737. *The Use of the Spekker Photoelectric Absorptiometer for the Determination of* pH.

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The use of several buffer solutions to determine the pK of an indicator not only provides an essential datum but also enables the suitability of the indicator for the proposed method to be tested. Precautions are considered whereby the sum of the errors of measurement and of the assessment of activity effects may be kept within desired limits. If the recommended procedure is adopted, the pK may be determined to within 0·02 unit, and in favourable cases to better than 0·01. pK values are determined for the nitrophenols, and the behaviour of methyl-red is considered in some detail.

Lothian (*Trans. Faraday Soc.*, 1937, **33**, 1239) proposed the use of the Spekker photoelectric absorptiometer for determination of pH with a white light source and special filters, and gave calibration curves for several indicators. Such curves would give accurate results only for solutions of about the same ionic strength as that of the buffer solutions used in the calibration. Moreover, the method requires the accurate reproduction of concentrations of stock indicator solutions—an exacting requirement—and does not use the simple relation between drum-readings and concentrations which should make applicable an indicator equation of the Ostwald type, *viz.*, $HIn \rightleftharpoons H^+ + In^-$ ($HIn =$ indicator). By contrast, the method described below utilises the capacity of the Spekker instrument to measure optical density, and its validity has been demonstrated by the accurate determination of pK_{In} values for some common indicators.

From the equation defining the dissociation constant (K_{In}) of a typical simple indicator of the pseudo-acid type it follows that

$$pK_{In} = p\{H^+\} + \log_{10} [HIn]/[In^-] + \log_{10} f_{HIn}/f_{In^-} \quad . \quad . \quad . \quad . \quad (1)$$

(see T. B. Smith, "Analytical Processes," Edward Arnold & Co., London, 1940, pp. 229—231). An analogous formula can be applied to a pseudo-base. In equation (1) the relation between pK_{In} and $p\{H^+\}$ can be derived if the other two terms can be determined. Measurement of the ratio $[HIn]/[In^-]$ by means of absorptiometer is equivalent in principle to determination of the concentration of one species only, since a wave-length would be chosen to exclude the other. Hence, ideally, water would be suitable for establishing one of the scale-readings required; but since some departure from ideal conditions is often inevitable, it is safer to use the extreme colour of the indicator for this purpose. Any solution of pH not less than 3 units from the p*K* is suitable. The concentration of other species will then be not greater than 0·1%. Cases where such a simple arrangement is not practicable are discussed later.

If α and β are the Spekker drum-readings corresponding with the fully non-ionised and with the fully ionised condition respectively, and if R is the reading for an intermediate state, then

$$[HIn]/[In^-] = (R - \beta)/(\alpha - R) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This ratio should be evaluated accurately, especially for determination of p*K* which enters into any subsequent calculation of pH.

The term $\log (f_{HIn}/f_{In^-})$ of equation (1) involves assessment of activity effects. Unless the solutions are unduly concentrated, it should be possible to calculate these effects from one of the well-known approximate equations. Of these, by far the most convenient is Davies's form (*J.*, 1938, 2093) since, unlike such earlier equations as those of Debye and Hückel, Brønsted, and Guggenheim, it contains no constants which have to be specially evaluated for each application. This simplification may, of course, lead to some loss of accuracy, but that the equation is entirely adequate for present purposes is shown in the Experimental section in connection with the preparation of buffers.

The activity coefficient, f_i, of an ion of valency z_i at 25° is then represented by

$$\log f_i = -0{\cdot}5\, z_i^2 \phi(I) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where I is the ionic strength and

$$\phi(I) = \sqrt{I}/(1 + \sqrt{I}) - 0{\cdot}2(I)$$

Equation (1) then becomes

$$pK_{In} = p\{H^+\} + \log [HIn]/[In^-] + 0{\cdot}5\phi(I) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since f_{HIn} may be taken as unity.

EXPERIMENTAL

Instrument.—For approximate work the Spekker Photoelectric Absorptiometer model H 560 can be used as supplied by the makers; for the highest accuracy, however, a few modifications to the instrument were made, and certain precautions observed.

(*a*) *Voltage stabilisation.* A BISRA study group has concluded that, for many purposes, most instruments are sufficiently self-compensating to eliminate effects of the usual voltage fluctuations. This property depends on the critical matching of the photocells, and, in the instrument used in these investigations, changes of drum-reading of about 0·02 unit were observed for a 5-v change in the supply when a Wratten 74 (green) filter was used. Consequently the voltage used in all the experiments described here was controlled at 195 ± 0·5 volts, by a carbon-pile regulator.

