Analysis

"That's not a regular rule: you invented it just now." "It's the oldest rule in the book," said the King. "Then it ought to be Number One," said Alice.

LEWIS CARROLL

EXPERIMENT No. 1

THE BEER-LAMBERT LAW

(Including Vierordt's Method)

(D. T. Englis and D. A. Skoog, *Ind. Eng. Chem.* (*Anal.*), 1943 **115**, 748)

Theory

According to the Beer-Lambert law

$$A = \log \frac{I_0}{I} = \varepsilon l C, \qquad (1)$$

The optical density or absorbance, A, at a constant width of the solution, l, is proportional to the concentration C of the solute in solution; ε is the molar extinction coefficient.[1] If the incident radiation contains the wavelengths λ_1 and λ_2, then

$$A_1 = \log \left(\frac{I_0}{I}\right)_1 = \varepsilon_1 l C \quad \text{and} \quad A_2 = \log \left(\frac{I_0}{I}\right)_2 = \varepsilon_2 l C \qquad (2)$$

where I_0 and I are the intensities of the incident and emergent beams respectively at λ_1 and λ_2. The total absorbance

$$A = \log \frac{(I_0)_1 + (I_0)_2}{I_1 + I_2}$$

is different from both A_1 and A_2 except when $\varepsilon_1 = \varepsilon_2$, i.e. when the molar absorption coefficient is independent of wavelength in the given range. It has also been shown[2] that the largest possible variation in transmittancy $T (T = I/I_0)$ for a given change in concentration is produced near $T = 0{\cdot}368$ (in practice, $0{\cdot}1 < T < 0{\cdot}75$). For highly dilute solutions, however, the optimum range of absorbances is at the maximum of the absorption curve, while for highly concentrated solutions $(A > 1)$ either a standard solution of known concentration must be substituted for the blank[3] as in the differential methods, or the solution must be diluted.

[1] A. Beer, *Ann. Physik Chem.*, 1852, **86**, 78; F. Bernard, *Ann. Chim. Phys.*, 1852, **35**, 385.

[2] F. Twyman and G. F. Lothian, *Proc. phys. Soc. Lond.*, 1933, **45**, 643; A. Ringborn, *Z. anal. Chem.*, 1939, **115**, 332.

[3] G. Kortüm, *Angew. Chem.*, 1937, **50**, 193.

For solutions containing several solutes (Vierordt's method) the absorbances are additive, provided that there is no reaction between the components of the solution. Thus

$$A_{\lambda_1} = A_{1,a} \,.\, l \,.\, C_a + A_{1,b} \,.\, l \,.\, C_b$$

and

$$A_{\lambda_2} = A_{2,a} \,.\, l \,.\, C_a + A_{2,b} \,.\, l \,.\, C_b$$

where $A_{1,a}$ and $A_{1,b}$ are the optical densities of substances a and b at λ_1; those at λ_2 are $A_{2,a}$ and $A_{2,b}$; C_a and C_b are the molar concentrations of the solutions. The solution of these simultaneous equations is by the method of determinants or successive approximation. It is essential to have at one wavelength a wide variation between the absorbances of the compounds, and at the other wavelength fairly strong absorption of both substances. The wavelengths chosen must coincide with fairly flat parts of the absorption curves.

Apparatus

Spectrophotometer (ultra-violet range); 1-cm quartz cells (thermostatically controlled at 25°C); solutions of sulphanilamide and sulphathiazole in water (4 mg per litre each); mixed solution of sulphanilamide and sulphathiazole containing 3·2 (x) and 0·8 (y) mg per litre of water respectively.

Procedure

Find the absorption peaks of the pure substances at 25°C. Measure the optical densities of the solutions of the pure components and of the mixed solution at the peaks thus found. Multiply each density by 250, in order to obtain the result in grammes per litre, and set up the two simultaneous equations. Solve the equations for x and y.

