750. *The Effect of Pressure on the First Dissociation Constant of "Carbonic Acid."*

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The apparent first dissociation constant of "carbonic acid" has been determined for pressures up to 3000 atm. in the temperature range 25—65° c. An increase of 2500 atm. increases this constant approximately ten-fold owing largely to the increased hydration of carbon dioxide to H_2CO_3 at high pressure.

The effects of pressure on the molar conductances of potassium chloride, hydrochloric acid and potassium hydrogen carbonate in water at these temperatures are compared with previous results. There is little change in the effects of pressure in the concentration range 0·0001—0·1M.

As only 0·259% of the equilibrium mixture, $CO_2 + H_2O$, or "carbonic acid," is hydrated to H_2CO_3 in water at 25°,[1] increased pressure influences two equilibria

$$H_2O + CO_2 \rightleftharpoons H_2CO_3; \quad H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

For comparison, the effects of pressure on the dissociation of simple weak acids such as formic, acetic, propionic acid, are available from the reviews of Cohen and Schut,[2] and Hamann.[3]

Davies's method[4] was used to obtain the acid dissociation constants for "carbonic acid" between 25° and 65°, and at various pressures. The degree of dissociation, α, of the mixture $CO_2 + H_2O$ into H^+ and HCO_3^- ions was assumed to equal the ratio Λ/Λ', where Λ is the molar conductance of the mixture and Λ' the sum of the molar conductances of the ions H^+ and HCO_3^- at the ionic strength of the solution examined. Λ' was obtained by interpolation of conductance values for hydrochloric acid, potassium chloride, and potassium hydrogen carbonate solutions at various concentrations, temperatures, and pressures. As indicated by Hamann[3] it is safe to assume that Kohlrausch's law of independent ionic mobilities is obeyed under the conditions used.

The thermodynamic apparent dissociation constant K_a is given on the molal scale by the expression

$$K_a = [\alpha^2 m/(1 - \alpha)]\gamma_\pm{}^2/\gamma_{\mathrm{HA}}$$

where m is the molal concentration of total carbon dioxide, and $\gamma_\pm$ the mean activity coefficient of the H^+ and the HCO_3^- ion. γ_{HA}, the activity coefficient of the undissociated acid, was taken as unity at all pressures and temperatures. Values for $\gamma_\pm$ were obtained from the Debye–Hückel equation in the form

$$-\log f_\pm = \{1{\cdot}8123 \times 10^6(DT)^{-3/2}c^{\frac{1}{2}}\}/\{1 + 50{\cdot}29 \times 10^8(DT)^{-\frac{1}{2}}ac^{\frac{1}{2}}\}$$

a was taken as 5×10^{-8} cm., and changes of the molar concentration c and the dielectric constant D with pressure were taken into consideration. At the low ionic strengths used, the molar activity coefficient $f_\pm$ can be taken as equal to the molal activity coefficient $\gamma_\pm$. As the term DT changes little with temperature in the range 25—65°, it was sufficient for the accuracy of the experiments to apply the 25° values of $\gamma_\pm$ for various pressures and concentrations at all the temperatures.

A comparison of Hamann's results[3] with earlier data[2,5] for the conductance of strong electrolytes in water at high pressures showed that there were appreciable deviations and

[1] Wissbrun, French, and Patterson, *J. Phys. Chem.*, 1954, **58**, 693.
[2] Cohen and Schut, "Piezochemie Kondensierter Systeme," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1919.
[3] Hamann, "Physico-chemical Effects of Pressure," Butterworths, London, 1957.
[4] Davies, *J. Phys. Chem.*, 1925, **29**, 977.
[5] Zisman, *Phys. Review*, 1932, **39**, 151.

these are discussed below in relation to the values obtained for solutions of potassium chloride and hydrochloric acid in the process of obtaining dissociation constants.

EXPERIMENTAL

Apparatus.—The stainless-steel pressure vessel (25 c.c.; 3 in. diam.) had two manganin wire electrical leads through its walls; these were insulated in a packing gland of compressed polystyrene. Into the vessel was placed the conductivity cell containing the solution, and the appropriate electrical leads were soldered together inside the vessel.

The conductivity cell (constant $0{\cdot}365$ cm.$^{-1}$) was a Teflon cylinder, open at one end, of 7 c.c. capacity. A tight-fitting Teflon piston supporting the electrodes separated the solution in the cell from medicinal paraffin used to transmit pressure within the pressure vessel. The electrode assembly in the cell consisted of platinum foil electrodes tightly bound by fine platinum wire to the arms of a U-shaped Pyrex glass piece. A thick platinum lead from one electrode supported the assembly from the Teflon piston, and a lead of fine wire from the other electrode to the piston allowed for the slight play caused by the contraction of Teflon under pressure. The cell therefore incorporated the advantages of the sliding piston design of Jamieson,[6] and almost constant spacing of the electrodes by glass. The platinum in the cell was lightly coated with platinum black.

Sealed platinum-in-glass electrodes are usually broken by the application of a few thousand atm. pressure. In cells with electrodes spaced by plastic, corrections are needed for the high and often irreproducible compressibility of these substances. For example, a marked discontinuity is apparent in the conductivity results of Hamann and Strauss [7] at 5000 atm. where Weir [8] reported a phase change in Teflon with a 2% decrease in volume. Disadvantages of other cells used previously include direct contact of the solution with kerosene [5] and with mercury.[9]

Pressures were developed by hand hydraulic pumps and a pressure intensifier. Bourdon gauges were calibrated against a Harwood manganin-coil resistance gauge supplied calibrated to $\pm 0{\cdot}1\%$. With allowance for small variations in the Bourdon gauges, the pressures reported should be accurate to within $\pm 0{\cdot}5\%$.

