taken to be constant over the temperature range. The accuracy of its determination is of the order of ±5 cal.

Summary

1. From measurements of the cells, $H_2|NaOH$ (m_1), NaCl (m_2), Dioxane (X), H_2O $(Y)|AgCl$–Ag, the ionization constant of water has been determined in 20, 45 and 70% dioxane mixtures, and at 5° intervals from 0 to 50° inclusive.

2. The heat content and heat capacity changes of the ionization reaction have been evaluated.

3. The uncertainty in the determination of the ionization constant increases with the dioxane content of the solvent. This is caused by the change in relative solubility of silver chloride and hydroxide and cannot be remedied as long as silver–silver chloride electrodes are employed. Cells containing silver–silver bromide or iodide electrodes would probably be more suitable, but, unfortunately, their standard potentials are not known in these media.

NEW HAVEN, CONN.   RECEIVED JULY 5, 1939

The Properties of Electrolytes in Mixtures of Water and Organic Solvents. III. Ionization Constant of Acetic Acid in an 82% Dioxane–Water Mixture

BY HERBERT S. HARNED AND LESLIE D. FALLON

From the measurements of the electromotive forces of the cells

$H_2|HAC$ (m_1), NaCl (m_2), NaCl (m_3), Dioxane (X),
$$H_2O \ (Y)|AgCl\text{–}Ag$$

Harned and Kazanjian[1] determined the ionization constant of acetic acid in 20, 45 and 70% dioxane-water mixtures. The first computations depended on standard potentials derived by the Debye-Hückel theory without the use of the extended terms, and have been revised somewhat by Harned.[2] These results have now been extended to 82% dioxane mixtures.

Experimental Results

It was more difficult to obtain high accuracy with these cells than with those containing mixtures of higher dielectric constant. This is caused by the long period of time for equilibrium to be reached, particularly in the cases of cells containing ions at low ionic strengths. However, the average reproducibility of the cells was of the order of ±0.3 mv. The concentrations of acetic acid, sodium acetate and sodium chloride were made equal. These concentrations were known with an accuracy of 0.1% and, consequently, any error from this source was less than that caused by error in the electromotive force measurements. Cells were run in triplicate and the mean values of the electromotive forces taken. These results are compiled in Table I.

(1) Harned and Kazanjian, THIS JOURNAL, 58, 1912 (1936).
(2) Harned, J. Phys. Chem., 43, 275 (1939).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $H_2|HAc$ (m_1), NaAc (m_2), NaCl (m_3), DIOXANE (X), H_2O $(Y)|AgCl$–Ag $X = 82\%$ BY WEIGHT IN SOLVENT, $m_1 = m_2 = m_3 =$ MOLES PER 1000 G. SOLVENT; $\mu = m_2 + m_3$

t	0.01	0.02	0.03	0.05	0.068	0.08	$K \times 10^{11}$
5	0.6903	0.6715	0.6637	0.6501	0.6404	0.6362	7.4
10	.6911	.6739	.6644	.6508	.6413	.6372	7.6
15	.6929	.6750	.6656	.6519	.6423	.6379	7.6
20	.6945	.6766	.6663	.6532	.6432	.6384	7.6
25	.6962	.6782	.6671	.6540	.6440	.6391	7.2
30	.6978	.6795	.6688	.6549	.6448	.6399	6.9
35	.6994	.6808	.6698	.6559	.6458	.6406	6.6
40	.7011	.6821	.6714	.6568	.6465	.6413	6.0
45	.7028	.6834	.6730	.6577	.6472	.6420	5.4

Ionization Constant

The equation for the cell may be written in the form[3]

$$\frac{F(E - E_0)}{2.303 \, RT} + \log \frac{m_1 m_3}{m_2} = - \log \frac{\gamma_H \gamma_{Cl} \gamma_{HAc}}{\gamma_H \gamma_{Ac}} -$$
$$\log K = - \log K' \quad (1)$$

If the left side or $-\log K'$ is plotted against μ, the intercept at zero μ equals $-\log K$. In Fig. 1, plots of $\log K'$ versus μ are shown and it is clear that the values of $-\log K$ can be determined to within ±0.005, or about ±0.2 mv. This uncertainty is very much less than that in the values of the standard potentials, E_0. The difficulty of obtaining E_0 in media of as low a dielectric constant as the present one $(D_{25} = 9.53)$ has been discussed carefully by Harned, Walker and Calmon.[4]

This situation suggests that the present cell

(3) Harned and Ehlers, THIS JOURNAL, 54, 1350 (1932).
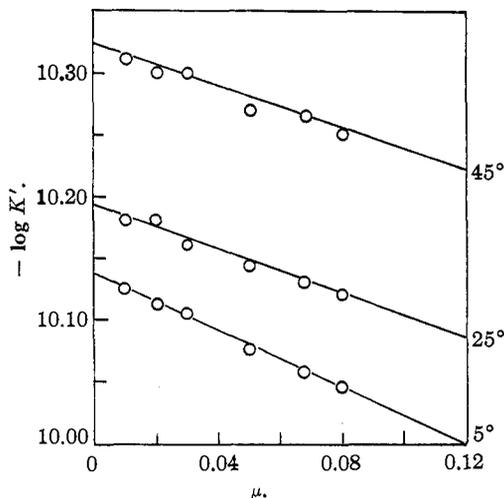(4) Harned, Walker and Calmon, ibid., 61, 44 (1939).

