The substance fluoresces bright blue under ultraviolet light.

Anal. Calcd. for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 95.11; H, 4.86.

The *di-picrate* forms fine, orange needles from benzene, m. p. 201–201.5° corr.

Anal. Calcd. for $C_{35}H_{20}O_{14}N_6$: C, 56.13; H, 2.69. Found: C, 56.55; H, 2.71.

3-[α-Naphthoyl]-acenaphthene.—The condensation of α-naphthoyl chloride (33.4 g.) with acenaphthene (30 g.) was carried out in 250 cc. of tetrachloroethane at 20–25°, using 26 g. of aluminum chloride. After working up the product in the usual way and distilling the neutral fraction in vacuum, 48 g. (89%) of a light yellow solid was obtained, b. p. 299–302° (7.5 mm.). Recrystallization from benzene–ether gave 41 g. (76%) of the pure 3-isomer as yellow prisms, m. p. 159–160° corr.

Anal. Calcd. for $C_{23}H_{16}O$: C, 89.75; H, 5.10. Found: C, 89.49; H, 5.37.

The oily residue was collected from the mother liquors and subjected to pyrolysis. This afforded 0.2 g. of purified hydrocarbon identical with the material (II) prepared by the other method.

Summary

A hydrocarbon having the cholanthrene ring system and one additional benzene ring has been synthesized.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

RECEIVED JULY 12, 1935

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Thermodynamic Ionization Constants of Carbonic Acid at 38° from Electromotive Force Measurements

BY D. A. MACINNES AND DONALD BELCHER

In a recent paper from this Laboratory[1] the authors described measurements, at 25°, on concentration cells without liquid junctions, leading to the determination of the two ionization constants of carbonic acid. The measurements have been repeated at body temperature, 38°, with the results and conclusions to be outlined in this paper.

(a) The First Ionization Constant.—As in our previous work, the potentials, E'_{A}, were obtained of cells of the type

$$\text{Ag; AgCl, KHCO}_3\text{, KCl, CO}_2\text{ (dissolved), } \textit{glass}\text{, 0.1 } N\text{ HCl, AgCl; Ag} \qquad \text{(A)}$$

in which the concentrations of potassium chloride and potassium bicarbonate were kept equal. The results were interpreted with the aid of the equation

$$pK_1' = pK_1 - \log f_{H}f_{Cl}/f_{H}f_{HCO_3} = -\frac{E_A - E_0 + E_g}{(RT/F)} + \log SP_{CO_2} \qquad (1)$$

Here pK_1 is the negative logarithm of the thermodynamic ionization constant, f_H, f_{Cl} and f_{HCO_3} are the activity coefficients of the indicated ion constituents, E_A is the potential of Cell A, after correction for the asymmetry potential of the glass electrode, E_0 is the limiting potential of the cell

$$\text{Ag; AgCl, HCl; H}_2 \qquad \text{(B)}$$

E_g is the potential of the cell

$$\text{Ag; AgCl, HCl (0.1 } N\text{); H}_2 \qquad \text{(C)}$$

S is the Henry law constant, and P_{CO_2} is the partial pressure of carbon dioxide. Since the activity coefficients approach unity as the concentration is decreased, pK_1 may be obtained by a suitable extrapolation from a series of values of pK_1'.

Except for the change of temperature the experimental arrangements, the preparation of solutions, etc., were exactly as described in our previous paper. The new experimental data are given in Table I, which is self-explanatory. To compute pK_1' values the potentials of Cells B and C are necessary. The first of these, $E_0 = -0.2135$, was obtained from the work of Harned and Ehlers,[2] who give a formula connecting E_0 of this cell with the temperature, based on their extensive experimental work. The second, $E_g = -0.3495$, was interpolated from the same measurements, and agrees closely with direct measurements made in this Laboratory. The Henry law constant, $S = 0.02443$ mole/liter/atm., was obtained from the data of Van Slyke, Sendroy, Hastings and Neill,[3] and has been corrected for the deviation of the equation of state of carbon dioxide from that of a perfect gas. The partial pressure, P_{CO_2}, was obtained from the barometric pressure, the analysis of the tank gas and the vapor pressure of water. The small correction arising from the formation of bicarbonate ion

---

[1] MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933).

