HIGH FREQUENCY TITRATIONS IN ACETIC ACID MEDIA

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MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
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High frequency titration is an electrometric technique of end point detection. It possesses the advantage over existing techniques in that it eliminates the necessity of internal electrodes.

The purpose of this investigation was the study of the advantages and disadvantages inherent in the method and a comparison of this method to conventional methods of end point detection.

The instrument used was a conventional tuned plate, tuned grid, 3600 KC crystal oscillator utilizing a 6E5 triode. Measurements were made by a capacitive loading of the plate circuit. The effect measured was the maximum biased grid voltage of the loaded circuit while the instrument was in oscillation. The end point detected by the instrument as used is explained in terms of conventional conductometric titrations which may be related to this technique by ordinary methods of electronic circuit reduction.

Of the factors evaluated most important are the effects of solvent system, dissociation of the substance titrated, and the concentration. The effect of the solvent system is conventional and in accordance with the Brønsted theory of acids and bases. It was found that weak bases such as dimethylaniline, pyridine, hexamethylenediamine, 8-hydroxyquinoline, aniline, p-toluidine, and β-alanine, when titrated with a strong acid such as perchloric acid gave better end points in acetic acid media than in water or dioxane. The degree of dissocia-

tion of the substance titrated in a particular solvent system had a profound effect. The more highly ionized substances gave better end points than the less dissociated or "weak" substances. The effect of concentration is perhaps the most unconventional aspect of the high frequency technique in that sensitivity of response is not a linear function of concentration. The methods utilized gave two regions of maximum sensitivity separated by a region of low sensitivity. It was found that each system titrated had a unique region of highest sensitivity. The location of this maximum region of sensitivity depends upon the kind of ions present. The regions of maximum sensitivity varied from 0.05M-0.002M for aniline to 0.1M-0.01M for diethylaniline.

In acetic acid media the precision of high frequency end points compares favorably with potentiometric end points where the concentration of maximum sensitivity is utilized. In most cases of weak bases the high frequency region of maximum sensitivity extends to lower concentrations than does the potentiometric concentration range. The potentiometric method in acetic acid systems extends to weaker bases than does the high frequency method studied here. Thus high frequency techniques and potentiometric methods are complementary to the study of acetic acid systems.

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INTRODUCTION

High frequency titration is a relative newcomer to the field of electrometric analysis, consequently most studies have been primarily concerned with instrumentation and the theoretical basis for measurement. Only few papers have dealt with problems of construction and operation.

Although high frequency methods possess unique properties only a few of its possibilities have been realized. Potentially such an instrument could be widely useful wherever a measure of solution concentration is desired. Most studies to date have used high frequency methods on classical determinations for instrumental and theoretical background, rather than for the purpose of improving the determination. This is to be expected, since instrumentation and theoretical ramifications must be understood, prior to application.

Several excellent review articles have appeared (9,11,33, 57) and reviewers agree concerning the nature of the measurements, however instrumentation seems to be a matter of individual preference.

In light of the foregoing, this study stresses application of high frequency techniques to analytical problems, rather than theoretical aspects. An investigation was made of various operating techniques on a simple high frequency titrimeter of the type described by Hall (39). Various cells

were evaluated from the operational standpoint. Finally a study was made of hi h frequency applications to nonaqueous acid-base titrations. Since this is not an exhaustive report on the subject of high frequency analysis in nonaqueous media the study is specifically limited to some acetic acid systems.

HISTORICAL BACKGROUND

High frequency analysis, a method in the general field of electrometric analysis has gained widespread attention in the past few years. This method possesses certain advantages over standard methods of electro-analysis. Conductometric, potentiometric and allied methods do not give satisfactory results with a great many important systems, and many systems which give adequate results are contaminated by the immersion of electrodes or deactivate the electrodes unless elaborate precautions are taken.

Applications

The high frequency methods, even though they have inherent limitations, have been used for many diverse determinations. Successful high frequency analytical procedures have been reported for: classical acidimetry, (2,4,11,22,36,39, 40,45,53,66); nonaqueous acidimetry, (45,65); oxidimetry, (45); general precipitation reactions, (21,30,40,45,62,66); adaptation to continuous reading and constant recording apparatus, (21,64); kinetic studies, (25,30,32,46); beryllium determination, (3); mercurimetric determination of chloride, (12); micro titrations (16); volumetric thorium determination, (14); determination of calcium and magnesium ions, (10,47); analysis of mixtures, (67); detection of chromatographic zones, (52); sulfate determination, (51,62); determination of water

in alcohols, (68); moisture tester, (6); indicator for pipeline liquid separation, (26); measurement of dielectric constants, (1,5,25,31,33,37,58); dipole moment measurement, (27); a comparator for solutions, (19); capacity measurement, (24); argentometric titrations, (8); versenate titrations, (10); and dimethylglyoxime chelation, (53).

Instrument Classification

A brief survey of the literature on this subject, would seem to indicate that these methods, each using different techniques, instruments, and measuring different electrical properties, are only related by their use of a high frequency alternating current. This observation gives rise to the general characteristic common to all high frequency measuring devices. When a solution is placed in the tank circuit of an oscillator, circuit parameters due to the solution alter the characteristics of that oscillator to a degree determined by the nature and concentration of the solution, and as the concentration of the solution changes, these oscillator characteristics are further altered. Ideally, for analytical purposes, a change of solution concentration should cause a linear response of a single variable characteristic. In practice the oscillator changes that are noted in conjunction with solution changes are change in frequency and change in power loss. In the language of current literature the solution changes measured are capacitance and high frequency conductance or a combination of the two (57).

This dual nature of the change offers a convenient distinction between types of instruments for purposes of description. They can be classified as instruments which measure change of frequency (capacitance), those which measure a function of power loss (conductance), and those which measure a combination of the two.

Frequency measurement. The frequency measuring instrument has a response of the type, shown in Figures 1, 2 and 2a, and can be further broken down into two subgroups depending upon actual operation of the instrument. One subgroup utilizes two oscillators to measure the change of frequency, an indicator oscillator and a reference oscillator. This is the so called beat frequency technique (11-14,37,52,54,64,66,68). The indicator oscillator contains the unknown to be analyzed in its tank circuit. During the determination the characteristic frequency of the indicator oscillator is changed. The degree to which the frequency changes is primarily a function of the change of capacitance of the cell containing the unknown. The alternating current of different frequencies from the two oscillators is fed into a mixer amplifier circuit and the change in the frequency of the indicator oscillator is recorded as a beat frequency change. This beat frequency change can be determined with a frequency meter or by determining the appropriate lissajous pattern of an oscilloscope. The reference oscillator may be an unloaded indicator oscillator or any stable oscillator operating at an appropriate frequency. It has been suggested (48) that by using a stable

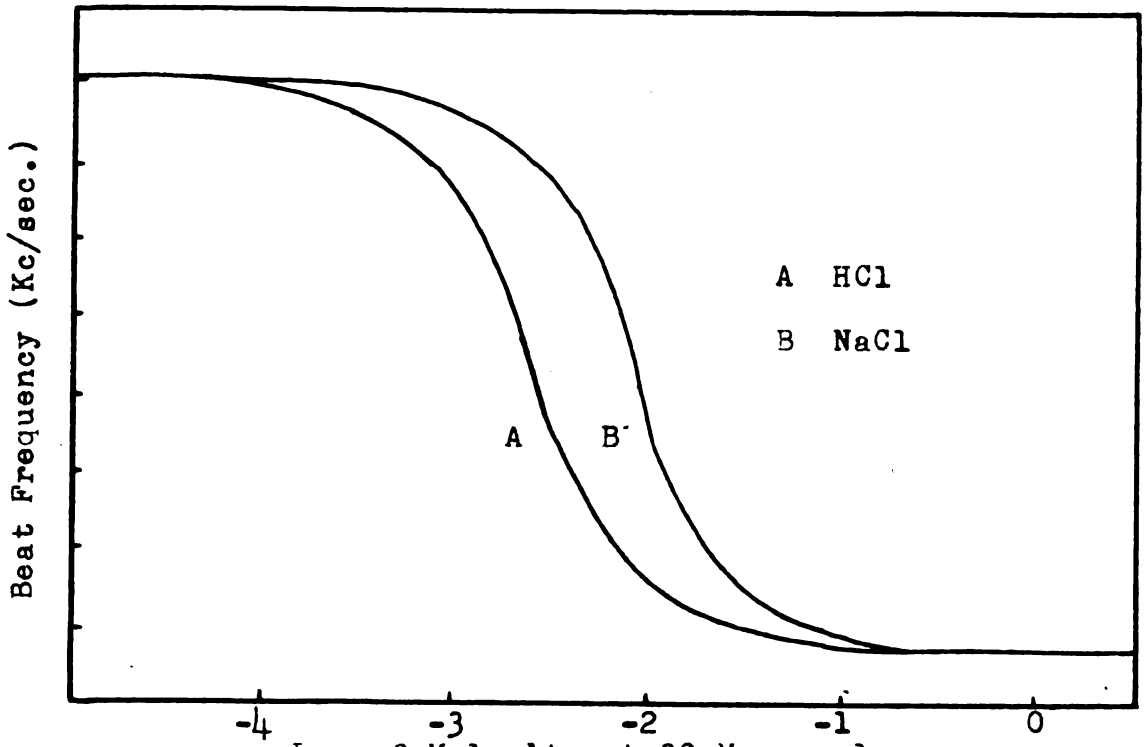

Fig. 1. Frequency Change Instrument Response

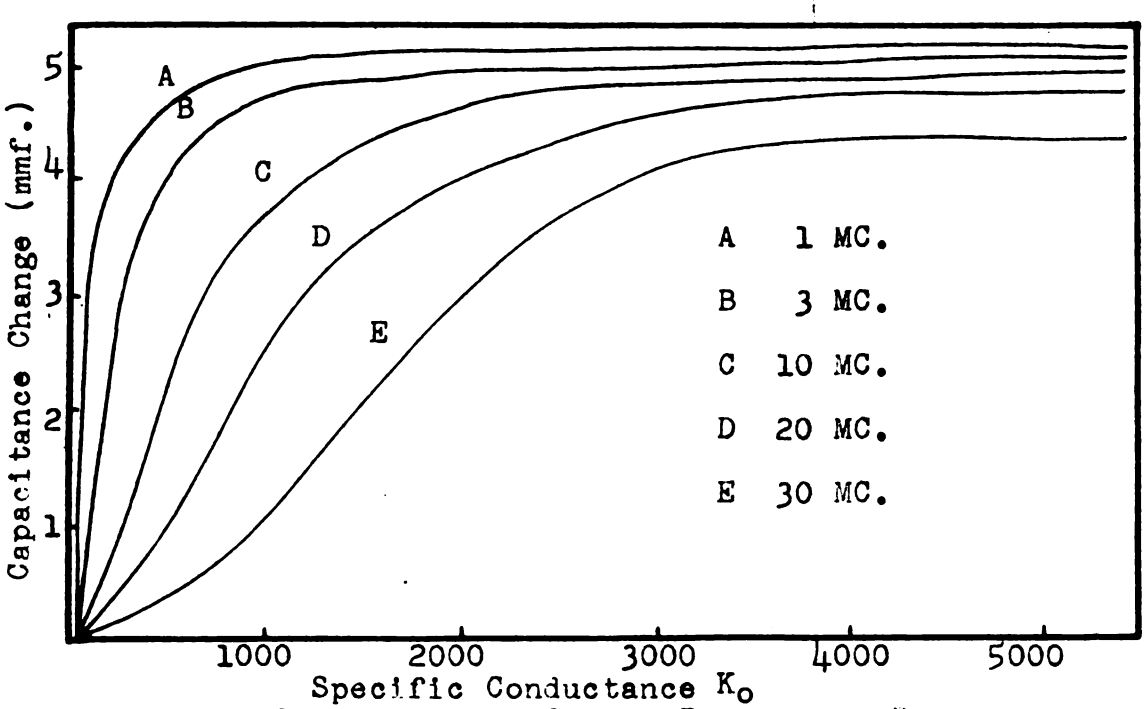

Fig. 2. Frequency Change Instrument Response

receiver a beat can be taken on the tone of National Bureau of Standards station W.W.V.

In the second subgroup of frequency measuring methods an indicator oscillator is used, which by suitable tuning devices in its circuit is returned to its original frequency (8,25,27, 31,39,40,57,61,62,68). Usually the tuning is achieved by removing capacitance from the tank circuit although it has been suggested that slug tuning of the inductance may serve the same purpose. In this method a reference oscillator may or may not be used. The tuning usually is to the original resonant frequency which may be determined by means of a frequency meter or a suitable detector with a "magic eye" indicating device. If a reference oscillator is used, tuning is carried out on the indicator oscillator until a zero beat results on the recorder, which may be a null-point galvanometer connected to a rectifier circuit, an oscilloscope, by earphones or some audio method when suitably amplified.

Power loss measurement. The second general technique of high frequency analysis is the method using power loss measurements which is a function of conductance. Changing the concentration of a solution, which is part of a tank circuit of an oscillator, changes the characteristics of that circuit through change of the resistance of the solution and its subsequent absorption of real power from the oscillator circuit. This power loss when the frequency remains constant, manifests itself by changes in the electrical properties of the oscilla-

tor tube in the tank circuit. The changes and measurements which have been reported are plate voltage or current (14,27, 31,51,65), and grid voltage or current, (2,3,4,29,33,53,58). The characteristic responses for this type of measurement are shown in Figures 3 and 4. Measurements of the real component of impedance in which the amount of radio frequency current transmitted through a cell is rectified and measured have been described by Blake (16-20, 22-25).

Dual response measurement. A third type of instrument gives measurements dependent upon changes of both frequency and conductance. These are the instruments which measure voltage or current change in a tuned circuit which may (2,3) or may not (44-47) be operated at resonant frequency. Some devices measuring impedance directly have been reported, (36, 39,40,57).

Circuit Characteristics

The specific response obtained is dependent upon the relationship and values of the circuit parameters. The parameters may be expressed as complex vector operators arising from instantaneous values and operating upon the network quantities of current, voltage and frequency. The vector operators derived from the parameters are variable in two senses, directly and indirectly (not to be construed as linear and non-linear relationships). Directly variable are those vectors which change due to changed parameter values such as changed conductance or capacitance caused by solution change.

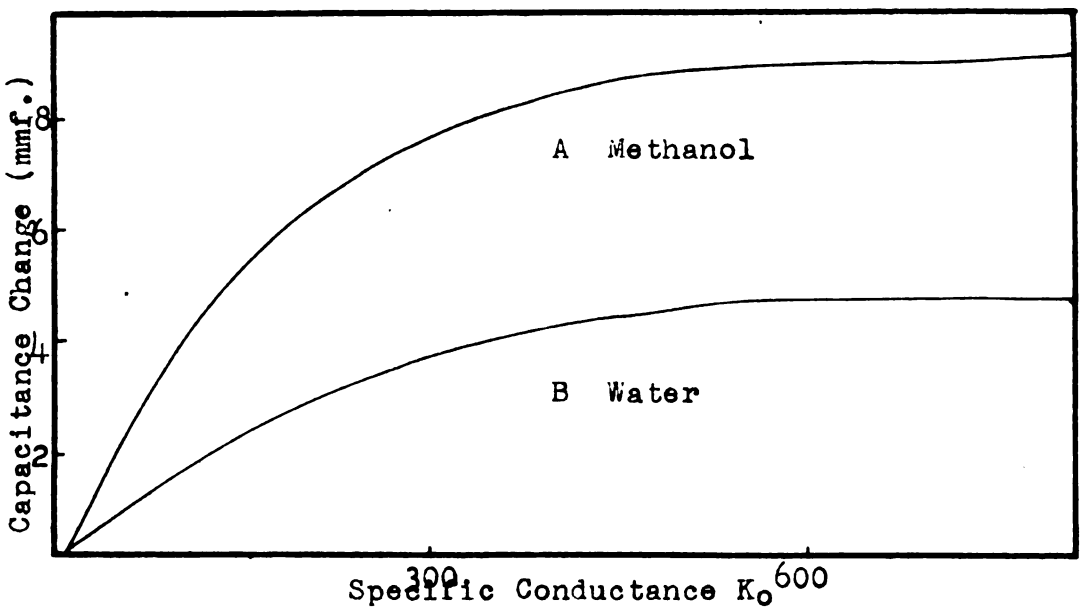

Fig. 2a. Sensitivity Curves for Frequency Change Instruments

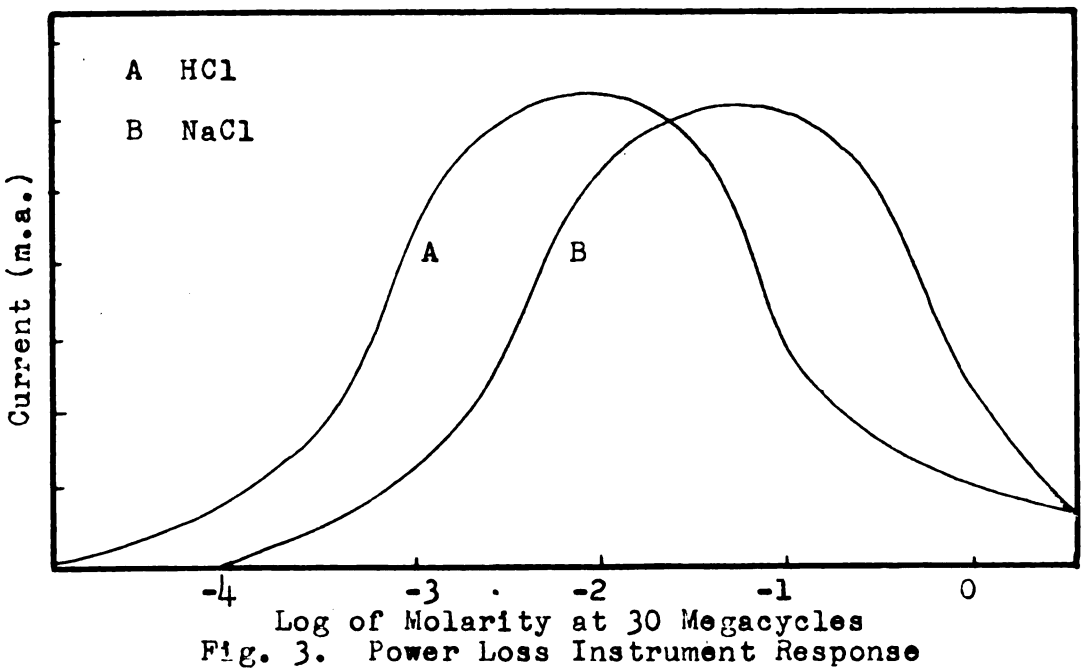

Fig. 3. Power Loss Instrument Response

Changes due to a volitional change of one or more of the multivalued parameters installed in the circuit are also direct variables. Indirectly variable are those vectors which are changed not by a change in circuit parameter values but rather a vector readjusted by a changed circuit quantity, chiefly frequency change due to a directly changed vector. Individual circuit components give rise to one, both or neither directly or indirectly variable vector quantities.

Oscillators. A discussion of oscillator network parameters must of necessity recognize the inherent differences in different types of oscillators. To date a wide variety of different oscillators have been used. Workers have reported successful use of; tuned plate oscillator (24,45,54), Colpitts oscillator (11,12,14,15,47,66), tuned plate and tuned grid oscillator (4,32,44,46,47,51,52,64), and the crystal oscillator, (25,27,31,39) and others less frequently reported include cathode coupled, magnetic feedback and quarter wave length concentric oscillators. The criterion for choosing an oscillator is its stability and reproducibility.

Equivalent circuit. High frequency measuring devices may be resolved into an equivalent admittance network system. The admittance network of Figure 4 composed of non directly variable vector quantities is a general representation of any high frequency instrument. The values of the admittances Y_1-Y_6 determine the characteristics of the instrument. The difference between instruments arises from the characteristic measured, the manner of measurement (A-A') and the experimental set

up of the solution measured across B - B'. Thus the manner of measurement and the circuit quantity account for differences between frequency change, power loss, and dual response instruments. The network is the equivalent circuit of the specific oscillator used. The solution-cell equivalent circuit is the representation of the experimental set up. Figure 5 is the equivalent circuit of a solution in a capacitance type cell in parallel with a variable restoring capacitor. With the aid of specific equivalent circuits the response of an instrument may be calculated as a function of solution concentration.

Response curve. The response obtained or measurement is a function of current, voltage, and frequency, operated upon by complex operators, the directly (Y_x) and indirectly variable (Y_a) admittances. Considering the cell-solution equivalent circuit analysis the expression $Y_x = G_p + jB_p$ is obtained where $G_p = (w^2kC_c^2)/[k^2+w^2(C_s+C_c)^2]$

and $B_p = [\{wC_ck^2+w^3C_cC_s(C_c+C_s)\} / \{k^2+w^2(C_s+C_c)^2\}]+[wC_2]$

Y_x the net admittance of equivalent circuit Figure 4

G_p high frequency conductance term

B_p imaginary part of the admittance

w $2\pi f$, where f is the frequency

k low frequency conductance

C_c capacitance due to walls of container

C_s capacitance due to solution

C_2 the variable capacitor for circuit adjustment

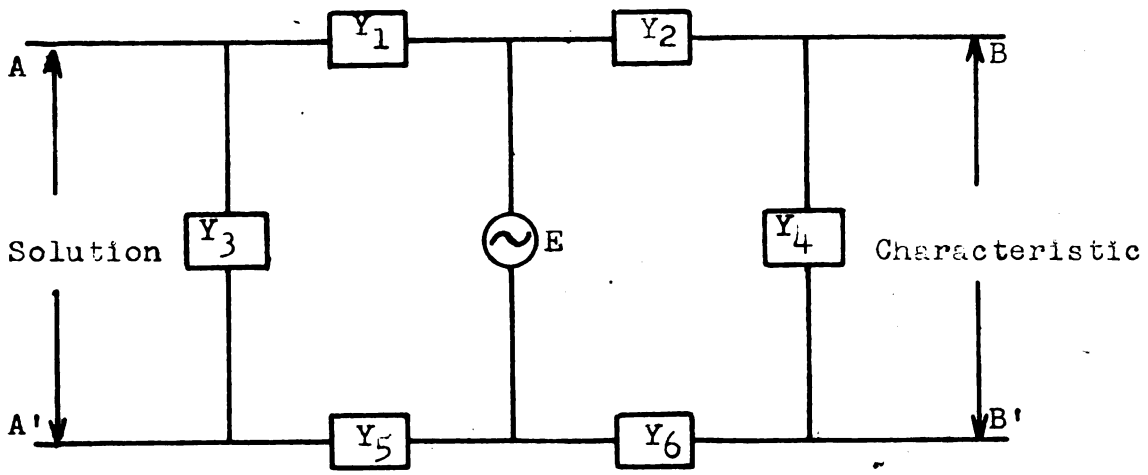

Fig. 4. Equivalent admittance network

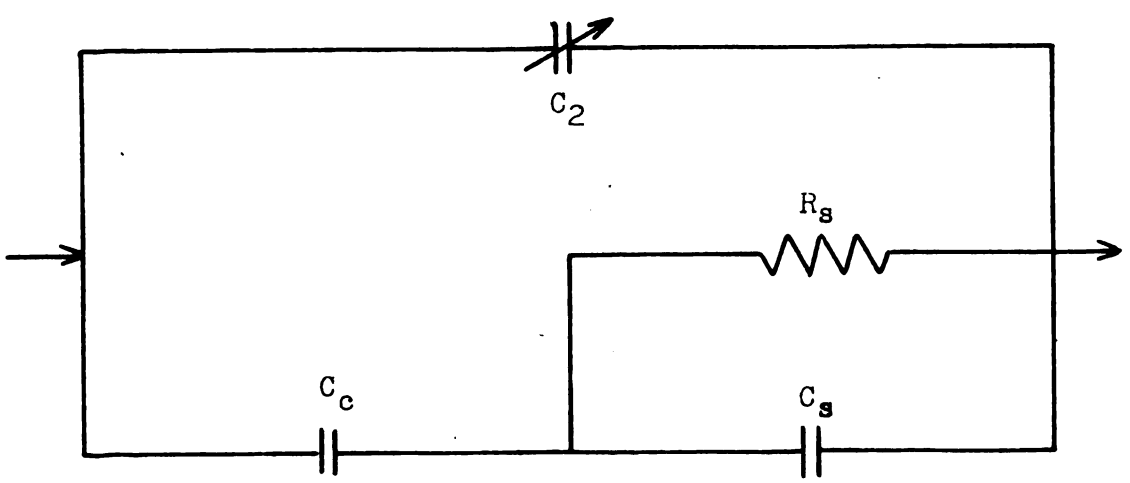

Fig. 5.. Equivalent Circuit

C_2 Instrument control

C_c Capacitance through the container

C_s Solution capacitance

R_s Resistance of solution

J is an operator. If C_2 is set equal to zero the expression reduces to that of Reilly and McCurdy (57).