Fig. 1.—Extrapolation plots, diameter of circles equals 0.01 in log K' or approximately 0.4 mv.

may prove important in determining the standard potential in these media of low dielectric constant. It is clear from the nature of the extrapolation plots that an accurate determination of E_0 is possible if the ionization constant is known. A good determination of this quantity by conductance measurements combined with these results would permit the evaluation of E_0 to within ±0.2 mv. Further, there is reason to believe that with an altered technique the accuracy of the present results may be increased.

As previously observed for acetic acid in water and water–organic solvent mixtures of lower dielectric constant, the ionization constant has a maximum value which in this case occurs at about 15°. Owing to the uncertainty of the temperature variation in E_0 and the resulting error in K, we cannot regard the heat data derivable from these results with a high degree of certainty, and have omitted their calculation.

Variation of log K with Mole Fraction of Dioxane–Interpolation Functions.—It has been shown[2] that the plots of log K, or log K_0 — log K, where K_0 is the value of the ionization constant in water, versus $1/D$ show considerable curvature both for acetic acid and water. On the other hand, as indicated by Fig. 2, the plot of this quantity against the mole fraction of water or dioxane is nearly linear. This fact can be employed for interpolation by using the equation

$$\log K = -C - C'N_2 \qquad (2)$$

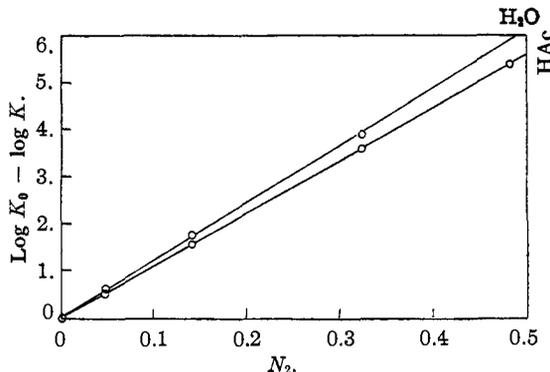where C and C' are constants and N_2 is the mole fraction of dioxane. The constants were deter-

mined from the values of log K in water and 82% dioxane–water mixtures so that the deviations at these solvent compositions are zero. The values of C and C' are given in Table II at all temperatures. The last three columns contain the deviations of the observed results from equation (2) at the concentrations at which K was determined. From these deviations plots can be constructed readily from which log K can be read with an accuracy of the order of 0.002.

Fig. 2.—Variation of log K of acetic acid and water with mole fraction of dioxane, N_2: upper curve, water, lower curve, acetic acid.

TABLE II

CONSTANTS OF EQUATION (2) AND DEVIATIONS, Δ LOG K, OF OBSERVED VALUES OF LOG K FROM THOSE CALCULATED BY THIS EQUATION

Δ log K to be added to calculated value of log K.
$N_2 = 0$, $\Delta \log K = 0$; $N_2 = 0.4823$ ($X = 82$), $\Delta \log K = 0$

	C	C'	$\Delta \log K$		
			$N_2 = 0.0486$ ($X = 20$)	$N_2 = 0.1433$ ($X = 45$)	$N_2 = 0.3231$ ($X = 70$)
0	4.7807	11.1100	−0.001	0.057	0.052
5	4.7695	11.1121	− .001	.053	.045
10	4.7622	11.1148	.000	.045	.040
15	4.7584	11.1231	.003	.0485	.038
20	4.7562	11.1397	.005	.049	.038
25	4.7560	11.1650	.007	.0475	.040
30	4.7570	11.2025	.008	.0480	.044
35	4.7625	11.2407	.012	.050	.051
40	4.7668	11.2898	.014	.052	.060
45	4.7773	11.3468	.016	.055	.071
50	4.7870	11.4150	.018	.059	.084

Summary

1. From measurements of the cells $H_2 | HAc$ (m_1), NaAc (m_2), NaCl (m_3), dioxane (X), H_2O $(Y) | AgCl$–Ag, the ionization constant of acetic acid has been determined from 5 to 45° in a solvent containing 82% by weight of dioxane, the dielectric constant of which is 9.3 at 25°.

