



1942

Titration Curves of Indicators

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TITRATION CURVES OF INDICATORS

by

Marvin F. L. Johnson

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of Master
of Science in Loyola University

February

1942

Theoretical Discussion

The original purpose of this work was to find out if, when acid-base indicators were titrated potentiometrically against standard acids or bases, the typical pH-volume curves would be obtained. An indicator is a weak acid or base, colored in solution, which changes color as the hydrogen ion concentration changes; for every indicator there is a certain pH range in which there is a sharp color change. Indicators are used in volumetric analysis to show by this change of color when the end-point in a titration has been reached. Hitherto, no work has been published about titration curves of these indicators. The large amount of work that has been done on them has been in finding the pH region of the sharp color change, and in finding the equilibrium constant of dissociation.

According to the Bronsted theory, an acid is a "proton donor", while a base is a "proton acceptor"; in considering this statement, remember that a hydrogen ion is nothing more or less than a proton. The older idea of an acid is that of a substance which produces hydrogen ions in solution, a base one which produces hydroxyl ions. These acids and bases are still considered such by Bronsted, but so are many others. The old, or Arrhenius, theory of ionization writes the ionization of an acid, such as hydrochloric, as a break-down: $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$; Bronsted writes it differently: $\text{HCl} + \text{HOH} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$.

Thus, the ionization of hydrochloric acid becomes nothing more than a reaction with the solvent, water: HCl is an

acid (proton donor), water a base (proton acceptor); H_3O^+ and Cl^- are the acid and base, respectively, formed by this reaction.

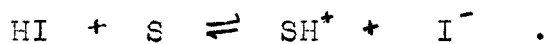
Let us next consider a case in which water acts as an acid: $\text{NH}_3 + \text{HOH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$; here the acid, water, donates a proton to the base, ammonia, forming a new acid, the ammonium ion, and a new base, hydroxyl ion. By the old definition of acids and bases no substance could interchangeably act as either an acid or as a base. The reason for this possibility now is that the new idea of acidity and basicity is relative. For example, HCl is more acidic than water, therefore acts as an acid in water solution: it is more willing to donate a proton than is water. Similarly, in the second example, ammonia is less acidic than water, and therefore tends to accept this proton. By the term "less acidic" we also mean "more basic".

The effect of the solvent upon the acidity or basicity of a substance may be seen from this discussion. Suppose a certain substance is acidic in water. If it is dissolved in a solvent which is also more acidic than water, although less so than the solute, the latter will not be as acidic as it is in water: the new solvent will not be as willing to accept protons. If a solvent is used which is more acidic than either water or our solute, then, of course, the latter will act as a base.

I have used two criteria for comparing acidities from the titration curves: the equilibrium constant, and the sharpness of the break in the titration curve.

Let us consider an indicator acid, HI, where I

represents the molecule with H removed. Suppose it is dissolved in a basic solvent, S; it will ionize in the following manner:



The equilibrium constant for this reaction is given by:

$$K = \frac{[\text{SH}^+][\text{I}^-]}{[\text{HI}]} ; \quad \text{pK} = -\log K .$$

The concentration of solvent, since it is comparatively very large, and only negligibly changed during the course of the reaction, is included in the constant. The equilibrium constant of an indicator is usually very small, so that $[\text{HI}]$ is very large compared to the numerator. If a base, such as sodium hydroxide solution, is now added, it will react with SH, shifting the above equilibrium to the right. At the end-point, when equimolar amounts of sodium hydroxide and indicator have been allowed to react, $[\text{HI}]$ is comparatively very small. If only half enough base is added, then $[\text{I}^-] = [\text{HI}]$, and $K = [\text{SH}^+]$, or $\text{pK} = \text{pH}$.

Thus, the pK is known if the pH value at the half-titration point is known; it is, of course, indicative of the acid strength of the indicator. Experimental means will be discussed later.

When a strong acid is titrated against a strong base, the break in the titration curve is much larger and sharper than if a weak acid or base were used. For this reason, the sharpness of the break may be used as a qualitative comparison of acidity, providing the same base be used for all titrations. By plotting the slope of the titration curve against the volume

of base added these differences are accentuated.

The dielectric constant of the solvent also has an effect upon the acidity of a solute - or, rather, the observed acidity. By Coulomb's law: $f = \frac{q_1 \cdot q_2}{Dr^2}$, where: f is the force of attraction or repulsion between charged particles; q_1 and q_2 are the magnitudes of the two charges; r is the distance between the centers of charges; D is the dielectric constant, peculiar to the individual. In a solvent such as water, having a dielectric constant of a high magnitude, the forces of attraction between ions of opposite charge are low, so that their tendency to associate will not be strong, but they will tend to remain dissociated. In a solvent such as benzene or dioxane, with low dielectric constants, the forces of attraction will be much higher, and dissociation will be low. Therefore, as the dielectric constant is increased, dissociation increases, and pK decreases.