Circuit reductions of other experimental set ups have been reported (39,57). Approximations can and have been made of the function, $f(Y_x, Y_a, V, K, f)$ knowing the appropriate circuit parameters of Y_x with the attendent assumptions as to the nature of the changes or constancy of Y_a, V, I, f (39). Because of the nature of the assumptions and the fact that the equivalent network is also a simplified approximation, perfect agreement was not expected between calculated and experimental results. The equivalent circuit of the solution (Figure 5) and its calculated admittance can yield a great deal of information concerning the response of a given type instrument and the correlation of this response to earlier experimental results.

In the frequency measuring methods, frequency which is a function of capacitance, or beat frequency itself, is plotted against concentration change of the solution. The plots give rise to curves similar to Figures 1, 2, and 2a. To explain the shape of these curves it is necessary to refer back to the equivalent circuit, Figure 5, assuming C_2 to have infinite impedance. When the impedance of R_s becomes small compared to C_s (at high electrolyte concentration) C_s is almost shorted out and the frequency approaches $1/(2\pi\sqrt{LC})$ asymptotically. In dilute solutions in which the impedance of R_s is large compared to that of C_s the frequency approaches

$(1/2\pi)[\sqrt{(C_s+C_c)/(LC_sC_c)}]$ asymptotically. In the intermediate concentration regions where the impedances of R_s and C_s are of the same order, the frequency varies monatonically with concentration between the two limits.

For conductance (power loss methods) an explanation of the shape of Figure 3 is based on the assumption that the resistance R_s of the solution is changing while the other properties remain approximately constant. At high concentrations R_s is small and passes the current with little absorption, however, absorption increases with increasing R_s. Above a certain limit the capacitance of the solution C_s begins to shunt greater portions of the current and when R_s is large enough, absorption is small because the current in R_s is small. Thus the power absorption passes through a maximum as does the plate current, etc. From Figure 3 it can be seen that there are two regions of maximum sensitivity (on either side of the hump). Consequently the concentration limitations are much less severe than those for frequency measuring instruments. The dual response instrument which measures the effect of both dielectric change and power loss change has given excellent results (44,45), however, in some titrations a rapid conductance change near the end point may work in opposition to the capacitance change and make the end point determination less sharp than would otherside be expected (38).

In the preceding discussion little has been said concerning the effect of conductance on frequency measurement.[1] In most cases it affects the frequency only slightly, however in cases of larger conductance change (overloading the oscillator) it is possible to dampen oscillation completely. Whenever conductance is sufficient to change the frequency appreciably the oscillator must be brought back to maximum resonance by adjustment of a variable capacitor in the tank circuit.

These conclusions are in agreement with the conclusions drawn by earlier workers. Forman and Crisp (33) showed that change in frequency was due to change in dielectric constant of the solution (or change in capacitance of the cell) and power loss was primarily a function of the conductance of the solution, remembering that in cases of measurement with rapidly changing polarity, with the electrodes isolated from solution, the ordinary ohmic conception of conductance is invalid. The G_p term is the real component of the complex admittance function. This real conductance component in ionic solution is the result of the movement of molecules relative to their[2]

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[1] In electronic terminology, change of frequency due to loading.

[2] The absorption of power manifests itself by a heating effect. A rise in temperature or change in viscosity of a solution in a tank circuit, other things remaining unchanged, will cause a change in the characteristics of that tank circuit. This could conceivably be a source of error in titrations, however, the voltages used are low, consequently the amount of power dissipated is low enough so that temperature effects can be ignored.

neighbors. The power loss (conductance) effect is concerned with the storage of energy and its subsequent return to the signal source. If the source and the system did not have their inherent energy losses it would be possible to transfer energy from source to system without attenuation. The nature of the conductance change has been investigated by Forman and Crisp (33) and Richards and Loomis (53), who have derived mathematical expressions relating power loss to specific conductivity and dielectric constant of the solvent. An empirical relationship of frequency corresponding to maximum energy loss has been shown to be $\lambda\gamma = K_e$ by Forman and Crisp (33), in which λ is the wave length, for maximum power loss, γ is the concentration of the solution and K_e is a particular constant for each simple electrolyte. This relationship was determined by means of the temperature rise of a solution tested in a calorimeter during a definite time interval. This relationship is indicative of the concentration limitations of the method, since outside of a certain concentration region, the degree to which power loss or wave length (frequency) changes with respect to concentration falls of sharply. Consequently outside of this region the sensitivity is not great enough to satisfactorily indicate an end point in a titration.

Cell Types

Earlier workers used inductance type cells, (31,44,45). Unknowns were placed in a glass container which in turn was placed in the inductance coil of the oscillator circuit.

Several disadvantages are said to be attendent upon coil type cells which are said to be overcome by using the capacitance type cells (11). Reported disadvantages are a lack of reproducibility and a lower order of sensitivity than that of the capacitance cell. Recently Fujiwara and Hajashi (36) have reported overcoming these difficulties by modifying the oscillator circuit, and measuring technique. The capacitance type cell is a container, usually glass, with external condenser plates which are part of the oscillator circuit. The geometry of the cells reported has been diverse and greatly dependent upon the system analyzed and the particular use. Most employ a pair of metal bands about a glass cylinder. Several studies of cell geometry have been made (54,57) and it has been found that plate size affects the loading of the oscillator. Cells have been designed for special purposes, flow cells for constant recording apparatus, covered cells for inert atmosphere studies, finger type cells, and cells for studying chromatographic zones.

The TITRATION CURVE

The shape of a titration curve can be explained pictorally by considering the titration graph to be the locus of a point moving on the appropriate response curve. For a specific example relating concentration to grid current by means of the response curve of Figure 7, consider a titration occuring in a concentration range where the initial and end point concentrations are on opposite sides of the "hump". In this case the grid current increases at the beginning of the titration until the "hump" is passed, after which the current decreases as the end point is approached. After the end point is passed the grid current increases passing over the "hump" and decreases again. The resultant titration graph has a "pip" shaped appearance. Depending upon the starting point and the concentration changes which occur, a large variety of complicated titration curves can be obtained.

For the case of an aqueous titration the graph is similar to that of a conductometric titration, provided the titration is carried out on the linear portion of the concentration-frequency change or concentration-power loss change relationship. Up to the end point the change is due to the sum of the changes from decrease in concentration of substance titrated, the increase of reaction product, and dilution factor due to increased volume upon addition of titrant. After the end point,

the change is due to the sum of changes from addition of excess titrant, and the dilution factor. In order to obtain a sharp break at the end point and linear response during the titration it is necessary that the substance being titrated and the titrant both be in the concentration range[1] of greatest sensitivity (greatest change) for that particular frequency. Assuming linearity of the graph, a second optimum condition exists. For sharper end point breaks, the excess titrant should change the direction of the response, or at least change the slope of the graph sharply. Non-linear curves should have a cusp or inflection at the end point. The considerations mentioned above hold true for both power measuring instruments and frequency measuring instruments.

The concentration and non-linearity limitations can be overcome somewhat by the use of higher working frequencies (Figures 2 and 2a).

If an ideal high frequency titration can be postulated, a graph of this titration will possess certain attributes against which the properties of actual high frequency titration graphs can be contrasted. The comparison will show the advantages, disadvantages, optimum working conditions, and the greatest sources of error inherent in the methods used here.

The ideality strived for in the graphical representation is primarily based upon two conditions: a sharp break at the

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[1] Near the end point the presence of reaction product, if a highly ionized substance, will influence the optimum concentration for the greatest change.

end point, and a linear response of the dependent variable.[2] Thus the ideal high frequency graph would resemble a typical conductometric titration graph. A high degree of curvature indicates a great departure from linearity and aside from other considerations a more inferior graph. These other considerations, which are often mitigating factors justifying conclusions, are: symmetry, number of points, and angle of break. The most important of the three is the angle of the break at the end point. Ideally the break at the end point should be as sharp as possible, thus the smaller the angle between the tangents at the end point, the sharper the end point, and conversely no break at all would result in an angle between the tangents of 180°. Unfortunately two opposing tendencies are present here, each limiting the angle of the end point break. The smaller the break i.e., as the tangents approach 180°, the greater is the effect of random errors in changing the location of the break. The larger the break, i.e., as the tangents approach 0°, the greater the range necessary for the

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[2]A more linear response for a particular concentration range can be achieved by increasing the working frequency of the instrument and/or within limits, changed cell geometry and plate size.

Reilley and McCurdy (57), have shown that for a particular concentration and a particular system, the cosine projection of the admittance of the parallel equivalent circuit for the instrument used under specified conditions when made a function of specific conductivity will yield a transfer plot by means of which the equivalent conductometric titration graph may be prepared. This is mathematically equivalent to allowing the response to become a parameter of a function of specific conductance which is in turn plotted against the independent variable yielding a linear graph.

measuring instrument, which in this case is a vacuum tube voltmeter (V.T.V.M.). Thus the minimum angle of the break is limited by the maximum voltage obtainable due to the nature of the oscillating triode and also the maximum range of the vacuum tube voltmeter. The optimum angle of the tangents at the break due to these considerations is in the vicinity of 90°.

It can be said from a qualitative standpoint, that if a curve possesses axes of symmetry the smaller is the probability of random errors present causing a distortion of the end point. It can also be said qualititively, for a greater number of points the probability is larger that in a smoothed curve the positive and negative random errors cancel.

EXPERIMENTAL METHOD AND DISCUSSION OF RESULTS

Preparation of Reagents

All chemicals used were of reagent grade. No special purification of reagents was carried out except in the case of dioxane as mentioned and the aluminum oxinate which was reprecipitated from a dilute acetic acid solution several times. Melting points were taken on the organic solids to confirm their purity, agreeing to $\pm 1^{\circ}$, except glycine which decomposed at a point 10° lower than the theoretical decomposition point.

Solids used were weighed out to the nearest 0.1 of a milligram employing weights calibrated against Bureau of Standard weights. All solutions were compared against standard solutions using potentiometric, conductometric or visual indicators, as a means of detecting titration end points, wherever these means were applicable. Liquids were measured in calibrated glassware.

Aqueous acids and bases were prepared to the approximate desired normality and standardized against known acids or bases. Primary standard grade potassium acid phthalate was used as the primary standard. End points were detected conductometrically or visually with methyl red or phenolphthalein indicator. The reagents used for aqueous studies were reagent grade, acetic acid, hydrochloric acid, oxalic acid, orthophosphoric acid, phenol, potassium hydroxide, sodium chloride, sodium hydroxide, and sulfuric acid.

Acids and bases in dioxane media were prepared with dioxane redistilled over sodium. The bases were compared against a standard perchloric acid solution in dioxane using methyl violet in chlorobenzene as the indicator. The perchloric acid solution was standardized against reagent grade diphenylguanidine using methyl violet indicator (34). The reagents used for studies in dioxane media were, aniline diphenylguanidine, perchloric acid 70-72%, pyridine, and p-toluidine.

The acetic acid media acids and bases were prepared from duPont C.P. glacial acetic acid and C.P. acetic anhydride. The reagents used were, β-alanine, aluminum oxinate, p-amino acetophenone, α-amino-isobuteric acid, aniline, benzidene, benzoic acid, diethylaniline, glycine, hexamethylenediamine, β-napthylamine, 8-hydroxyquinoline, perchloric acid, phenol, phthalic acid, potassium acid phthalate, pyridine, sodium acetate, sodium perchlorate, p-toluidine, and urea.

The glacial acetic acid was assumed to contain 0.5% of water. Enough acetic anhydride was added to react with 50% of the water present. Fifty percent was chosen so that the final solution would contain less than 0.3% of water and no excess of acetic anhydride. The 0.3% or less water level was shown by earlier workers not to affect the solution measurements (34,65). In the preparation of perchloric acid solutions enough acetic anhydride was added to react with 95% of the water present. Perchloric acid solutions were standardized against primary standard potassium acid phthalate dis-

solved in acetic acid (61). Comparisons of solutions were made conductometrically, potentiometrically and visually using methyl violet indicator.

Incidental Instrumentation

Aside from high frequency measurements on the instrument, which will be described below, comparisons and incidental measurements were carried out on other instruments. A Beckman model H-2 line operated pH meter using type #4990-80 red label glass electrode and a calomel type #4970 fiber electrode, was used for titrations in acetic acid media, in the manner reported by previous workers (34,55,56,59,63). An Industrial Instruments conductivity bridge model RC-1B at 1000 cycles per second with Beckman platinized platinum immersion electrodes, was used for titrations in aqueous media and for some acetic acid media titrations in the usual manner. A Heathkit vacuum tube voltmeter model V-5A which was used to measure the grid potential of the high frequency titrimeter. Line voltage was controlled by a 120 volt Sola constant voltage transformer Serial D-73537. A U.S. Army Signal Corps surplus frequency meter type BC-221D was used to determine frequency reproducibility of the experimental instrument. A Fischer electric block melting point apparatus was used to determine the purity of the organic solids.

Apparatus

The titrimeter used with few modifications, chiefly in the power supply, has a circuit (Figure 6) which has been re-

corded by Hall and others (1,5,39). A 3500 kilocycle crystal with the appropriate coil was used rather than the two megacycle crystal used by Hall, the variable capacitor utilized a national geared drive, and the 20 volt direct current was taken from a line operated, half wave voltage regulator power supply, employing a selenium rectifier, (Figure 6).

A short description will be given here of the function and operation of the various components of the circuit. The 6E5 "magic eye" tube functions both as an oscillator triode and a resonance indicator. The triode oscillator circuit is of the tuned plate tuned grid type with a piezo-active quartz crystal as the grid portion of the resonant circuit and as the frequency controlling device. The circuit oscillates whenever the plate parallel resonant circuit is tuned to the same frequency as the fixed quartz crystal. The transfer of energy between plate and grid circuits takes place through the plate-grid capacitance of the tube. Oscillation exists when $f = [2\pi\sqrt{(LC)}]^{-1}$ where f is the crystal frequency, L is the inductance and C the capacitance of the parallel resonant circuit. The state of oscillation is marked by a decrease in plate current, grid current, and grid voltage. Graph B, Figure 7 is a representation of the grid dip response for a tuned plate tuned grid oscillator as described by J.L. Hall (39). The instrument used here being essentially the same instrument with a few modifications has a similar response.

In the grid circuit the R.F. choke prevents the high frequency alternating current from short circuiting the crystal through the grid leak resistor.

The 6E5 "magic eye" also functions as a cathode tube indicator. When there is no oscillation the plate current is high, thus the tube target is maintained at its lowest potential with respect to the cathode. A control electrode is connected through a resistor to the plate of the triode and is therefore at a higher potential than the plate, due to the potential drop across the plate resistor. The shadow angle is the widest at this point. When the circuit is in oscillation there is a redistribution of potential around the plate circuit. The potential drop from the cathode to the plate increases because the effective resistance of this unit increases while the plate load resistor remains constant. The plate current decreases and hence the voltage drop across the plate load resistor decreases and the voltage of the plate approaches the voltage on the control electrode and the shadow angle becomes smaller.

If the capacity in the plate tuning circuit is increased or decreased beyond certain limits it will no longer be in resonance with the quartz crystal and oscillation will stop. At this point there will be a sudden jump in plate current, the potential of the plate with respect to the cathode decreases and as a consequence the shadow angle will widen abruptly. This point is reproducible and can be used as a basis for measurements.

In parallel with the capacitance type cell is a series of capacitors, C_1 through C_6 inclusive, Figure 6. The C_1 variable capacitor is the rough adjustment, the C_2 variable capacitor, with the national reducing drive, is the fine adjustment for the proper capacitance to produce oscillation. The fixed capacitors C_3 through C_6 allow the circuit network capacitance to be roughly adjusted to proper range for oscillation to occur depending on switch position.

The R_3 variable resistor acts as a potentiometer which gives an opposing voltage, balancing the measured grid voltage. The opposing voltage serves to bias the vacuum tube voltmeter (V.T.V.M.) by a predetermined constant potential.

The response curve of graph B, Figure 7 is given in terms of the absolute grid voltage. In the titrations of this study a bias was placed on the vacuum tube voltmeter. If a bias whose value is larger than the maximum value of the grid voltage is imposed, an example of which might be a twenty volt bias, on the grid dip response curve of graph B Figure 7, a reversal of the response is obtained as depicted in graph A Figure 7. It can be seen that a twenty volt bias will result in voltage readings such that a twenty volt grid voltage gives a reading of 0 volts on the V.T.V.M., nineteen grid volts, gives a one volt reading etc. The purpose of biasing the voltage was so that by choosing the proper bias voltage the range measured could cover the entire voltmeter scale and so increase the pointer deflection thereby decreasing the reading

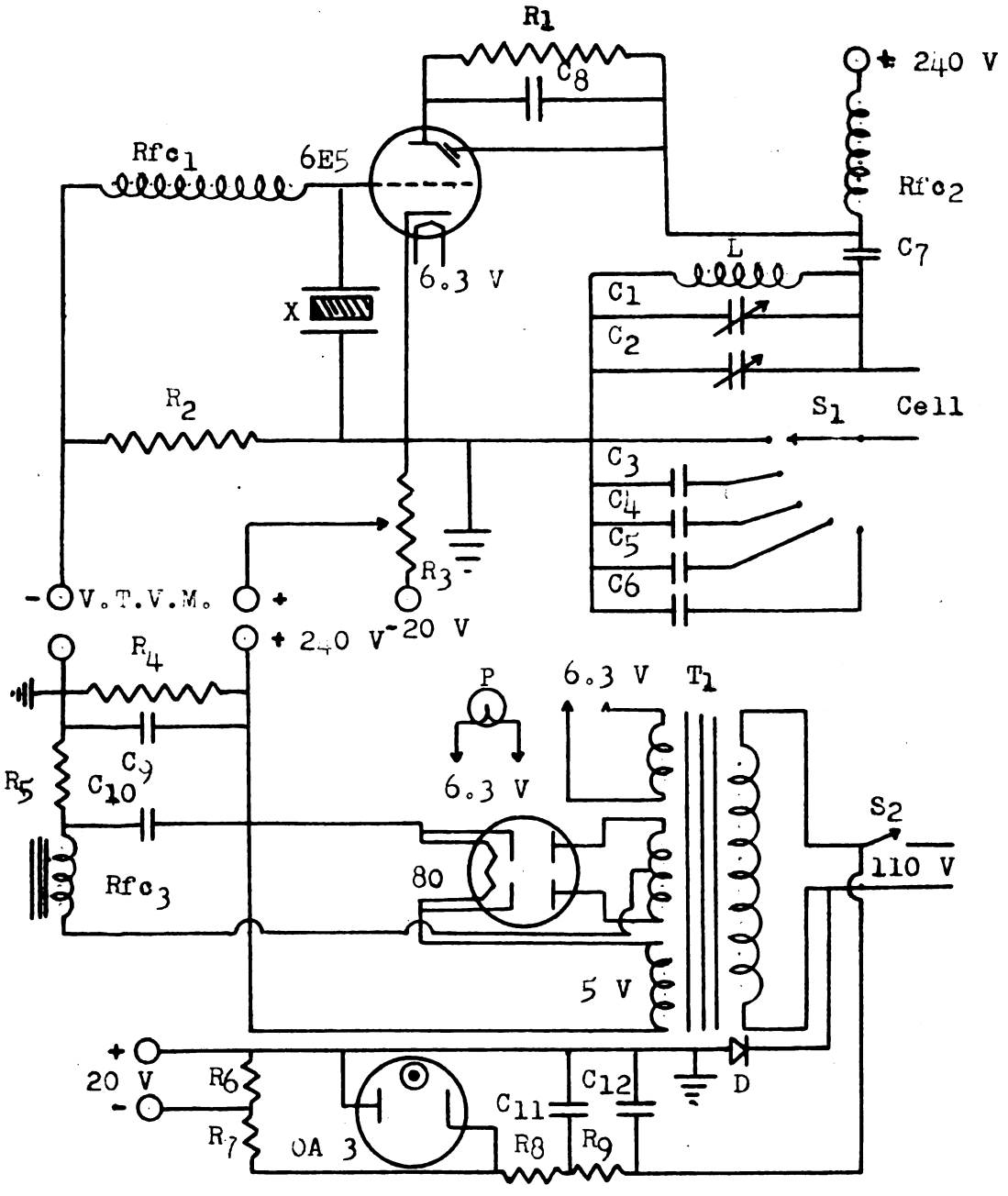

Fig. 6. Circuit diagram of titrimeter and power supply*

*A parts list may be found in the appendix.

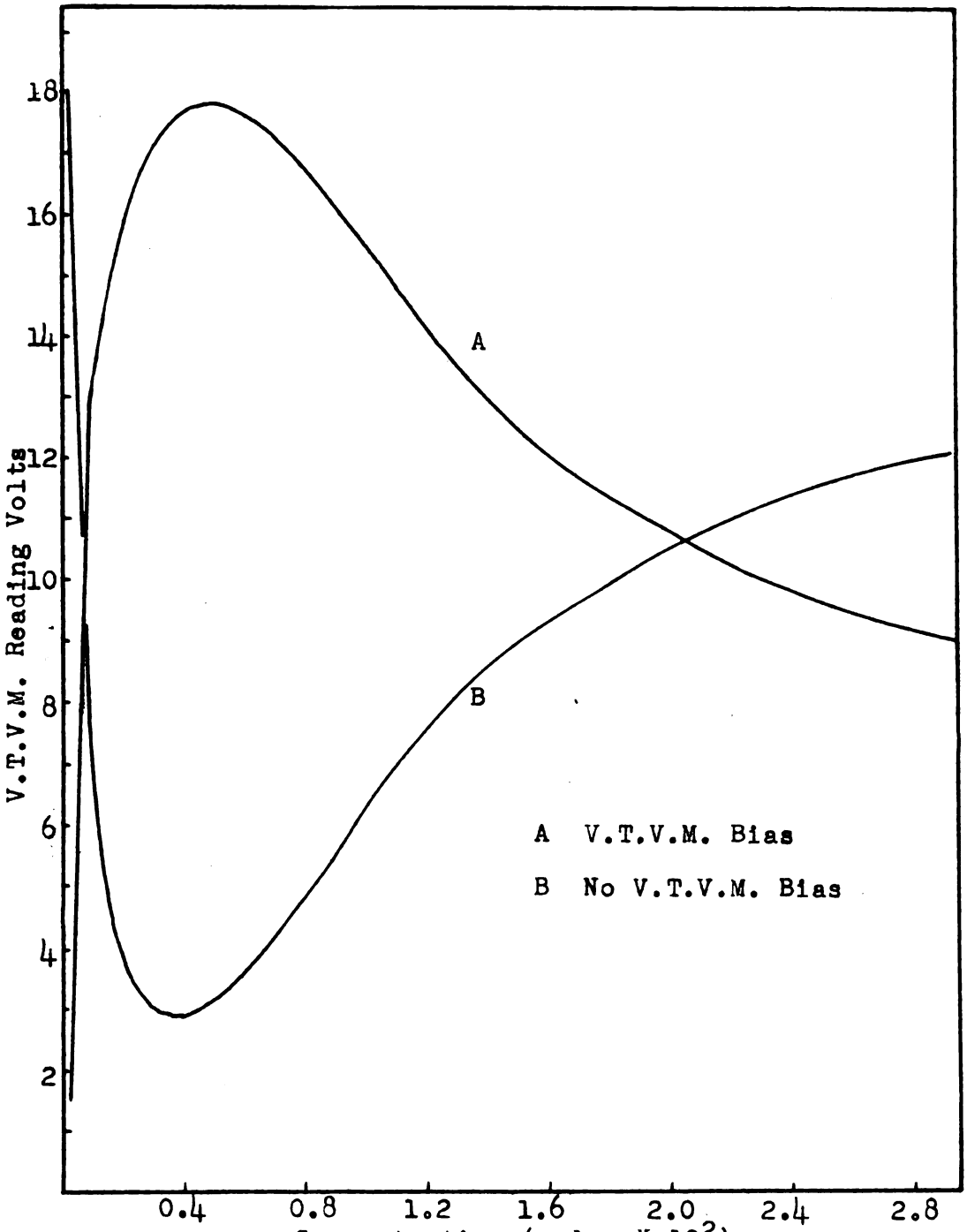

Fig. 7. Response Curve of a Tuned Plate Tuned Grid Instrument

error.[1] Thus the response of this instrument can be discussed in terms of two different curves.