Results

The absorption curves show peaks at 260 mμ for sulphanilamide and 286 mμ for sulphathiazole; the latter compound shows considerable absorption at 260 mμ as well. The optical densities found are shown in the table below.

Substance	Optical density	
	260 mμ	286 mμ
Sulphanilamide .	0·403	0·127
Sulphathiazole .	0·272	0·315
Mixture . .	0·392	0·176

Calculations

$$0{\cdot}392 = 0{\cdot}403 \times 250x + 0{\cdot}272 \times 250y$$

$$0{\cdot}176 = 0{\cdot}127 \times 250x + 0{\cdot}315 \times 250y$$

Hence $x = 0{\cdot}0033$ and $y = 0{\cdot}0009$ grammes per litre.

Comment

Although there are a large number of deviations from the Beer-Lambert law (cf. Exp. No. 51), it is possible to apply spectrophotometry in quantitative analysis with marked success, provided that necessary precautions are taken to control experimental conditions. The method can also be applied to cases in which the Beer-Lambert law is not obeyed but the absorbances are additive. The optical densities are then functions of concentrations, and the latter can be calculated by successive approximations. It is also possible to deal in certain cases with mixtures of substances for which the absorbances are not additive.[1]

While the Beer-Lambert law can be used for accurate analysis of solutions containing one or two solutes, considerable errors result with solutions of three or more solutes. Theoretically, sets of n simultaneous equations at n wavelengths for n solutes would give their concentrations. The accuracy is, however, poor, especially in the narrow visible range where there is considerable interference. On the other hand, it is possible to determine simultaneously six compounds in the much wider infra-red region.[2]

Other applications of Beer-Lambert's law include photometric titrations[3] of various types, determination of equilibrium constants,[4] methods of continuous variation,[5] and determination of degree of oxidation.[6]

[1] M. G. Mellon, *Analytical Absorption Spectroscopy* (New York, Wiley, 1950).
[2] C. F. Hiskey and D. Firestone, *Analyt. Chem.*, 1952, **24**, 342.
[3] R. F. Goddu and D. N. Hume, *Analyt. Chem.*, 1954, **26**, 1740.
[4] J. M. F. Fortuin *et al.*, *Analyt. chim. acta*, 1954, **10**, 356.
[5] P. Job, *Ann. Chim.*, 1928, **9**, 113; G. Charlot and R. Gauguin, *Les Méthodes d'Analyse des Réactions en Solution* (Paris, Masson, 1951).
[6] J. C. Hindman *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 687.

EXPERIMENT No. 2

CHRONOPOTENTIOMETRIC ANALYSIS

(P. Delahay and G. Mamantov, *Analyt. Chem.*, 1955, **27**, 478; L. Gierst and A. Juliard, *J. phys. Chem.*, 1953, **57**, 701)

Theory

In chronopotentiometry the potential of a polarizable electrode is measured during constant-current electrolysis of a depolarizer in an unstirred solution containing a supporting electrolyte. It is assumed that during electrolysis the availability of the depolarizer at the electrode surface is limited only by semi-infinite linear diffusion from a uniform bulk solution to the electrode surface. There is a rapid change in potential at the electrode when the concentration of the depolarizer there approaches zero, and the duration of the electrolysis required to produce this effect is known as the "transition time" τ and is given by

$$\tau^{\frac{1}{2}} = \frac{nFA\pi^{\frac{1}{2}}D^{\frac{1}{2}}C}{2i} \quad . \quad . \quad . \quad (3)$$

where C is the concentration (moles/ml) of the depolarizer having a diffusion coefficient D (sq cm-sec^{-1}), A is the area of the electrode (sq cm), and i (amp) is the current intensity; F is the faraday and n is the number of equivalents involved in the process. For a mixture of two depolarizers, of concentrations C_1 and C_2, undergoing reaction at different potentials, the transition times of each being τ_1 and τ_2, the relation is

$$(\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}} = \frac{n_2F\pi^{\frac{1}{2}}D_2C_2}{2i} \quad . \quad . \quad (4)$$

