orientation in the field around the dropping mercury electrode may be one contributing factor. An additional factor of probable significance is the greater thermodynamic stability of the *trans* isomer of many coördination compounds as compared with the corresponding *cis* isomer.

The half-wave potential for the first reduction wave becomes more negative and the diffusion current constant decreases with increasing concentrations of tartrate and of citrate. These trends, which hold true for both the *cis* and *trans* isomers, are in line with the postulate of Laitinen, Bailar, Holtzclaw and Quagliano[2] of a "super-complex" of multivalent anions clustered about the central complex by electrostatic and ion-dipole attraction. An interesting observation for which an explanation is not readily apparent is the effect of increased chloride concentration upon the half-wave potential of the *cis* isomer but not upon that of the *trans*.

Acknowledgment.—The author is indebted to the Research Council of the University of Nebraska for a grant which aided in carrying out this work.

LINCOLN, NEBRASKA RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Ionization Constant of Sulfanilic Acid from 0 to 50° by Means of E.m.f. Measurements[1]

BY RICHARD O. MACLAREN AND D. F. SWINEHART

The ionization constant of sulfanilic acid has been determined from 0 to 50° by the use of cells without liquid junction. The equation $-\log K = 1143.71/T + 0.0023142T - 1.2979$ expresses the experimental data as a function of the temperature in the above temperature range with a standard deviation of 0.00063 in $-\log K$ for eleven experimental prints.

Introduction

The ionization constant of sulfanilic acid at a single temperature has been measured by several investigators and reported at four temperatures in one paper. All these investigations were carried out by means of conductivity measurements and modern methods of accounting for interionic attraction were not applied. These results are:

Investigator	$K \times 10^4$	t, °C.
Ostwald[2]	5.81	25
Winkelblech[3]	6.20	25
White and Jones[4]	3.26	0
	3.93	6
	6.55	25
	8.20	35
Boyle[5]	7.05	25
Stearn[6]	7.05	21

Sulfanilic acid has been shown to exist in solution as the zwitterion by the dielectric constant data of Carr and Shutt[7] and as may be concluded from the mere fact that it is a moderately weak acid. The ionization constant is that for the reaction

$$^{+}H_3NC_6H_4SO_3^- = H_2NC_6H_4SO_3^- + H^+$$

It is the object of this investigation to present accurate values of the ionization constant of sulfanilic acid determined over the temperature range 0 to 50° by the measurement of the electromotive force of cells without liquid junction following the general method developed by Harned and coworkers.[8] The cells were of the type Pt, H_2/HSu(m_1), NaSu(m_2), NaCl(m_3)/AgCl–Ag, in which HSu and NaSu are sulfanilic acid and its sodium salt and m_1, m_2 and m_3 are weight molalities. The potential of this cell is given by

$$E = E^0 - \frac{2.3026RT}{F} \log m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-} \qquad (1)$$

where E^0 is the molal electrode potential of the silver–silver chloride electrode which has been determined by Harned and Ehlers[9] and where γ is an activity coefficient. By elimination of $m_{H^+}\gamma_{H^+}$ from equation (1) and the expression for the thermodynamic ionization constant

$$K = \frac{m_{H^+}m_{Su^-}}{m_{HSu}} \times \frac{\gamma_{H^+}\gamma_{Su^-}}{\gamma_{HSu}} \qquad (2)$$

the following relation is found

$$\frac{(E - E^0)F}{2.3026RT} + \log \frac{m_{HSu}m_{Cl^-}}{m_{Su^-}} = -\log K - \log \frac{\gamma_{HSu}\gamma_{Cl^-}}{\gamma_{Su^-}} \qquad (3)$$

The usual method of using equation (3) for the calculation of the ionization constant of weak acids, as, for example, in the case of acetic acid,[10] is not suitable for sulfanilic acid since it involves a long series of successive approximations which converge slowly. Instead a procedure developed by Hamer[11] was used. First approximations to m_{H^+}, called m'_{H^+}, were calculated directly from (1) using the Debye–Hückel limiting law[12] to evaluate the activity coefficients. Then values of a first approximation to the ionization constant, K', were calculated from (2), again using the limiting law and $m'_{HSu} = m_1 - m'_{H^+}$ and $m'_{HSu^-} = m_2 + m'_{H^+}$. The negative logarithms of these values were plotted *vs.* the ionic strength and extrapolated to $\mu = 0$. Using this value of K', the limiting law and equation (2), second approximations to m_{H^+},

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[1] Taken from the master's thesis of Richard O. MacLaren.