The pressure vessel and a paraffin reservoir were heated in an oil-bath controlled to $\pm 0{\cdot}05°$. The mass of the vessel damped out temperature variations in the bath. About 2 hr. were required for the apparatus to reach initial thermal equilibrium, and a further 30 min. were required after a change of pressure for equilibrium to be regained.

The resistances were measured with a capacity-compensated non-inductive Wheatstone bridge using a 1000 c.p.s. valve oscillator as an A.C. source. Corrections to the conductances were made for the resistance of lead wires and the change in cell constant with pressure. The latter was $0{\cdot}1\%$ change per 1000 atm.

Measurements of the cell resistance were taken again at 1 atm. pressure at the end of each run. In no case were hysteresis effects important.

Materials and Method.—Solutions of potassium chloride, hydrochloric acid and potassium hydrogen carbonate were prepared from "AnalaR" reagents. A large volume of "carbonic acid" solution was prepared in a closed flask, and the liquid and the gas phase were allowed to equilibrate. A portion of this solution was run into the conductance cell, and another portion analysed.

Throughout the experiments with "carbonic acid" the pressure on the cell was kept above 50 atm. to prevent bubbles forming in the cell. A short extrapolation was made to get conductances at 1 atm. No significant amount of carbon dioxide was lost from the cell during the measurements.

The distilled water in the cell was assumed to have two types of impurity, *viz.*, carbon dioxide and stray strong electrolyte ions. The conductance blank due to the latter, κ_i changes very little with pressure, while that of ionised carbonic acid, κ_c, increases considerably. From the conductance of the solvent at various pressures it was possible to obtain the values of κ_i and κ_c. As an example, for the water used in the experiment at 25° and 1 atm., κ_i was approximately $1{\cdot}0 \times 10^{-6}$ and κ_c $0{\cdot}5 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$.

[6] Jamieson, *J. Chem. Phys.*, 1953, **21**, 1385.
[7] Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51**, 1684.
[8] Weir, *J. Res. Nat. Bur. Stand.*, 1953, **50**, 95; 1954, **53**, 245.
[9] Buchanan and Hamann, *Trans. Faraday Soc.*, 1953, **49**, 1425.

When corrections for the solvent were made to the conductances of potassium chloride solutions ($\kappa_l + \kappa_c$) was subtracted, but for hydrochloric acid and potassium hydrogen carbonate only the blank κ_l, for pressure and temperature, was applied.

The correction for solvent conduction was of the order of a few units % for solutions with an ion concentration of 10^{-3}m, but reached a maximum of 20% of the total conduction for 10^{-4}m potassium chloride at 25° and 3000 atm. The blank correction to the "carbonic acid" conductivities was greatest at 65° and 1 atm. where it amounted to about 10%.

TABLE 1.

P (atm.)	500	1000	1500	2000	2500	3000
ρ_r	1·021	1·039	1·058	1·073	1·088	1·103

TABLE 2. *Hydrochloric acid: values of* $\Lambda^P\rho_r/\Lambda^1$ (M = *molar concentrations at* P = 1).

(Owen and Sweeton's values [11] of Λ^1 in parentheses.

Temp.	M	P (atm.) 1	500	1000	2000	3000
25°	0·1	(391·3)	1·050	1·088	1·152	1·193
25°	0·01	(412·0)	1·051	1·089	1·152	1·191
25°	0·01	(421·4)	1·050	1·087	1·151	1·191
25°	0·0001	(424·7)	1·05	1·10	1·16	1·21
35°	0·1	(447·3)	1·040	1·074	1·127	1·164
35°	0·01	(472·3)	1·041	1·075	1·128	1·162
35°	0·001	(483·3)	1·041	1·070	1·126	1·165
35°	0·0001	(487·0)	1·04	1·09	1·14	1·18
45°	0·1	(502·2)	1·034	1·068	1·120	1·158
45°	0·01	(530·5)	1·034	1·066	1·118	1·156
45°	0·001	(544·2)	1·033	1·067	1·117	1·154
55°	0·1	(554·0)	1·032	1·062	1·112	1·148
55°	0·01	(586·5)	1·032	1·063	1·113	1·149
55°	0·001	(602·3)	1·033	1·065	1·115	1·150
65°	0·1	(603·0)	1·031	1·060	1·105	1·142
65°	0·01	(640·5)	1·030	1·060	1·106	1·140
65°	0·001	(657·5)	1·029	1·062	1·108	1·142

Values of Λ_0^P/Λ_0^1 *for hydrochloric acid solutions.*

Temp.	P (atm.) 1	500	1000	2000	3000
25°	(426·2)	1·028	1·048	1·074	1·080
35	(489·2)	1·020	1·034	1·051	1·056
45	(550·3)	1·013	1·027	1·042	1·048
55	(609·5)	1·012	1·025	1·039	1·043
65	(666·8)	1·009	1·022	1·032	1·035

TABLE 3. *Potassium chloride: values of* $\Lambda^P\rho_r/\Lambda^1$.

(Λ^1 values in parentheses up to 45° from Gunning and Gordon,[12] and at 55° and 65° from the present work.)