The above method has been applied to multicomponent systems in aqueous solutions[1] and fused salt solutions.[2]

In general, the method consists in allowing a solution of an electro-active compound or compounds to come to a complete state of rest, and then suddenly applying a constant current across an electrode-surface interface; the resulting transient potential variation occurring at the interface is followed as a function of time. Under conditions of linear diffusion of the

[1] R. C. Turner and C. A. Winkler, *J. electrochem. Soc.*, 1952, **99**, 78; C. N. Reilley *et al.*, *Analyt. Chem.*, 1955, **27**, 483; C. N. Reilley and W. G. Scribner, ibid., 1955, **27**, 1210.

[2] H. A. Laitinen and W. S. Ferguson, ibid., 1957, **29**, 4.

active species to the surface the interface potential progresses rapidly, on the application of a current, to the decomposition potential of the species present. After a certain interval of time (τ) the concentration of that species at the interface is reduced to an extremely small value, and the potential then rises rapidly to the decomposition potential of some other species present or that of the solvent. It follows that if chronopotentiograms for a species are taken at a given current density during a titration, then the plot of $\tau^{\frac{1}{2}}$ versus volume of titrant will yield two straight lines whose intersection gives the end-point.

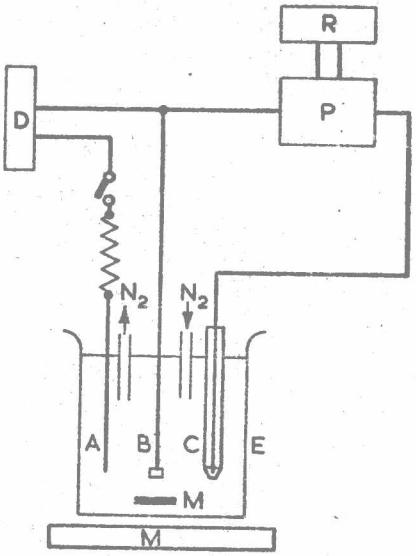

FIG. 1. SCHEMATIC DIAGRAM OF THE CIRCUIT FOR CHRONOPOTENTIOMETRIC ANALYSIS

A, platinum wire electrode; B, platinum foil (2 sq cm); C, saturated calomel electrode; D, constant current supply (10 μA to 1000 μA) *see* Fig. 2; E, cell on rubber mountings on a solid stand; M, magnetic stirrer; P, direct-reading millivolt-metre of high input resistance; R, potentiometric recorder, full-scale scanning speed of 5 sec.

Apparatus

A schematic circuit of the apparatus is shown in Fig. 1, and details of the constant-current supply in Fig. 2. Also required are an accurate stopwatch or electrical timer; 0·1N solutions of copper sulphate, disodium ethylenediamine-tetraacetic acid (magnesium-free), ferrous ammonium sulphate, ceric ammonium sulphate, potassium sulphate, and sulphuric acid; 2×10^{-4}N solution of (each) zinc, lead and cadmium ions in 0·1N potassium nitrate; 2×10^{-4}N solution of (each) lead and cadmium in 0·1N potassium nitrate; nitrogen supply.

Procedure

(*a*) Dilute 5 ml of the copper sulphate solution to 100 ml with the 0·1N potassium sulphate solution and place the solution in the cell. Pass nitrogen through the solution for 10 minutes. Use as an electrode (B in Fig. 1) a platinum foil of

2 sq cm plated with mercury (the plating is done by first depositing a thin film of copper on a freshly cleaned platinum foil at 50 μA for a few seconds and then immersing in mercury). Select a current of 500 μA. Disconnect the nitrogen supply, start the magnetic stirrer and add 4 ml of the disodium ethylenediamine-tetraacetic acid titrant; stop the stirrer, and after 5 minutes rest connect the current and observe the transition time at —0·2 volt with respect to the saturated calomel