Minnick and Kilpatrick^{1a} made a study of the equilibrium constants of various organic acids in solvents of various dielectric constants. However, I have been unable to find any work of this sort done with indicators. Several men have determined pK for various indicators spectrophotometrically or colorimetrically. I shall mention some values later.

To the best of my knowledge, no work has been done on this topic at Loyola.

Experimental Procedure

Purification of materials

Pyridine-----Used Eastman Kodak technical grade. Let stand a few days over sodium hydroxide pellets to remove water and acids. Then distilled, using the fractionating column of Snyder and Shriner¹ and collected the fraction distilling between 114.5° C and 114.7° C. Stored in a glass-stoppered bottle.

Methyl Orange--Used student preparation. Recrystallized twice from hot water, washed with copious quantities of alcohol, then ether, and dried.

p-Nitrophenol--Used Eastman Kodak reagent grade.

Recrystallized from hot water, washed with cold water, dried, and stored in a desiccator. Had to experiment in order to find the proper amount of water to use, as a hard, dark solid precipitates from a too concentrated solution, instead of the long, white, silky needles which I finally obtained.

Dioxane-----Eastman Kodak practical.

Alcohol-----Used the ordinary "95%". By hygrometer bulbs, found density = 0.8116; by extrapolation from data in Lange's handbook, I found that I had 92.4% alcohol. Ran titrations in alcohol as fast as possible, to keep composition constant.

Stored in a glass-stoppered bottle.

Water-----Distilled.

I did not purify the other indicators used any further, mainly because I didn't have enough on hand. Used Eastman Kodak.

Standardization of solutions

I made up a solution of hydrochloric acid, less than 0.1 N; I titrated this against a standard silver nitrate solution, after neutralizing with an excess of calcium carbonate powder. I obtained far better precision by using the method of Fajan²•, with dichlorofluorescein as an adsorption indicator, than by that of Mohr²•, with potassium chromate as indicator. The titer of the silver nitrate solution was known because it was weighed out into a volumetric flask, and dissolved in enough water to fill the flask up to its mark.

I used this acid to standardize my 0.1 N sodium hydroxide, with methyl orange xylene cyanole as an indicator. The precision of both standardizations was close to 0.1%.

Apparatus and procedure

I used a Coleman pHmeter, employing a glass indicator electrode and a calomel reference electrode; I calibrated the instrument with buffer solutions of known pH before using. I found it unnecessary to check the instrument more than once, as the calibration did not change.

I dissolved a weighed quantity of the indicator in 50.0 ml. of solvent in a beaker, inserted electrodes and a mechanical stirrer, then made measurements as I added the standard acid or

base from a burette.

I plotted pH against volume. From these curves I obtained the slope curves in the following manner: between any two points on the drawn curve I calculated ΔpH and ΔV , and thus $\Delta\text{pH}/\Delta V$; I plotted this slope against the average volumes between each pair of points, and obtained a curve with a high peak at the end-point. A higher peak is indicative of a sharper slope at the end-point.

From the original curve it was simple to interpolate in order to find the pH at the half-titration point, and thus the pK value. Since the weight of the sample and the titer of the base are known, the theoretical end-point can be calculated, in case there is any doubt about the observed end-point, and the half-titration point.

The end-points obtained from the potentiometric titrations checked almost perfectly with the calculated values, providing a check on my measurements. The check was apparently perfect, except that the graphs could not be interpolated closely enough.

Preparation of dioxane-water mixtures

I measured the quantities of dioxane and water at room temperature with Exax pipettes. For the densities I used the values³: water = 0.998; dioxane = 1.033; from these values I was able to calculate the compositions in weight percent. From the data given by Krauss and Fuoss⁴. I plotted percent composition against dielectric constant; I have not included

this curve. I interpolated this curve to find the dielectric constants of my mixtures. These data are given in Table I.

Data -- Titrations of p-Nitrophenol

Table I

Composition			Dielectric
ml. dioxane	ml. water	%dioxane	Constant
50	0	100	2.20
50	10	83.8	7.6
50	25	67.4	21.0
25	35	42.5	38.8
10	50	17.2	62.6
0	50	0.0	78.6

Table II

% Dioxane	$\Delta\text{pH}/\Delta V$ max.	pK
0.0	1.500	6.93
17.2	2.880	7.28
42.5	2.313	8.24
67.4	1.640	8.77
83.8	2.200	9.39
100.0	1.000	9.86

Solvent:

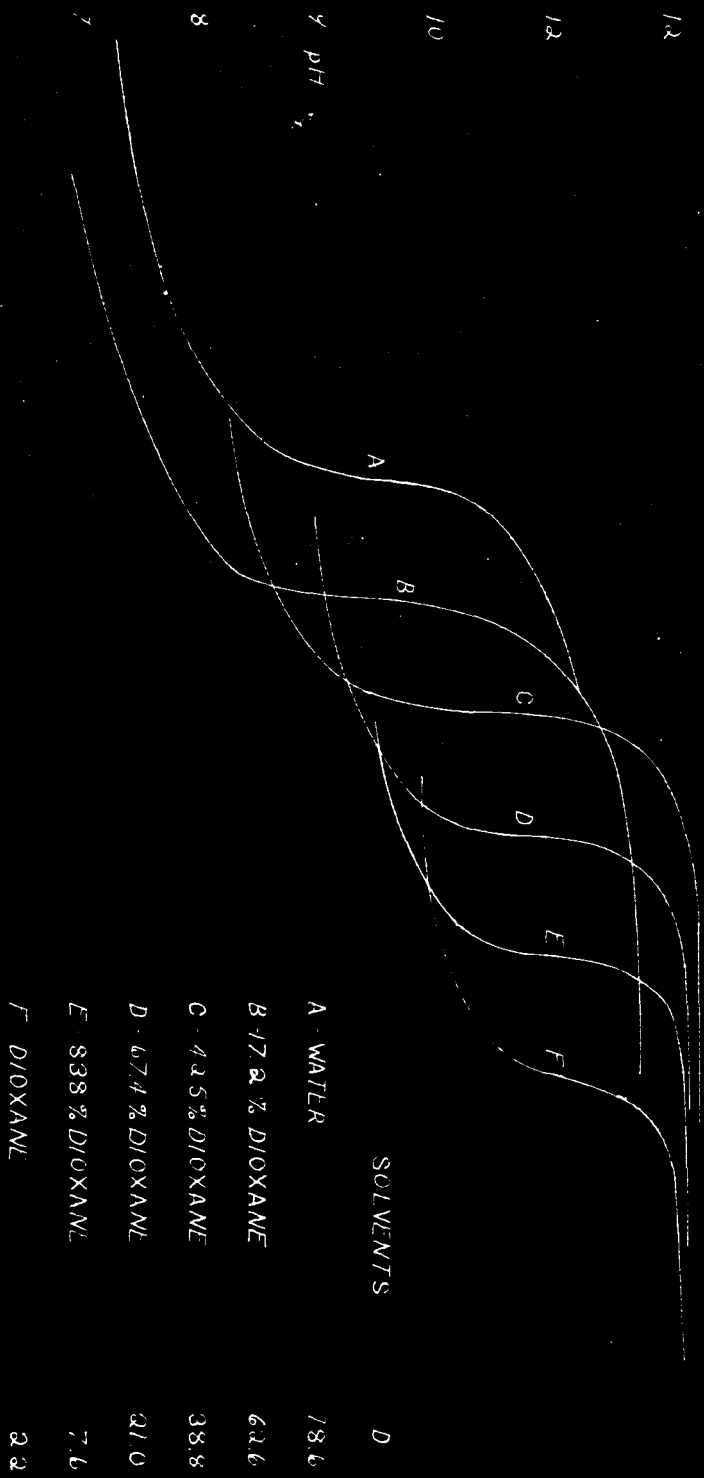
95% alcohol	1.550	8.24
aq. 50% pyridine	3.250	8.06
Pyridine	2.425	9.36

The rest of the data is given in the following curves.

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Fig. 1

TITRATIONS of p-NITROPHENOL vs. NaOH
 IN WATER-DIOXANE MIXTURES



VOLUME NaOH ADDED (1 cm division = 2 cc based)