Titrations for this study were carried out using both the "bowl" shaped response and the "hump" shaped response. No difference was expected or found in the observations or conclusions from these observations except the inversion of the relationship between conductance and response. The inclusion of curves from both types of response (which are merely horizontal mirror images of each other) was for the purpose of showing the complete convertability of one identity to the other. Unless, otherwise specified, the voltage measurements are of the "hump" shaped response. For any related set of curves on any one figure the use of a particular response measurement is consistent.

Instrument characteristics. Reproducibility of the instrument was determined using an Army surplus frequency meter. Cut in and cut out points as determined by sudden opening and closing of the "magic eye", were exactly reproducible when determined as the null-point of beat frequency by using earphones. The variable condenser dial reading was reproducible to ± 0.3 dial units. This was tested on various portions of the variable capacitor range by the expedient of using different concentrations of hydrochloric acid solutions in the cell. The variability of the dial readings was found to be greater

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[1] The reading error of the V.T.V.M. in the three volt range estimated as being ± 5 millivolts.

at the first 5% and the last 5% of the capacitor range. Peak voltage[2] measurements were exactly reproducible with respect to voltage and frequency for several different cell loads. At the peak voltage relative capacitor readings were reproducible to ± 2 dial units. At the peak voltage point the frequency was found to be constant even under changing load conditions in the cell. At other grid voltages not on the flat top portion of the characteristic grid voltage capacitance curve the frequency changed different amounts. Reproducibility of grid voltage during loading measurements was possible but only if great care was taken with repeating the prearranged capacitor setting.

Stability measurements were made at various grid voltages and it was found that at all grid voltages there was a slow steady rise which ceased after a period of 90 minutes. The rise at the peak voltage was slower than that for lower grid potentials. The cause of this, although not definitely ascertained can logically be attributed to heating of the crystal during oscillation and cooling of the triode during oscillation and their subsequent attainment of thermal equilibrium with the surroundings.

Stability with respect to stirring was measured using both magnetic stirrer and motor driven paddle stirrer. It.

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[2]A hump shaped curve skewed to the right with a flat top resulted when capacitance removed from circuit is plotted against grid voltage. The grid voltage on the flattened top portion is the "peak voltage".

was found that the glass paddle stirrer when motionless in any position or rotated at any speed had no effect on the grid potential, unless air was beaten into the solution. At a speed which air was beaten into the solution, violent fluctuations of grid potential occurred. With the magnetic stirrer the same effect was noted. Also noted was generally lowered sensitivity (identical solutions titrated under identical conditions had a less sharp end point break). A motionless magnetic stirrer gave varied readings, depending upon the orientation of the stirrer element. The two latter effects were attributed to the presence of a mass of metal in the stirrer element.

Cell Types and Characteristics

Several different type cells were tested for applicability to the present project. The cells described here are typical high frequency titration cells in that the electrodes are electrically insulated from the solution by the container walls. The electrodes are suitably coupled, by means of coaxial cable or by direct connection[3], to the plate circuit of the oscillator (Figure 6).

In the finger type cell (Figure 3) a glass test tube or "finger" was fused over a circular opening in the bottom of

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[3]Direct connection was achieved by fastening a male coaxial connector to the cell and the female coaxial connector to the instrument in such a manner that they could be connected without an intervening cable.

a beaker-like container. On the outside surfaces of the container copper foil was cemented resulting in two cylindrical concentric condenser plates, with the solution concentrically contained between the two plates. Mechanical difficulties in construction and inefficient stirring made the use of other cells described here more feasible.

Dip electrodes (Figure 9) of different sizes, shapes and modes of shielding were devised. These consisted of two condenser plates coated with an insulating material, immersed in the solution, allowing the solution to flow between and around the plates. The chief difficulty incurred in such arrangement was that the level of the liquid changed with respect to the electrodes, consequently a very large part of the change measured was due to volume change.

The cylinder type cell (Figure 10) consisted of a beaker type container on the outside of which two hemi-cylinders of copper foil were cemented as condenser plates. This cell proved to be entirely satisfactory in use, provided sufficient solution was used to minimize the volume change effect. One defficiency of cell design for all of the above mentioned cells which was not overcome, but with careful titration techniques could be minimized, was shielding the cell from stray external capacitance and radiations.

The band type cells consisted of a series of glass containers on which two metal bands were placed, one above the other (Figure 11). Bands of brass, aluminum, copper and gal-

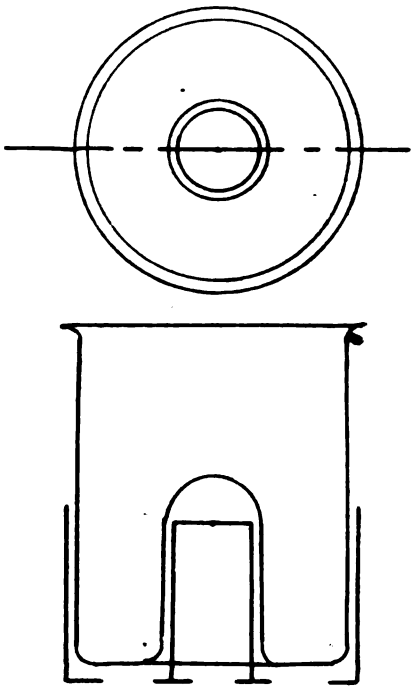

Fig. 8. Finger Cell

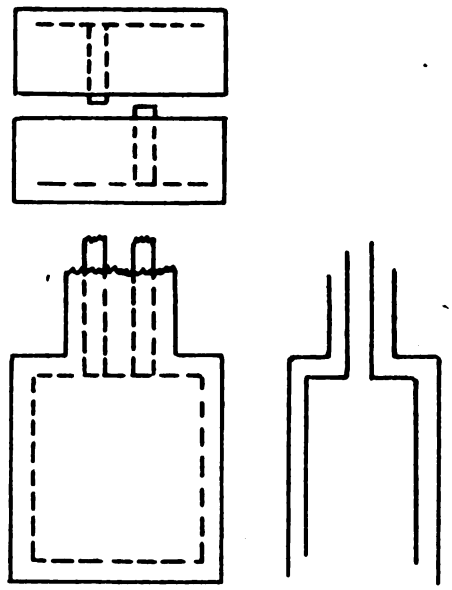

Fig. 9. Dip Electrodes

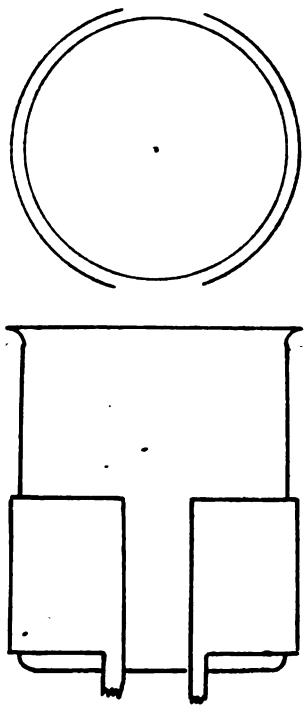

Fig. 10. Cylinder Cell

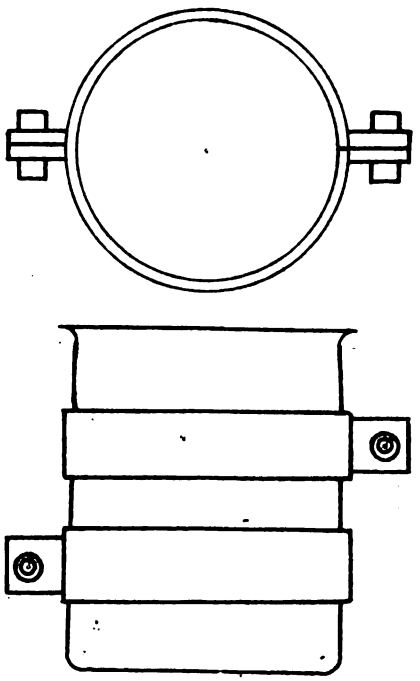

Fig. 11. Band Cell

vanized iron of different widths and with different coupling arrangements on the outside of the container, were tried. One cell with the plates inside the container, insulated from the solution by laquer was tested. Factors which affected the sensitivity of the response for this type cell were found to be, size of plates, thickness and kind of insulation, and separation of plates. These factors were noted qualitatively rather than quantitatively and further investigation along this line was precluded by other unsuitable features of band type cells. The chief difficulty was to design adequate shielding for a cell on which coupling protuberances extended. A second difficulty was present in the form of response change due to volume change. Other studies of this type cell have been reported previously (54,57).

The last type cell tested consisted of a polyethylene container with electrodes imbeded in the bottom (Figure 12). This was the cell subsequently used for all quantitative non-aqueous high frequency titrations. The advantages observed in this cell compared to the others were, a high degree of sensitivity, probably due to the use of polyethylene rather than glass as an insulating material, a smaller change due to volume change by placing the electrodes at the bottom of the cell, ease of construction and shielding, which was achieved by fastening the entire assembly to the bottom of a heavy copper cup.

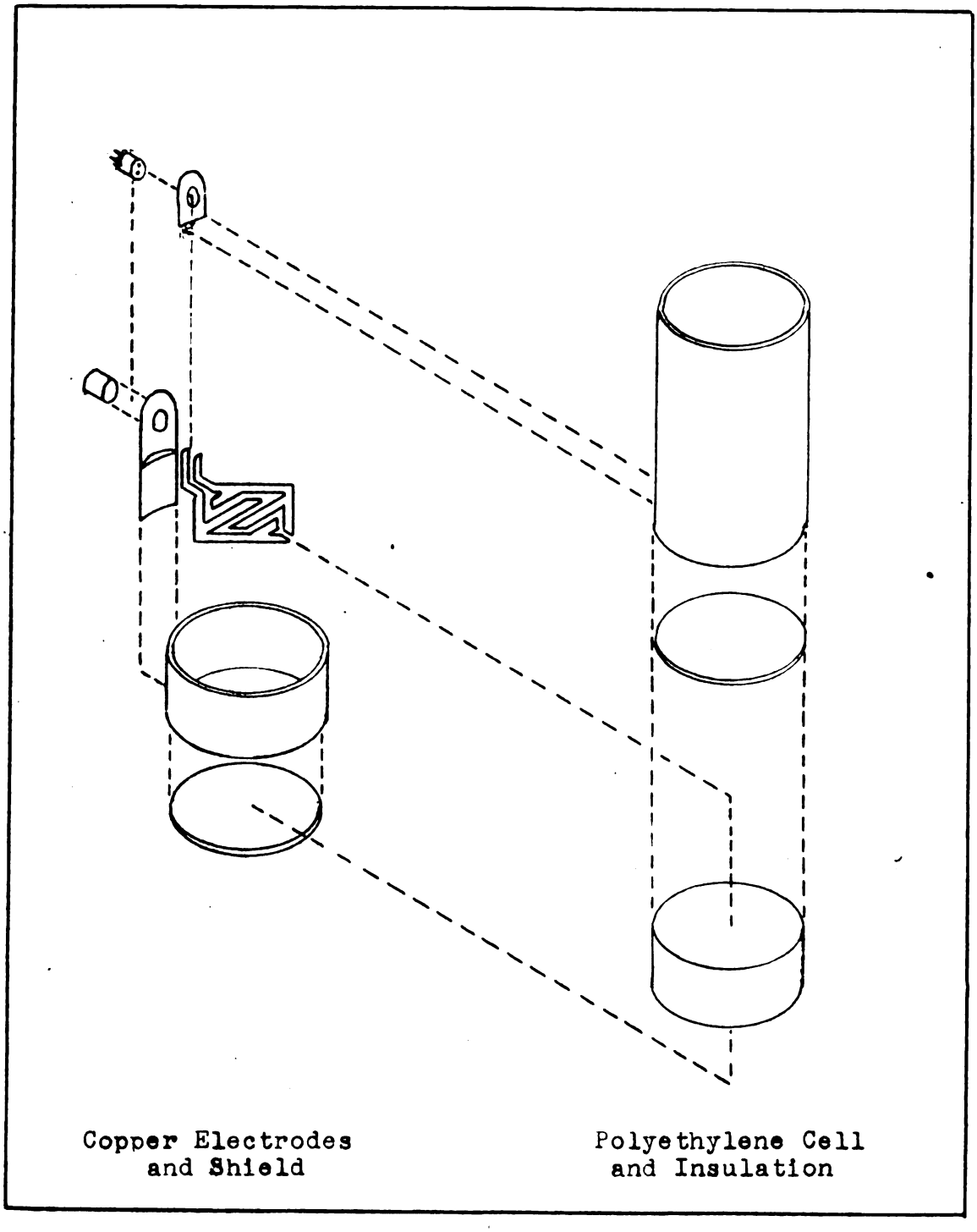

Fig. 12. Polyethylene Base Electrode Cell

General Experimental Procedure

Solutions of known concentrations were pipeted into the experimental cell. Volumes of solution from one ml. to 50 ml. were used. Additional solvent was then pipeted into the titration vessel to increase the volume so that the electrodes were well below the solution surface. Solvent was added in 25 ml., 50ml., or 100 ml. portions depending upon the particular cell used and the volume of solution already present. The instrument was then adjusted to proper working range for the concentration of solution used. This was done by a trial and error choice of a series fixed condenser and adjustment of the C_1 variable capacitor (Figure 6). Upon final adjustment these controls remained fixed throughout the titration. The voltage bias as determined by the R_3 variable resistor up to this point has been zero. The V.T.V.M. is adjusted to the 30 volt range. The R_3 potentiometer is then adjusted, while the instrument is in oscillation, so that the voltage measured is within the proper range[4] and is positive or negative[5] depending upon the choice of "bowl" or "hump" shaped response.

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[4]The proper range choice is an instance of a priori knowledge, however this knowledge is of a general sort which can be determined by a preliminary titration carried out with no bias on the 30 volt scale. In general it was found for the aqueous titrations the range was rarely greater than 3 volts and for non aqueous titrations the range was rarely greater than 1.5 volts.

[5]Since D.C. measurements are being made on the V.T.V.M. it is necessary to reverse the polarity each time the response curve is inverted.

Thus for aqueous titrations the R_3 was adjusted so that the V.T.V.M. registered 0 or 3 volts, with the instrument in oscillation at the initial point of the titration, and with the appropriate polarity for the response desired. For nonaqueous titrations R_3 is adjusted so that the V.T.V.M. registers 1.5 volts with the appropriate polarity. For any one titration the R_3 setting remains constant.

Measurements were made by recording grid voltage or C_2 variable capacitor reading versus ml. of titrant added. Methods of measurement will be discussed below. During the titration the buret tip was below the surface of the solution titrated except where otherwise noted, the stirrer was adjusted to the maximum speed at which no solution swirling occurred. Measurements were taken between 45 and 60 seconds after addition of the titrant except as otherwise noted. This was to permit complete stirring of the solution to take place. The size of titrant increments was such that a greater number readings was taken just before and just after the end point. End points were detected by graphing the oscillator characteristic versus ml. of titrant. At the end point a break in the graph was observed.

Several different techniques were used for obtaining high frequency measurements. One group of related techniques were based on power loss measurements, indicated by change in grid voltage when the circuit was in oscillation. In the other group the change in capacitance necessary to return the in-

strument to its resonant frequency was used as a basis for measurement.

The power loss measurements are made by observing the following characteristics at constant frequency; "cut in voltage", the grid potential at which oscillation just begins, when the "eye" snapped shut as capacitance is removed from the circuit by means of the variable capacitor; "cut out voltage", the grid potential just before oscillation ceases when the "eye" snapped open as capacitance is added to the circuit by means of the variable capacitor; "peak voltage measurement", the maximum potential by adjusting the variable capacitor so that a change in either direction will cause a lowering of the potential as indicated by the V.T.V.M.

Another power loss measurement records the grid potential as increments of titrant are added during titration without changing the variable capacitor from some pre-arranged setting. In this type of measurement the frequency does not remain constant. This is essentially a loading measurement because capacitance and conductance are lumped into a single measurement. Excellent results have previously been reported for this type of measurement (44,45).

Capacitance change measurements were made by two techniques corresponding to cut in and cut out voltage measurements described above. Instead of recording grid potential at the points mentioned, the relative variable capacitor settings in dial units to the nearest tenth of a dial unit were recorded.

These methods will be referred to as cut-in and cut-out capacitance change methods, respectively.

Graphing Procedure

Figures 13 through 27 are selected graphs of the titrations carried out with the instrument described. The graphs represented here are depicted as oscillator characteristic versus percentage of the theoretical amount neutralized. The abcissa is represented in unit of percent of the stoichiometric end point with the center mark equal to 100%. A few of the larger scale graphs start with 60% and 80%. The ordinate is represented in units of millivolts except for Figure 16. Both the independent and dependent variables are recorded as relative units.

Most of the individual graphs are smoothed to minimize end point errors.[6] The individual point probable reading errors, in keeping with the established convention of showing the error as being completely contained in the dependent variable, are shown by circle size in Figures 14-17, 22a-27, the scale of the other figures preclude the use of this convention. The uncertainty shown is the reading uncertainty, other sources of error are discussed below.

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[6]Figure 15 shows both smoothed and non-smoothed graphs for the same titrations. Smoothing graphical results is not uncommon for titrations and consists of drawing as smooth a curve as possible through the probable location of the greatest number of points.

Sources of Error

The error of the method studied, is the error of the location of the end point break with respect to the appropriate percentage values located on the abcissa. Pictorally this error may be represented as the algebraic sum of two errors, displacement of the break on a stationary graph and the displacement of the abcissa values with respect to the break.

The random sources of error can be summarized as errors of standardization, the drawing error, and the error of the individual points. The errors of the individual points are reading errors and instrument errors, such as the change of thermal equilibrium, dilution during the titration, fluctuation of the supply voltage and fluctuation of the circuit parameters due to stray radiation, capacitance, or other undetermined causes. Individual points displaced by random errors did not effect the location of the end point greatly since the graph was recorded as a smoothed curve.

Determinant errors were kept at a minimum by a method of cross checks, such as double readings, and graphing in a manner to minimize prejudgement.

Predictable condition errors such as the cubical expansion of acetic acid solutions (0.11 percent per ^{o}C) standardized at one temperature titrated at another, were either minimized by making the conditions constant or making the appropriate corrections in the calculations.

Discussion of Results

Power loss measurements in aqueous media. The power loss measured here was the loading measurement technique utilizing the "hump" shaped response. The cell used was the polyethylene cell of Figure 12, with a paddle stirrer. The solution consisted of a measured volume of the standardized base diluted with a measured volume of solvent so that the total volume was greater than 50 ml. The parallel capacitors were adjusted so that the V.T.V.M. registered in the region of the first 20 per cent of the frequency resonance curve (an absolute grid voltage of approximately 5 volts). The appropriate V.T.V.M. range was selected by adjusting the R_3 resistor. The titration was carried out using a standard acid solution with the buret tip below the surface. During the titration the instrument controls were fixed. The result was a graph of the volume of titrant versus the scale reading of the biased V.T.V.M.

The purpose of the aqueous titrations was to test the stability and sensitivity of the instrument and to determine the effect of cell geometry and design. These results have been summarized under instrument and cell characteristics.

The aqueous hydrochloric acid, sodium hydroxide titrations of Figure 13 and Table I show the effect of working on different portions of the response curve of Figure 7. In general the curves of Figure 13 give a synopsis of all previously reported curve shapes for this type of titration (4,22,45), from the almost linear (A) through various degrees of curvature (B, C,D) to the inverted one (E,F). The explanation is that the

response voltage is a function of conductance. The titration curve is the locus of a point following the conductance changes on the response curve of Figure 7. Consider the initial point of curve A to be on the left side of the "hump", as the titration progresses and conductance decreases, the locus of the point moves down the graph and the response voltage decreases until the end point is reached. After the end point the conductance increases and the point moves back up the response curve to the right. Consequently when titrant added is plotted against V.T.V.M. readings, or in terms of Figure 7 the vertical position of the moving point, a V shaped curve results.

TABLE I

LOADING MEASUREMENT TITRATIONS OF AQUEOUS HYDROCHLORIC ACID WITH 1.5936 N POTASSIUM HYDROXIDE

Figure 13	Normality	Meq. Taken	Meq. Found	Deviation P.P.T.
A	0.0475	4.767	4.767	0
B	0.0361	8.602	8.602	0
C	0.1927	19.23	19.01	11.5
D	0.3668	36.61	37.00	-10.5
E	0.7163	35.76	35.85	2.4
F	1.494	37.43	37.51	2.0

Similar explanations may be advanced to explain the shapes of the curves B,C,D,E,F, of Figure 13. Thus all the curves of Figure 13 can be considered plots of a moving point to the

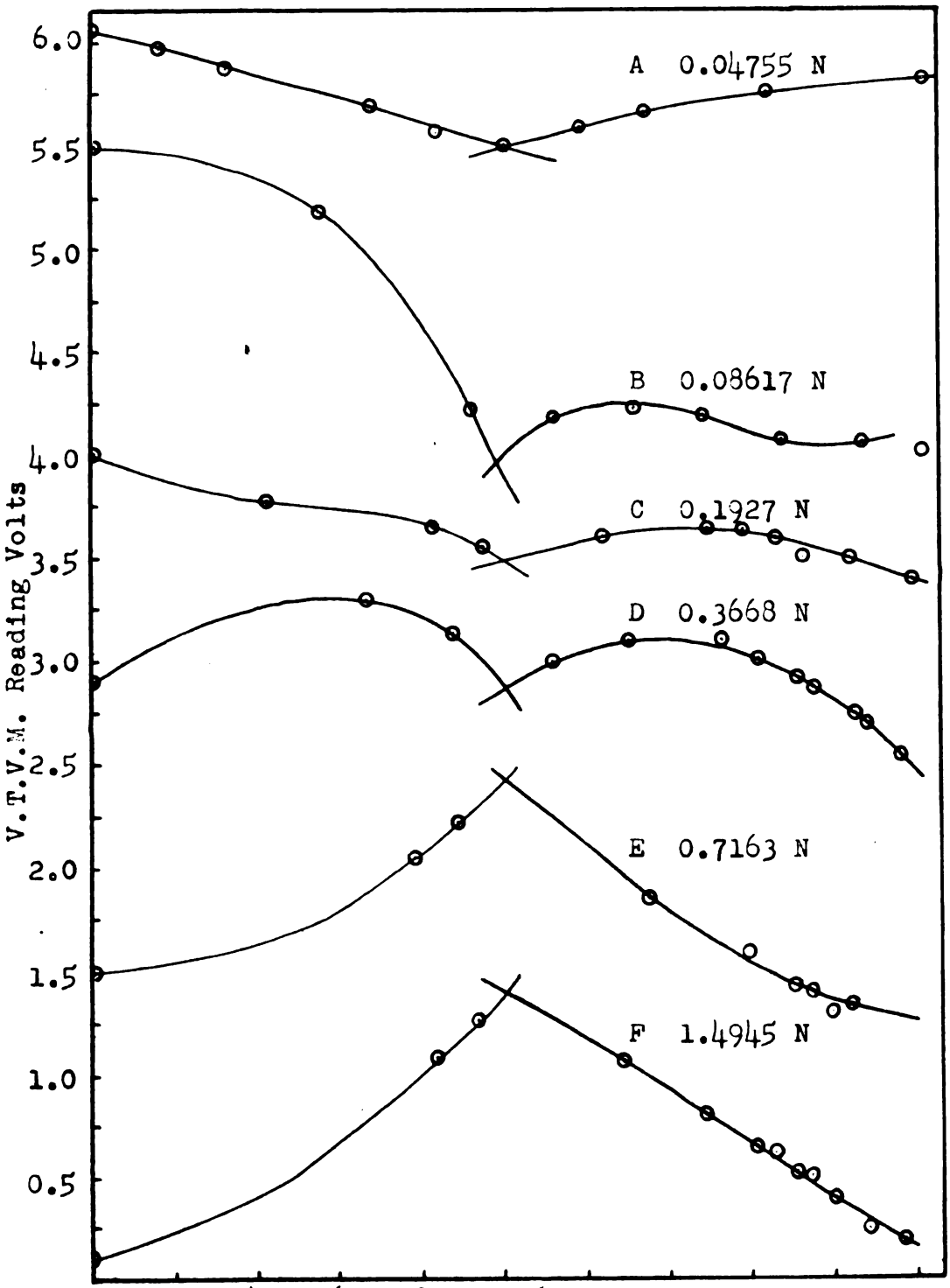

Fig. 13. Aqueous titration of hydrochloric acid solution with 1.5936 N potassium hydroxide

left up to the end point, to the right after the end point, on the "hump" curve of Figure 7. The curved graphs (B,C,D) are a result of the point moving over the curved top portion of the "hump". The inverted graphs (E,F) are a result of the starting point being on the right side of the "hump".