[2] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[3] Van Slyke, Sendroy, Hastings and Neill, *J. Biol. Chem.*, **78**, 765 (1928).

TABLE I

DATA FOR THE COMPUTATION OF THE FIRST DISSOCIATION CONSTANT OF CARBONIC ACID AT 38°

Solutions: Equal Concentrations of $KHCO_3$ and KCl

Ionic strength, μ	E'_A	Asymmetry potential	E_A	Barometric pressure	pK' Observed	pK' Computed
0.01036	−0.3532	−0.0019	−0.3551	751.7	6.309	6.308
	− .3539	− .0012	− .3551			
	− .3572	+ .0018	− .3554			
.01511	− .3475	− .0076	− .3551	755.1	6.308	6.308
	− .3479	− .0070	− .3549			
	− .3481	− .0070	− .3551			
.02014	− .3522	− .0026	− .3548	757.3	6.308	6.307
	− .3521	− .0028	− .3549			
.02444	− .3473	− .0075	− .3548	755.1	6.305	6.307
	− .3473	− .0073	− .3546			
	− .3479	− .0071	− .3550			
.03218	− .3502	− .0044	− .3546	755.1	6.303	6.306
	− .3487	− .0060	− .3547			
	− .3505	− .0044	− .3549			
.04230	− .3505	− .0040	− .3545	762.2	6.306	6.306
	− .3487	− .0059	− .3546			
	− .3505	− .0042	− .3547			
.05020	− .3496	− .0048	− .3544	764.0	6.305	6.305
	− .3475	− .0069	− .3544			
	− .3497	− .0050	− .3547			
.06286	− .3495	− .0048	− .3543	764.0	6.304	6.304
	− .3474	− .0070	− .3544			
	− .3494	− .0052	− .3546			
.07694	− .3491	− .0052	− .3543	759.3	6.301	6.303
	− .3466	− .0077	− .3543			
	− .3490	− .0056	− .3546			
.09570	− .3490	− .0054	− .3544	759.3	6.303	6.301
	− .3466	− .0080	− .3546			
	− .3487	− .0058	− .3545			
.1415	− .3484	− .0060	− .3544	754.7	6.298	6.297
	− .3456	− .0078	− .3543			
	− .3481	− .0064	− .3545			
.1919	− .3479	− .0061	− .3540	754.7	6.292	6.293
	− .3452	− .0088	− .3540			
	− .3479	− .0060	− .3539			

from the dissolved carbon dioxide discussed in the previous paper is negligible in the present case. The resulting "observed" values of pK_1' are given in the next to the last column of Table I, and can be expressed by means of the equation

$$pK_1' = 6.309 - 0.082\,\mu \qquad (2)$$

in which μ is the ionic strength and the constant has been obtained by means of least squares. The limiting value of $\mu = 0$ corresponds to a thermodynamic ionization constant, K_1, of 4.91×10^{-7}.

(b) The Second Ionization Constant.—As with the work at 25° the second ionization constant of carbonic acid, K_2, was determined at 38° by means of measurements on cells of the type

$$Ag; AgCl, K_2CO_3, KHCO_3, KCl; H_2 \qquad (D)$$

with the aid of the equation

$$pK_2' = pK_2 - \log\frac{f_H f_{HCO_3} f_{Cl}}{f_H f_{CO_3}} = -\frac{E - E_0}{RT/F} + \log\frac{[HCO_3^-]\,[Cl^-]}{[CO_3^=]} \qquad (3)$$

in which E is the potential of Cell D, E_0 is again the limiting potential of Cell B and $pK_2 = -\log K_2$, and the other terms have their customary meaning. The data are given in Table II. The potential E has been corrected to 1 atm. pressure of hydrogen, otherwise the table is self-explanatory. In computing the values in the column headed "pK_2' observed" a correction was made for the hydrolysis

