STUDIES ON THE HETEROPOLYMER: MALEIC ANHYDRIDE-STYRENE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Edward Robert Garrett

1948

This is to certify that the

thesis entitled

STUDIES ON THE HETEROPOLYMER, MALEIC ANHYDRIDE-STYRENE

presented by

Edward Robert Garrett

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemistry

Ralph L. Smile
Major professor

Date August 31, 1948

M-795

STUDIES ON THE HETEROPOLYMER:
MALEIC ANHYDRIDE-STYRENE

By

EDWARD ROBERT GARRETT

A THESIS

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

1948

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. Ralph L. Guile for his counsel and guidance and to Dr. R.C. Huston and Dr. F.R. Duke for their helpful assistance.

******
*****
**

*

CONTENTS

INTRODUCTION

Styrene and maleic anhydride in all proportions were reported to always form a heteropolymer with a 1:1 composition. Since accurate data on this fact, the rate of reaction, the exact structure of the polymer and properties of the polymer were lacking or inadequately proven by publisned data an investigation to determine these by use of precise analytical techniques was desirable and is the subject of this thesis.

HISTORICAL

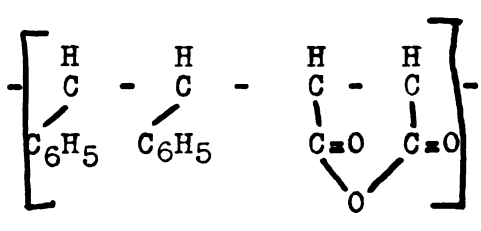
Literature on the detailed study of the copolymerization process and copolymer structure is of comparatively recent date and thus has not been adequately reviewed; in fact more than half of the accumulated data on the subject that is suitable for a true scientific study has been in publication for less than a year.[15-18, 20] The patent literature for a decade[2-10] has abounded in recipes but these give little inkling of the true nature of copolymers. Because of this fact, it has been deemed advisable to devote more space in this thesis to a review of the existing literature than is usual in order to acquaint the reader with the problems and methods of attack in this new field. In the following historical discussion, special reference has been given to copolymers with properties analogous to the maleic-anhydride - styrene heteropolymer.

It was recognized at an early date that the polymer product of copolymerization possesses properties that differ from a mixture of the homopolymerization products of each separate monomer.

The term "heteropolymerization" was proposed by Wagner-Jauregg[1] in 1930 to include those additive

heteropolymers of two different monomers, one of which showed no tendency to polymerize by itself. In these studies, maleic-anhydride (m.a.) was used as representative of the latter class of monomers. Representatives of the ethylenic class in additive heteropolymerization included stil-bene, benzal fluorene, 1,4 diphenyl butene-1 and dimethyl maleate. These non catalyzed reactions were carried out in refluxing solvents; the polymerization of maleic-anhydride and stil-bene in boiling xylene. This product has an average molecular weight of 4200 and from the data of elementary analysis it appeared that with a reactant ratio of 2:1 (stil-bene: m.a.), the heteropolymer was 1:1; with a reactant ratio of 1:1, the heteropolymer was .95:1.

It was suggested by Wagner-Jauregg[1] that the amorphous, white, infusible xylene insoluble polymer consisted of an alternating series of hydrocarbon and maleic-anhydride units linked thru the reaction of the individual double bonds:



Similarly a 1:1 reactant ratio (m.a.:benzal fluorene)

gave a 1:1 copolymer, whereas a 2:1 reactant ratio resulted in a 1:.9 copolymer.

Wagner-Jauregg[1] proposed that the tendency for an excess of m.a. could be explained on the premise of a chain ending with m.a. in these instances. Analogous results that tended to confirm this premise were obtained from the heteropolymer of m.a. with 1,4 diphenyl butene-1 which gave lower molecular weight polymers. Mass polymerization of styrene with maleic anhydride was also carried out but no significant data obtained.

Voss and Dickhauser[2] have copolymerized maleic anhydride and various ethylenic compounds in mass and solution by both heat and peroxide catalyst. They produced a m.a. -styrene heteropolymer by heat catalyzed mass polymerization that yielded a resin insoluble in benzene but soluble in acetone and dilute aqueous alkali. Using acetone as a solvent, a heat catalyzed soluble polymer was also obtained which could be precipitated by alcohol and had the same solubility properties. These polymerizations were greatly accelerated by the use of peroxide catalysts. The resultant products were capable of esterification during and after the polymerization process to yield esterified copolymers possessing different solubility properties than the original heteropolymer. The copolymer underwent the other usual reactions of carboxyl containing compounds.

For some time the m.a.-ethylenic hydrocarbon heteropolymer was considered as a phenomenon apart from true co-polymerization due to the stoichiometric proportions of the constituents in the polymer as evidenced by the studies of Wagner-Jaureggl and the unique prefix "hetero" applied. Wall[11] in his first theoretical development of relative reactivities of monomers in copolymerization ignored any specificity of attack of one type of monomer free radical upon an other of a different kind; such specificity may be considered extreme in the m.a. cases cited. His differential equation for the rate of copolymerization was based solely on the first order rate hypothesis for the disappearance of each monomer and is:

$$(1) \quad \frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{k_{M_1}\left[M_1\right]}{k_{M_2}\left[M_2\right]} = \frac{\alpha\left[M_1\right]}{\left[M_2\right]}$$

where $\left[M_1\right]$ and $\left[M_2\right]$ are the concentrations of unreacted monomer; where α is the relative reactivity of the two monomers in the copolymerization, a quotient of the rate constants for the individual polymerizations k_{M_1}, (rate constant of polymerization M_1) and k_{M_2}, (rate constant of polymerization M_2) respectively. When $\alpha = 1$, the polymer composition will be the same as the monomer reaction mixture. When $\alpha \neq 1$, the polymer composition will be proportional to, but not the same as, the reaction mixture.

Mayo and Lewis[12] studied the copolymerization of styrene and methyl methacrylate and, attempting to utilize the above equation, found that α varied with the $[M_1]/[M_2]$ ratio. They also stated that this equation could not account for the specificity of the several maleic anhydride heteropolymers to occur in a stoichiometric ratio as indicated by Wagner-Jauregg[1].

The differential equation of copolymerization as proposed by Mayo and Lewis[12] and based on the work of Norrish and Brookman[13] is formulated thusly:

Consider the two monomers M_1 and M_2 that copolymerize and the two kinds of free radicals that form the growing ends of the polymer molecules $M_1\cdot$ and $M_2\cdot$ The reactions that occur are:

(2) $M_1\cdot + M_1 \xrightarrow{k_1} M_1\cdot$

(3) $M_1\cdot + M_2 \xrightarrow{k_2} M_2\cdot$

(4) $M_2\cdot + M_2 \xrightarrow{k_3} M_2\cdot$

(5) $M_2\cdot + M_1 \xrightarrow{k_4} M_1\cdot$

The rates of disappearance of M_1 and M_2 alone are:

(6) $-d[M_1]/dt = k_1[M_1][M_1\cdot] + k_4[M_1][M_2\cdot]$

(7) $-d[M_2]/dt = k_2[M_2][M_1\cdot] + k_3[M_2][M_2\cdot]$

and thus: (8) $$\frac{d[M_1]}{d[M_2]} = \frac{k_1[M_1][M_1\cdot] + k_4[M_1][M_2\cdot]}{k_2[M_2][M_1\cdot] + k_3[M_2][M_2\cdot]}$$

Assuming a steady state where $M_1\cdot$ type radicals are converted to $M_2\cdot$ type radicals at a rate equal to which $M_2\cdot$ type radicals are converted to $M_1\cdot$ type radicals we have:

$$(9)\quad k_2 [M_2] [M_1\cdot] = k_4 [M_1] [M_2\cdot]$$

$$\text{or:}\quad [M_1\cdot] = \frac{k_4}{k_2} \frac{[M_1] [M_2\cdot]}{[M_2]}$$

$$\text{Thus:}\quad \frac{d[M_1]}{d[M_2]} = \frac{\frac{k_1}{k_2}[M_1] \frac{k_4 [M_1] [M_2\cdot]}{[M_2]} + k_4 [M_1] [M_2\cdot]}{k_2 [M_2] \frac{k_4 [M_1] [M_2\cdot]}{k_2 [M_2]} + k_3 [M_2] [M_2\cdot]}$$

And multiplying numerator and denominator by $[M_2] / k_4 [M_2\cdot]$ we have:

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_1}{k_2}[M_1]^2 + [M_2][M_1]}{[M_1][M_2] + \frac{k_3}{k_4}[M_2]^2}$$

$$\text{or (10)}\quad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{\frac{k_1}{k_2}[M_1] + [M_2]}{\frac{k_3}{k_4}[M_2] + [M_1]}$$

$$\text{and (11)}\quad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]}$$

In equation (11), r_1 and r_2 are termed the monomer reactivity ratios; r_1 is the ratio of the

rate constants for the reaction of M_1 type radical with M_1 and M_2 respectively while r_2 is the ratio for the reaction of M_2 type radical with M_2 and M_1 respectively.

The simple Wall[11] equation (1) states that rate of monomer consumption in the polymer depends solely on relative concentrations of unreacted monomer i.e. collision probability. It does not consider any possible specificity of attack of one free radical monomer on a molecule of the other kind, which consideration is included in the Mayo and Lewis[12] equation (11). If $r_1r_2 = 1$, $M_1\cdot$ is just as apt to attack M_1 (or M_2) as $M_2\cdot$ is to attack M_1 (or M_2) and thus we can expect the "ideal" copolymer of Wall[14], purely random and dependent on feed ratios entirely. But if $r_1r_2 = 0$, then either M_1 or M_2 will not react with itself and if $r_1 = 0$ and r_2 is very small, M_1 exclusively attacks M_2 and M_2 has extreme preference for M_1 and thus we have the "alternating" type polymer[15,16] proposed by Wagner-Jauregg[1]. If the r_1r_2 product has intermediate values, there is a variation in degree between the alternating and random effects. A product greater than unity indicates that the copolymer has the greatest tendency not to copolymerize but to homopolymerize.

The Mayo and Lewis technique[12,15-20] involved precipitation of the copolymer, solvent

extraction of monomer, drying and elementary analysis. This data, coupled with the yield data at precipitation, allowed them to calculate the monomer concentration at the time of polymerization cessation. These values of $[M_1]$ and $[M_2]$ plus the $[M_1]_o$ and $[M_2]_o$ values, the monomer concentrations at the start of the reaction, were substituted into an integrated form of equation (11)[4]. For a particular reaction (i.e. specific molar ratios at start and specific yield), a series of r_1 and r_2 values satisfied this integrated equation. When these values were plotted on rectangular coordinates r_1 vs. r_2, they gave a straight line as per the linear differential equation (11). Another reaction is necessary, using another initial monomer ratio and yield to determine another linear plot. The point of intersection theoretically defines a unique point giving the values of r_1 and r_2 for the copolymerization. In general, however, several such reactions are made and the center of the focal area is chosen as the closest approximation to the r_1 and r_2 values.

Wall[14] in a further theoretical study along the lines of Mayo and Lewis[12] states that if r_1 (or r_2) is equal to zero, there is a marked tendency to form a 1:1 copolymer "azeotrope" which cannot have this composition exactly as no such copolymer can

have a composition with maleic anhydride greater than .5 due to the latter's inability to react with itself. He calculates that the "azeotrope" of an analogous system would contain .474 mole fraction as a maximum i.e. when the m.a. monomer mole fraction is initially greater or equal to .5. For a .25 mol fraction of m.a., his theoretical system predicts a mol fraction of m.a. in the copolymer of .43.

This theoretical development also brings Wall[14] to the conclusion that if such a copolymerization is carried out with an excess of styrene, the first polymer formed will be close to the azeotrope but the last polymer formed will be pure styrene. He states, however, that we cannot assume that polymer chains would not have intermediate compositions.

In the light of the Mayo and Lewis[12] copolymer equation (11), Bartlett and Nozacki[21] have studied an azeotropic copolymer with a marked tendency toward a 1:1 composition. The yield of the peroxide catalyzed copolymer is determined at different intervals and the copolymer constitution of maleic anhydride and allyl acetate is determined by analysis of the remaining monomers using a specific unsaturation analytical technique. It is interesting to note that they effected a self-polymerization of maleic anhydride in these studies. The rate of copolymerization is

greater than either homopolymerization of the monomers and resulted in a molecular weight of 40,000 with high peroxide catalyst concentration and a lower molecular weight with decreased peroxide concentration. They note that the copolymerization showed great sensitivity to air inhibition.

With as high as 58:1 molar ratio of reactants (allyl acetate: m.a.) Bartlett and Nozacki[21] showed that the monomers entered into the copolymer mole for mole. However, with a m.a. excess over .8 mole fraction in the monomer mixture, they concluded that a definite tendency existed to have a greater mole fraction of m.a. in the copolymer. Their stated experimental error of 10% does not allow this assertion to be too valid.

No characteristic abnormalities in vapor pressures, mutual solubilities and viscosities of mixtures of monomers showing tendency toward 1:1 copolymerization were evident although concentrated mixtures of such monomers as stillbene, styrene, 1,1 diphenyl ethylene gave decided colors when mixed in solution with m.a. These compounds all contain aromatic groups and all tend to 1:1 copolymers[1]. Bartlett and Nozacki[21] suggested that resonant structures and polarities may allow the co-monomers to act as electron donors and acceptors respectively. Thus polar

chromophoric intermediates may occur that facilitate the "alternating tendencies " in the copolymer.

In a series of recent publications[16,18,20] more detailed attention has been given to the alternation tendency in copolymerization. The relative reactivity ratios have indicated a qualitative relation between an increasing tendency of monomers to alternate with styrene and the tendency of substituents on olefinic carbons to accept electrons from double bonds[16]. However, this relationship is not quantitative and other effects must be postulated to account for the observed relative alternation tendencies, such as specific resonance interactions between certain radicals and monomer, perhaps even involving actual electron transfer. Steric effects may also inhibit or abet alternation.

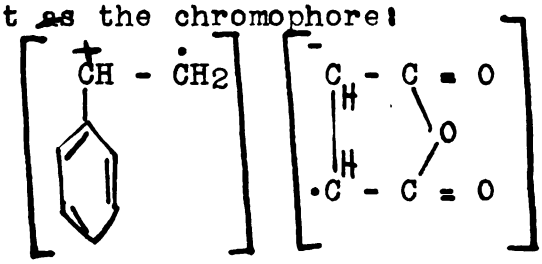
Mayo, Lewis and Walling[16] have established a donor-acceptor series which is, in a sense, a relative measure of electrophilicity (electronegativity). From the position of these radical groups in the series, alternation tendencies may be predicted. If two monomers are close together they will be "ideal" or random copolymers (e.g. styrene-butadiene). However, the position of the monomers in an activity series must also be considered, since the further apart they lie in this latter series the more the reactive monomer will predominate in

the copolymer (e.g. styrene-vinyl acetate). It can be noted that these copolymerizations will fit the simple equation (1) of Wall[11] and the copolymer constitution will depend solely on the feed ratio of the monomers. With two monomers well separated in the donor acceptor series, they will tend to alternate. If neither monomer polymerizes easily by itself (e.g. stillbene-m.a.) or if they lie close together in the average activity series (e.g. styrene-acrylonitrile) the tendency toward a 1:1 copolymer is high.

Since polarity considerations do not fully account for all alternation tendencies, cis and trans forms of various monomers were copolymerized[17]. In general the cis form (e.g. maleate ester with styrene) was less reactive than the trans form (e.g. fumarate ester with styrene) due to the non coplanar configuration of the cis form which decreases the ability of resonance to stabilize the activated complex. Thus, it became apparent that steric inhibition of resonance, when resonance can occur, affects the relative reactivities of geometrical isomers.

The comparison of copolymerizations of various substituted styrenes with methyl methacrylate[18] gave relative reactivity values for various substituents on the styrene radical. On comparison with the absorption spectra of these styrenes mixed with maleic anhydride, an excellent correlation

is found with the intensity of the color formation. This lends credence to the intermediate complex postulate which may facilitate alternation and, in general, increased rates of copolymerization over homopolymerization. In this regard, a radical-ion resonant hybrid is postulated which may act as the chromophore:



Further work along these lines has been conducted by the same school[20] utilizing monomers that tend toward complete alternation. A terpolymerization system was utilized of substituted alpha methylstyrenes and maleic anhydride. In this regard, the competing of two different alpha methyl styrenes to alternate with maleic anhydride served as an index to the effect of the substituent on the reactivity of the alpha methyl styrene. The terpolymeration equation is greatly simplified when the monomer reactivity ratios are essentially zero:

$$(12) \qquad \frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{k_1\left[M_1\right]}{k_2\left[M_2\right]}$$

Elementary analysis of the copolymers demonstrated that the increased reactivity of the styrenes

paralleled their tendencies to form colored molecular complexes with conjugated carbonyl systems. This serves as additional evidence that the alternating tendency arises from the presence of resonant structures in the previously postulated radical-ion. Thus it seems possible that the mechanism of alternation depends on the attack of a radical on the molecular complex i.e. polar resonance forms.

Alfrey and Lavin[22] have conducted a study of maleic anhydride-styrene copolymerization based on their derivation of the copolymerization equation:

$$(13)\quad b/a = B/A \cdot \alpha \cdot \frac{\beta B + A}{\alpha B + A}$$

where in terms of equations (2 through 5)

$$(14)\quad \alpha = k_2/k_1 \qquad \beta = k_3/k_4$$

and B is [styrene] and A is [maleic anhydride]. b/a is the ratio of monomer components in the copolymer (styrene: m.a.) From equations (10) and (11) it is apparent that:

$$(15)\quad \alpha = 1/r_1$$

$$(16)\quad \beta = 1/r_2$$

If we assume that there is no tendency for an m.a. radical to attack an m.a. molecule then:

$$(17)\quad \beta = 0$$

and equation (13) simplifies to:

$$(18)\quad a/b = 1 + 1/\alpha \cdot A/B$$

Alfrey and Lavin[22] in an industrial laboratory conducted these polymerizations in benzene solvent

with peroxide catalysis and when precipitation of the copolymer was first noted, it was filtered, thrice refluxed with benzene and vacuum dried. Yield was determined and the polymer dissolved in .2N NaOH. The maleic anhydride content was analyzed by electrometric titrations, which data is not given in the paper. This procedure was used at different molar ratios of styrene-maleic anhydride and the α values calculated by means of equation (18) since a/b, A and B were known. The α value was 24 ± 5 i.e. $r_1 \sim .025$ indicating that a styrene radical prefers an m.a. molecule 25 times more than it prefers a styrene molecule. The data in this paper is meager and only the per cent monomer in the reaction mixture, percentage composition of the copolymer, per cent yield at time of precipitation has been given. No experimental data or techniques are published.

Katchalsky and Spitnik[23] provide data and curves in their study of potentiometric titrations of carboxyl containing polymer. In their study of the polymeric acid polymethacrylic acid they found that the pH of the solutions fulfills a modification of the Henderson-Hasselbalch equation:

$$(19)\quad pH = pK - n \log \frac{1-\alpha}{\alpha}$$

where the exponent n has to be introduced as an empirical factor. α is the fraction of carboxyls that have

dissociated. Katchalsky and Spitnik also mention that polydibasic acids, as in the case of the copolymer polyallyl acetate - maleic acid, act in themselves as dibasic acids and conform to the polymeric acid conditions for each distal part of the titration curve in their agreement with equation (19). No data or curves are offered to substantiate this point.

EXPERIMENTAL

PART I

COMPARISON OF SOLUTION COPOLYMERIZATION TECHNIQUES

REACTION A

Materials: The benzene was c.p., thiophene free. Eastman technical maleic anhydride was used without further purification. The benzoyl peroxide was Eastman. Tertiary butyl catechol inhibitor was removed from Eastman styrene by washing twice with aqueous 10% NaOH and twice with distilled water. The uninhibited styrene was of a straw yellow color, u_D = 1.5468 at 20° C whereas the colorless inhibited styrene index of refraction was 1.5448 at 23° C. The handbook value was 1.5449 u^D at 20°, indicating that polymeric impurities appear in caustic uninhibited styrene.

Equipment: A 500 ml 3 necked flask with thermometer, reflux condenser and stirrer attachments was suspended in a water bath heated on a hot plate.

Recipe: 300 ml benzene
10.4 g maleic anhydride (.106 mole)
9.8 g styrene (.094 mole)
.1 g benzoyl peroxide

Procedure: Benzoyl peroxide was dissolved in benzene and added to the reaction flask with stirring. Maleic anhydride was added and stirred until dissolution and then the styrene was added through the condenser.

Observations:

Time Minutes	Temp. Reaction	Temp. bath	Remarks
0	25° C		- Heating begun
15	70		- Solution appears milky. Heating bath removed
20	55		- Replaced heating bath
25	80		- Reflux started. Removed water bath
27	72		- No great exothermality involved in reaction. Replaced heating bath
45	81.5	92°	- Solution is greatly turbid.
65	83	90	- Reflux rate appears slower
70	84	98	- Viscous white solution
80	81.5	100	- More viscous, splatters on sides of flask
81	82.5	100	- Motor speed of stirrer increased to maximum
82	83	100	
85	88	100	
90			- Removed water bath from flask

REACTION B

Materials: The materials used were the same as Reaction A except that c.p. acetone was substituted for the benzene.

Equipment: A 500 ml 3 necked flask with thermometer, reflux condenser, and stirrer attachments was used. In addition, the flask was fitted with a gas inlet tube under the surface of the solution leading from a nitrogen tank purified through 10% pyrogallol and a trap.

Recipe[25]: 150 ml acetone
12.5 g styrene (.12 mole)
13.5 g maleic anhydride (.138 mole)
.04g benzoyl peroxide

Procedure: Benzoyl peroxide was dissolved in acetone and added to the reaction flask with stirring. Maleic anhydride was added and stirred until dissolution and then the styrene was added through the condenser. Prior to monomer addition nitrogen gas was bubbled through 10% pyrogallol and under the surface of the solvent providing a nitrogen atmosphere for the reaction.

Observations:

Time Minutes	Temp. Reaction	Temp. Bath	Remarks
0	20°		- Heating in water bath begun
15	45		- Reflux started. Removed bath
20	40		- No exothermality noted. Replaced bath
25	57		- Refluxed from 40° up to 57°, temp. rose quite swiftly.
55	62	78°	- Clear slightly yellow solution
65	63	83	
80	63	82	
85	63.2	82	
145	64.6	86	- Solution is definitely viscous
150			- Removed water bath, added 150 ml acetone and refluxed for 7 more hours.

Summary and Comparison of Experimental Observations of Polymers A and B.

1. No apparent exothermality or reaction violence was indicated with the volume of solvent required by the recipes[24,25].

2. With benzene solvent (A) the reaction temperature was comparatively consistent at 80° C and the polymer precipitated as a granular white powder while with the acetone solvent (B) the reaction temperature did not appear consistent.

3. Polymer B was less easily worked and washed than Polymer A as the latter needs but to be filtered, benzene washed and dried. The former tends to coagulate as an unworkable sticky mass on being precipitated out of its acetone solvent with water. Qualitatively, it

appears to have a much greater excess of dissolved styrene. This latter polymer was broken up and washed in benzene which tended to remove some of its gelatinous, sticky nature.

4. Both polymers were dried at 40° C for five weeks. The total yield of (A) was 83.1%, of (B) 15%.

5. Weighed samples of the polymers were dissolved in acetone and titrated to phenolphthalein endpoint with aqueous alkali. By this method, the acid number[28] of (A) was 8.5 and of (B) 346.5. The value for B corresponds to a maleic anhydride - styrene ratio in the heteropolymer of 1:2 whereas the value for A indicates 15.4 gram styrene in the copolymer whereas the initial amount of styrene was only 9.8 grams. These results show that new titration techniques were necessary.

PART II

STUDIES ON THE RATE OF COPOLYMERIZATION

STUDY A

Materials: The materials were the same as Reaction A, Part I except that Dow specially distilled unhibited styrene was used without further purification.

Equipment: The reaction was carried out in a 1 liter round bottom three necked flask, equipped with a thermometer, vacuum sampler, reflux condenser, stirrer with mercury seal and heating mantle. All the glass equipment was fitted with ground joints.

Recipe: 615.2 grams benzene
22.881 grams maleic anhydride (.233 mole)
24.266 grams styrene (.231 mole)
.2333 gram benzoyl peroxide

Procedures:

1. The Polymerization: Benzene solvent was heated to reflux temperature 80°C. Maleic anhydride was washed into the solvent by a portion of the benzene. Similarly, the styrene and benzoyl peroxide were washed into the reaction mixture by a portion of the benzene.

2. Sampling and polymer treatment: Samples of the reaction mixture were taken periodically in tared 50 ml erlenmeyers and the polymer frozen in the benzene solvent until it could be filtered through tared asbestos-matted gooch crucibles. The copolymer was washed several times with benzene, dried for one week at 80°C, and weighed (see Table I).

3. Method of determination of unreacted monomer: The filtrate and benzene washings of a copolymer sample were titrated with standard bromine in glacial acetic acid to test for unsaturation by the direct bromine titration method developed by Uhlrig and Levin[27]. Validity of this method was based on preliminary work by Morgan[26] who proposed that although maleic anhydride did not undergo bromine addition alone, it did so in styrene mixtures. (See Table 2).

4. Comparative molecular weight determinations: Although no empirical constant was available for this copolymer to correlate viscosity in acetone solvent with molecular weight by Staudinger's viscosity method[29,30], it was believed relative values could be obtained by this method. (See Table 3).

5. Analysis of polymer constitution: Due to the relative stability of the anhydride linkage to direct caustic titration as evidenced in Part I, the dried polymer samples were dissolved in acetone and treated with a probable excess of standard aqueous NaOH, brought to the boiling point, cooled and titrated with standard acid to a phenolphthalein endpoint. The entire gooch crucible with its contents was introduced into the acetone solvent. (See Table 4).

Observations: Cloudiness due to polymer formation was first noted at 7 minutes after monomer addition to reaction flask. The reaction was conducted for five hours.