The greatest sensitivity, that is the greatest change of power loss per unit change in concentration and consequently the sharpest end point break, occurs on the straight line side portions of the response curve. Examination of Figure 13 confirms this. Curve A is the only one that does not conform to this general tendency and this is very likely due to the very dilute state of the solution since the change of conductance is small due to the reduced number of ions involved.

The considerations given above for aqueous titrations are analogous to factors present in non-aqueous titrations.[7] However the effects noted are considerably reduced since the substances involved are less ionizable and consequently have a smaller conductance. The solvent systems themselves are inherently less conducive to high conductivities.

In general aqueous titrations gave the most satisfactory results for strong acids titrated with strong bases (Figure 13) and vice versa. Acids such as hydrochloric, sulfuric, and

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[7]Acid base titrations in their widest sense do not necessarily involve interaction of hydroxyl and hydronium ions (34,35,41,42,60). Since high conductivities in the aqueous titrations of Figure 13 are due chiefly to these two ions, it is reasonable to expect that in the absence of one or the other or both, the conductive character of the solution is lowered and considerably altered.

tribasic phosphoric, and bases such as sodium hydroxide, and potassium hydroxide gave excellent results. Weak acids such as dibasic phosphoric, acetic, and monobasic oxalic, when titrated with a strong base gave fair results, end points were not as sharp as those for strong acids. Very weak bases and acids, aniline, phenol, and monobasic phosphoric hitherto unreported in the literature of high frequency titration, when titrated with strong acids or bases respectively, showed no end point break.

Power loss measurements in dioxane media. A series of preliminary titrations were made in dioxane to determine its suitability for adaptation to high frequency techniques. Some comparisons of titrations in each of the respective media are shown in Figure 14. Dioxane, and aprotic solvent, gave a sharp end point where both acid and base were strong, such as pyridine (Figure 14 curve B) titrated with perchloric acid. Weak and intermediate bases, such as aniline, when titrated with perchloric acid (Figure 14 curve A) gave irregular graphs. The titrations represented in Figure 14 curves A and B were carried out at the optimum concentration (approximately 0.01M) for these compounds in dioxane. Other high frequency titrations in dioxane (not shown here) verified these results i.e., diphenylguanidine a strong base gave a relatively sharp end point break, p-toluidine a weak base gave no end point.

Power loss measurements in acetic acid media. Titrations of aniline and pyridine at approximately 0.01M concentration were carried out in acetic acid media (Figure 14 curve C ani-

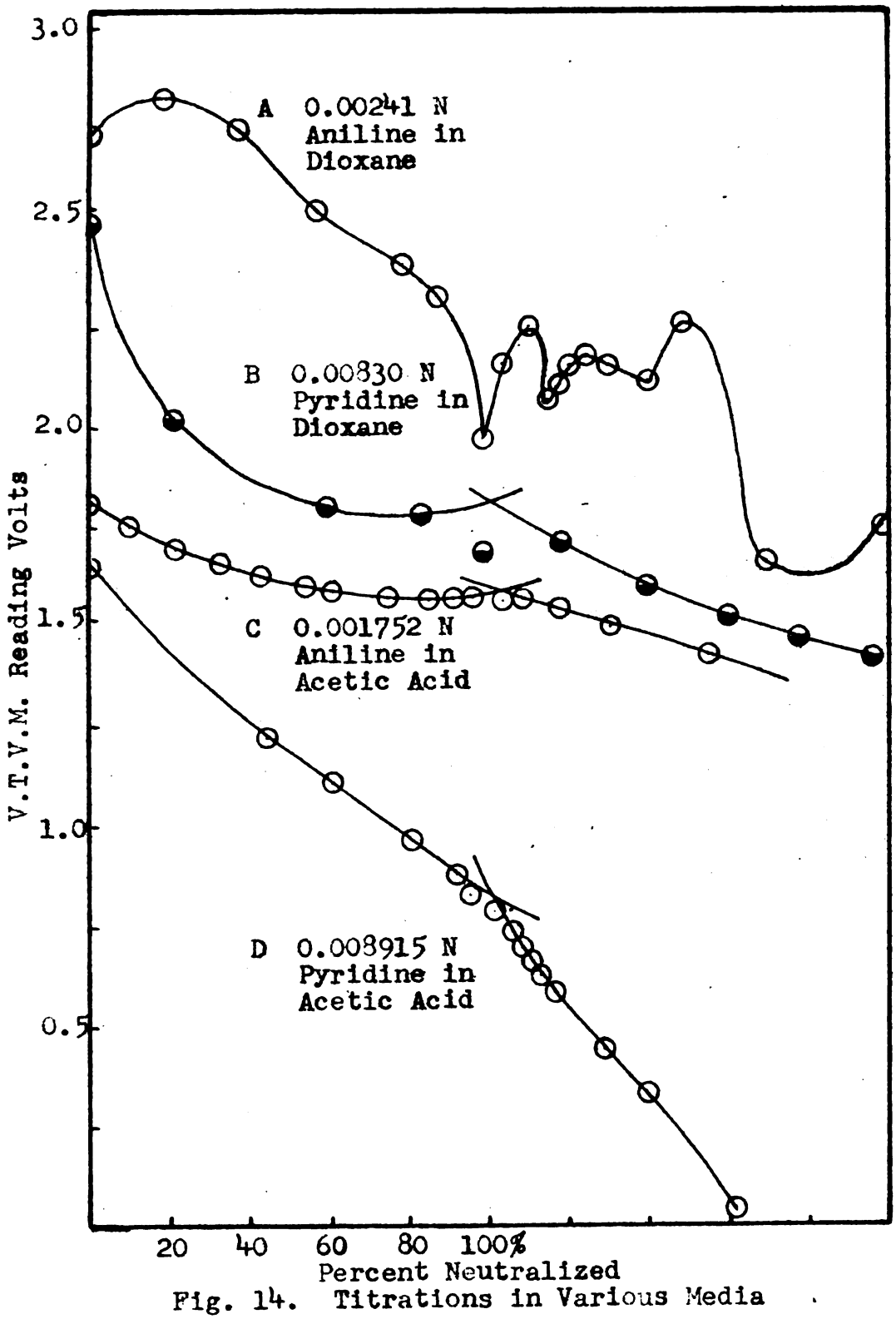

Fig. 14. Titrations in Various Media

line, curve D pyridine) for purposes of comparison with dioxane as a solvent. It will be noted tat the magnitude of the end point break for pyridine in both media is approximately the same even though dioxane measurement was taken in the optimum concentration range and acetic acid measurement was not. Comparison with titrations carried out in the optimum concentration ranges for aniline (Figure 20 curve A) and pyridine (Figure 22 curve C) show much sharper end points in the acetic acid media.

Conventional theories of solvency state that acetic acid as a solvent causes a greater degree of dissociation of weak bases than does water or dioxane as a solvent (34). Thus acetic acid systems allow greater conductance changes during the course of a titration, giving a sharper end point. Theoretically and experimentally acetic acid systems showed a wider range of applicability for weak bases than did water or dioxane systems. For this reason it was decided to confine the investigation of the titration of weak bases to the acetic acid media. One limitation of acetic acid was its power of solvency. Some substances such as aluminum oxinate could not be titrated because of limited solubility.

Concurrent with the study of solvent systems was an investigation of the various possible measurement techniques. Some techniques were superior to others and although each solvent system was tested by each possible technique, the previous discussion was condensed and confined to loading measurements for reasons which will become apparent in the discussion of measurement techniques.

Various operating procedures are feasible as mentioned in the section on experimental methods. The previously described methods of cut in voltage, cut in capacitance, peak voltage, and loading measurements were utilized for the titration of sodium acetate, 8-hydroxyquinoline, and β-alanine, with perchloric acid as the titrant in acetic acid media. (A,B, and C curves respectively for Figure 15,16,17 and 18).

Cut in voltage measurements. The general procedure for this measurement involves the same preliminary steps used for loading measurements. The response measured, was the scale reading of the V.T.V.M. at the onset of oscillation as indicated by the sudden closure of the 6E5 eye. This measurement was obtained by increasing the capacitance, using the C_2 variable capacitor until the instrument was out of oscillation, then carefully adjusting the C_2 capacitor until oscillation just started[3] when the voltage reading was taken.

Curves of the cut in voltage (Figure 15) show the extreme irregularity and a complete lack of end point for this operating procedure. The curves are shown by a dotted line connecting the points, but a more accurate representation comensurating with the uncertainty and irreproducibility of the individual points might be given by the solid curves of Figure 15. The change of voltage at the end point break was of the same magnitude as the uncertainty of the voltage read-

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[3] The stopping of oscillation for each reading is an undesirable characteristic of this method and allied methods, since the instrument is not allowed to reach equilibrium.

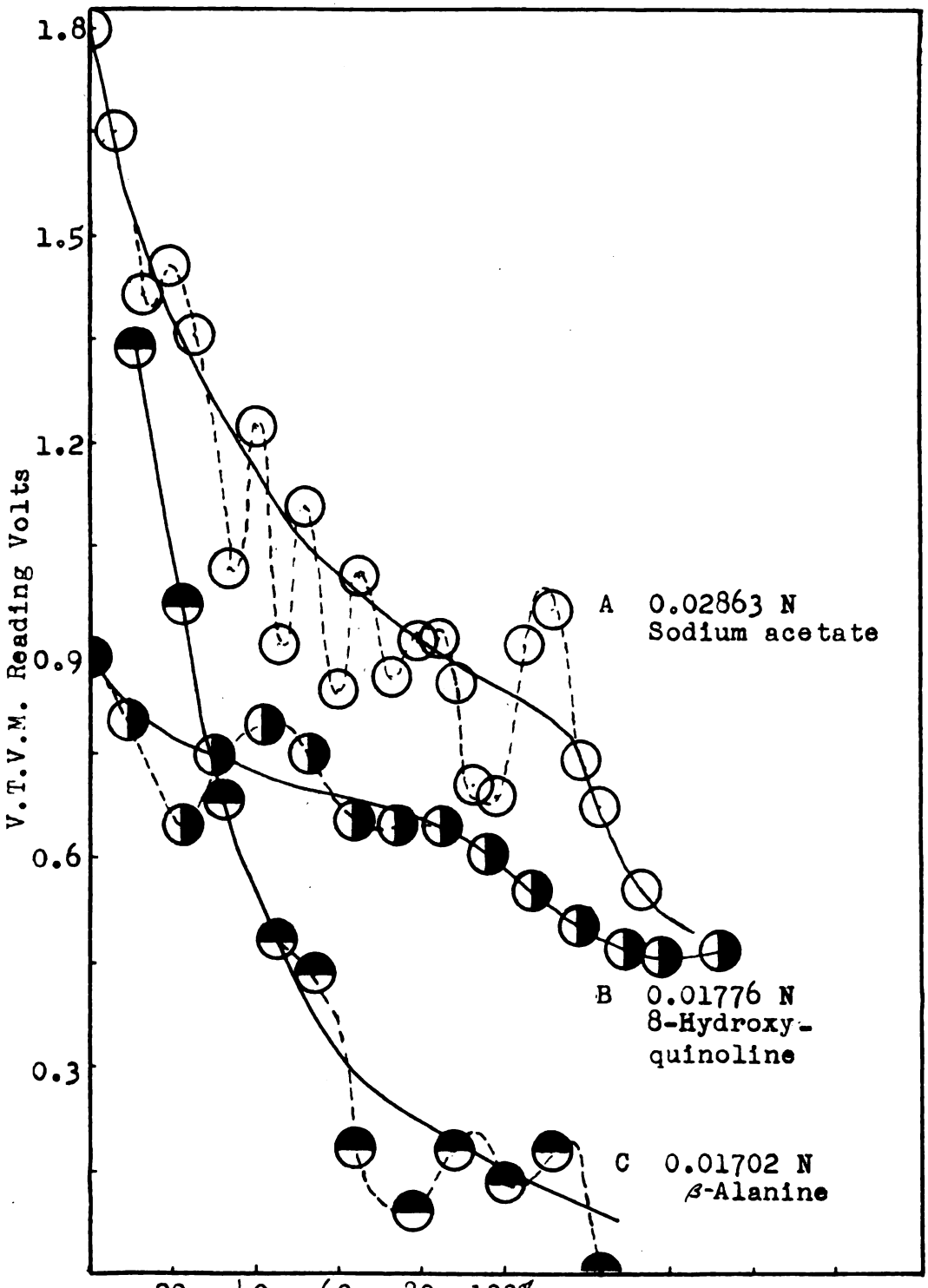

Fig. 15. Cut in Voltage in Acetic Acid Media With 0.1132 N Perchloric Acid

ing (on the order of 250 m.v.). At the start of oscillation for the first 0.3 unit of the C_2 dial (approx. 0.02 mf) the voltage increase was on the order of 2.5 volts. Due to the relatively coarse dial control[9] compared to the voltage change at the onset of oscillation, it was impossible to take a voltage reading and specify it as the cut in voltage. A further defect was an upward creep of the voltage which leveled out after 90 minutes.[10]

Cut in capacitance measurement. Figure 16 and Table II show the results of the same titrations using the cut in capacitance technique. The procedure involved for this measurement is identical to the procedure of the cut in voltage measurements except that the C_2 variable capacitor setting is the dependent variable rather than the measured voltage. Under ideal conditions of concentration end points were observed using this operating procedure, however many of the defects present in cut in voltage measurement are also present here.

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[9]The reaction time of the operator turning the dial at different speeds was a large factor here. Possibly a constant speed mechanical drive electronically operated by the instrument may have decreased this mechanical disadvantage, however it is thought that sufficient backlash in the gear train exists to make even this unworkable. Another possible solution to this problem of refining a coarse adjustment, is to use a smaller C_2 capacitor, however this would effectively cut down the range of the instrument and titrations involving large changes could not be made.

[10]The upward climb of measured voltage is equivalent to a downward creep of grid voltage. The time (t) of the climb of measured voltage is a reciprocal function of the magnitude of the voltage.

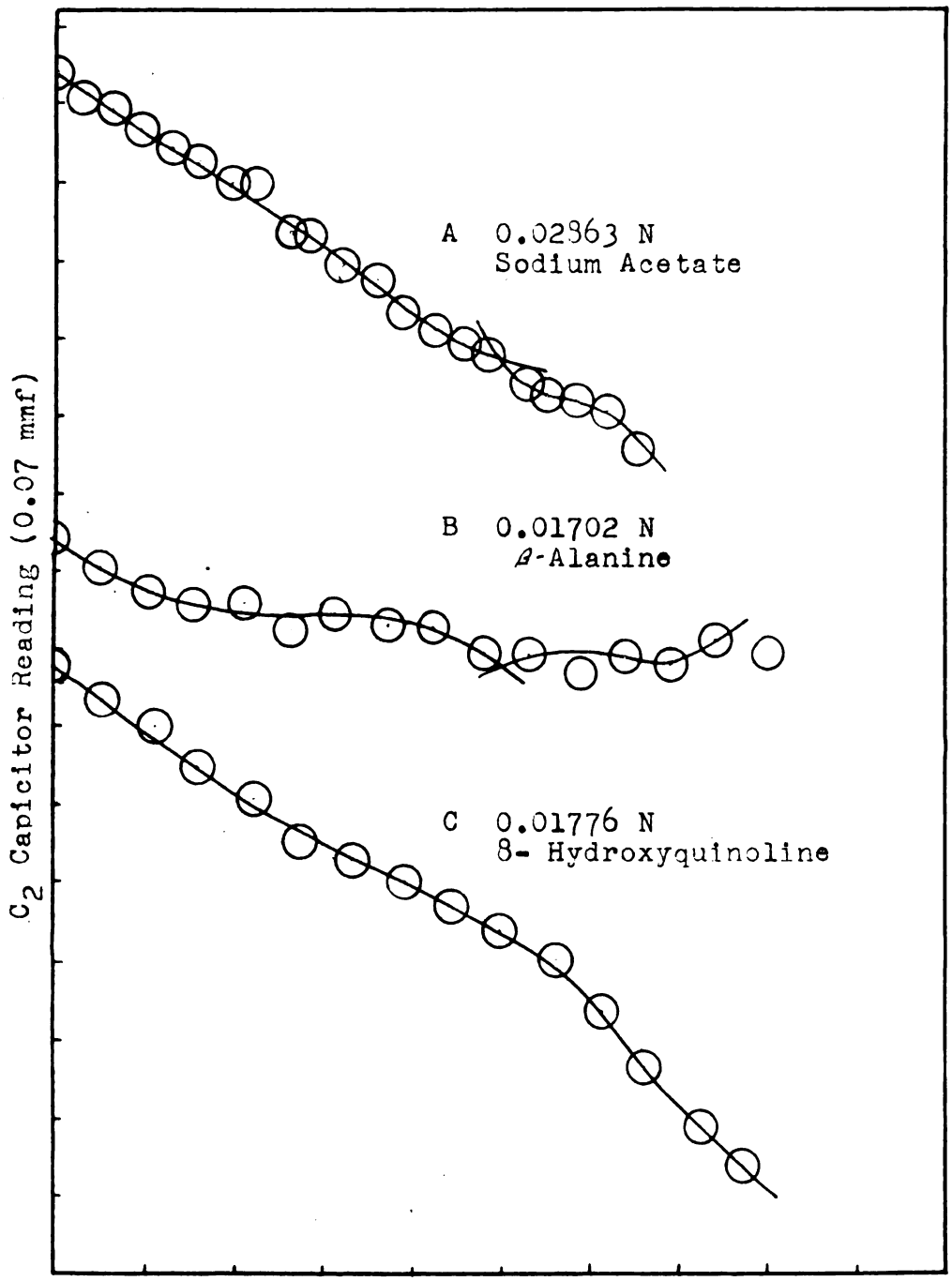

Fig. 16. Cut in Capacitance in Acetic Acid Media with 0.1132 N Perchloric Acid.

TABLE II

TITRATIONS IN ACETIC ACID MEDIA BY DIFFERENT MEASUREMENT TECHNIQUES WITH .1132 N PERCHLORIC ACID

Figure	Substance Titrated	Normality	Meq. Taken	Meq. Found	Deviation P.p.t.
16					
A	Sodium Acetate	0.02363	1.713	1.724	6.4
B	8-Hydroxy-quinoline	0.01776	1.064	1.074	9.3
C	β-Alanine	0.01702	1.019	1.119	83.8
17					
A	Sodium Acetate	0.01702	1.019	1.021	1.9
C	β-Alanine	0.01031	1.131	1.131	0.0
13					
A	Sodium Acetate	0.00357	0.4276	0.4303	2.8
B	8-Hydroxy-quinoline	0.1065	5.307	5.322	2.3
C	β-Alanine	0.01702	1.019	1.019	0.0

It will be noted from Figure 16 and Table II that the end point breaks in terms of dial units were very small (±0.3), since the uncertainty of reproducing a dial setting was ±0.1 the end points obtained were unreliable. The time required (3/4 to 1 hour) to carry out a titration using the method of cut in voltage or cut in capacitance is a disadvantage of the method. The techniques (not recorded here) of cut out voltage and cut out capacitance, in which the procedures are identical with those above except that the point recorded was just before oscillation ceased, suffer the same defects and gave less reproducible results.

Loading measurements. At constant conductance the grid voltage passes through a typical parallel resonance curve with respect to changing capacitance. Any portion of the resonance curve could be used for the titration response if the frequency were kept constant. In practice adjustment of the capacitance is not fine enough to keep the frequency constant except on the flattened maxima of the resonance curve. Due to this instrument characteristic two types of measurement are possible. The first is to allow both the net cell capacitance and conductance to change. The measured voltage is then a function of the lumped parameters, the so-called loading measurement. The second is the so called peak voltage measurement, i.e., the measurement of the maximum grid voltage after each increment of titrant is added, keeping the frequency constant by adjusting the C_2 capacitor. The capacitor adjustment is not critical since the frequency at the maximum grid voltage remains constant over a range of 3.0 capacitor dial units. The resultant graphs of the titrations of both methods are reproducible and in most cases gave good end points. Since the instrument was allowed to warm up for over an hour and was not out of oscillation at any time, thermal equilibrium was maintained.

