)$; and from equations already given $(H^+) = K'_1 c_{30} P/(HCO_3^-)$; wherefore

$$E_1 = -E^\circ_{Cl^-} - 0.05915 \log \frac{K'_1 c_0 P [KCl]}{[KHCO_3]} - 0.05915 \log \psi/\alpha \qquad (7)$$

ψ being the activity coefficient of chloride ion in the carbonate-chloride solution at the silver-silver chloride electrode, and α, as before, the activity coefficient of bicarbonate ion in the solution about the hydrogen electrode. $E^\circ_{Cl^-}$ is —0.2226, as derived by Scatchard[20] from the measurements of Linhart on hydrochloric acid by extrapolation by means of the Debye-Hückel equation. At 25°, $K'_1 = 3.50 \times 10^{-7}$ and $c_0 = 0.0341$; the other three quantities in the second term of Equation 7 are listed in Table X. Thus we are enabled to calculate values of $\log \psi/\alpha$, hence of α if ψ were known; but we may not here make use of the principle of ionic strength, especially at the higher concentrations, which in any case would yield only the mean activity coefficient of potassium chloride, this being undoubtedly lower than ψ for the un-common ion Cl^-. Consequently, we

TABLE X

THE OBSERVED POTENTIAL DIFFERENCE E_1, AT 25°, BETWEEN A Pt-H_2 ELECTRODE IN A $KHCO_3$-K_2CO_3 SOLUTION OF IONIC STRENGTH μ, AND A Ag-AgCl ELECTRODE IN THE IDENTICAL SOLUTION CONTAINING ALSO KCl

μ	$[KHCO_3] \times 10^3$	$[K_2CO_3] \times 10^3$	$[KCl] \times 10^3$	E_1, volts	$P \times 10^6$	$-\log \psi$	$-\log \alpha$
0.0100	7.33	0.90	9.71	0.8990	236	0.051	0.044
.0101	7.25	.96	9.71	.9009	216	.051	.044
.0541	40.93	4.39	9.99	.8889	1809	.066	.083
.1268	39.41	29.03	10.06	.9236	288	.075	.115
.1279	39.75	29.50	10.06	.9329	288	.075	.116

[20] Scatchard, THIS JOURNAL, **47**, 641 (1925). Randall and Vanselow [*ibid.*, **46**, 2418 (1924)], from freezing-point measurement of hydrochloric acid solutions, derive the concordant value —0.2230.

shall derive both ψ and α from the measurements themselves, by a method discussed after the other experimental data have been presented; the final values of log ψ and log α are, however, included in Table X.

(B) **Measurements with a Silver-Silver Carbonate Electrode.**—Abegg and Cox,[21] and later, Spencer and Le Pla[22] attempted the use of a silver-silver carbonate electrode. Their silver carbonate was microcrystalline, and therefore possibly contaminated with material absorbed from the solution in which the carbonate was precipitated, and their silver was plated onto a platinum wire from a cyanide solution. With such materials we were unable to secure quite constant or reproducible potentials, but overcame this difficulty by making use of definitely crystalline silver carbonate and by preparing silver electrodes free from strains or absorbed impurities.

Crystalline Silver Carbonate.—To get good crystals of a sparingly soluble substance, it is necessary to precipitate it quite slowly, which can be achieved only if at any moment the concentrations of the pair of precipitating ions are maintained very slightly in excess of the solubility product; also, it is convenient to have a reservoir which will furnish the ions as fast as they are used. In the preparation of silver carbonate these conditions were fulfilled by passing a slow stream of carbon dioxide through a filtered solution of the silver-ammonia complex, made by addition of ammonia to 0.3 *N* silver nitrate solution until the precipitate had just disappeared. This process yields glistening crystals of silver carbonate, which can readily be made in any desired quantity, though some of the silver in the solution remains unprecipitated in accordance with the equilibrium conditions.

The crystals obtained in this way proved by analysis (both by thermal decomposition and by precipitation as chloride) to be pure silver carbonate. They are a beautiful sulfur yellow in color, but darken upon even a brief exposure to a bright light. They have high indices of refraction, above 1.88, and show parallel extinction and pleochroism; interference patterns indicate that they are biaxial.