Temp.	M	P (atm.) 1	500	1000	2000	3000
25°	0·1	(129·0)	1·031	1·052	1·069	1·061
25°	0·01	(141·3)	1·031	1·052	1·068	1·058
25°	0·001	(147·0)	1·032	1·054	1·069	1·064
25°	0·0001	(149·3)	1·03	1·06	1·08	1·07
35°	0·1	(154·7)	1·023	1·044	1·052	1·044
35°	0·01	(169·9)	1·024	1·040	1·049	1·042
35°	0·001	(176·9)	1·025	1·04(5)	1·05(5)	1·05(0)
45°	0·1	(180·3)	1·020	1·038	1·044	1·030
45°	0·01	(199·7)	1·021	1·035	1·040	1·026
45°	0·001	(208·1)	1·02(0)	1·03(5)	1·04(1)	1·03(0)
55°	0·1	(208·3)	1·015	1·026	1·035	1·023
55°	0·01	(230·1)	1·017	1·028	1·033	1·021
55°	0·001	(241·0)	1·02	1·03(1)	1·04(0)	1·03(0)
65°	0·1	(235·5)	1·014	1·026	1·026	1·011
65°	0·01	(262·3)	1·015	1·025	1·027	1·012
65°	0·001	(278·2)	1·01(5)	1·02(3)	1·02(6)	1·01(7)

Values of Λ_0^P/Λ_0^1 *for* KCl *solutions.*

(Λ_0^1 values to 45° from Gunning and Gordon [12] in parentheses.)

Temp.	P (atm.) 1	50	1000	2000	3000
25°	(149·9)	1·011	1·014	0·996	0·964
35	(180·5)	1·004	1·004	0·979	0·947
45	(212·5)	1·000	0·997	0·971	0·931
55	(246·0)	0·996	0·989	0·965	0·927
65	(281·3)	0·994	0·987	0·957	0·917

Buchanan and Hamann [9] defined the molal conductance of an electrolyte as Λ (molal) = $1000L'/m$, where m is the molality of the electrolyte, which is independent of pressure, and L' the specific conductance of the solution corrected for the solvent blank.

At low ionic strengths the following approximate relation holds, Λ (molal) = Λd, where d is the density of the solution. This equation is valid at all concentrations used in the present experiments within the possible experimental error.

In this work the product Λd is used instead of the term molal conductance, as the former emphasises that the increase in conductance with pressure is due to both a volume factor and one involving the mobility of the ions.

The results are reported as the ratios $\Lambda^P\rho_r/\Lambda^1$ where Λ^P and Λ^1 are the molar conductances of the electrolytes at a pressure P and at 1 atm., respectively. ρ_r is the corresponding density ratio ρ^P/ρ^1 for water at the temperature. Values of ρ_r taken from Dorsey [10] and given in Table 1 represent the solution densities within $\pm 0{\cdot}2\%$ in the temperature range 25—65°.

Electrolyte solutions ranging from 0·1 to 0·0001M were examined up to 3000 atm. at temperatures between 25° and 65°. The results for 10^{-4}M-solutions were of little significance above 35° because of the high solvent correction to the conductances.

TABLE 4. *Potassium hydrogen carbonate: values of $\Lambda^P\rho_r/\Lambda^1$.*

(Λ^1 values in parentheses based on Shedlovsky and MacInnes's results [13] up to 40°, and the present work.)

Temp.	M	P (atm.) 1	500	1000	2000	3000
25°	0·1	(97·7)	1·025	1·041	1·050	1·034
	0·01	(110·1)	1·026	1·042	1·048	1·031
	0·001	(115·3)	1·024	1·041	1·049	1·033
	0·0001	(117·3)	1·03	1·05	1·06	1·04
35°	0·1	(118)	1·019	1·031	1·034	1·019
	0·01	(131·8)	1·018	1·030	1·033	1·017
	0·001	(139·2)	1·020	1·032	1·032	1·016
45°	0·1	(138)	1·014	1·020	1·021	1·004
	0·01	(155·0)	1·013	1·022	1·023	1·002
	0·001	(163·5)	1·115	1·024	1·025	1·005
55°	0·1	(158)	1·012	1·016	1·014	0·994
	0·01	(178·5)	1·010	1·015	1·012	0·992
	0·001	(189·0)	1·014	1·014	1·015	0·996
65°	0·1	(181)	1·008	1·013	1·002	0·986
	0·01	(202·8)	1·007	1·010	1·004	0·984
	0·001	(189·0)	1·009	1·012	1·004	0·987

Values of $\Lambda_0{}^P/\Lambda_0{}^1$ for $KHCO_3$ solutions.

Temp.	P (atm.) 1	500	1000	2000	3000
25°	(118·0)	1·005	1·002	0·978	0·937
35	(141·5)	0·999	0·992	0·963	0·922
45	(179·3)	0·993	0·985	0·954	0·909
55	(192·8)	0·989	0·977	0·944	0·901
65	(219)	0·987	0·974	0·936	0·894

TABLE 5. *The effect of pressure on the conductance of the distilled water used in the experiments: Typical values of specific conductivity* $\times 10^6$ (ohm^{-1} cm.$^{-1}$).

Temp.	P (atm.) 1	1000	2000	3000
25°	1·5	2·1	2·7	3·0
45	3·2	5·0	5·9	6·5
65	5·1	7·4	9·3	11·5

Tables 2 to 4 give, in order, the change in conductivity with pressure for solutions of hydrochloric acid, potassium chloride, and potassium hydrogen carbonate. Table 5 gives the change in conductivity for water in equilibrium with the cell assembly.