Figure 17 represents the results obtained for loading measurements, using the procedure of page 43. The voltage range utilized was the first 20 percent of the resonance curve. Curve A of Figure 17 is one of a series of reverse titrations carried out in this study. In this example the titrant was

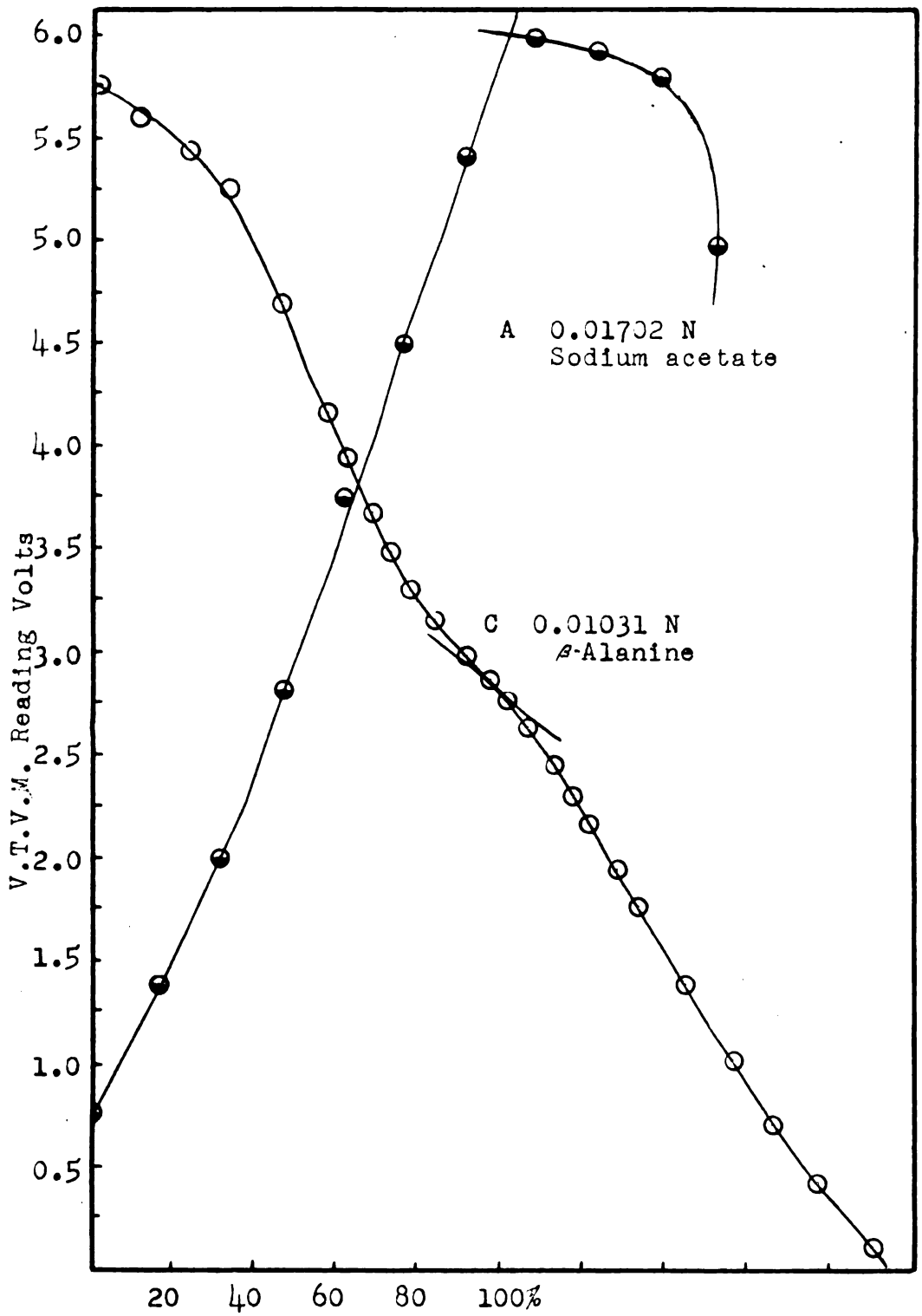

Fig. 17. Loading Voltage in Acetic Acid Media with 0.1132 N Perchloric Acid

sodium acetate and the substance titrated perchloric acid. The emphasized break mentioned above was not noted in the conventional titration of sodium acetate with perchloric acid. In general not all reverse titrations showed this emphasized end point break. From the standpoint of conventional titrations with perchloric acid the reverse titrations for both loading and peak voltage measurements were less satisfactory.

Peak voltage measurements. This is a conductance measurement technique utilizing both "hump" and "bowl" shaped response curves. The titrations listed here have all been carried out using the cell of Figure 12 utilizing a paddle stirrer as previously described. The solution titrated consisted of a measured volume of the standardized base diluted with a measured volume of solvent so that the total volume was greater than 50ml. The parallel capacitors were adjusted so that the V.T.V.M. registered the maximum (about 18 v) or minimum voltage possible depending upon the response used. The appropriate V.T.V.M. range was selected by adjusting the R_3 resistor. The titrations were carried out using standard perchloric acid as titrant.[11] During the titration the C_2 capacitor was adjusted after each increment of titrant so that the maximum or minimum voltage, as the case may be, was registered. The resultant series is plotted as a graph of the percent titrated versus the scale reading of the biased V.T.V.M.

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[11] Several titrations, as noted, are so-called reverse titrations, that is, titration of perchloric acid wih the appropriate base as a titrant.

The graphs of Figure 18 are titrations of (A) sodium acetate (B) 8-hydroxyquinoline, and (C) β-alanine using the peak voltage method of measurement. Acceptable end points are present except for curve C and this is probably due to the very low ionization of β-alanine, (on the order of $K_{B_{H_2O}} = 10^{-13}$).

Comparison of a large number of titrations carried out using both peak voltage and loading techniques gave comparable results with reference to accuracy and reproducibility however in most cases the end point break was noticeably less sharp for the loading measurements. Comparison of curves C of Figure 17 and 18 shows this for the case of β-alanine. This leveling effect was caused by allowing the capacitance to vary during the titration. Several exceptions to this leveling effect were noted in some loading measurement titrations. The sharper than ordinary break of Figure 17 curve A is an example.

Peak voltage measurement was chosen in favor of loading measurements for this study. The reasons are, slightly sharper end points obtained by peak voltage measurements, and the fact that the more concentrated solutions tend to load the tank circuit out of oscillation.

Effect of concentration. A series of titrations on a variety of weak bases was carried out in acetic acid solution, perchloric acid being the titrant. The purpose was to check the characteristic curves obtained for any one substance and the changes that occur in these curves when the solution concentration is varied.

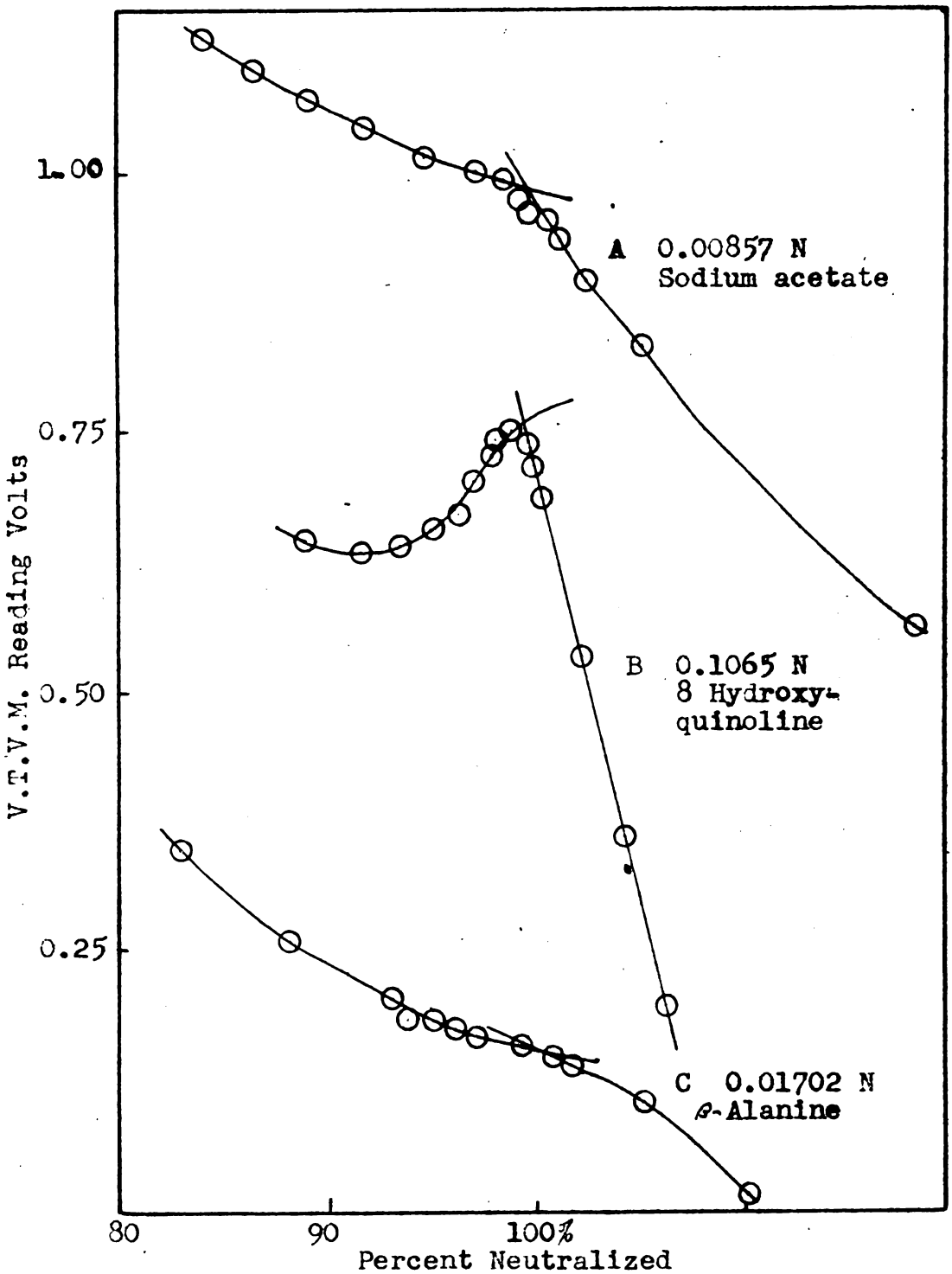

Fig. 18. Peak Voltage Measurement in Acetic Acid Media with 0.1132 N Perchloric Acid

The first series of Titrations were carried out on the base 8-hydroxyquinoline as represented in Figures 19, 19a and Table III.

TABLE III

8 HYDROXYQUINOLINE TITRATIONS IN ACETIC ACID MEDIA WITH .1132 N PERCHLORIC ACID

Figure	Normality	Meq. Taken	Meq. Found	Deviation P.p.t.
19 A	0.1065	5.307	5.292	-2.8
B	0.05261	2.655	2.655	0.0
C	0.00,683	0.5314	0.5314	0.0
19a A	0.002458	0.159	0.1602	5.0
B	0.001774	0.1063	0.1053	-9.4

The most concentrated solutions, curves A and B Figure 19 show a characteristic dip before the end point, most pronounced for curve A. This is caused by the formation of a precipitate which effectively removes the participating ions from solution. Curve C further indicates this tendency although only in a very mild form. During the titration represented by curve C the precipitate formed was evident by only a slight opalescence whereas in titrations A and B large crystals formed. The dip was caused by the summation of two non-linear voltages, one increasing the other decreasing. The depth of the dip depends upon the rate of change of the two voltages.

The tendency observed for 8-hydroxyquinoline is that the end point breaks become more obtuse as the concentration decreases. The titrations of Figures 19 and 19 a were carried

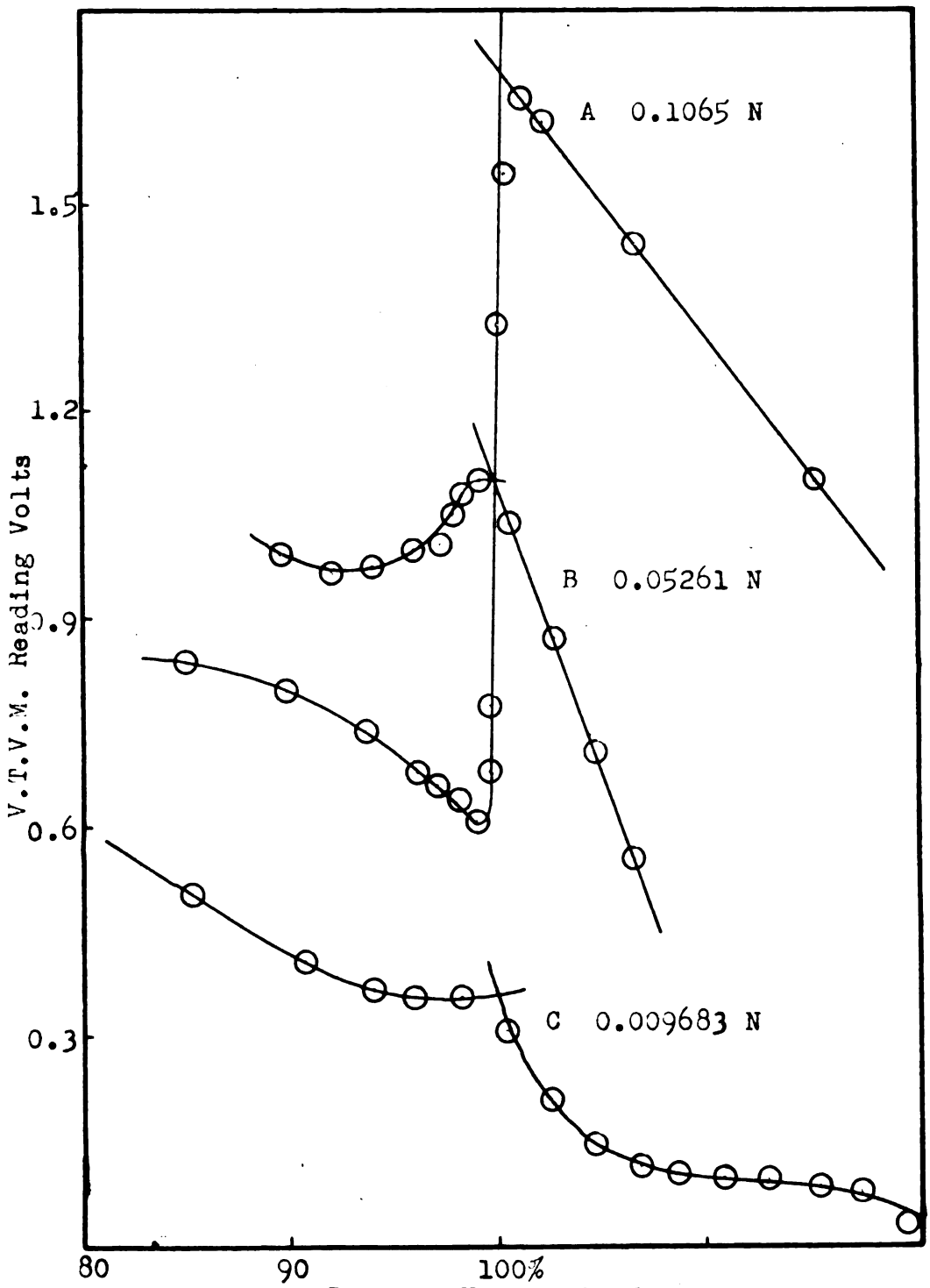

Fig. 19. Peak Voltage Measurements of 8 Hydroxyquinoline in Acetic Acid Media with 0.1132 N Perchloric Acid

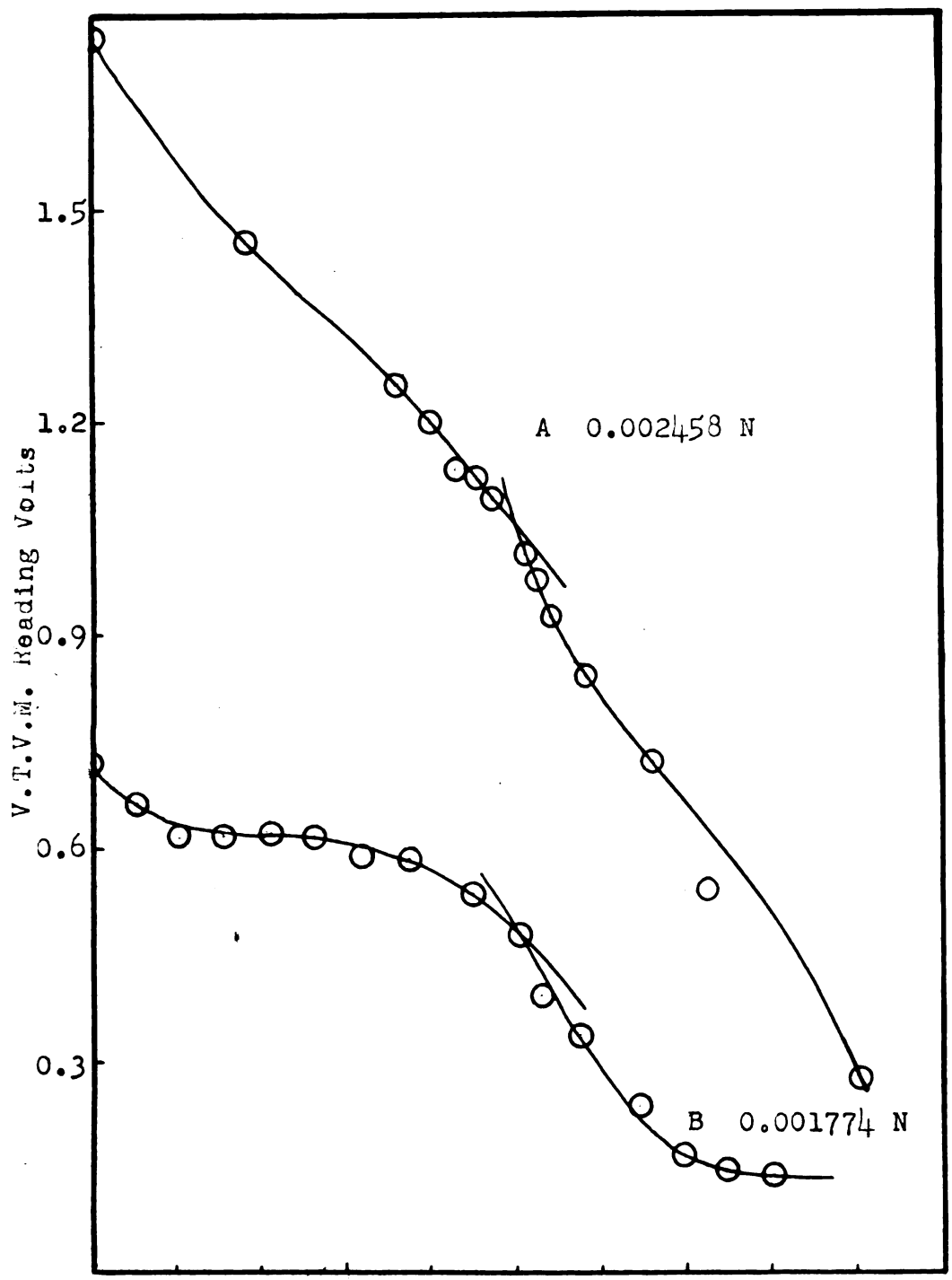

Fig. 19a. Peak Voltage Measurements of 8 Hydroxyquinoline in Acetic Acid Media with 0.1132 N Perchloric Acid

out on the right side of the "hump". In curve C of Figure 19 and curves A and B of Figure 19a the top of the "hump" was approached from the right as is indicated by the shape and direction of the curvature. The decreasing sharpness of the curve at the lower concentrations on the right side of the "hump" corresponds to the higher error level of these titrations shown in Table III. The left side of the "hump" with the corresponding increase of sensitivity evidently occurs at concentrations too low for practical analysis. The more reliable results occur at higher concentrations, however a specific optimum concentration cannot be predicted since the sharpness of the end point break due to sensitivity is obscured by the precipitate dip.

Figure 20 and Table IV are titrations of various concentrations of aniline in acetic acid media using perchloric acid titrant.

TABLE IV.

ANILINE TITRATIONS IN ACETIC ACID MEDIA WITH .1132 N PERCHLORIC ACID

Figure 20	Normality	Meq. Taken	Meq. Found	Deviation P.p.T.
A	0.05288	2.643	2.663	8.0
B	0.01765	1.056	1.066	9.4
C	0.00525	0.2630	0.2593	-14.2
D	0.00175	0.1049	0.1038	-10.0

Wagner and Kaufman have reported results for this particular system (65) using the technique of frequency change

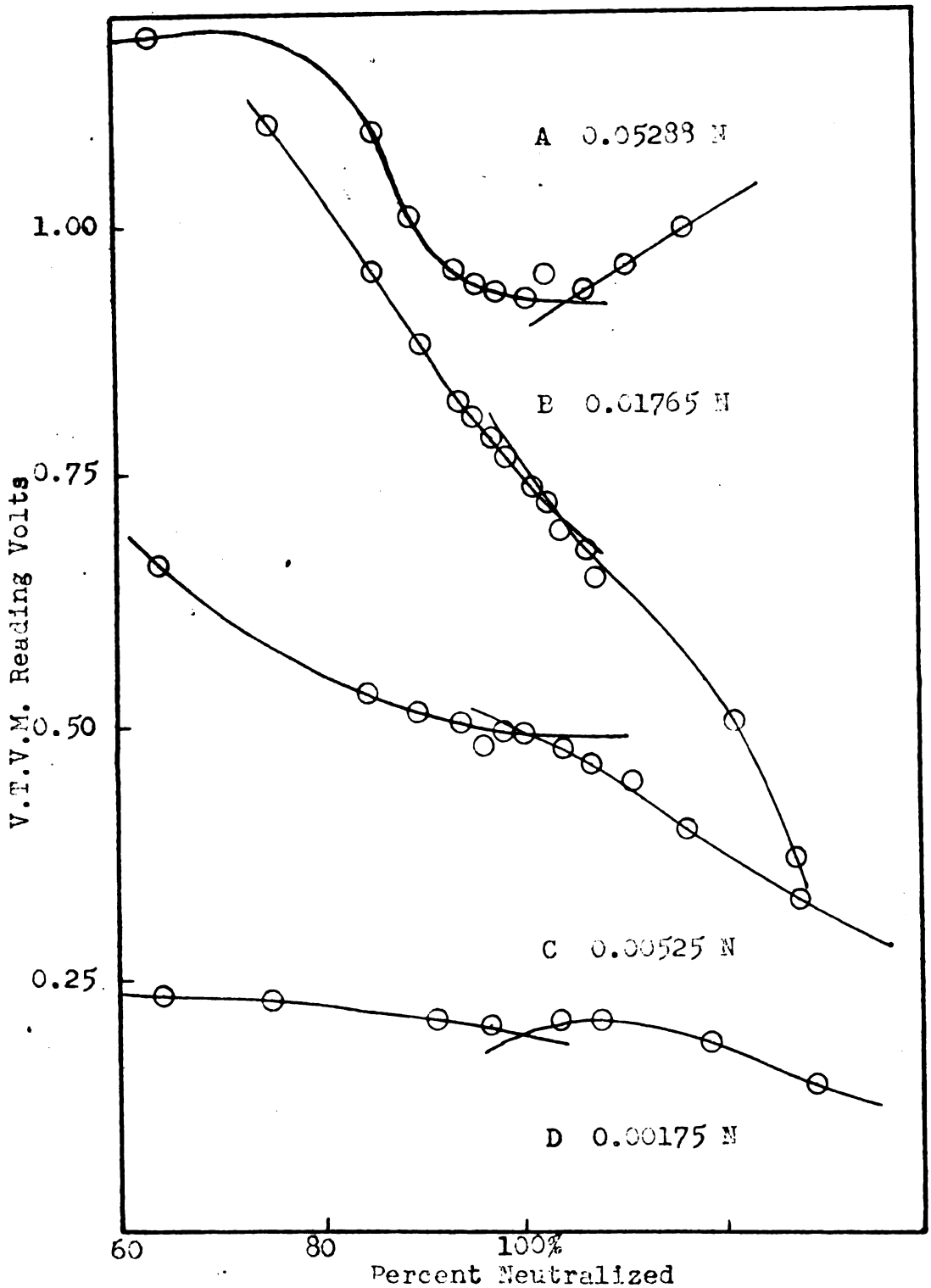

Fig. 20. Peak Voltage Measurement of Aniline in Acetic Acid Media with 0.1132 N Perchloric Acid

measurement. The relative sharpness of the end point breaks are approximately the same for the two methods. The graphs of Wagner and Kaufman show a more linear relationship of the response than do the graphs on Figure 20. The relative accuracy of the two methods will be discussed in the final section.

In the curves of Figure 20 titrations were made on both sides of the "hump" shaped response curve (Figure 7). The curves may be explained in terms of changing conductances. The K_B of aniline is small and the conductance change due to the removal of the base by titration is negligible. The conductance change due to the salt which is appreciably highly dissociated is relatively large. During a titration, up to the end point, the conductance for dilute solutions increases due to the formation of a salt more ionizable than the original base. After the end point the conductance increased at a greater rate than before due to addition of the excess acid which has a higher conductance than the salt. In terms of voltage from the right side of the "hump" (Figure 12) the voltage decreases up to the end point at a certain rate and decreases at a faster rate after the end point. Since the overall conductance change depends upon overall concentration change, the more concentrated solutions will have a larger total voltage change. This can be seen by comparing curves B and C of Figure 20. The size of the end point break depends upon the difference of the conductance change before and after the end point.

