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The D o Acidity Function for Aqueous Sodium Hydroxide Solutions

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THE D_0 ACIDITY FUNCTION
FOR AQUEOUS SODIUM HYDROXIDE SOLUTIONS

by
James T. ^{Thomas} MacGregor UC 1965
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Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY
UNION COLLEGE
MAY 1965



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This Thesis

Submitted by

James L. MacGregor

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

Kewok V. Nahbedian

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INTRODUCTION AND SUMMARY

The H_0 acidity function developed by Hammett and Deyrup (11) is well known, and values for this function are established for solutions of various acids. This function is derived from the equilibrium



where B is an uncharged indicator base.

Another type of equilibrium is possible, one in which the reaction is



and the indicator base is ROH.

The only difference between the above reactions is that in the latter a molecule of water is split out rather than the indicator merely becoming protonated. Denb, Jaruzelski, and Schriesheim (6, 7, 8) have done the most extensive work on the function derived from the second ionization equilibrium (the J_0 function), and it was found that this function differed from the H_0 function, although the actual and theoretical differences are as yet not well correlated.

Nevertheless, it has been established that the kinetics of some acid-catalyzed reactions are related to the H_0 function, while others are related to the J_0 function. These functions are therefore useful in

the study of the kinetics and mechanisms of acid-catalyzed reactions (2).

The purpose of this project is to establish a basicity function analogous to the H_0 function which is defined by the equilibrium.



and is a quantitative measure of the basicity of the medium. The function may be defined either as an acidity function or as a basicity function, since these can be related through the ionization constant of water, just as the pH and pOH scales may be related.

A system of indicators which will allow these measurements has been developed. The ratio of free indicator to its hydroxylated form is determined by observing the ultraviolet spectra of the indicators.

Values for this function, which will be called the D_0 function when defined as an acidity function, have been measured in aqueous sodium hydroxide solutions from concentrations of about .02M to about 12 M.

An attempt has been made to correlate these values with values of the H_- function developed by Schwarzenbach and Sulzberger (14). The

H₋ function is derived from an ionization equilibrium of the type,



and should theoretically differ from the D₀ function by,

$$\log a_{\text{H}_2\text{O}} + \log \frac{f_{\text{D}}}{f_{\text{DOH}}} \frac{f_{\text{A}^-}}{f_{\text{HA}}}$$

where the f's are the activity coefficients of their respective species.

The right-hand term is ideally zero or at least a constant (see History and Theory).

The correlation with Schwarzenbach's values yields fair results, but correlation with a set of theoretical values calculated by Anbar and Yagil (3) is excellent.

The correlation between the two functions should provide a very useful tool for studies of the kinetics and mechanisms of base-catalyzed reactions. It has already been established by Anbar and Yagil (3) that certain base-catalyzed reactions have rates correlated by the H₋ function, while others are correlated by H₋ + log aH₂O.

HISTORY AND THEORY

The acidity of dilute solutions of acids and bases is adequately described by the pH scale. According to this scale the acidity of a solution is defined by:

$$\text{pH} \equiv \log \frac{1}{[\text{H}^+]} .$$

Alternatively, the basicity is defined by:

$$\text{pOH} \equiv \log \frac{1}{[\text{OH}^-]} .$$

The acidity and basicity are related through the ionization constant of water, namely,

$$\text{pH} + \text{pOH} = -\log K_w = 14 .$$

The pH scale, however, is useful only in dilute solutions of acids and bases, specifically from about $[\text{H}^+] = 1\text{M}$ to about $[\text{OH}^-] = 1\text{M}$. Outside this dilute range the activity coefficient of H^+ becomes very significant, and it is found that the acidity of concentrated solutions increases much more rapidly than would be expected if it were dependent only on the concentration of acid. This "super-acidity" has been explained in part by Bascombe and Bell (4), who showed that this high acidity is due primarily to strong hydration of the proton. A similar phenomenon is observed

in strongly basic solutions and is explained in an analogous manner by hydration of the OH^- ion (3).

In 1932 Hammett and Deyrup (11) published a paper in which they had developed an acidity function to serve as a quantitative measure of acidity outside the dilute range. In the pH range their function becomes equal to the pH. This is the H_0 function already mentioned and is based on the reaction of a proton with an indicator base:



The dissociation constant of the protonated base is

$$K_{\text{BH}^+} = \frac{a_{\text{B}} a_{\text{H}^+}}{a_{\text{BH}^+}}$$

From this the H_0 function can be derived.

$$K_{\text{BH}^+} = \frac{a_{\text{B}} a_{\text{H}^+}}{a_{\text{BH}^+}} = \frac{[\text{B}]}{[\text{BH}^+]} \cdot \frac{f_{\text{B}} a_{\text{H}^+}}{f_{\text{BH}^+}}$$

where f_{B} , f_{BH^+} are activity coefficients.

$$\frac{f_{\text{B}} a_{\text{H}^+}}{f_{\text{BH}^+}} = K_{\text{BH}^+} \frac{[\text{BH}^+]}{[\text{B}]}$$

$$\text{or } -\log a_{\text{H}^+} \frac{f_{\text{B}}}{f_{\text{BH}^+}} = -\log K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

$$\text{but } -\log K_{\text{BH}^+} = \text{p}K_{\text{BH}^+}$$

and H_0 is defined as (13)

$$(I) \quad H_0 = -\log a_{H^+} \frac{f_B}{f_{BH^+}} = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

From equation (I) it can be seen that values of H_0 may be determined by measuring the indicator ratio, $\frac{[BH^+]}{[B]}$, and pK_{BH^+} . Values of H_0 have been measured for aqueous solutions of HNO_3 , HCl , $HClO_4$, H_2SO_4 , H_3PO_4 , HF , and HBr (13) using spectrophotometric or colorimetric methods to determine the indicator ratio and pK_{BH^+} . From these values it is observed that the acidity increases much more rapidly than would be expected if it were dependent on the concentration of H^+ alone, as has already been noted.

The J_0 function, originally proposed by Westheimer and Kharach (15), is also based on the reaction of a proton with an indicator base, but in this case a molecule of water is formed.



The J_0 function is derived in a manner analogous to the H_0 function.

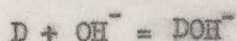
$$(II) \quad J_0 = -\log \frac{a_{H^+} \cdot f_{ROH}}{a_{H_2O} \cdot f_{R^+}} = -pK_{ROH} - \log \frac{[R^+]}{[ROH]}$$

If equation (I) is substituted in equation (II) we find that (13)

$$(III) \quad J_0 = H_0 + \log a_{H_2O} - \log \frac{f_{BH^+} f_{ROH}}{f_B f_{R^+}}$$

It has been suggested (10) that the term on the right might cancel out, in which case the two functions should differ by $\log a_{H_2O}$. The J_o function was indeed found to differ from the H_o function, although the assumption that the right-hand term would cancel out is not realized. Nevertheless, the two functions are very useful in the study of acid-catalyzed reactions, since some reaction rates are correlated to the H_o function while others are correlated by the J_o function (12).

This project is concerned with developing a function which is a quantitative measure of the basicity of a medium and is derived from the reaction of a charged base (OH^-) with an indicator that is acidic in the Lewis sense:



A basicity function may be derived from this equilibrium in a manner analogous to the derivation of the H_o function.

$$K_{DOH^-} = \frac{a_D a_{OH^-}}{a_{DOH^-}} = \frac{[D]}{[DOH^-]} \cdot \frac{f_D a_{OH^-}}{f_{DOH^-}}$$

$$a_{OH^-} \frac{f_D}{f_{DOH^-}} = K_{DOH^-} \frac{[DOH^-]}{[D]}$$

or

$$-\log a_{\text{OH}^-} \frac{f_D}{f_{\text{DOH}^-}} = -\log K_{\text{DOH}^-} - \log \frac{[\text{DOH}^-]}{[D]}$$

Our new function may now be defined as a basicity function as follows (denoting it D'_0):

$$(IV) \quad D'_0 = -\log a_{\text{OH}^-} \frac{f_D}{f_{\text{DOH}^-}} = pK_{\text{DOH}^-} - \log \frac{[\text{DOH}^-]}{[D]}$$

If we wish to define the same function as an acidity function, we may recall that

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}},$$

where K_w is the ionization constant of water.

$$D'_0 = -\log a_{\text{OH}^-} \frac{f_D}{f_{\text{DOH}^-}} = -\log K_w \frac{a_{\text{H}_2\text{O}}}{a_{\text{H}^+}} \cdot \frac{f_D}{f_{\text{DOH}^-}} = pK_{\text{DOH}^-} - \log \frac{[\text{DOH}^-]}{[D]}$$

$$(V) \quad -\log \frac{a_{\text{H}^+}}{a_{\text{H}_2\text{O}}} \frac{f_{\text{DOH}^-}}{f_D} = -\log K_w - D'_0 = -\log K_w - pK_{\text{DOH}^-} - \log \frac{[D]}{[\text{DOH}^-]}$$

Therefore the D'_0 function defined as an acidity function (which will be called the D_0 function) is

$$(VI) \quad D_0 = -\log \frac{a_{\text{H}^+} f_{\text{DOH}^-}}{a_{\text{H}_2\text{O}} f_D}$$

From equation (V) we see that

$$(VII) \quad D_o = 14 - D'_o$$

or

$$D_o = -\log K_w - pK_{DOH^-} - \log \frac{[D]}{[DOH^-]}$$

Now that the D_o function has been theoretically derived, it must be measured. It was decided to determine values of D'_o and then calculate D_o values from equation (VIII).

Since

$$D'_o = pK_{DOH^-} - \log \frac{[DOH^-]}{[D]},$$

it is obvious that we must measure both the dissociation constant of the complex, DOH^- , and the indicator ratio, $\frac{[DOH^-]}{[D]}$, in order to obtain values of D'_o .

The measurement of the indicator ratio will be discussed first.

It has already been stated that the method used was ultraviolet spectroscopy. For any solution containing the indicator in a partly dissociated form,

$$A_t = A_D + A_{DOH^-},$$

where A_t is the total absorbancy, A_D is the absorbancy due to the free indicator, and A_{DOH^-} is the absorbancy due to the hydroxylated form of the indicator.

Then:

$$([D] + [DOH^-])\epsilon_t = A_D + A_{DOH^-} ,$$

where brackets denote concentrations, in moles/liter, and ϵ_t is the extinction coefficient of the total solution.

Therefore,

$$\epsilon_t [D] + \epsilon_t [DOH^-] = \epsilon_D [D] + \epsilon_{DOH^-} [DOH^-]$$

rearranging

$$[DOH^-] (\epsilon_t - \epsilon_{DOH^-}) = [D] (\epsilon_D - \epsilon_t)$$

or

$$(VIII) \quad \frac{[DOH^-]}{[D]} = \frac{\epsilon_D - \epsilon_t}{\epsilon_t - \epsilon_{DOH^-}}$$

It is now apparent that the extinction coefficient of the indicator and of the indicator in its completely hydroxylated form must be measured. Then, from the extinction coefficient of any partly dissociated solution and equation (VIII), we may determine the indicator ratio.

Of course we have assumed that concentrations of the indicator are low enough so that the Beer-Lambert law is obeyed. Since the indicator concentrations used were of the order of 10^{-4} M, this should be a valid assumption.

It is also obvious that the absorption of the medium must be corrected for in these measurements.

The definition of pK_{DOH^-} is

$$pK_{DOH^-} \equiv \log \frac{[DOH^-]}{[D][OH^-]} + \log \frac{f_{DOH^-}}{f_D f_{OH^-}}$$

Since the concentration of the indicator is always very small and activity coefficients approach unity at zero concentration, we may write:

$$(IX) \quad pK_{DOH^-} = \lim_{[OH^-] \rightarrow 0} \left[\log \frac{[DOH^-]}{[D]} - \log [OH^-] \right]$$

Because of equation (IX) the pK_{DOH^-} may be obtained by plotting $\left[\log \frac{[DOH^-]}{[D]} - \log [OH^-] \right]$ vs. $[OH^-]$ and extrapolating to zero. It should be apparent that this method can be used only for sufficiently acidic indicators (i.e., those which are partly hydroxylated in the $[OH^-]$ range 0-2M). For less acidic indicators, a stepwise comparison analogous to that described by Paul and Long (13) for the H_o function may be used. If the indicators are of similar structure, then for a

given basic solution, we may assume that the indicator ratios for the two indicators are related to each other as follows:

$$(X) \quad pK_{DOH^-} - pK_{BOH^-} = \log \frac{[DOH^-]}{[D]} - \log \frac{[BOH^-]}{[B]},$$

in analogy to the situation discussed by Paul and Long (13).

If $\log \frac{[DOH^-]}{[D]}$ is plotted vs. $[OH^-]$, we should find that the various indicators give parallel plots if the D_o function is truly a function of the medium alone, and not dependent on the particular indicator used. In this case the difference in the logarithm of the indicator ratio between each indicator is also the difference in pK_{DOH^-} between these indicators according to equation (X). Therefore, if the pK of any single indicator can be directly obtained from equation (IX), the absolute values of the pK 's of all the indicators can be determined from equation (X), provided, of course, that the plot of each indicator overlaps with the plot of the one above and below it.