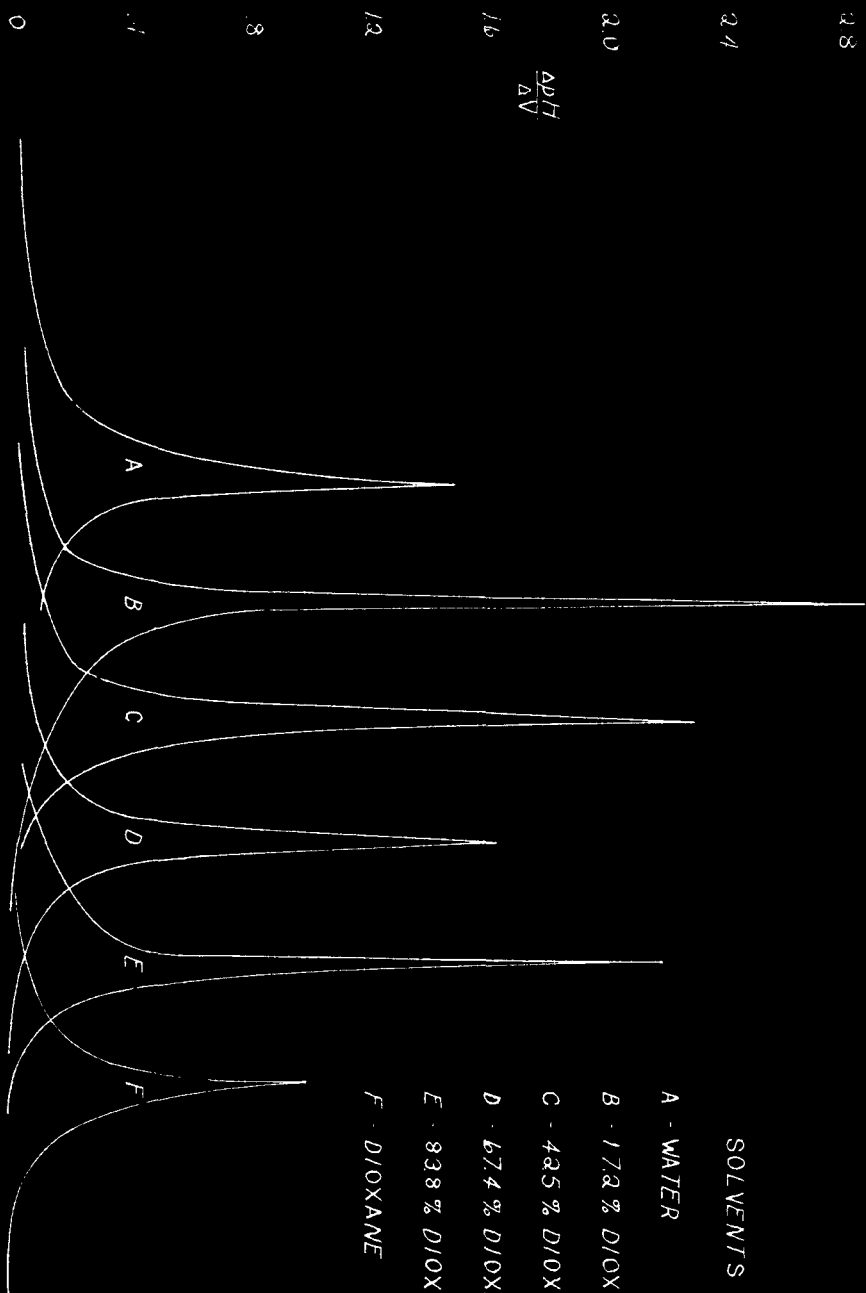
SOLVENTS	D
A - WATER	18.6
B - 17.2% DIOXANE	6.26
C - 42.5% DIOXANE	38.8
D - 67.4% DIOXANE	21.0
E - 83.8% DIOXANE	7.6
F - DIOXANE	2.2

Fig. 2

VOLUME NaOH ADDED

(1 cm. division = 2 cc base)

TITRATIONS of p-NITROPHENOL vs. NaOH
in WATER-DIOXANE MIXTURES



SOLVENTS	D
A - WATER	7.86
B - 17.2% DIOXANE	6.26
C - 42.5% DIOXANE	3.88
D - 67.4% DIOXANE	2.10
E - 83.8% DIOXANE	1.6
F - DIOXANE	2.2