(*b*) *Temperature effects.* (i) The perceptible absorption of the usual heat filters in the visible spectrum alters appreciably for the temperature increases which inevitably occur when light is being transmitted. The only simple cure is to permit passage of light for very short intervals of time. The gelatin light-filters may also be affected if placed adjacent to the heat-filters, but an improvised position on the opposite side of the glass cell (except when 4-cm. cells render this impossible) practically eliminates the effect. (The Spekker model H 760 has incorporated a filter holder in this position.) (ii) Both indicator and buffer characteristics may vary with temperature, and consequently temperature control is essential for accurate work. This was achieved by storing the solutions in a thermostat at 28° and allowing them to cool in the cell on the instrument at a known rate, to 25° ± 0·1°. The glass cells were also fitted with cover slips to eliminate evaporation, to reduce the rate of cooling, and to minimise meniscus reflections by facilitating complete filling of the cells. (iii) The general heating of the apparatus from the lamp causes an additional (and avoidable) change in the transmission of the filters. It is also liable to produce a shift of the light image relative to the photocell surface; this image is larger than the photocell surface and is of non-uniform intensity. The use of a water-cooled lamp-house minimises these effects and has other advantages; its adoption follows the practice of the Bragg Laboratory, N.O.I.D., Sheffield.

(*c*) *The light beam.* Since the mercury-arc lamp does not provide a point source, the resulting beam cannot be both parallel and of uniform intensity; for large apertures considerable divergence occurs. This causes the beam to strike the bottom of the glass cells with consequent variable reflection errors. (If the cell is raised to avoid meniscus reflections at the liquid surface, there is even a danger of the light passing through the glass base of the cell.) In all experiments recorded here, apertures larger than correspond to a drum-reading of 0·2 were therefore avoided. Photocell fatigue effects were also thereby reduced.

(*d*) *Extraneous light.* This should be excluded as far as possible. All the cells were covered with black " Perspex " hoods during use.

(*e*) *The calibrated aperture.* A check should be made on all sections of the scale within the working limits, with a neutral filter of low optical density (*e.g.*, H 503). The Spekker used was satisfactory in this respect.

Procedure for the Accurate Determination of pK_{In}, *the Approximate Value being known.*—In all determinations a mercury-arc lamp, with appropriate heat- and light-filters, was used, to give an effectively monochromatic source. A series of buffer solutions covering the range of about 1 unit of pH on either side of the change-point of the indicator, and a stock solution of the indicator itself (preferably in water), were first prepared. Each of the buffer solutions was then mixed with 5 ml. of indicator solution and diluted so as to give a total volume of 100 ml. Standards for the " acid " and " alkaline " forms of the indicator were produced from any solution of pH at least 3 units from the change-point of the indicator in question. Mineral acid and alkali of approximately N/100 concentration were convenient for the nitrophenols. Difficulties may arise if the indicator has more than one change-point, in which case extrapolation methods can be employed (see results for methyl-red). Indicator concentrations were chosen so that the 4-cm. glass cells could be used to give readings between 0·2 and 0·9 on the drum. The fully coloured form was used as the standard, and was rechecked at frequent intervals during each determination, but no wandering of the drum-reading was observed when the precautions outlined above were taken. Filters were chosen to transmit light of wave-length as near as possible to the absorption maximum of the indicator.

Nitrophenols.—The behaviour of simple indicators of the pseudo-acid type, such as nitrophenols, is adequately represented by equation (4). The more highly coloured (alkaline) form of the indicator is represented by In^-, so that, from equations (2) and (4), we obtain

$$pK_{In} = p\{H^+\} + \log(R - \beta)/(\alpha - R) + 0{\cdot}5\phi(I) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The several values of pK_{In} shown in Tables 1—3 for *m*-, *p*-, and *o*-nitrophenol have been calculated with the aid of this equation.

Methyl-red (p-*Dimethylaminoazobenzene*-o-*carboxylic Acid*).—This exemplifies relatively complicated cases. Since methyl-red contains both a basic and an acidic group, changes are produced (i) by addition of a proton to the basic nitrogen atom in more acid solutions, forming a singly charged cation, *i.e.*, $HIn + H^+ \rightleftharpoons H_2In^+$ (ion of quaternary salt, known as Red I), and (ii) by reversal of this process in more alkaline solution, and ionisation of the carboxyl group producing a singly charged anion, $HIn \rightleftharpoons H^+ + In^-$ (ion of yellow salt). There is some doubt whether the intermediate form (Red II) is properly represented as an uncharged molecule (HIn), or as a zwitterion ($^+HIn^-$) (see Kolthoff, " Acid-base Indicators," The MacMillan Co., New York, 1937, p. 146). For present purposes the former assumption is made, and the activity coefficient of HIn is taken to be 1 at the concentrations used (see, however, p. 3853). Then

$$K_1 = \{H^+\}[HIn]/[H_2In^+]f_I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$K_2 = \{H^+\}[In^-]f_I/[HIn] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where f_I represents the activity coefficient of a univalent ion.