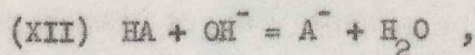
The H_- function is defined as (13),

$$(XI) \quad H_- \equiv -\log a_H + \frac{f_B^-}{f_{BH}^-}$$

and derives from the equilibrium,



However, if one considers the standard neutralization reaction,



we see that it differs from the equilibrium from which the D_o function was derived only in that a water molecule is formed in this case. For reaction (XII) we may write:

$$K_A = \frac{a_{A^-} a_{H_2O}}{a_{HA} a_{OH^-}} = \frac{\left[\frac{A^-}{HA} \right] a_{H_2O}}{a_{OH^-} \frac{f_{A^-}}{f_{HA}}}$$

$$-\log \frac{a_{H_2O}}{a_{OH^-}} \frac{f_{A^-}}{f_{HA}} = -\log K_{HA} - \log \left[\frac{HA}{A^-} \right]$$

substituting

$$K_w = \frac{a_{OH^-} a_{H^+}}{a_{H_2O}}$$

$$-\log \frac{a_{H_2O} a_{H^+}}{K_w a_{H_2O}} \frac{f_{A^-}}{f_{HA}} = -\log K_{HA} - \log \left[\frac{HA}{A^-} \right]$$

or

$$(XIII) \quad -\log a_H + \frac{f_{A^-}}{f_{HA}} = pK_{HA} - \log \left[\frac{HA}{A^-} \right] - \log K_w$$

It is seen that the left-hand side of equation (XIII) is exactly the definition of the H_- function, equation (XI). Thus we see that the acidity function for the standard neutralization reaction (XII) is the H_- function.

Upon inspection it is seen that the D_o function (VI) should be related to the H_- function as follows:

$$(D_o - H_-) = -\log \frac{a_{H^+}}{a_{H_2O}} \frac{f_{DOH^-}}{f_D} + \log a_{H^+} \frac{f_{A^-}}{f_{HA}}$$

or

$$(XIV) \quad (D_o - H_-) = \log a_{H_2O} + \log \frac{f_{A^-}}{f_{HA}} \frac{f_D}{f_{DOH^-}}$$

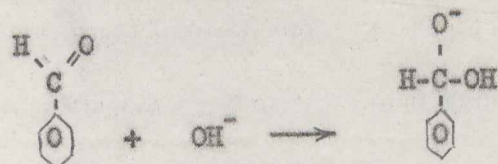
This is analagous to the theoretical difference between the H_o and J_o functions. Ideally the second term on the right will equal zero or a constant.

Both experimental and theoretical values of the H_- function are available. Experimental values have been determined by Schwarzenbach and Sulzberger (14) and are listed in a paper by Anbar and Yagil (3). In this same paper Anbar and Yagil have calculated theoretical values of H_- by assuming the OH^- ion has a hydration number of three in concentrated basic solutions.

Once values for the D_o function are measured, they should be correlated by the H_- function by equation (XIV).

When the two functions are fully developed and related to each other they should be useful in the study of base-catalyzed reactions. The work by Anbar (3) has already been mentioned.

It might be added here that the system of indicators developed for the D_0 function consists of derivatives of benzaldehyde. These compounds all have very strong absorption maxima around 230 mμ to 280 mμ and undergo hydroxylation according to the general reaction:



The hydroxylated form is stable, except for the well-known Canizzaro reaction, which was found to be so slow that it did not interfere with the necessary measurements. Care must be taken, however, to exclude oxygen from the solutions, since the aldehydes are oxidized in the presence of oxygen. The use of these compounds has the added advantage that many of them are solids, and are, therefore, easy to purify and handle.

EXPERIMENTAL PROCEDURE

The experimental work consisted of two separate phases:

1. The semi-quantitative work necessary to determine if a given compound would be a suitable indicator.

2. The actual quantitative measurement of the D_0 function, once the system of indicators was developed.

I. Development of the Indicator System

A series of indicators which would undergo partial hydroxylation in hydroxide ion concentration range 0-12 molal, and which could be studied by spectrophotometric techniques had to be found. Since no single indicator could cover the entire range, it was necessary to find an overlapping series of successively weaker acids (acids in the Lewis sense).

The ultraviolet region was chosen because many organic substances absorb very strongly in this region, while few absorb in the visible region. It was soon found that the sodium hydroxide solutions themselves absorbed very strongly below 220-230 mμ, depending on their concentrations. This limited useful indicators to those compounds having absorption maxima above 230 mμ.

For this preliminary work sodium hydroxide solutions were made from a 10M stock solution, prepared with distilled water which had been deaerated by boiling. This stock solution was kept in poly-ethylene containers to prevent the solution from dissolving any contaminants out of a glass container.

Practically all the compounds studied required a solution of approximately 10^{-4} M to give meaningful absorbancies, but since many of these compounds were only sparingly soluble in water the solutions could not be prepared directly. For this reason the general method used by Gedansky (9) was followed:

1. A 1.0×10^{-2} solution in methanol was prepared, the indicator being weighed on an analytical balance.
2. A 10 ml. aliquot of this solution was diluted to 100 ml. with water, giving a 10^{-3} M solution with 10% methanol content.
3. An appropriate aliquot to give the final concentration desired was added to a 100 ml. volumetric flask in which there was already a sodium hydroxide solution of the appropriate concentration, and the flask was then

diluted to the mark with water. (i.e.: for a 0.5×10^{-4} M indicator solution in 1.0M NaOH, 5 ml. of the 10^{-3} M solution would be added to a flask containing 10 ml. of 10M NaOH stock solution and approximately 80 ml. of water and then the flask would be diluted to the mark with water.) The final solution was always 1% or less methanol.

The indicator used was purified by distillation if it was a liquid, or by recrystallization from an appropriate solvent if it was a solid. Distilled water, which was boiled to remove dissolved gases, was used in the preparation of all solutions. If the solutions were air sensitive, as is the case with all aldehydes, nitrogen was also bubbled through the solution to eliminate air.

Each potential indicator was first examined to see if it had an absorption maximum in the range 230 mμ to about 360 mμ. If this qualification was met it was examined in base to determine the range of base concentrations over which it would be partially hydroxylated. Timed readings were made to determine if the hydroxylated species was stable, or whether it broke down to yield another product.

Since some of the aldehydes examined slowly underwent the Canizzaro reaction, the following experiment was introduced. After each timed spectrum was run, a portion of the solution was neutralized with dilute HCl and its spectrum run again. If only the hydroxylated form was present before neutralization, the original aldehyde band would be regenerated. However, if some of the aldehyde had undergone the Canizzaro reaction, the original band would only be partially regenerated. In this way, it was possible to determine the extent of any reactions beyond mere hydroxylation. This technique was also applied to other indicators which were found to undergo complicating reactions.

These preliminary measurements were made on a Perkin and Elmer Model 202 automatic recording spectrophotometer which scans the entire region from 190 mμ to 390 mμ in two minutes.

II. Quantitative Measurement of D_0 Values

After the preliminary work was done, it was no longer necessary to observe the entire spectrum of the indicator, and the Beckman D.U., which was fitted with a water jacket to maintain a constant temperature, was used. All measurements were made at $(25 \pm 1)^\circ \text{C}$.

The system of indicators used in the quantitative work consisted entirely of derivatives of benzaldehyde. The liquids were purified by distillation in a nitrogen atmosphere (benzaldehyde), or by vacuum distillation in a stream of nitrogen (O-anisaldehyde, p-anisaldehyde), while the solids were purified by recrystallization from an alcohol-water solvent pair. The purified compounds were kept in a nitrogen atmosphere and all solutions were de-aerated by bubbling nitrogen through them. Distilled water, which had been de-aerated by boiling, was used in the preparation of all solutions.

Since the exact hydroxide ion concentration now had to be determined, it was necessary to have pure, carbonate-free sodium hydroxide solutions. Carbonate-free sodium hydroxide was made by preparing a saturated solution of sodium hydroxide. According to Akerlof and Kegeles (2) the ratio between carbonate and hydroxide in a saturated solution is 0.001 or lower. The saturated sodium hydroxide solutions were kept in polyethylene containers, to prevent the solution from dissolving any contaminants out of a glass container, and all solutions were made up directly from this saturated stock solution immediately before use.

To determine the hydroxide ion concentration the solutions were titrated with standard HCl immediately after the spectrophotometric measurements were made. The HCl solutions were standardized against special grade sodium carbonate, following the procedure given in Willard, Furman, and Bacon (16). The NaOH concentration was determined as follows:

1. An aliquot of the solution was weighed.
2. The solution was titrated with standard HCl, using phenolphthalein as an indicator.
3. From the weight of the solution titrated and the volume of HCl required, the molality of the solution was calculated.
4. Since the density of NaOH solutions of molality 0-14 is accurately known (2), the volume of the solution titrated, and hence the molarity, can be calculated.

The actual solutions were prepared by essentially the same procedure given in part (I), except that the saturated NaOH stock solution was used. In the few cases where the Canizzaro reaction caused the absorbancy to change with time, an extrapolation to zero time was made.

For each indicator the absorbancy of a known concentration in water was measured to obtain the extinction coefficient of the pure aldehyde. The absorbancy of a known concentration of indicator in a solution basic enough to convert the indicator completely to its hydroxylated form was measured in order to obtain the extinction coefficient of the hydroxylated form. One exception to this was the determination of the extinction coefficient of the hydroxylated form of p-anisaldehyde, for which an approximation was made. The reasons for this will be discussed later.

Finally, a series of sodium hydroxide solutions of known concentration were run on the P and E 202. From the spectra of these solutions solvent correction curves were drawn for each wavelength run on the Beckman D.U. The methanol was found not to absorb in the region of interest.

COMPOUNDS INVESTIGATED AND RESULTS

The search for compounds useful as indicators for the D_o function was begun last year by Gedansky (9) at Union College. He definitely eliminated p-nitrobenzaldehyde and substituted benzeneboronic acids as possible indicators. The peak he observed in o-nitrobenzaldehyde is definitely too low to be of use because of the solvent absorption in this region. While he experienced a good deal of trouble with benzaldehyde, reinvestigation by the procedures just described showed no complications.

The data collected in the investigation of these compounds is far too extensive to be included here, but a table of the compounds investigated, along with the results, is given on the following page.

2,4-dimethoxybenzaldehyde was also considered briefly, but insufficient work has been done with it. Its low solubility does not appear favorable, but it could possibly be used as one of the very weakly acidic indicators. 2,4,6-trimethoxybenzaldehyde is another possible indicator in the very weakly acidic range which has not yet been investigated.

The first six useful indicators listed in the following table are the ones actually used to date in the measurement of D_o values.

TABLE 1. - Compounds Investigated and ResultsA. Useful Indicators

<u>Compound</u>	<u>Useful Range of [OH⁻]</u>	<u>$\lambda_{\text{max.}}$</u>	<u>ϵ_D</u>	<u>ϵ_{DOH^-}</u>	<u>M.P.</u>	<u>B.P.</u>
1. m-nitro-benzaldehyde	0-0.6 molal	234 mμ	20,550	3327	58°C.	-
2. 2,4-dichloro-benzaldehyde	0-0.6 "	264 mμ	12,980	634	71°C.	-
3. p-chloro-benzaldehyde	.15-2.5 "	261 mμ	16,190	324	47.5°C.	214°C.
4. benzaldehyde	.4-5.5 "	251 mμ	12,830	596	-	179.5°C.
5. o-anisaldehyde	1.5-8 "	256.5 mμ	10,450	463	-	243°C.
6. p-anisaldehyde	3.3-12.2 "	286 mμ	16,340	-	-	247°C.
7. o-chloro-benzaldehyde	.2-3(?) "	254 mμ	-	-	-	208°C.
8. piperonal	3-11(?) "	232.5, 278, 318 mμ	-	-	37°C.	-

B. Compounds Not Useful

<u>Compound</u>	<u>Reason Not Useful</u>
o-nitrobenzaldehyde	$\lambda_{\text{max.}}$ too low
p-dimethylaminobenzaldehyde	insufficient solubility
triphenylboron	rapid oxidation
benzophenone	insufficient solubility
m-dinitrobenzene	complicating reactions
benzoquinone	complicating reactions
duroquinone	complicating reactions

MEASUREMENT OF THE D_0 FUNCTION AND RESULTS

The data taken for each of the six indicators used is given in the following tables. Data for the titrations of the sodium hydroxide solutions is not given, but the method of determining the concentrations follows that given in the section on experimental procedure.

The irregularities in the absorbancy readings taken within the first few minutes after the solutions are made up are probably due to the fact that thermal equilibrium has not yet been reached. In most cases the readings become constant after a few minutes. In these cases this constant value was used in subsequent calculations. In the few cases where the readings did not become constant (due to the Cannizzaro reaction) over the interval of observance, an extrapolation to zero time was made. The graphs used for extrapolation to zero time follow the data. (Figures 1-4)

The reason readings were not begun sooner at the higher base concentrations was that a cloudiness occurred upon the addition of the indicator solution. This is no problem up to about 5m, and from 5m to 12m it clears up in a few minutes. At higher base concentrations it takes much longer to clear up, and it could present a real problem at these concentrations. This phenomenon also occurs upon the addition

of the same volume of deaerated distilled water, and has been attributed to the decrease in solubility of minute amounts of dissolved gas in the water upon dilution of the very strong base. Because of this cloudiness it was not possible to make measurements with p-anisaldehyde above 12 molal base. This made it necessary to approximate the extinction coefficient of the hydroxylated form of this indicator. This approximation will be discussed later.