Silver for Electrodes.—Silver electrodes prepared by heating silver oxide proved to be better[23] than plated electrodes,[24] but we found them less satisfactory than those made up by electrolysis of a silver nitrate

[21] Abegg and Cox, *Z. physik. Chem.*, **46**, 1 (1903).

[22] Spencer and Le Pla, *Z. anorg. Chem.*, **65**, 10 (1909).

[23] Compare Lewis, THIS JOURNAL, **28**, 158 (1906). Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[24] Several investigators have observed constant and reproducible potentials with silver chloride electrodes made by electroplating silver chloride, from the solution in which the electrode is to be used, upon a platinum gauze electrode previously coated with silver from silver oxide, or by plating from a cyanide solution; it may be that the inhomogeneities in the silver disappear during the process of forming the chloride layer.

solution.[25] The cathode, a large platinum wire sealed through a glass tube, was attached to a shaking device; the anode was put inside a porous cup to prevent contamination of the silver by black crystals, which appeared at the anode and were of the composition Ag_2O_3 and presumably the oxide reported by Yost.[26] The silver crystals were left in contact with silver nitrate solution for a day, washed a dozen times by decantation and finally filtered and washed. They were kept under distilled water until used, as electrodes made up from solid materials which have never dried seem to be somewhat more satisfactory.

The Electrodes.—If an electrode comprising a sparingly soluble salt is to attain rapidly a constant reproducible potential, it is advisable to secure in advance substantial equilibrium between this salt and the solution to be used.[27] This was achieved by leaving the silver carbonate crystals, previously washed with some of the solution to be used, in intimate contact for several hours with the solution. The silver crystals were likewise washed with the solution saturated with the carbonate, and kept immersed in a portion of it until its transfer to the electrode vessel. The electrode vessels, of Pyrex, were of the type shown in Fig. 3; each contains three identical electrodes and thus affords a ready means of intercomparison.

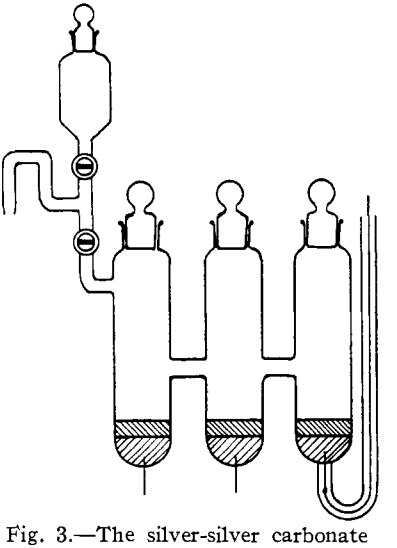

Fig. 3.—The silver-silver carbonate electrode vessel.

The silver-silver chloride reference electrodes were immersed, as before, in the identical solution which surrounded the carbonate electrode, but made by the addition of potassium chloride about 0.005 M with respect to chloride. All measurements were made in an air thermostat at 25.00°, the electrodes being protected from illumination because of the light-sensitiveness of the materials. The concentration of bicarbonate and of carbonate in the solution was determined by the procedure described earlier.

Experimental Results

The results are listed in Table XI, in the first five columns, at five concentrations, each e.m.f. recorded being the average of measurements of at

[25] Linhart, THIS JOURNAL, **41**, 1175 (1919).

[26] Yost, *ibid.*, **48**, 374 (1926).

[27] This is achieved very neatly by the form of electrode vessel recently described by Brönsted [*Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **3**, No. 9 (1920)] in which the solution flows down to the electrode through a deep layer of the salt.

least three of each electrode, which differed from this mean by not more than 0.1 millivolt. The values of ionic strength (μ) refer to the carbonate electrode side; that for the chloride side would have to be increased by an amount corresponding to the molality of potassium chloride.