2. The principal source of error in this determination is caused by the uncertainty in the

determination of the standard potential, E_0.

3. The results indicate a maximum in the ionization constant which occurs at 15°.

4. Log K does not vary linearly with the reciprocal of the dielectric constant.

5. The plot of log K versus the mole fraction of dioxane at a given temperature is nearly linear.

Numerical equations expressing this linear relationship have been constructed and a table of deviations compiled from which K may be evaluated in all solvents containing 0 to 82% dioxane and at 5° intervals from 0 to 50° with an accuracy comparable to the experimental error.
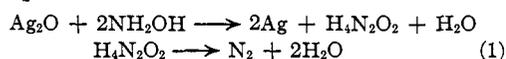

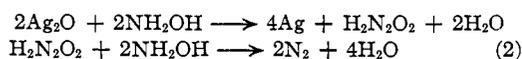# The Reduction of Silver Ions by Hydroxylamine

BY T. H. JAMES

Hydroxylamine appeared to be ideally suited for use in a continuation of the investigation of the reduction of silver ions by developing agents.[1]

The reaction rate can be followed by two independent methods, i. e., optical determination of silver, as previously described, and measurement of nitrogen evolution. The reaction has been subjected to analytical study.[2] Further, it was found that this reaction supplied a transition between the relatively simple kinetics of the hydroquinone reduction and the complicated behavior encountered in a study of the reduction by p-phenylenediamine.

Nichols showed that ammoniacal silver nitrate reacts with hydroxylamine to give pure nitrogen. Strongly alkaline silver nitrate–sodium sulfite solution, on the other hand, yields a mixture of nitrogen and nitrous oxide, but the amount of nitrous oxide produced decreases with decreasing alkalinity. For the production of nitrogen, Nichols postulates the alternative mechanisms

$$Ag_2O + 2NH_2OH \longrightarrow 2Ag + H_4N_2O_2 + H_2O$$
$$H_4N_2O_2 \longrightarrow N_2 + 2H_2O \qquad (1)$$

or

$$2Ag_2O + 2NH_2OH \longrightarrow 4Ag + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 + 2NH_2OH \longrightarrow 2N_2 + 4H_2O \qquad (2)$$

Nitrous oxide, when formed, is considered to arise from the decomposition of hyponitrous acid. Sheppard and Mees showed that the rate of reaction between silver ions and hydroxylamine is accelerated by the addition of alkali, and they concluded that the active species is the ion NH_2O^-. They further observed a catalysis by finely divided silver.

Under the conditions employed in the present investigation, only nitrogen was obtained as reaction product, and this was invariably in the theoretical amount. All measurements were made at $20 \pm 0.02°$, and a solution volume of 75 ml. was employed. The reactions were carried out in total darkness, or under a no. 1 Wratten safelight.

Materials and Procedure

Hydroxylamine Sulfate.—Eastman Kodak Company preparation recrystallized and dried in vacuum, m. p. 172°.

Colloidal Gold.—Phosphorus reduction[3] failed to show the Tyndall cone.

Salts.—General Chemical Company reagent grade. The reaction mixture was prepared in two parts, one containing the silver nitrate and buffer solution, the other containing the hydroxylamine, 2 ml. of 5% gum arabic solution, and, in general, 2 ml. of gold sol. The solutions were freed from oxygen by means of a stream of pure nitrogen, allowed to attain the temperature of the thermostat, and mixed rapidly at time 0. When nitrogen evolution was employed to follow the reaction course, the apparatus previously employed in the measurement of autoxidation rates[4] was used. The reaction chamber was filled with nitrogen and the buret with water at thermostat temperature. The shaking rate employed was adequate to prevent supersaturation of the reaction mixture with nitrogen. When silver determinations were made, a special apparatus was employed which permitted removal of samples at suitable intervals without allowing air to enter the reaction vessel. The solution was stirred by pure nitrogen throughout the course of reaction.

The reduction of silver ions by hydroxylamine is catalyzed by colloidal gold, and more strongly by colloidal silver. Beyond a nitrogen evolution of 0.08–0.10 ml., a plot of $V^{1/3}$ against t yields a straight line for about one-fourth of the entire reaction. This method of the treatment of the

(1) T. H. James, THIS JOURNAL, **61**, 648 (1939).

(2) S. E. Sheppard and C. E. K. Mees, "Investigations of the Theory of the Photographic Process," Longmans, Green and Company, New York, 1907, 141 pp.; M. L. Nichols, THIS JOURNAL, **56**, 841 (1934).

(3) H. B. Weiser, "Inorganic Colloid Chemistry," J. Wiley and Sons, Inc., New York, N. Y., Vol. I, 1933, p. 38.

(4) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937).