TABLE 2. Data Using m-nitrobenzaldehyde

 $\lambda_{\max} = 234 \text{ m}\mu$ $T = 25^{\circ}\text{C}$

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
4	$0.5330 \times 10^{-4} \text{ M}$	0.1804	2 1/4 min	.562
			3 3/4 "	.566
			6 1/2 "	.578
			7 1/2 "	.585
			10 1/2 "	.585
			15 "	.586
5	$0.5330 \times 10^{-4} \text{ M}$	0.2890	3 1/2 min	.470
			5 "	.473
			6 3/4 "	.481
			10 1/4 "	.487
			13 "	.489
			15 "	.489
6	$0.5330 \times 10^{-4} \text{ M}$	0.3679	2 1/2 min	.440
			3 1/2 "	.442
			7 "	.446
			12 "	.456
			16 1/2 "	.456
			20 1/2 "	.457
9	$0.5110 \times 10^{-4} \text{ M}$	0.03048	2 1/2 min	.890
			3 3/4 "	.890
			7 "	.890
			15 "	.890
10	$0.5110 \times 10^{-4} \text{ M}$	0.08450	2 3/4 min	.711
			3 3/4 "	.709
			5 "	.710
			13 "	.711
			17 1/2 "	.711
11	$0.5110 \times 10^{-4} \text{ M}$	0.2836	2 1/4 min	.476
			4 "	.476
			12 "	.476

TABLE 2. (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>Molality</u>	<u>Time</u>	<u>Absorbancy</u>
12	0.5110×10^{-4} M	0.6343	2 3/4 min	.373
			6 "	.374
			13 1/2 "	.376
			17 "	.376
13 (complete hydroxylation)	0.5110×10^{-4} M	2.021	2 1/2 min	.337
			4 1/2 "	.337
			9 "	.337
1'	0.5110×10^{-4} M	0		1.050

TABLE 3. Data Using 2,4-dichlorobenzaldehyde $\lambda_{\text{max}} = 254 \text{ m}\mu$ $T = 25^{\circ}\text{C}$

<u>Sol. No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
1	$0.9943 \times 10^{-4} \text{ M}$	0	-	1.274
2	$0.9943 \times 10^{-4} \text{ M}$	0.05666	2 3/4 min	.892
			4 1/2 "	.895
			8 1/2 "	.895
			12 1/4 "	.895
3	$0.9943 \times 10^{-4} \text{ M}$	0.08666	3 min	.729
			9 "	.756
			10 "	.758
			13 1/2 "	.759
			19 3/4 "	.769
			29 "	.766
4	$0.9943 \times 10^{-4} \text{ M}$	0.1800	3 min	.482
			5 1/2 "	.509
			9 1/2 "	.527
			12 1/2 "	.533
			15 3/4 "	.536
			19 1/4 "	.534
			26 "	.536
			33 1/2 "	.534
			2 3/4 min	.360
5	$0.9943 \times 10^{-4} \text{ M}$	0.3134	4 1/4 "	.364
			7 1/2 "	.372
			11 1/2 "	.375
			14 1/2 "	.377
			17 1/2 "	.379
			25 "	.380
			36 1/4 "	.379
6 (complete hydroxylation)	$0.9943 \times 10^{-4} \text{ M}$	1.571	2 3/4 min	.108
			4 "	.109
			8 "	.109
			11 1/2 "	.109

TABLE 3. (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
1	$0.9971 \times 10^{-4} \text{ M}$	0	-	1.310
			3 min	1.099
			4 1/4 "	1.107
7	$0.9971 \times 10^{-4} \text{ M}$	0.02402	5 "	1.107
			8 1/2 "	1.107
			10 "	1.107
			2 3/4 min	.757
			4 3/4 "	.760
8	$0.9971 \times 10^{-4} \text{ M}$	0.09578	8 1/2 "	.761
			11 "	.761
			12 "	.761
			2 1/4 min	.437
			3 3/4 "	.439
9	$0.9971 \times 10^{-4} \text{ M}$	0.2805	6 1/2 "	.440
			11 1/2 "	.441
			17 "	.442
			24 "	.442
			3 min	.288
			5 "	.293
			9 "	.295
10	$0.9971 \times 10^{-4} \text{ M}$	0.4931	12 "	.297
			14 "	.297
			19 "	.297
			2 3/4 min	.249
			4 "	.249
			6 "	.249
11	$0.9971 \times 10^{-4} \text{ M}$	0.6185	11 "	.252
			16 "	.253
			19 "	.253
			23 "	.252

TABLE 4. Data Using p-chlorobenzaldehyde $\lambda_{\max} = 261 \text{ m}\mu$

T = 25°C

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
1	$0.7988 \times 10^{-4} \text{ M}$	0	-	1.293
			3 1/2 min	1.189
			4 "	1.191
			6 3/4 "	1.194
			8 1/2 "	1.192
2	$0.7988 \times 10^{-4} \text{ M}$	0.1946	12 1/2 "	1.185
			16 1/4 "	1.183
			21 3/4 "	1.186
			27 "	1.185
			3 1/2 min	1.098
			4 3/4 "	1.099
			8 3/4 "	1.100
			13 1/4 "	1.104
3	$0.7988 \times 10^{-4} \text{ M}$	0.3759	17 1/4 "	1.109
			21 1/2 "	1.110
			33 1/2 "	1.113
			49 "	1.115
			3 1/2 min	1.062
			5 "	1.063
4	$0.7988 \times 10^{-4} \text{ M}$	0.4946	7 1/2 "	1.062
			14 1/2 "	1.060
			16 "	1.059
			3 1/2 min	.981
			6 1/2 "	.990
5	$0.7988 \times 10^{-4} \text{ M}$	0.6843	8 1/2 "	.990
			12 1/2 "	.990
			3 min	.925
			4 1/2 "	.925
6	$0.7988 \times 10^{-4} \text{ M}$	0.7992	9 "	.935
			15 "	.935
			17 3/4 "	.935

TABLE 4. (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
7	$0.7988 \times 10^{-4} \text{ M}$	0.9398	3 min	.895
			4 1/2 "	.895
			10 "	.895
8	$0.7988 \times 10^{-4} \text{ M}$	1.196	3 1/2 min	.795
			5 "	.800
			7 1/2 "	.805
			11 1/2 "	.800
			13 "	.800
9	$0.7988 \times 10^{-4} \text{ M}$	1.480	2 1/2 min	.731
			10 "	.730
			13 "	.730
10	$0.7988 \times 10^{-4} \text{ M}$	1.996	4 min	.619
			6 1/4 "	.619
			14 "	.614
			17 "	.614
			2 1/2 min	.561
11	$0.7988 \times 10^{-4} \text{ M}$	2.360	3 3/4 "	.560
			8 "	.559
			9 1/2 "	.559
			19 1/4 min	.125*
15	$0.8033 \times 10^{-4} \text{ M}$	10.45	27 "	.134
			34 1/2 "	.141
			45 1/2 "	.145
			57 1/2 "	.135

* For solution No. 15 - reference cell found to absorb
0.050 - this must be added to observed readings.

TABLE 5. Data Using Benzaldehyde $\lambda_{\max} = 251 \text{ m}\mu$

T = 25°C

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
1	$1.073 \times 10^{-4} \text{ M}$	0	-	1.377
			3 min	1.304
			4 "	1.312
			5 1/2 "	1.302
2	$1.073 \times 10^{-4} \text{ M}$	0.4404	9 1/2 "	1.290
			12 1/4 "	1.290
			20 "	1.290
			24 "	1.290
			3 min	1.210
			4 1/4 "	1.212
3	$1.073 \times 10^{-4} \text{ M}$	0.7964	7 "	1.210
			9 1/2 "	1.212
			15 1/2 "	1.212
			3 1/2 min	1.057
			5 "	1.059
5	$1.073 \times 10^{-4} \text{ M}$	1.518	9 "	1.053
			15 "	1.053
			20 "	1.053
			3 1/2 min	.980
			5 1/4 "	.980
6	$1.073 \times 10^{-4} \text{ M}$	1.995	8 "	.980
			10 "	.980
			3 1/4 min	.915
7	$1.073 \times 10^{-4} \text{ M}$	2.358	4 1/4 "	.915
			8 "	.915
			15 "	.915
			3 1/4 min	.815
			5 1/2 "	.810
8	$1.073 \times 10^{-4} \text{ M}$	2.963	7 1/2 "	.815
			10 1/4 "	.810
			4 min	.759
			5 1/4 "	.759
9	$1.073 \times 10^{-4} \text{ M}$	3.254	10 "	.757
			16 "	.757
			30 "	.756

TABLE 5 - (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
10	$1.073 \times 10^{-4} M$	3.636	3 3/4 min	.700
			5 3/4 "	.696
			10 1/2 "	.690
			13 1/4 "	.690
			19 1/4 "	.691
			26 "	.691
11	$1.073 \times 10^{-4} M$	4.097	3 min	.639
			6 1/2 "	.629
			11 3/4 "	.629
			15 1/2 "	.629
12	$1.073 \times 10^{-4} M$	4.898	7 1/4 min	.528
			10 "	.528
			16 "	.526
			20 1/2 "	.524
			27 1/4 "	.522
13	$1.073 \times 10^{-4} M$	5.513	8 min	.463
			10 1/2 "	.459
			14 3/4 "	.458
			24 "	.457
			42 "	.452
14 (complete hydroxylation)	$1.073 \times 10^{-4} M$	10.55	12 1/2 min	.242
			13 1/2 "	.243
			21 1/2 "	.236
			31 1/2 "	.234
			39 1/2 "	.233
			53 "	.232

TABLE 6 - Data Using o-anisaldehyde $\lambda_{\text{max}} = 256.5 \text{ m}\mu$ $T = 25^{\circ}\text{C}$

<u>Sol. No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy*</u>
1	$0.9934 \times 10^{-4} \text{M}$	0	-	1.023
2	$0.9934 \times 10^{-4} \text{M}$	1.568	6 1/4 min	.890
			10 1/2 "	.885
			18 "	.885
3	$0.9934 \times 10^{-4} \text{M}$	2.367	6 min	.790
			19 "	.790
			26 "	.790
4	$0.9934 \times 10^{-4} \text{M}$	3.173	10 min	.712
			15 "	.712
			22 "	.712
5	$0.9934 \times 10^{-4} \text{M}$	3.950	7 min	.636
			18 1/4 "	.631
			25 1/4 "	.632
			28 1/4 "	.632
6	$0.9934 \times 10^{-4} \text{M}$	4.704	9 min	.550
			16 "	.550
			20 "	.550
			10 min	.471
			17 1/4 "	.474
			24 "	.478
7	$0.9934 \times 10^{-4} \text{M}$	5.617	28 1/2 "	.478
			33 "	.472
			46 "	.462
			10 min	.387
			20 "	.384
8	$0.9934 \times 10^{-4} \text{M}$	6.540	27 "	.384
			37 "	.381
			44 "	.381

* Due to absorption by the cells, the following corrections must be made: Sol Nos. 1,3,4,7,8,13 - add 0.015 to readings in table. Sol Nos. 2,5,6,9,10 - add 0.010 to readings in table.

TABLE 6 - (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy*</u>
9	$0.9934 \times 10^{-4} \text{M}$	7.440	10 1/2 min	.331
			17 "	.330
			24 "	.330
10	$0.9934 \times 10^{-4} \text{M}$	8.050	14 1/4 min	.292
			23 "	.283
			33 "	.283
			40 "	.283
			20 min	.197
13 (complete hydroxylation)	$0.9934 \times 10^{-4} \text{M}$	11.34	28 "	.198
			41 1/2 "	.187
			52 "	.186
			60 "	.186

* Due to absorption by the cells, the following corrections must be made: Sol Nos. 1,3,4,7,8,13 - add 0.015 to readings in table. Sol Nos. 2,5,6,9,10 - add 0.010 to readings in table.

TABLE 7 - Data Using p-enisaldehyde

 $\lambda_{\text{max}} = 286 \text{ m}\mu$

T = 25°C

<u>Sol. No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
1	$0.8325 \times 10^{-4} \text{M}$	0	-	1.360
4	$0.8325 \times 10^{-4} \text{M}$	3.363	6 min	1.299
			9 "	1.299
			18 "	1.286
			23 1/2 "	1.299
6	$0.8325 \times 10^{-4} \text{M}$	4.945	8 1/4 min	1.172
			11 1/4 "	1.167
			16 1/2 "	1.172
			20 1/2 "	1.167
			31 "	1.165
8	$0.8325 \times 10^{-4} \text{M}$	7.324	9 min	.945
			11 1/2 "	.930
			15 1/2 "	.920
			24 "	.915
			30 "	.905
9	$0.8325 \times 10^{-4} \text{M}$	8.085	13 min	.820
			21 1/2 "	.799
			31 1/2 "	.790
			44 1/2 "	.762
			53 "	.739
10	$0.8325 \times 10^{-4} \text{M}$	9.093	12 min	.689
			13 1/2 "	.679
			18 "	.647
			25 1/2 "	.621
			32 1/2 "	.601
11	$0.8325 \times 10^{-4} \text{M}$	10.02	13 1/4 min	.566
			20 1/2 "	.523
			29 "	.499
			43 "	.447
			49 "	.427