TABLE XI

THE OBSERVED POTENTIAL DIFFERENCE E_2, at 25°, BETWEEN A Ag-Ag_2CO_3 ELECTRODE IN A $KHCO_3$-K_2CO_3 SOLUTION OF IONIC STRENGTH μ, AND A Ag-AgCl ELECTRODE IN THE IDENTICAL SOLUTION CONTAINING ALSO KCl

μ	$[KHCO_3] \times 10^3$	$[K_2CO_3] \times 10^3$	$[KCl] \times 10^3$	E_2 (volts)	$-E^\circ_{CO_3^=}$	$-\log \beta$	$-\log \psi$
0.0148	1.87	4.30	5.38	0.1880	0.4719	0.208	0.051
.0367	2.74	11.32	7.07	.1840	.4713	.292	.061
.0795	5.40	24.68	4.99	.1677	.4716	.382	.069
.1428	9.71	44.37	5.03	.1624	.4715	.458	.075
.2174	14.30	67.77	5.54	.1603	.4705	.522	.080
				Av.	0.4716		

In this case we have, $E^\circ_{CO_3^=}$ denoting the standard potential of $CO_3^=$

$$E^\circ_{CO_3^=} + E_2 = E^\circ_{Cl^-} + 0.02957 \log [KCl]^2/[K_2CO_3] + 0.02957 \log \psi^2/\beta \quad (8)$$

where, as before, ψ is the activity coefficient of chloride ion and β is the activity coefficient of carbonate ion. In this equation there are three unknowns, $E^\circ_{CO_3^=}$, ψ and β; the method of evaluation will be discussed later but the definitive values of these quantities are included in Table XI.

The Solubility-Product Constant of Silver Carbonate

This is defined by the equation $(Ag^+)^2 (CO_3^=) = K$, from which, by combination with Equations 4 and 6, we have

$$(Ag^+)^2(HCO_3^-)^2/P = K\varphi_0 \quad (9)$$

and may, therefore, for our experimental conditions, write

$$[AgHCO_3]^4/P = K\varphi_0/\gamma_\pm^4 \quad (10)$$

$\gamma_\pm$ being the mean activity coefficient of silver bicarbonate. Thus, we can derive a value of K if we can measure the gross concentration of silver bicarbonate in a solution in equilibrium with silver carbonate crystals and a measured partial pressure of carbon dioxide; this can be done readily at 1 atm. of carbon dioxide because then the concentration of carbonate in the saturated solution is so small relative to that of bicarbonate that we may set the total silver concentration, [Ag], determined by analysis, as equal to $[AgHCO_3]$ in Equation 10.

The experimental procedure was to pass carbon dioxide at 1 atm. pressure for several days through a solution in contact with excess of silver carbonate crystals, contained in a 1-liter flask of the type illustrated in Fig. 1. A 500g. sample was withdrawn through a cotton filter, the first portion being rejected, and the silver determined as chloride. The carbon dioxide, from a commercial tank two-thirds used, was analyzed repeatedly in a Schiff azotometer filled with 60% potassium hydroxide solution, with

completely concordant results. Four entirely distinct determinations at 25° yielded the following results.

$[Ag]^4 \times 10^8$, millimoles/kg. of H_2O	P, atm. of CO_2	$10^8[Ag]^4/P$
8.375	0.946	5.20
8.338	.943	5.12
8.353	.943	5.17
8.437	.975	5.20
	Av.	5.18

Inserting this value in Equation 10, we may either assign a value to $\gamma_{\pm}$ and calculate K, or preferably calculate $\gamma_{\pm}$ by making use of the value of K derivable from the normal potential, $E^{\circ}_{CO_3^-}$, of the silver-silver carbonate electrode, combined with $E^{\circ}_{Ag^+}$, the normal potential of silver. For, in a carbonate solution saturated with silver carbonate in which the activity of carbonate ion is unity, $(Ag^+) = \sqrt{K}$; the silver-silver carbonate electrode is reversible with respect to both silver and carbonate ions, and thus $0.02957 \log K = E^{\circ}_{Ag^+} - E^{\circ}_{CO_3^-}$. For $E^{\circ}_{Ag^+}$ we take —0.7995, according to Lewis and Randall,[28] who derive it from the measurements of Noyes and Brann[29] in the cell Ag, AgCl, $AgNO_3$ (0.1 M), KNO_3 (0.1 M), KCl (0.1 M), HgCl, Hg, with the aid of estimates of the junction potential and of the activity coefficient of the silver ion; for $E^{\circ}_{CO_3^-}$ we take 0.4716, the mean derived from the data in Table XI. On this basis $K = 8.2 \times 10^{-12}$,[30] whence $\gamma_{\pm}$ is 0.84. This result, which is inherently not unreasonable, depends, of course, upon the value assigned to the normal potential of silver; in this connection we may recall the fact that there is still a difference of 0.4 millivolt between the two best values of the silver-silver chloride electrode and of 1.1 millivolts between the measured and calculated e.m.f. of the Ag, AgCl, HgCl, Hg combination.[31]