Curve D, shows even less of an overall voltage change in addition to having a V shape caused by a crossing over the "hump" at the end point. Titration A departs from the above considerations of shape and overall slope in that the concentration of the solution is high enough to supress the ionisation of the salt formed. In this respect it is essentially a non aqueous buffer solution with respect to the salt. These observations verify the fact that aniline is a weak base in acetic acid, and postulates that aniline perchlorate though not a "weak" salt is not completely ionized in acetic acid. Aniline in acetic acid is a relatively weak base, therefore an optimum concentration for titration as such does not exist, however a greater overall conductance change occurs at the higher concentrations.

A series of titrations were made of various concentrations of hexamethylenediamine in acetic acid media with perchloric acid as the titrant. The results of these titrations are shown in Figures 21 and 21a and Table V. The hexamethylenediamine titrations are straight forward in every respect, the salt is strongly ionized, the base moderately so, and there is no precipitate formation. There is but a single end point break, this indicates that the basic groups are indistinguishable and that hexamethylenediamine acts as a mono-acid base.

The overall grid voltage change in the dilute curves is toward increase in conductance on the left side of the "bowl" for Figure 21 curve C and D, and Figure 21a curves A,B, and C. This indicates that the conductance increase prior to the

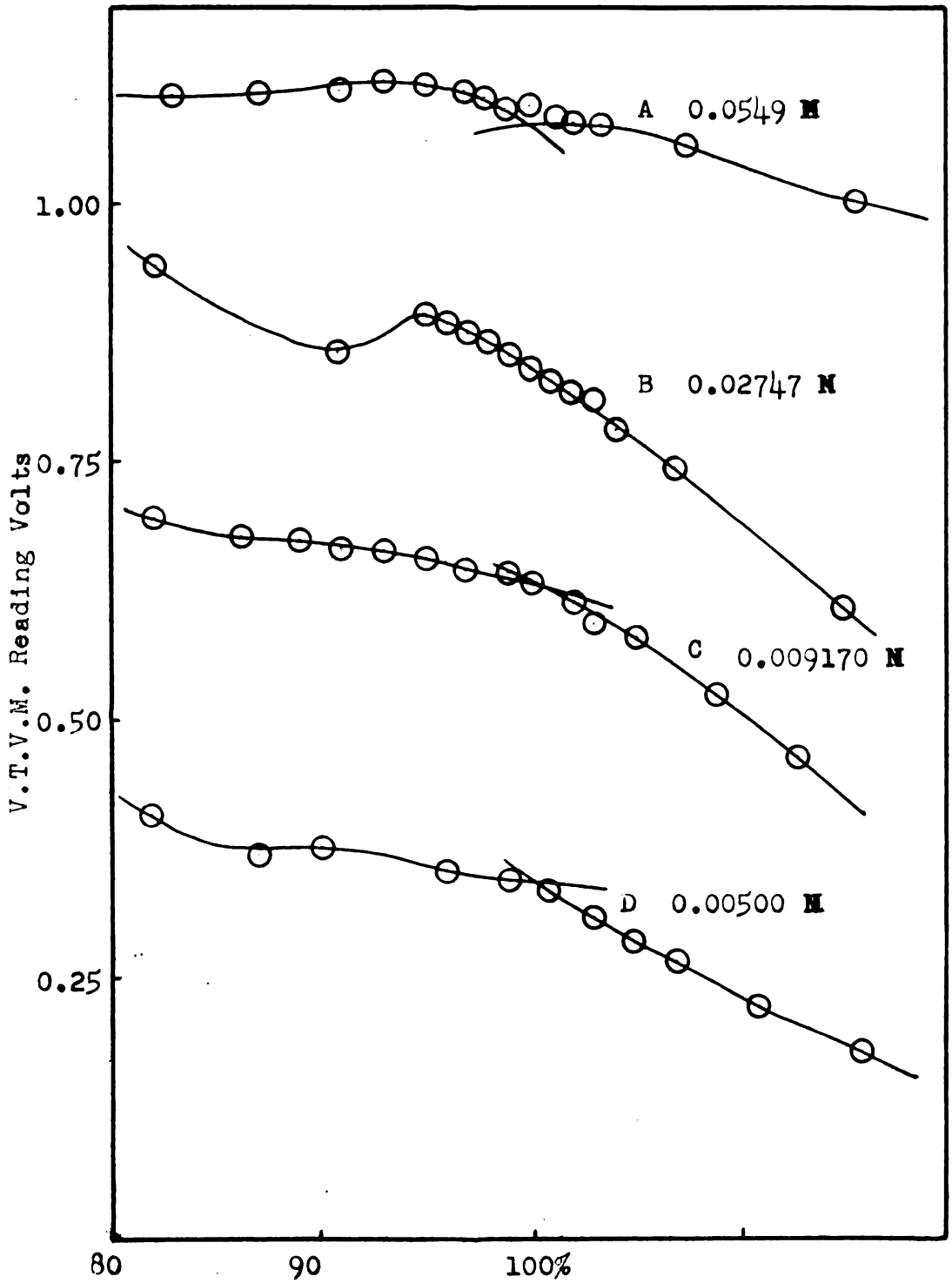

Fig. 21. Peak voltage measurement of hexamethylenediamine in acetic acid media with 0.1132 N perchloric acid.

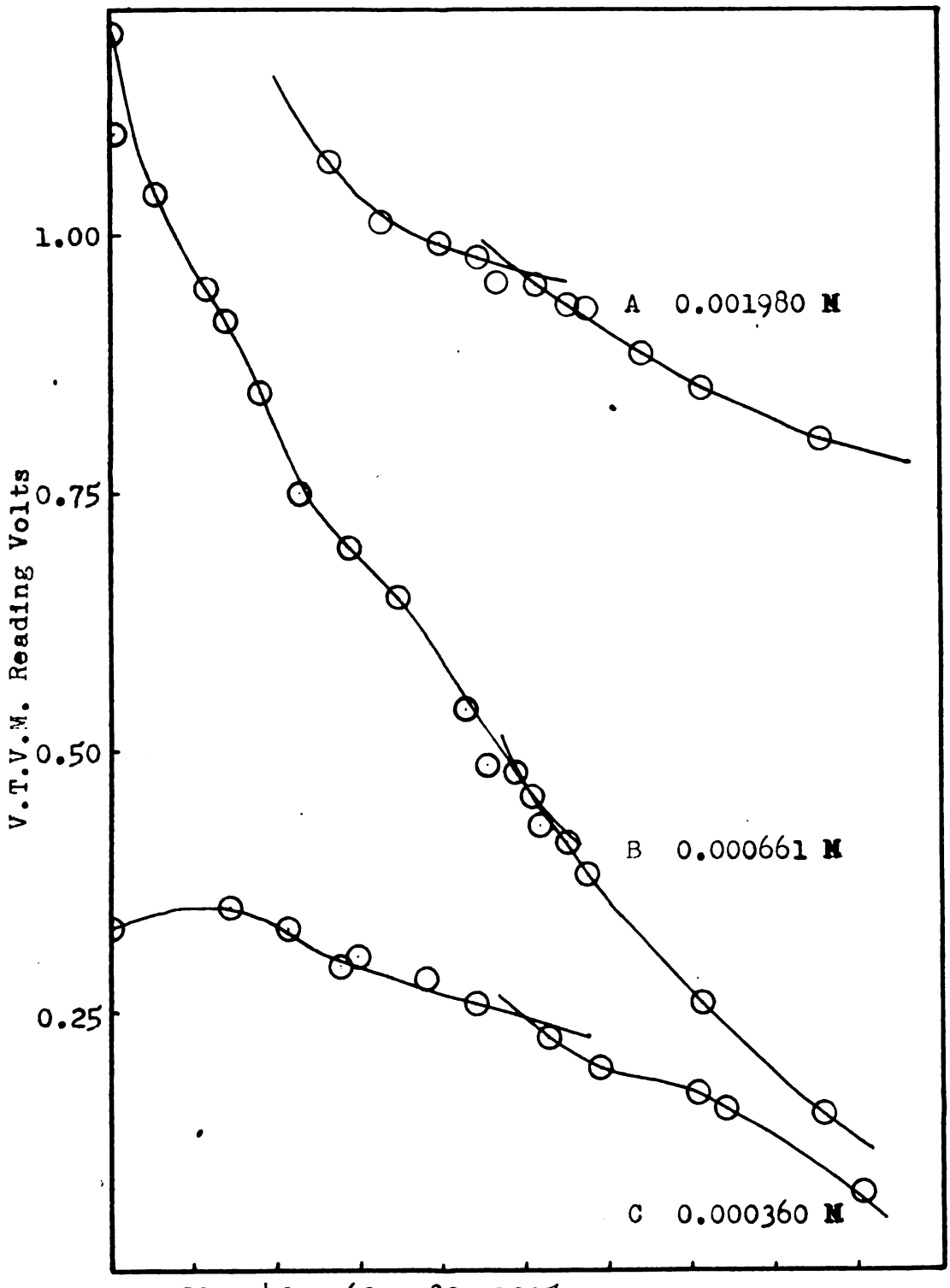

Fig. 21a. Peak voltage measurements of hexamethylenediamine in acetic acid media with 0.1132 N perchloric acid.

end point, due to salt formation is greater than the conductance decrease due to base titration. The end point of curve B Figure 21 occurs at the minima of the "bowl" and consequently displays no break. Titration A Figure 21 occurs on the right side of the "bowl" and consequently displays a V shape. It can also be noted that the degree of curvature remains relatively constant while the sharpness of the breaks decrease with decreased concentration. Optimum concentration for titration occurs in the more concentrated region.

TABLE V.

HEXAMETHYLENEDIAMINE TITRATIONS IN ACETIC ACID MEDIA WITH .1132 N PERCHLORIC ACID

Figure	Molarity	Mmo. Taken	Mmo. Found	Deviation P.p.T.
21 A	0.0549	2.736	2.734	-.8
B	0.02747	1.375	1.376	0.2
C	0.00917	0.5484	0.5463	-3.6
D	0.00500	0.2740	0.2740	0.0
21a A	0.00198	0.09920	0.09970	5.0
B	0.000661	0.03956	0.03956	0.0
C	0.000360	0.01976	0.02016	20.0

Figures 22 and 22a and Table VI represent a series of titrations of various concentrations of pyridine in acetic acid media with perchloric acid as the titrant. The curves of these Figures show the typical dip prior to the end point due to the formation of a precipitate (65). The dip is most evident in curve C of Figure 22, less so in curve D and vanishes

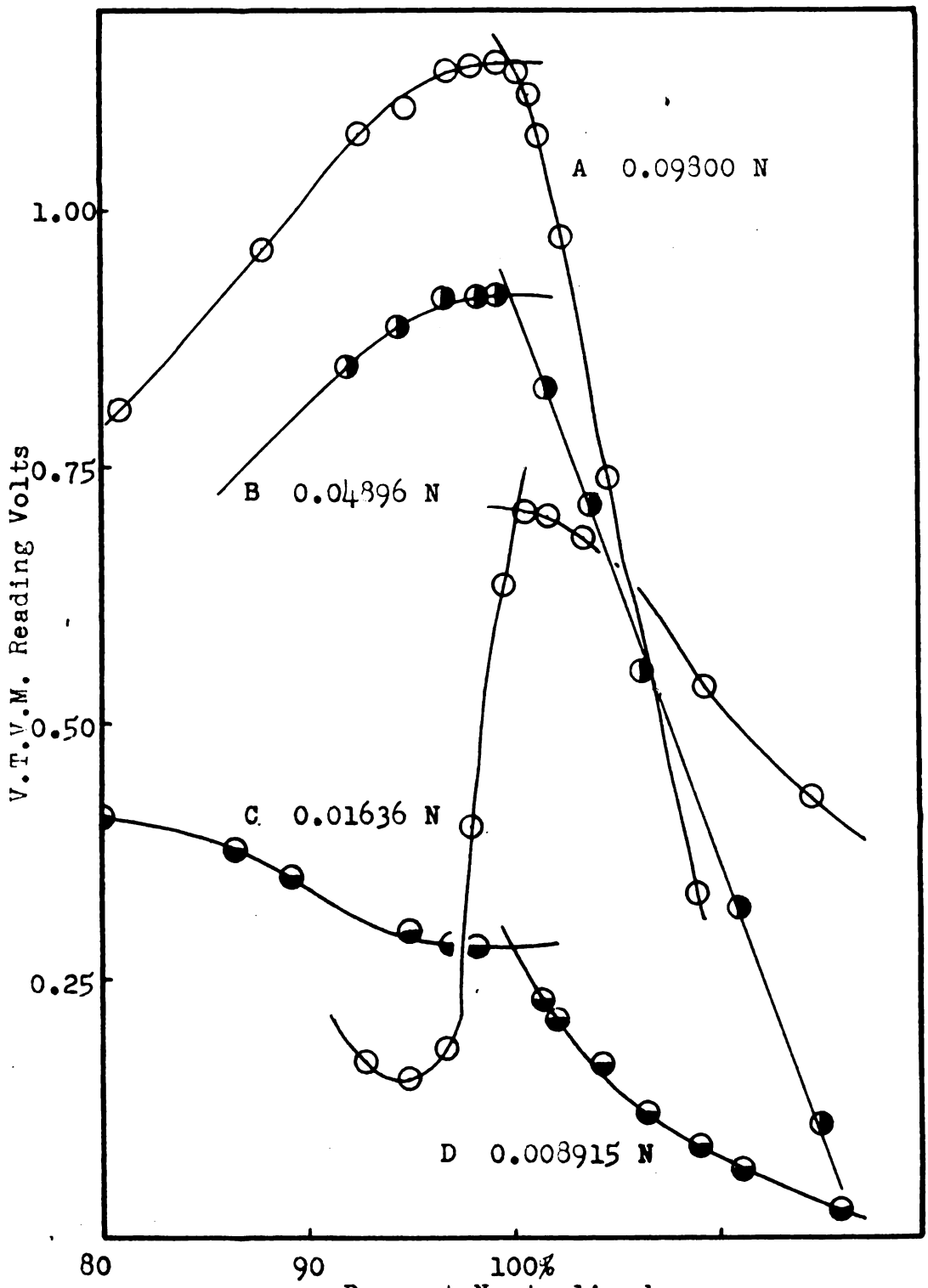

Fig. 22. Peak voltage measurement of pyridine in acetic acid media with 0.1132 N perchloric acid.

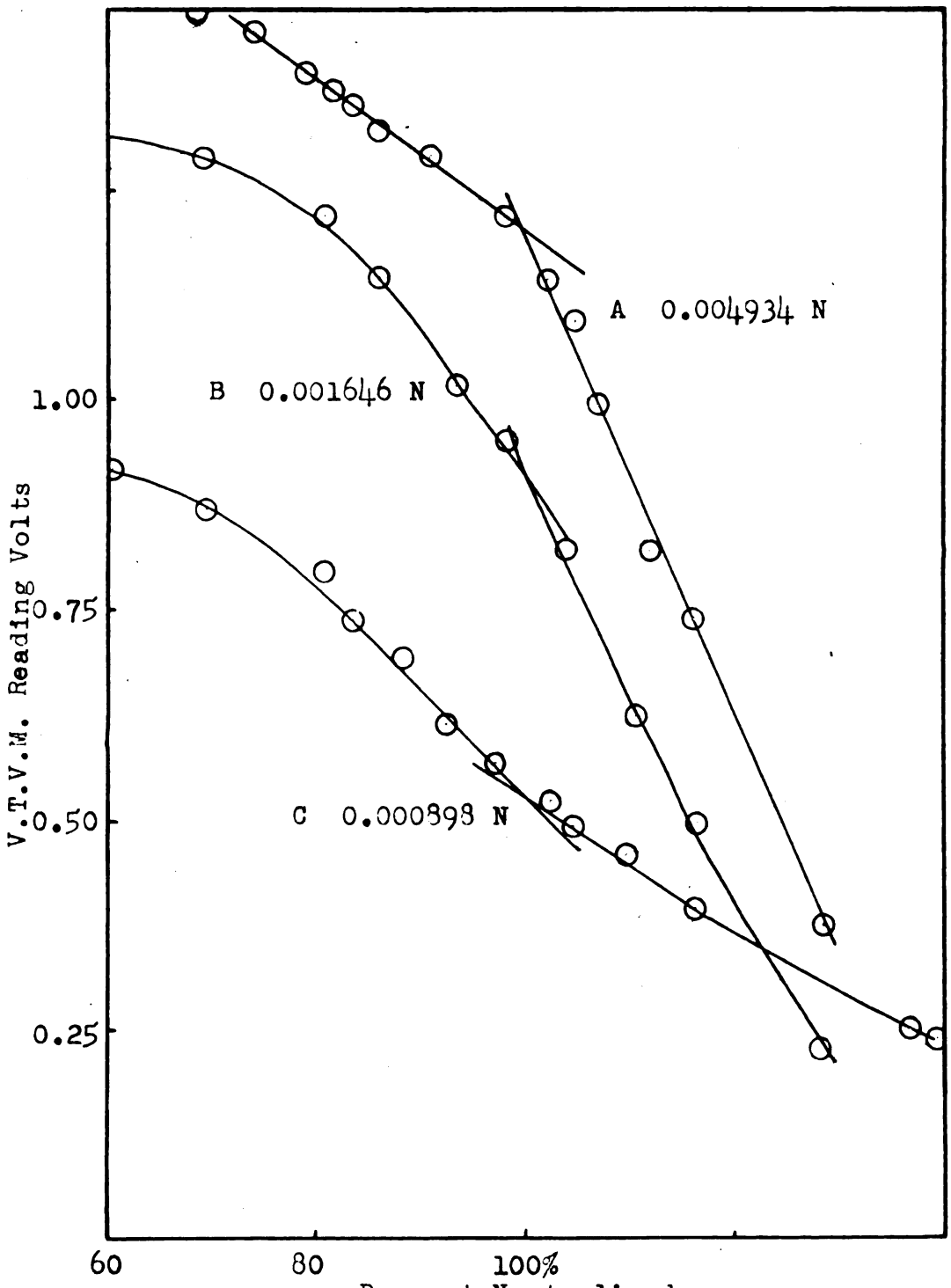

Fig. 22a. Peak voltage measurement of pyridine in acetic acid media with 0.1132 N perchloric acid.

completely in the graphs of Figure 22a. The precipitate dip, of curves A and E, Figure 22, are not shown since the abcissa coordinate starts at 80 percent. All the titrations except C of Figure 22a had their initial inception on the right side of the "hump" shaped response curve. As the concentration decreases for this series of titrations so does the sharpness of the end point. Optimum concentration here is in the more concentrated regions as it was for 8-hydroxyquinoline.

TABLE VI.

PYRIDINE TITRATION IN ACETIC ACID MEDIA WITH .1132 N PERCHLORIC ACID

Figure	Normality	Meq. Taken	Meq. Found	Deviation P.p.T.
22 A	0.09800	4.883	4.9126	0.6
B	0.04896	2.014	2.0360	1.1
C	0.01636	0.9790	0.9790	0.0
D	0.008915	0.4880	0.4978	2.0
22a A	0.004934	0.2022	0.2022	0.0
B	0.001646	0.09850	0.09358	-5.0
C	0.000898	0.04919	0.04722	-4.0

The graphs of Figures 23, 23a, and 23b represented in Table VII are the titrations of various concentrations of diethylaniline in acetic acid media with perchloric acid as the titrant. The titrations of Figures 23 through 23b show the results which would have been predicted except for curve B Figure 23a. These curves, "tent" or V shaped depending upon whether the left or the right side of the "bowl" curve was used to show typical titration curves resulting from the con-

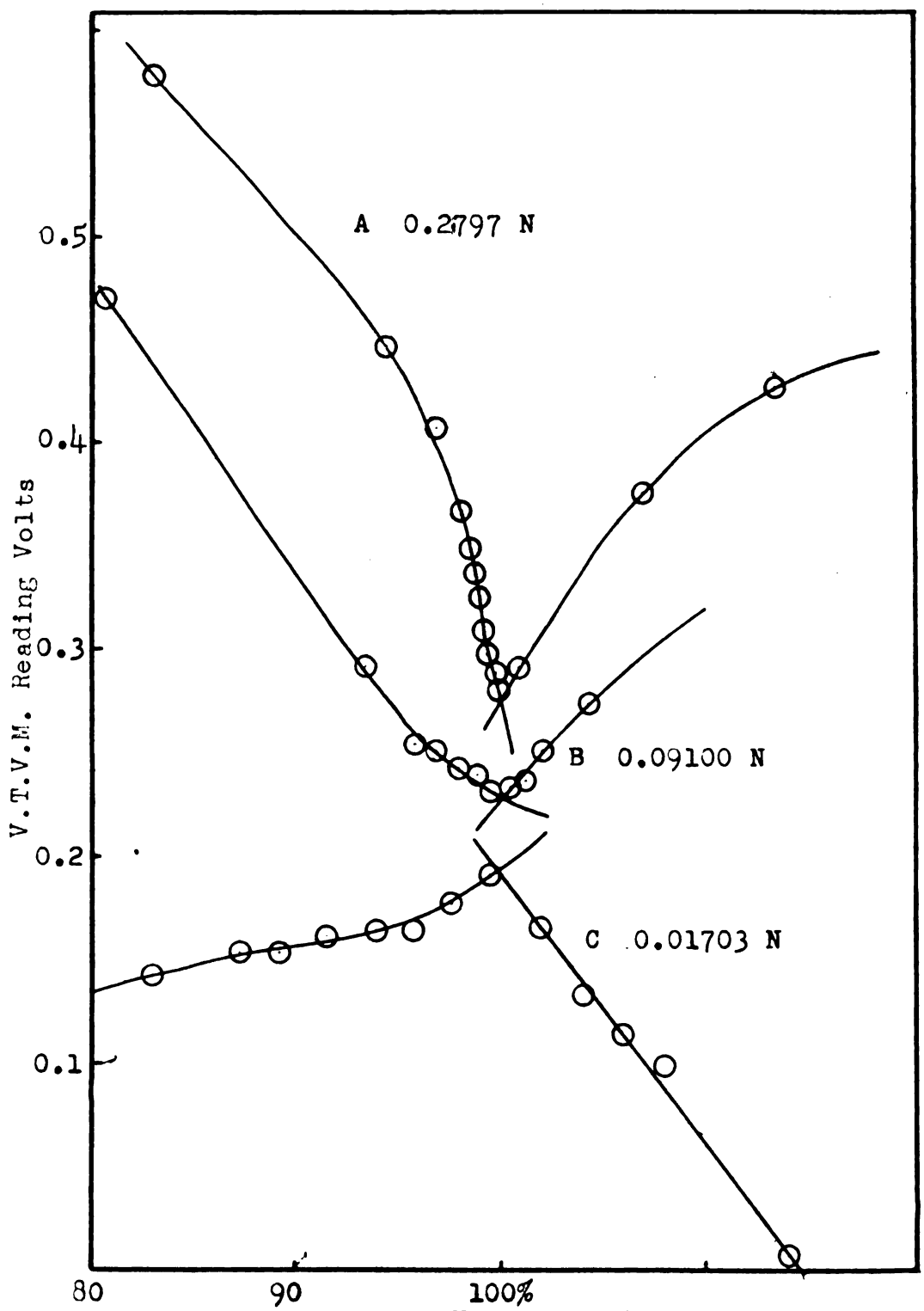

Fig. 23. Peak voltage measurement of diethylaniline in acetic acid media with 0.1132 N perchloric acid.