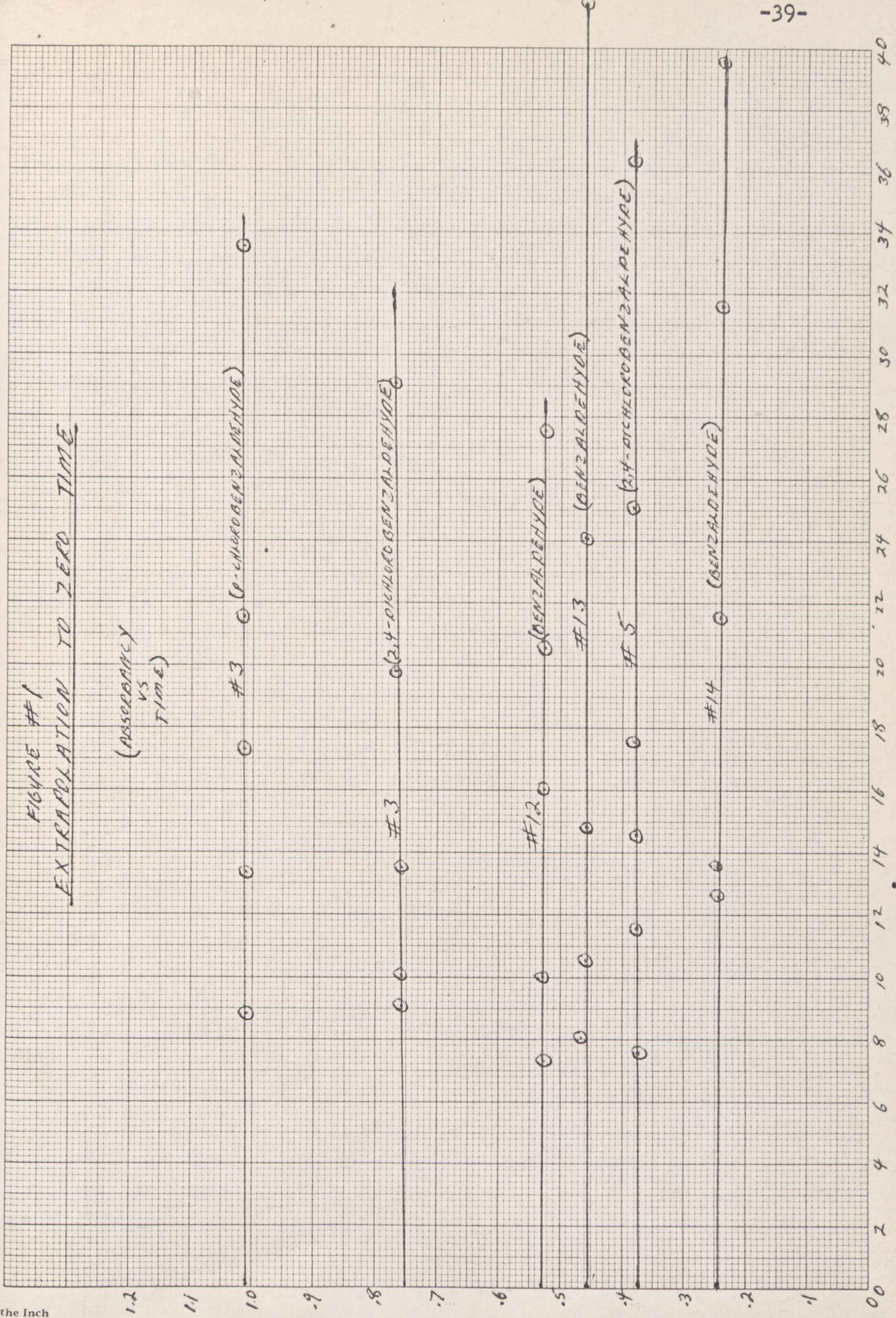
TABLE 7 - (Continued)

<u>Sol No.</u>	<u>Indicator Concentration</u>	<u>OH⁻ Molality</u>	<u>Time</u>	<u>Absorbancy</u>
12	0.8325×10^{-4} M	12.31	16 1/2 min	.369
			18 "	.366
			23 "	.350
			28 1/2 "	.326
			36 1/2 "	.309
			47 "	.294
			63 "	.262

FIGURE #1
EXTRAPOLATION TO ZERO TIME

(ABSORBANCE
VS
TIME)

ABSORBANCE



TIME (MINUTES)

FIGURE #2

EXTRAPOLATION TO ZERO TIME

(p-CHLOROBENZALDEHYDE)

ABSORBANCE
VS
TIME

ABSORBANCE

TIME (MINUTES)

#15

1.0

.9

.8

.7

.6

.5

.4

.3

.2

.1

0.0

10

20

30

40

50

60

70

FIGURE #3

EXTRAPOLATION TO ZERO TIME
(o-ANISALDEHYDE)

(ABSORBANCE
VS
TIME)

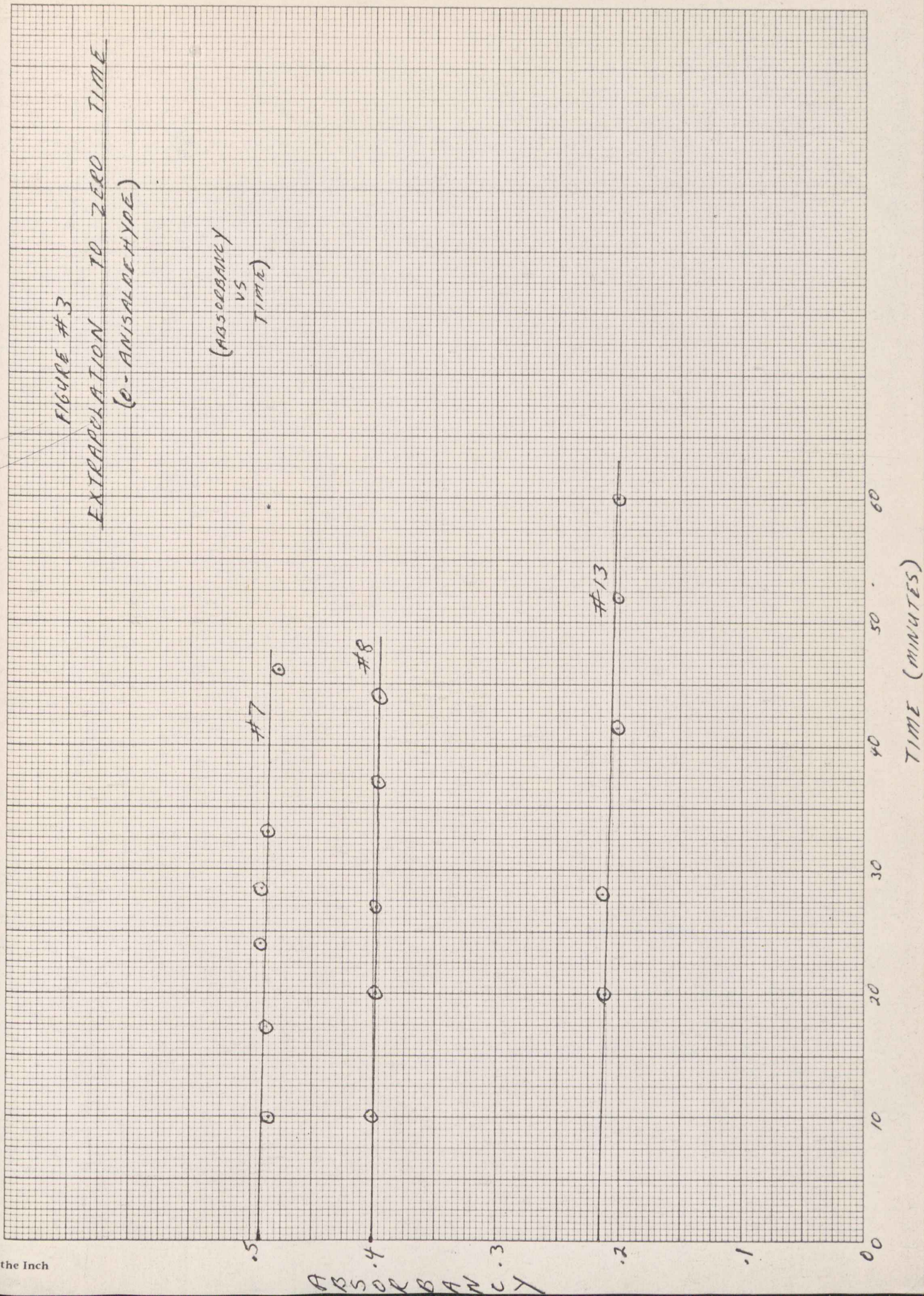
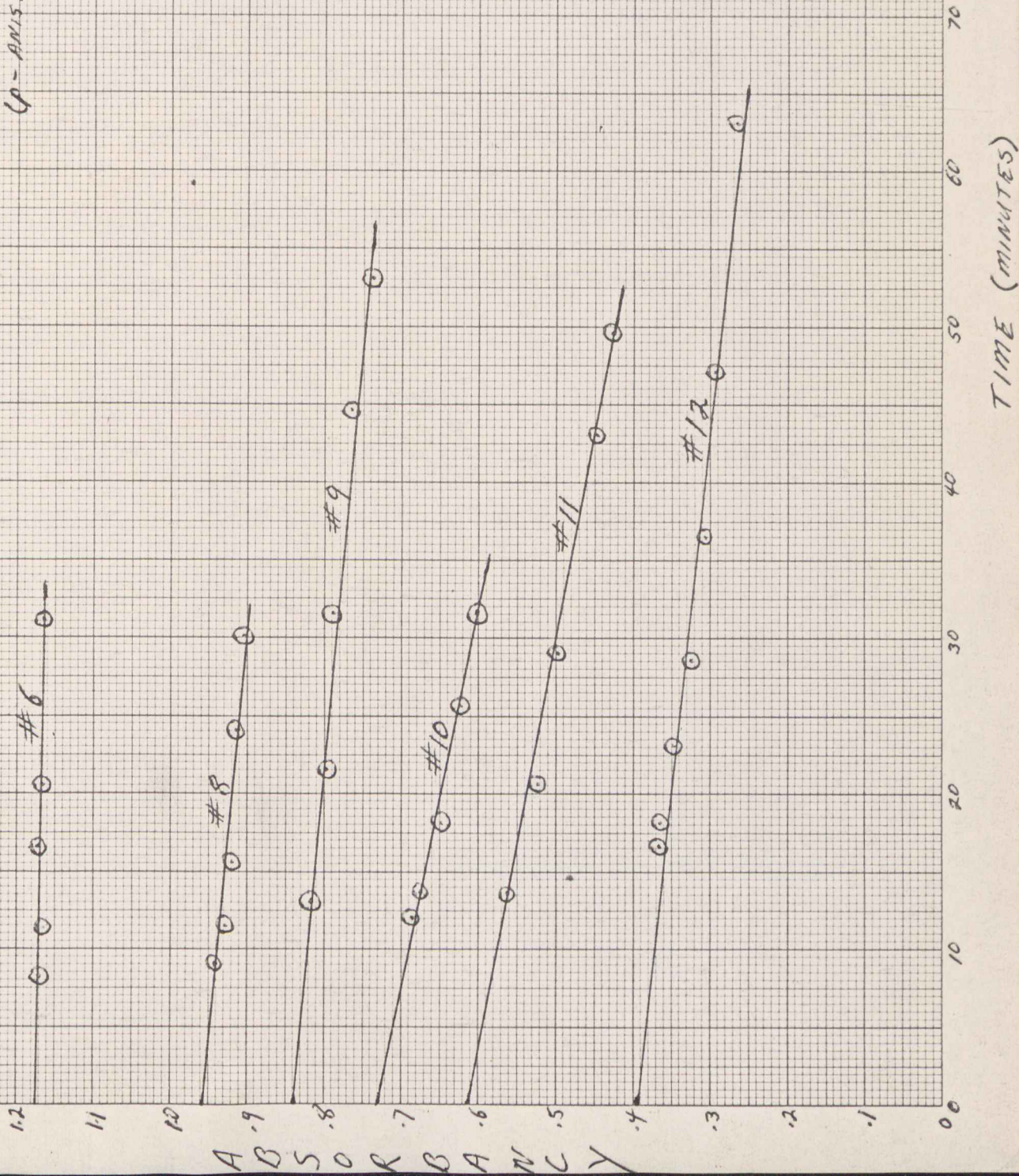