The values of $\Lambda^P\rho_r/\Lambda^1$ did not change significantly with concentration in the range 0·1—0·0001M. At the end of each of the Tables 2—4 values for the ratio $\Lambda^P{}_0/\Lambda^1{}_0$ are given for the electrolytes. To obtain these values it was assumed that the effects of pressure on conductance remained constant down to infinitely small electrolyte concentrations.

[10] Dorsey, "Properties of Ordinary Water-substance," Amer. Chem. Soc. Monograph No. 81, 1940.

TABLE 6. *"Carbonic acid."*

100 × concn. (molal)	P (atm.)	Λ_{ρ_r}	$\Lambda^1{}_{\rho_r}$	$\gamma_\pm{}^2$	$K_a{}^P/K_a{}^1$ * (molal scale)
		At 25°			
2·56	1	1·606	394	0·977	(4·2 × 10⁻⁷)
,,	2080	5·332	454	0·966	8·26
,,	2930	7·821	468	0·961	16·7
2·91	1	1·528	394	0·974	(4·3 × 10⁻⁷)
,,	1050	2·918	430	0·969	3·04
,,	2040	4·945	454	0·963	7·85
,,	2930	7·455	468	0·958	16·7
2·92	1	1·493	394	0·974	(4·1 × 10⁻⁷)
,,	1270	3·243	435	0·969	3·85
,,	2540	6·147	463	0·960	12·2
2·73	1	1·538	394	0·976	(4·1 × 10⁻⁷)
,,	1050	2·951	431	0·972	3·07
,,	2070	5·071	455	0·969	8·14
,,	2860	7·532	468	0·960	16·9
2·05	1	1·777	394	0·979	(4·1 × 10⁻⁷)
,,	1030	3·353	430	0·975	2·98
,,	2010	5·725	454	0·970	7·81
,,	2930	8·743	469	0·963	17·0
3·20	1	1·402	394	0·976	(4·0 × 10⁻⁷)
,,	1010	2·606	439	0·972	2·90
,,	2010	4·458	454	0·963	7·54
,,	2850	6·873	467	0·959	16·9
$\Delta V^1 = -26·5$ c.c. mole⁻¹; $\Delta V^{3000} = -20·7$ c.c. mole⁻¹; Average $\Delta K = -0·0019$ atm.⁻¹ c.c. mole⁻¹.					
		At 35°			
3·32	1	1·696	448	0·974	(4·7 × 10⁻⁷)
,,	1390	3·809	492	0·966	4·16
,,	2930	7·791	521	0·956	15·5
3·19	1	1·714	448	0·974	(4·6 × 10⁻⁷)
,,	1030	3·161	481	0·969	2·93
,,	2040	5·343	507	0·962	7·54
,,	2930	7·968	521	0·956	15·9
3·46	1	1·695	448	0·974	(4·9 × 10⁻⁷)
,,	1010	3·066	481	0·968	2·82
,,	2040	5·261	507	0·961	7·46
,,	2930	7·856	521	0·955	15·8
1·51	1	2·558	448	0·978	(4·9 × 10⁻⁷)
,,	1030	4·720	482	0·973	2·94
,,	2030	7·940	507	0·968	7·51
,,	2930	11·85	521	0·963	15·9
1·18	1	2·970	448	0·979	(5·1 × 10⁻⁷)
,,	1390	6·386	492	0·974	3·83
,,	2640	12·01	517	0·966	12·3
2·53	1	1·972	448	0·977	(4·8 × 10⁻⁷)
,,	1390	4·397	492	0·970	4·11
,,	2780	8·527	519	0·961	13·9
3·40	1	1·674	448	0·975	(4·7 × 10⁻⁷)
,,	1050	3·130	482	0·970	3·00
,,	2030	5·144	507	0·964	7·33
,,	2930	7·700	521	0·959	15·6
$\Delta V^1 = -25·4$ c.c. mole⁻¹; $\Delta V^{3000} = -20·0$ c.c. mole⁻¹; Average $\Delta K = -0·0018$ atm.⁻¹ c.c. mole⁻¹.					
		At 45°			
2·99	1	2·066	506	0·976	(4·9 × 10⁻⁷)
,,	1320	4·250	547	0·968	3·61
,,	2500	7·397	576	0·960	9·83
2·48	1	2·276	506	0·975	(4·9 × 10⁻⁷)
,,	1030	4·117	540	0·970	2·85
,,	2010	6·728	565	0·965	6·99
,,	2930	10·11	586	0·960	14·7
3·74	1	1·903	506	0·972	(5·2 × 10⁻⁷)
,,	1030	3·420	540	0·967	2·83
,,	2030	5·614	565	0·961	6·95
,,	3000	8·544	587	0·954	14·9

* Values of K_a at $P = 1$ in parentheses.