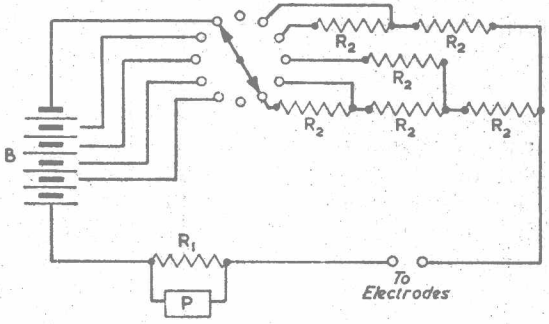

FIG. 2. CONSTANT-CURRENT SUPPLY
B, six 45-volt dry batteries in series with tap for 90–225 volts; P, potentiometer; R_1, standard resistance box; R_2, series of fixed resistances to give currents from 10 to 1,000 μA.

electrode. Repeat this operation and take the mean of the two readings.

Add a further 0·2, 0·4, 0·6, and 0·8 ml of the titrant and repeat the above procedure after each addition. Plot the square root of the transition times (τ) thus obtained against volume of titrant added (V) and extrapolate to zero time. The intercept on the V-axis at $\tau^{\frac{1}{2}} = 0$ gives the end-point in terms of the titrant added. Repeat above at 10 μA.

(*b*) Dilute 25 ml of the ferrous solution with 0·1N sulphuric acid to 200 ml. Repeat procedure (*a*) using the ceric solution as a titrant and a 2 sq cm platinum foil as the anode (current 150 μA or 50 μA). Add 24 ml of the ceric solution and then 0·2 ml at a time. Plot the curve of $\tau^{\frac{1}{2}}$ versus volume of titrant (voltage —0·9 to —0·5 versus the saturated calomel electrode).

(*c*) Measure the transition times (current of 50 μA) at various potentials with respect to the saturated calomel electrode (—0·2 to —1·2 volt) for the solution of zinc, cadmium and lead ions in potassium nitrate solution. Plot τ against potential and note the three breaks in the curve. Repeat with the solution containing lead and cadmium in the presence of potassium nitrate.

Results

(*a*)

Volume of titrant (ml) .		4·0	4·2	4·4	4·6	4·8
τ (sec)	10 μA . .	134·6	86·5	49·0	21·2	4·8
	500 μA . .	20·3	13·0	7·3	3·3	0·8

Plot the values of $\sqrt{\tau}$ against volume of titrant (Fig. 3).

(*b*)

Volume of titrant (ml) .		24·0	24·2	24·4	24·6	24·8
τ (sec)	50 μA . .	25	16	9	4	1
	150 μA . .	5·8	3·3	2·0	1	0·4

Plot the values of $\sqrt{\tau}$ against volume of titrant added (Fig. 4).

(*c*)

Potential (volts) . .		−0·3	−0·34	−0·4	−0·5	−0·56	−0·59	−0·64	−0·68	−0·8	−0·98	−1·02	−1·1	−1·2	−1·3	−1·38
τ (sec)	$Zn^{2+}+Cd^{2+}+Pb^{2+}$	0	8·2	12·0	14·0	14·2	18·3	36·2	40·1	40·0	40·1	48·2	68·1	80·0	84·2	84·2
	$Zn^{2+}+Cd^{2+}$	0	8·0	12·2	14·0	14·0	18·1	36·0	39·8	40·0	40·0	40·1	40·2	40·0	40·0	40·1

Plot the values of τ (sec) against the potentials used (Fig. 5).

Conclusions

Figs. 3 and 4 show that accurate end-points can be obtained in complexiметric and redox titrations, while multicomponent mixtures of metallic ions in aqueous solutions can be resolved by chronopotentiometry (Fig. 5).