[2] W. Ostwald, *Z. physik. Chem.*, **3**, 406 (1889).

[3] K. Winkelblech, *ibid.*, **36**, 568 (1901).

[4] G. F. White and H. C. Jones, *Am. Chem. J.*, **44**, 159 (1910).

[5] M. Boyle, *J. Chem. Soc.*, **115**, 1505 (1919).

[6] A. E. Stearn, *J. Gen. Physiol.*, **10**, 379 (1926).

[7] W. Carr and W. J. Shutt, *Trans. Faraday Soc.*, **35**, 579 (1939).

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1942.

[9] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).

[10] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932).

[11] W. J. Hamer, *ibid.*, **56**, 860 (1934).

[12] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

called m''_{H^+}, were calculated. These values were used with (3) to again extrapolate to $\mu = 0$ to obtain $-\log K''$. This last step was repeated again and in every case the third approximation, using (3), gave the same value of $-\log K$ as the second approximation. This whole procedure was repeated at each temperature.

Experimental

Water.—The water used had a conductivity less than 1×10^{-6} mho.

Sodium Carbonate.—Reagent grade sodium carbonate was recrystallized once as the decahydrate. A concentrated solution of this product was saturated with carbon dioxide and the precipitated bicarbonate was filtered, washed and ignited for 2 hr. at 280°.

Sodium Chloride.—Reagent grade sodium chloride was dissolved and precipitated by addition of hydrogen chloride generated from reagent grade hydrochloric acid, sodium chloride and sulfuric acid. The product was fused in platinum.

Hydrogen.—Tank hydrogen was passed over copper (made by reducing copper oxide wire) at 470°.

Sulfanilic Acid.—J. T. Baker C.P. "Analyzed" sulfanilic acid recrystallized from water in large plates of the dihydrate. Samples of this product, ground and dried at 105° for 2-3 hr., were analyzed by weight buret titrations with carbonate-free sodium hydroxide standardized against Bureau of Standards acid potassium phthalate and indicated 100.02 ± 0.05% sulfanilic acid. This heat-dried product gave a faint yellow color in solution which deepened in color on standing due to atmospheric oxidation. For preparing cell solutions, finely ground samples were dried over 90% sulfuric acid in a vacuum desiccator for one week and analyzed as above showing an average of 99.88% sulfanilic acid and the remainder was assumed to be water. Each batch was analyzed separately.

Cell Solutions.—Stock solutions were not used since such solutions, even when stored under hydrogen, showed a yellow color on standing a week or more, presumably due to a trace of oxygen not removed by bubbling hydrogen through the solution for three hours. The cell solutions were prepared directly from the solid materials before each run by weighing the appropriate amounts of sulfanilic acid, sodium carbonate, sodium chloride and water, dissolving as rapidly as possible and bubbling hydrogen through the solution protected by a presaturator. Weights were corrected to vacuum where significant. No cell solution was more than 36 hr. old before the completion of a run. Using this procedure, no yellow color could be detected in the solution after the completion of a run. Due to this procedure, the ratios m_1/m_2 and m_1/m_3 were not exactly constant but were nearly so, m_1, m_2 and m_3 being equal within 1% in each case.

Procedure of the Measurements.—The general procedure was similar to that described by Harned and Owen.[13] The cells were U-shaped with two hydrogen and four silver-silver chloride electrodes in each.

The silver-silver chloride electrodes were Type II electrodes as described by Harned.[14] Silver oxide was decomposed thermally on a platinum spiral and the silver was annealed at 430° for 5 hours before electrolyzing in hydrochloric acid.

The potentials were measured with a Rubicon Type B potentiometer using a Leeds and Northrup No. 2430 galvanometer with a sensitivity of 3.2×10^{-9} amp. per mm. and a standard cell certified by the National Bureau of Standards in absolute volts.

Cells were run in duplicate providing ten independent potential difference measurements. The initial equilibration was carried out at 50° since it was found that the last traces of carbon dioxide were removed quite slowly at 25°. This equilibration required 4 to 8 hr., including 1 to 2 hr. during which the potentials were constant to 0.03 mv. The temperature was then changed directly to 25°. The temperature was raised in 5° intervals to 50°, then back to 25°, lowered in 5° intervals to the lowest temperature permitted by the relatively low solubility of sulfanilic acid,[15] then back to 25°. In general 1.5 hours were required to be certain that equilibrium had been attained after each temperature change except where that change was greater than 5° when a somewhat longer time was required. No run required more than 36 hr. for completion. In most cases the second and third checks at 25° agreed within 0.05 mv. and always within 0.1 mv.