III. Discussion of Results

In Equations 6, 7 and 8 we have relations between measured quantities and α, β, ψ and $E^{\circ}_{CO_3}$; but these cannot be evaluated until we make some assumption. For this, instead of assigning to ψ values which would in effect be arbitrary, we have preferred to make a new postulate, namely, that in carbonate-bicarbonate solutions, $d \log \beta / d \log \alpha = 4$ throughout the range of concentration. At very low concentrations this postulate is in accord with the Debye-Hückel theory, for the initial slopes of the curves

[28] Ref. 16, p. 414.

[29] Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

[30] The values of K given by Abegg and Cox and by Spencer and Le Pla, from electrometric determinations, are 4.0 and 6.4×10^{-12}, respectively, the differences being largely in the mode of interpretation of the experiments.

[31] Ref. 16, p. 407. Gerke, THIS JOURNAL, **44**, 1684 (1922). Scatchard, *ibid.*, **47**, 707 (1925).

of log α and log β against $\mu^{1/2}$ are, respectively, —0.5 and —2.0, so that we are postulating merely that the ratio of the slopes of the two curves remains constant as the concentration increases. On the modern view of the constraints due to the charges, the constancy of this ratio is not implausible, because the positive ion is identical and the negative ions bicarbonate and carbonate differ only by one hydrogen atom and one charge.

With the aid of this postulate and the relation expressed in Equation 6, namely, $\beta/\alpha^2 = \varphi/\varphi_0$, we are enabled to compute values of β and α from the analytical results alone. Accordingly, from the log φ curve for each of the bases potassium, sodium, lithium, by familiar mathematical methods, the log α and log β curves were constructed, the former with one-half, the latter with twice the (negative) slope of the log φ curve throughout its course,[32] the position of the pair of points (at given ionic strength) being fixed by the relation

$$\log \beta - 2 \log \alpha = \log \varphi - \log \varphi_0 \qquad (6a)$$

Values read from these curves at a series of ionic strengths are given in the columns headed α' and β' in Table XII.

The several quantities were now evaluated by the following procedure, which is in effect a series of successive approximations, the final values being virtually independent of the postulate. Values of log α' for potassium bicarbonate appropriate to the several ionic strengths were substituted, along with the relevant data from Table X, in Equation 7, and the resulting preliminary values of log ψ were plotted. From this plot were taken values of log ψ for the ionic strengths of Table XI and substituted, together with the appropriate values of log β' and the other relevant data, in Equation 8; this yielded preliminary values of $E^\circ_{CO_3^-}$ which showed a range, in the five measurements, of only 1.5 millivolts, the average being —0.4715. This average value was now substituted in Equation 8, log ψ was recomputed, re-plotted against $\mu^{1/2}$, and a smooth curve drawn. Values of log ψ from this definitive curve were now again substituted in Equation 7, the resulting values of log α were plotted and a smooth curve was drawn; from this the values of log α given in Tables X and XII were read. Values of log α were now substituted in Equation 6a, and from the resulting values of log β, together with the definitive values of log ψ and the relevant data of Table XI, final values of $E^\circ_{CO_3^-}$ were calculated; these are given in Table XI. Finally, this average value of $E^\circ_{CO_3^-}$, —0.4716, was used to compute definitive values of β which were plotted and a smooth curve was drawn; from this were read the values of log β given in Tables XI and XII.