Due to the asbestos used in the gooch crucible, the extent of polymer dissolution during the titrations could not be followed although it appeared that different samples gave differing clarity in the titrated solutions. There was difficulty in determining the endpoint with phenolphthalein indicator due to the slow change in indicator color.

PART II STUDY A

Table 1

DETERMINATION OF % POLYMERIZATION

BY AMOUNT OF PRECIPITATED POLYMER

(as per procedure 2)

No. of Sample	Time Minutes	Net wt. Sample	Net wt. Polymer	% Polymer in Sample	%Monomer Polymerized
1	5.83	25.861	.0015	.006	.008
2	18.33	19.021	.1720	.904	12.7
3	18.33	23.787	.2551	1.071	12.8
4	42.45	17.714	.7001	3.94	55.3
5	42.45	19.189	.7949	4.14	59.1
6	68.17	11.487	.6476	5.64	79.2
7	68.17	19.137	.9817	5.13	72.0
8	100.75	24.890	1.4881	5.98	84.0
9	100.75	22.924	1.3351	5.83	81.9
10	171.67	24.267	1.5142	6.24	87.5
11	171.67	21.219	1.3542	6.38	89.6
12	250.00	18.090	1.3028	7.21	101.0
13	250.00	27.430	1.9008	6.93	97.2

Reaction Weights

Benzene 615.2 g
M.A. 22.881g (.2333 mole)
Benzoyl Peroxide .2333g
Styrene 24.266g (.2333 mole)

662.5803g

Total Weight of Monomers: 47.147g

% Monomers in Initial Reaction Mixture: 7.12%

PART II STUDY A

Table 2

DETERMINATION OF % POLYMERIZATION

BY BROMINE TITRATION OF UNSATURATION

(as per procedure 3)

sample	Br_2 (ml)	Grams Br_2	Unreacted Monomer-wt	Net wt. sample	Total Mon. in Sample	% Unreacted Monomer	% Polymerization
1	25.3	1.533g	1.022g	25.861	1.843g	55.4	44.6
2	17.2	1.042	.764	19.021	1.354	56.4	43.6
3	24.7	1.500	1.000	23.787	1.69	59.0	41.0
4	5.7	.345	.253	17.714	1.262	20.0	80.0
5	3.7	.224	.164	19.189	1.368	12.0	88.0
6	.7	.042	.031	11.487	.818	3.8	96.2
7	2.2	.133	.098	19.137	1.362	7.2	92.8
8	.7	.042	.031	24.890	1.772	1.8	98.2
9	1.7	.103	.076	22.924	1.633	4.7	95.3
10	1.2	.073	.054	24.267	1.730	3.1	96.9
11	.8	.049	.036	21.219	1.512	2.4	97.6
12	.3	.018	.013	18.090	1.289	1.0	99.0
13	.4	.024	.018	27.430	1.959	.7	99.3

METHOD OF CALCULATION:

(1) 1 ml Br_2 = 60.59 mg/ml = .0606g Br_2/ml

(2) M.W. styrene = 104

M.W. M.A. = 98

average 101

(3) M.W. Br_2 = 159.8, therefore $\frac{159.8g\ Br_2}{101g\ Mon.}$ = 1.5g Br_2 per (1 g. Monomer

(4) g Br_2 consumed • 1.5 = g. unreacted Monomer.

(5) 7.12% of sample wt. = g. monomer in sample.

(6) G. unreacted monomer/Total g Mon. in sample • 100 = (% unreacted monomer.

(7) 100 - % unreacted monomer = % Polymerization.

PART II STUDY A

Table 3

VISCOSIMETER MEASUREMENT

(a) Size Ostwald Viscosimeter used: 100

Solvent: Acetone Molarity of Polymer: .02N

Temperature: 20.00° ± .05 (.2020g polymer / 100 ml)

The molecular weight of each monomer in the copolymer was assumed to be the average of the molecular weights of styrene and maleic anhydride i.e. 101.126g = 1 mole. This assumes a 1:1 relation.

Sample	Efflux Time Seconds	Deviation from Pure solvent efflux	Reproducibility
Blank	26.25	0	± .05
5	29.7	3.45	± .05
7	28.9	2.65	± .05
9	29.8	3.55	± .1
11	29.3	3.05	± .2
13	28.4	2.15	± .1
Final	28.6	2.35	± .08

(b) All data is the same as (a) except that a size 50 Ostwald Viscosimeter was used.

Sample	Efflux time Seconds	Deviation from Pure solvent efflux	Reproducibility
Blank	116.0	0	± .3
5	163.7	47.7	±0.00
7	163.7	47.7	± .15
9	164.1	48.1	± .15
11	160.7	44.7	±0.00

PART II STUDY A

Table 4

DETERMINATION OF MALEIC ANHYDRIDE CONTENT OF COPOLYMER BY AQUEOUS TITRATION WITH PHENOLPHTHALEIN INDICATOR

(as per procedure 5)

Sample	ml NaOH	ml HCl	Net Mequ wt. M.A.	Wt. M.A. in Copolymer	% M.A. in Copolymer
1*	5.00	1.75	.345	.017	-
2	55.00	41.60	1.67	.082	47.6
3	45.4	22.4	2.52	.123	48.8
4**	90.0	41.2	4.97	.243	34.7
6	80.0	30.0	5.10	.250	38.6
8	125.0	4.50	12.32	.604	40.6
10	125.0	2.30	12.54	.615	40.6
12	100.0	7.00	9.50	.465	35.7

* In samples 1 through 3, .1022N NaOH and .0952NHCl used.

** In samples 4 through 12, .1022N NaOH and .1026N HCl used.

METHOD OF CALCULATION:

(1) Ml • n = Mequ. wts.

(2) Mequ. wts. of NaOH used - mequ. wts. HCl used = mequ. wts Maleic Anhydride

(3) M.w. of M.A. = 98.06, therefore meq. wt. of M.A. is .049

(4) # mequ. wts. of M.A. • .049 = wt. M.A. copolymerized

(5) $\frac{\text{Wt. M.A. copolymerized}}{\text{Wt. sample}} \cdot 100 = \%$ M.A. copolymerized in sample.

Heterogeneous Polymerization of Maleic Anhydride-Styrene in Benzene Solvent

Data in Experimental Part I
Study 1, Tables 1, 2, 7

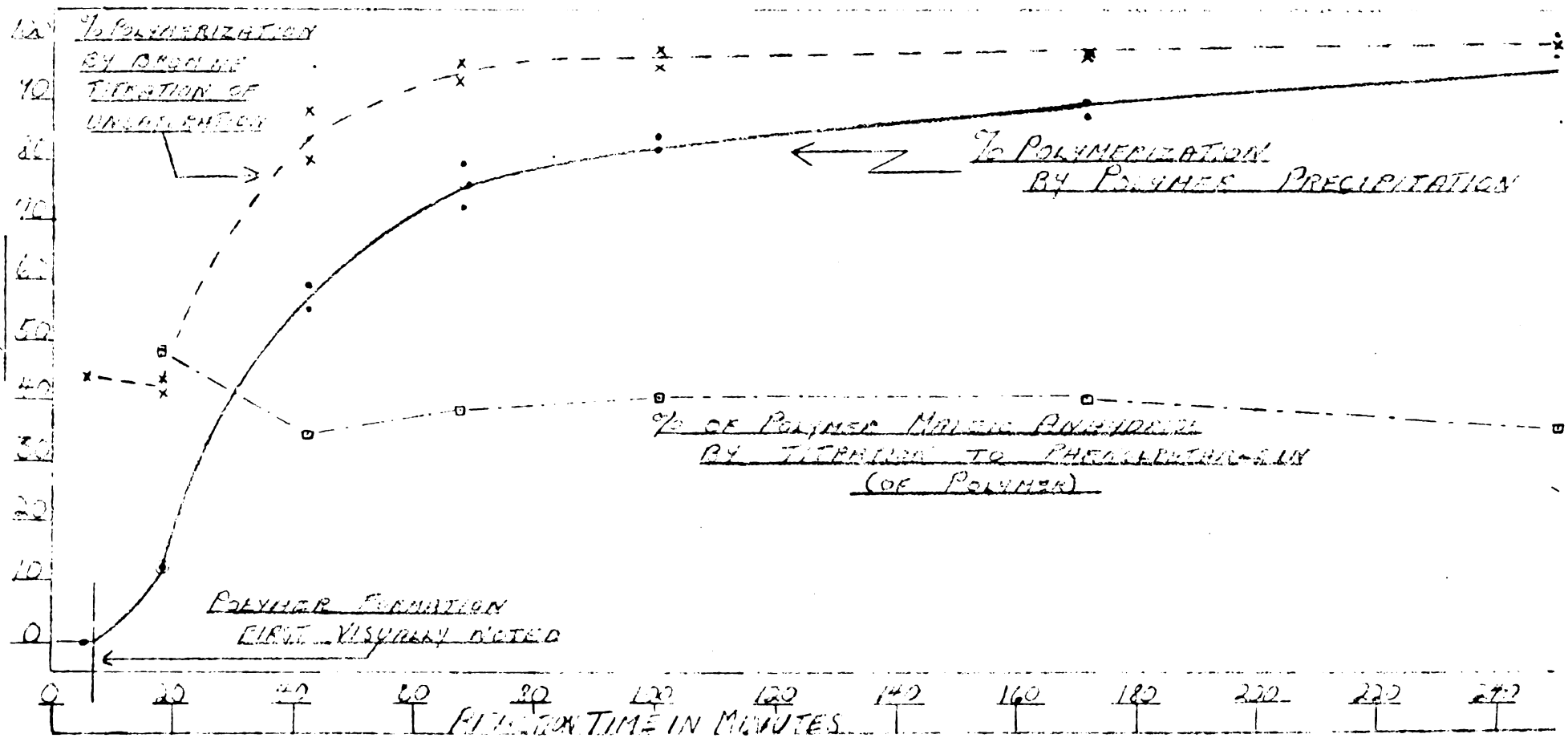


FIGURE 1

Thomas L. Chapman
M.S.C. 1948

HETEROPOLYMERIZATION OF MALEIC ANHYDRIDE-STYRENE IN BENZENE SOLVENT

DATA IN EXPERIMENTAL, PART II
STUDY 7, TABLES 1, 2, 4

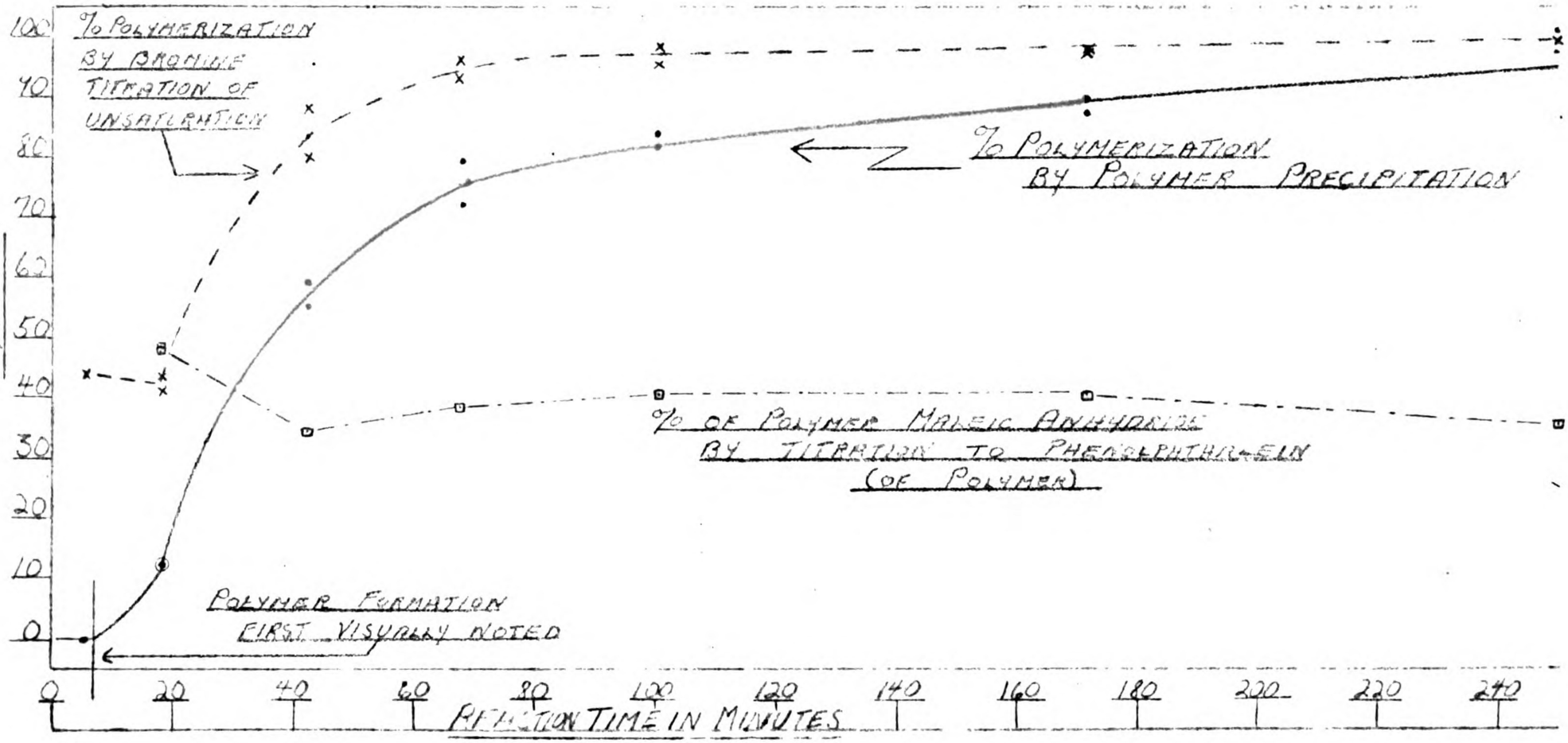


FIGURE 1

EDWARD R. GARRETT
M.S.C. 1948

STUDY B

Materials, equipment, recipe and procedure No.(1) were the same as in Study A. Procedure No.(2) was modified so that filter crucibles were used instead of asbestos matting in gooches (see Table 5). The crucible polymer samples were vacuum dried (3mm at 80° C) for 12 hours. Procedures Nos. (3) and (4) were not used due to the fact that they did not provide significant data in Study A. Procedure No. (4) was used on the filtrate from the weighed reaction samples to determine the amount of maleic anhydride not in the precipitated polymer.

Observations: Cloudiness due to polymer formation was first noted at 6 1/3 minutes after monomer addition to the reaction flask and the total reaction time was 2 hours.

PART II STUDY B

Table 5

DETERMINATION OF % POLYMERIZATION BY AMOUNT OF PRECIPITATED POLYMER

(as per procedure 2)

No. of Sample	Time Minutes	Net wt Reaction Sample	Net wt. Polymer	% Polymer in Sample	% Polymerization
1	4.5	11.393	.0003	.003	.004
2	6.0	3.790	.0001	.002	.003
3	8.6	16.277	.0428	.263	3.8
4	9.6	10.652	.0392	.368	5.4
5	11.7	19.560	.1342	.687	10.00
6	14.2	15.470	.1622	1.05	15.3
7	18.8	15.122	.2783	1.84	26.8
8	20.4	17.035	.3644	2.14	31.10
9	30.6	21.560	.7716	3.58	52.1
10	34.8	13.150	.5342	4.06	59.0
11	46.3	17.00	.8361	4.92	71.6
12	58.3	25.99	1.4123	5.43	79.1
13	63.0	18.025	.9696	5.38	78.3
14	85.5	22.145	1.4453	6.54	95.0
15	114.5	21.565	1.3716	6.37	92.7

% Monomer in Initial Reaction Mixture: 7.12%

PART II STUDY B

Table 6

DETERMINATION OF MALEIC ANHYDRIDE CONTENT OF COPOLYMER BY AQUEOUS TITRATION OF UNREACTED MONOMERS WITH PHENOLPHTHALEIN INDICATOR

(as per procedure 5)

Sample	ml NaOH	ml HCl	Unreacted Monomer %	Unreacted Monomer in grams	% M.A. in Polymer
1	61.95*	13.65	7.12	.812	60.1
2	25.00	11.30	7.12	.270	72.6
4	43.00	2.20	6.75	.719	71.3
5	89.5	2.20	6.43	1.259	65.1
6	36.00	4.10	6.07	.939	82.9
7	50.00	9.60	5.28	.800	74.6
8	49.00**	9.00	4.98	.852	77.9
9	45.00	9.00	3.54	.763	77.8
10	25.00	4.00	3.06	.402	75.4
11	25.00	2.20	2.20	.374	71.1
12	25.00	2.70	1.69	.439	76.1
13	25.00	10.00	1.74	.314	78.0
14	25.00	12.50	.58	.129	56.6
15	25.00	18.00	.75	.161	82.0

* Samples 1 through 7; .1027N NaOH and .1026N HCl

** Samples 8 through 15; .0970N NaOH and .1026 N HCl

METHODS OF CALCULATION:

1. (ml NaOH used • Normality NaOH) - (ml HCl used • Normality HCl) = net meq. wts. M.A. in sample's unreacted monomer.

2. Net meq. wts. M.A. • Meq. wt. M.A. (.049) = grams M.A. in sample's unreacted monomer.

3. % monomer in initial reaction mixture (7.12%) - % Polymer in sample = % Unreacted monomer in sample.

4. % Unreacted monomer in sample • wt. of sample = grams unreacted monomer in sample.

5. $100 - \frac{\text{g. unreacted M.A. in sample}}{\text{g. unreacted monomer in sample}} = \%$ M.A. in (polymer.

HETEROPOLYMERIZATION OF MALEIC ANHYDRIDE - STYRENE IN BENZENE SOLVENT

DATA IN EXPERIMENTAL, PART II
STUDY B, TABLES 5 & 6

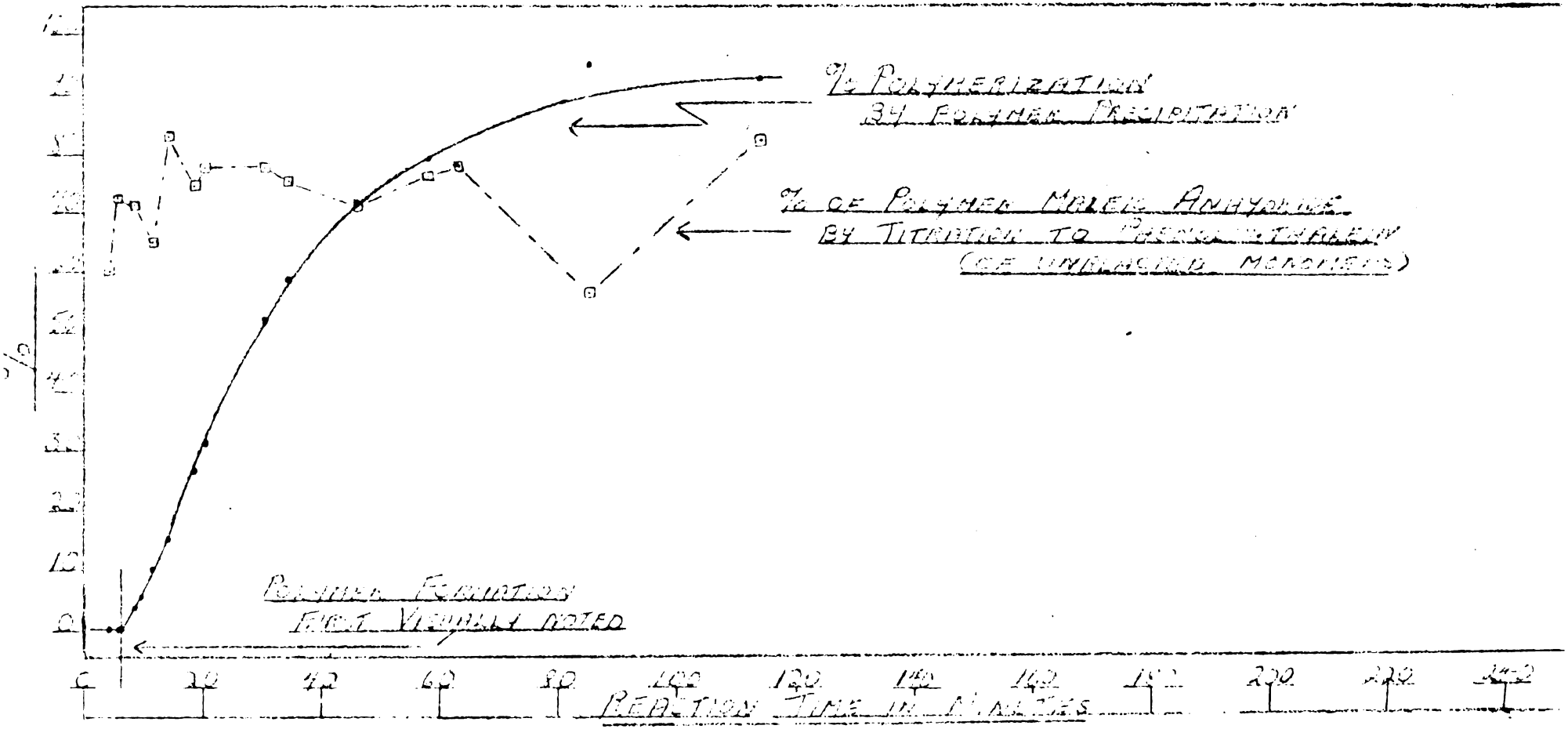


FIGURE 2

EDWARD R. GUREWITZ
M.S.C. 1948

PART III

AQUEOUS POTENTIOMETRIC TITRATIONS OF THE HETEROPOLYMER: MALEIC ANHYDRIDE-STYRENE

General Method of Preparation of Copolymer Samples for Titration: The weighed copolymer samples 1 through 11, 13 and 14 were taken from the final product of Study A, Part II, (1:1 molar ratio of reactants), the result of a five hour reaction. Sample 12 was from Study B, Part II, same molar ratio.

The amorphous, powdery material was weighed on tared watch glasses and washed with C.P. acetone into covered 400 ml beakers. Sufficient acetone was added to effect solution of the material. Standard alkali was added to the acetone solution with constant stirring and decided turbidity resulted. (N.B.: In the cases of samples 1 and 2, a definite precipitate occurred.) The solution samples were boiled on the hot plate until the acetone odor could not be discerned and at which time the solution generally became transparent. The solution sample was potentiometrically titrated several times with standard acid, then standard alkali, etc., using the glass electrode. Comments on the particular quantitative treatment of each sample as well as remarks on the titrations will be found in the tables corresponding to the specific samples (Tables I through XIV).

Samples 1 through 14 were washed with cold benzene and dried at 85° C under 3 mm vacuum.

Sample 5 was exposed to the carbon dioxide of the air for one week before being potentiometrically titrated (Table V).

Samples 6 and 7 were potentiometrically titrated with an indicator, brom cresol purple, being used. (Tables VI and VII).

In Samples 9 and 10, weighed amounts of pure maleic anhydride were dissolved prior to the potentiometric titrations. (Tables IX and X).

Samples 10 through 14 were refluxed twice with benzene and were also dried at 110°C, 14mm pressure. (Tables X through XIV).

Samples 13 and 14 were also dried at 135°C (Tables XIII and XIV).

TABLE I

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE #1: Initially dissolved in 100 ml. .0970N NaOH.

weight: 1.000gram

Titration A: .1141N HCl

Titration B: .097N NaOH

Equipment: Beckman Portable pH meter, standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst, washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3 mm pressure. Weighed sample dissolved in 100-150 ml. acetone. 100 ml .097N NaOH added quickly. Some sticky string-like precipitate noted, which did not dissolve on the boiling off of the acetone.

