

209. *The Dissociation Constants of Organic Acids. Part XII.*
A New Buffer: Phenylacetic Acid-Sodium Phenylacetate.

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THE use of phenylacetic acid as a convenient standard in the measurement of dissociation constants of monobasic acids has been described in Part VIII (J., 1934, 166). The ready availability of this acid in a state of high purity suggested the use of its partially neutralised solutions as buffers, and measurements of the p_H of such solutions have been made with the quinhydrone electrode at 25°. The hydrogen electrode could not be employed owing to the catalytic reduction of the acid (see Experimental) which resulted in unsteady and drifting potentials. The new buffer solutions cover the p_H range 3.16—4.66. The advantages are: (1) convenience of preparation from a solid, non-hygroscopic acid, the purity of which can be readily checked, and (2) stability, owing to absence of mould growth.

Prideaux and Ward (J., 1924, 125, 428) incorporated phenylacetic acid as a constituent of their universal buffer mixture; they employ a value for $K_{\text{class.}}$ of 5.4×10^{-5} ; in view of the work described in Part VIII of this series (*loc. cit.*), a slight revision of their p_H values is necessary.

A potentiometric titration of phenylacetic acid with sodium hydroxide solution was carried out at 25° with the quinhydrone electrode. The value of $K_{\text{therm.}}$, 4.89×10^{-5} , calculated from the results agrees well with the value 4.884×10^{-5} deduced by conductivity. The buffer solutions give $K_{\text{therm.}} = 4.87 \times 10^{-5}$ (compare acetic acid buffer, Morton, *Trans. Faraday Soc.*, 1928, 24, 1; J., 1928, 1401) and this provides evidence in support of their trustworthiness.

EXPERIMENTAL.

Preparation of Materials.—Phenylacetic acid. The commercial acid was purified through the ethyl ester (J., 1934, 166) and had m. p. 76.5—77° after two recrystallisations from benzene-light petroleum (b. p. 100—120°). It was kept in a vacuum desiccator over calcium chloride until required.

Sodium hydroxide solutions. These were prepared by the electrolysis of "AnalaR" sodium chloride with a mercury cathode (compare Jeffery and Vogel, *Phil. Mag.*, 1933, 15, 400) in an all-Pyrex apparatus. The amalgam was run out into a Jena-glass weighing bottle containing conductivity (equilibrium) water and provided with a soda-lime guard tube. The aqueous solution was decanted after 12 hours into a Jena-glass flask, suitably diluted with equilibrium water, and standardised with methyl-red as indicator immediately before use against constant b. p. hydrochloric acid, prepared by means of the apparatus described in Part V (J., 1932, 409), and diluted with a weight pipette.

Quinhydrone. This was prepared by the oxidation of quinol with ferric alum (Bilmmann, *Bull. Soc. chim.*, 1927, 41, 23), and recrystallised from water at about 70° in an atmosphere of nitrogen. The crystals which separated on cooling were collected on a Jena-glass sintered

funnel and dried between good-quality filter paper. They were stored in a brown-glass stoppered bottle. One or two days before use, a sample was washed with conductivity water and then dried in a desiccator over calcium chloride.

Calomel electrode materials. The mercury was redistilled, the calomel was prepared electrolytically from this pure mercury and pure hydrochloric acid, and the potassium chloride was the "AnalaR" quality. All solutions were made up with conductivity (equilibrium) water.

Apparatus.—The *E.M.F.* measurements were made with a Cambridge potentiometer reading to 0.1 millivolt, a Tinsley standard Weston cell, and a Tinsley mirror galvanometer of high sensitivity. Two Tinsley–Weston cells, with N.P.L. certificate, were employed as standards; these were repeatedly checked against the Weston cell in use with the potentiometer, but no variation could be detected.

All measurements were carried out in an electrically controlled thermostat at $25^\circ \pm 0.01^\circ$. The volumetric apparatus was carefully calibrated before use.

The titration vessel consisted of a 250-c.c. Pyrex bottle provided with four apertures. These were used severally for the saturated calomel electrode, a pair of quinhydrone electrodes sealed through a stopper, and a mercury-sealed stirrer; all these fitted into the apparatus with interchangeable ground-glass joints. The fourth aperture carried the Grade A burette, provided with a soda-lime guard tube, and fitted into the titration vessel with a specially treated rubber stopper.

The titration cell was cleaned between each experiment by soaking in chromic acid mixture, washed with distilled water, steamed for 6 hours, and then dried in an electric oven at 120° .

Stirring was also carried out by a stream of nitrogen (Morgan, Lammert, and Campbell, *J. Amer. Chem. Soc.*, 1931, **53**, 597) derived from a cylinder and purified by passage through alkaline pyrogallol solution, conductivity water, solid calcium chloride, and purified cotton-wool. The calomel electrode vessels, in Pyrex, were a modification of Clark's type *A* ("The Determination of Hydrogen Ions," 1928, p. 304); an ungreased, well-ground stopcock in the arm of the electrode prevented diffusion of the saturated potassium chloride into the titration vessel. The electrodes consisted of two bright platinum sheets, 1.2 cm. square, sealed into a ground-glass stopper. Several pairs of these were made, and all fitted into the cell by interchangeable ground-glass joints. The readings of any individual pair employed in the titrations did not differ by more than 0.2 millivolt. After use, they were cleaned by 12 hours' immersion in chromic acid mixture, washed well, left for a few days short-circuited in distilled water, and then dried in a desiccator. Electrodes which had not been submitted to the last two processes did not give consistent results.