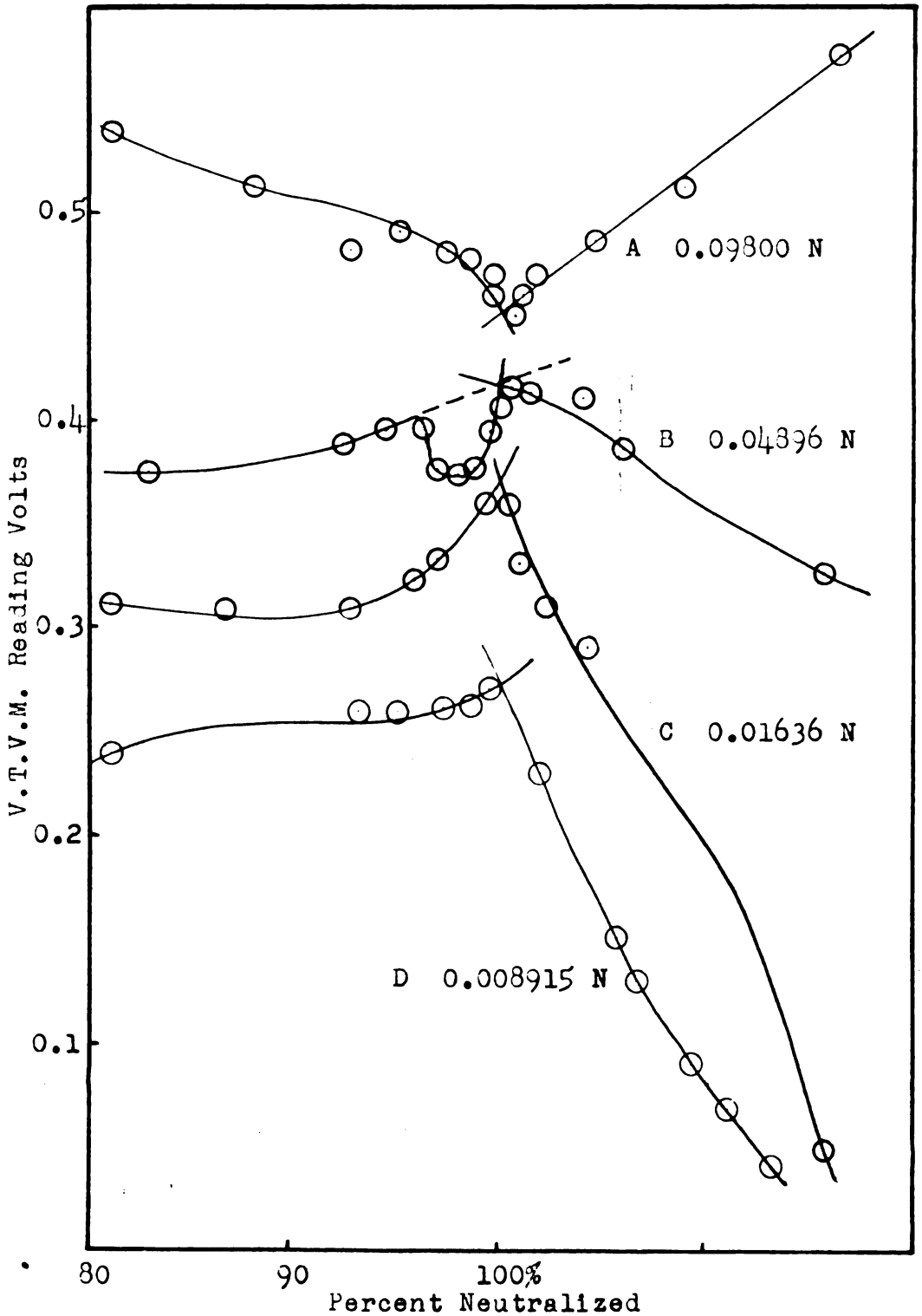

Fig. 23a. Peak voltage measurement of diethylaniline in acetic acid media with 0.1132 N perchloric acid.

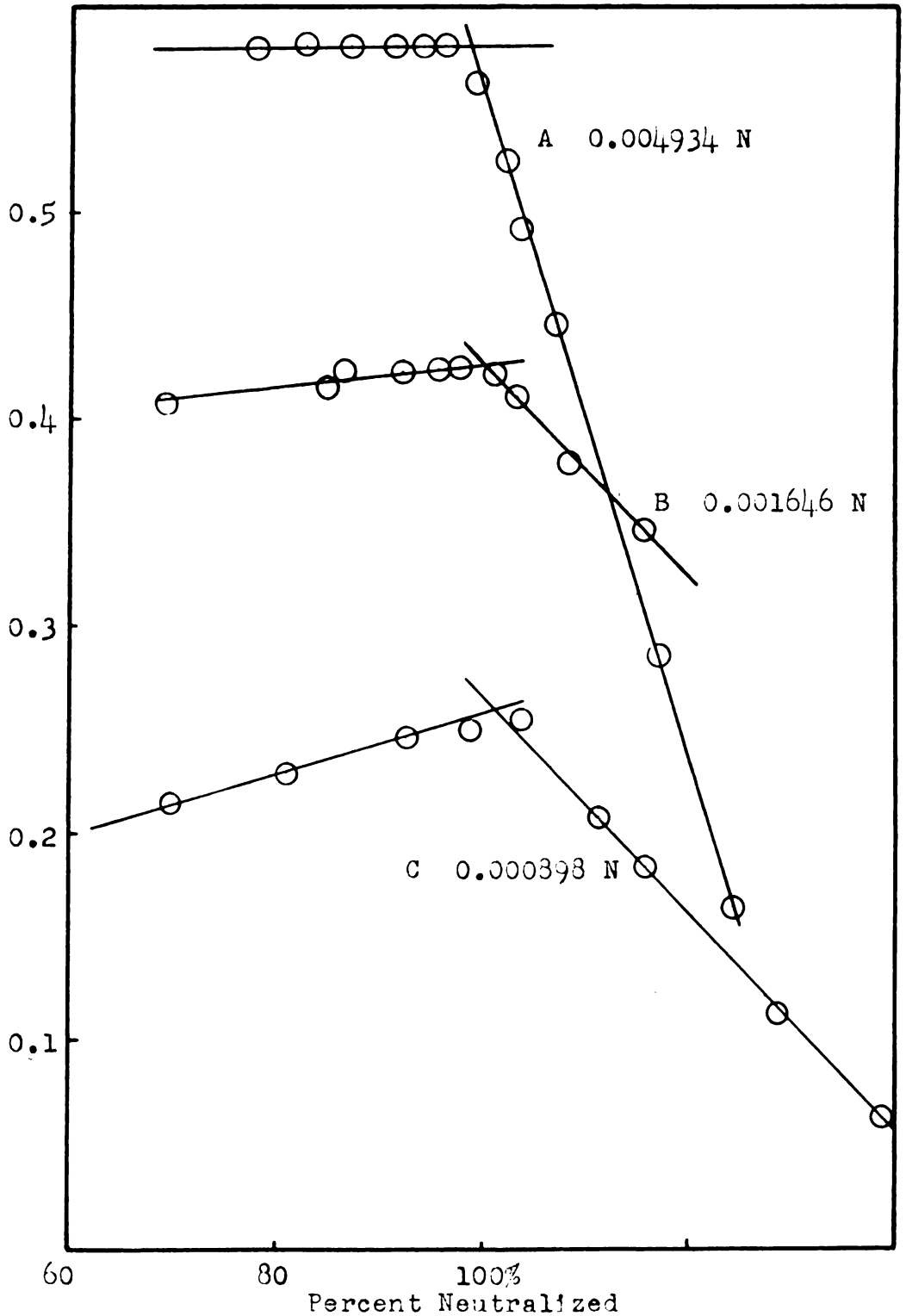

Fig. 23b. Peak voltage measurement of diethylaniline in acetic acid media with 0.1132 N perchloric acid.

ductance changes when a medium strength base is titrated with a strong acid and the salt formed is soluble and highly ionized. The titrations of Figures 23 through 23b could be termed the titrations of a well behaved system.

TABLE VII.

DIETHYLANILINE TITRATIONS IN ACETIC ACID - DIOXANE

.1132 N PERCHLORIC ACID

Figure	Normality	Meq. Taken	Meq. Found	Deviation P.p.T.
23 A	0.2717	9.099	9.099	0.0
B	0.09100	5.440	5.440	0.0
C	0.01073	0.5445	0.5445	0.0
23a A	0.09300	4.833	4.893	2.0
B	0.04896	2.455	2.455	0.0
C	0.01636	0.9790	0.9741	-5.0
D	0.008915	0.4890	0.4890	0.0
23b A	0.004934	0.2470	0.2450	-8.1
B	0.001646	0.09850	0.09850	0.0
C	0.000898	0.04920	0.0487	-10.1
23c A	0.000898	0.04920	0.04959	8.0
B	0.000898	0.04920	No E.P.	No E.P.

The graphs of Figure 23b were made for the expressed purpose of showing that a perfectly linear response can be obtained with a well behaved system provided that the response range is so chosen that the straight side of the "bowl" curve is utilized. In Figure 23b, as in Figures 23 and 23a, a decrease of sensitivity results with a decrease in concentration. Ti-

tration B of Figure 23a displays a small dip before the end point, the cause of which is not known. This dip could not be duplicated, and all subsequent titrations of this system at and near this concentration, yielded graphs whose appearance is a graph indicated by the dotted line replacing the dip. A plausible explanation of this effect is, that at the time of measurement there was a variation in supply voltage.

The curves of Figure 23c are of titrations identical with the C graph of Figure 23b except for the addition of the neutral salt, sodium perchlorate, which was added for the purpose of determining the result of lowering the total resistance of the solution. In curve A Figure 23c the solution is 0.0227 N sodium perchlorate and curve B is 0.0455 N sodium perchlorate. The addition of a small amount of a neutral salt to the solution titrated in curve C Figure 23b resulted in a decrease of sensitivity (curve A Figure 23c). This lessening of the end point break was generally noted where the concentration of the neutral salt was not sufficient to dampen oscillation completely. The more concentrated the neutral salt in the titrated solution the greater the uncertainty and random spreading of individual points (Curve B Figure 23c).

Effect of base strength. Titrations in acetic acid media using conventional methods of end point detection have been investigated by a great number of workers. A few of these investigators have made an attempt to put acetic acid systems on the same mathematical footing as aqueous systems. (41 to 43

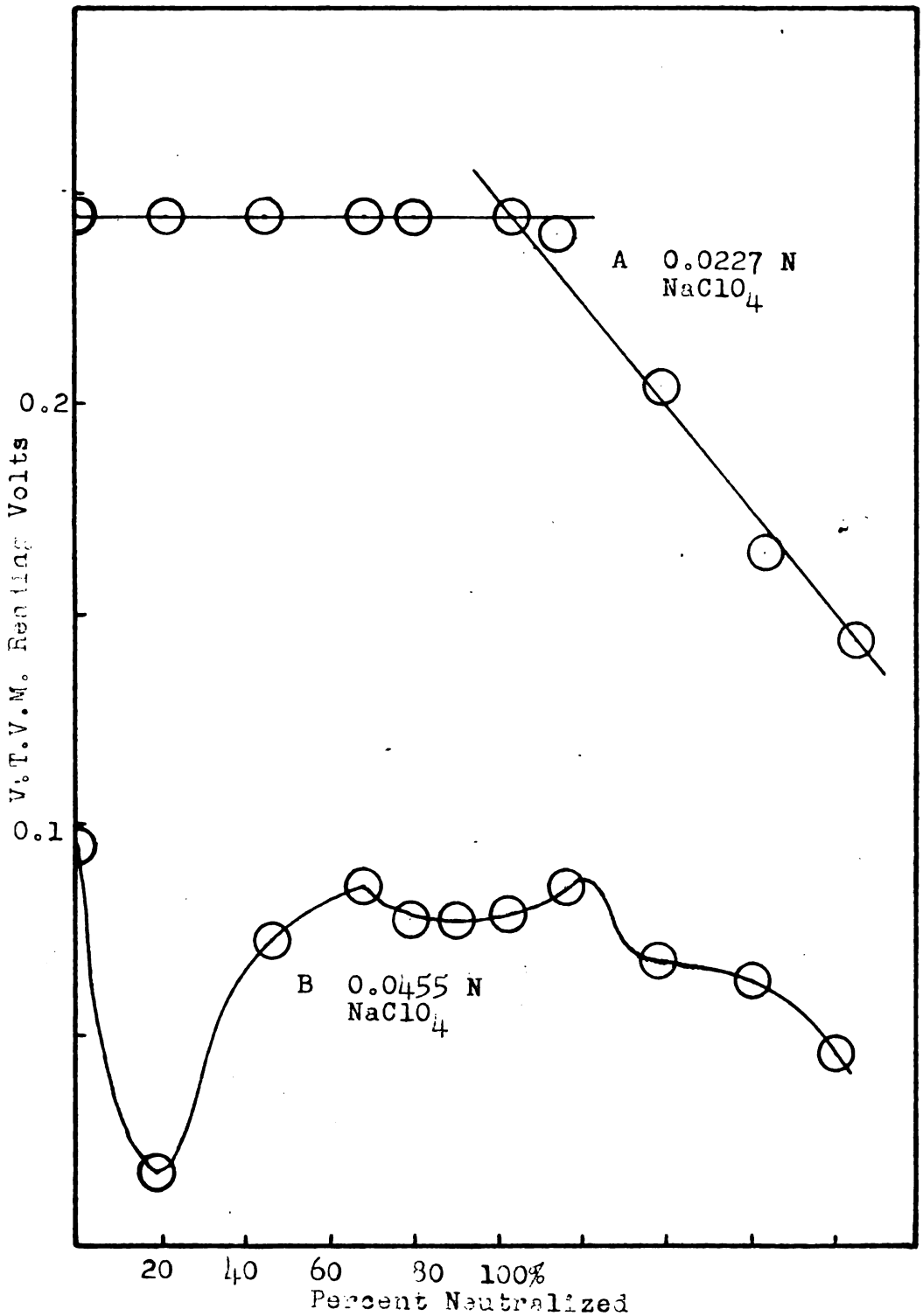

Fig. 23c. Peak voltage measurement of 0.000838 N diethylaniline with neutral salt added in acetic acid media with 0.1132 N perchloric acid

and 63). This numerical classification of acetic acid-weak base systems though not complete and of questionable absolute value (59), allows an ordering of the bases titrated in this study, from strongest to weakest. With the bases thus ordered according to strength, titrations under identical conditions should show characteristic differences due to the base itself and differences in degree of ionization. The ordered titrations of bases are shown in Figures 24, 24a and Table VIII. These titrations have been carried out using the peak voltage technique in acetic acid media with perchloric acid as the titrant.

TABLE VIII.

COMPARISON OF TITRATIONS OF BASES OF DIFFERENT STRENGTHS IN ACETIC ACID MEDIA WITH .1132 N PERCHLORIC ACID

Figure	Base Titrated	Normality	Meq.Taken	Meq.Found	Deviation P.p.T.
24 A	Pyridine	0.01636	0.9790	0.9790	0.0
B	Diethyl-aniline	0.008915	0.4890	0.4890	0.0
C	Hexame-thylene-diamine	0.009170	0.5484	0.5484	0.0
24a A	Aniline	0.01765	0.056	1.066	9.4
B	β-Alanine	0.009290	0.5090	0.5905	1.0
C	Urea	0.009175	0.5030	No E.P.	No.E.P.

Comparison of the titration curves show a progressively poorer end point break as the basicity decreases until no end point at all is evident for the urea titration (curve C Figure 24a). Curve A of Figure 24 shows the typical tent shape

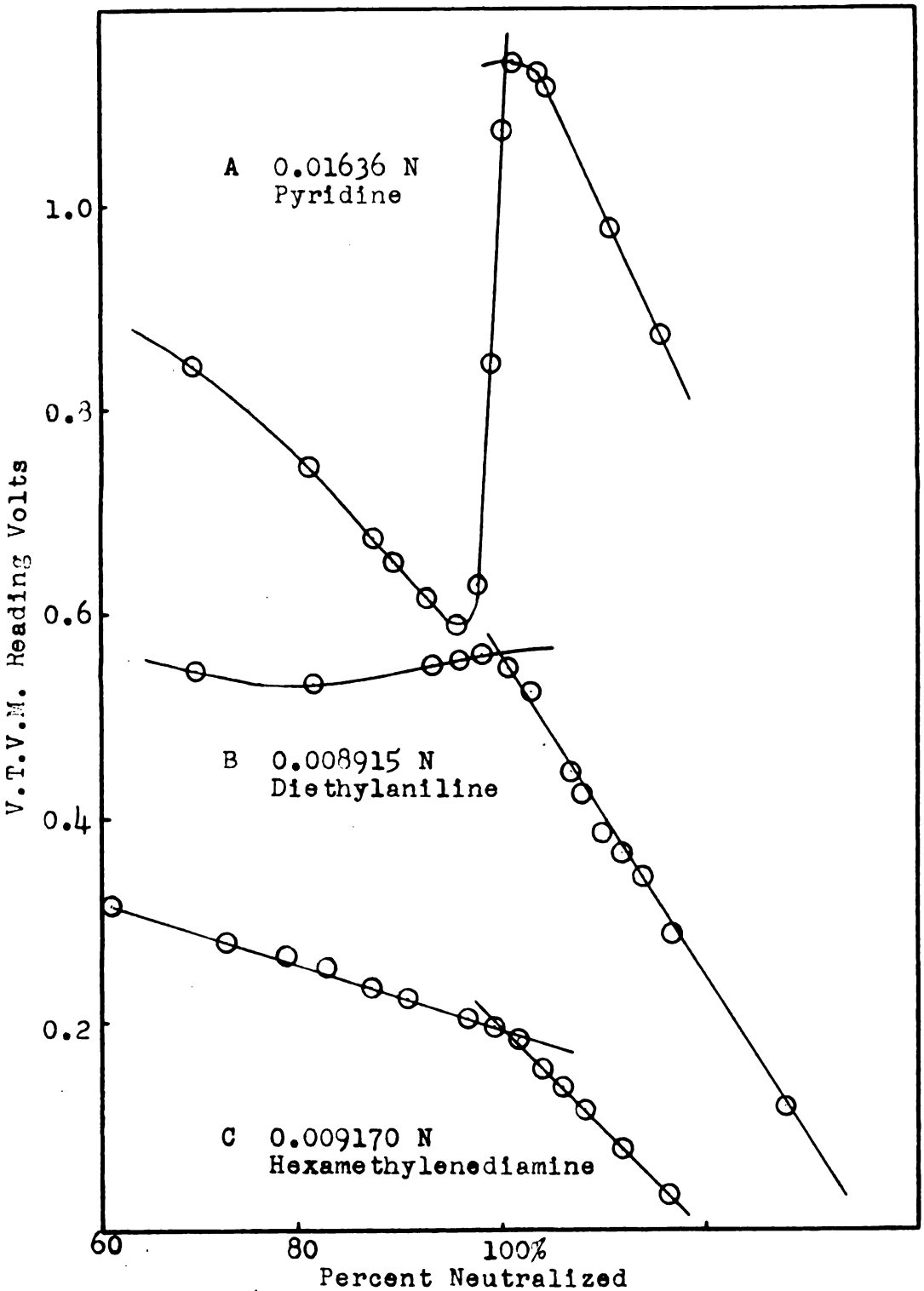

Fig. 24. Peak voltage measurement of base strength in acetic acid media with 0.1132 N perchloric acid.

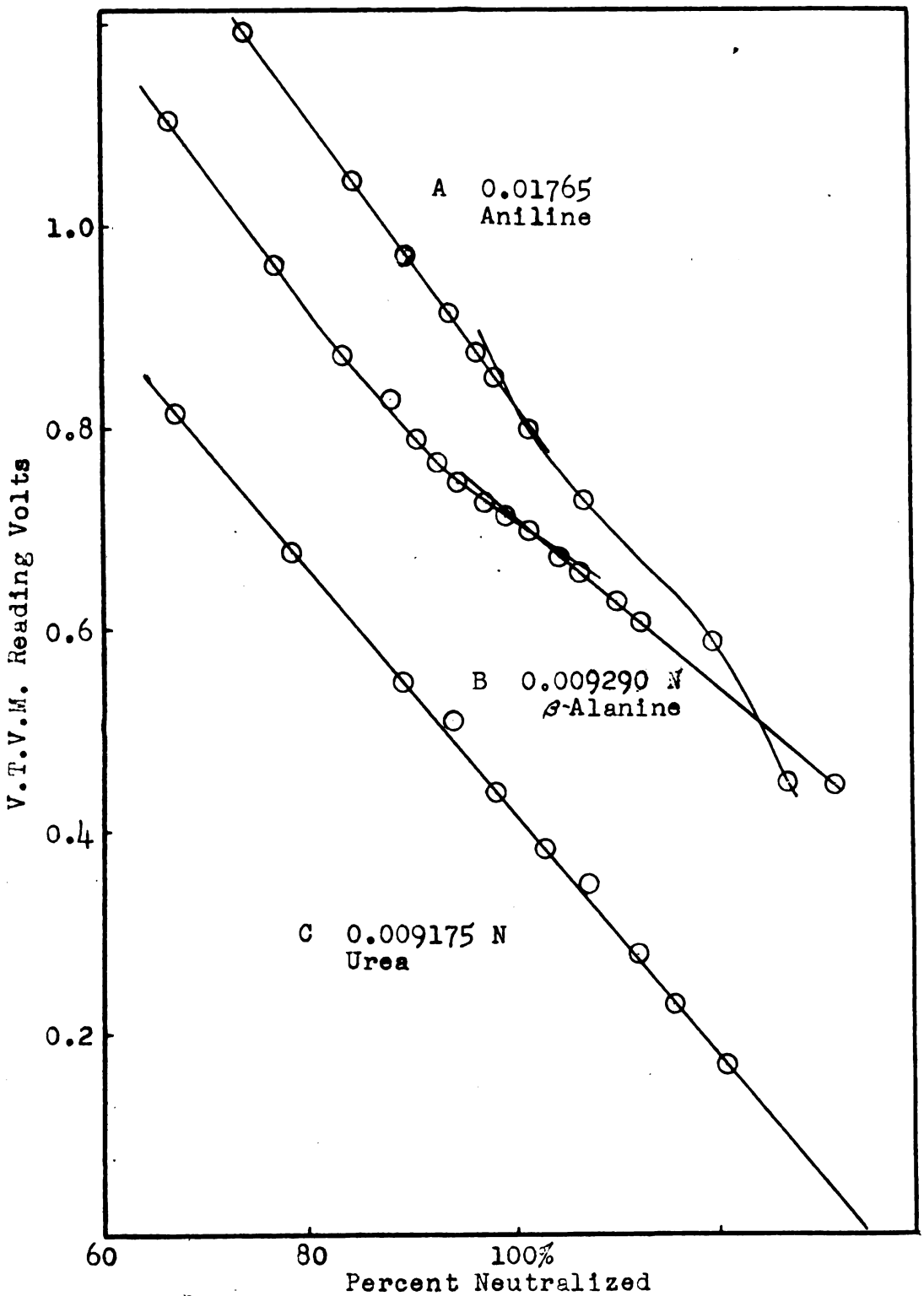

Fig. 24a. Peak voltage measurement of base strength in acetic acid media with 0.1132 N perchloric acid.

curves of the right side of the "hump" while curve B and C show the tent shape of the left side of the "bowl". This indicates a decrease of conductance up to the end point and increase after. As the base becomes progressively weaker the change of conductance is no longer dependent upon the change of concentration of the base but rather upon the concentration of the salt formed. This trend in its extreme is shown in Curve A of Figure 24a where the right side of the "bowl" shaped curve produces a typical V shaped curve. Curve B of Figure 24a shows the V shape of the left side of the "hump". Titration A Figure 24 is an extreme example of the precipitation formation dip. The titrations although done at optimum concentrations, show progressively poorer end point breaks as the base becomes weaker.

Other methods of end point detection. The titrations of the acetic acid systems discussed from the standpoint of high frequency end point detection were also carried out using conventional methods, some were carried out using a beat frequency method. These analyses by other methods were made for the purpose of determining the accuracy of the high frequency method studied here and for the purpose of comparing the quality of the end point obtained against the end points of conventional methods.