TITRATION A

Total ml solution	Ml. .1141N HCl	pH	Remarks
100	0	11.53	Pink to phth.
100.5	0.5	11.52	
101.5	1.5	11.51	
102.5	2.5	11.50	
104.0	4.0	11.48	
106.0	6.0	11.47	
108.0	8.0	11.37	
110.0	10.0	11.23	
111.0	11.0	11.18	
112.0	12.0	11.09	

TITRATION A (continued)

Total ml solution	Ml. .1141N HCl	pH	Remarks
113.0	13.0	11.01	
114.0	14.0	10.92	
115.0	15.0	10.83	
116.0	16.0	10.76	
117.5	17.5	10.61	
119.0	19.0	10.48	
120.5	20.5	10.33	
121.5	21.5	10.22	
123.0	23.0	10.12	
124.5	24.5	9.98	
126.0	26.0	9.78	
127.0	27.0	9.65	
128.0	28.0	9.57	
129.0	29.0	9.48	
130.0	30.0	9.33	
130.5	30.5	9.28	
131.0	31.0	9.18	phth. pink lightening
131.6	31.6	9.10	
132.5	32.5	9.08	
133.5	33.5	8.99	
134.5	34.5	8.88	faint pink
135.6	35.6	8.77	
136.5	36.5	8.66	
137.5	37.5	8.52	extremely faint trace of pink
138.0	38.0	8.48	
138.5	38.5	8.38	clear

TITRATION A (continued)

Total ml solution	Ml .1141N HCl	pH	Remarks
139.0	39.0	8.35	Shreds ppt. still here
140.0	40.0	8.20	As HCl hits solution, noted cloudiness, disappears on stirring.
140.5	40.5	8.13	
141.0	41.0	8.07	
141.5	41.5	8.00	
142.0	42.0	7.92	
142.5	42.5	7.87	
143.0	43.0	7.72	Suds developed on stirring
143.5	43.5	7.68	
144.0	44.0	7.57	
144.5	44.5	7.42	
145.0	45.0	7.35	
145.5	45.5	7.21	
146.0	46.0	7.03	
146.5	46.5	6.89	
147.0	47.0	6.69	
147.5	47.5	6.51	
148.0	48.0	6.38	
148.5	48.5	6.22	
149.0	49.0	6.03	With steady stirring the pH reading held constant.
150.0	50.0	5.69	On halting stirring, the galvanometer needle
150.5	50.5	5.53	tended to backtrack toward alkaline side.
151.0	51.0	5.40	
151.5	51.5	5.28	
152.5	52.5	5.08	

TITRATION A (continued)

Total ml solution	Ml .1141N HCl	pH	Remarks
153.5	53.5	4.89	
154.6	54.6	4.77	
155.6	55.6	4.65	
157.0	57.0	4.52	
158.5	58.5	4.42	
160.0	60.0	4.32	
162.0	62.0	4.22	
164.0	64.0	4.15	
166.0	66.0	4.08	
169.0	69.0	3.96	
173.0	73.0	3.76	
177.0	77.0	3.48	
180.0	80.0	3.10	
181.0	81.0	3.00	
182.0	82.0	2.89	
183.0	83.0	2.81	
184.5	84.5	2.68	
186.0	86.0	2.59	
188.0	88.0	2.45	
190.0	90.0	2.33	cloudiness seems to persist at this point
192.0	92.0	2.26	
194.0	94.0	2.19	
196.0	96.0	2.11	
198.0	98.0	2.08	Cloudiness obviously persists
200.0	100.0	2.00	
202.0	102.0	1.97	Almost opaque
204.0	104.0	1.92	
208.0	108.0	1.88	
225.0	125.0	1.70	

TITRATION B

Total ml solution	Ml .097N NaOH	Ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
225.0	0	0	1.7	24°
245.0	20	17	1.94	
250.0	25	21.23	2.02	
255.0	30	25.5	2.12	
260.0	35	29.75	2.25	
265.0	40	34.0	2.42	
270.0	45	38.2	2.57	
272.0	47	39.92	2.68	Cloudiness clearing
273.0	48	40.8	2.74	Almost gone
273.5	48.5	41.2	2.77	Faint haze
274.0	49	41.6	2.81	
275.0	50	42.5	2.88	
277.5	52.5	44.6	3.00	
280.0	55	46.7	3.22	
282.5	57.5	48.8	3.43	
285.0	60.0	50.95	3.62	
287.5	62.5	53.1	3.75	
290.0	65.0	56.1	3.85	
295.0	70.0	59.5	3.96	
298.0	73.0	62.0	4.04	
301.0	76.0	64.6	4.19	
305.0	80.0	68.0	4.42	
307.0	82.0	69.6	4.59	
309.0	84.0	71.4	4.82	
311.0	86.0	73.1	5.22	
313.0	88.0	74.8	5.89	

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
314.0	89.0	75.6	6.41	
315.0	90.0	76.5	6.75	
316.0	91.0	77.3	7.06	
317.0	92.0	78.2	7.31	
318.0	93.0	79.0	7.52	
319.0	94.0	79.8	7.69	
320.0	95.0	80.8	7.88	
321.0	96.0	81.5	7.98	
322.0	97.0	82.4	8.10	
323.0	98.0	83.3	8.21	
324.0	99.0	84.1	8.30	Machine corrected
325.0	100.0	85.0	8.38	Pink tinge of phth
326.0	101.0	85.8	8.5	Slight pink
327.0	102.0	86.7	8.62	
328.0	103.0	87.6	8.71	
330.0	105.0	89.3	8.9	Decided pink
332.0	107.0	91.0	9.07	
335.0	110.0	93.5	9.32	
338.0	113.0	96.1	9.55	
341.0	116.0	98.6	9.79	
345.0	120.0	102.0	10.08	
350.0	125.0	106.2	10.40	
355.0	130.0	110.5	10.7	
360.0	135.0	114.8	10.81	
365.0	140.0	119.0	11.0	
375.0	150.0	127.5	11.18	

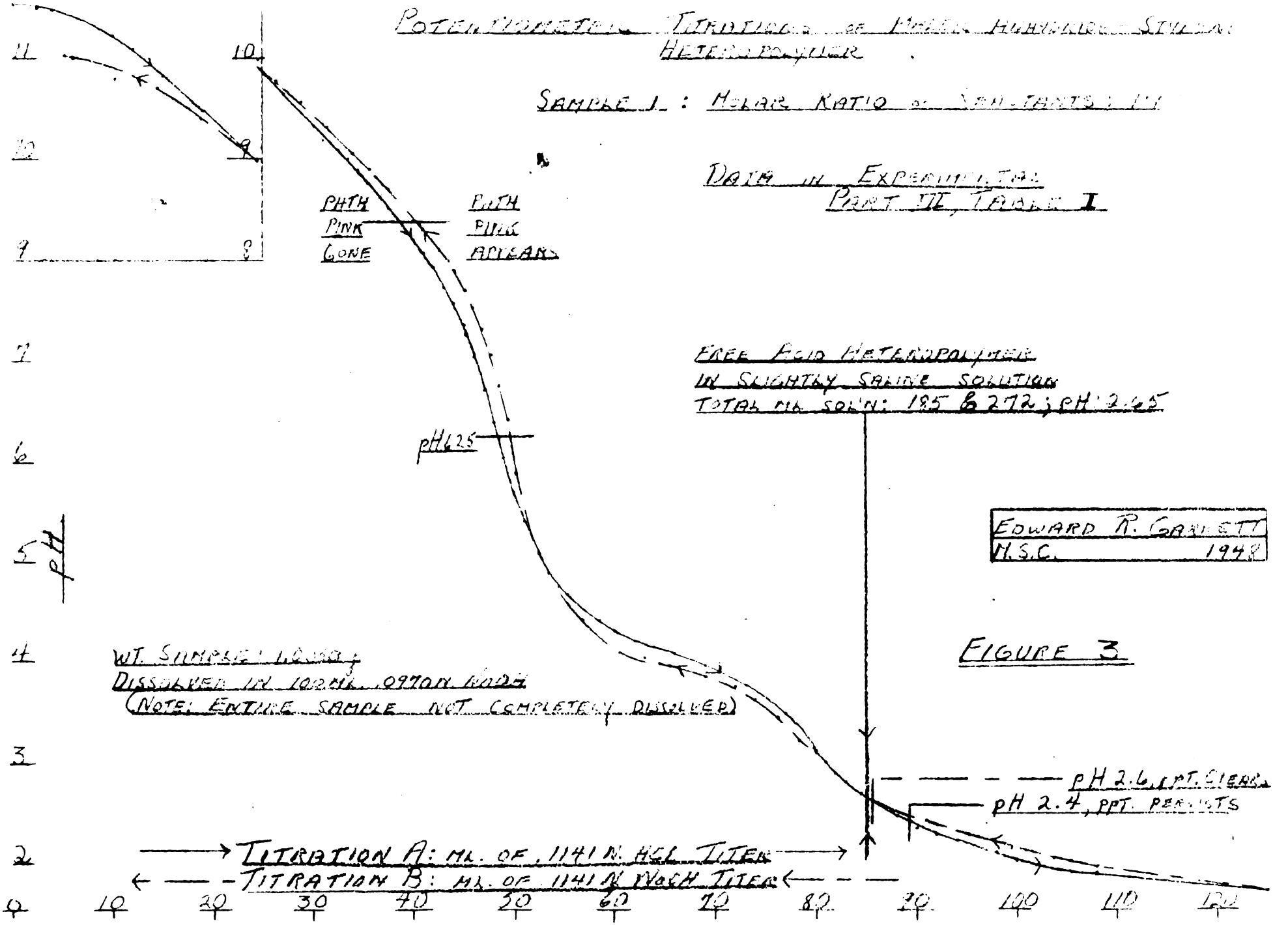

POTENTIOMETRIC TITRATION OF MIXED HYDROXIDE STILLAGE HETEROPOLYMER
SAMPLE 1 : MOLAR RATIO OF SOLUTANTS : 1/1
DATA IN EXPERIMENTAL PART VI, TABLE I
PATH PINK GONE
PATH PINK A CLEAR
FREE ACID HETEROPOLYMER IN SLIGHTLY SALINE SOLUTION
TOTAL ML SOLN: 185 & 272 ; pH 2.65
pH 6.25
EDWARD R. GARNETT
M.S.C. 1948
FIGURE 3
WT SAMPLE 1.0000 g
DISSOLVED IN 102 ML .0970 N NaOH
(NOTE: ENTIRE SAMPLE NOT COMPLETELY DISSOLVED)
pH 2.6 PPT. SLIGHT
pH 2.4 PPT. PERCEPTS
TITRATION A: ML. OF .1141 N. HCl TITER
TITRATION B: ML. OF .1141 N NaOH TITER
pH
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
110
120

TABLE II

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE

STYRENE HETEROPOLYMER

SAMPLE #2: Initially dissolved in 75 ml .097N NaOH wt: 1.00g.

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .097N NaOH Standard outside glass electrode

Titration C: .1141N HCl

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with Bz_2O_2 catalyst, washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hrs. 85°C, 3 mm pressure. Weighed sample dissolved in 100-150ml acetone. 75 ml .097N NaOH added quickly. Some sticky string-like ppt. noted, which did not dissolve on the boiling off of acetone.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
75.0	0	9.52	23° Shreds of white material in solution
78.0	3	9.28	
80.0	5	9.10	
83.0	8	8.85	
86.0	11	8.42	Pink lightening..solution slightly cloudy
89.0	14	8.11	
91.0	16	7.73	
92.0	17	7.61	
93.0	18	7.39	Slow in coming to equilibrium
94.0	19	7.17	
95.0	20	6.91	
96.0	21	6.62	
98.0	23	5.97	Appears to lather well
99.0	24	5.69	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
100.0	25	5.42	
101.0	26	5.20	
102.0	27	5.02	
103.0	28	4.89	
104.0	29	4.78	
106.0	31	4.60	
109.1	34.1	4.40	
112.0	37	4.28	
114.0	39	4.19	
116.0	41	4.12	
117.0	42	4.08	
118.0	43	4.02	
119.0	44	3.98	
120.0	45	3.94	
121.0	46	3.91	
122.0	47	3.88	
123.0	48	3.83	
124.0	49	3.78	
125.0	50	3.72	
126.0	51	3.68	
127.0	52	3.60	
128.0	53	3.52	
129.0	54	3.45	
130.0	55	3.37	
131.0	56	3.23	
131.5	56.5	3.18	
132.0	57	3.13	
133.0	58	3.01	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
134.0	59	2.90	
136.0	61	2.70	
137.0	62	2.62	
137.5	62.5	2.58	
138.0	63	2.52	
138.5	63.5	2.49	
139.0	64	2.43	
139.5	64.5	2.41	
140.0	65	2.38	
140.5	65.5	2.32	
141.0	66	2.29	
141.5	66.5	2.29	Corrected pH meter
142.0	67	2.25	Slightly more cloudy
142.5	67.5	2.22	Hazier
143.0	68	2.18	
143.5	68.5	2.15	Definite cloudiness
144.0	69	2.14	
144.5	69.5	2.12	
145.0	70	2.10	Can barely see electrode
145.5	70.5	2.08	Electrode no longer seen
146.0	71	2.07	
147.0	72	2.02	
148.0	73	1.98	White, no translucence
149.0	74	1.98	
150.0	75	1.94	
151.0	76	1.89	
152.0	77	1.88	
160.0	85	1.74	

TITRATION B

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
160.0	0	0	1.74	
170.0	10	8.5	1.92	
172.0	12	10.2	1.98	
174.0	14	11.9	2.02	
176.0	16	13.6	2.08	
177.0	17	14.43	2.12	
178.0	18	15.30	2.18	
179.0	19	16.17	2.22	
180.0	20	17.00	2.22	Corrected pH meter
182.0	22	18.7	2.31	
183.0	23	19.55	2.36	
184.0	24	20.4	2.42	
185.0	25	21.23	2.48	Lightening
186.0	26	22.1	2.52	
187.0	27	22.97	2.62	
187.5	27.5	23.4	2.62	Clear
188.0	28	23.8	2.65	
191.0	31	26.38	2.88	
195.0	35	29.77	3.19	
197.0	37	31.45	3.32	
199.0	39	33.17	3.48	
201.0	41	34.83	3.59	
205.0	45	38.5	3.75	
210.0	50	42.5	3.94	
216.0	56	47.6	4.1	
220.0	60	51.0	4.2	
225.0	65	55.2	4.52	

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
230.0	70	59.5	5.33	
235.0	75	63.75	7.02	
237.0	77	65.5	7.40	
238.0	78	66.3	7.58	
240.0	80	68.0	7.88	
242.0	82	69.7	8.12	
245.0	85	72.2	8.42	Light pink
250.0	90	76.5	8.88	
255.0	95	80.8	9.29	
260.0	100	85.0	9.68	

TITRATION C

Filtered Sample #2 at this point to remove insolubles. Let stand for 3 days.

Total ml solution	ml .1141N HCl	pH	Remarks
260.0	0	9.32	
263.0	3	9.12	
266.0	6	8.88	
269.0	9	8.58	
272.0	12	8.22	Phth cleared
274.0	14	7.98	
276.0	16	7.64	
278.0	18	7.17	
279.0	19	6.88	
280.0	20	6.62	
281.0	21	6.34	
282.1	22.1	6.08	
283.0	23	5.88	
284.0	24	5.65	
285.0	25	5.48	
287.0	27	5.13	
290.0	30	4.82	
294.0	34	4.58	
298.0	38	4.41	
302.0	42	4.29	
306.0	46	4.15	
310.0	50	3.99	
313.0	53	3.80	
315.0	55	3.65	
316.0	56	3.58	
317.0	57	3.50	

TITRATION C (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
319.0	59	3.31	
321.0	61	3.17	
324.0	64	2.98	
325.0	65	2.90	Stood 48 hours
325.0	65	2.80	Corrected pH meter
328.0	68	2.67	
331.0	71	2.55	Let stand 1½ hr., no ppt.
334.0	74	2.35	
335.0	75	2.30	
337.0	77	2.23	Let stand 40 min., no ppt.
337.0	77	2.23	
338.0	78	2.19	Appears more cloudy
339.0	79	2.12	
340.0	80	2.09	Let stand 15 hours, slight ppt. settled
340.0	80	2.32	
343.0	83	2.25	
346.0	86	2.20	
349.0	89	2.17	
352.0	92	2.12	
357.0	97	2.03	
360.0	100	2.00	Seems a bit more cloudy Allowed to stand 7 hours. Considerable amount ppt. on bottom of beaker but supernatant liquid still cloudy. Let stand 15 hours, great deal ppt. settled but supernatant liquid not clarified, added reagent HCl and let stand. Reagent HCl fully pptd. and clarified supernatant liquid.

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE - STYRENE HETEROPOLYMER

SAMPLE 2: MOLAR RATIO OF REACTANTS: 1:1

DATA IN EXPERIMENTAL PART III, TABLE II

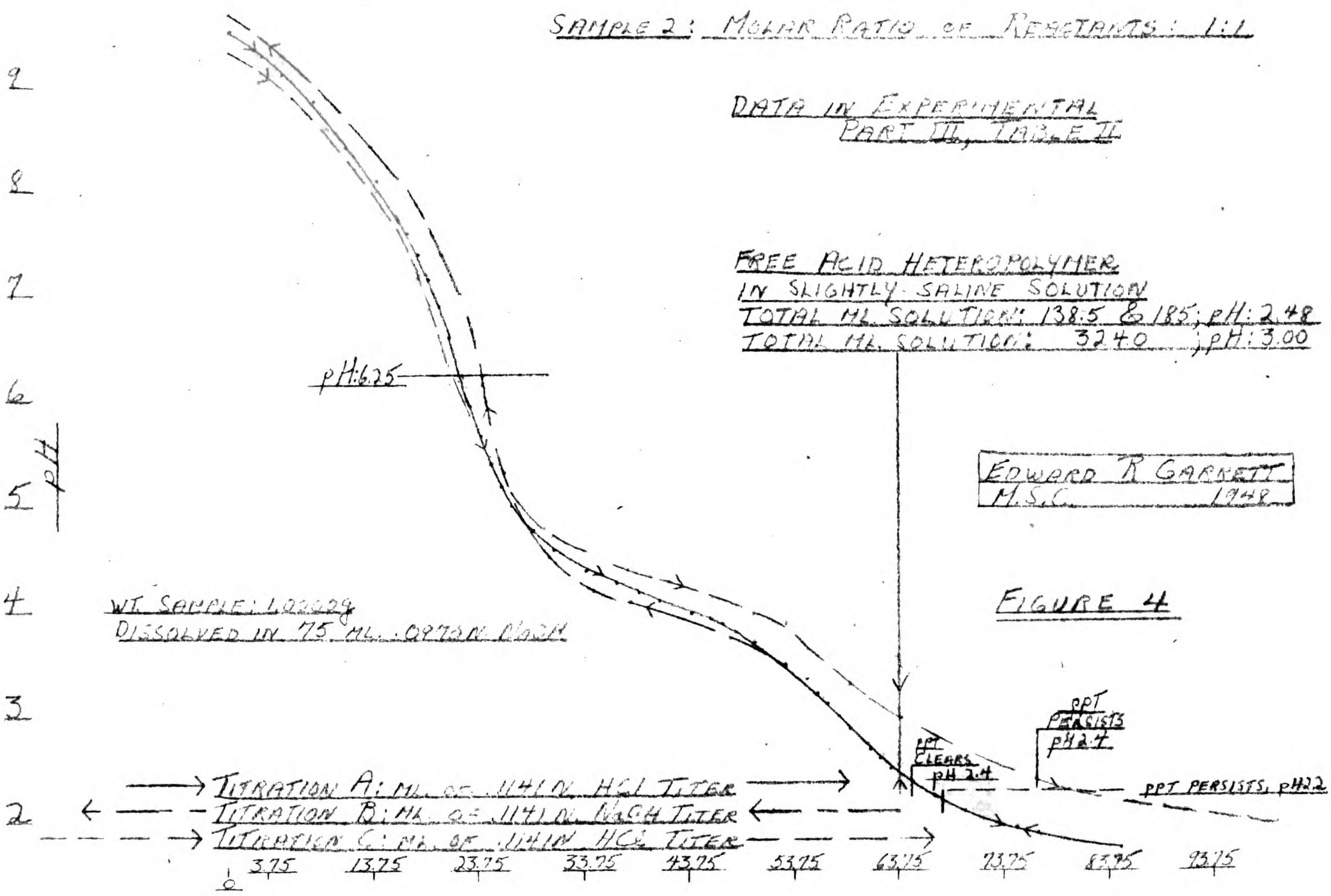


FIGURE 4

TABLE III

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE

STYRENE HETEROPOLYMER

SAMPLE #3: Initially dissolved in 75 ml. .097N NaOH. wt.: 1.0000g.

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .097N NaOH Standard outside glass electrode

Titration C: .1141N HCl

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85° C., 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 75 ml. .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
75.0	0	9.39	26°
77.0	2	9.21	
79.0	4	9.02	
81.0	6	8.82	
83.0	8	8.61	
85.0	10	8.39	
87.0	12	8.15	
88.0	13	8.03	
89.0	14	7.91	
90.0	15	7.75	
91.0	16	7.61	
91.5	16.5	7.50	
92.0	17	7.39	
92.5	17.5	7.28	
93.0	18	7.18	
93.5	18.5	7.09	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
94.0	19	6.92	
94.5	19.5	6.77	
95.0	20	6.62	
95.5	20.5	6.48	
96.0	21	6.28	
96.5	21.5	6.11	
97.0	22	5.92	
97.5	22.5	5.73	
98.0	23	5.58	
98.55	23.55	5.42	
99.05	24.05	5.31	
99.5	24.5	5.21	
100.0	25	5.11	
101.0	26	4.95	
102.0	27	4.82	
103.0	28	4.72	
105.0	30	4.58	
107.0	32	4.43	
109.0	34	4.32	
111.0	36	4.23	
114.0	39	4.12	
117.0	42	4.02	
120.0	45	3.94	
122.0	47	3.86	
125.0	50	3.72	
127.0	52	3.59	
129.0	54	3.42	
130.0	55	3.32	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
131.0	56	3.21	
131.5	56.5	3.15	
132.0	57	3.10	
132.5	57.5	3.02	
133.0	58	2.99	
134.0	59	2.88	
135.0	60	2.78	
136.0	61	2.68	
136.5	61.5	2.62	
137.0	62	2.59	
137.5	62.5	2.52	
138.0	63	2.49	
138.5	63.5	2.47	
139.5	64.5	2.40	
140.0	65	2.35	
140.5	65.5	2.31	
141.0	66	2.27	
141.5	66.5	2.23	
142.0	67	2.22	Some stringy ppt.
142.5	67.5	2.20	
143.0	68	2.18	
143.5	68.5	2.15	More definite ppt.
144.0	69	2.12	
144.5	69.5	2.11	
145.0	70	2.08	
146.05	71.05	2.05	Can no longer see electrode
147.0	72	2.01	
150.0	75	1.94	

TITRATION B

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
150.0	0	0	1.94	
154.0	4	3.4	2.07	
157.0	7	5.95	2.15	
159.0	9	7.65	2.22	
161.0	11	9.36	2.32	
162.0	12	10.20	2.38	Lightening
163.0	13	11.05	2.41	Clears more on standing-- apparently all in solution
163.5	13.5	11.48	2.43	
164.5	14.5	12.32	2.50	
166.0	16	13.6	2.58	
167.0	17	14.45	2.63	Washed electrode with HOH,allowed to stand 15 hrs.
167.0	17	14.45	2.73	
168.0	18	15.3	2.82	
169.0	19	16.15	2.89	
170.0	20	17.0	2.98	
171.0	21	17.85	3.06	
172.0	22	18.7	3.13	
173.0	23	19.55	3.23	
174.0	24	20.4	3.31	
175.0	25	21.24	3.41	
176.0	26	22.1	3.48	
177.0	27	22.93	3.53	
179.0	29	24.65	3.62	
181.0	31	26.35	3.72	
185.1	35.1	29.75	3.83	
189.0	39	33.15	3.92	
193.0	43	36.55	4.02	

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
197.0	47	39.95	4.18	
200.0	50	42.5	4.29	
203.0	53	45.1	4.47	
205.0	55	46.9	4.68	
208.0	58	49.3	5.02	
210.0	60	51.0	5.47	
211.55	61.55	52.2	5.97	
212.0	62	52.7	6.14	
213.0	63	53.6	6.56	
214.0	64	54.4	6.88	
215.0	65	55.2	7.15	
216.0	66	56.1	7.34	
218.0	68	57.7	7.66	
220.0	70	59.5	7.91	
223.0	73	62.1	8.22	
226.0	76	64.6	8.52	
230.0	80	68.0	8.88	
234.0	84	71.4	9.18	
238.24	88.24	75	9.50	

TITRATION C

Total ml solution	ml .1141N HCl	pH	Remarks
238.24	0	9.45	
241.24	3	9.20	
244.24	6	8.92	
247.24	9	8.62	
250.24	12	8.33	
252.25	14	8.10	
254.24	16	7.82	
257.24	19	7.32	
259.24	21	6.75	
260.24	22	6.32	
260.74	22.5	6.08	
261.24	23	5.88	
261.74	23.5	5.69	
262.25	24.01	5.51	
263.24	25	5.28	
264.24	26	5.09	
266.24	28	4.82	
268.24	30	4.66	
272.24	34	4.41	
277.24	39	4.21	
282.24	44	4.07	
288.24	50	3.82	
290.24	52	3.72	
292.24	54	3.49	
293.24	55	3.49	Adjusted pH meter
294.24	56	3.32	
295.24	57	3.22	
296.24	58	3.12	

TITRATION C (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
297.24	59	3.05	
298.24	60	2.98	
299.24	61	2.89	
300.34	62.1	2.79	
301.24	63	2.77	
303.24	65	2.62	Corrected PH meter-- let stand one hour
303.24	65	2.55	
304.24	66	2.52	
306.24	68	2.48	
308.24	70	2.42	
310.24	72	2.32	
312.24	74	2.30	
314.24	76	2.26	
316.24	78	2.22	
318.24	80	2.18	
320.24	82	2.15	Opalescent?
322.24	84	2.12	More opalescent
324.24	86	2.09	
326.24	88	2.07	Definitely more cloudy
329.24	91	2.05	On standing clouds up moreso.
329.24	91	2.08	After 7 minutes, cant see electrodes
329.24	91	1.88	After 1½ hours
332.24	94	1.82	
335.24	97	1.79	
338.24	100	1.75	After rechecking against buffer, pH reads 2.07

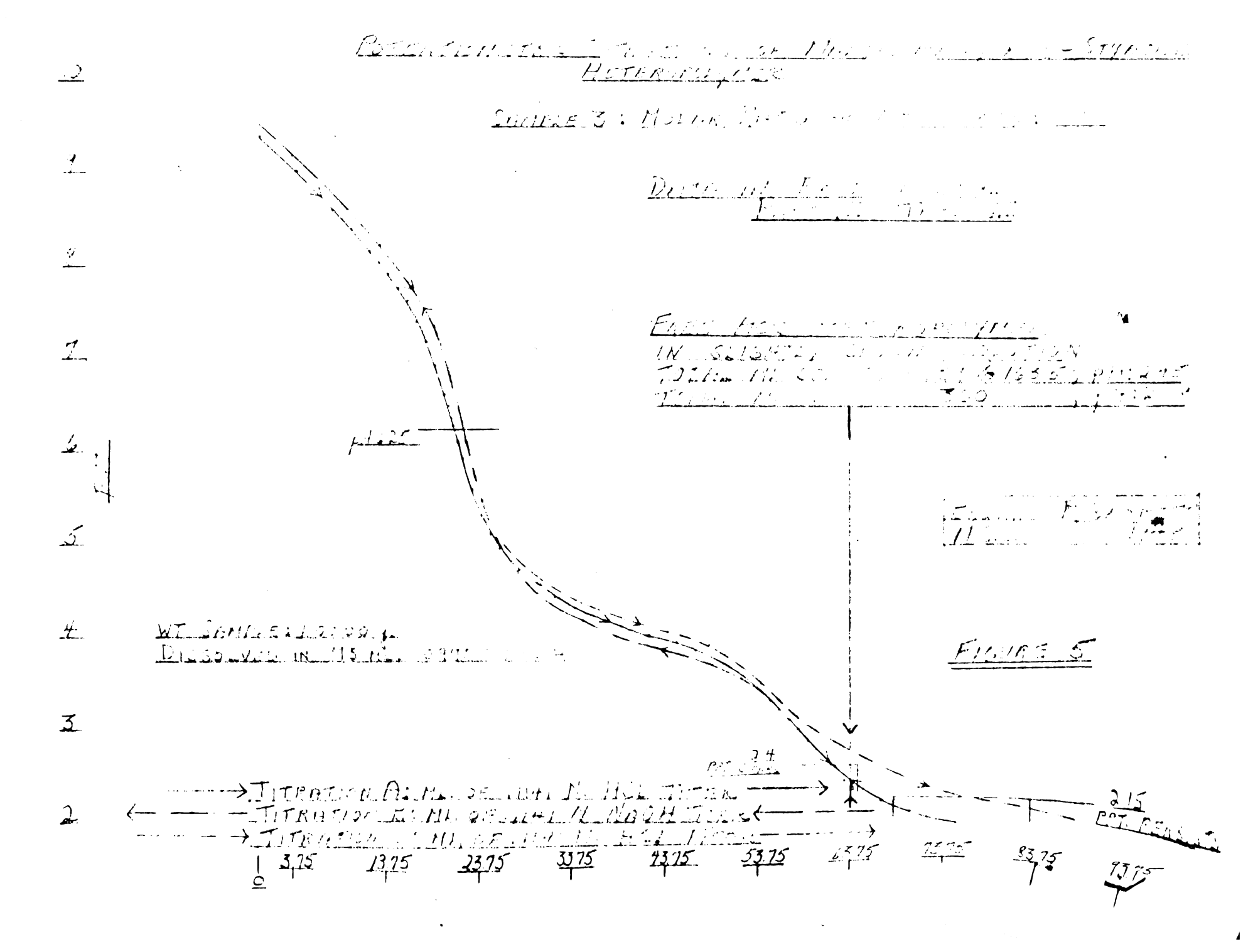


FIGURE 5

TABLE IV

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE #4: Initially dissolved in 75 ml .097N NaOH wt.: 1.0000g.