TABLE 6. (*Continued.*)

100 × concn. (molal)	P (atm.)	Λ_{ρ_r}	$\Lambda^1_{\rho_r}$	$\gamma_{\pm}^2$	K_a^P/K_a^1 * (molal scale)
			At 45°		
3·71	1	1·850	506	0·972	(4·8 × 10^{-7})
,,	1010	3·238	539	0·968	2·70
,,	2010	5·328	565	0·962	6·63
,,	2780	7·487	582	0·957	12·3
,,	2930	7·933	585	0·956	13·7
2·94	1	2·075	506	0·976	(4·8 × 10^{-7})
,,	1020	3·633	539	0·970	2·70
,,	2010	5·951	565	0·964	6·57
,,	3000	9·192	587	0·959	14·5
2·48	1	2·264	506	0·975	(4·9 × 10^{-7})
,,	1390	4·931	549	0·969	4·03
,,	2780	9·30	583	0·961	12·7
,,	3000	10·16	588	0·959	14·9
$\Delta V^1 = -24·8$ c.c. mole^{-1}; $\Delta V^{3000} = -18·4$ c.c. mole^{-1}; Average $\Delta K = -0·0021$ atm.$^{-1}$ c.c. mole^{-1}.					
			At 55°		
3·71	1	2·009	550	0·973	(4·8 × 10^{-7})
,,	1350	4·195	595	0·963	3·70
,,	2850	7·996	632	0·958	11·9
2·50	1	2·544	550	0·974	(5·2 × 10^{-7})
,,	1020	4·444	584	0·970	2·71
,,	2010	7·159	613	0·965	6·37
,,	2780	9·932	631	0·961	11·6
2·37	1	2·549	550	0·974	(5·0 × 10^{-7})
,,	1740	6·291	606	0·967	5·01
,,	2850	10·15	631	0·961	12·05
2·49	1	2·443	550	0·974	(4·8 × 10^{-7})
,,	1020	4·295	585	0·970	2·73
,,	2440	8·252	622	0·963	8·90
,,	2840	9·740	632	0·960	12·0
,,	2940	10·12	634	0·960	12·9
1·45	1	3·297	550	0·978	(5·1 × 10^{-7})
,,	1020	5·865	586	0·972	2·79
,,	2010	9·373	613	0·970	6·52
,,	2810	13·11	631	0·965	12·0
,,	2930	13·70	634	0·964	13·1
3·37	1	2·116	550	0·973	(4·9 × 10^{-7})
,,	720	3·189	574	0·969	2·08
,,	1770	5·364	607	0·967	5·28
,,	3000	9·133	635	0·966	14·0
2·72	1	2·353	550	0·974	(4·9 × 10^{-7})
,,	1420	5·017	596	0·968	3·87
,,	2930	9·857	634	0·959	13·19
$\Delta V^1 = -24·3$ c.c. mole^{-1}; $\Delta V^{3000} = -17·5$ c.c. mole^{-1}; Average $\Delta K = -0·0023$ atm.$^{-1}$ c.c. mole^{-1}.					
			At 65°		
2·46	1	2·706	606	0·975	(4·8 × 10^{-7})
,,	1080	4·726	644	0·971	2·70
,,	2080	7·558	671	0·966	6·34
,,	2850	10·45	689	0·963	11·5
2·32	1	2·845	606	0·975	(5·0 × 10^{-7})
,,	1010	4·922	642	0·972	2·67
,,	2010	7·886	669	0·965	6·30
,,	2700	10·44	685	0·961	10·5
,,	2780	10·87	687	0·961	11·3
3·71	1	2·193	606	0·974	(4·8 × 10^{-7})
,,	1060	3·840	642	0·968	2·72
,,	2080	6·127	671	0·962	6·33
,,	2790	8·215	687	0·959	10·8
1·59	1	3·380	606	0·978	(4·9 × 10^{-7})
,,	1400	6·997	653	0·972	3·68
,,	2790	12·69	688	0·965	10·9
2·50	1	2·724	606	0·975	(5·0 × 10^{-7})
,,	1040	4·729	642	0·970	2·67
,,	2570	9·531	683	0·963	9·62
$\Delta V^1 = -23·6$ c.c. mole^{-1}; $\Delta V^{3000} = -16·8$ c.c. mole^{-1}; Average $\Delta K = -0·0023$ atm.$^{-1}$ c.c. mole^{-1}.					

* Values of K_a at $P = 1$ in parentheses.

Wherever possible, accurate values of Λ^1 from other measurements [11–13] are included with the conductance ratios in the Tables. The units of the Λ values reported are cm.^{2} ohm^{-1} mole^{-1}.

Table 6 gives the results for the changes with pressure of the apparent dissociation constant K_a of carbonic acid. The product $\Lambda\rho_r$ (and hence $\alpha = \Lambda\rho_r/\Lambda'\rho_r$) was obtained from the specific conductivities L' by the relation $\Lambda\rho_r = 1000L'/m\rho^1$, where ρ^1 is the density of the acid solution ($\sim$water) at 1 atm. pressure.

The volume change on ionisation at infinite dilution was calculated from the slope of log $(K_a{}^P/K_a{}^1)$ *versus* pressure graphs at 1 atm. (ΔV^1) and at 3000 atm. (ΔV^{3000}).

