In our first experiments a Pirani gage for determination of gas composition by measurement of thermal conduction has been substituted for the water reservoir in an apparatus otherwise similar to that of the previous work. The procedure was then to fill the system to (total) pressures between 2 and 4 cm. with hydrogen and water vapor in about equimolal proportions. After standing until the gases were thoroughly mixed, their composition was determined by the gage. The (empty) equilibrium tube was then heated to about 800° and the temperature held constant for periods of about an hour, the total pressure and gage readings being taken at short intervals. When corrected for the pressure change the readings showed an increase of 10–20% in the mole fraction of water vapor of the gas in the gage. This increase was completed in the few minutes required to secure constancy in temperature of the furnace.

To make sure that the excess water vapor did not result from desorption from the walls of the tube on heating, a second series of experiments has been made. In these, a horizontally placed tube, 2.5 cm. in diameter and 30 cm. long, one end of which was heated to 800° over a distance of 15 cm., was employed. The apparatus was filled while the tube was hot to some 15–20 mm. of water vapor, and hydrogen added until a pressure about double the original was reached. Stopcocks in capillaries leading from the hot end and the cold end of the tube to the thermal conductivity gage were then closed, and the gage and connecting manometer evacuated. Samples of gas from the tube were then introduced into the gage–manometer system, being taken alternately from the hot and cold ends, with evacuation of the gage between samples. The thermal conductivity of the samples showed an accumulation of water vapor in the cold end of the tube, approximately equivalent to that in the experiments first described. Here again the time of establishment of the composition difference was less than that required in the preliminary manipulation.

We agree therefore with the conclusions of Emmett and Shultz. We also agree that thermal diffusion may affect not only the Deville and other static measurements but may be important also in dynamic methods at low rates of flow, as it apparently was in the experiments of Eastman and Robinson[3] in the tin system, and of Chipman and

(3) Eastman and Robinson, THIS JOURNAL, **50**, 1106 (1928).

Fontana[4] with liquid iron. Presumably it would also affect measurements in which a heated filament is employed, such as Langmuir's[5] on the dissociation of water vapor. Unpublished experiments of Sermattei[6] lend some support to this last idea. Sermattei undertook to measure the water gas constant by observing pressure changes produced in various mixtures of the reacting gases, in which the partial pressure of water vapor was fixed by a reservoir of liquid water as in the Deville method, when a platinum wire in the gas phase was glowed at constant temperatures (known from its resistance) between 800 and 1200°. Near 800° the results were in good agreement with the indirect results, but at the higher temperatures tended toward the direct values. We interpret this as due to a differential thermal diffusion, the effect of which was offset to an increasing degree with increasing temperature of the filament by some other factor, perhaps increased convection of the gases.

A few points concerning the probable variation of the effect in systems of different types are perhaps worth noting. Since relative molecular weight largely determines the magnitude of the effect, it will be particularly important in mixtures containing hydrogen but not large in many others. The evidence from the indirect calculations of the water-gas constant, for example, is that carbon monoxide–carbon dioxide mixtures in horizontal tubes and at pressures of the order of an atmosphere are little influenced by it. At low pressures, or in vertical tubes, where the full equilibrium effect may be established, any system in which substances differing significantly in molecular weight are involved may show a considerable effect.

(4) Chipman and Fontana, *ibid.*, **56**, 2011 (1934).
(5) Langmuir, *ibid.*, **28**, 1357 (1906).
(6) Sermattei, Thesis, University of California, 1929.

Theory of the Error of Acid–Base Titration[1]

BY PAUL S. ROLLER[2]

In this note the titer error and electrometric titer deviation in titrating with a weak base is

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(2) Associate Chemist, U. S. Bureau of Mines, Nonmetallic Minerals Experiment Station, Rutgers University, New Brunswick, N. J.

considered in detail, and correction made for this special case in the general formulations previously given.[3] Since weak acid salts occurring in the titrating solution enter into the formulations in the same way as a weak base, the present considerations apply also to such salts.

