chain-branching rate expression. Similarly, if deuterium is substituted for hydrogen, one would expect the rates of reactions e and g to be decreased much more than that of reaction f. Hence one expects the deuterium pressure to appear in the chain branching rate expression at lower temperatures than those at which the hydrogen pressure appears. Using the data of Frost and Alyea[7] for deuterium–oxygen explosions and a value of 0.5 for K_1'/K_1 of equation (4) the lines of Figure 5 for D_2 were obtained. It is apparent that the substitution of D_2 for H_2 practically obliterates the temperature effect observed for H_2.

The authors wish to express their sincere appreciation for many helpful criticisms made by Dr. L. S. Kassel.

Summary

An equation has been suggested for representing the explosion limits of hydrogen–oxygen mixtures as a function of the partial pressures of the reactants. This equation is shown to be qualitatively consistent with a series of possible reactions for the chain branching and chain breaking mechanisms; and it is in quantitative agreement with most of the available data.

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[7] Frost and Alyea, THIS JOURNAL, **56**, 1251 (1934).

NOTES

Boron Arsenate

BY WALTER C. SCHUMB AND WINSLOW H. HARTFORD

In connection with our study of the compounds of boron described elsewhere,[1] we have prepared the relatively little known boron arsenate,[2] and have determined certain of its properties. The method of Meyer[3] for the preparation of boron phosphate was employed, but modifications were necessary due to the greater tendency of boron arsenate to hydrolyze. The best results were obtained by the following procedure: 100 g. of arsenic acid was dissolved in water, the solution was filtered from any suspended matter, heated to boiling, and 20 g. of boric acid then was added. The liquid was maintained at the boiling point until, suddenly, a viscous, white precipitate formed, which was washed rapidly by decantation, filtered and dried; 24.5 g. of a pure white product was obtained. This product still contained a small amount of boric acid, but when boiled with ethyl alcohol, in which boric acid is somewhat soluble and hydrolysis does not occur, a substance was obtained which analysis showed to be very nearly pure boron arsenate. Boron and arsenic were determined on separate samples, using the standard Chapin method for boron, and the U. S. Department of Agriculture method for arsenic.[4] *Anal.* Calcd. for $BAsO_4$: B, 7.27; As, 50.34. Found: B, 7.21, 7.27; As, 50.17, 50.07, 50.20.

The ready hydrolysis of boron arsenate is indicated by the facts that in contact with water the substance was wholly decomposed after three days, and that even in acid solution hydrolysis slowly progressed.

The specific gravity of this substance was found to be, at room temperature, 3.40, a fact which, taken in comparison with the much lower specific gravities of the reactants, indicates a highly condensed internal structure. Its index of refraction (n_D) was 1.66. It is readily decomposed by hot water or warm solutions of sodium carbonate or sodium hydroxide; concentrated hydrochloric acid dissolves it on warming, forming arsenic trichloride and liberating chlorine. It is soluble in dilute sulfuric acid but not in the cold, concentrated acid. It is slowly dissolved by dilute or concentrated nitric acid. At red heat it is slightly decomposed without melting.

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[1] Schumb and Hartford, THIS JOURNAL, **56**, 2613 (1934).

[2] Berger, *Compt. rend.*, **170**, 1492 (1920); Schulze, *Naturwiss.*, **21**, 562 (1933); *Z. physik. Chem.*, **B24**, 215 (1934); Gruner, *Z. anorg. allgem. Chem.*, **219**, 181 (1934).

[3] Meyer, *Ber.*, **22**, 2919 (1889).

[4] Chapin, THIS JOURNAL, **30**, 1687 (1908); U. S. Dept. of Agriculture, Bull. 107, p. 239.

Occurrence and Position of the Principal Inflection Point in Certain Acid–Base Titration Curves

BY E. D. EASTMAN

This note comprises a refutation of the statements of P. S. Roller[1] concerning my previous

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[1] Roller, THIS JOURNAL, **54**, 3485 (1932).

work[2] on this subject. It also includes certain new results and simplifications, and a recapitulation of the main theoretical expectations relating to the titration of monobasic acids by monacid bases.

The passages (numbered for convenience, and in order of importance) from Roller's paper with which I disagree are cited below, accompanied in each case by my comment.

I (a) (Ref. 1, p. 3494).—"The conclusion of Eastman that an inflection point may not appear in the (symmetrical) titration of a weak base is in the light of these results seen to be incorrect."

(b) (Ref. 1, pp. 3494–3495).—"The deduction of Eastman that for the symmetrical titration of a weak acid by a weak base there is a titer deviation of the inflection point from the stoichiometric point is seen to be erroneous."