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .097N NaOH Standard outside glass electrode

Titration C: .1141N HCl

Titration D: .097N NaOH

Titration E: .1141N HCl

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hrs. at 85°C, 3mm pressure. Weighed sample dissolved in 100-150ml acetone. 75 ml .097N NaOH added slowly. All ppt. dissolved on the boiling off of acetone.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
75.0	0	9.17	
79.0	4	8.78	
83.0	8	8.37	
87.0	12	7.91	
91.05	16.05	7.27	
93.0	18	6.83	
94.0	19	6.61	
95.0	20	6.38	
96.0	21	6.11	
97.0	22	5.80	
98.0	23	5.52	
99.0	24	5.29	
100.0	25	5.11	
102.0	27	4.84	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
105.0	30	4.58	
109.0	34	4.35	
113.0	38	4.20	
117.0	42	4.09	
121.0	46	3.94	
125.0	50	3.75	
127.0	52	3.62	
129.0	54	3.48	
131.0	56	3.29	
132.0	57	3.14	
133.0	58	3.03	
134.0	59	2.95	
135.0	60	2.84	
137.0	62	2.68	
139.0	64	2.50	
140.0	65	2.42	Rinsed off electrodes, allowed to stand..no ppt.
140.0	65	2.38	
142.0	67	2.22	Allowed to stand, slight ppt.
142.0	67	2.19	
143.0	68	2.12	Seems more cloudy
144.0	69	2.25	Some ppt. settled
145.0	70	2.21	
146.0	71	2.17	Definite ppt.
147.0	72	2.11	Allowed to stand
147.0	72	1.92	Opaque, but will not settle
149.0	74	1.88	
150.0	75	1.80	Allowed to stand 2 hours, some settled but still milky supernatant liquid.

TITRATION B

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
150.0	0	0	1.81	
153.0	3	2.55	1.89	
156.0	6	5.1	2.00	
159.0	9	7.65	2.10	Not clear, allowed to stand
159.0	9	7.65	2.37	Still not clear
160.0	10	8.5	2.38	
161.0	11	9.35	2.34	Still settles
162.0	12	10.2	2.43	Let stand
162.0	12	10.2	2.37	20 min. later still settles
163.0	13	11.05	2.40	
164.0	14	11.9	2.45	
164.0	14	11.9	2.38	after 2½ hrs. still settles
166.0	16	13.6	2.47	Allowed to stand
167.0	17	14.45	2.52	Apparently less opaque, clearing somewhat in 45 min.
168.0	18	15.3	2.58	Clearing further 40 min. later clear as usual
169.0	19	16.13	2.69	
170.0	20	17.0	2.78	
171.0	21	17.83	2.78	Adjusted pH meter
172.0	22	18.7	2.82	
174.0	24	20.4	3.01	
175.0	25	21.23	3.09	
176.0	26	22.1	3.19	Adjusted pH meter
176.0	26	22.1	3.47	
177.0	27	22.97	3.52	
179.0	29	24.65	3.67	
181.0	31	26.35	3.75	

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
185.0	35	29.77	3.89	
189.0	39	34.13	4.00	
193.0	43	36.6	4.09	
197.0	47	39.97	4.20	
200.0	50	42.5	4.29	Adjusted pH meter
204.0	54	45.9	4.42	
208.0	58	49.3	4.71	
213.0	63	53.6	5.64	
215.0	65	55.25	6.41	
217.0	67	57.0	7.02	
221.0	71	60.4	7.71	
223.0	73	62.1	7.98	
225.0	75	63.8	8.18	
227.0	77	65.4	8.48	
229.0	79	67.1	8.58	
231.0	81	68.9	8.70	
233.0	83	70.6	8.87	
239.0	89	75.6	9.31	
241.0	91	77.4	9.42	
245.0	95	80.75	9.72	
247.0	97	82.4	9.87	
249.04	99.04	84.2	10.01	
250.0	100	85.0	10.08	
254.0	104	88.3	10.33	
255.0	105	89.3	10.41	
257.0	107	91.0	10.51	
259.0	109	92.6	10.61	
262.0	112	95.2	10.77	
269.0	119	101.1	11.00	

TITRATION C

Total ml solution	ml .1141N HCl	pH	Remarks
269.0	0	11.0	
272.0	3	10.89	
274.0	5	10.80	
276.0	7	10.69	
278.0	9	10.58	
279.0	10	10.51	
280.0	11	10.42	
281.0	12	10.38	
282.0	13	10.29	
283.0	14	10.20	
284.0	15	10.12	
285.0	16	10.03	
286.0	17	9.98	
287.0	18	9.89	
288.0	19	9.81	
289.0	20	9.72	
291.0	22	9.58	
294.0	25	9.31	
297.0	28	9.05	
300.0	31	8.79	
303.0	34	8.49	
306.0	37	8.15	
309.0	40	7.79	
311.0	42	7.50	
313.05	44.05	7.02	
315.0	46	6.3	
316.0	47	5.88	
317.1	48.1	5.30	

TITRATION C (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
318.05	49.05	5.23	
319.0	50	5.08	
320.0	51	4.90	
321.0	52	4.79	
323.0	54	4.59	
326.0	57	4.41	
330.0	61	4.22	
335.0	66	4.09	
340.0	71	3.92	
344.0	75	3.78	
347.0	78	3.59	
350.0	81	3.48	
353.0	84	3.12	
355.0	86	3.00	
357.0	88	2.86	
359.0	90	2.74	
362.0	93	2.62	
365.0	96	2.51	
369.0	100	2.38, 2.33	
373.0	104	2.32	
378.0	109	2.15	
384.0	115	2.08	
396.0	127	1.98	Allowed to stand--- Definitely becoming opaque.

TITRATION D

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
396.0	0	0	1.97	
401.0	5	4.25	1.98	
406.0	10	8.5	2.02	Clearing?
411.0	15	12.75	2.09	
416.0	20	17	2.16	Clearing.
421.0	25	21.25	2.21	Allowed to stand
426.0	30	25.55	2.28	Not clearing more
431.0	35	29.75	2.37	
435.0	39	33.15	2.49	Practically clear
440.0	44	37.4	2.62	
446.0	50	42.5	2.89, 292	
448.0	52	44.2	3.10	
450.0	54	45.9	3.23	
452.0	56	47.6	3.39	
454.0	58	49.2	3.57	
456.0	60	51.0	3.68	
458.0	62	52.7	3.74	
463.0	67	56.9	3.9	
468.0	72	61.2	4.01	
473.0	77	65.4	4.15	
478.0	82	69.7	4.32	
483.0	87	73.9	4.65	
488.0	92	78.3	5.42	
489.0	93	79	5.75	
490.0	94	79.9	6.16	
491.0	95	80.7	6.52	
492.0	96	81.6	6.87	

TITRATION D (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH
496.0	100	85.0	7.61
501.0	105	89.3	8.19
506.0	110	93.5	8.68
511.0	115	97.8	9.03
516.0	120	102.0	9.39
517.0	121	102.9	9.45
518.0	122	103.8	9.51
520.0	124	105.9	9.68
523.0	127	108.0	9.83
524.0	128	108.9	9.91
525.0	129	109.8	9.975
527.0	131	111.2	10.08
529.0	133	113.0	10.20
531.0	135	114.8	10.29
533.0	137	116.4	10.39
536.0	140	119	10.51

TITRATION E

Total ml solution	ml .1141N HCl	pH	Remarks
536.0	0	10.51	
541.0	5	10.23	
542.0	6	10.18	
543.0	7	10.12	
544.0	8	10.04	
546.0	10	9.90	
548.0	12	9.78	
550.0	14	9.61	
552.0	16	9.43	
554.0	18	9.28, 9.30, 9.29	
556.0	20	9.12	
558.0	22	8.98	
560.0	24	8.78	
562.0	26	8.60	
564.0	28	8.38	
566.0	30	8.16	
568.0	32	7.92	
570.0	34	7.68	
572.0	36	7.29	
574.0	38	6.78	
576.0	40	5.92	
577.0	41	5.56	
578.0	42	5.27	
579.0	43	5.03	
581.0	45	4.72	
586.0	50	4.42, 4.43, 4.48	
596.0	60	4.09	

TITRATION E (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
601.0	65	3.92	
611.0	75	3.41	
616.0	80	3.09	
618.0	82	3.00	
620.0	84	2.90	
624.0	88	2.77	
628.0	92	2.63	
632.0	96	2.57	
636.0	100	2.48	
641.0	105	2.40	
646.0	110	2.32	
651.0	115	2.27	Still clear

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMER

SAMPLE 4: MOLAR RATIO OF REACTANTS: 1:1

DATA IN EXPERIMENTAL
PART III TABLE IV

FREE ACID HETEROPOLYMER
IN SLIGHTLY SALINE SOLUTION
TOTAL ML. SOLUTION: 139 & 164 ; pH: 2.5
TOTAL ML. SOLUTION: 359 ; pH: 2.75
TOTAL ML SOLUTION: 619 ; pH: 2.95

EDWARD R. GARRETT
M.S.C. 1946

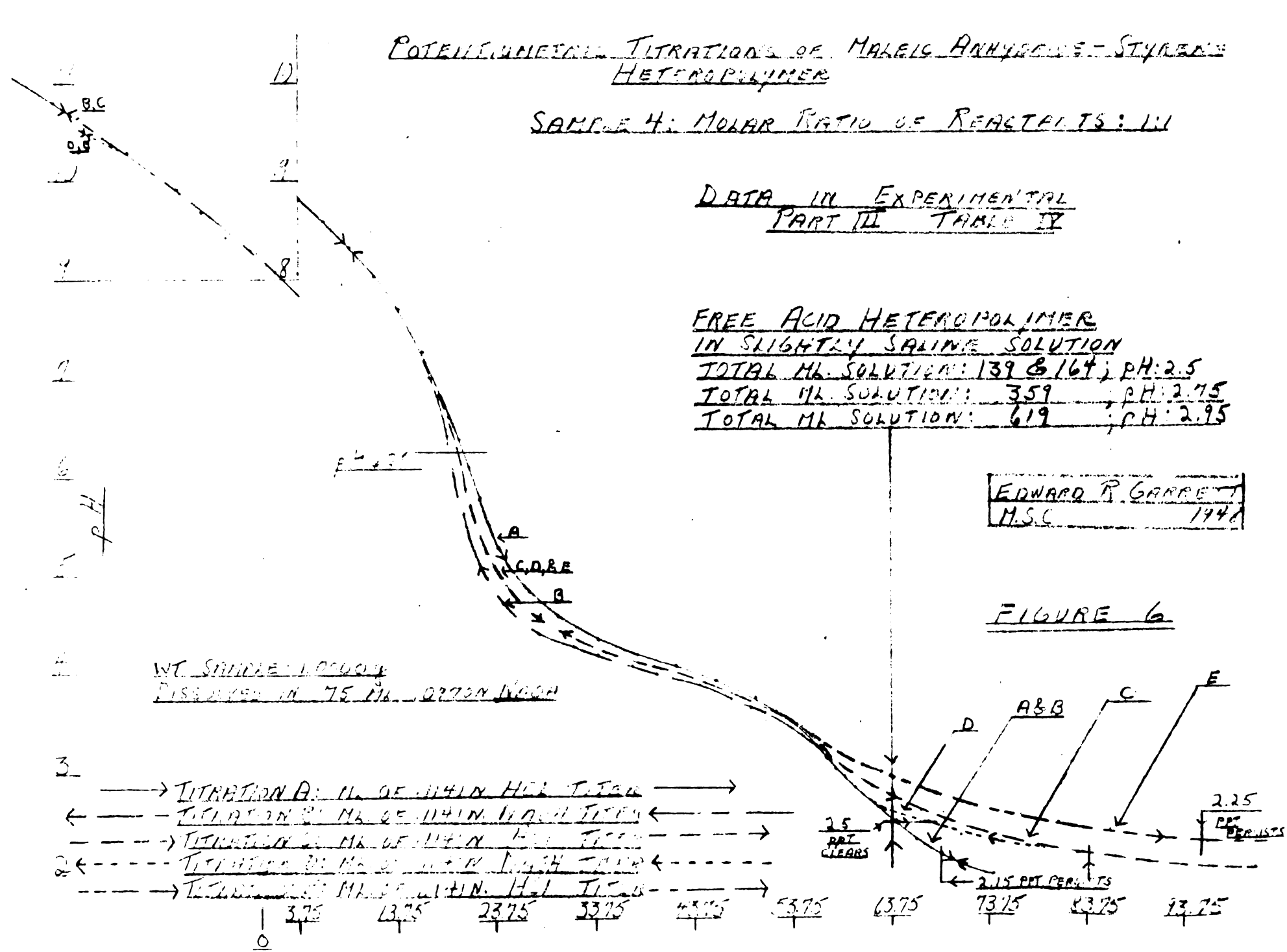


FIGURE 6

TABLE V

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE #5: Initially dissolved in 100 ml .097N NaOH.

wt.: 1.0000 gram

Titration A: .1141N HCl
Titration B: .097N NaOH
Titration C: .1141N HCl

Equipment: Beckman Portable pH meter. Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with BzO_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C., 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Exposed one week to CO_2 of air.

TITRATION A

Total ml solution	ml .1141N HCl	pH
100	0	10.32
102	2	10.20
104	4	10.03
106	6	9.92
108	8	9.81
110	10	9.68
112	12	9.52
114	14	9.39
116	16	9.22
118	18	9.09
120	20	8.91
123	23	8.63
126	26	8.32

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH
130	30	7.90
133	33	7.48
135	35	7.15
137	37	6.88
139	39	6.52
140	40	6.38
141	41	6.19
142	42	6.02
144	44	5.58
146	46	5.15
148	48	4.89
150	50	4.69

TITRATION B

100 ml distilled water added before titration.

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH
250	0	0	4.71
252	2	1.7	4.88
254	4	3.4	5.11
256	6	5.1	5.51
257	7	5.95	5.80
258	8	6.8	6.13
259	9	7.64	6.55
260	10	8.5	6.89
261	11	9.4	7.19
262	12	10.2	7.41
263	13	11.05	7.61
265	15	12.72	7.91
268	18	15.29	8.23
271	21	17.85	8.53
275	25	21.22	8.87
280	30	25.5	9.24
285	35	29.75	9.61
290	40	34.0	9.95
294	44	37.4	10.22
296	46	39.1	10.34
298	48	40.8	10.47
300	50	42.5	10.53
302	52	44.15	10.66
304	54	45.9	10.73
308	58	49.3	10.90

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH
310	60	51.0	10.98
312	62	52.7	11.02
314	64	54.4	11.08
316	66	56.1	11.12
318	68	57.8	11.13
321.5	71.5	60.75	11.21
325	75	63.7	11.27

TITRATION C

Total ml solution	ml .1141N HCl	pH
325	0	11.27
330	5	11.14
333	8	11.09
335	10	11.00
337	12	10.93
339	14	10.83
341	16	10.75
343	18	10.65
345	20	10.52
347	22	10.41
349.5	24.5	10.26
352	27	10.03
355	30	9.81
360	35	9.40
365	40	9.02
370	45	8.51
373	48	8.27
375	50	7.88
377	52	7.58
380	55	6.79
381	56	6.45
382	57	6.08
384	59	5.42
385	60	5.22
389	64	4.72
391	66	4.57
393	68	4.43
395	70	4.32

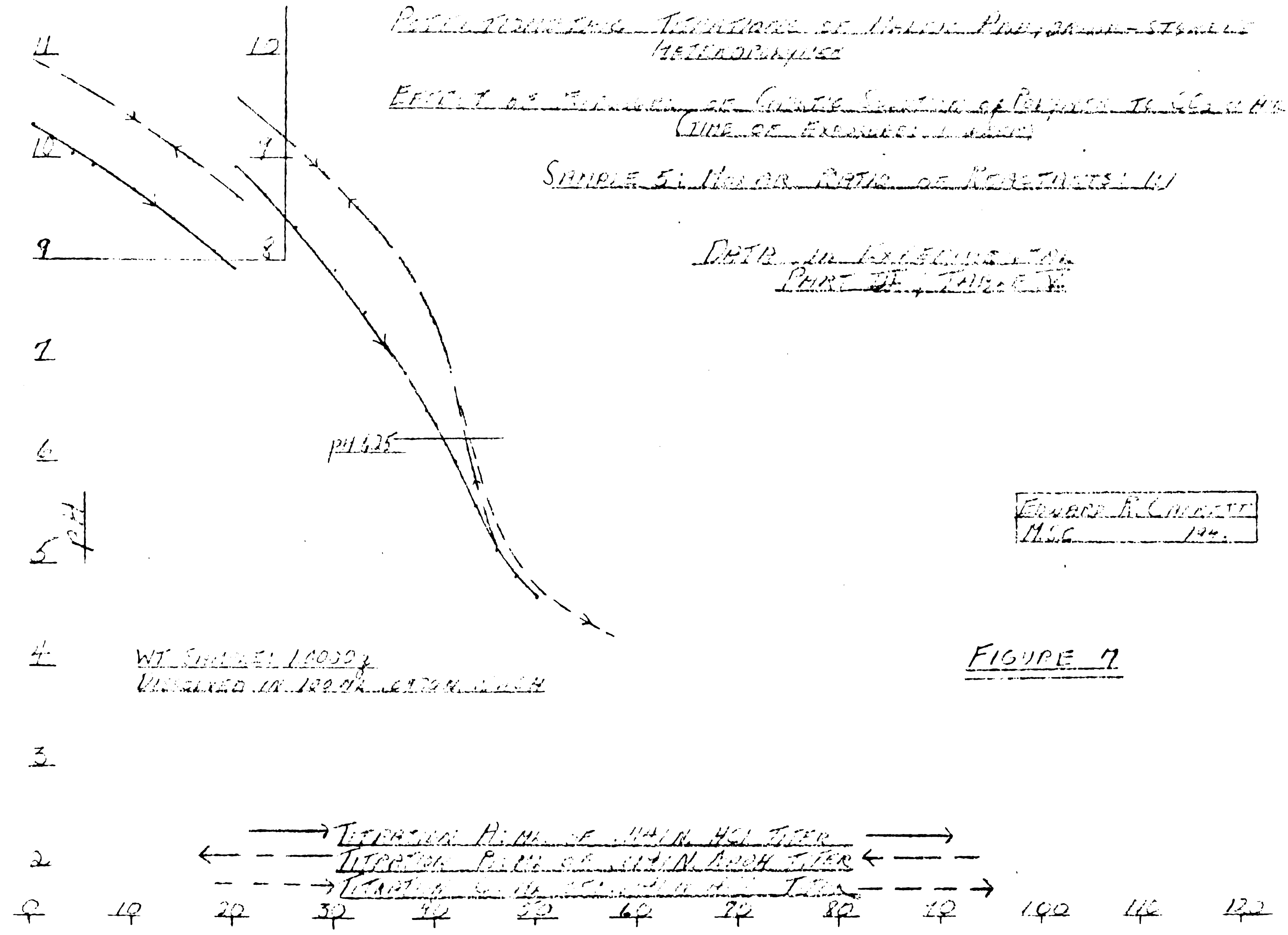

pH 4.25
pH
WT. SAMPLE: 1.0000 g
0
10
20
30
40
50
60
70
80
90
100
110
120
2
3
4
5
6
7
8
9
10
11
12

FIGURE 7

TABLE VI

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 6: Initially dissolved in 100 ml .097N NaOH. wt.: 1.000g

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with Bz_2O_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85° C, 3mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Diluted to 275 ml with dist. HOH. Titration of alkaline solution with Brom cresol purple as indicator. 15 drops

Total ml solution	ml .1141N HCl	pH	Remarks
275	0	9.78	purple
285	10	9.19	"
290	15	8.81	"
295	20	8.37	"
300.5	25.5	7.69	"
303	28	7.19	lighter..still purple
305	30	6.82	" " "
306	31	6.69	" " "
307	32	6.53	lighter..still purple
308	33	6.43	" " "
309	34	6.31	" " "
310	35	6.22	
311	36	6.12	light purple
312	37	6.03	
313	38	5.93	
314	39	5.85	slight purplish tint
315	40	5.73	dirty brown tint
316	41	5.62	amber
317	42	5.52	yellow

TABLE VI (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
318	43	5.4	
319	44	5.29	
320	45	5.18	
325	50	4.69	

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMER

SAMPLE 4: MOLAR RATIO OF REACTANTS: 1:1

DATA IN EXPERIMENTAL
PART III TABLE IV

FREE ACID HETEROPOLYMER
IN SLIGHTLY SALINE SOLUTION
TOTAL ML SOLUTION: 139 & 164; pH: 2.5
TOTAL ML SOLUTION: 359 ; pH: 2.15
TOTAL ML SOLUTION: 619 ; pH: 2.95

EDWARD R. GARRETT
M.S.C. 1962

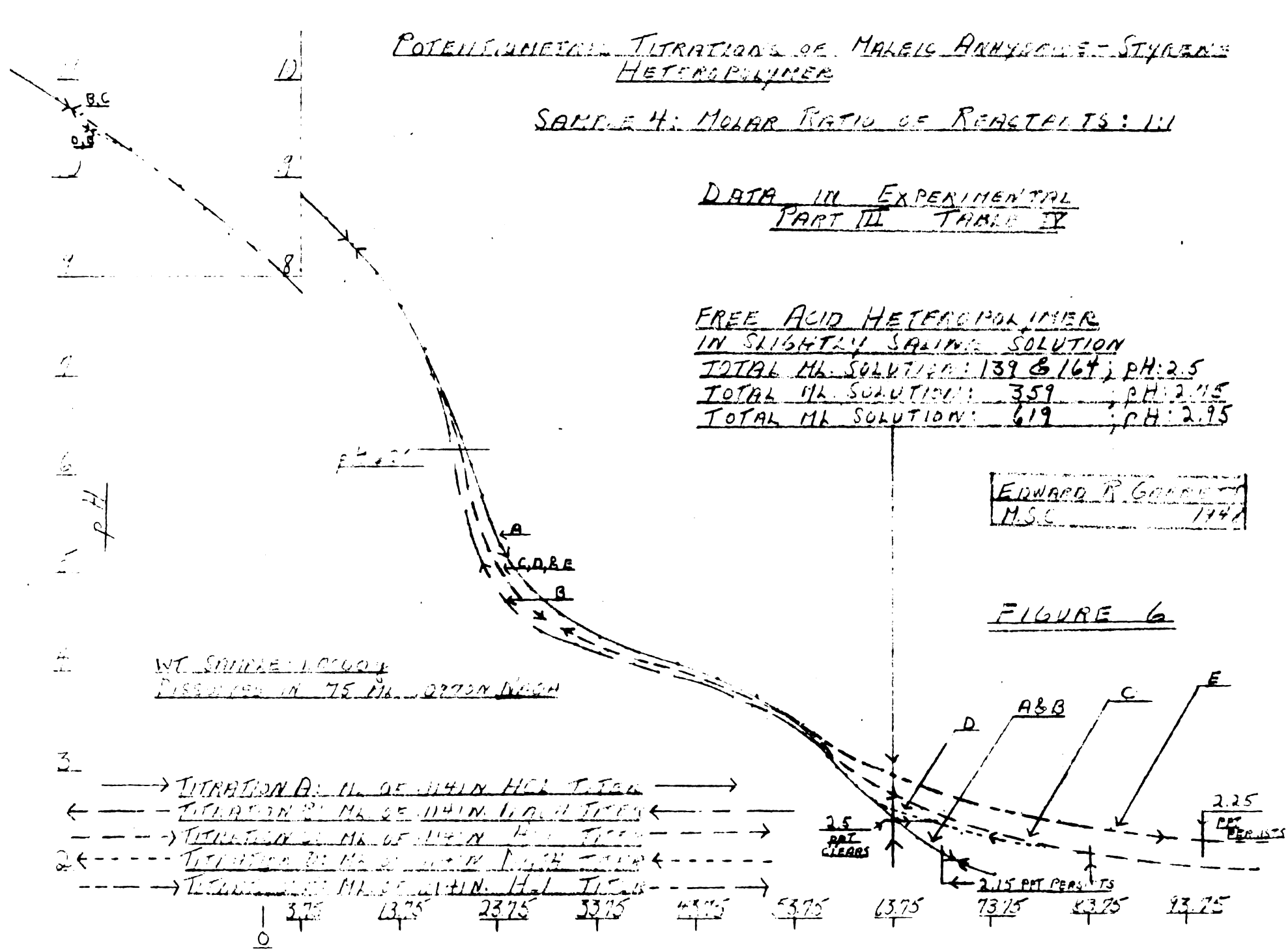


FIGURE 6

TABLE V

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE #5: Initially dissolved in 100 ml .097N NaOH.

wt.: 1.0000 gram

Titration A: .1141N HCl
Titration B: .097N NaOH
Titration C: .1141N HCl

Equipment: Beckman Portable pH meter. Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C., 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Exposed one week to CO_2 of air.