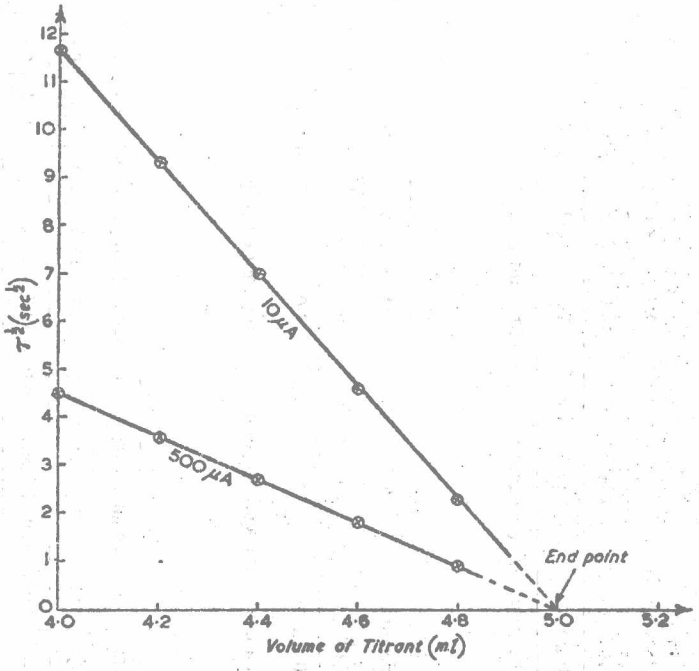

FIG. 3. TITRATION OF COPPER SULPHATE WITH DISODIUM ETHYLENEDIAMINE-TETRAACETIC ACID

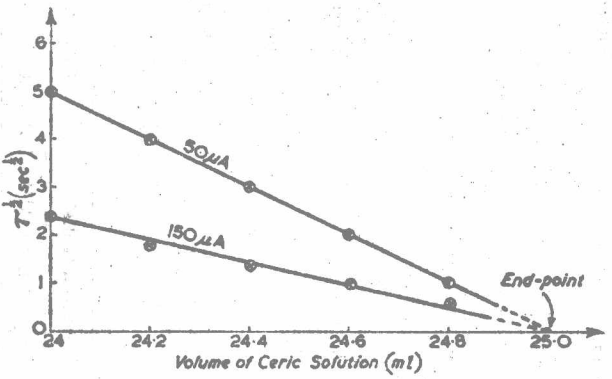

FIG. 4. TITRATION OF FERROUS IRON WITH CERIC CERIUM

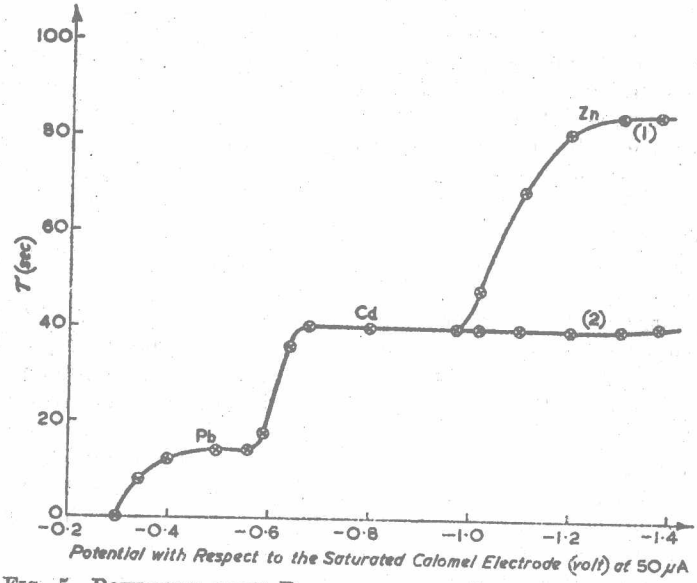

FIG. 5. POTENTIAL WITH RESPECT TO THE SATURATED CALOMEL ELECTRODE (VOLTS) AT 50 μA

(1) 2×10^{-4}N solution of Zn^{2+}, Cd^{2+}, and Pb^{2+};
(2) 2×10^{-4}N solution of Cd^{2+} and Pb^{2+}.