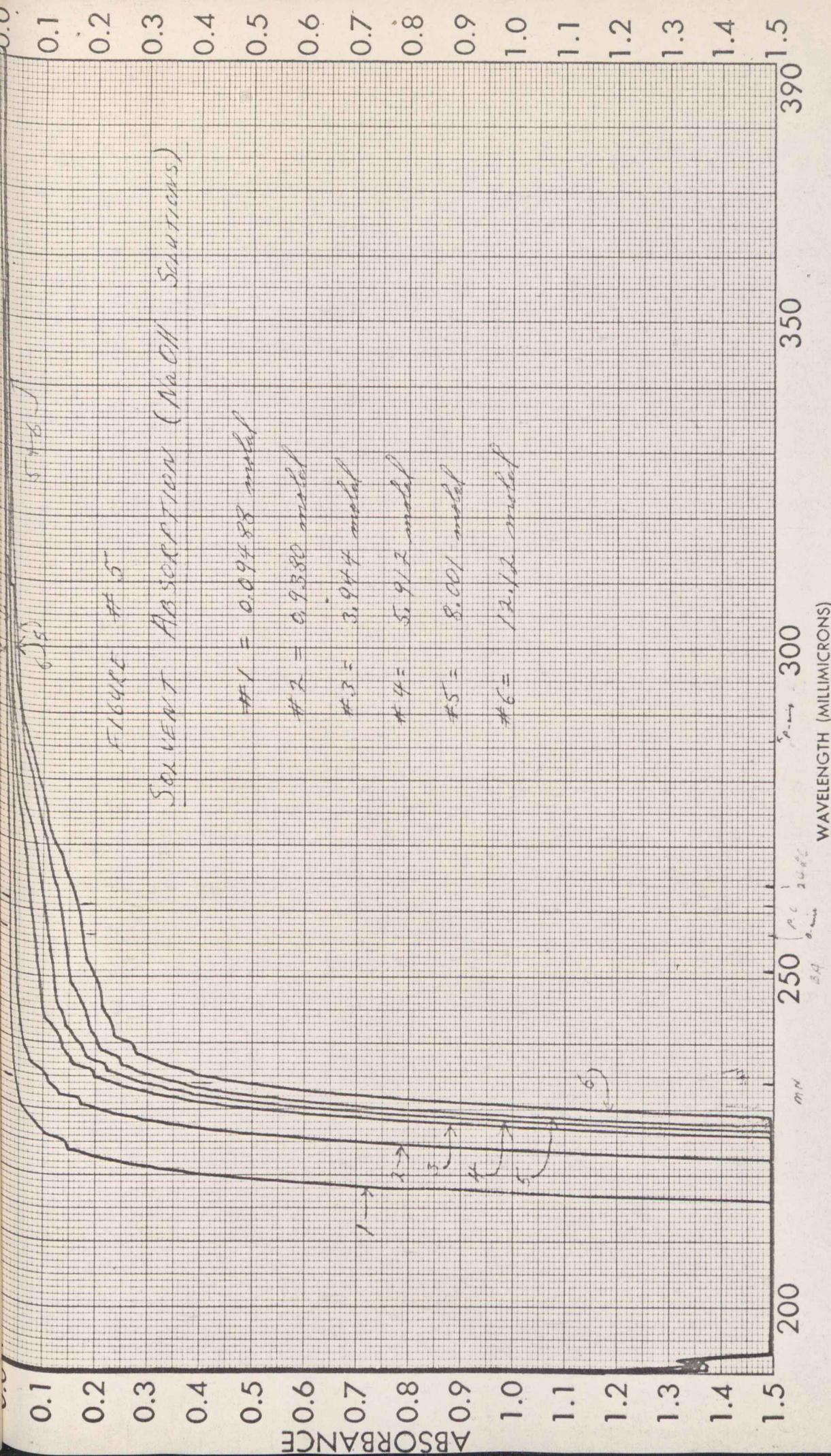
FIGURE #4
EXTRAPOLATION TO ZERO TIME
(p-ANISALDEHYDE)

(ABSORBANCY
VS
TIME)



Since it was necessary to correct for the absorption of the solutions themselves, a series of sodium hydroxide solutions of known concentration were run on the Perkin and Elmer 202. These solutions also contained 1% methanol, although the absorbancy due to the methanol was found to be entirely negligible. These spectra are given in Figure 5. From these spectra, plots of the solvent correction necessary at each NaOH molality were made for each wavelength used on the Beckman D.U.. These solvent correction curves appear in Figure 6.

It was also necessary to convert the molality of the sodium hydroxide solutions into molarity. To do this it was necessary to know the density of the sodium hydroxide solutions at each molality. This data was available in the literature (2) at 20°C and 30°C. To obtain values at 25°C these values were averaged. Table 8 gives these values and they are plotted in Figure 7. The density at each molality required was read from Figure 7.



SAMPLE <u>NaOH solutions</u>	CURVE NO. <u>92</u>	SCAN SPEED <u>2.000</u>	OPERATOR <u>JTM</u>
app. conc = #1 (1.0 ml), 2 (1.0 ml), 3 (5 ml), 4 (2.5 ml), 5 (1.0 ml), 6 (5 ml)	CONC.	SLIT <u>30</u>	DATE <u>2/11/68</u>
ORIGIN	CELL PATH <u>1 cm</u>	REMARKS	
SOLVENT <u>H₂O - 1% methanol</u>	REFERENCE <u>H₂O</u>		

282

ABSORBANCE

Squares to the Inch

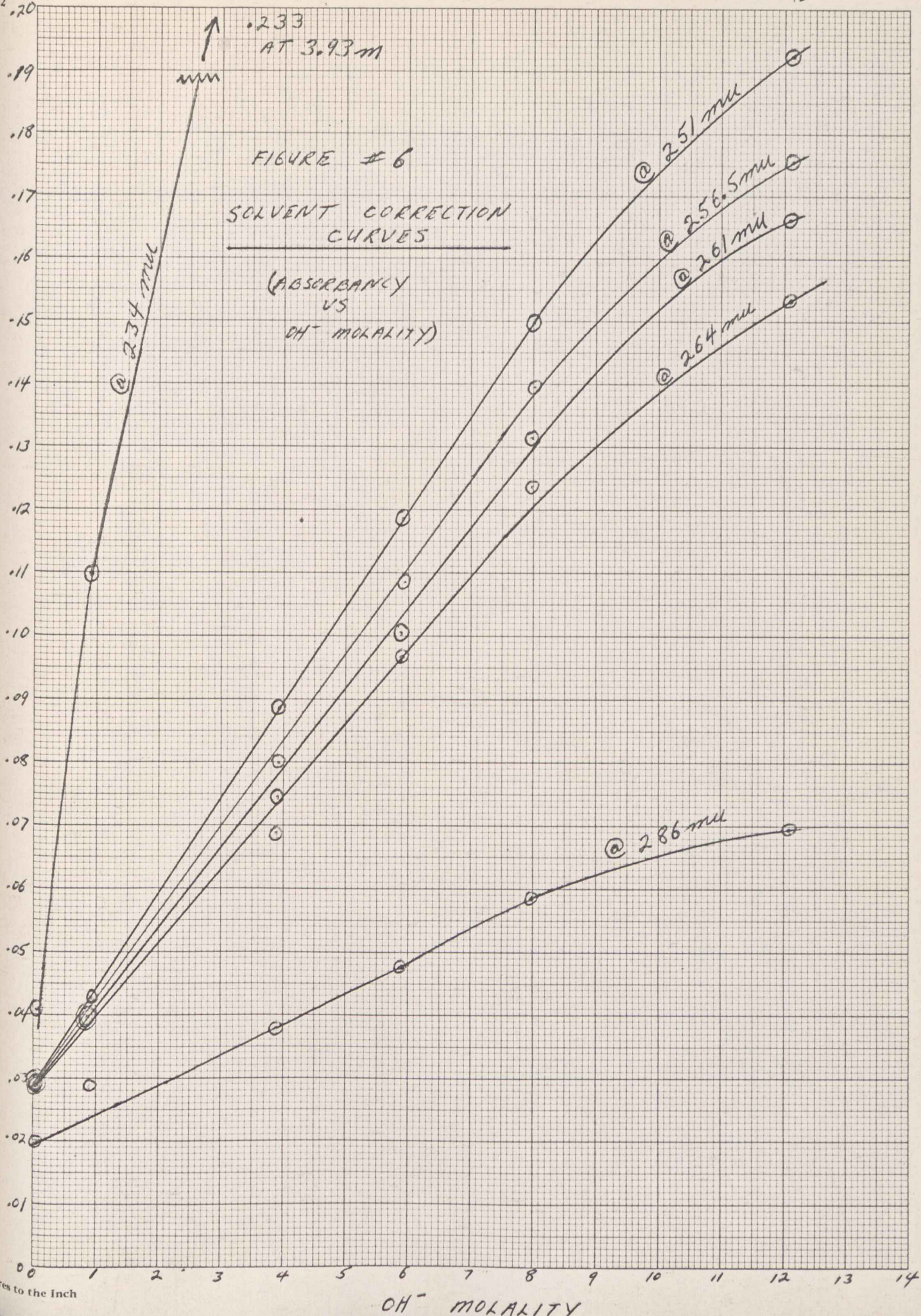


TABLE 8 - Density of Aqueous NaOH Solutions(taken from Akerlof, Kegeles; J. Am. Chem. Soc. 61, 1027 (1939))

<u>Molality</u>	<u>Density at 20°C</u>	<u>Density at 30°C</u>	<u>Density at 25°C*</u>
0.0000	.9980	.9955	.9968
0.5101	1.020	1.017	1.019
1.0415	1.042	1.039	1.040
1.5955	1.064	1.060	1.062
2.1736	1.086	1.082	1.084
2.7774	1.108	1.103	1.105
3.4087	1.130	1.125	1.127
4.0693	1.152	1.147	1.149
4.7613	1.174	1.169	1.171
5.4871	1.196	1.191	1.194
6.2492	1.218	1.213	1.216
7.0504	1.241	1.235	1.238
7.8938	1.262	1.257	1.260
8.7827	1.284	1.279	1.281
9.7210	1.305	1.300	1.303
10.7129	1.326	1.321	1.324
11.7632	1.346	1.342	1.344
12.8772	1.366	1.362	1.364
14.0607	1.388	1.381	1.384

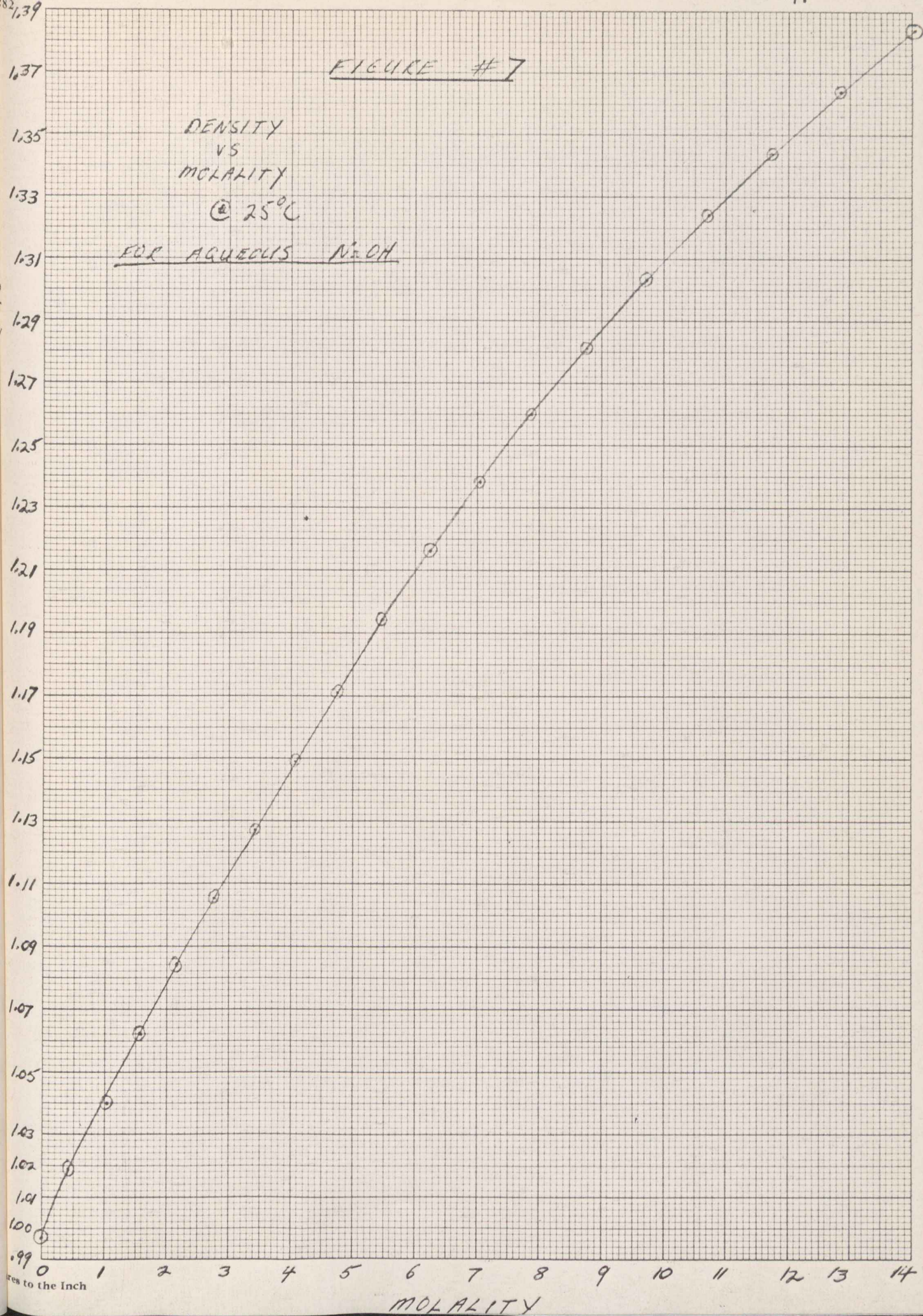
*(average of density at 20°C and 30°C)

1.39

FIGURE #7

DENSITY
VS
MOLALITY
@ 25°C

FOR AQUEOUS NaOH



All the data necessary to calculate D_0 values has now been described. The calculations were carried out as outlined in the section, History and Theory, and the results are tabulated in the following tables.

Tables 9 - 14 give calculations of the logarithm of the indicator ratios and the logarithm of the NaOH molarity, where it is required.

As stated before, the extinction coefficient of the hydroxylated form of p-anisaldehyde had to be estimated, since it could not be determined directly. It was found that the extinction coefficient of the hydroxylated form of each indicator corresponded quite closely to the extinction coefficient of the corresponding compound without the aldehyde group. Examples are given below:

	ϵ_{DOH^-}		ϵ
p-chlorobenzaldehyde	324	chlorobenzene	310 (5)
o-anisaldehyde	463	anisole	501 (exptl.)
m-nitrobenzaldehyde	33327	nitrobenzene	2570*
benzaldehyde	596	benzene	250 (5)

*Dr. Kevork Nahabedian, Doctoral Thesis

Examination shows that an error of ± 100 in the extinction coefficient of the hydroxylated form of p-anisaldehyde will give a maximum error of 0.01 in the logarithm of the indicator ratio. On this basis the extinction coefficient of the hydroxylated form of p-anisaldehyde was taken to be 500, since the extinction coefficient of anisole at 286 m μ is about 500. This approximation should introduce no appreciable error.