TITRATION A

Total ml solution	ml .1141N HCl	pH
100	0	10.32
102	2	10.20
104	4	10.03
106	6	9.92
108	8	9.81
110	10	9.68
112	12	9.52
114	14	9.39
116	16	9.22
118	18	9.09
120	20	8.91
123	23	8.63
126	26	8.32

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH
130	30	7.90
133	33	7.48
135	35	7.15
137	37	6.88
139	39	6.52
140	40	6.38
141	41	6.19
142	42	6.02
144	44	5.58
146	46	5.15
148	48	4.89
150	50	4.69

TITRATION B

100 ml distilled water added before titration.

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH
250	0	0	4.71
252	2	1.7	4.88
254	4	3.4	5.11
256	6	5.1	5.51
257	7	5.95	5.80
258	8	6.8	6.13
259	9	7.64	6.55
260	10	8.5	6.89
261	11	9.4	7.19
262	12	10.2	7.41
263	13	11.05	7.61
265	15	12.72	7.91
268	18	15.29	8.23
271	21	17.85	8.53
275	25	21.22	8.87
280	30	25.5	9.24
285	35	29.75	9.61
290	40	34.0	9.95
294	44	37.4	10.22
296	46	39.1	10.34
298	48	40.8	10.47
300	50	42.5	10.53
302	52	44.15	10.66
304	54	45.9	10.73
308	58	49.3	10.90

TITRATION B (continued)

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH
310	60	51.0	10.98
312	62	52.7	11.02
314	64	54.4	11.08
316	66	56.1	11.12
318	68	57.8	11.13
321.5	71.5	60.75	11.21
325	75	63.7	11.27

TITRATION C

Total ml solution	ml .1141N HCl	pH
325	0	11.27
330	5	11.14
333	8	11.09
335	10	11.00
337	12	10.93
339	14	10.83
341	16	10.75
343	18	10.65
345	20	10.52
347	22	10.41
349.5	24.5	10.26
352	27	10.03
355	30	9.81
360	35	9.40
365	40	9.02
370	45	8.51
373	48	8.27
375	50	7.88
377	52	7.58
380	55	6.79
381	56	6.45
382	57	6.08
384	59	5.42
385	60	5.22
389	64	4.72
391	66	4.57
393	68	4.43
395	70	4.32

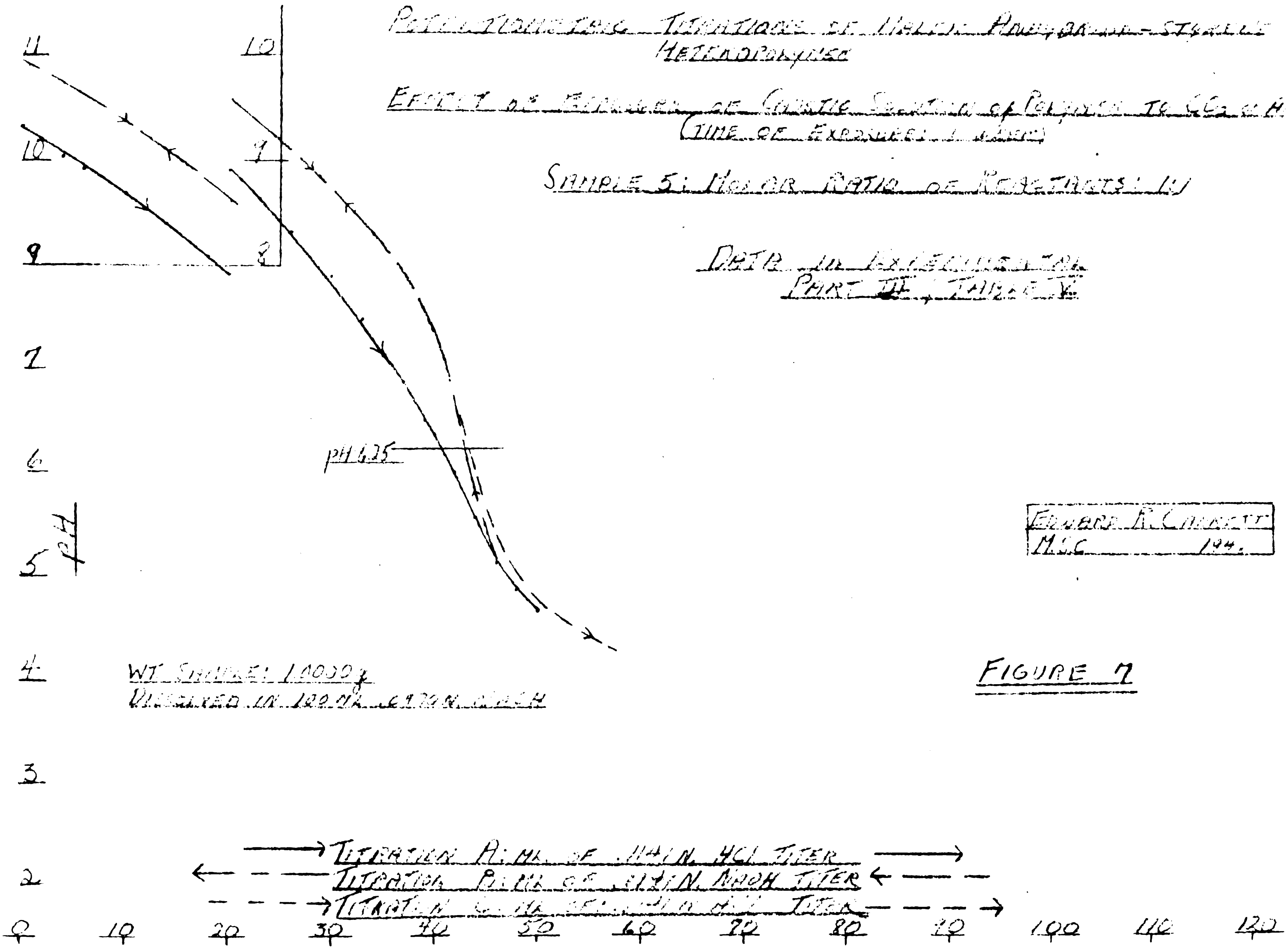

SAMPLE 5: MOLAR RATIO OF REACTANTS: 1/1
DATA IN EXPERIMENTAL PART III, TABLE V
pH 6.25
pH
WT. SAMPLE: 1.0030 g
TITRATION A: ML. OF .1 N. HCl TITER
11
10
9
7
6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100
110
120

FIGURE 7

TABLE VI

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 6: Initially dissolved in 100 ml .097N NaOH. wt.: 1.000g

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with Bz_2O_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85° C, 3mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Diluted to 275 ml with dist. HOH. Titration of alkaline solution with Brom cresol purple as indicator. 15 drops

Total ml solution	ml .1141N HCl	pH	Remarks
275	0	9.78	purple
285	10	9.19	"
290	15	8.81	"
295	20	8.37	"
300.5	25.5	7.69	"
303	28	7.19	lighter..still purple
305	30	6.82	" " "
306	31	6.69	" " "
307	32	6.53	lighter..still purple
308	33	6.43	" " "
309	34	6.31	" " "
310	35	6.22	
311	36	6.12	light purple
312	37	6.03	
313	38	5.93	
314	39	5.85	slight purplish tint
315	40	5.73	dirty brown tint
316	41	5.62	amber
317	42	5.52	yellow

TABLE VI (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
318	43	5.4	
319	44	5.29	
320	45	5.18	
325	50	4.69	

TABLE VI (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
318	43	5.4	
319	44	5.29	
320	45	5.18	
325	50	4.69	

TABLE VII

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 7: Initially dissolved in 100 ml .097N NaOH

wt.: 1.0000 gram

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with BzO_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Diluted to 325 ml with distilled HOH. Brom Cresol Purple, Indicator.

Total ml solution	ml .1141N HCl	pH	Remarks
325	0	9.68	
335	10	9.1	
345	20	8.23	
350	25	7.57	
355	30	6.62	
356	31	6.5	
357	32	6.41	
358	33	6.32	Faint purple
360	35	6.12	
362	37	5.98	Amber
364	39	5.79	
366	41	5.6	
368	43	5.39	
370	45	5.17	
372	47	4.98	
375	50	4.72	
378	53	4.53	
384	59	4.29	

TABLE VIII

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 8: Initially dissolved in 100 ml .097N NaOH. wt.: 1.0000g

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .097N NaOH Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Added .3525 g. C.P. Maleic-Anhydride to above solution. Heated on steam bath until dissolved.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
100	0	5.60	
101	1	5.52	
104	4	5.41	
110.05	10.05	5.02	
115	15	4.67	
120	20	4.38	
125	25	4.17	
130.05	30.05	4.01	Quite a bit of foan dissolved CO_2
135	35	3.88	
140	40	3.67	
143	43	3.48	
145	45	3.30	
147	47	3.13	
149	49	3.01	
150	50	2.91	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
152	52	2.79	
154	54	2.69	
156	56	2.59	
158	58	2.49	
160	60	2.41	
162	62	2.32	
164	64	2.27	
167	67	2.19	Cloudy
170	70	2.10	Thick ppt.
175	75	2.00	
180	80	1.93	
182	82	1.89	
184	84	1.87	
186	86	1.82	Removed sample. Heated on steam bath to drive out CO_2. Balled up into a sticky mass.

TITRATION B

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
186	0	0	2.01	Hard ball ppt.
196	10	8.5	2.18	
206	20	17.0	2.38	
216	30	25.5	2.72	
226	40	34.0	4.2 -	Galvonometer needle drifting to lower reading
226	40	34.0	2.88-	After standing 16 hrs. almost dissolved
231	45	38.22	3.13-	Allowed to stand 4 hrs. all in solution.
234	48	40.8	3.35	
236	50	42.5	3.43	
238	52	44.2	3.52	
241	55	46.7	3.7	
244	58	49.3	3.81	
247	61	51.8	3.91	
251	65	55.2	4.07	
254	68	57.8	4.12	
257	71	60.3	4.22	
261	75	63.7	4.37	
266	80	67.9	4.60	
270	84	71.4	4.88	

Potentiometric Titration of Maleic Anhydride-Styrene
Interpolymer

Effect of Added Maleic Acid on Titration Curve

Sample 38: Molar Ratio of Monomers 1:1

DATA IN EXPERIMENTAL
PART III. TABLE III

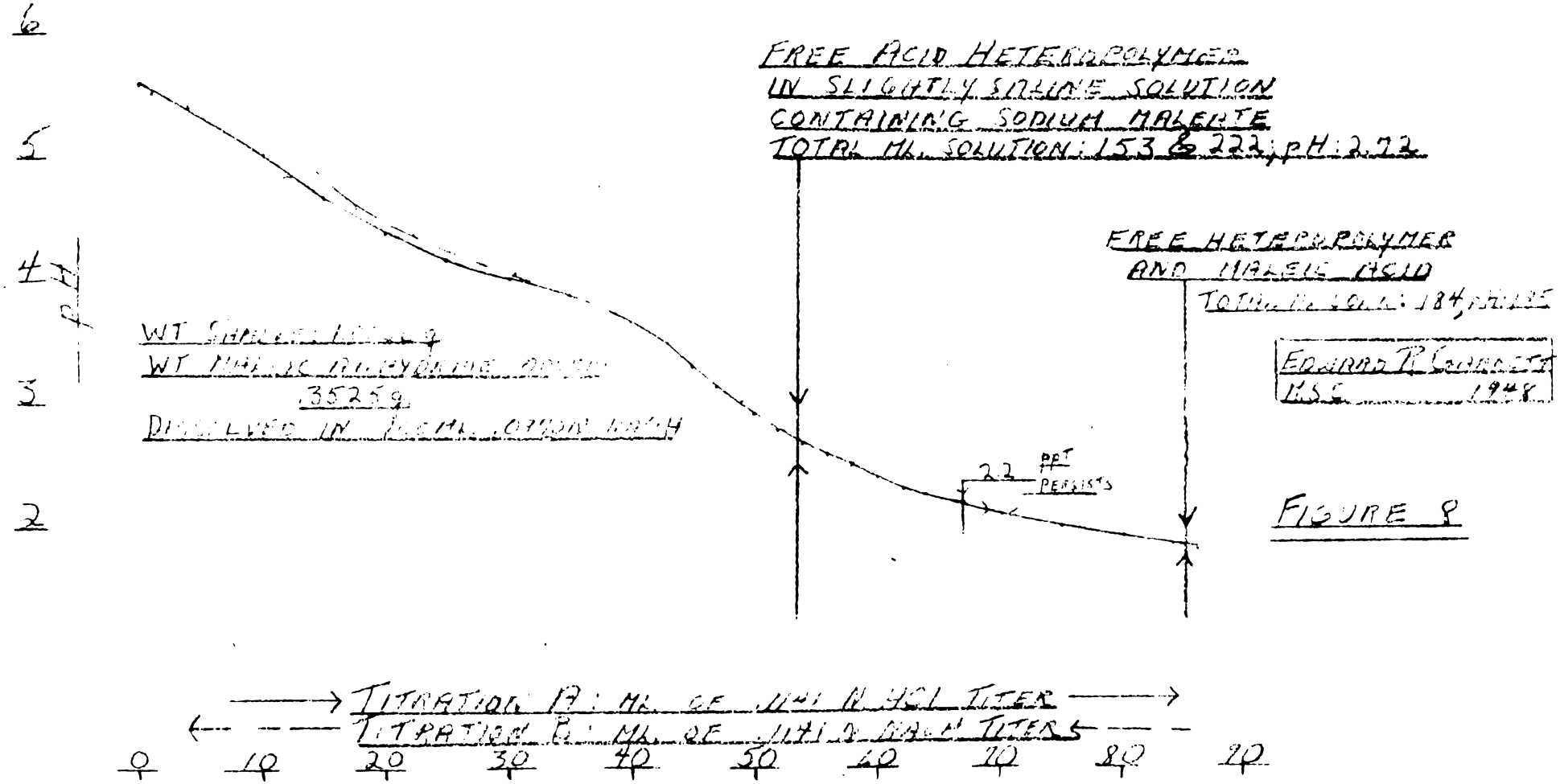


TABLE IX

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE

STYRENE HETEROPOLYMER

SAMPLE # 9: Initially dissolved in 100 ml .097N NaOH.

wt.: 1.0000 gram

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .097N NaOH Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with BzO_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85° C, 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. 100 ml .097N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone. Added .1534 g. C.P. Maleic-Anhydride to above solution. Heated on steam bath until dissolved.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
100	0	7.49	
105	5	7.00	
110	10	6.51	
115	15	6.15	
120	20	5.82	
125	25	5.48	
130	30	5.00	
135	35	4.58	
140	40	4.29	
145	45	4.16	
150	50	3.97	
155	55	3.79	
160	60	3.52	
165	65	3.10	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
167	67	2.92	
169	69	2.77	
171.5	71.5	2.60	
174	74	2.48	
177	77	2.32	
179	79	2.25	Little cloudy ppt.
181	81	2.18	Good ppt.
183	83	2.12	
185	85	2.07	
187	87	2.01	

TITRATION B

Total ml solution	ml .097N NaOH	ml .097N NaOH used corresponds to following # ml .1141N NaOH	pH	Remarks
187	0	0	2.01	
197	10	8.5	2.29	
207	20	17.0	2.70	
212	25	21.22	3.00	Clear
214	27	22.95	3.12	
216	29	24.62	3.31	
218	31	26.35	3.42	
220	33	28.03	3.52	
222	35	29.75	3.62	
224	37	31.43	3.72	
227	40	34.0	3.79	
232	45	39.25	3.94	
237	50	42.5	4.00	
242	55	46.75	4.22	
247	60	51.0	4.49	
252	65	55.3	4.89	
254	67	57.0	5.11	
256	69	58.7	5.31	
258	71	60.4	5.54	
260	73	62.1	5.68	
262	75	63.7	5.81	
266	79	67.2	6.13	
270	83	70.6	6.49	
272	85	72.3	6.87	
274	87	74.0	7.13	
276	89	75.7	7.42	

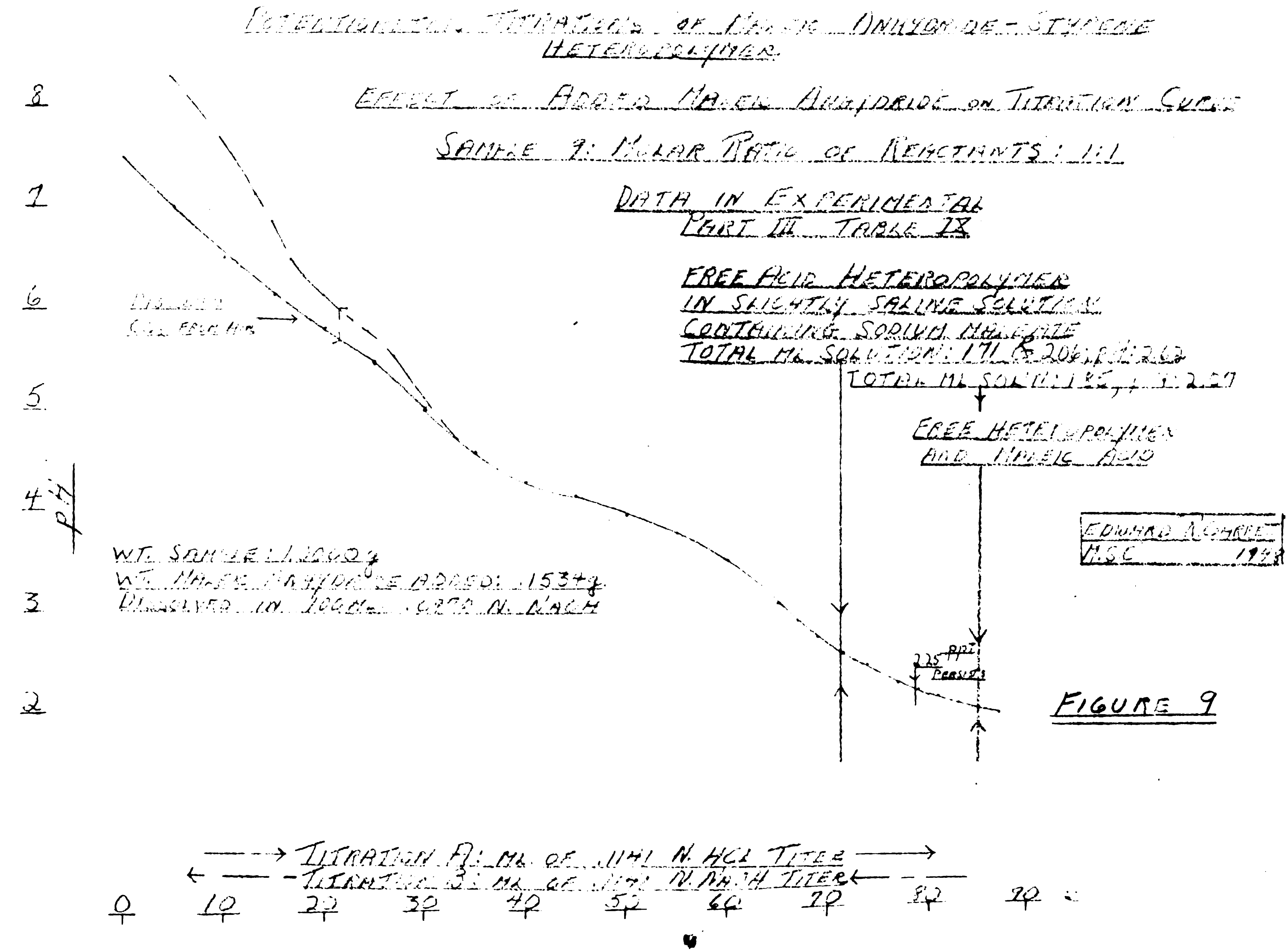

HETEROPOLYMER
SAMPLE 9: MOLAR RATIO OF REACTANTS: 1:1
DATA IN EXPERIMENTAL
PART III TABLE IX
FREE ACID HETEROPOLYMER
IN SLIGHTLY SALINE SOLUTION
CONTAINING SODIUM MALEATE
FREE HETEROPOLYMER
AND MALEIC ACID
EDWARD
M.SC
pH
8
7
6
5
4
3
2
WT. SAMPLE
TITRATION A: ML OF .1141 N. HCL TITER
0
10
20
30
40
50
60
70
80
90

FIGURE 9

TABLE X

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 10: Initially dissolved in 75 ml .0923N NaOH* wt.: 1.0007 gram

Titration A: .1141N HCl Equipment: Beckman Portable
Titration B: .0923N NaOH pH meter..Standard outside
Titration C: .1141N HCl glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3mm pressure. Weighed sample dissolved in 100-150ml acetone. Added 75 ml .0923 N NaOH. Material washed by refluxing 2 hours twice with fresh C.P. benzene. Dried in an Aberhalden drying pistol at 110° C at 14 mm pressure for two days.

* An apparent error in caustic normality was evident.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
75	0	9.10	
79	4	8.72	
83	8	8.28	
87	12	7.79	
91	16	7.13	
93	18	6.68	
94	19	6.51	
95	20	6.28	
96	21	6.00	
97	22	5.72	
98	23	5.49	
99	24	5.22	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
100	25	5.02	
101	26	4.89	
103	28	4.66	
105	30	4.50	
109	34	4.27	
113	38	4.10	
117	42	3.97	
121	46	3.92	
125	50	3.62	
128	53	3.42	
130	55	3.22	
132	57	3.02	
133	58	2.90	
134	59	2.81	
135	60	2.71	
137	62	2.52	
139	64	2.32	
141	66	2.18	ppt persists

TITRATION B

Total ml solution	ml .0923N NaOH	Correction to ml of .1141N NaOH	pH	Remarks
141	0	0	2.17	
144	3	2.43	2.31	
147	6	4.86	2.50	Clear
150	9	7.28	2.72	
152	11	8.90	2.91	
154	13	10.51	3.10	
156	15	12.13	3.38	
158	17	13.77	3.48	
166	25	20.22	3.79	
171	30	24.25	3.91	
176	35	28.33	4.02	
181	40	32.35	4.22	
186	45	36.5	4.52	
191	50	40.4	5.28	
193	52	42.1	5.82	
195	54	43.7	6.48	
197	56	45.3	7.00	
199	58	46.9	7.37	
201	60	48.6	7.62	
206	65	52.6	8.16	
211	70	56.7	8.58	
216	75	60.7	8.97	
220	79	63.9	9.21	
225	84	67.9	9.58	
230	89	72.0	9.87	
235	94	76.1	10.13	
239.05	98.05	79.3	10.37	
241	100	80.9	10.45	

TITRATION C

Total ml solution	ml .1141N HCl	pH	Remarks
241	0	10.45	
251	10	9.74	
261	20	8.94	
271	30	7.92	
276	35	7.12	
278	37	6.61	
279	38	6.33	
280	39	6.08	
281	40	5.81	
282	41	5.58	
283	42	5.33	
284.05	43.05	5.12	
285	44	4.98	
288	47	4.61	
291	50	4.41	
301	60	4.01	
306	65	3.83	
311	70	3.59	
313	72	3.42	
315	74	3.27	
317	76	3.09	
319	78	2.93	
321	80	2.79	
323	82	2.68	
326	85	2.52	
331	90	2.32	
336	95	2.21	
341	100	2.09	Ppt., but not fully even on standing 24 hours.

TABLE XI

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 11: Initially dissolved in 100 ml .0923N NaOH*

wt.: 1.0012 gram

Titration A: .1141N HCl Equipment: Beckman Portable pH meter

Titration B: .0923N NaOH Standard outside glass electrode

Titration C: .1141N HCl

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. Added 100 ml .0923N NaOH. Material washed by refluxing 2 hours twice with fresh C.P. benzene. Dried in an Aberhalden drying pistol at 110°C at 14 mm pressure for 2 days.

* An apparent error in caustic normality was evident.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
100	0	10.0	
102	2	9.98	
104	4	9.77	
106	6	9.63	
108	8	9.52	
110	10	9.39	
115	15	9.02	
120	20	8.63	
125	25	8.13	
130	30	7.51	
135	35	6.72	
136	36	6.58	
137	37	6.42	

TITRATION A (continued)

Total ml solution	ml .1141 HCl	pH	Remarks
138	38	6.31	
140	40	6.09	
141	41	5.97	
143	43	5.59	
145	45	5.19	
150	50	4.57	
160	60	4.09	
165	65	3.92	
170	70	3.72	
175	75	3.33	
176	76	3.25	
177	77	3.17	
178	78	3.03	
179	79	2.97	
180	80	2.83	
181	81	2.72	
182	82	2.63	
185	85	2.42	
186	86	2.38	Very slight ppt. On standing 24 hrs., solution is clear.

TITRATION B

Total ml solution	ml .0923N NaOH	Correction to ml of .1141N NaOH	pH
188	0	0	2.08
194	6	4.86	2.37
197	9	7.28	2.59
200	12	9.79	2.79
203	15	12.13	2.98
206	18	14.58	3.17
209	21	17.0	3.32
212	24	19.41	3.52
215	27	21.83	3.72
219	31	25.07	3.97
223	35	28.33	4.08
228	40	32.35	4.24
233	45	36.41	4.57
238	50	40.4	5.22
240	52	42.1	5.67
242	54	43.7	6.21
244.1	56.1	45.3	6.72
247	59	47.75	7.23
250	62	50.2	7.63
253	65	52.7	7.93
258	70	56.7	8.38
268	80	64.7	9.09
278	90	72.8	9.72
283	95	76.8	10.00
286	98	79.3	10.18
288	100	80.9	10.28

TITRATION C

Added 10 drops Brom Cresol Purple to solution.