Comment

The accuracy of the chronopotentiometric method of analysis is, of course, dependent on that of determining the end-points; the latter are related to the slopes of the titration curves, while the sensitivity depends very markedly on the steepness of the slope. The slope, in its turn, is nearly proportional to $\sqrt{\tau}$ for a given variation in the concentrations of the analytical species, viz.

$$\text{Slope} = \frac{d\sqrt{\tau}}{dC} = \frac{nF\pi^{\frac{1}{2}}AD^{\frac{1}{2}}}{2iV}$$

where V is the volume of the solution containing C m equiv. of the species; the other terms have the same significance as those of equation (3). Since for a given species D, F, and n are constants, then the experimentally variable factor (f) controlling the sensitivity is

$$f = \frac{A}{iV}$$

i.e. greater sensitivity is obtained by having a large electrode area, small volume of solution and small current intensity. On the other hand, an excessively large area may bring about a

considerable depletion of the ions at the interface owing to extensive electrolysis; low results will thus be obtained. Furthermore, high currents will lead to excessively long transition times, which lead to variations of the density of the solution across the diffusion layer and thus to convection. Under such conditions the transfer of the active species to the interface is controlled by both thermal diffusion and convection, and equation (3) is not obeyed. It is advisable, in general, to select first the optimal electrode area and volume and then find a current to yield satisfactory sensitivity.

Another point of importance is the relation between potentiometric and chronopotentiometric titrations. The initial voltage (zero time) of the chronopotentiogram (plot of τ against potential) corresponds to the potentiometric voltage. By observing the change in voltage during titration it is possible to predict the points at which chronopotentiometric titrations should be carried out. The actual selection of voltage at which the transition times are measured depends upon the shape of the chronopotentiograms. It is desirable to carry out the experiment in the region where the curve is fairly flat and horizontal.

The advantages of this method over other electrochemical analytical procedures are good precision, high sensitivity (down to 10^{-6}M), no fluctuations in the measured quantity, and the use of solid platinum or liquid mercury electrodes. Chronopotentiometry is also useful in electrochemical kinetics.[1] Another recent application[2] is in the realm of studies of the behaviour of the solvent during the electrolysis of a solution of sodium perchlorate in acetic anhydride–acetic acid solvent mixture. In general, the method partakes of the advantages of amperometry and can be applied to any titration system involving an electroactive species. In fact, the reactant, titrant and product of reaction do not need to undergo a reversible electrode reaction, so long as diffusion of the titrated species is the controlling factor of transition time. It must also be noted that the method has several disadvantages. No steady reading is actually observed; there is larger consumption of mercury (if a mercury electrode is used) than in polarography; titrations in the negative potential region must be performed in the absence of oxygen, with intervals between the additions of the titrant; the electrode surfaces have to be renewed before each run in precipitation titrations.

[1] P. Delahay and T. Berzins, *J. Amer. chem. Soc.*, 1953, **75**, 2486; P. Delahay and C. C. Mattax, ibid., 1954, **76**, 874.
[2] W. B. Mather and F. C. Anson, *Analyt. Chem.*, 1961, **33**, 1634.

EXPERIMENT No. 3

"DEAD-STOP" END-POINT TITRATIONS (AMPEROMETRIC)

(K. G. Stone and H. G. Scholten, *Analyt. Chem.*, 1952, 24, 671; C. W. Foulk and A. T. Bowden, *J. Amer. chem. Soc.*, 1926, 48, 2045)