The pK's of m-nitrobenzaldehyde, 2,4-dichlorobenzaldehyde, and p-chlorobenzaldehyde were determined by direct extrapolation, according to equation (IX). The necessary data is given in Table 15, and the graphs showing the extrapolation follow this table. (Figure 8)

TABLE 9 - Calculation of Log (Indicator Ratio) and Log (NaOH Molarity) - m-nitrobenzaldehyde

Sol No.	Molality	Molarity	Solvent Correction	A _T	$\epsilon_{\text{DOH}^-} = 3327$				$\epsilon_D = 20,550$			
					ϵ_T	$\epsilon_D - \epsilon_T$	$\epsilon_T - \epsilon_{\text{DOH}^-}$	$\frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\log \frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\log \frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\log [\text{OH}^-]$
4	0.1805	0.1800	.051	.585	10,000	10,550	6,700	1.57	+0.196	-0.745	-0.745	
5	0.2891	0.2883	.061	.489	8,030	12,520	4,700	2.66	+0.425	-0.540	-0.540	
6	0.3679	0.3669	.068	.456	7,280	13,270	3,950	3.36	+0.526	-0.435	-0.435	
9	0.03048	0.03039	.038	.890	16,700	3,850	13,400	0.287	-0.542	-1.517	-1.517	
10	0.08450	0.08426	.041	.711	13,100	7,450	9,800	0.760	-0.119	-1.074	-1.074	
11	0.2836	0.2829	.060	.476	8,140	12,410	4,810	2.58	+0.412	-0.548	-0.548	
12	0.6343	0.6335	.090	.376	5,600	14,950	2,270	6.59	+0.819	-0.198	-0.198	

TABLE 10 - Calculation of Log (Indicator Ratio) and Log (NaOH Molarity) - 2,4-dichlorobenzaldehyde

$\lambda_{\max} = 234 \text{ m}\mu$		$\epsilon_{\text{DOH}^-} = 3327$		$\epsilon_D = 20,550$						
Sol. No.	Molality	Molarity	Solvent Correction	A_T	ϵ_T	$\epsilon_D \epsilon_T$	$\epsilon_T \epsilon_{\text{DOH}^-}$	$\frac{\epsilon_D \epsilon_T}{\epsilon_T \epsilon_{\text{DOH}^-}}$	$\text{Log } \frac{\epsilon_D \epsilon_T}{\epsilon_T \epsilon_{\text{DOH}^-}}$	$\text{Log } [\text{OH}^-]$
2	0.05664	0.05646	.029	.895	8,710	4,270	8,080	0.528	-0.277	-1.248
3	0.08666	0.08640	.029	.751	7,260	5,720	6,630	0.863	-0.064	-1.063
4	0.1800	0.1795	.030	.535	5,080	7,900	4,450	1.78	+0.250	-0.746
5	0.3132	0.3124	.031	.373	3,440	9,540	2,810	3.40	+0.531	-0.505
7	0.02402	0.02395	.028	11.107	10,820	2,160	10,190	0.212	-0.674	-1.621
8	0.09578	0.09551	.029	.761	7,340	5,640	6,710	0.841	-0.075	-1.020
9	0.2805	0.2798	.031	.441	4,110	8,870	3,480	2.55	+0.407	-0.553
10	0.4931	0.4921	.034	.297	2,640	10,340	2,010	5.14	+0.711	-0.307
11	0.6185	0.6174	.035	.253	2,190	10,790	1,560	6.92	+0.840	-0.209

TABLE 11 - Calculation of Log (Indicator Ratio) and Log (NaOH Molarity) - p-chlorobenzaldehyde

$\lambda_{\text{max}} = 261 \text{ m}\mu$		$\xi_{\text{DOH}} = 3247$		$\xi_{\text{D}} = 16,190$						
Sol No.	Molality	Molarity	Solvent Correction	A_T	ξ_T	$\xi_{\text{D}} - \xi_T$	$\xi_T - \xi_{\text{DOH}}$	$\frac{\xi_{\text{D}} - \xi_T}{\xi_T - \xi_{\text{DOH}}}$	$\text{Log } \frac{\xi_{\text{D}} - \xi_T}{\xi_T - \xi_{\text{DOH}}}$	$\text{Log } [\text{OH}^-]$
2	0.1946	0.1945	.030	1.185	14,460	1,730	14,140	0.122	-0.914	-0.711
3	0.3759	0.3763	.033	1.099	13,350	2,840	13,030	0.318	-0.662	-0.424
4	0.4946	0.4957	.034	1.060	12,840	3,350	12,520	0.268	-0.572	-0.305
5	0.6843	0.6854	.037	.990	11,930	4,260	11,610	0.367	-0.435	-0.164
6	0.7992	0.8010	.038	.935	11,230	4,960	10,910	0.455	-0.342	-0.096
7	0.9398	0.9412	.040	.895	10,700	5,490	10,400	0.528	-0.277	-0.026
8	1.196	1.196	.043	.800	9,480	6,710	9,160	0.733	-0.135	+0.078
9	1.480	1.479	.047	.730	8,550	7,640	8,230	0.928	-0.032	+0.170
10	1.996	1.991	.053	.614	7,020	9,170	6,700	1.37	+0.137	+0.299
11	2.360	2.352	.058	.559	6,270	9,920	5,950	1.67	+0.223	+0.371

TABLE 12 - Calculation of Log (Indicator Ratio) - benzaldehyde

$\lambda_{\text{max}} = 251 \text{ m}\mu$		$\epsilon_{\text{DOH}} = 596$		$\epsilon_{\text{D}} = 12,830$					
Sol No.	Molality	Molarity	Solvent Correction	A_{T}	ϵ_{T}	$\epsilon_{\text{D}} - \epsilon_{\text{T}}$	$\epsilon_{\text{T}} - \epsilon_{\text{DOH}}$	$\frac{\epsilon_{\text{D}} - \epsilon_{\text{T}}}{\epsilon_{\text{T}} - \epsilon_{\text{DOH}}}$	$\text{Log } \frac{\epsilon_{\text{D}} - \epsilon_{\text{T}}}{\epsilon_{\text{T}} - \epsilon_{\text{DOH}}}$
2	0.4104	0.4115	.034	1.290	11,710	1,120	11,110	0.101	-0.996
3	0.7964	0.7980	.040	1.211	10,910	1,920	10,310	0.186	-0.730
5	1.518	1.518	.052	1.053	9,329	3,500	8,733	0.401	-0.397
6	1.995	1.992	.059	.980	8,580	4,250	7,980	0.533	-0.273
7	2.358	2.352	.064	.915	7,930	4,900	7,330	0.668	-0.175
8	2.963	2.943	.074	.813	6,890	5,940	6,290	0.944	-0.025
9	3.254	3.227	.078	.757	6,330	6,500	5,730	1.13	+0.053
10	3.636	3.599	.084	.691	5,660	7,170	5,060	1.42	+0.152
11	4.097	4.046	.090	.629	5,020	7,810	4,420	1.77	+0.248
12	4.898	4.812	.104	.530	3,970	8,860	3,370	2.63	+0.420
13	5.513	5.400	.113	.459	3,220	9,610	2,620	3.67	+0.565

TABLE 13 - Calculation of Log (Indicator Ratio) - o-anisaldehyde

$\lambda_{\text{max}} = 256.5 \text{ m}\mu$		$\epsilon_{\text{DOH}} = 463$		$\epsilon_{\text{D}} = 10,450$					
Sol No.	Molality	Molarity	Solvent Correction	A_{T}	ϵ_{T}	$\epsilon_{\text{D}} - \epsilon_{\text{T}}$	$\epsilon_{\text{T}} - \epsilon_{\text{DOH}}$	$\frac{\epsilon_{\text{D}} - \epsilon_{\text{T}}}{\epsilon_{\text{T}} - \epsilon_{\text{DOH}}}$	$\text{Log } \frac{\epsilon_{\text{D}} - \epsilon_{\text{T}}}{\epsilon_{\text{T}} - \epsilon_{\text{DOH}}}$
2	1.568	1.566	.049	.895	8,520	1,930	8,060	0.239	-0.622
3	2.367	2.359	.060	.805	7,500	2,950	7,040	0.419	-0.378
4	3.173	3.147	.071	.727	6,600	3,850	6,140	0.627	-0.203
5	3.950	3.902	.082	.642	5,640	4,810	5,180	0.929	-0.032
6	4.704	4.629	.092	.560	4,710	5,740	4,250	1.35	+0.130
7	5.617	5.500	.105	.494	3,920	6,530	3,460	1.89	+0.276
8	6.540	6.351	.118	.401	2,850	7,600	2,390	3.18	+0.502
9	7.440	7.161	.130	.340	2,110	8,340	1,650	5.05	+0.703
10	8.050	7.704	.138	.293	1,560	8,890	1,100	8.08	+0.907

TABLE 14 - Calculation of Log (Indicator Ratio) - p-anisaldehyde

$\lambda_{\text{max}} = 286 \text{ m}\mu$		$\epsilon_{\text{DOH}^-} = 500^*$		$\epsilon_D = 16,340$				
Sol No.	Molality	Molarity	Solvent Correction	A_T	ϵ_T	$\frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$	$\text{Log } \frac{\epsilon_D - \epsilon_T}{\epsilon_T - \epsilon_{\text{DOH}^-}}$
4	3.363	3.333	.036	1.299	15,170	1,170	14,670	0.0798
6	4.945	4.859	.044	1.175	13,590	2,750	13,090	0.210
8	7.324	7.061	.056	.959	10,800	5,540	10,300	0.538
9	8.085	7.728	.059	.840	9,380	6,960	8,880	0.784
10	9.093	8.595	.063	.730	8,010	8,330	7,510	1.11
11	10.02	9.376	.066	.614	6,580	9,760	6,080	1.61
12	12.31	11.16	.071	.392	3,860	12,480	3,360	3.71

*estimated from the spectrum of anisole

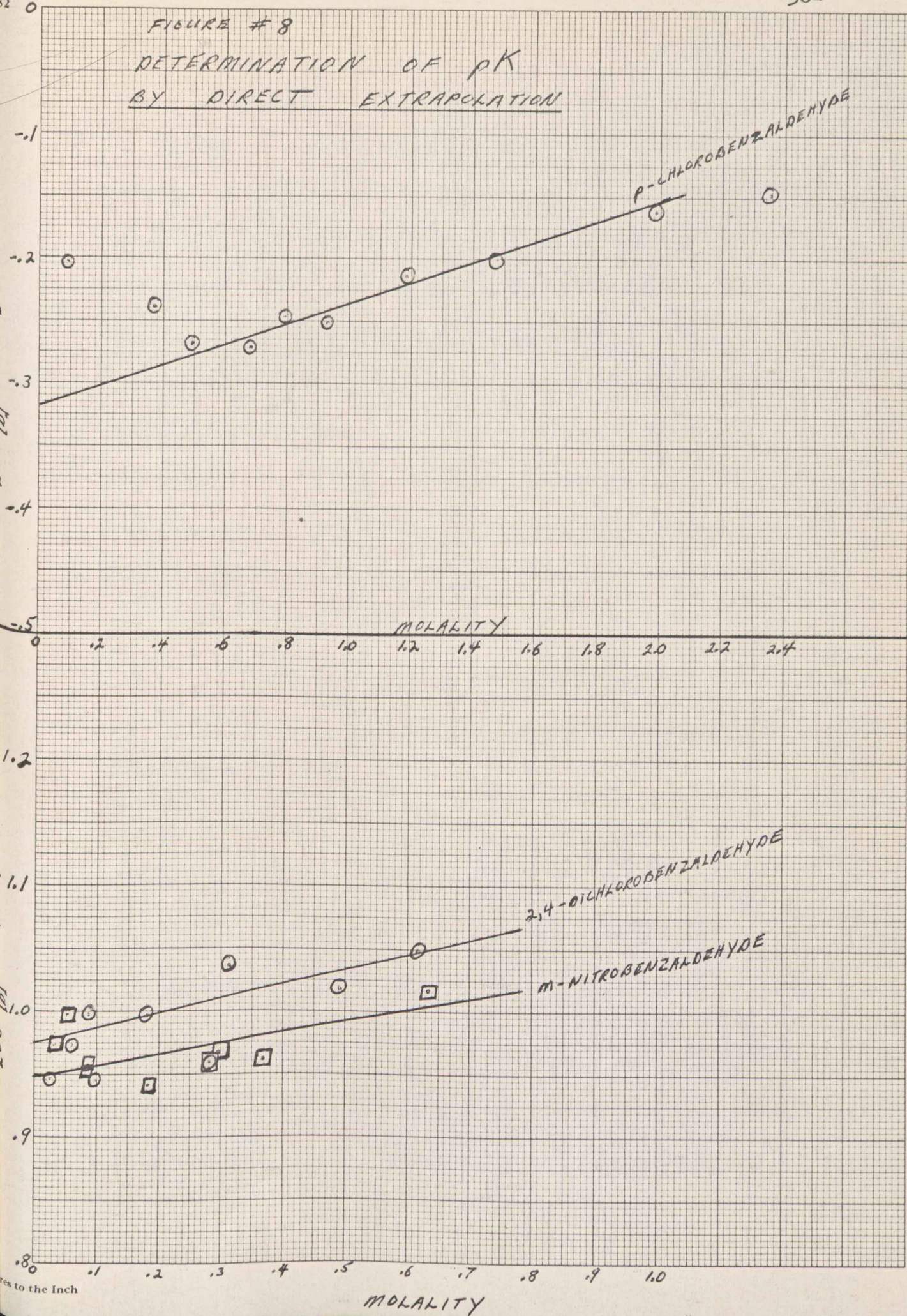
TABLE 15 - Determination of pK by Direct Extrapolation2,4-dichlorobenzaldehyde