Acid–base titrations previously were divided into two classes, symmetrical and unsymmetrical.[3] For the symmetrical case (titration of all H but the last of a polybasic acid, titration of the first of two weak acids of equal concentration, by a strong base, etc.), the inflection point always appears and agrees exactly with the stoichiometric or equivalence point; this conclusion has again been verified in connection with this work. For the unsymmetrical case (titration of a weak acid, or of the last H of a polybasic acid, by a strong base, etc.), the inflection point may not appear, and in general does not coincide with the stoichiometric point.

It appeared characteristic of the symmetrical titration that the concentration does not enter into the equation for $p\mathrm{H_S}$, the $p\mathrm{H}$ at the stoichiometric point. In titrating with a weak base, $p\mathrm{H_S}$ is independent of concentration. It would appear, therefore, that titration with a weak base would also be symmetrical. However, detailed examination shows that this is not so. This is in agreement with Eastman's previous conclusions[4] to the effect that in titrating with a weak base the inflection point may not appear, and that it does not agree in general with the stoichiometric point. The previous criticism[3] of these conclusions is therefore withdrawn. It appears also that for the special case treated by Eastman of titration of a monobasic weak acid by a weak or a strong base the results of the latter as now given[5] and those of the present author are in practical numerical agreement.

The reason that titration with a weak base is not, as might be expected, symmetrical, lies in the fact that in addition to considering the strength of the base, one must consider also the quantity of reagent added. This is seen by comparing on the one hand the equation for titration of two weak acids by a strong base (symmetrical), and on the other hand the equation for titration of one weak acid by a weak base (unsymmetrical). The same nomenclature is used as before.

(3) Roller, This Journal, **54**, 3485 (1932).
(4) Eastman, *ibid.*, **47**, 332 (1925).
(5) Eastman, *ibid.*, **56**, 2646 (1934).

$$C_{\mathrm{OH'}}\frac{N}{V} = C_{\mathrm{HA_1}}^0 - \frac{V+N}{V}\left(H - \frac{K_w}{H}\right) -$$
$$\frac{C_{\mathrm{HA_1}}^0 H}{K_{A_1}+H} + C_{\mathrm{HA_2}}^0\frac{K_{A_2}}{K_{A_2}+H} \quad (1)$$

$$C_{\mathrm{BOH'}}\frac{N}{V} = C_{\mathrm{HA_1}}^0 - \frac{V+N}{V}\left(H - \frac{K_w}{H}\right) -$$
$$\frac{C_{\mathrm{HA_1}}^0 H}{K_{A_1}+H} + C_{\mathrm{BOH'}}\frac{N}{V}\frac{K_w/K_B}{K_w/K_B+H} \quad (2)$$

Equation (2) for titration of a weak acid by a weak base contains a coefficient $C_{\mathrm{BOH'}}$ (N/V) on the right-hand side which is absent in equation (1) for two weak acids titrated by a strong base. This titer coefficient cancels out in the expression for $p\mathrm{H_S}$. However, it does not cancel out in the expression for the titer error and titer deviation obtained by differentiation of the original titration equation, and so leads to an unsymmetrical result.

The new result for the special case of titration by a weak base, or of weak acid salts present in the titrating solution, is sufficiently described by making the following changes in the expressions previously derived.[3] If f_A is a factor equal to

$$1 - (K_w/K_B) + \ldots + K_A + \ldots + 0/\sqrt{\sigma_A}$$

in which K_B and K_A in the numerator refer to the titrating solution only, multiply equation (2) for κ_A by $1/f_A$. In equations 8, 9 and 10 omit in the parentheses terms referring to K_B'' for a weak base and to K_A'' for a weak acid salt in the titrating solution, just as K_w is already omitted. It appears also that equation (10) for the titer deviation between the stoichiometric and inflection points is to be multiplied by $(1/f_A)$,[3] and therefore equation (9) for the deviation in $p\mathrm{H}$ is to be multiplied by $(1/f_A)$.[2] With $f_B = 1 - ((K_w / K_A)\ldots + K_B + \ldots + 0)/\sqrt{\sigma_B}$, analogous corrections are to be made to equations (2'), (8'), (9') and (10') for titration by a weak acid. The expressions modified as above for titration by a weak base or a weak acid have been checked by numerical calculation, plotting as before $dp\mathrm{H}/dN/N_S$ against $(N/N_S) - 1$.