Theory

In this method a voltage of small amplitude is applied to two stationary polarized platinum electrodes in a stirred solution, and the current measured during titration. From the analysis of curves of current *v.* potential at various stages of titration, it is found that, for a given voltage, the current shows a maximum and decreases as the equivalence point is approached,[1] the maximum occurring at the midpoint of the titration. The current beyond the end-point is nearly zero, provided a reversible couple (iodine-iodide) is titrated with an irreversible one (tetrathionate-thiosulphate), as in the analysis of iodine by thiosulphate. In the opposite case, i.e. titration of an irreversible by a reversible couple, the current is nearly zero before the end-point and increases rapidly beyond this point. In a titration involving two reversible couples the equivalence point is indicated by a sharp minimum.[2]

Apparatus

The circuit is shown in Fig. 6. Also required are solutions of 0·1N sodium thiosulphate and iodine; starch indicator solution; 0·1N sulphuric acid; 0·1N sodium hydroxide; 3 per cent alcoholic iodine.

Procedure

Pipette 10 ml of the thiosulphate solution into a 250 ml beaker and stir the solution. Close key K (zero current on G). Titrate the solution with 0·1N iodine. As soon as the galvanometer spot shows signs of moving titrate much more slowly. Note the first *permanent* deflexion of the spot. Do a duplicate and then carry out a conventional titration using starch as an indicator. Dilute both solutions a hundred-fold and repeat the titrations.

[1] P. Delahay, *Instrumental Analysis*, p. 113 (New York, Macmillan, 1957).
[2] H. A. Laitinen, *Analyt. Chem.*, 1952, 24, 46; ibid., 1956, 28, 666.

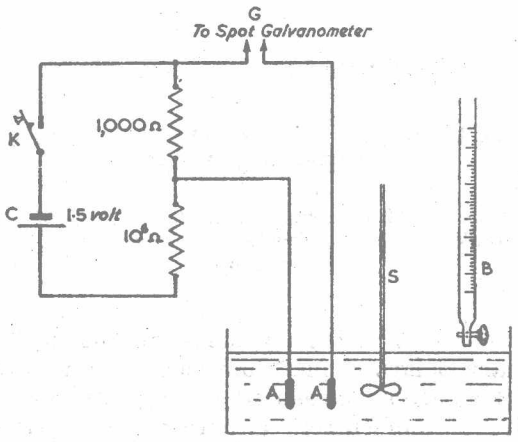

FIG. 6. "DEAD-STOP" END-POINT APPARATUS
A, bright platinum electrodes; B, burette; C, accumulator (1·5 volt); K, key; S, stirrer.

Carry out similar titrations of the sulphuric acid solution by means of the standard sodium hydroxide solution in the presence of 1 drop of the alcoholic iodine solution. Compare this with the volumetric titration, in the presence of phenolphthalein indicator.

Results

	Ml of iodine solution added to thiosulphate		Ml of sodium hydroxide added to sulphuric acid
Dead-stop end-point titration	0·1N	10·05	10·00
		10·00	
	0·001N	10·1	10·10
		10·1	
Volumetric titration	10·00 (Starch)		10·00 (Phenolphthalein)
	10·00 (Starch)		10·00 (Phenolphthalein)

Conclusions

It is seen from the above results that the accuracy of data obtained by the "dead-stop" end-point method is similar to that obtained by volumetric titrations.

Comment

In the iodine-thiosulphate titrations, when no free iodine is present, the platinum cathode is polarized and hence practically no current flows through the galvanometer G. As soon as free iodine appears, this cathode is depolarized and a large permanent deflexion is registered on G.

In the acid-alkali titrations the iodine acts as an electrometric indicator keeping the cathode depolarized. At the end, when there is a slight excess of alkali, the anode depolarizes, owing to the formation of iodine ions. Of course, the addition of the titrant in this and other titrations can be stopped automatically at the equivalence point by substituting a sensitive relay for G, and a magnetic valve for the stopcock of the burette.[1]