<u>Molality</u>	<u>Molarity</u>	<u>Log $\frac{[\text{DOH}^-]}{[\text{D}]} - \text{Log } [\text{OH}^-]$</u>
0.02402	0.02395	+0.947
0.05664	0.05646	+0.971
0.08666	0.08640	+0.999
0.09578	0.09551	+0.945
0.1800	0.1795	+0.996
0.2805	0.2798	+0.960
0.3132	0.3124	+1.036
0.4931	0.4921	+1.018
0.6185	0.6174	+1.049

m-nitrobenzaldehyde

<u>Molality</u>	<u>Molarity</u>	<u>Log $\frac{[\text{DOH}^-]}{[\text{D}]} - \text{Log } [\text{OH}^-]$</u>
0.03048	0.03039	+0.975
0.08450	0.08426	+0.955
0.1805	0.1800	+0.941
0.2836	0.2829	+0.960
0.2891	0.2883	+0.965
0.3679	0.3669	+0.961
0.6343	0.6335	+1.017

FIGURE #8
DETERMINATION OF pK
BY DIRECT EXTRAPOLATION

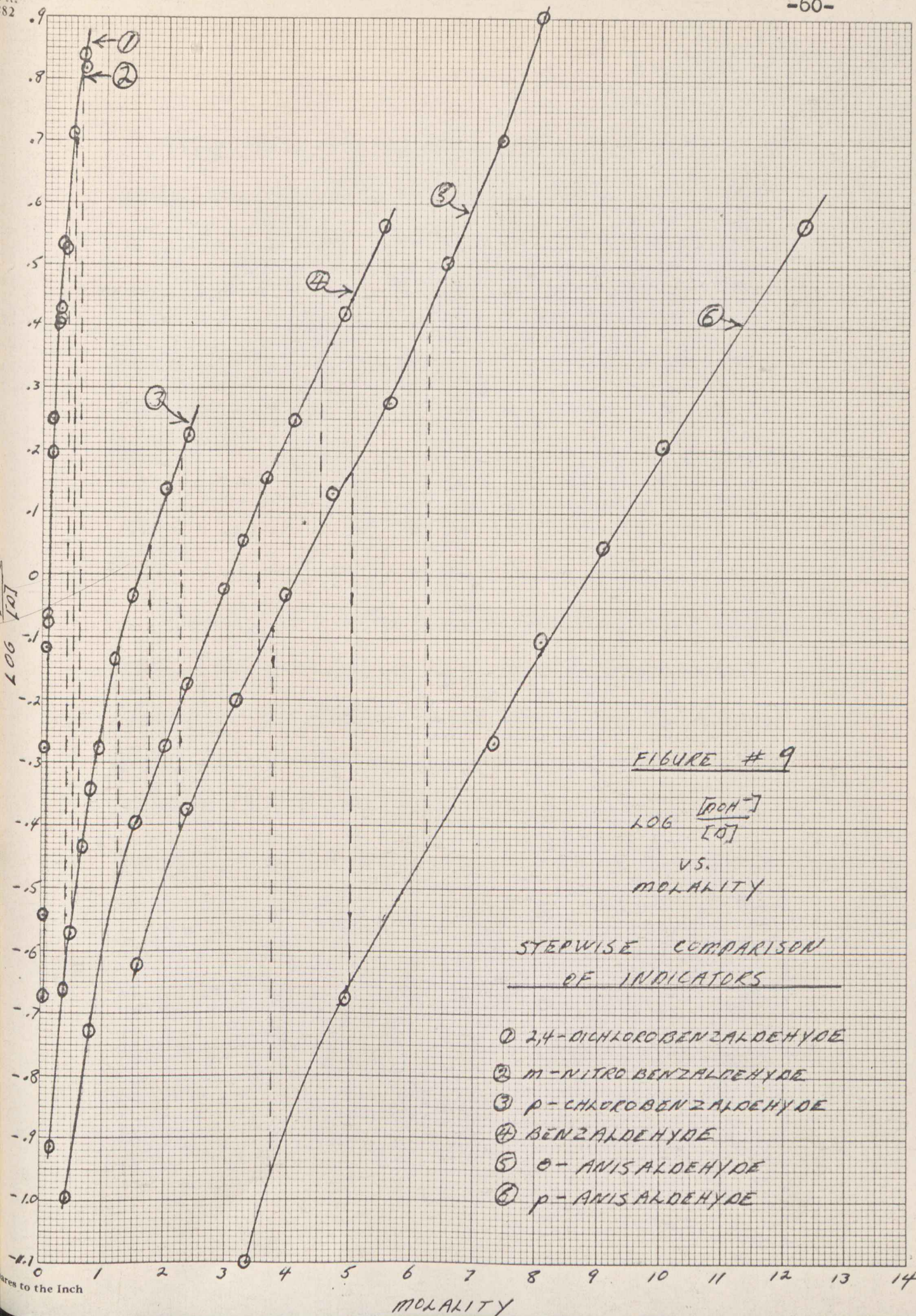


If the logarithm of the indicator ratio is plotted vs. NaOH molality, the plots for each indicator should be parallel (see History and Theory). Moreover, the difference between the plot of each indicator should also be the difference in the pK's of each indicator. From Figure 9 it can be seen that parallel plots are indeed obtained, indicating that the function being measured is independent of the indicator, and is dependent only on the basicity of the medium. Each dotted line in Figure 9 indicates a determination of the difference in pK between indicators. An average of three values was used in each case. The pK values which were obtained for each indicator are given in Table 16 below:

TABLE 16 - pK Values of the Indicators

<u>Indicator</u>	<u>pK (DOH⁻)</u>	<u>Method of Determination</u>
m-nitrobenzaldehyde	0.95	direct extrapolation
2,4-dichlorobenzaldehyde	0.98	direct extrapolation
p-chlorobenzaldehyde	-0.32	direct extrapolation
p-chlorobenzaldehyde	-0.32	comparison with ave. value of 0.97 for m-nitro and p-chloro B.A.
benzaldehyde	-0.68	comparison with ave. value of 0.97 for m-nitro and p-chloro B.A.
o-anisaldehyde	-0.96	comparison with ave. value of 0.97 for m-nitro and p-chloro B.A.
p-anisaldehyde	-1.89	comparison with ave. value of 0.97 for m-nitro and p-chloro B.A.

(NOTE: Since 2,4-dichlorobenzaldehyde and m-nitrobenzaldehyde are indistinguishable in Figure 9, an average value of 0.97 was used for comparison with other indicators.)



The D'_0 and D_0 values for each indicator and each base concentration measured are given in Table 17.

In order to illustrate the "super-basicity" discussed earlier, a plot of D'_0 vs. $\log \frac{1}{[\text{OH}^-]}$ is given in Figure 10. If the basicity were dependent only on the negative logarithm of the hydroxide ion concentration, a straight line of unit slope (dotted line) would be expected. It is seen that the basicity increased much more rapidly, showing that a "super-basicity" does occur in the more concentrated solutions.

Since it was desired to check the validity of equation (XIV), values of the H_- function and $\log a_{\text{H}_2\text{O}}$ were obtained from the literature. Anbar and Yagil (3) give both Schwarzenbach and Sulzberger's values (14) and theoretical values calculated on the assumption of a hydration number of three for the hydroxide ion. Schwarzenbach and Sulzberger arbitrarily assumed a value of 14.00 for the H_- function for a 1 molar solution. Anbar and Yagil added 0.26 to the values of Schwarzenbach and Sulzberger for the purposes of comparison with their theoretical values. Since the D_0 and H_- functions should be identical at low base concentrations, and since only relative values are of interest, the values of both Anbar and Yagil and of Schwarzenbach and Sulzberger were arbitrarily set equal

to the value of the D_0 function at 1 molar base concentration for the purposes of comparison. This was accomplished by subtracting 0.19 from all H_- values given in the paper by Anbar and Yagil (3).

The $\log a_{H_2O}$ in aqueous sodium hydroxide solutions is given in a paper by Akerlof and Kegeles (1) at 20°C.

Figure 11 is a plot of both H_- and D_0 values vs. molarity of NaOH. It should be noted that the D_0 values were measured at 25°C, while the H_- values were measured at 20°C, but this should not be a significant temperature difference. It can be seen that the two functions diverge as the base concentration increases. Anbar and Yagil's theoretical H_- values differ from the D_0 values by the $\log a_{H_2O}$ (within 0.05 logarithm units), as predicted.

Table 18 gives values of H_- , D_0 , and $H_- + \log a_{H_2O}$ for 1 to 10 molar NaOH solutions. Figure 12 is a plot of D_0 vs. $H_- + \log a_{H_2O}$. If equation (XIV) is obeyed, a straight line of unit slope (indicated by dotted line) would be expected. It can be seen that Anbar and Yagil's values agree with this prediction (within 0.05 logarithm units) while Schwarzenbach and Sulzberger's values deviate considerably.

Although more extensive work should be done with the D_0 and H functions, it appears that the theoretical considerations involved are upheld experimentally. It seems definite that the difference in the two functions will be useful in the study of base-catalyzed reactions.

TABLE 17 - D_o Values2,4-dichlorobenzaldehyde ($pK = 0.97$)

<u>Molality</u>	<u>Molarity</u>	<u>D'_o</u>	<u>D_o</u>
0.02402	0.0239	+1.64	12.36
0.05664	0.0565	+1.25	12.75
0.08666	0.0864	+1.03	12.97
0.09578	0.0955	+1.05	12.95
0.1800	0.180	+0.72	13.28
0.2805	0.280	+0.56	13.44
0.3132	0.312	+0.44	13.56
0.4931	0.492	+0.26	13.74
0.6185	0.617	+0.13	13.87

m-nitrobenzaldehyde ($pK = 0.97$)

<u>Molality</u>	<u>Molarity</u>	<u>D'_o</u>	<u>D_o</u>
0.03048	0.0304	+1.51	12.49
0.08450	0.0843	+1.09	12.91
0.1805	0.180	+0.77	13.23
0.2836	0.283	+0.56	13.44
0.2891	0.288	+0.54	13.46
0.3679	0.367	+0.44	13.56
0.6343	0.634	+0.15	13.85

TABLE 17 (Continued)

p-chlorobenzaldehyde (pK = -0.32)

<u>Molality</u>	<u>Molarity</u>	<u>D'</u> <u>D₀</u>	<u>D₀</u>
0.195	0.195	+0.59	13.41
0.376	0.376	+0.34	13.66
0.495	0.496	+0.25	13.75
0.684	0.685	+0.12	13.88
0.799	0.801	+0.02	13.98
0.940	0.941	-0.04	14.04
1.196	1.196	-0.18	14.18
1.480	1.479	-0.29	14.29
1.996	1.991	-0.46	14.46
2.360	2.352	-0.54	14.54

benzaldehyde (pK = -0.68)

<u>Molality</u>	<u>Molarity</u>	<u>D'</u> <u>D₀</u>	<u>D₀</u>
0.410	0.412	+0.32	13.68
0.796	0.798	+0.05	13.95
1.518	1.518	-0.28	14.28
1.995	1.992	-0.41	14.41
2.358	2.352	-0.50	14.50
2.963	2.943	-0.65	14.65
3.254	3.227	-0.73	14.73
3.636	3.599	-0.83	14.83
4.097	4.046	-0.93	14.93
4.898	4.812	-1.10	15.10
5.513	5.400	-1.25	15.25

TABLE 17 (Continued)

o-anisaldehyde (pK = -0.96)

<u>Molality</u>	<u>Molarity</u>	<u>D'_o</u>	<u>D_o</u>
1.568	1.566	-0.34	14.34
2.367	2.359	-0.58	14.58
3.173	3.147	-0.76	14.76
3.950	3.902	-0.93	14.93
4.704	4.629	-1.09	15.09
5.617	5.500	-1.24	15.24
6.540	6.351	-1.46	15.46
7.440	7.161	-1.66	15.66
8.050	7.704	-1.87	15.87

p-anisaldehyde (pK = -1.89)

<u>Molality</u>	<u>Molarity</u>	<u>D'_o</u>	<u>D_o</u>
3.363	3.333	-0.79	14.79
4.945	4.859	-1.21	15.21
7.324	7.061	-1.62	15.62
8.085	7.728	-1.78	15.78
9.093	8.595	-1.94	15.94
10.02	9.376	-2.10	16.10
12.31	11.16	-2.46	16.46