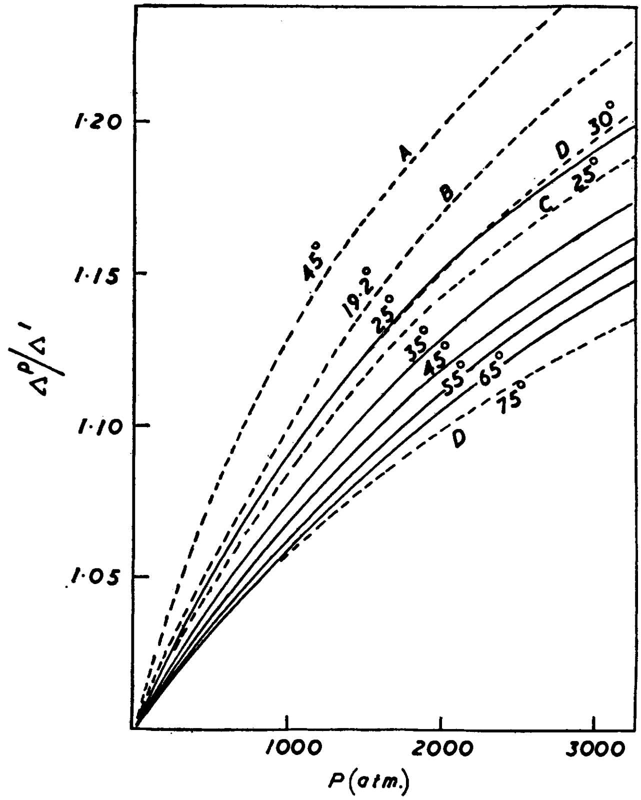
$$(\delta \ln K_a)/(\delta P)_{T,m} = -\Delta V/\boldsymbol{R}T \qquad (-\delta\Delta V/\delta P)_{T,m} = \Delta K \approx (\Delta V^{3000} - \Delta V^1)/3000$$

From the latter relation the average value for the change in compressibility (ΔK) on ionisation in the pressure range 1—3000 atm. was obtained at each temperature.

Discussion

Figs. 1—3 summarise the results for hydrochloric acid, potassium chloride, and potassium hydrogen carbonate, and also show some values of $\Lambda^P\rho_r/\Lambda^1$ obtained by previous

FIG. 1. 0·01m-*Hydrochloric acid.* —— *Our values.* ---- *Literature values: A, Hamann and Strauss, ref.* 7; *B, Korber, ref.* 14; *C, Buchanan and Hamann, ref.* 9; *D, Zisman, ref.* 5.



workers. The agreement is not good, and the results of Hamann and Strauss [7] are anomalous. The effect of pressure on conductance was found to decrease with temperature in the manner reported by Korber [14] and Zisman.[5]

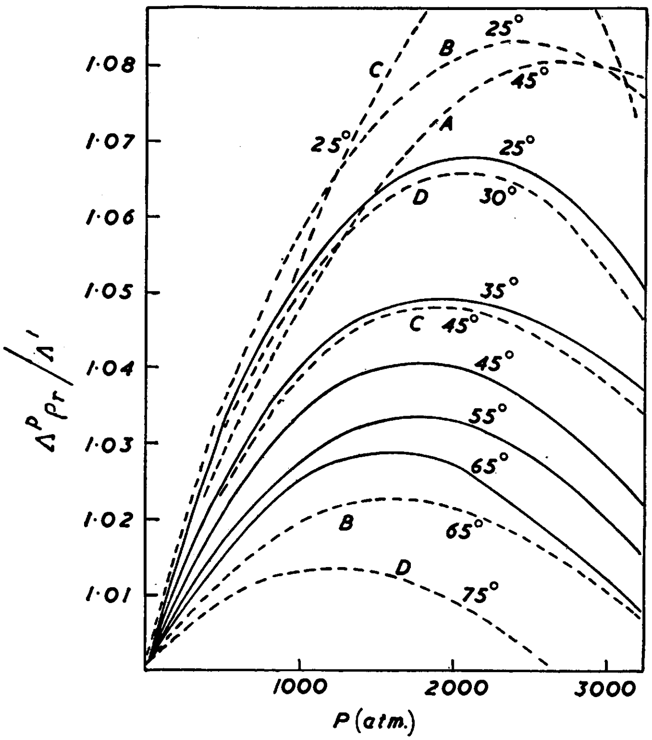
[11] Owen and Sweeton, *J. Amer. Chem. Soc.*, 1941, **63**, 2811.
[12] Gunning and Gordon, *J. Chem. Phys.*, 1942, **10**, 126.
[13] Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, 1935, **54**, 1429.
[14] Korber, *Z. phys. Chem.*, 1909, **67**, 212.

Zisman [5] and Hamann and Strauss [7] examined the effects of pressure on conductance up to pressures of 10,000 atm. The latter workers suggested that Zisman's results were in error by several units %, but the present observations do not support this suggestion.

Fig. 4 shows the ratios Λ_0^P/Λ_0^1 for potassium hydrogen carbonate solutions, together with Bridgman's ratios [15] of the viscosity η^1/η^P for 18°, 30°, and 75°. The variation of Λ_0^P/Λ_0^1 with pressure is similar for most salts in that the values pass through an initial maximum or a curvature in the same sense before decreasing steadily with increasing pressure.

For 16 salts Zisman [5] showed that at 30° and 75° the ratio Λ^P/Λ^1 decreased almost linearly with pressure in the range 3000—8000 atm., and always with the same slope.

FIG. 2. 0·01m-*Potassium chloride.*



The increase in the viscosity of water at these temperatures and pressures is also approximately linear with pressure, but the increase in viscosity is more rapid than the decrease in conductance for the same temperature.

The compressibility of ions, derived from measurements on crystals of the alkali halide type, is only about one tenth of the compressibility of water at moderate pressures.[15] The effect of pressure on conductance should therefore be related mainly to changes in solvent structure and in ion-solvent interaction.