TITRATIONS of p-NITROPHENOL vs NaOH
in DIOXANE-WATER MIXTURES

Fig. 3

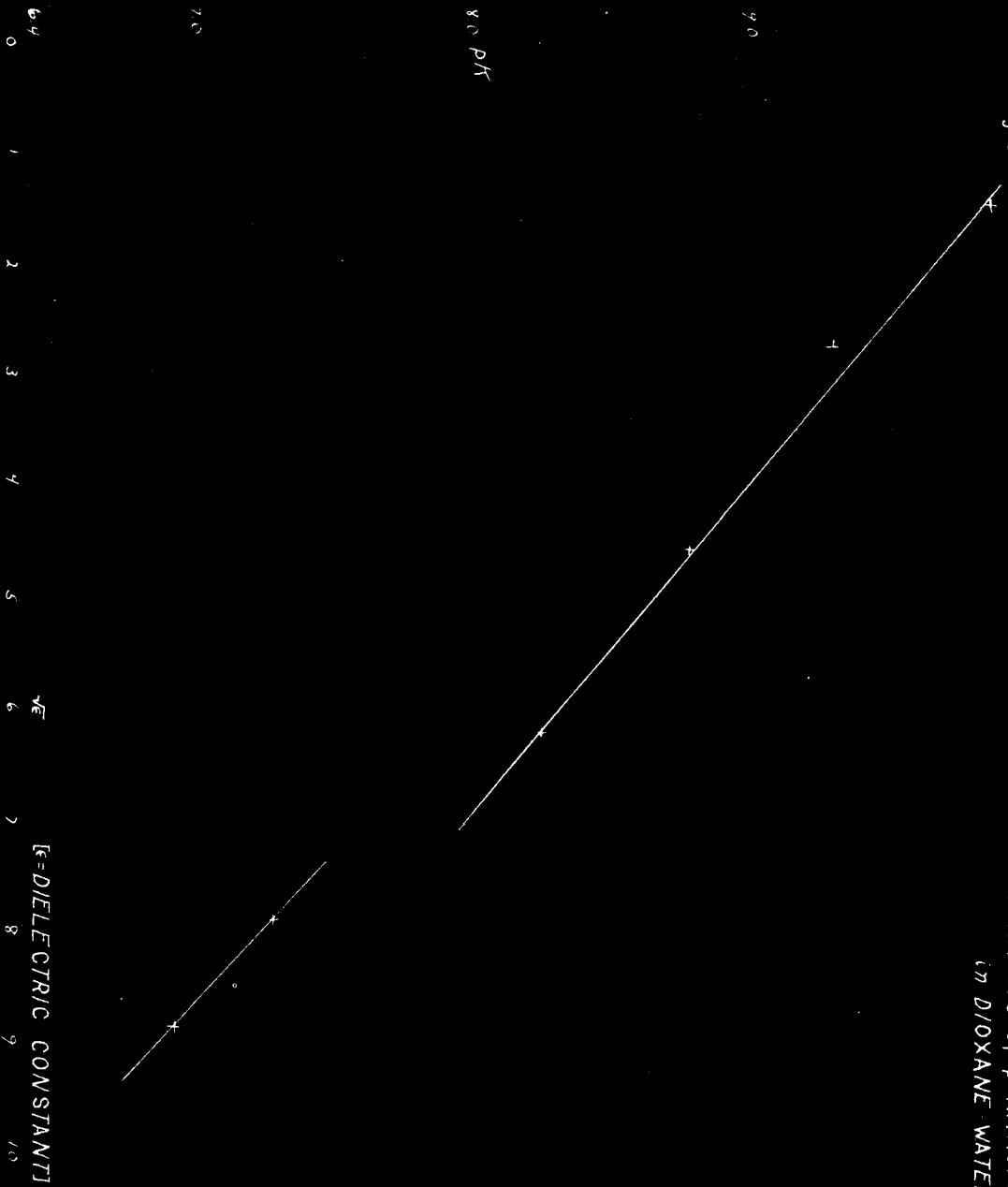
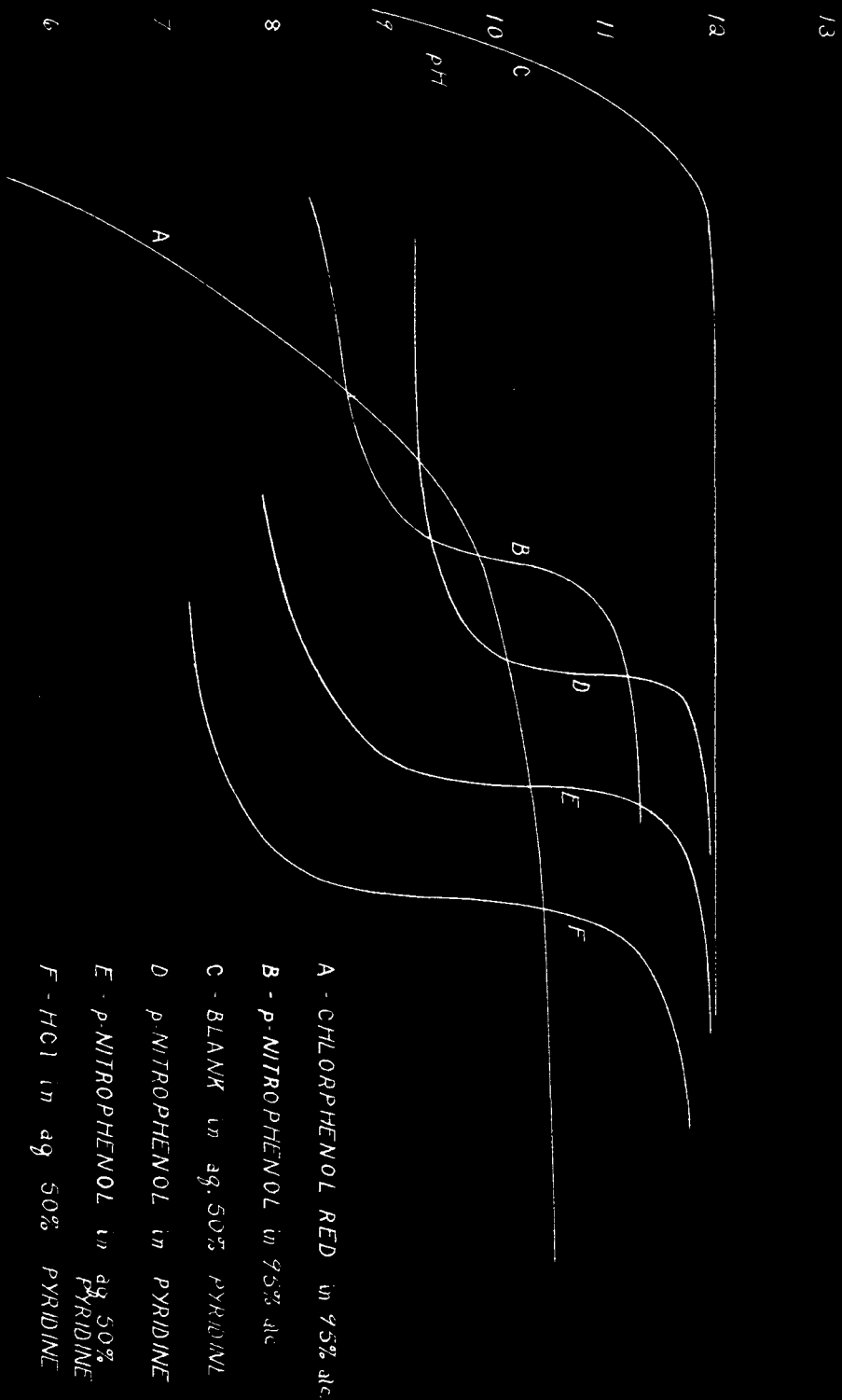