To make clear the differences in results implied in these statements, the behavior indicated by Equations 10 and 8 of my paper for the titration of a weak acid by an equally weak base will be given. At concentrations of either 1 *M* or 0.001 *M*, if $K_A = K_B = 10^{-5}$ the principal inflection occurs when H^+ concentration is about 2% greater and the "titer" 0.04% less than at the end-point. If $K_A = K_B = 10^{-6}$, the inflection point, at either concentration, is still found[3] but deviates by approximately 30% in (H^+) and 4.5% in titer from the end-point. If $K_A = K_B = 10^{-7}$, the inflection no longer appears. According to Roller the inflection *always* appears if $K_A = K_B$, and always coincides with the end-point in this case.

I have rechecked the derivation of my equations and calculations from them, confirming the above results. I have also checked these results from the expression for dpH/dV (pH = Sörensen number, V = moles of base added) and find maxima at the positions found from Eq. 10 for the inflections with $K = 10^{-5}$ and 10^{-6} and none if $K = 10^{-7}$. I have also verified these results by direct substitution in Eq. 7 of (H^+) values at intervals of 0.05 unit in pH, with the same results. I therefore reaffirm the former conclusions.

Qualitatively, the predicted disappearance of the inflection as the acid and base are progressively weakened is the normally expected result. On the other hand, the deviation of the inflection, when it does appear, from the end-point is disturbing in view of the apparent "symmetry" to which Roller refers. Actually, however, this symmetry does not exist. The ordinary plot of pH against titer is unsymmetrical about the end-point (or any other point). The principle of symmetry cannot therefore be invoked in the present discussion.

II (Ref. 1, p. 3495).—(a) Eastman's "estimate of the titer deviation in the unsymmetrical titration by a strong base of a 1 molar weak acid with $K_A = 10^{-12}$ is about ten-fold too low; (b) and his conclusion that the titer deviation for this titration does not vary with concentration of weak acid between 1 and 10^{-3} mole/liter is plainly in error."

The calculation mentioned in (a) corresponded to $K_A = 10^{-11}$ and not 10^{-12} as assumed by Roller. It is correct for the former value.

My conclusion mentioned in II (b) carried the proviso that the acid strength should be just sufficient (only integral powers of ten being considered in K_A) to produce an inflection. With this proviso the conclusion is correct. Thus with concentration 1 *M*, the limiting strength of acid is $K_A = 10^{-12}$ and the deviation in titer is about 3%. At 0.001 *M* the limiting strength is $K_A = 10^{-9}$ and the titer deviation again about 3%. These values are in complete agreement with Roller's calculations. In the former paper the limiting acid strength was mistakenly taken as 10^{-11} and 10^{-8} for the respective concentrations, the titer deviation then corresponding to 0.3%. There was no intention to imply that for a fixed value of K_A the titer deviation is independent of concentration.

III (Ref. 1, p. 3486).—(a) Eastman's "numerical result for the condition of the appearance of an inflection point was shown to be erroneous; (b) his other numerical results are also in error as shown below."

The errors mentioned in (a) are trivial and have been acknowledged previously (Ref. 2b). They resulted from the use of intervals (one power of 10) in (H^+) which were too large for solving the equation by successive approximations. Three of the calculations were affected by this error (one of these being recognized for the first time above). All other numerical results I believe to be correct under the (idealized) conditions to which they apply.

Although this completes my reply to Roller's criticisms, I shall take this opportunity of giving a more convenient form of Eq. 10 of my former

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[2] Eastman, (a) THIS JOURNAL, **47**, 332 (1925); (b) **50**, 418 (1928).

[3] In the former paper the limit in K_A for 0.001 *M* was incorrectly given as 10^{-5}.

paper, with a few further results based upon it. The equation of condition for appearance of an inflection may be written, with the same symbols as previously except that H replaces (H^+) as follows:

$$\begin{gathered}(1 - K_\mathrm{W}/K_\mathrm{B}\mathrm{H})(cK_\mathrm{A}/(K_\mathrm{A} + \mathrm{H})^2 + K_\mathrm{W}/\mathrm{H}^2 + 1) - \\ (K_\mathrm{W}/K_\mathrm{B}\mathrm{H}^2)(cK_\mathrm{A}/(K_\mathrm{A} + \mathrm{H}) + K_\mathrm{W}/\mathrm{H} - \mathrm{H}) - \\ 2(K_\mathrm{W}/K_\mathrm{B}\mathrm{H} + 1)(cK_\mathrm{A}\mathrm{H}/(K_\mathrm{A} + \mathrm{H})^3 + K_\mathrm{W}/\mathrm{H}^2) = 0\end{gathered}$$

Using this equation for several cases not previously considered in which acid and base are both weak, I find that if K_A or $K_\mathrm{B} = 10^{-3}$ the inflection occurs if the ionization constant of the titrating base or acid is as large as 10^{-9} but not if it is $= 10^{-10}$. Similarly, if K_A or K_B is taken as 10^{-9} the inflection occurs if the ionization constant of the titrating agent is 10^{-3}, but not if it is 10^{-4}.