Total ml solution	ml .1141N HCl	pH	Remarks
288	0	10.28	
293	5	9.92	
298	10	9.57	
308	20	8.78	
318	30	7.72	
323	35	6.80	
325	37	6.31	Lightened considerably
326	38	6.08	About clear
327	39	5.81	Clear (yellowish)
329	41	5.38	
333	45	4.70	
338	50	4.31	
348	60	3.99	
353	65	3.81	
358	70	3.58	
363	75	3.18	
368	80	2.8	
373	85	2.59	
378	90	2.41	
388	100	2.20	

TABLE XII

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 12: Initially dissolved in 50 ml .0923N NaOH*

wt.: .4143 gram

Titration A: .1141N HCl Equipment: Beckman Portable

Titration B: .0923N NaOH pH meter, Standard outside

Titration C: .1141N HCl glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio with Bz_2O_2 catalyst and refluxed with benzene for 20 hours. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3 mm pressure. Weighed sample dissolved in 100-150 ml acetone. Added 50 ml .0923N NaOH and 10 ml distilled HOH.

* An apparent error in the caustic normality is evident.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
65	0	10.68	
67	2	10.38	
69	4	10.09	
71	6	9.92	
73	8	9.58	
75	10	9.23	
77	12	8.91	
79	14	8.50	
81.05	16.05	8.00	
82	17	7.72	
83	18	7.38	
84	19	6.97	
85	20	6.61	
86	21	6.30	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
87	22	6.02	
89	24	5.38	
91	26	4.79	
93	28	4.47	
96	31	4.18	
99	34	3.93	
102	37	3.59	
104	39	3.19	
105	40	2.99	
106	41	2.79	
107	42	2.63	
108	43	2.50	
110	45	2.32	
113	48	2.13	Milky
115	50	2.02	Ppt. noted

TITRATION B

Total ml solution	ml .0923N NaOH	Correction to ml of .1141N NaOH	pH	Remarks
215	0	0	2.19	Added 100ml dist. HOH
219	4	3.4	2.32	
223	8	6.48	2.59	
226	11	8.9	2.92	
228.1	13.1	10.6	3.28	
229	14	11.33	3.42	
230	15	12.13	3.60	
235	20	16.18	3.98	
240	25	20.22	4.32	
243	28	22.65	4.69	
245	30	24.28	5.19	
246	31	25.1	5.59	
247	32	25.9	6.05	
248	33	26.72	6.62	
249	34	27.52	7.17	
250	35	28.33	7.58	
252	37	29.97	8.2	

TITRATION C

Total ml solution	ml .1141N HCl	pH
252	0	8.2
255	3	6.82
256	4	6.18
----------Added 100 ml distilled HOH		
356	4	6.28
357.5	5.5	5.57
359	7	5.08
369	17	3.93
375	23	3.09
376	24	2.94
377	25	2.86

TABLE XIII

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 13: Initially dissolved in 50 ml .1000N NaOH

wt.: .6033 gram

Titration A: .1141N HCl
Titration B: .1000N NaOH
Titration C: .1141N HCl
Titration D: .1000N NaOH

Equipment: Beckman Portable pH meter, Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with $Bz0_2$ catalyst and washed with cold benzene. Dried at atm. pressure and 80° one week, dried 24 hours at 85°C, 3mm pressure. Weighed sample dissolved in 100-150 ml acetone. Added 50 ml .1000N NaOH. Material washed by refluxing 2 hours twice with fresh C.P. benzene. Dried in an Aberhalden drying pistol at 110° C at 14 mm pressure for two days. Dried at 135° for two days.

TITRATION A

Total ml solution	ml .1141N HCl	pH	Remarks
100	0	10.19	
107	7	9.22	
110	10	8.80	
113	13	8.27	
115	15	7.78	
116.5	16.5	7.27	
118	18	6.52	
119	19	6.08	
120	20	5.62	
121	21	5.31	

TITRATION A (continued)

Total ml solution	ml .1141N HCl	pH	Remarks
122	22	5.04	
124	24	4.7	
127	27	4.40	
132	32	4.09	
137	37	3.68	
138	38	3.49	
139	39	3.44	
141	41	3.13	
142	42	2.99	
143	43	2.82	
144	44	2.70	
145	45	2.59	
146	46	2.49	
148	48	2.31	Slight ppt.
150	50	2.19	Definite ppt.

TITRATION B

Total ml solution	ml .1000N NaOH	Correction to ml .1141N NaOH	pH
152	2	1.75	2.27
154	4	3.30	2.48
155	5	4.38	2.47
156	6	5.26	2.53
157	7	6.13	2.62
158	8	7.01	2.72
159	9	7.88	2.88
160	10	8.77	3.03
161	11	9.65	3.22
162	12	10.52	3.33
163	13	11.39	3.48
164	14	12.28	3.57
165	15	13.14	3.63
172	22	19.28	3.99
177	27	23.65	4.31
180	30	26.28	4.62, 4.76
182	32	28.03	5.13
183	33	28.95	5.47
184	34	29.80	5.80
185.1	35.1	30.78	6.52
186	36	31.57	7.00
187	37	32.4	7.38
189	39	34.2	7.88
190	40	35.03	7.98
191	41	35.93	8.13
193	43	37.7	8.50
195	45	39.42	8.79
197	47	41.15	9.03

TITRATION C

Total ml solution	ml .1141N HCl	pH
199	2	8.75
201	4	8.4
203	6	8.01
204	7	7.81
205	8	7.52
206	9	7.21
207	10	6.72
208	11	6.17
209	12	5.62
210	13	5.25
211	14	4.98
213	16	4.61
215	18	4.40
218	21	4.19
223	26	3.84
226	29	3.62
228	31	3.42
230	33	3.13
231	34	3.01
232	35	2.91
233	36	2.78
234	37	2.69
235	38	2.61

TITRATION D

Total ml solution	ml .1000N NaOH	Correction to ml .1141N NaOH	pH
237	2	1.75	2.72
239	4	3.50	2.92
241	6	5.26	3.18
242	7	6.13	3.29
243	8	7.01	3.41
244	9	7.88	3.5
250	15	13.14	3.87
255	20	17.52	4.09
260	25	21.9	4.52
262	27	23.65	4.89
263	28	24.53	5.13, 5.19
264	29	25.41	5.59
265	30	26.28	6.02
266	31	27.17	6.60
267	32	28.03	7.00
268	33	28.95	7.32
269.5	34.5	30.21	7.70
271	36	31.57	8.2
273	38	33.30	8.38
275	40	35.02	8.67
280	45	39.42	9.23
285	50	43.80	9.85

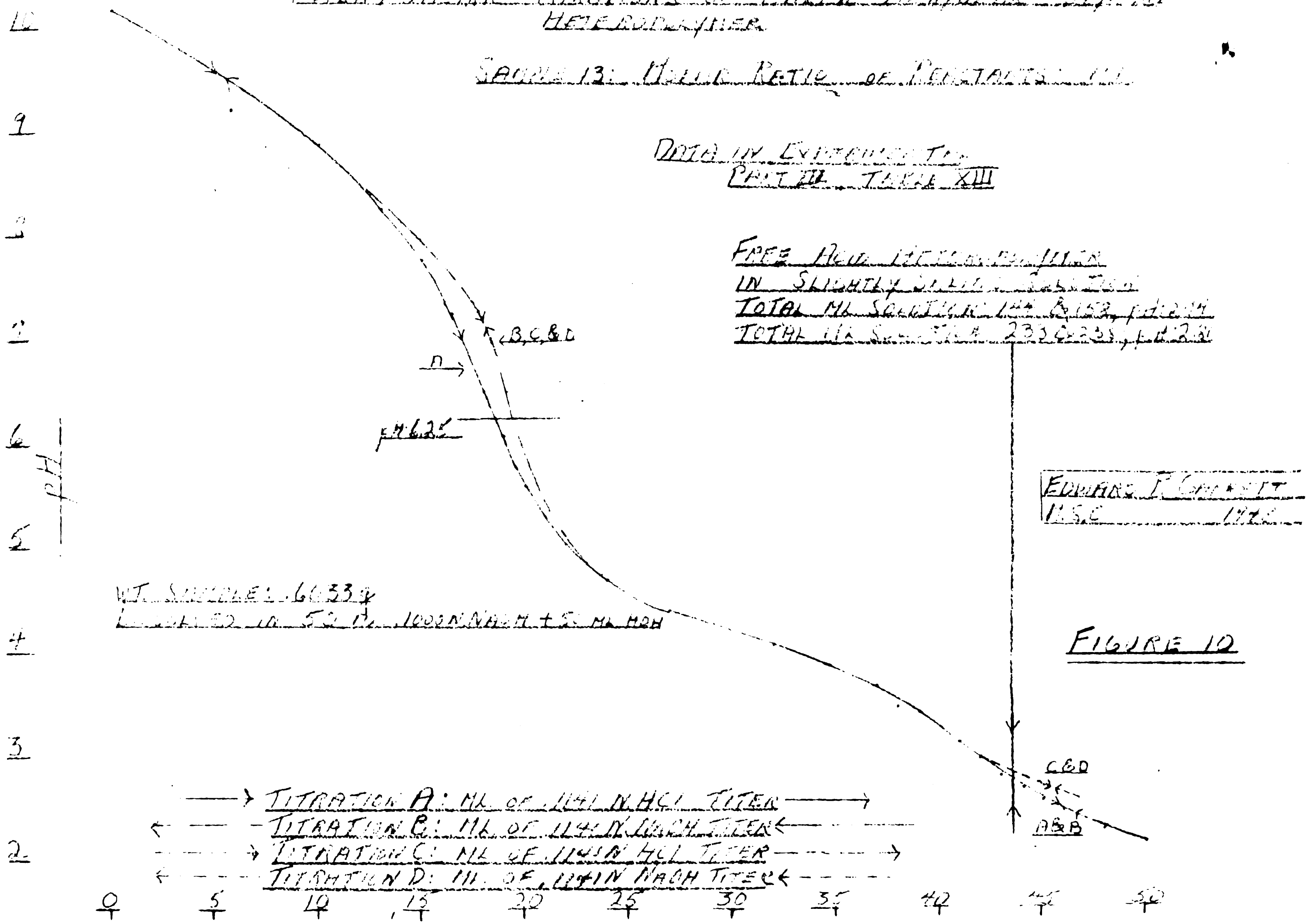

Data in Experimental
Part III Table XIII
Total ml Solution 144 & 152
pH
pH 6.25
B, C & D
D
C & D
A & B
Titration A: ml of .1141 N HCl Titer
Titration B: ml of .1141 N NaOH Titer
Titration C: ml of .1141 N HCl Titer
Titration D: ml of .1141 N NaOH Titer
0
5
10
15
20
25
30
35
40
45
50
2
3
4
5
6
7
8
9
10

Figure 10

TABLE XIV

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE

STYRENE HETEROPOLYMER

SAMPLE # 14: Initially dissolved in 50 ml .1000N NaOH

wt.: .6712 gram.

Titration A: .1141N HCl Equipment: Beckman Portable

Titration B: .1000N NaOH pH meter, Standard outside

Titration C: .1141N HCl glass electrode

COMMENTS: Same as Table XIII .

TITRATION A

Total ml solution	ml .1141N HCl	pH
100	0	9.32
105	5	8.67
110	10	7.72
112	12	7.08
114	14	6.33
115	15	6.08
116	16	5.80
117	17	5.52
118	18	5.28
119	19	5.08
121	21	4.72
124	24	4.42
130	30	4.09
134	34	3.88
136	36	3.48
138	38	3.22
139	39	3.16
140	40	3.01
142	42	2.71
143	43	2.59
150	50	2.08

TITRATION B

Total ml solution	ml .1000N NaOH	Correction to ml .1141N NaOH	pH
154	4	3.50	2.25
158	8	7.01	2.59
160	10	8.77	2.79
161	11	9.65	2.92
162	12	10.52	3.05
163	13	11.39	3.18
164	14	12.28	3.29
166	16	14.03	3.48
171	21	18.42	3.71
176	26	22.80	3.87
181	31	27.17	4.20
186	36	31.57	5.09
189	39	34.2	6.48
191	41	35.96	7.22
195	45	39.42	8.02
197	47	41.22	8.37

TITRATION C

Total ml solution	ml .1141N HCl	pH	
199	2	8.02	
201	4	7.65	
202	5	7.49	
203	6	7.22	
204	7	6.70	
205	8	6.17	
206	9	5.70	
207	10	5.24	
208	11	5.01	
210	13	4.63	
216	19	4.18	
221	24	3.91	Let stand 16 hours
221	24	3.72	
223	26	3.62	
225	28	3.48	
227	30	3.28	
229	32	3.08	
230	33	2.91	
231	34	2.81	
232	35	2.71	
233	36	2.62	
235	38	2.48	
237	40	2.35	

POTENTIOMETRIC TITRATION OF [illegible]
HETEROPOLYMER

SAMPLE 14: MOLAR RATIO OF REACTANTS: 1:1

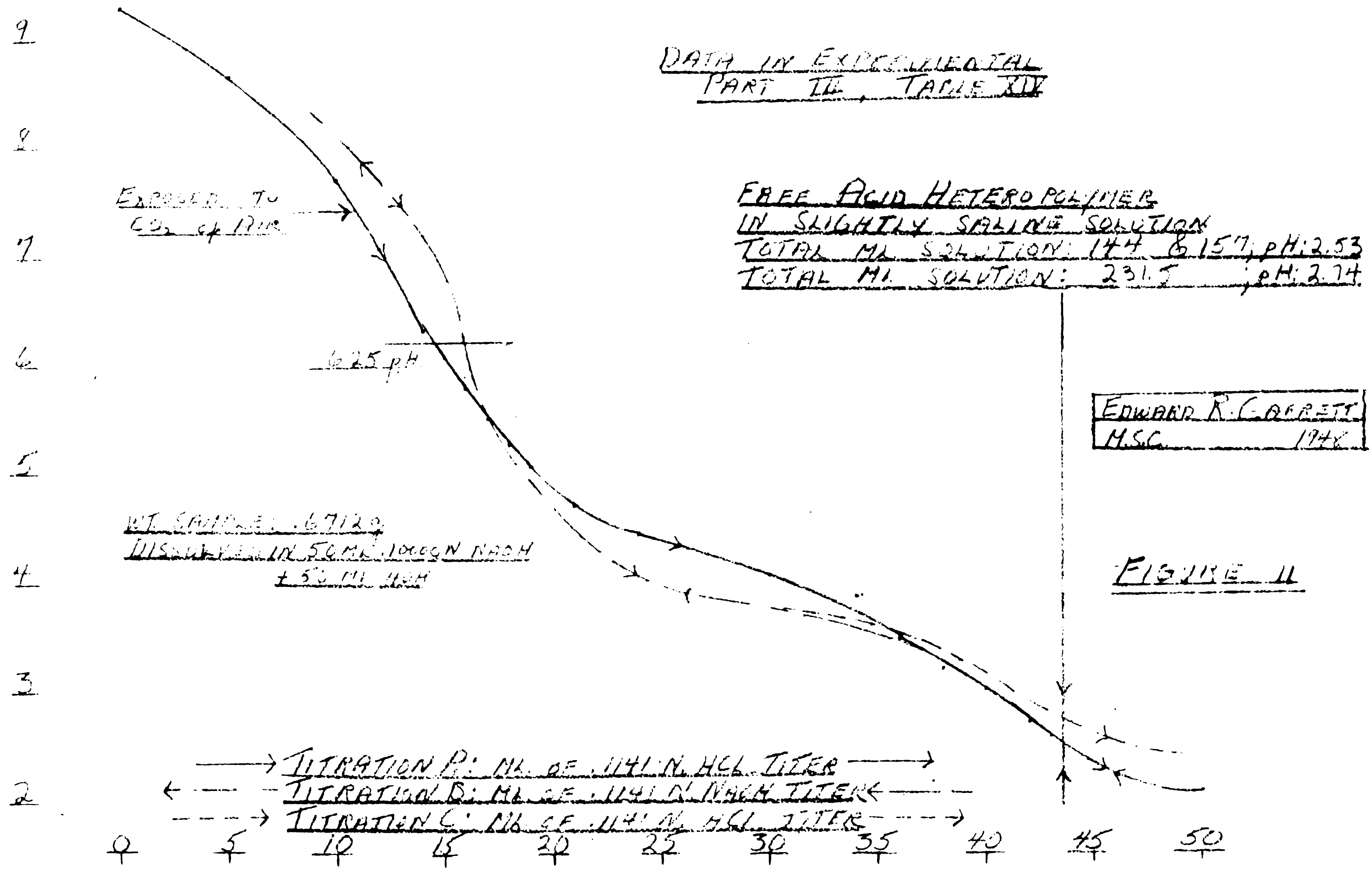


FIGURE 11

PART IV

ANALYSIS OF THE MALEIC ANHYDRIDE-STYRENE HETEROPOLYMER PREPARED FROM DIFFERENT MOLAR RATIOS OF REACTANTS BY MEANS OF POTENTIOMETRIC TITRATIONS

Materials: Eastman Styrene was vacuum distilled and the fraction distilling at 41-43°C, 14-16mm, $n^{20°}$ 1.5446, was used immediately after distillation. This is a standard method of styrene purification but determination of the freshly distilled styrene purity by the direct bromine titration of the double bond of Uhlrig and Levin[27] gave a % styrene purity value of 95.2%. By the mercuric acetate unsaturation method as described by Mihina[31] a % styrene value of 94.2% purity of freshly distilled styrene was obtained. In all probability, these methods, which depend on quantitative addition to the styrene double bond, are not adequate.

Eastman maleic anhydride was redistilled at 80mm Hg pressure, 135°C. 100% purity was certified by titration with anhydrous methanolic sodium hydroxide of weighed maleic anhydride samples dissolved in anhydrous acetone to phenolphthalein endpoint corresponding to half neutralization of the anhydride, according to the method of Moran and Siegel[32].

Nitrogen gas was passed through alkaline pyrogallol and under the surface of the solvent prior to and during the reactions so that the

copolymerization took place in the absence of oxygen.

The other materials were the same as used in the reactions of Studies A and B, Part II.

Procedures: The polymerization procedure was effected as per Part II, Study A, Procedure 1. The copolymer samples were prepared for potentiometric titration by the methods developed in Part III.

STUDY A

1:1 (Styrene: Maleic anhydride) molar ratio of reactants: (Samples 15 and 16, Tables XV and XVI).

Recipe: 24.2970 g styrene (.2333 mole)
22.8810 g maleic anhydride (.2333 mole)
615.2 grams benzene
.2333 g benzoyl peroxide

Total time of polymerization: 6 hours.

Treatment of Copolymer and Potentiometric titration data: See tables XV and XVI for Samples 15 and 16 respectively.

STUDY B

3:1 (Styrene:Maleic anhydride) molar ratio of reactants: (Samples 17 and 18, Tables XVII,XVIII).

Recipe: 36.8004 g styrene (.3500 mole)
11.4431 g maleic anhydride (.1167 mole)
615.2 grams benzene
.2333 grams benzoyl peroxide

Total time of polymerization: 6½ hours.

Treatment of copolymer and Potentiometric titration data: See Tables XVII and XVIII for Samples 17 and 18.

STUDY C

1:3 (Styrene-Maleic anhydride) molar ratio of reactants: (Samples 19 and 20, Tables XIX and XX).

Recipe: 12.1536 g styrene (.1167 mole)

34.3161 g M.A. (.3500 mole)

615.2 grams benzene

.2333 g benzoyl peroxide

Total time of polymerization: 8 hours

Treatment of copolymer and potentiometric titration data: See Tables XIX and XX for samples 19 and 20 respectively.

TABLE XV

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 15: Initially dissolved in 100 ml .0975N NaOH
wt.: 1.0000 gram

Titration A: .0949N HCl Equipment: Fischer Line
Titration B: .0975N NaOH Operated pH meter, Standard
Titration C: .0949N HCL outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants and washed with hot benzene. Polymer extracted in soxhelets by benzene for three weeks and vacuum dried at 3 mm pressure, 140° C for three weeks. 100 ml .0975N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone, but was slightly cloudy. Temperature of titrations 28°C.

TITRATION A

Total ml solution	ml .0949N HCl	pH
115.5	.5	10.42
116.0	1.0	10.41
117.0	2.0	10.37
118.0	3.0	10.32
119.0	4.0	10.28
120.5	5.5	10.19
122.0	7.0	10.11
124.0	9.0	10.01
126.0	11.0	9.9
128.0	13.0	9.78
129.0	14.0	9.75
131.0	16.0	9.63
132.5	17.5	9.50

TITRATION A (continued)

Total ml solution	ml .0949N HCl	pH	Total ml solution	ml .0949N HCl	pH
134.0	19.0	9.43	177.0	62.0	4.81
135.5	20.5	9.3	179.0	64.0	4.67
137.0	22.0	9.22	182.0	67.0	4.55
138.5	23.5	9.1	185.0	70.0	4.45
140.0	25.0	9.08	188.0	73.0	4.35
141.5	26.5	8.91	191.07	76.07	4.22
143.0	28.0	8.83	194.0	79.0	4.12
144.5	29.5	8.7	197.0	82.0	4.02
146.0	31.0	8.58	200.0	85.0	3.90
147.5	32.5	8.47	203.0	88.0	3.72
149.0	34.0	8.36	205.0	90.0	3.6
151.0	36.0	8.11	207.0	92.0	3.48
152.5	37.5	8.00	209.0	94.0	3.32
154.0	39.0	7.81	210.0	95.0	3.22
155.0	40.0	7.69	211.0	96.0	3.20
156.0	41.0	7.59	212.5	97.5	3.10
157.0	42.0	7.44	213.5	98.5	3.00
158.0	43.0	7.30	215.0	100.0	2.91
159.0	44.0	7.15	216.5	101.5	2.80
160.0	45.0	7.01	217.75	102.75	2.72
161.0	46.0	6.90	219.0	104.0	2.62
162.0	47.0	6.78	222.0	107.0	2.5
163.0	48.0	6.7	225.5	110.5	2.4
164.0	49.0	6.57	229.0	114.0	2.3
165.0	50.0	6.46	231.0	116.0	2.31
175.1	60.1	4.93	235.0	120.0	2.25

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml .0949N NaOH	pH
235	0	0	2.25
241	6	6.16	2.42
246	11	11.3	2.58
251	16	16.42	2.8
255	20	20.53	3.0
259	24	24.63	3.21
261	26	26.7	3.32
263	28	28.75	3.5
265	30	30.81	3.68
266	31	31.82	3.75
267	32	32.83	3.82
268	33	33.88	3.88
271	36	36.98	4.01
276	41	42.1	4.18
280	45	46.2	4.3
285	50	51.3	4.5
295	60	61.6	5.24
297	62	63.7	5.61
298	63	64.7	5.89
299	64	65.7	6.12
300	65	66.7	6.42
301	66	67.75	6.74
302	67	68.8	7.00
303.5	68.5	70.35	7.25
305	70	71.9	7.50
307	72	73.9	7.80
310	75	77.0	8.16

TITRATION C

Total ml solution	ml .0949N HCl	pH	Total ml solution	ml .0949N HCl	pH
310	0	8.15	363	53	3.42
312	2	7.88	364	54	3.38
315	5	7.52	365	55	3.31
317	7	7.22	367	57	3.2
318	8	7.1	368	58	3.11
319	9	6.79	369	59	3.08
320	10	6.59	371	61	3.01
321	11	6.29	374	64	2.9
322	12	6.02	378	68	2.78
323	13	5.78	383	73	2.7
324	14	5.51	389	79	2.57
325	15	5.3	395	85	2.48
326	16	5.2			
328	18	4.99			
331	21	4.79			
334	24	4.6			
339	29	4.48			
345	35	4.3			
350	40	4.15			
355	45	3.9			
357	47	3.81			
359	49	3.7			
360	50	3.62			
362	52	3.5			

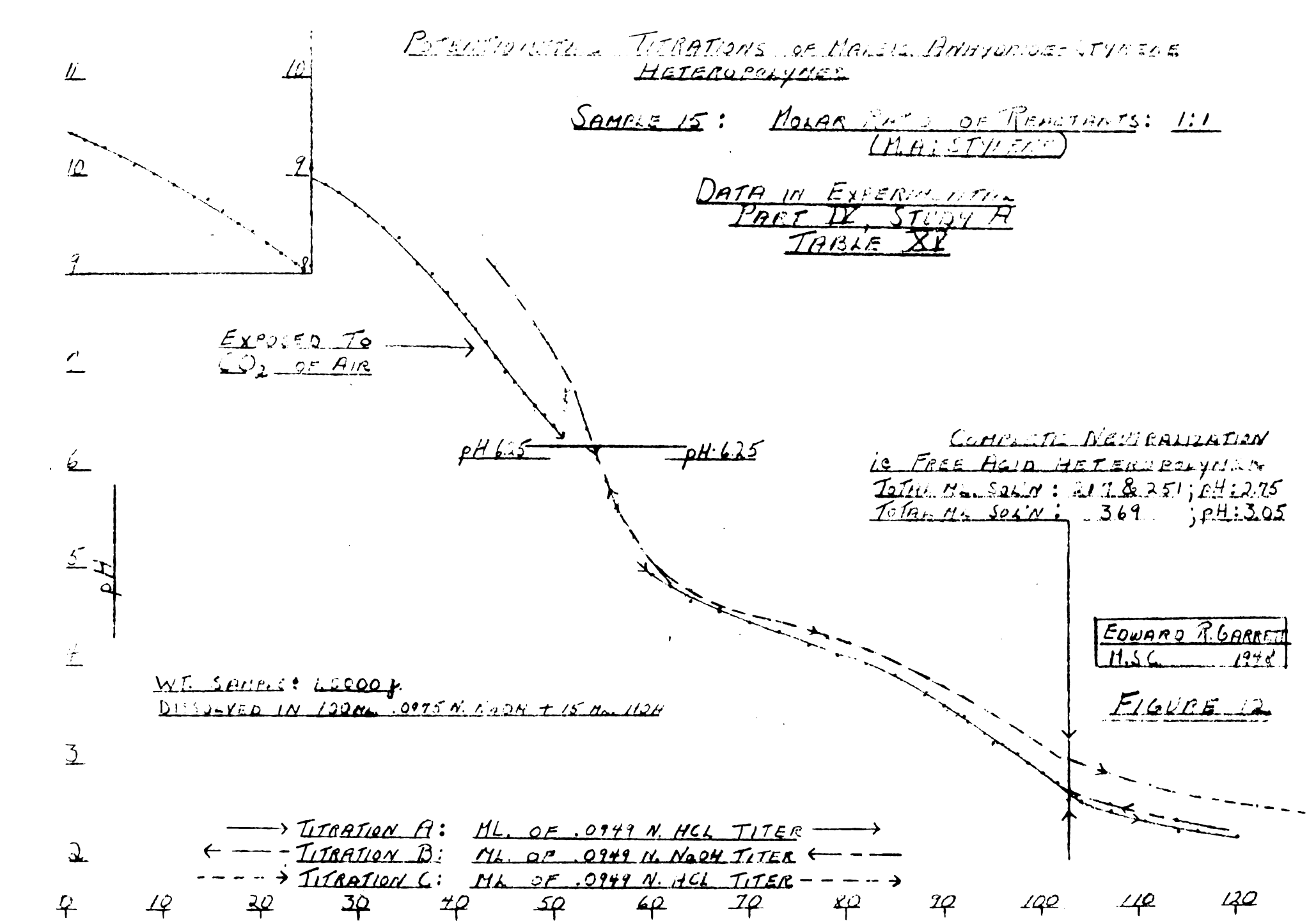

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMERS
SAMPLE 15: MOLAR RATIO OF REACTANTS: 1:1 (M.A.:STYRENE)
DATA IN EXPERIMENTAL PART IV, STUDY A TABLE XV
EXPOSED TO CO_2 OF AIR
pH 6.25
pH 6.25
COMPLETE NEUTRALIZATION
ie FREE ACID HETEROPOLYMER
TOTAL Ml. SOLN: 217 & 251; pH: 2.75
TOTAL Ml. SOLN: 369; pH: 3.05
WT. SAMPLE: 1.2000 g.
DISSOLVED IN 120 Ml. .0975 N. NaOH + 15 Ml. H2O
EDWARD R. GARRETT M.S.C. 1948
FIGURE 12
TITRATION A: ML. OF .0949 N. HCl TITER
TITRATION B: ML. OF .0949 N. NaOH TITER
TITRATION C: ML. OF .0949 N. HCl TITER
pH
11
10
9
8
7
6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100
110
120

TABLE XVI

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 16: Polymer sample treatment same as in Table XV.