The "dead-stop" end-point method is advantageous in the cases involving non-aqueous media, since no reference electrode is needed,[2] as in the Karl Fischer titration of water. The method is superior to potentiometric techniques when electrode potentials are only slowly established at zero current, since in amperometry the potentials acquire very quickly a steady value. A large number of titrations have been carried out by means of the "dead-stop" end-point method, e.g. ceric, permanganate, bromometric, titanometric, and other titrations. An instructive experiment is that involving the determination of gallium-(III) by means of ferrocyanide at pH = 2 and 50°C.[3] For comparison of various electro-analytical methods, *see* Kolthoff.[4]

It must be noted, however, that in all acid-base titrations in aqueous solutions there exists a discrepancy between the end-point and equivalence-point.[5] Thus, for the system strong acid-strong base the percentage difference ($E_{\%}$) is given by the relation

$$E_{\%} = 100(M_A + M_B)K_w/M_A M_B(\mathrm{H_{eq.}}^+)$$

where M_A and M_B are the concentrations of the acid and the base solution, respectively; K_w is the ionic product for water, and $(\mathrm{H_{eq.}}^+)$ is the hydrogen-ion concentration at the end-point of the titration. For a weak acid-strong base system, the

[1] H. A. Frediani, *Analyt. Chem.*, 1952, **24**, 1126.
[2] J. Mitchell and D. M. Smith, *Aquametry*, p. 86 (New York, Interscience, 1948).
[3] N. R. Fetter and D. F. Swinehart, *Analyt. Chem.*, 1956, **28**, 122.
[4] I. M. Kolthoff, *Analyt. Chem.*, 1954, **26**, 1685.
[5] E. Bishop, *Analyt. chim. acta*, 1960, **22**, 205.

relevant relation is

$$E_{\%} = 100(\mathrm{H_{eq.}}^{+})/K_a$$

where K_a is the ionization constant of the acid. Finally, for the strong acid-weak base system, the percentage difference is given by

$$E_{\%} = 100K_w/(\mathrm{H_{eq.}}^{+}) \cdot K_b$$

where K_b is the ionization constant of the base.

EXPERIMENT No. 4

DIFFERENTIAL CONDUCTIMETRIC TITRATION OF VERY WEAK BASES IN AQUEOUS SOLUTION

(F. Gaslini and L. Z. Nahum, *Analyt. Chem.*, 1960, **32**, 1027)

Theory

If a very weak base is titrated with a strong acid in an aqueous solution containing a weak acid, the conductance of the solution changes owing to replacement of the anion of the weak acid by that of the strong acid, the former combining with the hydrogen ions of the titrant. After the equivalence point the conductance rises very sharply owing to the rapid increase of the hydrogen ion concentration from the titrant. The point of intersection between these curves gives the end-point of the titration. Generally, in a weakly acidic solvent the dissociation of a weak base is greatly increased so that hydrolysis is reduced, especially in aqueous ethanol. This leads to a more accurate evaluation of end-points of titrations.

Apparatus

H.F. conductance bridge (ca. 2,500 c/s); conductance cell (constant 1·3–1·6); 50:50 aqueous ethanol containing 0·75 moles of acetic acid per litre; 0·985M trichloroacetic acid; solutions, each 0·07M, of *p*-toluidine, glycine, *p*-phenylenediamine and a mixture of *p*-toluidine (0·035M) and glycine (0·035M) in the above solvent; thermostatic bath at 25°C; burette (±0·01 ml).

Procedure

Place all the solutions in the bath for 30 minutes. Titrate 50 ml of each solution with the trichloroacetic acid noting the conductance of the solution after each addition of the titrant.

Results

TABLE OF CONDUCTANCES (MHOS × 10^4) DURING TITRATION

Ml of titrant	0	1	2	3	4	5	7	8	10	12	14
p-Toluidine	6·7	6·8	7·1	7·2	12·0	20·0	37·0	45·0	63·0	79·0	97·0
Glycine	1·78	4·0	6·0	9·0	14·0	22·0	39·0	47·0	64·0	81·0	97·0
p-Phenylene-diamine	8	8	8·2	8·2	8·2	8·2	8·2	14·0	27·0	40·0	53·0