Temperatures were established by means of a platinum resistance thermometer. Temperature regulation was to ±0.01°.

Results

The data are shown in Table I. Each potential difference is an average as indicated in the experimental section. In a few cases one or more indi-

TABLE I

ELECTROMOTIVE FORCE OF THE CELL: $Pt, H_2(p = 1)/HSu(m_1), NaSu(m_2), NaCl(m_3)/AgCl\text{-}Ag$

International volts

m_1	0.00997_0	0.02002_9	0.02995_5	0.03998_5	0.04976_2	0.04961_3
m_2	$.01003_6$	$.02002_0$	$.03042_0$	$.04000_0$	$.05003_4$	$.04992_4$
m_3	$.01001_9$	$.02003_1$	$.03022_9$	$.03973_7$	$.05003_7$	$.04996_0$
t (°C)						
0	.53798	.52130	......	......	......	.....
5	.53781	.52075	.51155	......	......	......
10	.53755	.52005	.51064	.50380	......	.....
15	.53713	.51920	.50954	.50249	.49706	.....
20	.53659	.51822	.50834	.50110	.49564	......
25	.53594	.51710	.50700	.49952	.49404	.49386
30	.53520	.51576	.50546	.49793	.49230	.49182
35	.53434	.51450	.50389	.49634	.49047	.49005
40	.53346	.51310	.50223	.49455	.48844	.48816
45	.53246	.51164	.50058	.49267	.48638	.48622
50	.53131	.51001	.49868	.49076	.48414	.48406

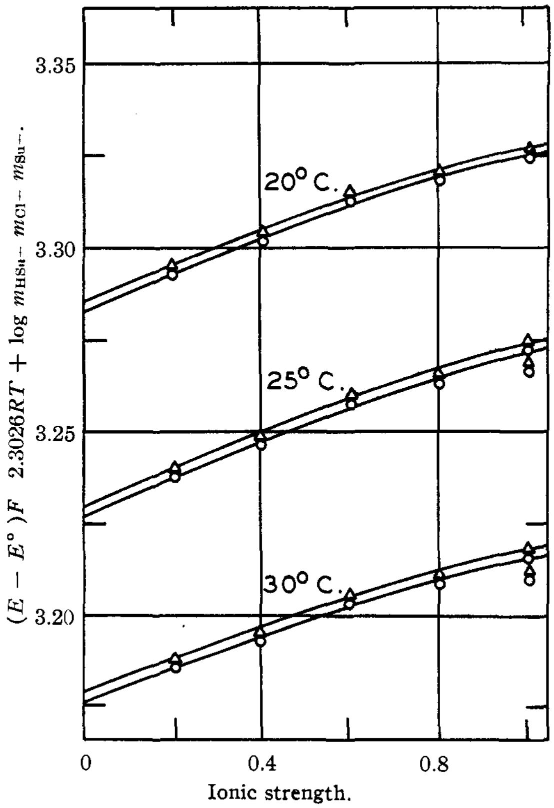

Fig. 1.—Representative extrapolations for the evaluation of $-\log K$: △, first approximation; O, second approximation.

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[13] H. S. Harned and B. B. Owen, *Am. J. Science*, **233**, 161 (1937).

[14] H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

[15] A. Seidell, "Solubilities of Organic Compounds," Vol. I, 3rd Edition, D. Van Nostrand and Co., New York, N. Y., 1941, p. 423.

vidual electrodes were rejected where it deviated from the average by more than about 0.1 mv. The agreement among the silver–silver chloride electrodes was better, in general, than that for the hydrogen electrodes and narrower limits were used for the former than for the latter.

An attempt to make a run with m_1, m_2 and m_3 approximately 0.005 resulted in potentials that drifted badly and these results were discarded entirely.

The measured values of the potential differences in absolute volts were divided by the factor 1.000330 to convert them into international volts.[16] This was done so that the E^0 values of Harned and Ehlers[9] and the constants of Manov, Bates, Hamer and Acree[17] could be used in the calculations.

The data were treated as indicated in the introduction and representative extrapolations at three temperatures are shown in Fig. 1.

The results showing K at the various temperatures are shown in Table II. The experimental values of $-\log K$ were fitted by the method of least squares by the empirical equation $-\log K = (A/T) + CT - D$, yielding the values 1143.71, 1.2979 and 0.0023142 for A, D and C, respectively. The calculated values of $-\log K$ using these constants are shown in Table II. The standard deviation of the calculated values from the experimental ones is 0.00063 in $-\log K$.