Results.—The p_H values were computed from the formula $E = E_0 + (RT/F) \log a_H$; E_0 , the normal potential of quinhydrone at 25° , was taken as 0.69969 volt (Harned and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 4586; cf. Biilmann and Krarup, *J.*, 1924, **125**, 1954); the potential of the saturated calomel electrode used was determined by standardisation against the *N/10*-calomel electrode, for which a value of 0.3376 volt was assumed (Clark, *op. cit.*, p. 480), and was further checked against *M/20*-AnalaR potassium hydrogen phthalate ($p_H = 3.974$; *idem*, *ibid.*), the value 0.2458 volt being obtained.

The cell employed was $Hg|Hg_2Cl_2, KCl (satd.)||phenylacetate\ buffer, quinhydrone|Pt$, and the liquid-junction potential was assumed to be negligible.

The true dissociation constants were calculated from the formula

$$p_{K\text{therm.}} = p_H + \log ([acid] - [H^+]) - \log ([salt] + [H^+]) + 0.505 \mu^{\frac{1}{2}} - B\mu$$

(cf. Cohn, *J. Amer. Chem. Soc.*, 1927, **49**, 185; Cohn, Heyroth, and Menken, *ibid.*, 1928, **50**, 696; Glasstone, "The Electrochemistry of Solutions," 1930, pp. 125, 211). Now μ , the ionic strength, is small (0.0007—0.005) for the experiments described, so the *B* term was neglected.

The p_H values of the buffer solutions are given below, and also the values of $p_{K\text{therm.}}$ calculated from the above equation: *x* c.c. of 0.01*N*-sodium hydroxide were added to 50 c.c. of 0.01*N*-phenylacetic acid and made up to 100 c.c.

<i>x</i>	0.00	2.50	5.00	10.00	15.00	20.00	25.00	30.00	35.00
p_H	3.160	3.449	3.562	3.779	3.966	4.140	4.308	4.473	4.658
$p_{K\text{therm.}}$	—	4.310	4.314	4.314	4.310	4.313	4.316	4.312	4.311

The details of the potentiometric titration of 100 c.c. of 0.01*N*-phenylacetic acid with 0.01*N*-sodium hydroxide are in the table below, together with the values of the ionic strength

and $p_{K_{\text{therm.}}}$; the two values of E refer to the two electrodes employed. In deducing the mean value of $K_{\text{therm.}}$, 4.89×10^{-5} , the figures in parentheses, where the solutions are poorly buffered, *viz.* at the beginning and the end of the titration, have been omitted.

Potentiometric titration of 100 c.c. of 0.01N-phenylacetic acid with 0.01N-sodium hydroxide.

NaOH, c.c.	$E.M.F. \times 10^4$, volt.		p_{H}	μ	10^5 , $K_{\text{therm.}}$	NaOH, c.c.	$E.M.F. \times 10^4$, volt.		p_{H}	μ	10^5 , $K_{\text{therm.}}$
	E_1	E_2					E_1	E_2			
0.00	2676	2674	3.160	0.00069	—	45.00	2054	2054	4.211	0.00316	4.88
5.00	2578	2578	3.326	0.00095	[5.04]	50.00	2004	2004	4.297	0.00338	4.86
10.00	2484	2482	3.485	0.00124	4.94	55.00	1956	1956	4.379	0.00359	4.89
15.00	2396	2396	3.627	0.00154	4.85	60.00	1903	1903	4.468	0.00378	4.83
20.00	2332	2332	3.740	0.00185	4.94	65.00	1848	1848	4.554	0.00397	4.92
25.00	2266	2264	3.854	0.00214	4.84	70.00	1790	1790	4.653	0.00414	4.90
30.00	2220	2220	3.932	0.00242	4.88	75.00	1716	1716	4.778	0.00430	[4.71]
35.00	2150	2150	4.057	0.00277	4.90	80.00	1628	1628	4.927	0.00446	[4.44]
40.00	2104	2104	4.127	0.00293	4.88	90.00	1306	1306	5.478	—	—
											Mean 4.89

Catalytic Reduction of Phenylacetic Acid.—5 G. of phenylacetic acid in rectified spirit were shaken in an atmosphere of hydrogen in the presence of 0.1 g. of Adams's platinum oxide catalyst; about 75% of the theoretical quantity of hydrogen was absorbed during the first 6 hours, and the remainder more slowly. The alcohol was distilled off, and the ester in the residue hydrolysed by 6 hours' boiling with 50% potassium hydroxide solution. An excellent yield of cyclohexylacetic acid was obtained on acidification.

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