Fig. 4

TITRATIONS of INDICATORS



VOLUME NaOH ADDED (1 cm. division = 2 cc. base)

- A - CHLORPHENOL RED in 95% alc
- B - p-NITROPHENOL in 95% alc
- C - BLANK in 50% PYRIDINE
- D - p-NITROPHENOL in PYRIDINE
- E - p-NITROPHENOL in 50% PYRIDINE
- F - HCl in 50% PYRIDINE

Fig. 5

VOLUME NaOH ADDED (1 cm³ division = 2 cc base)

TITRATIONS of INDICATORS

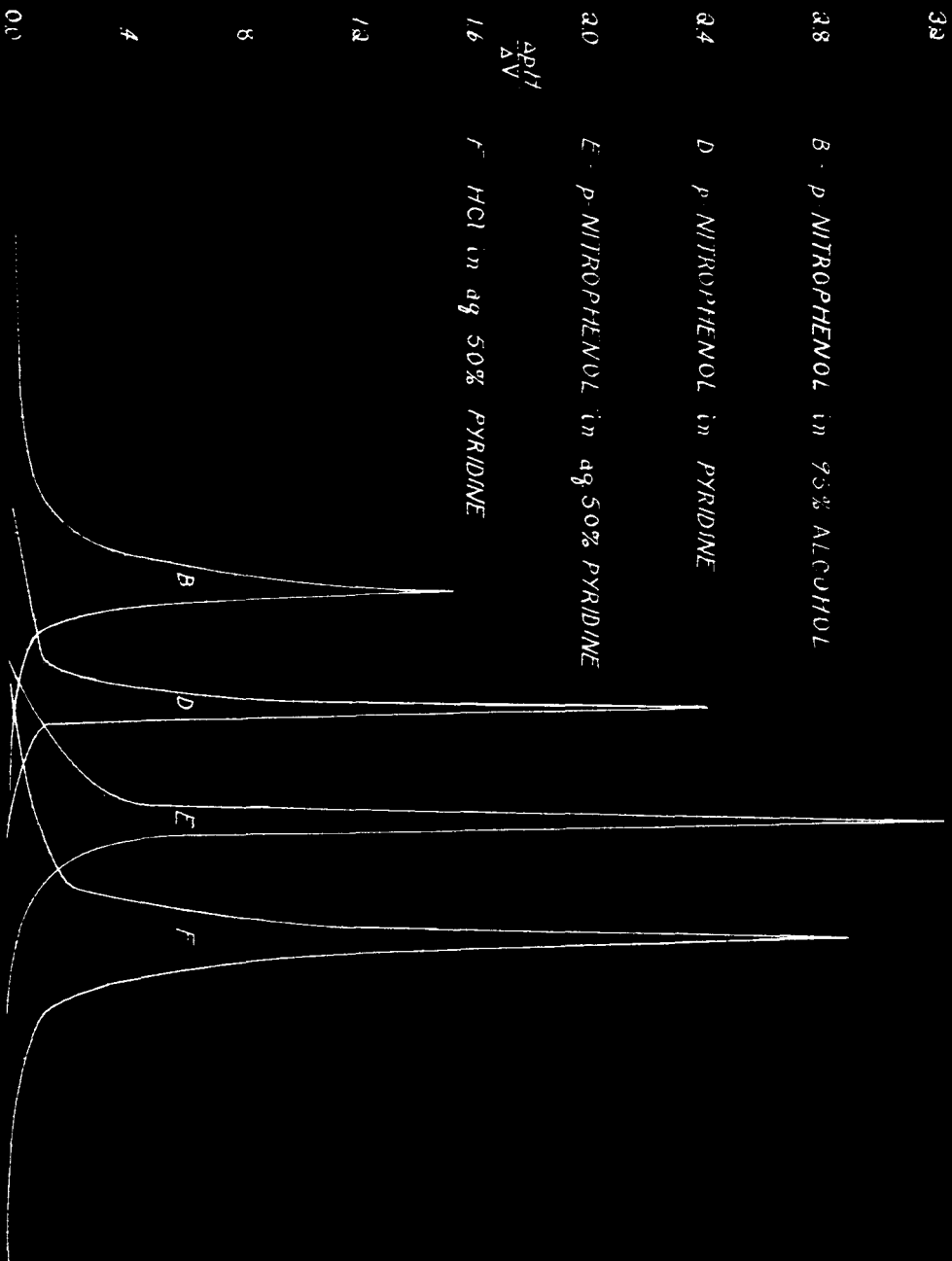
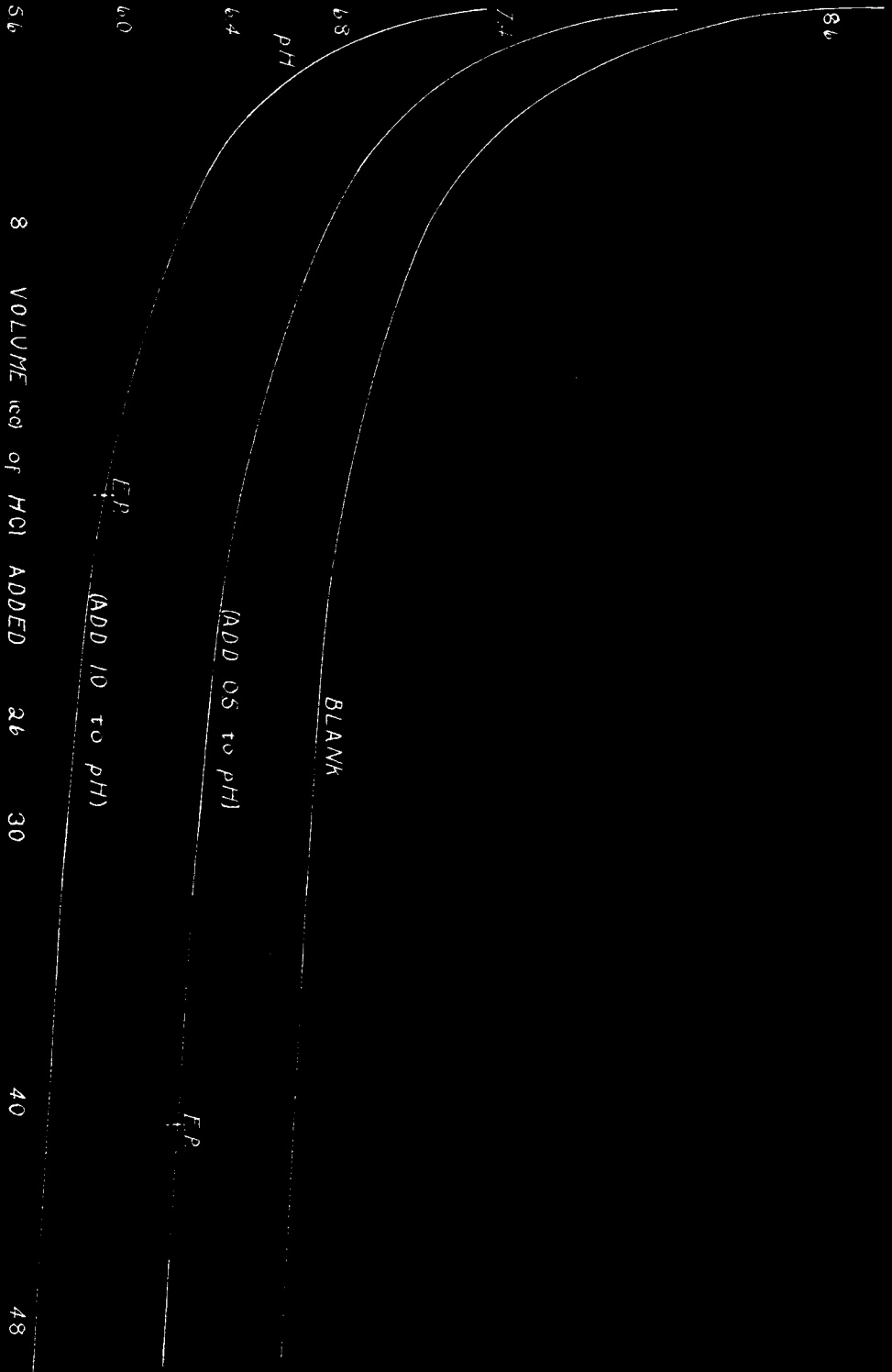