At the wave-length used, the absorption of Red I is less than that of Red II and, because of some overlap of the two indicator stages, there is in the region of pH 3—4 a minimum in the drum-readings which does not correspond with the indicator's being wholly in the Red II form. The drum-reading for the latter condition, though inaccessible to direct measurement, can be derived by calculation. Thus, let a, b, c, respectively denote drum-readings which correspond ideally with the indicator's being wholly in the forms H_2In^+, HIn, and In^- respectively; further let R (or R') represent any other reading between a and b (or b and c). Then the ratios $[HIn]/[H_2In^+]$ and $[In^-]/[HIn]$ in equations (6) and (7) become respectively $(a - R)/(R - b)$ [and $(R' - b)/(c - R')$] for all solutions in which one of the three forms is negligible. Hence, from equation (6),

$$R = (a - R)\{H^+\}/f_I(K_1) + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, from equation (7),

$$R' = [K_2(c - R')/\{H^+\}f_I] + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It is clear that, by plotting R against the coefficient of $1/K_1$ in equation (8), and R' against the coefficient of K_2 in equation (9), two independent values of b can be derived as the intercepts on the axis of R. The relevant experimental data are quoted in Tables 4 and 5, where values of the coefficients of $1/K_1$ and K_2 are given (column 4). The divergencies from linearity are negligible. Application of the method of least squares to the data gave:

$$pK_1 \text{ range}: b = 0{\cdot}197;\ pK_1 = 2{\cdot}33;$$
$$pK_2 \text{ range}: b = 0{\cdot}203;\ pK_2 = 5{\cdot}01.$$

The agreement between the b values obtained from the two ranges is reasonable but, in view of the small difference in drum-readings involved in the pK_1 measurements, the b values from the pK_2 range are regarded as much more reliable. For the present purpose, it is of interest to investigate the variability of pK as obtained from individual buffers; by using, therefore, $b = 0{\cdot}203$, the pK_2 values recorded in column 5 of Table 5 have been obtained.

For these calculations it has been assumed, as a first approximation, that the constant a was measured sufficiently accurately by use of 0·1N-hydrochloric acid. The approximate pK_1 values so obtained show, however, that in such an acid there would remain about 4% of Red II; accordingly, a more accurate value of a has been calculated by simple proportion and used in deriving the pK_1 values of Table 4.

Materials.—*m*-Nitrophenol was of B.D.H. Indicator quality; the stock solution contained 0·26 g./l. *p*-Nitrophenol was of B.D.H. Indicator quality; the stock solution contained 0·025 g./l. *o*-Nitrophenol was resublimed; the stock solution contained 0·1 g./l. Methyl red of B.D.H. Indicator quality was recrystallised; the stock solution contained 0·02 g./l.

Phosphate buffers. $\{pH^+\}$ values for NaH_2PO_4–Na_2HPO_4 mixtures (of "AnalaR" quality) (of ionic strength shown in Tables 1—3) were derived from the tables of Cohn *et al.* (*J. Amer. Chem. Soc.*, 1927, **49**, 173; 1928, **50**, 696).

Borax buffers. 0·05M-Borax of "AnalaR" quality was used. $p\{H^+\} + 0{\cdot}5\phi(I)$ at 25° = 9·29 (see Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1943, p. 321).

Acetate buffers. The $p\{H^+\}$ values for sodium acetate–acetic acid mixtures have been calculated by the Davies formula (equation 3) with pK_a for acetic acid = 4·756 (from the best values quoted by Harned and Owen, *op. cit.*, p. 515). Values calculated in this way were in excellent agreement with the experimental standards quoted by Harned and Owen, *op. cit.*, p. 321).

Results.—See Tables.

TABLE 1. pK_{In} *for* m-*nitrophenol.* Filters: Wratten 2 and Chance OV 1, giving mainly the Hg line 4047 Å.

$p\{H^+\} + 0{\cdot}5\phi(I)$		Drum reading	I	$0{\cdot}5\phi(I)$	pK_{In}
N/100-H_2SO_4		0·801			
N/100-NaOH		0·300			
6·95	PO_4''' buffers	0·784	0·100	0·110	(8·40)
7·55		0·730	0·130	0·120	8·33
7·65		0·720	0·160	0·127	8·36
7·94		0·664	0·151	0·124	8·36
8·34		0·560	0·150	0·124	8·37
9·29	Borax buffer	0·364	0·100	0·110	8·35

TABLE 2. pK_{In} *for* p-*nitrophenol.* Filters as for *m*-nitrophenol.