Conventional conductometric titrations with a bridge were attempted on acetic acid systems. In a few cases detectable end points were obtained, however the breaks were small.

The bulk of the non-high frequency titrations were potentiometric titrations carried out in the usual manner (34,

41,42,43,50,56,63). It was found that a great majority of titrations cited here gave satisfactory titration curves potentiometrically. (Figures 25,26, and 27 are selected examples.)

Several titrations in acetic acid media were carried out with a thirty megacycle beat frequency, high frequency device (49). The results were inconclusive, in comparison to the power loss titrimeter, some titrations had better breaks, others poorer. A plausible explanation for this, drawn from the general characteristics of the two types of instruments, is that within a certain range, the beat frequency instrument at 30 megacycles is more sensitive than the power loss instrument at 3.6 megacycles. Since the range of the power loss instrument is larger than the range of the beat frequency instrument, the above apparently anomolous results are explained.

Summary and Conclusion

Many factors are capable of affecting the quality of an end point. Some factors and their effects are quite obvious and corrections can be made to minimize the errors they may cause. Expansion of the solutions with increased temperature, and predictable instrument changes, are correctable factors.

Possible random errors have been minimized by the appropriate treatment of data, however the conventional methods used as reference methods are relatively unprecise[12] therefore

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[12] The precision of acetic acid media titrations has been variously reported as ±0.2% for the potentiometric method (32, 47) and ±0.3% for the Indicator methods (32).

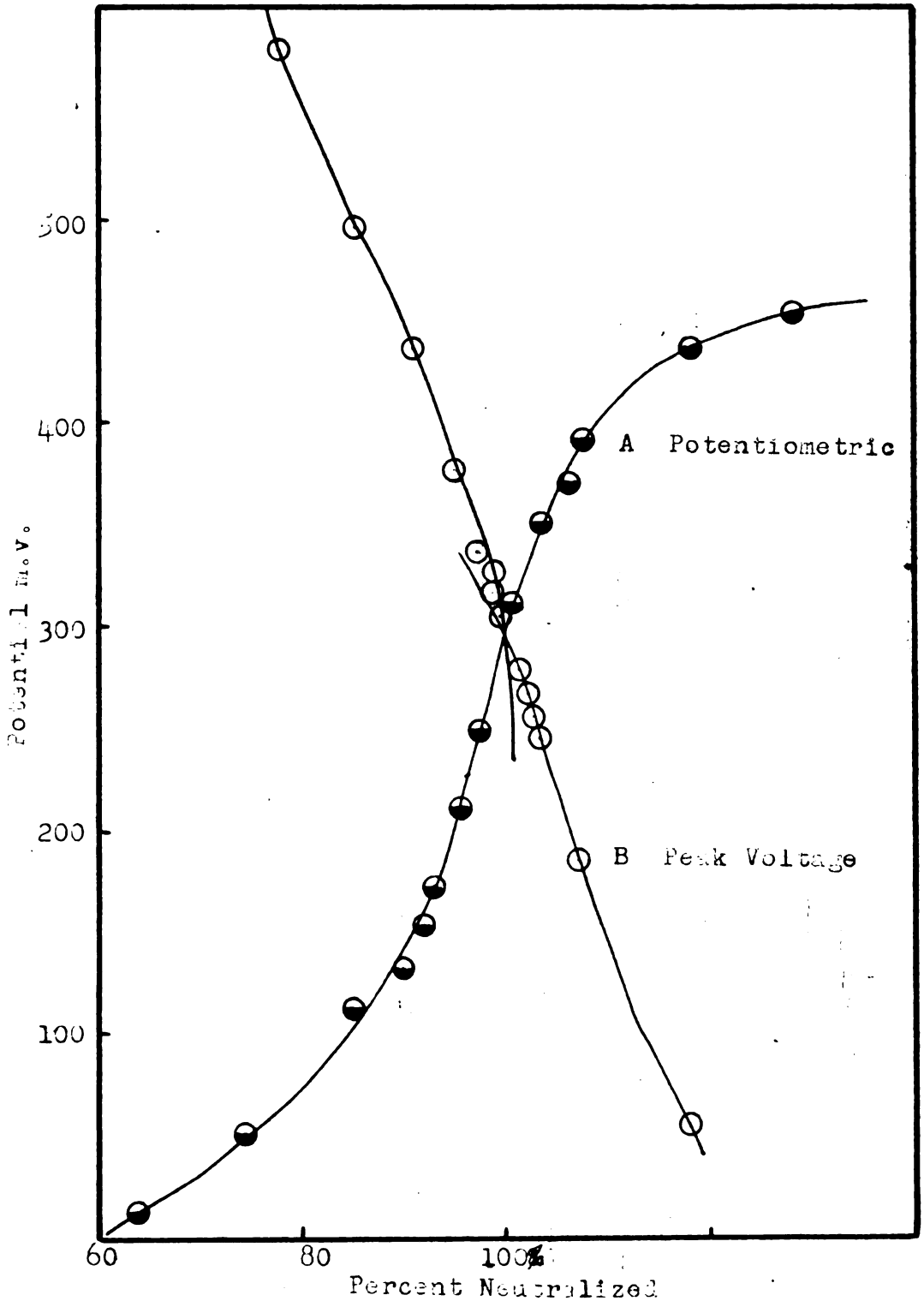

Fig. 25. Comparison of peak voltage and potential measurements of 0.0176 N aniline in acetic acid media with 0.1132 N perchloric acid

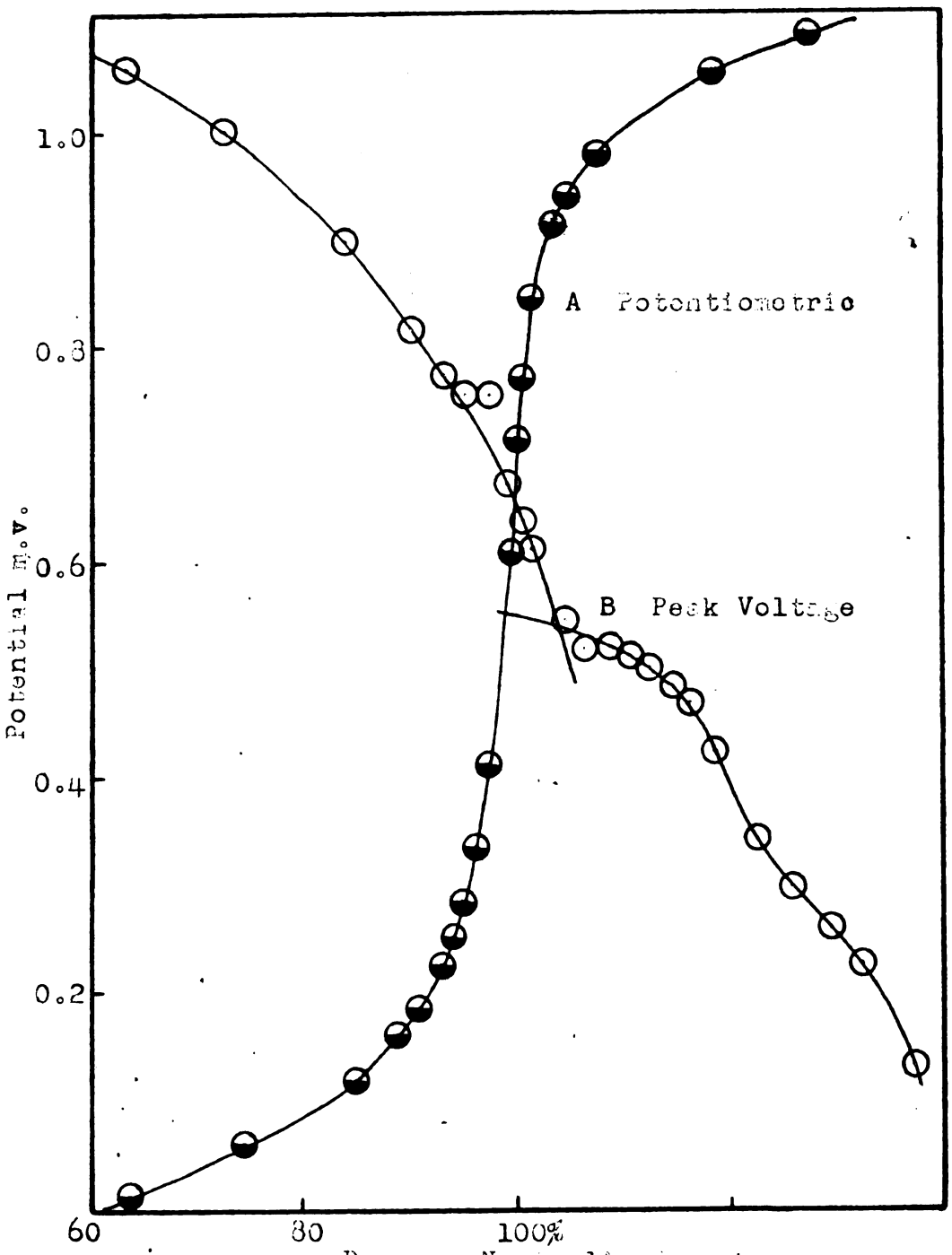

Fig. 26. Comparison of peak voltage and potential measurements of 0.009633 N 8-hydroxyquinoline in acetic acid media with 0.1132 N perchloric acid

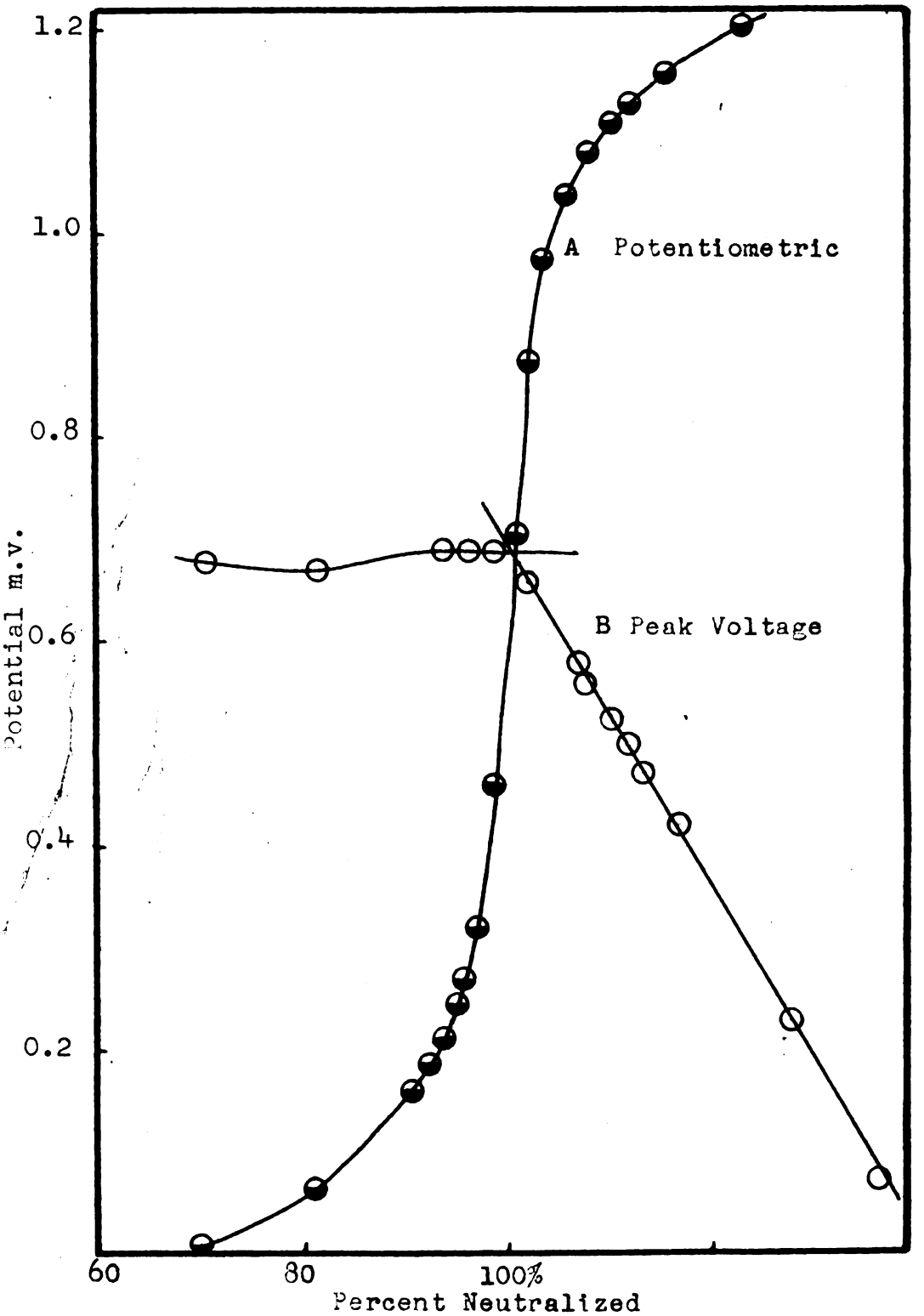

Fig. 27. Comparison of peak voltage and potential measurements of 0.008915 N diethylaniline in acetic acid media with 0.1132 N perchloric acid.

it should be expected that this be reflected in the precision of the data of the present study. A calculation of average and standard deviations[13] on the incorrect assumption that the reference methods are precise yields a result (average deviation is 0.24%, σ is 0.7%) which compares favorably with the standard methods.

Two factors found not to affect the end point in any way, are immersion of the buret tip, and the magnitude of the bias of the V.I.V.M.. Though no effect was noticed by changing these factors, most titrations were carried out with the buret tip immersed and a bias sufficiently great to give the "hump" shaped response for reasons of manipulative convenience.

Stirring speed was not a critical factor if beating did not occur. The glass paddle stirrer was found to be superior to the magnetic stirrer which had a tendency to decrease sensitivity.

The method of measurement is a factor affecting the quality of the end point and can be discussed by comparing the advantages and disadvantages of the six methods studied. The loading measurements and peak voltage measurements presented a greater number of advantages in the acetic acid system than did the other four methods.

The cut in and cut out voltage methods, though satisfactory in aqueous media for strong acids and bases where the

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[13]Calculations were made on the 47 peak voltage titrations rather than the total of 213 titrations performed, since a great many of these titrations were of an exploratory nature.

overall voltage change was large compared to the uncertainty of the individual points, could not be utilized for weak bases in the acetic acid system since the uncertainty of the readings were of the same order of magnitude as the end point break.

The cut in and cut out capacitance methods gave satisfactory results in aqueous media for strong and intermediate acids and bases. In the acetic acid media these two methods showed small end point breaks for strong and intermediate bases, none for weak bases. The uncertainty of the readings, though of considerably less magnitude than the end point breaks, are still a large accuracy reducing factor. A further encountered difficulty, where the oscillator is constantly taken in and out of oscillation, is the matter of the upward creep of voltage as crystal and triode reach thermal equilibrium.

Two factors which have a profound influence on the quality of the end point are the order of titration and the presence of a neutral electrolyte. Where both acid and base are strong the order of titration has no effect, where one or the other is weak the weak member must be titrated with the strong to avoid adverse effects. This observation is analogous to the same effect noted in conventional conductometric titrations. The desensitization due to a neutral electrolyte is also analogous to the effect noted in conventional conductometric titrations.

No significant change in response was noted when the order of solvent-sample introduction was reversed. Peak vol-

tage timed readings indicated that for the systems studied here the interval between successive increments of titrant, is not a significant factor.

Back titration in the usual sense where a weak base was over titrated with a strong standard acid then back titrated to an end point with a strong standard base, was found to have no advantages over the conventional titration to the direct end point. In a few cases back titration gave a lower sensitivity than the conventional titration.

The importance of the solvent can be extrapolated from the results obtained for aqueous, dioxane, and acetic acid media. In general the properties of a solvent which allows it to increase the dissociation of a weak acid or base and thereby increase the conductance, are advantageous to high frequency end points.

High frequency methods of analysis in non-aqueous media possess definite concentration limitations. The more versatile instruments, such as the one discussed in this study, having a more extended concentration range tends to have other off setting defects. Extension of the concentration range usually results in a lowered sensitivity. Increasing frequency usually extends the concentration range without a decrease in sensitivity, however in most cases the instrument becomes more complex with attendent undesirable complications.

The effect of concentration in peak voltage measurement is predictable from the general characteristics of high frequency instruments. Since capacitance is adjusted to remain

constant during a series of measurements the response noted is almost completely due to change in conductance. Conductance of a solution depends upon the number and mobility of the ions present, that is, the concentration and kind of ions present. Considering a response for a particular system the concentration defines the magnitude of the response. The particular system defines the functional relationship between concentration and response, which is in all probability unique for each system and is a function of the dissociation of the particular substance in that system. Thus the optimum concentration for greatest sensitivity cannot be calculated from the present development of the method it must be determined experimentally. A general observation in this study was that the lower the degree of ionization the higher the concentration required for maximum sensitivity. A comparison of the potentiometric method of analysis to the high frequency peak voltage method of analysis will serve to show the relative advantages and disadvantages of the method. In the course of this study it was found that the potentiometric method had a more severe concentration limitation than did the high frequency method, that is, in the very dilute solutions where a potentiometric end point was unsatisfactory the high frequency method gave a better end point. The limitation of base strengths was less severe for potentiometric titrations than for high frequency, that is, bases which were too weak to show a high frequency end point, have reportedly been successfully titrated potentiometrically.

APPENDIX

Instrument Parts List (Figure 6)

Capacitors

C_1, 0-100 mmf midget air padder

C_2, 0-35 mmf midget air padder

C_3, 40 mmf mica

C_4, 25 mmf mica

C_5, 10 mmf mica

C_7, C_8, C_9, C_{10}, 0.001 mfd 450 volt paper

C_{11}, C_{12}, 40 mfd electrolytic can

Resistors

R_1, 150K 1 watt

R_2, 41K 1 watt

R_3, 10K wire wound pot.

R_4, 15K 1/2 watt

R_5, 2K 1/2 watt

R_6, 3900 ohms 1/2 watt

R_7, 1200 ohms 1/2 watt

R_8, 1/2 megohms 1/2 watt

R_9, 600 ohms 1/2 watt

Tubes

0A 3,

80 Diode rectifier

6E5 "Magic Eye"

Miscellaneous parts cont'd

T_1, power transformer

S_1, S.P.S.T. switch

S_2, 6 terminal rotary switch

X, crystal

L, Tuning coil

P, pilot light 6 volt

D, dry plate selenium rectifier

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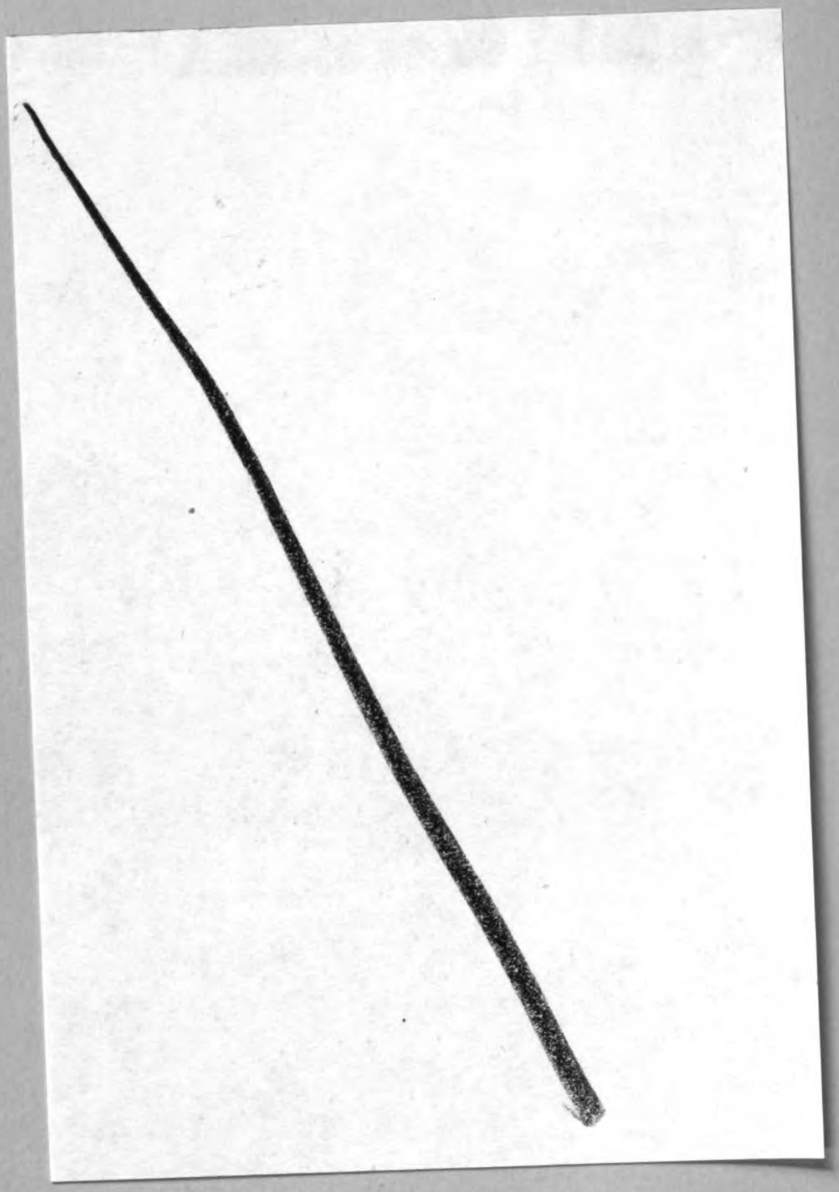

HIGH FREQUENCY TITRATIONS IN ACETIC ACID MEDIA

By

Conrad M. Jankowski

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1954

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Conrad M. Jankowski

High frequency titration is an electrometric technique of end point detection. It possesses the advantage over existing techniques in that it eliminates the necessity of internal electrodes.

The purpose of this investigation was the study of the advantages and disadvantages inherent in the method and a comparison of this method to conventional methods of end point detection.

The instrument used was a conventional tuned plate, tuned grid, 3600 KC crystal oscillator utilizing a 6L5 triode. Measurements were made by a capacitive loading of the plate circuit. The effect measured was the maximum biased grid voltage of the loaded circuit while the instrument was in oscillation. The end point detected by the instrument as used is explained in terms of conventional conductometric titrations which may be related to this technique by ordinary methods of electronic circuit reduction.

Of the factors evaluated most important are the effects of solvent system, dissociation of the substance titrated, and the concentration. The effect of the solvent system is conventional and in accordance with the Brønsted theory of acids and bases. It was found that weak bases such as dimethylaniline, pyridine, hexamethylenediamine, 8-hydroxyquinoline, aniline, p-toluidine, and -alanine, when titrated with a strong acid such as perchloric acid gave better end points in acetic acid media than in water or dioxane. The degree of dissocia-

tion of the substance titrated in a particular solvent system had a profound effect. The more highly ionized substances gave better end points than the less dissociated or "weak" substances. The effect of concentration is perhaps the most unconventional aspect of the high frequency technique in that sensitivity of response is not a linear function of concentration. The methods utilized gave two regions of maximum sensitivity separated by a region of low sensitivity. It was found that each system titrated had a unique region of highest sensitivity. The location of this maximum region of sensitivity depends upon the kind of ions present. The regions of maximum sensitivity varied from 0.05M-0.002M for aniline to 0.1M-0.01M for diethylaniline.

In acetic acid media the precision of high frequency end points compares favorably with potentiometric end points where the concentration of maximum sensitivity is utilized. In most cases of weak bases the high frequency region of maximum sensitivity extends to lower concentrations than does the potentiometric concentration range. The potentiometric method in acetic acid systems extends to weaker bases than does the high frequency method studied here. Thus high frequency techniques and potentiometric methods are complementary to the study of acetic acid systems.