Fig 6

TITRATIONS of METHYL ORANGE
SOLVENT 50% WATER-PYRIDINE



Discussion of data

I have already shown how I have obtained the values given in Table II from the curves (figs. 2 and 3, obtained from figs. 1 and 4). I included data on alcohol and pyridine solutions for comparison purposes. Using the data of Table II, I plotted, for the dioxane-water mixtures, pK against the square root of the dielectric constant (fig. 3). The results are unexpected. The results of Minnick and Kilpatrick^{1a} are quite different. They obtained a straight line by plotting log K against the reciprocal of the dielectric constant. This is to be expected on a theoretical basis: the electrostatic energy, E, of an ion may be expressed by $-E = q^2/2\epsilon r$, where r is its radius, and ϵ is the dielectric constant. Thus, the change in electrostatic energy would be proportional to $1/\epsilon$, and therefore so would ΔF and pK.

I used the square root of ϵ , because it was the only function even approaching a straight line. The four solutions rich in dioxane seem to follow one function, while the straight line drawn through the other two points seems to bear no relation to the other two points. I am unable to explain this.

My value of 6.93 for the pK of p-Nitrophenol in water agrees rather well with a value previously reported⁵ of 7.03

In the dioxane-water mixtures, pK increases as ϵ falls, as is expected. Also, my value for the pK in alcohol is higher than that in water; again there is agreement with theory, as alcohol is more acidic than water. However, the results in

pyridine and in pyridine-water are unexpected, as again the pK values are higher than in water. Because of the basicity of these solvents, the pK of the acidic solute should be decreased, due to increased dissociation. The explanation for this is undoubtedly that the solvent exerts a strong influence upon the pH of the solutions. The pK for pyridine itself, in water, is 8.76: Therefore, the method will not work in this case for getting pK values. The higher dissociation of *p*-nitrophenol in pyridine than in water seems to be indicated by the slope curves, as the maxima are higher.

The slope curves do not seem to be of value, as there is no correlation whatsoever. These were not constructed haphazardly, but I drew the titration and slope curves many times each to make sure the lack of correlation was not due to a drawing error.

I have included a blank titration of aqueous 50% pyridine against sodium hydroxide. Note that, as the base is added, pH rises quickly at first, then remains constant, due to buffer action.

For lack of any other solvent in which methyl orange is soluble, I found it necessary to titrate it against hydrochloric acid in aqueous 50% pyridine. This choice of solvent would be a bad one, were there any alternative, as we then have a basic solute in a basic solvent. The absence of any break in the curve shows that the indicator is weaker than the solvent; this is borne out by its pK value of 10.327, while, as I

mentioned, that of pyridine is 6.7, and thus a stronger base. I have included two such titration curves, and a blank titration for the solvent alone (fig. 6). All three are practically coincidental.

The case of Chlorphenol Red is analogous. I titrated in against sodium hydroxide in 95% alcohol, and found no break in the curve at the end-point in this acidic solvent (fig. 4). Using the value of the pH at half the theoretical end-point in order to get the pK, I obtained $pK = 6.13$; this is in good agreement with values reported of 5.98³., and 6.25⁵..

If hydrochloric acid and sodium hydroxide are titrated against each other in water, the break in the curve is very sharp; as a matter of fact, the slope seems to be infinity. I have included the titration curve for these two in aqueous 50% pyridine (fig. 4). The break here is not as large, due to the formation of the hydrochloride of pyridine which is not, by far, as strongly acidic as hydrochloric acid. On the same graph the blank titration of aqueous 50% pyridine is shown.

In order to facilitate comparison of the several curves on the same sheet (figs. 1, 2, 4, 5), I shifted each curve along the volume axis to the right or left, to space them evenly so that the actual volume of base added at the end-point is not shown in each case; the only comparisons desired are between the shapes of the curves. In drawing fig. 6 I shifted the curves along the pH axis, for the same reason.

I attempted the titrations of Thymol Blue, Bromthymol Blue, Phenol Red, and Aniline Blue in alcohol and water, but was unsuccessful. I used from 0.20 to 0.24 gm. of sample in 50.0 ml. of solvent, and was never able to dissolve the sample; even if this amount would dissolve, the molecular weights are so high that the theoretical end-points would be reached at about 5 ml. of base added, so no good titration curve could be drawn. I attempted the titrations with some insoluble matter present to be sure, but could make no readings because the meter kept drifting. I was unable to find other soluble indicators.

Further work could be done along these lines by titrating in a larger variety of solvents, such as amines and alcohols. I believe the pH meter I used is excellent for such work, providing the proper precautions are taken with the instrument.

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The thesis, "Investigation of Titration Curves of Acid-Base Indicators", written by Marvin F. Linton Johnson, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

Joseph D. Parent, Ph.D.

November 7, 1941

George M. Schmeing, Ph.D.

November 8, 1941