For a 1 : 1 electrolyte the Debye–Hückel–Onsager equation can be written [16] in the form

$$\Lambda_0 - \Lambda = \left[\frac{A\Lambda_0}{(DT)^{3/2}} + \frac{B}{\eta(DT)^{1/2}}\right]c^{1/2}$$

A and *B* are positive constants and *D* is the dielectric constant.

[15] Bridgman, " The Physics of High Pressures," G. Bell and Sons, London, 1931.
[16] MacInnes, " The Principles of Electrochemistry," Reinhold, New York, 1939.

Both D and η for pure water increase at high pressures and Λ_0 decreases. As discussed by Hamann,[3] the effect of pressure on conductance could be expected to decrease with increasing concentration. For example, for potassium chloride it would be expected that at 3000 atm. $\Lambda_0{}^P/\Lambda_0{}^1$ would be about 3·5% greater than Λ^P/Λ^1 for a 0·1M-solution.

Variations with concentration of this order were not found in the present experiments with solutions up to 0·1M. However, Korber's results [14] provide a good example of the decreasing pressure effect at higher concentrations.

The apparent disagreement with the Debye–Hückel–Onsager equation below 0·1M must result from the assumption that the values of D and η for the salt solutions at high

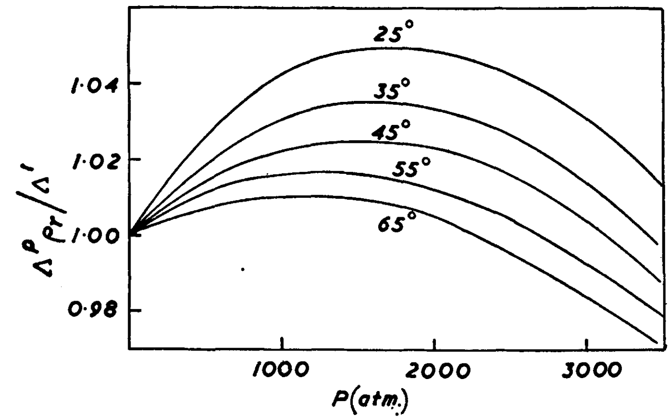


FIG. 3. 0·01M-*Potassium hydrogen carbonate.*

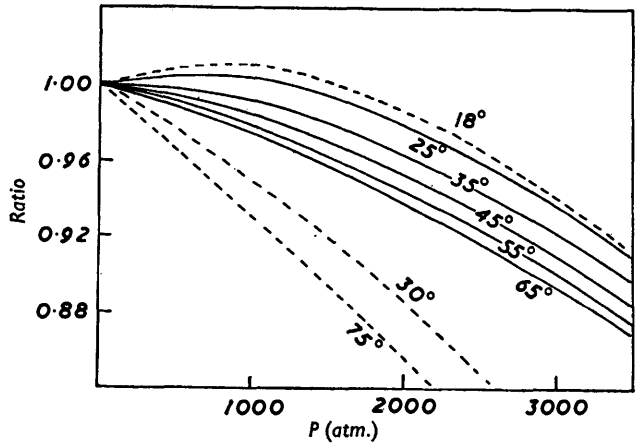


FIG. 4.

——— *Values of* $\Lambda_0{}^P/\Lambda_0{}^1$ *for* $KHCO_3$ *solutions at* 25°, 35°, 45°, 55°, *and* 65°.

- - - - *Bridgman's values for ratio* η^1/η^P *at* 18°, 30°, *and* 75°

pressures correspond to those for water at the same temperature. Zisman [5] showed that the initial maximum in the graph of Λ^P/Λ^1 for neutral salts was greatest and occurred at highest pressures for small ions of high valency. These are order-producing ions which, in the terminology of Frank and Evans,[17] lower the structural temperature of water. In Fig. 4 the variation of η^1/η^P with pressure corresponds to the ratio $\Lambda_0{}^P/\Lambda_0{}^1$ for a rather higher temperature. It is not sufficient to relate the changes in conduction at high pressure with the changes in physical properties of pure water at the same temperature.

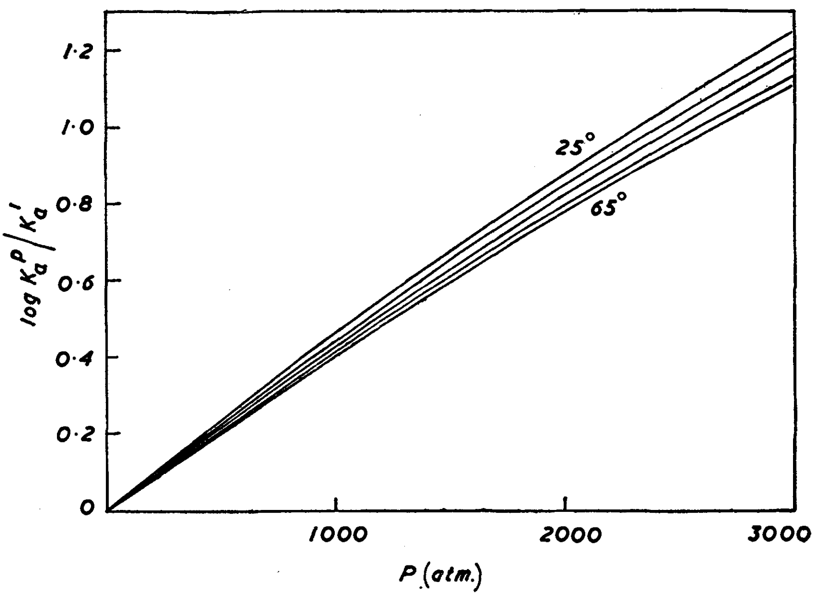
For aqueous solutions there appear to be two opposing factors in operation which tend to counterbalance each other with changing concentrations below about 0·1M. The

[17] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

decreased pressure effect on conductance predicted at higher concentrations by the Debye–Hückel–Onsager relationship is opposed by the lower structural temperature of water at increased salt concentrations. The pressure effect on conductance in water is greatest at low temperatures.