In titrating with a weak base as in titrating with a strong base, the inflection point is found to precede the stoichiometric point. With κ_A less than about 10^{-3}, the titer error and titer deviation are practically the same for both titrations. This is to be expected since f_A^3 generally is close to unity with κ_A less than 10^{-3}. For $\kappa_A = 10^{-3}$, the titer deviation is 0.30% for a strong base, and 0.33% for a weak base, and with $\kappa_A = 10^{-2}$, it is 3.0% (3.6% by exact numeral plot) for the

strong base, and 4.1% (4.6% by plot) for the weak base.

Just as the titer deviation in titration by a weak base exceeds that by a strong base, although κ_A is the same, so the titer error (of locating the end-point) is also in slight excess for the same value of κ_A and in proportion to the magnitude of $1/f_A$.

It is found by plot that for titration by a weak base the inflection point still appears if $\kappa_A = 10^{-1.5}$. The titer deviation is from the plot 20%. With κ_A decreased however to $10^{-1.4}$, the inflection point does not seem to appear. Thus the condition of the appearance of an inflection point for titration by a weak base is equal to or nearly so to that for titration by a strong base for which the condition is $\kappa_A < 10^{-1.42}$.[3]

Since the titer error and titer deviation are greater than when titrating with a strong base, theory requires that titration by a weak base be at all times avoided; likewise weak acid salts should be excluded from the titrating solution.

In connection with the general formulation for the titer error (equation (1) of reference 3) it may be remarked that for Δ small, sinh Δ may be taken equal to Δ. For all practical purposes, since the pH or m. v. error of titration is ordinarily small, equation (1) may therefore be simplified to

$$E = \pm 200 \sqrt{\kappa}\, \Delta \qquad (1a)$$

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The Limiting Effect of the Debye Equation on Polarization Concentration Curves

By W. D. Kumler

The polarization P_2 of most liquids possessing a permanent moment varies with the concentration c_2 when measured in a liquid with zero moment. The explanation given for this variation of P_2 with c_2 has been molecular association [Debye, "Handbuch der Radiologie," (Marx) Leipzig, 1925, p. 636; Höjendahl, Thesis, Copenhagen, 1928; Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., N. Y., 1931, p. 188; Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 170].

There is another factor affecting this variation. The mathematical nature of the Debye equation puts a limiting value on P_2 which without any recourse to association at all will account for most of the decrease in the value of P_2 at high concentrations. This limiting effect of the Debye equation has been observed in other connections by Wyman and by v. Arkel and Snoek [Wyman, This Journal, **56**, 536 (1934); v. Arkel and Snoek, Trans. Faraday Soc., **160**, 707 (1934)].

For nitrobenzene the value of P_2 goes from 330 cc. at infinite dilution to 90 cc. at pure nitrobenzene. Even if the dielectric constant of nitrobenzene were infinite the largest value the polarization could have for the pure substance as calculated by the equation is

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = 1 \times \frac{123}{1.2} = 102 \text{ cc.}$$

Thus the value of P_2 would have to decrease to less than 102 due to the limitation of the equation without any effect due to association. Even with a substance with as small a moment as ethyl alcohol 1.7 the limitation of the equation is affecting the polarization in the region of high concentration. The limiting value for the pure liquid is less than 58 cc.

$$P_2 = \frac{\epsilon - 1}{\epsilon + 1} \frac{M}{d} = 1 \times \frac{46}{0.79} = 58 \text{ cc.}$$

and the value of the polarization at mole fraction 0.5 is about 90 cc. Hence the downward slope of this curve at high concentrations is necessitated by the limitations of the equation.

With diethyl ether (moment 1.12) the value of $M/d(104)$ is sufficiently high in comparison with the value of $P_2(54)$ so that no such effect is introduced by the equation when the polarization is calculated for the pure substance. Its P_2, c_2 curve, as is well known, is a straight horizontal line.

Molecular association probably has some effect on polarization but it is apparent that no conclusions can be drawn from polarization concentration curves in regard to association unless the limiting factor due to the nature of the Debye equation itself is first excluded.

Department of Chemistry
University of California
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