N/100-H_2SO_4		0·899			
N/100-NaOH		0·300			
6·35	PO$_4'''$ buffers	0·817	0·07	0·098	7·14
6·64		0·665	0·10	0·110	7·14
6·95		0·753	0·10	0·110	7·13
7·23		0·576	0·14	0·122	7·17
7·55		0·471	0·13	0·120	7·15

TABLE 3. pK_{In} *for* o-*nitrophenol.* Filters : Wratten 50 and Chance OB 2, giving mainly the Hg line 4360 Å.

N/100-H_2SO_4		0·766			
N/100-NaOH		0·250			
6·35	PO$_4'''$ buffers	0·692	0·07	0·098	7·13
6·64		0·650	0·10	0·110	7·17
6·95		0·573	0·10	0·110	7·17
7·23		0·491	0·14	0·122	7·18
7·55		0·420	0·13	0·120	7·14

TABLE 4. *Methyl-red :* pK_1 *for the range Red I to Red II.* Filters : Wratten 74 and H 503, giving mainly the Hg line 5461 Å. $a = 0{\cdot}304$, calc. from an observational mean of 0·301 for N/10-hydrochloric acid ; $b = 0{\cdot}203$.

HCl normality (also = I)	p{H$^+$}	R	$10^4(0{\cdot}301 - R)\{H^+\}/f_I$	pK_1
0·01910	1·78	0·281	3·82	2·25
0·01433	1·90	0·275	3·72	2·24
0·00955	2·06	0·267	3·24	2·26
0·00478	2·35	0·249	2·48	2·24
0·00239	2·64	0·234	1·60	2·27
0·001433	2·86	0·220	1·16$_2$	2·14
0·000955	3·03	0·215	0·82$_1$	2·14

TABLE 5. *Methyl-red :* pK_2 *for the range Red II to yellow.* Acetate buffers. Filters as for pK_1. $c = 0{\cdot}842$ (mean of 10 readings for N/100-NaOH) ; $b = 0{\cdot}203$.

p{H$^+$}	R'	I	$10^{-4}(c - R')/\{H^+\}f_I$	pK_2
4·51	0·373	0·0250	1·782	5·02
4·68	0·430	0·0313	2·345	5·01
4·85	0·496	0·0375	2·958	5·00
5·04	0·564	0·0438	3·698	5·01
5·27	0·644	0·0500	4·52	5·01
5·62	0·735	0·0563	5·49	5·01
Buffers made 0·05M *with respect to* NaCl.				
4·48	0·362	0·0750	1·824	5·06
4·65	0·420	0·0813	2·400	5·04
4·83	0·485	0·0875	3·058	5·04
5·02	0·550	0·0938	3·89	5·05
5·25	0·638	0·1000	4·65	5·03
Buffers made 0·033M *with respect to* BaCl$_2$.				
4·48	0·364	0·0750	1·817	5·05
4·65	0·430	0·0813	2·348	5·02
4·83	0·490	0·0875	3·010	5·02
5·02	0·559	0·0938	3·768	5·03
5·25	0·636	0·1000	4·71	5·04
5·60	0·731	0·1063	5·70	5·03

TABLE 6. *Summary of mean* pK *values for methyl-red.*

		Theor. method ($f_{\mathrm{HIn}} = 1$)	Empirical method ($f_{\mathrm{HIn}} = f_I$)
b		0·203	0·186
pK_2	Buffers without additional salt	5·01 ± 0·01	4·91 ± 0·01
	Buffers containing NaCl	5·04 ± 0·02	4·91 ± 0·01
	Buffers containing BaCl$_2$	5·03 ± 0·02	4·90 ± 0·01
pK_1		2·23 ± 0·07	2·43 ± 0·09

DISCUSSION

The results in Tables 1—3 yield mean values of pK_{In} for *m*-, *p*-, and *o*-nitrophenol of 8·35, 7·14, and 7·16 respectively, all probably within ±0·02; the values are in reasonable agreement with those given in earlier literature, *viz.*, for *m*-nitrophenol, 8·30 (Michaelis), 8·30 (Kolthoff), 8·00 (Holleman), 8·28 (Lundén); for *p*-nitrophenol, 7·22 (Michaelis), 7·03 (Kolthoff), 7·16 (Lundén), 7·19 (Holleman); and for *o*-nitrophenol, 7·17 (Holleman), 7·12 (Hantzsch); see Landolt–Börnstein's "Tabellen, etc.," Eg II*b*, p. 1102, and Beilstein's "Handbuch, etc.," VI, 216, 222, 226.

