calculated to the formation of ammonium azide, as was done in the present work, the quantum yield becomes 3.7 ± 0.5, which is to be compared with the experimental value of 3.6 for the photosensitized decomposition.

One is led to the conclusion that the mechanism of the mercury photosensitized decomposition is probably identical with that of the photochemical decomposition. One may write, therefore, as a possible mechanism[5]

$$\begin{array}{rcll} h\nu + \mathrm{Hg} & = & \mathrm{Hg}^* & (1) \\ \mathrm{Hg}^* + \mathrm{HN_3} & = & \mathrm{Hg} + \mathrm{N_2} + \mathrm{HN} & (2) \\ \mathrm{HN} + \mathrm{HN_3} & = & \mathrm{H_2} + 2\mathrm{N_2} & (3) \\ \mathrm{HN} + \mathrm{HN_3} & = & \mathrm{N_2} + \mathrm{N_2H_2} & (4) \\ \mathrm{N_2H_2} + \mathrm{HN_3} & = & \mathrm{N_2} + \mathrm{NH_3} & (5) \\ \mathrm{NH_3} + \mathrm{HN_3} & = & \mathrm{NH_4N_3}\ \text{(solid)} & (6) \end{array}$$

with 18% of the hydrogen azide molecules reacting according to equations (2) and (3) and 82% according to equations (2), (4), (5) and (6).

Summary

The mercury photosensitized decomposition of gaseous hydrogen azide by monochromatic radiation of wave length 2537 Å. has been investigated over the pressure range 0.3 to 20 mm. The final products of the decomposition were found to be ammonia and nitrogen with ammonium azide and hydrogen as intermediate products during the earlier stages of the decomposition. The quantum yield for the initial stage of the decomposition was found to approach the value 2.86 molecules of hydrogen azide decomposed per quantum absorbed when calculated to the formation of ammonia or 3.6 when calculated to the formation of ammonium azide. It is shown that the photosensitized decomposition closely parallels the photochemical decomposition described by previous investigators.

PASADENA, CALIF. RECEIVED NOVEMBER 13, 1934

NOTES

The Iodimetric Determination of Copper[1]

BY JOHN R. CALDWELL

It is desirable to have a general method for reducing absorption by analytical precipitates in cases where the usual expedients are impracticable. It has been found that the presence of certain protective colloids, and of some organic compounds such as nitrobenzene, exerts a profound influence upon the physical nature of analytical precipitates. When used under appropriate conditions, these agents may have a twofold function, they not only bring about rapid flocculation and settling of the precipitate, but also alter the nature of its surface so that the adsorptive capacity and further reactivity are greatly reduced. This property of protective colloids is of general application and has been employed with considerable success in several standard analytical procedures. Among these are included modifications of the Volhard chloride titration[2] and the iodimetric determination of copper. The latter will be discussed in detail.

In the iodimetric determination of copper, blue iodo-starch is carried down by precipitated cuprous iodide and renders the end-point indistinct. At least two attempts have been made to remedy this condition[3,4] but both have certain disadvantages. It was found that a solution of white shellac in alcohol would alter the nature of the surface of the precipitate and reduce adsorption of blue iodo-starch color.

Experimental.—Standard sodium thiosulfate solution was added until most of the iodine was consumed. At this point, 0.5 to 1.0 ml. of 4% alcoholic solution of white shellac was added. This solution was put in slowly from a medicine dropper while swirling the contents of the flask. The precipitate was allowed to settle for twenty to thirty seconds, and the titration completed. Instead of a dark blue solid suspended in a turbid solution, there was a heavy cream-colored precipitate which settled out in a few seconds leaving a clear, blue supernatant liquid that contained practically all of the iodo-starch color.

Results.—Samples of electrolytic copper ranging from 0.05 to 0.31 g. were titrated according to the above procedure. In a series of twelve determinations, the sum of plus and minus errors was +0.0001 g., showing that no systematic error was introduced. Two copper ores were

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(1) Presented before the division of Colloid Chemistry at the 88th meeting of the American Chemical Society, Cleveland, Ohio, September 10–14, 1934.

(2) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(3) A. H. Low, "Tech. Methods of Ore Anal.," John Wiley and Sons, 1922, 9th ed., p. 79.

(4) E. H. Smith, *Chemist Analyst* **18**, 6 (1929).

analyzed by the short ammonium fluoride method[5] and satisfactory agreement with analyses by other methods obtained.

The shellac has a two-fold function: it causes the precipitated cuprous iodide to flocculate rapidly and settle out as heavy curds, and it also deactivates the surface so that further adsorption is reduced. In the ore analyses referred to above, iron is present as a colloidal complex and may inhibit to some extent the action of the shellac, but in any case the end-point is greatly improved.