TITRATION A

Total ml solution	ml .0949N HCl	pH	Total ml solution	ml .0949N HCl	pH
174	0	11.15	234	60	5.07
176	2	11.10	237	63	4.83
180	6	10.98	240	70	4.52
184	10	10.78	249.1	75.1	4.39
188	14	10.52	252	78	4.30
193	19	10.20	257	83	4.15
196	22	10.01	262	88	3.95
199	25	9.81	267	93	3.62
202	28	9.59	269	95	3.5
205	31	9.36	271	97	3.35
208	34	9.10	272	98	3.29
211	37	8.86	273	99	3.21
214	40	8.6	274	100	3.15
217	43	8.32	276	102	3.02
220	46	8.00	278	104	2.95
222	48	7.67	281	107	2.8
224	50	7.20	285	111	2.63
225	51	6.98			
226	52	6.67			
227	53	6.38			
228	54	6.10			
229	55	5.85			
230	56	5.6			
231	57	5.42			
232	58	5.30			

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml .0949N NaOH	pH
290	5	5.13	2.81
295	10	10.27	3.09
297	12	12.33	3.20
298	13	13.36	3.28
299	14	14.38	3.32
300	15	15.40	3.38
301	16	16.42	3.48
302	17	17.47	3.51
303	18	18.49	3.59
304	19	19.52	3.68
305	20	20.55	3.72
310	25	25.7	4.00
315	30	30.8	4.15
320	35	35.96	4.30
325	40	41.15	4.48
329	44	45.2	4.62
334	49	50.3	4.95
335	50	51.35	5.02
337	52	53.4	5.28
339	54	55.45	5.68
340	55	56.5	6.00
342	57	58.6	6.6
343	58	59.6	6.88
344	59	60.6	7.10
345	60	61.6	7.28
347	62	63.7	7.6
351	66	67.75	8.12

TITRATION C

Total ml solution	ml .0949N NaOH	pH
354	3	7.83
357	6	7.40
359	8	7.02
360	9	6.75
361	10	6.4
362	11	6.1
363	12	5.82
364	13	5.58
366	15	5.2
368	17	4.98
371	20	4.75
375	24	4.55
380	29	4.4
386	35	4.23
391	40	4.1
396	45	3.9
399	48	3.72
401	50	3.6
403	52	3.48
405	54	3.36
407	56	3.23
409	58	3.12
411	60	3.05
413	62	3.00

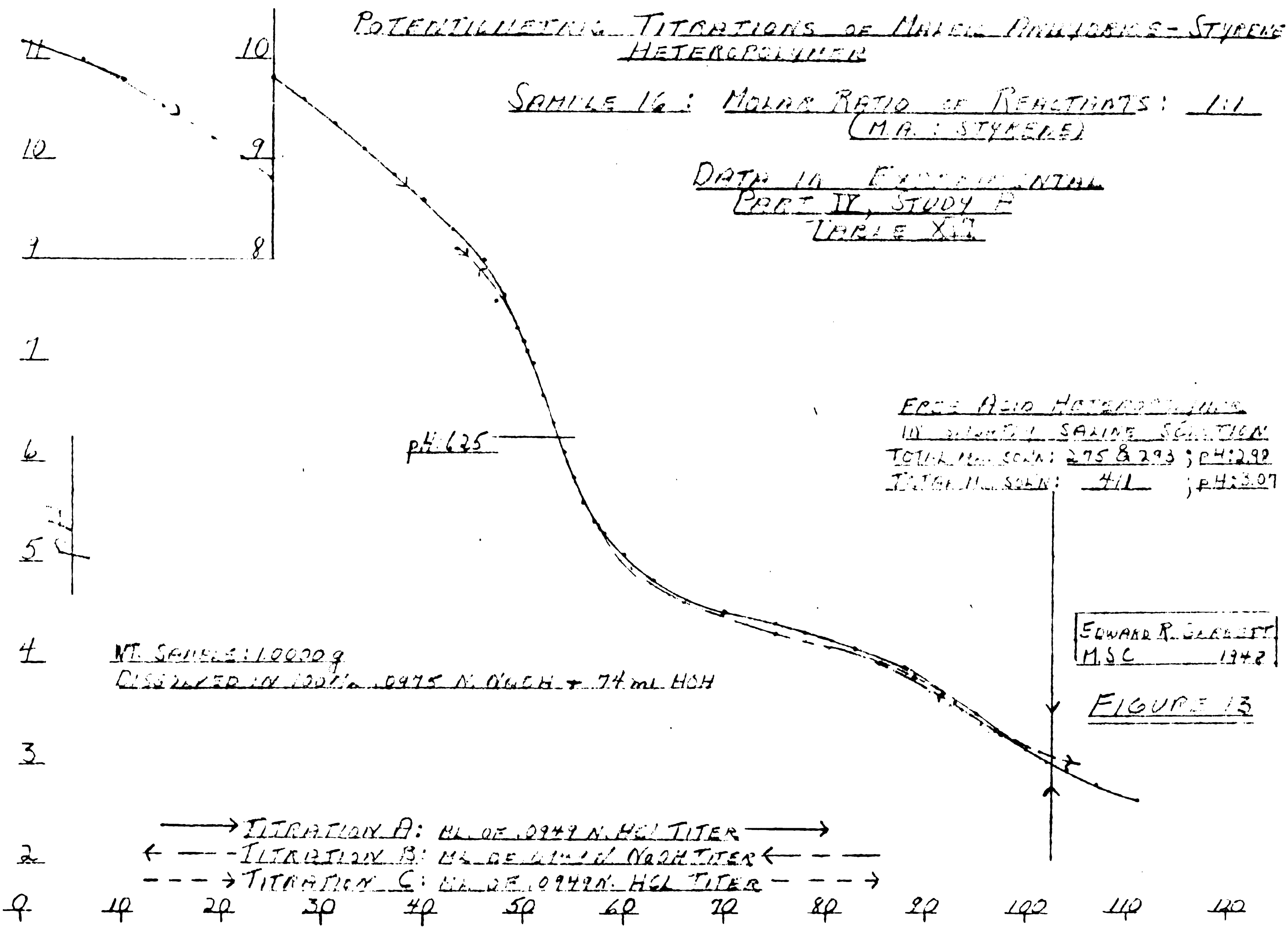

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMER
SAMPLE 16: MOLAR RATIO OF REACTANTS: 1:1
(M.A. : STYRENE)
DATA IN EXPERIMENTAL
PART IV, STUDY F
TABLE XII
pH 6.25
FREE ACID HETEROPOLYMER
IN SALINE SOLUTION
TOTAL ML. SOLN: 275 & 293; pH: 2.92
TOTAL ML. SOLN: 411; pH: 3.07
EDWARD R. GARRETT
M.S.C. 1948
WT. SAMPLE: 1.0000 g
DISSOLVED IN 100 ML .0975 N. NaOH + 74 ml HOH
TITRATION A: ML. OF .0949 N. HCl TITER
TITRATION B: ML. OF NaOH TITER
TITRATION C: ML. OF .0949 N. HCl TITER
pH
2
3
4
5
6
7
8
9
10
11
0
10
20
30
40
50
60
70
80
90
100
110
120
FIGURE 13

TABLE XVII

POTENTIOMETRIC TITRATIONS of MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 17: Polymer sample treatment same as Table XV.

COMMENTS: Heteropolymer was prepared from 1:3 (Maleic-Anhydride - Styrene) molar ratio of reactants with $Bz0_2$ catalyst and washed with hot benzene. Polymer extracted in soxhelets by benzene for three weeks and vacuum dried at 3 mm pressure, 140° C for three weeks. 100ml .0975N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone and the solution was clear.

TITRATION A

Total ml solution	ml .0949N HCl	pH
140	0	11.13
145	5	10.92
150	10	10.65
160	20	10.00
164	24	9.75
167	27	9.52
170	30	9.28
173	33	9.05
176	36	8.8
178	38	8.68
180	40	8.48
182	42	8.29
184	44	8.05
186	46	7.80
188	48	7.52
189	49	7.35
190	50	7.18

TITRATION A (continued)

Total ml solution	ml .0949N HCl	pH
191	51	7.00
192	52	6.85
193	53	6.65
194	54	6.40
195	55	6.20
196	56	5.98
197	57	5.77
198	58	5.55
199	59	5.38
200	60	5.22
202	62	5.02
204	64	4.85
207	67	4.7
211	71	4.52
216	76	4.4
222	82	4.2
227	87	4.0
231	91	3.71
233	93	3.58
235	95	3.42
237	97	3.28
238	98	3.17
239	99	3.11
240	100	3.08
244	104	2.79
248	108	2.60
250	110	2.52

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml .0949N NaOH	pH
255	5	5.13	2.8
257	7	7.19	2.9
258	8	8.22	2.95
259	9	9.24	3.01
260	10	10.27	3.09
261	11	11.29	3.17
262	12	12.33	3.22
263	13	13.36	3.30
264	14	14.38	3.38
265	15	15.40	3.45
267	17	17.47	3.61
271	21	21.54	3.9
274	24	24.6	4.03
278	28	28.7	4.22
283	33	33.78	4.38
289	39	40.1	4.58
293	43	44.2	4.75
298	48	49.3	5.1
300	50	51.35	5.39
301	51	52.4	5.58
302	52	53.4	5.85
303	53	54.4	6.15
304	54	55.45	6.51
305	55	56.5	6.82
306	56	57.5	7.00
308	58	59.6	7.40
310	60	61.6	7.72
314	64	65.7	8.17

TITRATION C

Total ml solution	ml .0949N HCl	pH
316	2	8.03
318	4	7.8
320	6	7.5
322	8	7.12
323	9	6.96
324	10	6.72
325	11	6.44
326	12	6.12
327	13	5.82
328	14	5.6
329	15	5.41
331	17	5.17
333	19	4.98
340	26	4.61
345	31	4.48
351	37	4.28
356	42	4.07
360	46	3.82
362	48	3.70
364	50	3.52
366	52	3.40
368	54	3.28
370	56	3.12
374	60	2.97
377	63	2.82
380	66	2.7
384	70	2.58

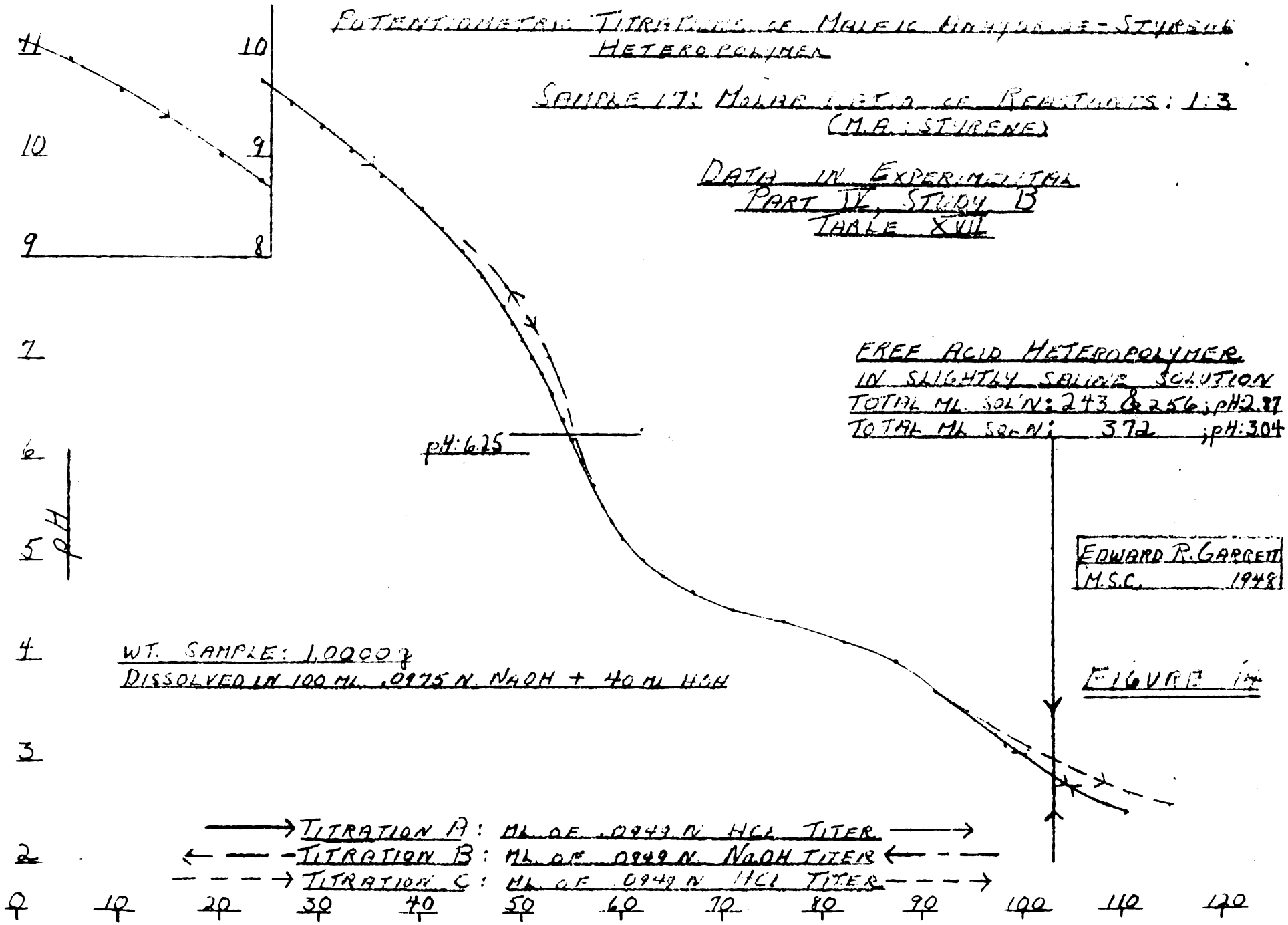

POTENTIOMETRIC TITRATION OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMER
SAMPLE 17: MOLAR RATIO OF REACTANTS: 1:3 (M.A.:STYRENE)
DATA IN EXPERIMENTAL PART IV, STUDY B TABLE XVII
FREE ACID HETEROPOLYMER IN SLIGHTLY SALINE SOLUTION
TOTAL ML. SOL'N: 243 & 256; pH 2.87
TOTAL ML SOL'N: 372 ; pH: 3.04
pH: 6.25
WT. SAMPLE: 1.0000 g
DISSOLVED IN 100 ML .0975 N. NaOH + 40 ML H2O
EDWARD R. GARCEN M.S.C. 1948
FIGURE 14
pH
TITRATION A: ML OF .0949 N HCl TITER
TITRATION B: ML OF 0949 N NaOH TITER
TITRATION C: ML OF 0949 N HCl TITER
0 10 20 30 40 50 60 70 80 90 100 110 120
2 3 4 5 6 7 8 9 10 11

TABLE XVIII

POTENTIOMETRIC TITRATIONS OF MALEIC-ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 18: Polymer sample treatment and COMMENTS are the same as Table XVII.

TITRATION A

Total ml solution	ml .0949N HCl	pH	Total ml solution	ml .0949N HCl	pH
174	0	11.05	236	62	5.43
179	5	10.98	238	64	5.02
184	10	10.78	241	67	4.78
189	15	10.52	244	70	4.92
			meter adjusted		
194	20	10.28	247	73	4.58
199	25	9.98	252	78	4.4
204	30	9.7	257	83	4.22
209	35	9.3	261	87	4.08
214	40	8.91	264	90	3.9
218	44	8.5	266	92	3.75
221	47	8.12	268	94	3.58
223	49	7.89	270	96	3.43
225	51	7.58	272	98	3.29
226	52	7.33	274	100	3.10
227	53	7.09	277	103	2.95
228	54	6.88	280	106	2.78
229	55	6.68	284	110	2.62
230	56	6.42			
231	57	5.93			
232	58	5.92			
233	59	5.80			
234	60	5.68			

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml. .0949N NaOH	pH
289	5	5.13	2.8
292	8	8.22	3.0
294	10	10.27	3.11
296	12	12.33	3.22
298	14	14.38	3.41
300	16	16.42	3.59
302	18	18.49	3.71
307	23	23.6	4.00
313	29	29.78	4.23
319	35	35.96	4.42
324	40	41.15	4.60
328	44	45.2	4.78
331	47	48.25	5.00
333	49	50.3	5.2
334	50	51.35	5.39
335	51	52.4	5.6
336	52	53.4	5.9
337	53	54.4	6.19
338	54	55.45	6.50
339	55	56.5	6.75
340	56	57.5	6.98
341	57	58.6	7.2
342	58	59.6	7.39
344	60	61.6	7.72

TITRATION C

Total ml solution	ml .0949N HCl	pH
347	3	7.32
349	5	6.97
350	6	6.72
351	7	6.45
352	8	6.12
353	9	5.85
354	10	5.6
356	12	5.28
359	15	4.99
364	20	4.71
371	27	4.48
377	33	4.3
382	38	4.1
387	43	3.81
391	47	3.52
393	49	3.41
394	50	3.35
396	52	3.21
399	55	3.02
402	58	2.90
409	65	2.65

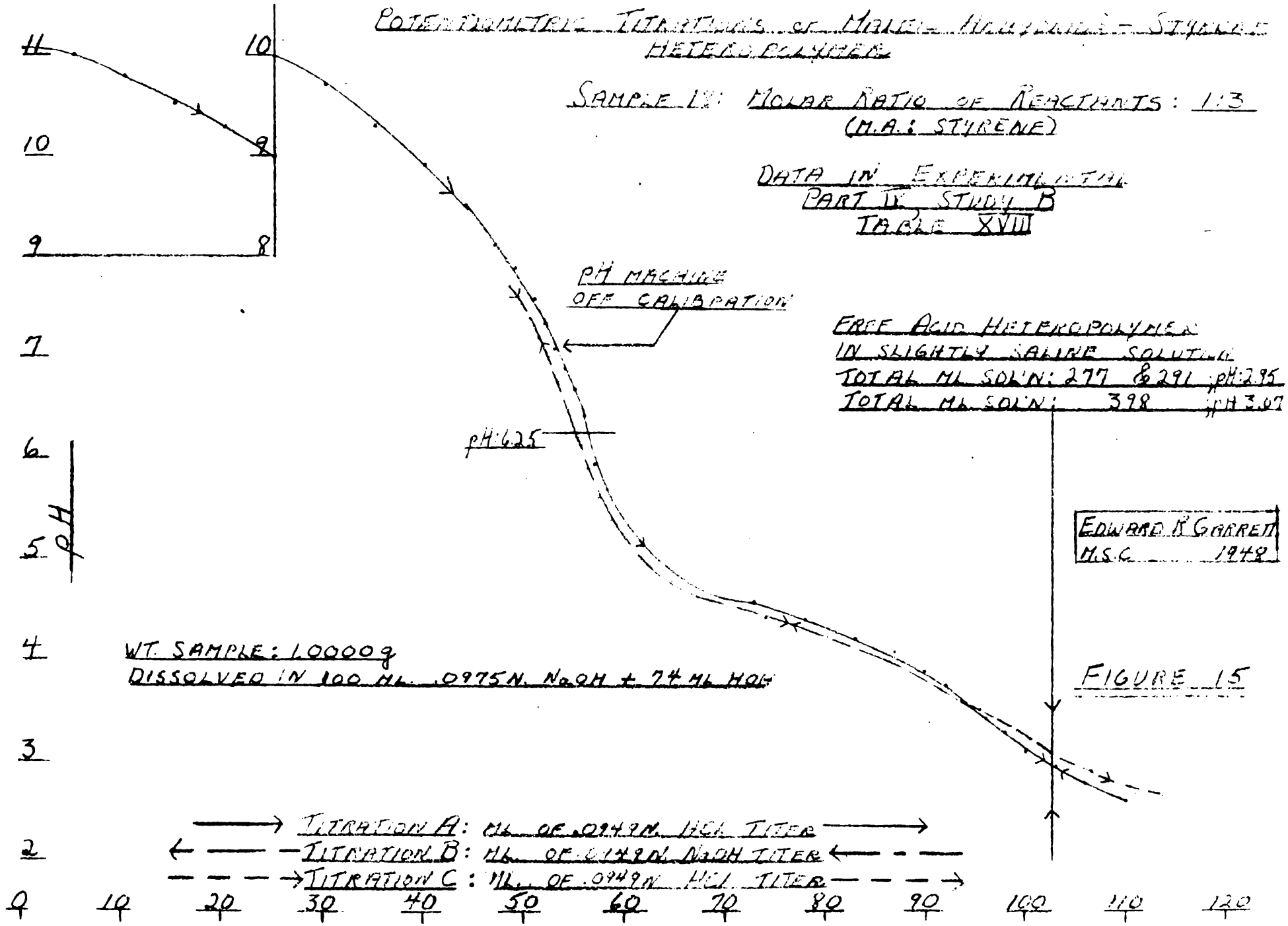

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE - STYRENE HETEROPOLYMERS
SAMPLE IX: MOLAR RATIO OF REACTANTS: 1:3 (M.A.: STYRENE)
DATA IN EXPERIMENTAL PART V STUDY B TABLE XVIII
PH MACHINE OFF CALIBRATION
FREE ACID HETEROPOLYMER IN SLIGHTLY SALINE SOLUTION
TOTAL ML SOLN: 277 & 291 pH: 2.95
TOTAL ML SOLN: 398 pH 3.07
pH: 6.25
EDWARD R. GARRETT M.S.C. 1948
WT. SAMPLE: 1.0000 g
DISSOLVED IN 100 ML .0975N. NaOH + 74 ML H2O
FIGURE 15
TITRATION A: ML OF 0.942N HCl TITER
TITRATION B: ML OF 0.1192N NaOH TITER
TITRATION C: ML OF 0.942N HCl TITER
pH
11
10
9
8
7
6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100
110
120

TABLE XIX

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 19: Initially dissolved in 100 ml .0975N NaOH
wt.: 1.0000 gram

Titration A: .0949N HCl
Titration B: .0975N NaOH
Titration C: .0949N HCl

Equipment: Fischer Line Operated pH meter, Standard outside glass electrode

COMMENTS: Heteropolymer was prepared from 3:1 (Maleic Anhydride - Styrene) molar ratio of reactants with Bz_2O_2 catalyst and washed with hot benzene. Polymer extracted in soxhelets by benzene for three weeks and vacuum dried at 3mm pressure, 140° C for one week. 100 ml .0975N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone and the solution was clear.