For "carbonic acid," ΔV^1 becomes more positive with increasing temperature. A similar behaviour was calculated by Owen and Brinkley [18] for ΔV^1 for the ionisation of water. They considered that ΔV^1 would continue to increase with temperature until at very high temperatures the ionisation of weak acids was decreased by pressure. It is thought more likely that ΔV^1 increases with temperature, passes through a maximum, and becomes increasingly negative at high temperatures. The present results for "carbonic acid" show that the increase in ΔV^1 for a given temperature rise becomes less at higher

FIG. 5. *The variation with pressure of the apparent dissociation constant of "carbonic acid" in the temperature range* 25—65°.



temperatures. It is known that at temperatures approaching, and exceeding the critical temperature of water, increased pressure greatly increases the ionisation of all electrolytes.[19]

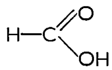
The effect of pressure on the ionisation of "carbonic acid" has not been studied before in detail, although Brander [20] found that pressure had an abnormally large influence on the conductance of carbon dioxide solutions. Owen and Brinkley [18] calculated ΔV^1 at infinite dilution by use of experimental values for the partial molal volumes of the hydrogen and bicarbonate ions, and of carbon dioxide in solution.

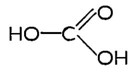
Owen and Brinkley's estimated value of ΔV^1 for "carbonic acid" at 25° was -29 c.c. mole^{-1}, but it was based on an early experimental value of the partial molar volume of carbon dioxide in solution. They assumed that $-\Delta K$ for ionisation was greater than $1{\cdot}0 \times 10^{-3}$; the present results show it to be equal to $1{\cdot}9 \times 10^{-3}$ at 25°.

True carbonic acid, H_2CO_3, has a dissociation constant at 25° and 1 atm. of $1{\cdot}72 \times 10^{-4}$, which is very close to the value of K_a given by Harned and Owen [21] for formic acid (1·772 ×

[18] Owen and Brinkley, *Chem. Rev.*, 1941, **29**, 461.
[19] Ellis and Fyfe, *Rev. Pure and Appl. Chem.*, 1957, **7**, 261.
[20] Brander, *Soc. Sci. Fenn., Phys. Math.*, 1932, **6**, 1.
[21] Harned and Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York, 1950.

10^{-4} at 25°). As the two molecules are very similar they would be expected to differ only slightly in properties:





If it is assumed that ΔV^1 at 25° for the ionisation of H_2CO_3 is equal to that for formic acid ($-8{\cdot}8$ c.c. mole^{-1}),[7] a value of ΔV_h for the hydration of carbon dioxide to carbonic acid can be obtained:

$$\Delta V_h \approx \Delta V^1 \text{ ("carbonic acid")} - \Delta V^1 \text{ (formic acid)} = -17{\cdot}7 \text{ c.c. mole}^{-1}.$$

It is evident that pressure has a considerable influence on the hydration of carbon dioxide, and it would be expected to have a similar effect on the hydration of other gases which form ionised solutions, *e.g.*, ammonia, amines, sulphur dioxide. In a 0·1M-ammonia solution, Moore and Winmill[22] found that NH_3 was present to the extent of 46·2% and $NH_4{\cdot}OH$ 52·4%. The true dissociation constant of $NH_4{\cdot}OH$ is about 4×10^{-5}.

Hamann[3] considered that the increased ionisation of weak electrolytes at high pressure was due essentially to the enhanced solvation of the ions with respect to the un-ionised molecules. He calculated the change in free energy of hydration of singly charged ions at high pressures using Born's formula:

$$\Delta G^\circ \text{ (solvation)} = -\frac{Ne^2}{2r}\left(1 - \frac{1}{D}\right)$$

where N is Avogadro's number, e the electronic charge, D the dielectric constant, and r the mean radius of the two ions. As r decreases and D increases with pressure, ΔG° (solvation) increases.

That this is an oversimplification for weak acids and bases of the hydrated gas type is shown by the present series of results. A calculation for the effect of pressure on ammonia ionisation was given by Hamann,[3] using the compressibility of cæsium fluoride as a model for the compressibilities of the ammonium and hydroxyl ions. The values obtained for the ratio $K_a{}^P/K_a{}^1$ were lower than those from experiment by a factor of about two over the pressure range 3000—6000 atm. This would indicate that ammonia is present in solution at these pressures almost entirely as $NH_4{\cdot}OH$.

If ΔV_h is assumed not to change appreciably with pressure at 25°, the fraction of carbon dioxide in solution present as H_2CO_3 rises from 0·259% at 1 atm. to 2·3% at 3000 atm.

It is evident therefore that the Born equation should not be used to predict the increase with pressure in the apparent ionisation constant for substances such as CO_2, SO_2, and NH_3, where a hydration step precedes ionisation.

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Dominion Laboratory, Department of Scientific and Industrial Research, Wellington, New Zealand. [*Received, January 16th*, 1959.]

[22] Moore and Winmill, *J.*, 1912, **101**, 1635.