(5) Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931)

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS, OHIO
RECEIVED JULY 26, 1934

A Note on the Calculation of Heat of Reaction from Values of the Equilibrium Constant at Two Temperatures

BY T. B. DOUGLAS AND H. D. CROCKFORD

The relation of the mass action constant to temperature is given by the equation

$$d \ln K = \Delta H \, dT/RT^2 \qquad (1)$$

If ΔH is a linear function of the temperature according to the equation

$$\Delta H = a + bT \qquad (2)$$

elimination of ΔH from (1) and integration lead to the equations

$$R \ln (K_2/K_1) = a[(1/T_1) - (1/T_2)] + b \ln (T_2/T_1) \qquad (3)$$

$$\frac{RT_1T_2 \ln (K_1/K_2)}{T_2 - T_1} = a + b \frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (4)$$

If now a temperature T_0 is defined by the equation

$$T_0 = \frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (5)$$

the right-hand member of (4) is ΔH_0, the value of ΔH for the temperature T_0. The resulting equation

$$\Delta H_0 = RT_1T_2 \ln (K_1/K_2)/(T_2 - T_1) \qquad (6)$$

is the same as is usually obtained from (1) by the use of the assumption that ΔH is independent of the temperature.

We have shown therefore that, when ΔH is a linear function of the temperature, (6) can still be used to calculate ΔH from two values of K and the two corresponding temperatures. The calculation does not require knowledge of the constants a and b and the ΔH thus calculated is for one particular temperature T_0, which is calculated by (5) without knowledge of a or b.

The authors recently published a paper[1] on the ionization constants of certain sulfur derivatives of phenylacetic acid at 0 and 25°. ΔH was calculated by equation (6) for these two temperatures. More exactly the ΔH values obtained are not average but are specifically for 12.1° as determined by substituting 0 and 25° in (5).

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[1] Crockford and Douglas, THIS JOURNAL, **56**, 1472 (1934).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.
RECEIVED AUGUST 21, 1934

Influence of Thermal Diffusion in Certain Equilibrium Measurements

BY E. D. EASTMAN AND SAMUEL RUBEN

Emmett and Shultz[1] find the Deville method of equilibrium measurement to be subject to large errors attributable to thermal diffusion in the gas phase. They account in this way for discrepancies of long standing in various metal–metal oxide reduction equilibria involving hydrogen and water vapor, and between direct and indirect values of the water gas equilibrium.

This factor was considered by Eastman and Evans[2] in their work by the Deville method in the iron–oxygen–hydrogen system. There were, however, several considerations which led them to believe it might be disregarded. Thus, the tube in which the temperature gradient occurred was of large diameter and was placed horizontally in the hope of securing rapid convection. The speed of attainment of equilibrium was taken as an indication that mixing in the gas phase was in fact rapid, and that in consequence no sort of Soret equilibrium was likely to be important. Moreover, it was believed that had a Soret effect been present, especially if only partially established and varying in completeness with the temperature, it would have been manifested in the plots of log K *vs.* $1/T$ as a divergence from linearity. In the Fe–FeO systems first investigated no such divergence was present. In the later experiments with FeO–Fe_3O_4 mixtures (at higher total pressures) there was some divergence which we now think might be ascribed to differing thermal diffusion effects in different parts of the temperature and pressure ranges. In view of these facts it has seemed desirable to look for Soret effects in blank experiments with apparatus duplicating the essential features of that employed by Eastman and Evans.

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[1] Emmett and Shultz, THIS JOURNAL, **55**, 1376 (1933).

[2] Eastman and Evans, *ibid.*, **46**, 888 (1924).

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 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.

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

[4] Chipman and Fontana, *ibid.*, 56, 2011 (1934).

[5] Langmuir, *ibid.*, 28, 1357 (1906).

[6] Sermattei, Thesis, University of California, 1929.

CHEMICAL LABORATORY
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RECEIVED OCTOBER 15, 1934

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

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[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 pH 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.

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

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

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

$$1 - (K_\mathrm{w}/K_\mathrm{B}) + \ldots + K_\mathrm{A} + \ldots + 0/\sqrt{\sigma_\mathrm{A}}$$

in which K_B and K_A in the numerator refer to the titrating solution only, multiply equation (2) for κ_A by $1/f_\mathrm{A}$. 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 $(1/f_\mathrm{A})$,[3] and therefore equation (9) for the deviation in pH is to be multiplied by $(1/f_\mathrm{A})$.[2] With $f_\mathrm{B} = 1 - ((K_\mathrm{w}\ /\ K_\mathrm{A})\ldots + K_\mathrm{B} + \ldots + 0)/\sqrt{\sigma_\mathrm{B}}$, 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 $\mathrm{d}p\mathrm{H}/\mathrm{d}N/N_\mathrm{S}$ against $(N/N_\mathrm{S}) - 1$.

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^3_A generally is close to unity with κ_A less than 10^{-3}. For $\kappa_\mathrm{A} = 10^{-3}$, the titer deviation is 0.30% for a strong base, and 0.33% for a weak base, and with $\kappa_\mathrm{A} = 10^{-2}$, it is 3.0% (3.6% by exact numeral plot) for the

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[3] Roller, This Journal, **54**, 3485 (1932).

[4] Eastman, *ibid.*, **47**, 332 (1925).

[5] Eastman, *ibid.*, **56**, 2646 (1934).

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 *p*H or m. v. error of titration is ordinarily small, equation (1) may therefore be simplified to

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

NEW BRUNSWICK, N. J. RECEIVED OCTOBER 18, 1934

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.

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RECEIVED NOVEMBER 30, 1934