It should be remarked that this rather involved series of approximations

[32] For by taking logarithms of Equation 6, differentiating, and combining with our postulate, we have d log $\alpha/d\mu^{1/2} = {}^1/_2$ d log $\varphi/d\mu^{1/2}$ and d log $\beta/d\mu^{1/2} = 2$ d log $\varphi/d\mu^{1/2}$.

makes very little difference in the final outcome, as is obvious from a comparison of the columns headed α and β (derived, as outlined above, from the e.m.f. measurements) with those, for potassium carbonate-bicarbonate, headed α' and β' (derived, on the basis of our postulate, from the analysis of equilibrated solutions). The fact that the various data are all so concordant, shown very well by the small range of $E^{\circ}_{CO_3}$- as calculated from the several measurements, corroborates the accuracy of the experimental work, and at the same time shows that our postulate is valid up to an ionic strength of 0.2, at least. By reason of this we venture to give, in Table XII, the calculated values α' and β' at ionic strengths up to 2.0, although beyond 0.2 there are no electrometric data with which to check them.

TABLE XII

THE ACTIVITY COEFFICIENTS, α' (FOR HCO_3^-) AND β' (FOR $CO_3^=$), DERIVED FROM THE ANALYSIS OF THE EQUILIBRATED SOLUTIONS; COMPARED, IN THE CASE OF POTASSIUM, WITH α AND β FROM THE POTENTIAL MEASUREMENTS

	Potassium				Sodium		Lithium	
μ	α	α'	β	β'	α'	β'	α'	β'
0.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
.01	0.904	0.904	0.663	0.667	0.901	0.658	0.896	0.646
.02	.876	.876	.585	.589	.871	.575	.862	.552
.04	.844	.843	.502	.503	.835	.485	.819	.451
.06	.821	.821	.452	.453	.810	.431	.790	.389
.08	.801	.803	.415	.415	.790	.389	.767	.345
.10	.785	.790	.388	.389	.773	.356	.747	.312
.20		.746	.308	.309	.710	.255	.683	.218
.40		.704		.246	.638	.165		
.60		.682		.216	.591	.122		
.80		.667		.198	.557	.096		
1.0		.654		.183	.529	.079		
1.5		.636		.164	.495	.055		
2.0		.627		.154	.452	.042		
2.5		.619		.147	.428	.033		

This rather remarkable agreement between the activity coefficients of bicarbonate and carbonate ions derived directly from electrometric measurements with those calculated, on the basis of our postulate, from the equilibrium data alone, suggests that this postulate could likewise be applied to other similar ion pairs of dibasic acids, such as sulfates, sulfites, sulfides; also it would be of interest to ascertain how it would apply to the more complex case of the phosphates where there are three negative ions which differ inappreciably except with respect to charge. The use of this postulate, if valid, would obviously also enable one to calculate, in this type of system, the change in equilibrium with change of ionic strength, if the activity of each of the pair of ions is known over a range of ionic strengths.

Summary

1. The carbonate-bicarbonate equilibrium in solutions of the carbonates of potassium, sodium and lithium, ranging in concentration from 0.01 to 2.5 M, and also in solutions of potassium and sodium carbonate containing the respective chloride at concentrations up to 2.5 M, has been determined by analytical methods at 25°, and in part also at 37°. The results are presented, in Table IX, free of all estimates of extent of ionization, so that they may be applied directly to the case of any solution of known ionic strength.

2. Measurements are presented of the potential of (*a*) a hydrogen electrode and (*b*) a silver-silver carbonate electrode, immersed in a potassium carbonate-bicarbonate solution of ionic strength ranging from about 0.01–0.2, against a silver-silver chloride electrode; from these the activity coefficients α and β, of bicarbonate ion and carbonate ion, respectively, were derived. The solubility product (in terms of activities) of crystalline silver carbonate proved to be 8.2×10^{-12}.

3. Values of the activity coefficients were also calculated from the equilibrium data, with the aid of the postulate that, as the ionic strength changes, the relative change in β (for carbonate ion) is always just four times as great as the relative change in α (for bicarbonate ion), a postulate which is, according to the Debye-Hückel theory, valid at ionic strengths approaching zero, and is plausible in view of the fact that the ions of this cognate pair differ only by a hydrogen atom and an electric charge; these values agree remarkably closely with those derived directly from the potential measurements. This agreement shows that the results of the several lines of work are in harmony and indicates that the postulate may be valid even when the ionic strength is considerable.

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