TABLE II

THE IONIZATION CONSTANT OF SULFANILIC ACID IN WATER FROM 0 TO 50°

T, °C.	$K \times 10^4$	$-\log K$ obsd.	$-\log K$ calcd.	$\Delta \times 10^4$
0	3.016	3.5206	3.5213	+ 7
5	3.488	3.4574	3.4576	+ 2
10	4.003	3.3976	3.3965	−11
15	4.588	3.3384	3.3380	− 4
20	5.218	3.2825	2.2819	− 6
25	5.925	3.2273	3.2280	+ 7
30	6.668	3.1760	3.1764	+ 4
35	7.482	3.1260	3.1267	+ 7
40	8.341	3.0788	3.0790	+ 2
45	9.249	3.0339	3.0332	− 7
50	10.252	2.9892	2.9892	± 0

Standard deviation = 0.0063

Standard thermodynamic quantities for the ionization reaction may be calculated from the above constants by well-known relations.[18] It is worthy of note that $\Delta C_p^0 = -2(2.3026)CRT$ yields −6.3 cal. mole^{-1} deg. $^{-1}$ at 25° which appears to be the smallest value for this quantity to appear in the literature for this type of reaction although it barely fits the range predicted on empirical grounds by Harned and Owen[19] for the standard heat capacity change for the ionization of a zwitterion.

Acknowledgment.—The authors are grateful to the Research Corporation for a grant in support of this investigation.

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[16] National Bureau of Standards, Circular 475, 1949.

[17] G. G. Manov, R. B. Bates, W. J. Hamer and S. F. Acree, THIS JOURNAL, **65**, 1765 (1943).

[18] Ref. 8, p. 583.

[19] Ref. 8, p. 533.

EUGENE, ORE. RECEIVED SEPTEMBER 18, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Experimental Vapor Heat Capacities and Heats of Vaporization of Seven Octanes

BY GORDON M. BARROW[1]

The vapor heat capacities at about 130, 190 and 250° and the heats of vaporization have been measured for *n*-octane, 3-ethylhexane, 2,3-dimethylhexane, 3,4-dimethylhexane, 2-methyl-3-ethylpentane, 3-methyl-3-ethylpentane and 2,3,4-trimethylpentane. The heat capacities of *n*-octane and 2,3,4-trimethylpentane have also been measured at a reduced pressure to obtain gas imperfection data. From average values of the gas imperfection corrections of these two compounds the heat capacities of all seven octanes in the ideal gas state have been obtained. A comparison of the results for *n*-octane with those of *n*-hexane and *n*-heptane and also with the statistically calculated values has been given. From this it appears that, while the calculated values are essentially reliable, they tend to be about 1% high for the *n*-paraffins.

The available thermodynamic properties of many of the paraffin hydrocarbons are the result of a necessarily approximate statistical calculation. It is desirable, therefore, to have experimentally determined values as checks on these calculations. Furthermore, the extension of this method of calculation to the branched compounds is sufficiently difficult that detailed statistical calculations do not appear to be feasible. Vapor heat capacity data for these compounds would then provide the basis for the empirical determination of otherwise undetermined factors.

The results presented here on the vapor heat capacities of seven of the paraffin octanes are part of the program in connection with the American Petroleum Institute Research Project 44 to provide the experimental results necessary to confirm and extend the tabulated thermodynamic properties of the paraffin hydrocarbons.

Apparatus and Material.—The vapor heat capacities and the heats of vaporization were measured in a new flow calorimeter. The calorimeter unit is similar to that recently described by Waddington, Todd and Huffman,[2] and will be described further elsewhere.

The vaporizer unit is essentially the same as that previously described by Pitzer.[3] The vaporizer heater consists of a 25 ohm coil of No. 30 chromel resistance wire supported on a light glass frame and suspended from a small glass float. With this arrangement the depth to which the heater was submerged remained constant. Two short sections of glass tubing attached to the float rode on the vertical tungsten leads and kept the float centered in the vaporizer.

The octanes used were already of high purity when re-

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[1] Physical Chemistry Laboratory, Oxford, England.

[2] G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947).

[3] K. S. Pitzer, *ibid.*, **63**, 2413 (1941); K. S. Pitzer and W. D. Gwinn, *ibid.*, **63**, 3313 (1941); R. Spitzer and K. S. Pitzer, *ibid.*, **68**, 2537 (1946).