Indefinite elaboration of such calculations is possible. I believe, however, that all that is ordinarily required for correct orientation is provided in the following summary.

If acid and base are both strong (ionization constant infinite) the inflection appears at all concentrations and always coincides with the endpoint.

If the acid is weak and the added base strong the inflection appears if $cK_\mathrm{A} > 2.7 \times 10^{-13}$, as shown by Roller. The inflection precedes the end-point by about 3% in titer if $cK_\mathrm{A} = 10^{-12}$. This last value decreases approximately 10-fold for each 10-fold increase in cK_A.

With acid and base both weak, and with c between 0.001 M and 1 M, the numerical results above may be generalized by the approximation that the inflection will appear if $K_\mathrm{A}K_\mathrm{B} \geqq 10^{-12}$, but not if $K_\mathrm{A}K_\mathrm{B} \leqq 10^{-13}$. The inflection in these cases does not coincide with the end-point. The deviation in titer is nearly independent of concentration in the indicated range. It is of the order of 5% if $K_\mathrm{A}K_\mathrm{B} = 10^{-12}$ and again decreases about 10-fold for each 10-fold increase in $K_\mathrm{A}K_\mathrm{B}$. It will be observed that the generalization above limits the critical value of $K_\mathrm{A}K_\mathrm{B}$ for the disappearance of the inflection only within one power of 10, and that it is based on examples in which neither constant exceeded 10^{-3}. It can no doubt be applied somewhat beyond this point, but must fail eventually if K_A or K_B is indefinitely increased. Further refinement of the criterion, within more restricted limits of K, is possible, but of little additional value.

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An Investigation of the Benzoate Method for the Separation of Iron, Aluminum and Chromium and Some Suggested Changes for its Application to Qualitative Analysis

BY LEO LEHRMAN AND JACOB KRAMER

Recently a method of separating aluminum, chromic and ferric ions, using ammonium benzoate as a precipitant, from the other ions of the third and fourth groups and magnesium was offered.[1] While the procedure was devised essentially for quantitative work the authors say it can be used in a qualitative scheme. However, certain features of the method seem not to be clearly developed for the qualitative analysis of the common metals and others may not be readily adaptable. These points in question, which we thoroughly investigated are: (A) the application of the procedure for 500 mg. total metallic ion content, the usual amount for qualitative work, especially when it is mostly trivalent; (B) diminution of the lengthy period of boiling required to precipitate the Cr^{+++}; (C) the possible difficulty of filtering the precipitate representing 500 mg. of trivalent metallic ion; (D) reduction of the number of washings and possible change of the wash solution. Our investigation, the results of which are given below, showed that with certain changes the method can be used for the qualitative analysis of the common metals.

With 500 mg. separately of each of the divalent ions of Groups 3 and 4 and Mg^{++}, no precipitation is obtained with 10% ammonium benzoate reagent in acetic acid solution. For separate solutions of 500 mg. each of Al^{+++}, Cr^{+++} and Fe^{+++}, 90 ml., 60 ml. and 40 ml., respectively, of the precipitant are needed to cause complete precipitation after one minute of boiling. Mixtures of 250 mg. of each of the trivalent metallic ions, Fe^{+++} and Cr^{+++}, Al^{+++} and Cr^{+++}, and Fe^{+++} and Al^{+++}, required 40 ml., 50 ml. and 60 ml., respectively, to give the same result. In all cases if not enough precipitant is originally added for complete precipitation, prolonged boiling has no effect. Thus it is possible to precipitate completely 500 mg. of Cr^{+++} in a short period of boiling (one minute). The size of the precipitate obtained with 500 mg. of the trivalent metallic ions is rather large but can be contained in an 11 cm. filter paper if filtered with suction. Under these conditions two or three washings with 10

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[1] Kolthoff, Stenger and Moskowitz, THIS JOURNAL, **56**, 812 (1934).