For methyl-red, the results for pK_2 are very consistent even after addition of sodium chloride and barium chloride. The comparatively low accuracy of the pK_1 values arises largely because an indicator concentration suitable for the study of the Red II–yellow stage is too low to secure adequate drum reading differences for change of the Red I to Red II; but since pK_1 was determined only to clarify the interpretation of the pK_2 range, high accuracy was not important. Kolthoff gives 5·05 for pK_2 and 2·60 for pK_1 (*Rec. Trav. chim.*, 1925, **44**, 75).

No colorimetric evidence was found for the existence of a third change-point for methyl-red in the region of pH 9, as claimed by Vlès *et al.* (*Arch. Phys. Biol.*, 1942, **16**, 5) from electrometric measurements. There certainly is, however, another colour change in the very low pH region which appears to have escaped attention hitherto. In 95% sulphuric acid methyl-red undergoes a further change to yellow which can be quantitatively reversed on reducing the acidity, and between this region and pH 0 the absorption in the green is *greater* than can be ascribed to Red I. Although in part this might be explained by the essential alteration of the solvent, it is probable that at least one new form of the indicator is involved. Because of these complications it would be unwise to determine the drum-reading equivalent to Red I by making the solution highly acid.

Procedure for Determination of pH.—It is clear from equation (1) that if, in any solution, the ionic strength is known, and the ratio of the two forms of the indicator can be measured on the absorptiometer, then either pK or pH can be derived if the other is known. The determination of pK_{In} here establishes the validity of the method, and since the nature of the errors involved in determining pH will be exactly similar, the useful range of any indicator is immediately apparent from the reproducibility of pK when solutions of known pH are used.

Now it might appear, from the overlapping of the K_1 and K_2 ranges of methyl-red, that this indicator is not suitable for pH determination. Certainly the initial investigation is complicated by this fact, but, once the essential data have been obtained, application of the indicator to pH determination is simple. The reading c corresponding with the yellow form can be arbitrarily chosen to be, say, 1·00 (or somewhat less) by balancing with the iris diaphragm when the right-hand cell contains a measured proportion of the indicator in dilute aqueous sodium hydroxide, conveniently about 0·01N. Now, although the hypothetical drum-reading b for 100% HIn form is not accessible to direct measurement, this always bears a fixed relation to any readings which *can* be readily reproduced. For convenience, therefore, we may take advantage of the flat minimum in the readings over the intermediate region, as illustrated by the following figures:

p{H$^+$}	3·0	3·1	3·2	3·3	3·4	3·5
R	0·217	0·214	0·213	0·213	0·215	0·217

Hence, to reproduce the minimum reading, no accurate buffers are needed; an acetic acid solution roughly diluted to be in the range N/30 to N/70 serves, and the value of b is then calculated directly by the formula: $b = 1{\cdot}016R_{\text{min.}} - 0{\cdot}016c$.

There is, however, another feature of indicators of this type which proves especially useful for the present purpose. The intermediate HIn form may be either a zwitterion or an uncharged molecule, and although the latter view seems now to be preferred in the case of methyl-red (Baggesgaard-Rasmussen and Reimers, *Dansk. Tidsskr. Farm*, ,1933, **7**, 225), Kolthoff has pointed out that it does not completely explain the salt-effects (*J. Amer. Chem. Soc.*, 1938, **60**, 2516). It is thus of interest that the complete omission of activity coefficients from equations (6) and (7), which amounts formally to setting the activity coefficient of HIn equal to that of a univalent ion (cf. Bjerrum, *Z. physikal. Chem.*, 1923, **104**, 147), leads to pK values which, although differing appreciably from those quoted above, are in as good agreement amongst themselves (see Table 6). From a practical point of view it is immaterial that this procedure has little theoretical justification, for, provided that a consistent pK_2 value is used (although merely an empirical value), the p$\{H^+\}$ of any solution can be determined with the same accuracy as with the more acceptable procedure, even in the presence of sodium or barium chloride. It is therefore recommended that the equation which bypasses activity assessments should be used, *viz.*, for methyl red :

$$p\{H^+\} = 4{\cdot}91 + \log (c - R) - \log (R - b)$$

in which b must now be consistently determined by the equation :

$$b = 1{\cdot}043R_{\text{min.}} - 0{\cdot}043c.$$

Indicators which are susceptible to this kind of empirical treatment should be selected for development of the method, since the correct assessment of activity effects constitutes its most serious difficulty.

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