FIGURE #10
COMPARISON OF D_o' AND $\log \frac{1}{[OH^-]}$
AS CRITERIA FOR BASICITY

D_o'
VS
 $\log \frac{1}{[OH^-]}$

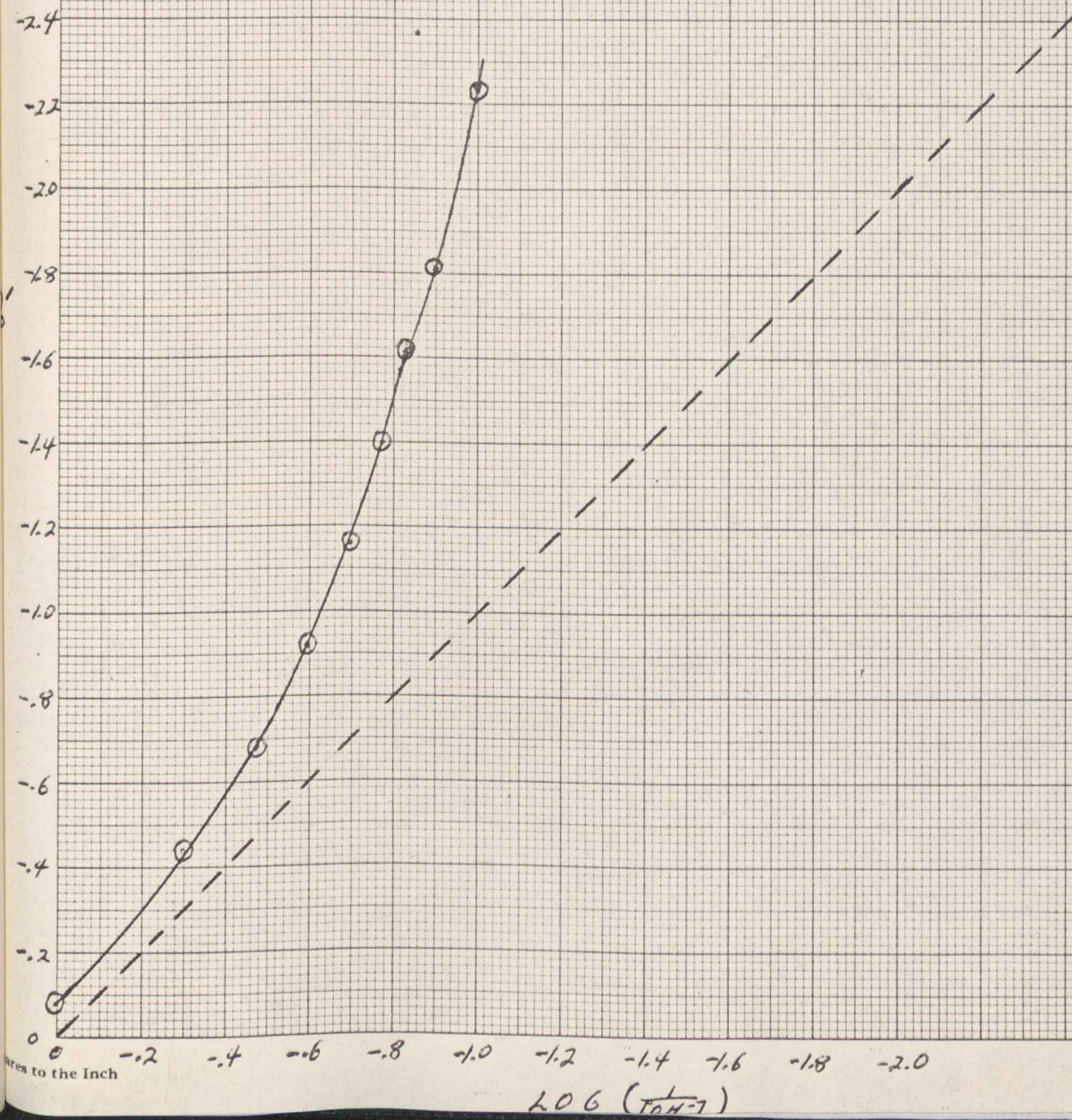


FIGURE # 11
 D_0 AND H_L VALUES
 VS
 OH^- MOLARITY

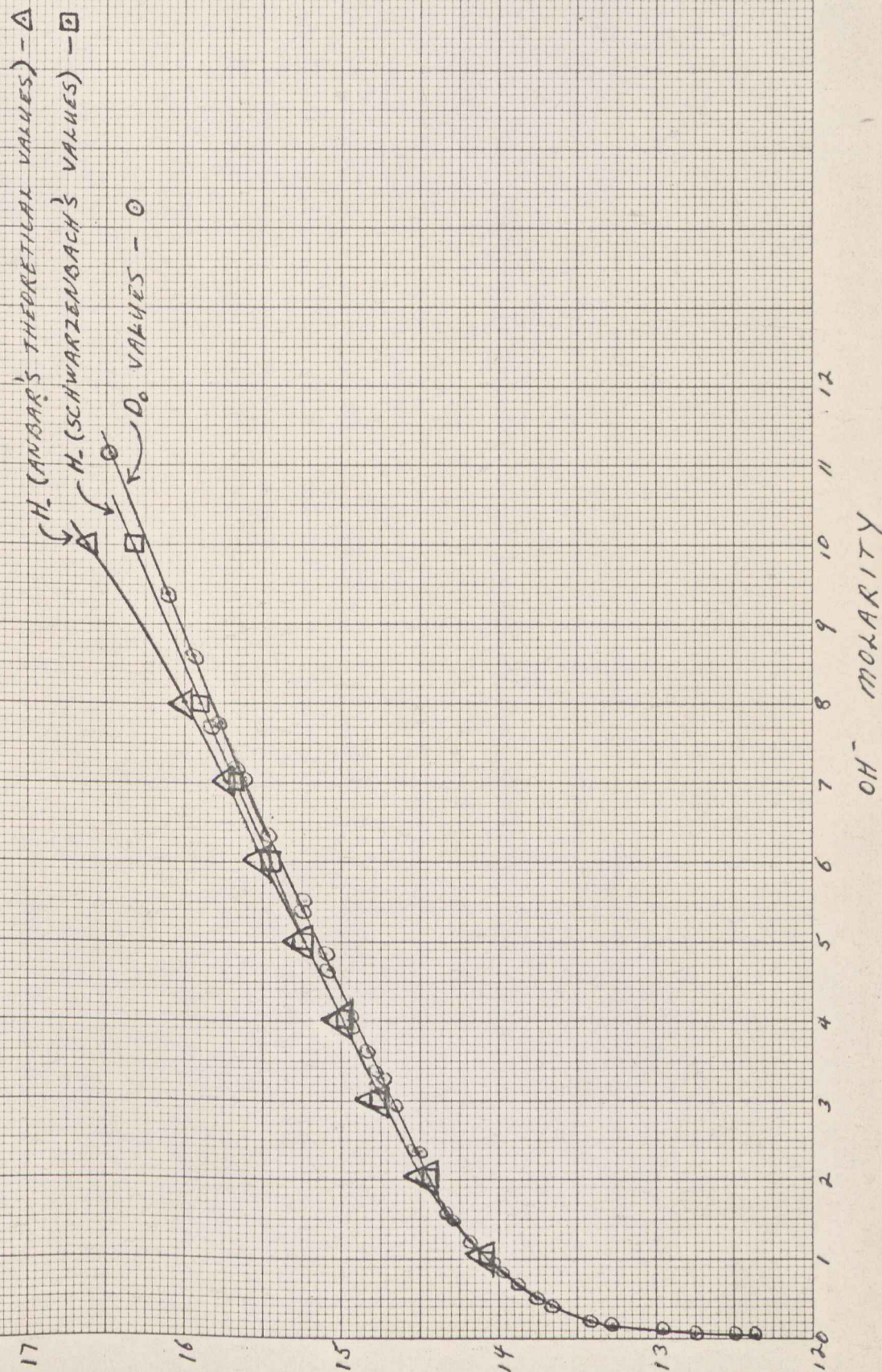


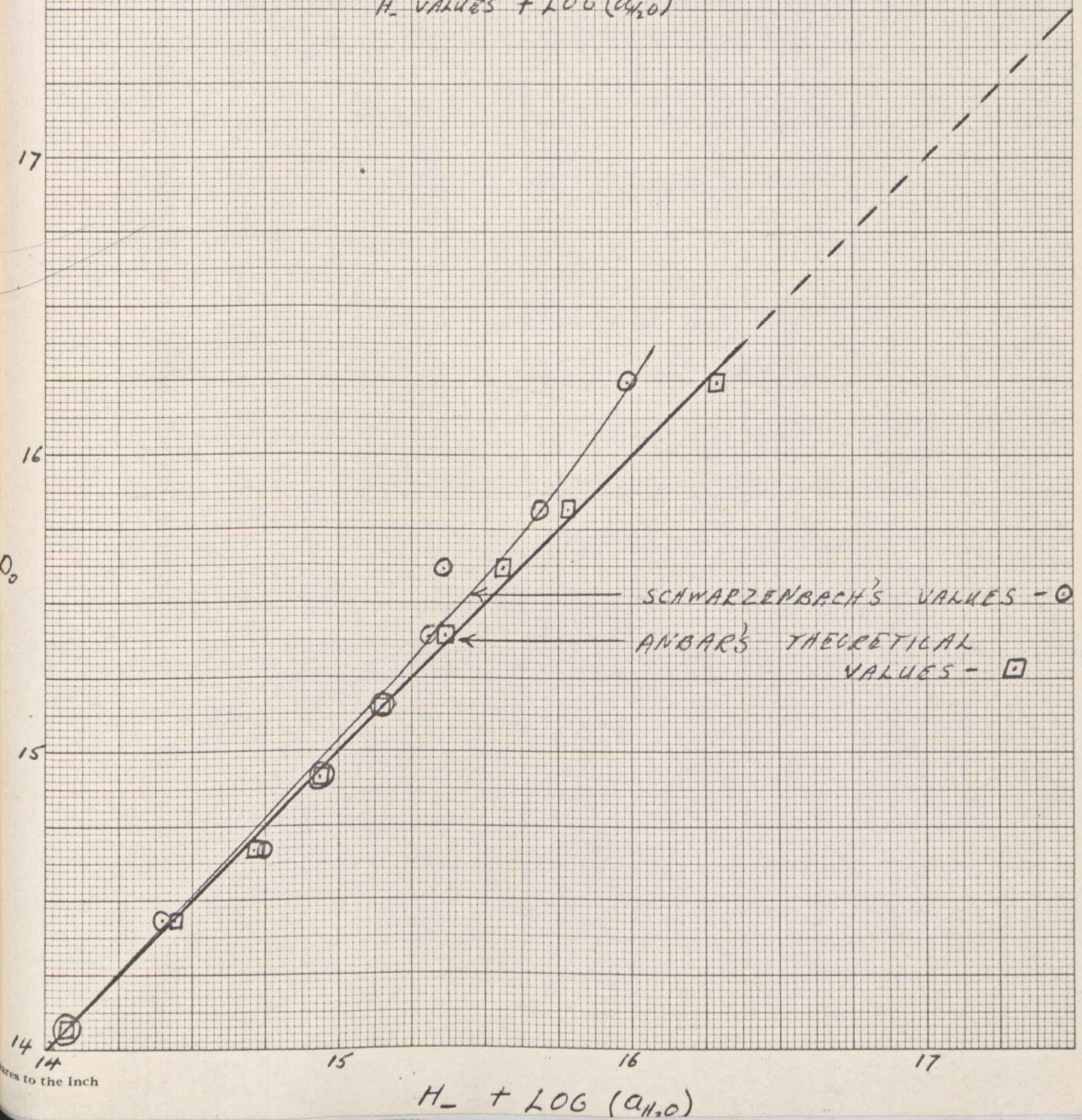
TABLE 18 - Comparison of H_L and D_O Values

Molarity	Anbar's* H_L at 20°C	Schwarzenbach's*		Anbar's		Schwarzenbach's	
		H_L at 20°C	Log a_{H_2O} at 20°C	$H_L + \text{Log } a_{H_2O}$	$H_L + \text{Log } a_{H_2O}$	$H_L + \text{Log } a_{H_2O}$	D_O at 25°C
1	14.07	14.07	-0.01	14.06	14.06	14.06	14.07
2	14.47	14.43	-0.03	14.44	14.40	14.40	14.43
3	14.76	14.78	-0.05	14.71	14.73	14.73	14.67
4	15.01	14.99	-0.08	14.93	14.91	14.91	14.91
5	15.25	15.25	-0.10	15.15	15.15	15.15	15.15
6	15.50	15.45	-0.14	15.36	15.31	15.31	15.39
7	15.74	15.66	-0.18	15.56	15.48	15.48	15.61
8	16.00	15.91	-0.22	15.78	15.69	15.69	15.81
10	16.61	16.31	-0.32	16.29	15.99	15.99	16.23

*0.19 has been subtracted from the values given in the paper by Anbar and Yagil (3)

FIGURE # 12

D_0 VALUES
VS
 H_- VALUES + $\text{LOG}(a_{H_2O})$



SUGGESTIONS FOR FURTHER STUDY

A system of indicators, consisting of eight derivatives of benzaldehyde, has been developed to enable measurements of the D_0 function. Measurements of this function in sodium hydroxide solutions from 0.02 to 12 molal have been completed, and satisfactory correlation of this function with the H_0 function has been made.

It has definitely been shown that the two functions diverge at higher base concentrations, and this fact should be useful in the study of base-catalyzed reactions.

It is suggested that the measurement of the D_0 function be carried into more concentrated sodium hydroxide solutions, where the difference between the H_0 and D_0 functions will be greater. If the problem of the cloudiness produced upon dilution of the very concentrated NaOH solutions becomes too serious, other techniques, such as using micropipettes to introduce a solution of the indicator in methanol directly into the NaOH solution (thereby eliminating dilution of the NaOH solution), might be tried.

Since excellent agreement with Anbar and Yagil's theoretical H_- values was obtained, while agreement with Schwarzenbach and Sulzberger's experimental H_- was poor, it would be desirable to check these experimental H_- values.

Measurement of the D_0 function should also be made in other bases, such as potassium hydroxide.

Another possibility, suggested by Dr. Kevork Mahabedian, is the study of these functions in mixed solvent media, such as aqueous dimethyl sulfoxide. In these solutions the basicity differences are much more pronounced, due to the decreased amount of water in the solutions.

Ultimately, of course, it is hoped that the kinetics of various base-catalyzed reactions can be correlated by the D_0 and H_- functions.

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