$$K_2CO_3 + H_2O = KHCO_3 + KOH$$

as described in the previous paper. For this

TABLE II

DATA FOR THE COMPUTATION OF THE SECOND DISSOCIATION CONSTANT OF CARBONIC ACID AT 38°

Concentration equivalents per liter				Ionic strength	pK_2'	
KCl	$KHCO_3$	K_2CO_3	E	μ	Obsd.	Compd.
0.001919	0.001843	0.002227	1.0030	0.009700	10.150	10.149
.002821	.002709	.003273	0.9942	.01454	10.134	10.137
.004430	.004254	.005140	.9834	.02319	10.120	10.119
.005661	.005436	.006568	.9769	.02986	10.106	10.108
.007608	.007306	.008828	.9690	.04044	10.091	10.092
.01001	.009615	.01162	.9612	.05355	10.071	10.075
.01288	.01237	.01495	.9537	.06911	10.061	10.057
.01949	.01872	.02262	.9415	.10498	10.022	10.023
.02987	.02869	.03466	.9278	.1616	9.978	9.980

purpose a preliminary series of pK' values were obtained, and a corresponding series of stoichiometric ionization constants, K_w', of water were interpolated from the work of Harned and Hamer.[4] A second approximation was not found necessary. The resulting pK_2' values may be expressed by means of the equation

$$pK' = 10.204 - 0.5577\sqrt{\mu}$$

in which the constants have been obtained by means of the method of least squares. The limiting value $pK_2 = 10.204$ corresponds to the ionization constant $K_2 = 6.25 \times 10^{-11}$. The Debye–Hückel theory, however, predicts a value of 1.04 instead of 0.5577 for the coefficient of the second term so that this extrapolation must be regarded as empirical. A similar lack of agreement between theory and observation was found in our work at 25° and by Hastings and Sendroy.[5] The difficulty may be due to our lack of a theory of solutions containing mixtures of singly and doubly charged ions.

Discussion

The first dissociation constant of carbonic acid, $K_1 = 4.91 \times 10^{-7}$ at 38°, as determined by the method reported in this paper, is in substantial agreement with the value $K_1 = 4.82 \times 10^{-7}$, based on conductance measurements, given in the accompanying paper by Shedlovsky and MacInnes, who are, in turn, in close accord with a recomputation by Sendroy of the results of Hastings and Sendroy which gave $K_1 = 4.83 \times 10^{-7}$. The determinations of this constant at 25° by the electromotive force method (MacInnes and Belcher) and by the conductance method (Shedlovsky and MacInnes) yielded, respectively, 4.45×10^{-7} and 4.31×10^{-7}, a difference which appears to be larger than the experimental error of either procedure. Both values are, however, in considerable disagreement with the value of $K_1 = 3.5 \times 10^{-7}$, which, until recently, had been generally accepted. Since the conductance method is the more sensitive one and is also independent of the measurements of other workers, we suggest that Shedlovsky and MacInnes' results be adopted.

The value of $K_2 = 6.25 \times 10^{-11}$ for the second constant at 38° is in good agreement with the figure $K_2 = 6.03 \times 10^{-11}$ reported by Hastings and Sendroy.[6] The K_1 and K_2 values determined by the latter authors depend upon the choice of a standard for the pH scale, a matter which will be the subject of a forthcoming paper from this Laboratory.

Summary

The first and second ionization constants for carbonic acid have been determined at 38° from electromotive force measurements on galvanic cells without liquid junctions.

NEW YORK, N. Y. RECEIVED JUNE 6, 1935

---

[4] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

[5] Hastings and Sendroy, *J. Biol. Chem.*, **65**, 445 (1925).

[6] The carbon dioxide in the solutions measured by these authors was determined gasometrically. Applying a small correction for this factor, based on a revision of constants by Van Slyke and Sendroy [*J. Biol. Chem.*, **73**, 127 (1927)] and treating their data by the metbod of least squares, the value obtained is $K_2 = 5.83 \times 10^{-11}$.