TITRATION A

Total ml solution	ml .0949N HCl	pH
135	0	10.78
137	2	10.68
140	5	10.49
145	10	10.19
150	15	9.89
155	20	9.55
158	23	9.35
161	26	9.12
164	29	8.92
167	32	8.7
170	35	8.48

TITRATION A (continued)

Total ml solution	ml .0949N HCl	pH	Total ml solution	ml .0949N HCl	pH
174	39	8.10	235	100	3.27
176	41	7.9	236	101	3.2
178	43	7.62	237	102	3.15
180	45	7.31	238	103	3.09
181	46	7.11	240	105	3.00
182	47	6.98	243	108	2.89
183	48	6.78	245	110	2.80
184	49	6.59			
185	50	6.39			
186	51	6.18			
187	52	6.00			
188	53	5.80			
189	54	5.68			
190	55	5.5			
192	57	5.22			
195	60	4.98			
199	64	4.77			
204	69	4.52			
210	75	4.38			
217	82	4.19			
222	87	4.00			
226	91	3.81			
229	94	3.65			
231	96	3.51			
233	98	3.38			

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml. .0949N NaOH	pH
250	5	5.13	3.00
253	8	8.22	3.10
255	10	10.27	3.22
257	12	12.33	3.39
259	14	14.38	3.5
261	16	16.42	3.61
263	18	18.49	3.72
266	21	21.54	3.91
270	25	25.7	4.1
275	30	30.8	4.23
281	36	36.98	4.39
286	41	42.1	4.52
290	45	46.2	4.72
293	48	49.3	4.88
295	50	51.35	5.09
297	52	53.4	5.30
299	54	55.45	5.61
300	55	56.5	5.83
301	56	57.5	6.02
302	57	58.6	6.30
303	58	59.6	6.55
304	59	60.6	6.75
305	60	61.6	7.00
306.5	61.5	63.2	7.25
308	63	64.7	7.55
310	65	66.7	7.79
312	67	68.8	8.01
315	70	71.9	8.25

TITRATION C

Total ml solution	ml .0949N HCl	pH
315	0	8.30
320	5	7.89
322	7	7.62
324	9	7.35
325	10	7.11
326	11	6.98
327	12	6.78
328	13	6.55
329	14	6.29
330	15	6.08
331	16	5.81
333	18	5.47
335	20	5.18
338	23	4.92
342	27	4.7
348	33	4.5
355	40	4.32
360	45	4.2
365	50	4.02
370	55	3.79
375	60	3.52
378	63	3.38
380	65	3.29
382	67	3.2
385	70	3.1
391	76	2.92
395	80	2.84

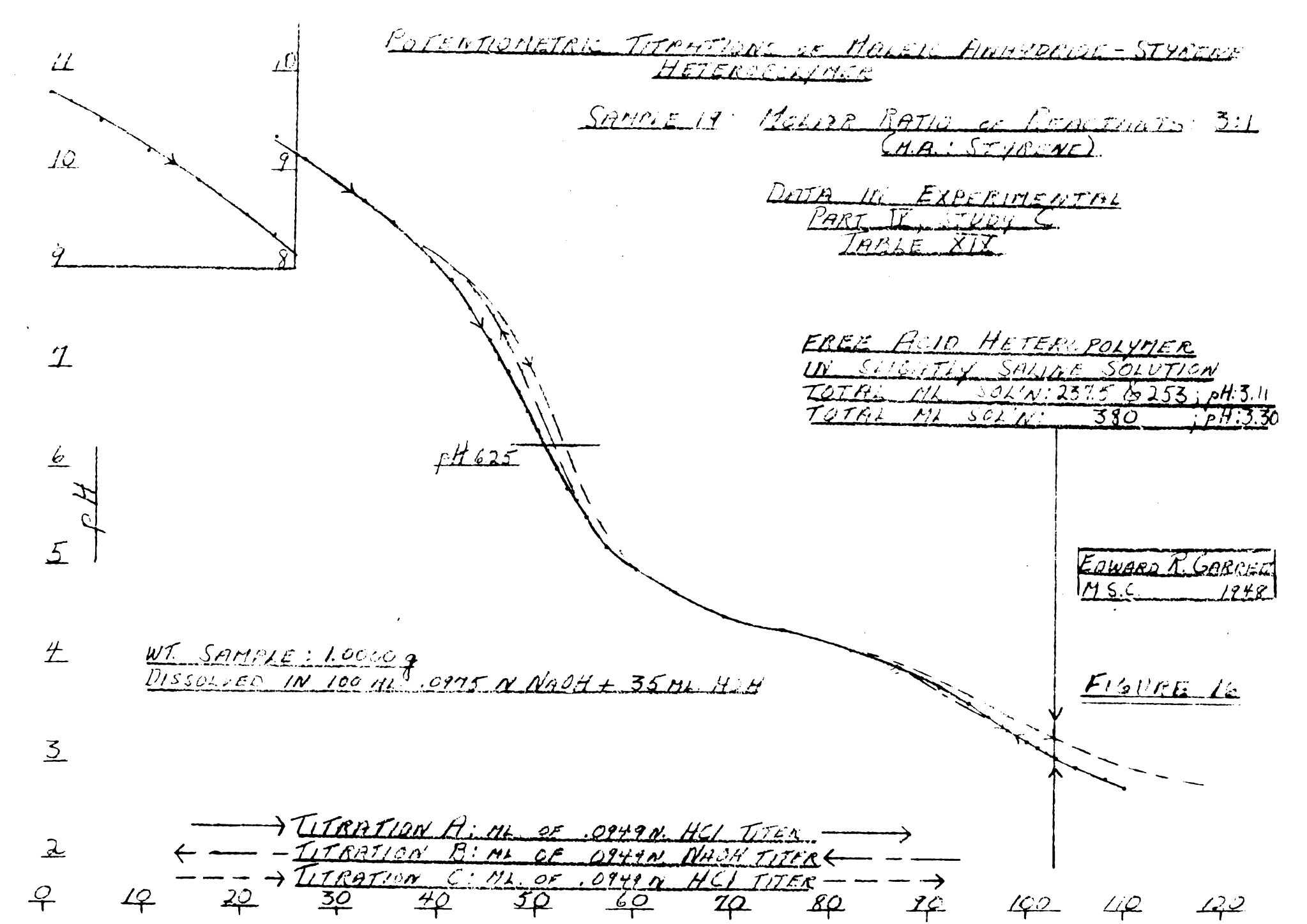

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE - STYRENE HETEROPOLYMER
SAMPLE 14 MOLAR RATIO OF REACTANTS: 3:1 (M.A.: STYRENE)
DATA IN EXPERIMENTAL PART IV STUDY C TABLE XIV
FREE ACID HETERO POLYMER IN SLIGHTLY SALINE SOLUTION
TOTAL ML SOL'N: 237.5 & 253 ; pH: 3.11
TOTAL ML SOL'N: 380 ; pH: 3.30
pH 6.25
EDWARD T. GARCEAU M.S.C. 1948
WT. SAMPLE: 1.0000 g
DISSOLVED IN 100 ML .0975 N NaOH + 35 ML H2O
FIGURE 16
TITRATION A: ML OF .0949 N. HCl TITER
TITRATION B: ML OF .0949 N NaOH TITER
TITRATION C: ML. OF .0949 N HCl TITER
pH
11
10
9
8
7
6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100
110
120

TABLE XX

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE STYRENE HETEROPOLYMER

SAMPLE # 20: Initially dissolved in 100 ml .0975N NaOH

wt.: 1.000 gram

Titration A: .0949N HCl Equipment: Fischer Line

Titration B: .0975N NaOH Operated pH meter, Standard

Titration C: .0949N HCl outside glass electrode

COMMENTS: Heteropolymer was prepared from 3:1 (Maleic Anhydride-Styrene) molar ratio of reactants with $Bz0_2$ catalyst and washed with hot benzene. Polymer extracted in soxhelets by benzene for three weeks and vacuum dried at 3mm pressure, 140° C for one week. 100 ml .0975N NaOH added very slowly. All ppt. dissolved on the boiling off of acetone and the solution was clear.

TITRATION A

Total ml solution	ml .0949N HCl	pH
146	0	10.80
156	10	10.22
166	20	9.60
172	26	9.19
178	32	8.78
183	37	8.35
187	41	7.95
190	44	7.51
192	46	7.17
194	48	6.81
195	49	6.6

TITRATION A (continued)

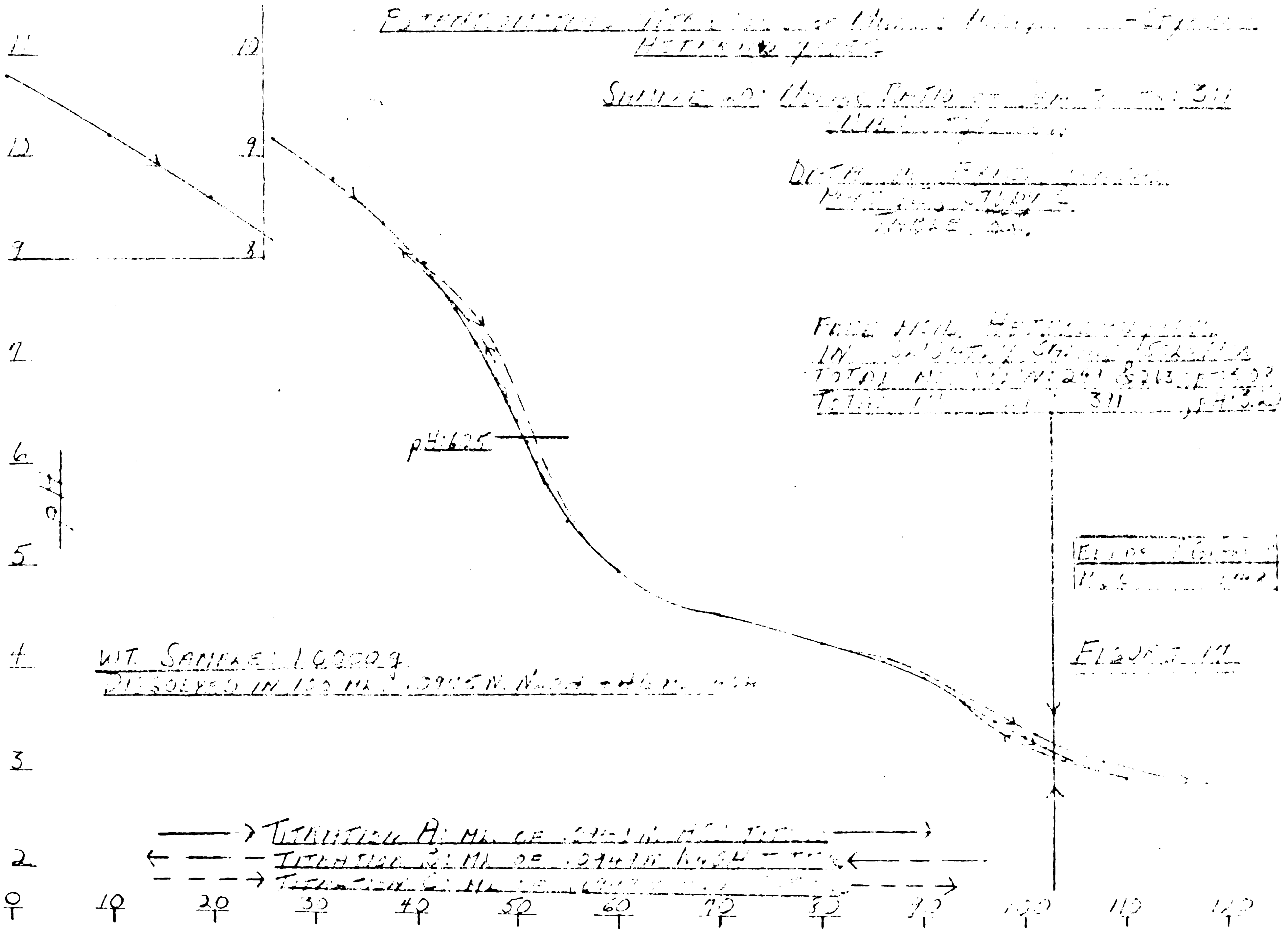
Total ml solution	ml .0949N HCl	pH
196	50	6.41
197	51	6.2
198	52	6.0
199	53	5.78
201	55	5.42
206	60	4.92
216	70	4.48
226	80	4.21
232	86	4.02
236	90	3.85
240	94	3.60
243	97	3.41
246	100	3.25
248	102	3.15
250	104	3.04
256	110	2.85

TITRATION B

Total ml solution	ml .0975N NaOH	Correction to ml .0949N NaOH	pH
256	0	0	2.85
261	5	5.13	3.00
264	8	8.22	3.10
266	10	10.27	3.20
268	12	12.33	3.32
270	14	14.38	3.45
276	20	20.55	3.80
286	30	30.8	4.20
296	40	41.15	4.47
302	46	47.25	4.7
306	50	51.35	4.99
309	53	54.4	5.3
311.5	55.5	57.0	5.75
313	57	58.6	6.15
314.5	58.5	59.1	6.50
316.5	60.5	62.1	6.98
319	63	64.7	7.39
322	66	67.75	7.70
326	70	71.9	8.15

TITRATION C

Total ml solution	ml .0949N HCl	pH
331	5	7.79
336	10	7.10
338	12	6.68
339	13	6.40
340	14	6.20
341	15	5.95
342	16	5.72
346	20	5.1
356	30	4.55
366	40	4.28
376	50	3.99
381	55	3.72
386	60	3.45
389	63	3.3
391	65	3.18
393	67	3.10
396	70	3.02
406	80	2.8


pH 6.25
WT. SAMPLE: 1.0000 g.
FIGURE
11
10
9
8
7
6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100
110
120

PART V

ANHYDROUS POTENTIOMETRIC TITRATIONS OF THE HETEROPOLYMER: MALEIC ANHYDRIDE-STYRENE

Treatment of the copolymer samples for Anhydrous Potentiometric Titration: The heteropolymer product from Study A, Part II was used. The treatment of the polymer and potentiometric titration data is given in Tables XXI, XXII and XXIII, corresponding to samples 21,22 and 23 respectively. Table XXIV is a blank titration of the pure solvent.

The procedure was based on the anhydrous titration of mono-esters of monomeric anhydrides with standard alcoholic caustic as proposed by Moran and Siegel[32]. The copolymer sample was dissolved in 250 ml acetone and potentiometrically titrated. Phenolphthalein indicator was also used as per the method of Moran and Siegel but due to polymer precipitation and indicator absorption by the polymer, no acute endpoint was discernable.

TABLE XXI

POTENTIOMETRIC TITRATIONS OF MALEIC ANHYDRIDE-STYRENE HETEROPOLYMERS WITH ABSOLUTE METHANOLIC NaOH IN ANHYDROUS ACETONE MEDIA

SAMPLE # 21: Initially dissolved in 250 ml anhydrous acetone wt.: 1.0062 gram

Titration: .0949N Methanolic NaOH

Equipment: Beckman Portable pH meter, Standard outside glass electrode

COMMENTS: Heteropolymer prepared from 1:1 molar ratio of reactants with BzO_2 catalyst and washed with cold benzene. Dried at atm. pressure and 80° C one week, dried 24 hours at 85° C, 3mm pressure. Added 1 ml absolute methyl alcohol.

ml .0949N NaOH	Correction to ml .1141N NaOH	pH	Remarks
1	.83	4.9	3 drops phth.
2	1.66	6.39	Clouding up
3	2.49	7.59	
4	3.32	7.19	
5	4.16	7.38, 7.29	
6	4.98	7.52, 7.48	
7	5.82	7.62, 7.58	
8	6.65	7.6 , 7.58	
9	7.48	7.68, 7.61	
13	10.80	8.15, 6.42	After 15½ hrs., still turbid.
14	11.62	6.48	No ppt., but not transparent
16	13.3	6.68	
18	14.96	7.03	

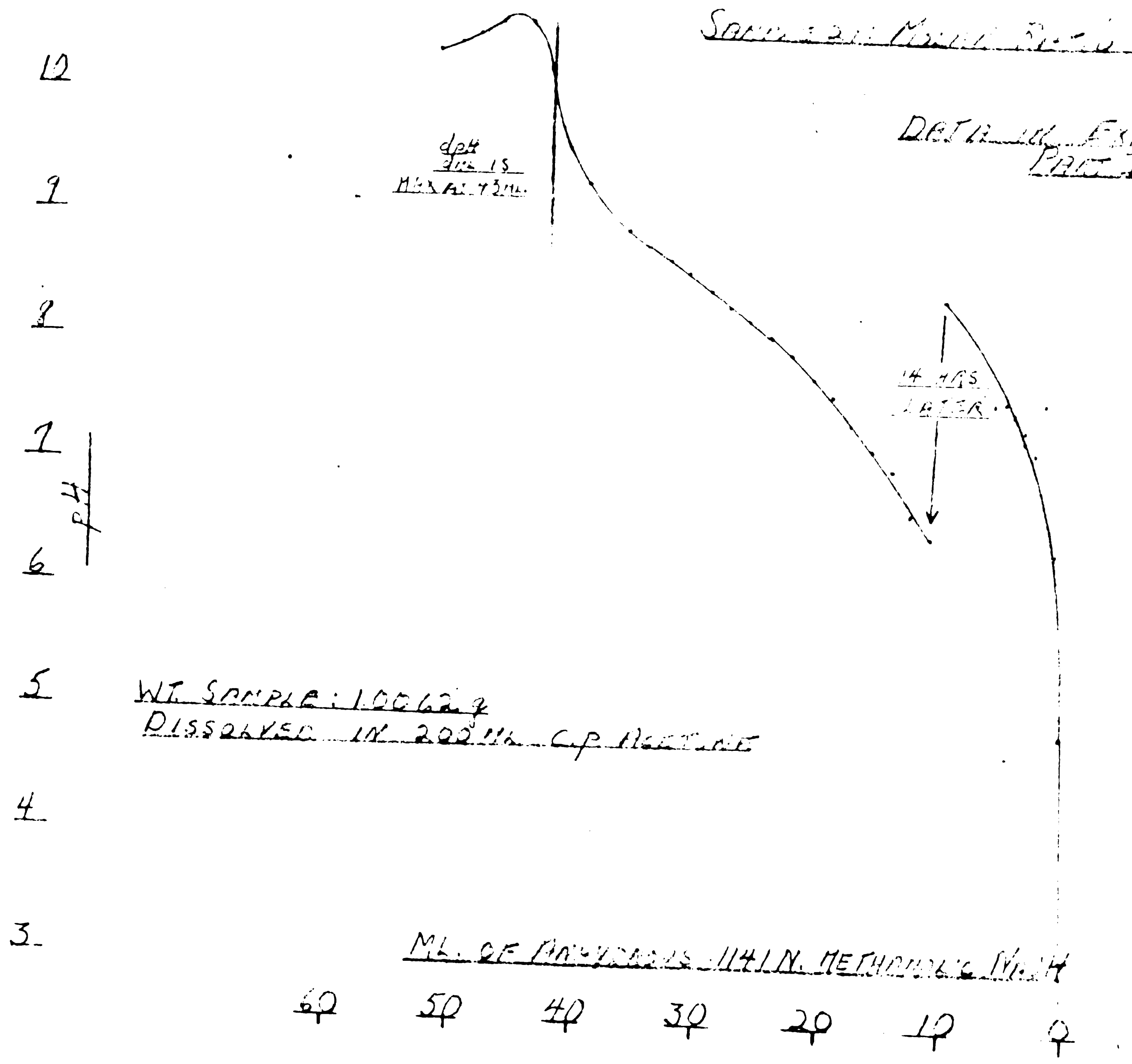
TABLE XXI (continued)

ml. .0949N NaOH	Correction to ml .1141N NaOH	pH	Remarks
20	16.61	7.19	
22	18.30	7.41	
24	19.95	7.6	
26	21.6	7.76	
28	23.25	7.93	
30	24.95	8.08	
32	26.6	8.20	
34	28.25	8.32	
36	29.92	8.44	
38	31.6	8.58	
40	33.25	8.68	
42	34.9	8.79	
44	36.6	8.92	
48	39.9	9.3	
50	41.6	9.58	
52	43.2	10.2	
54	44.9	10.58	
57	47.4	10.58	Slight pinkish cast
59.15	49.2	10.48	
61	50.7	10.42	Phth shows pink
63	52.3	10.35	
65	54	10.48	

ANHYDROUS POTENTIOMETRIC TITRATION OF [illegible]-STYRENE
HETERO[illegible]

SAMPLE [illegible] OF RE[illegible]

DATA IN EXPERIMENTAL
PART V, TABLE XI



EDWIN R. [illegible]
M.S.C. 1948

FIGURE 12

TABLE XXII

SAMPLE # 22: Same as TABLE XXI.

COMMENTS: Same as TABLE XXI.

ml. .0949 NaOH	Correction to ml .1141N NaOH	pH	Remarks
0	0	1.85	
2	1.66	7.8	Cloudy
4	3.33	8.23	
6	4.98	8.07	
8	6.64	8.10	Galv. jumpy when trying to read pH
12	9.98	8.19	
16	13.3	8.20	**(Difficult to see any phth color even by adding sev. drops on spot plate. However, phth drop atop sol. in beaker pink. Also, aqueous diluted anhydrous samples in spot plate are pink.)
20	16.6	8.38	
25	20.78	8.62	
30	24.9	8.79	
35	29.1	9.11	
40	33.21	9.38	
45	37.4	9.76	
47	39.05	9.82	Neg. to spot plate
49	40.7	10.12	"
50	41.6	10.32, 10.18	Neg.
51	42.5	10.67, 10.42	"
52	43.2	10.88, 10.73	"
53	44.1	10.98, 10.95 *	"
54	44.8	10.98	"
55	45.7	10.93	"
59	49	10.82 **	"
64	53.2	10.72	"
70	58.2	10.62	"
81	67.3	10.52	"

* Glass stirrer affects pH..From here, measured without glass rods in solution.

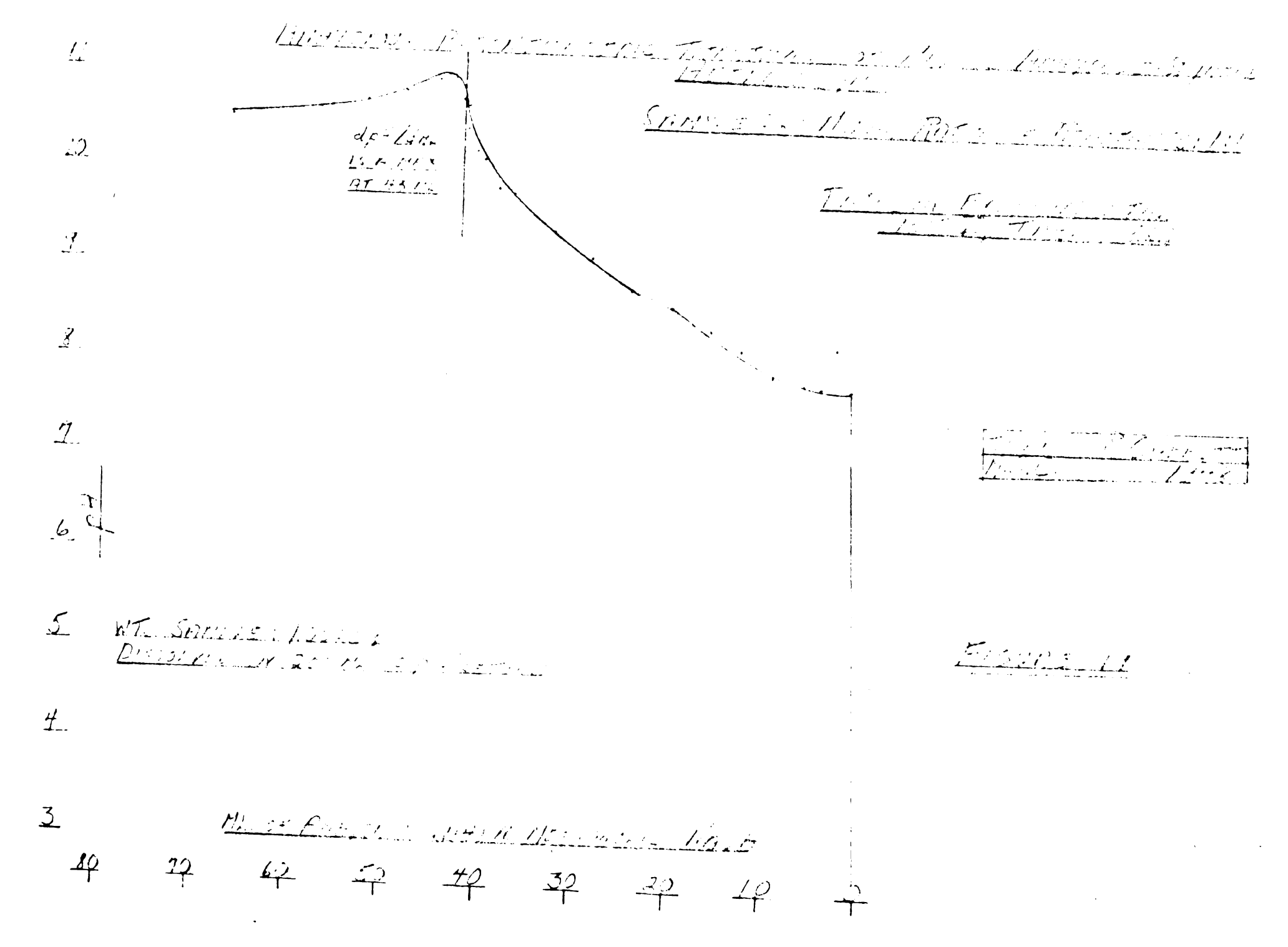

80
70
60
50
40
30
20
10
0

TABLE XXIII

SAMPLE # 23: Same as TABLE XXI.

COMMENTS: Same as TABLE XXI. wt. 1.0040 gram

ml. .0949N NaOH	Correction to ml .1141N NaOH	pH	Remarks
1	.83	6.0	
10	8.3	8.08	
20	16.62	7.7	
30	24.9	8.52	
40	33.22	9.02	
45	37.4	9.32	(Spot test: Colorless to 1 drop phth)
47	39.05	9.52	
48	39.9	9.59	Slight pink to spot test
49	40.7	9.72	Little more pink
50	41.6	9.81	Definite pink
51	42.4	10.02	
52	43.2	10.05	
53	44.1	10.37	
54	44.9	10.69	
55	45.7	10.67	
56	46.6	10.62	Slight pink
58	48.2	10.62	" "
60	49.8	10.52	
65	54	10.51	
70	58.2	10.28	
85	70.6	10.15	
100	83.1	10.12	

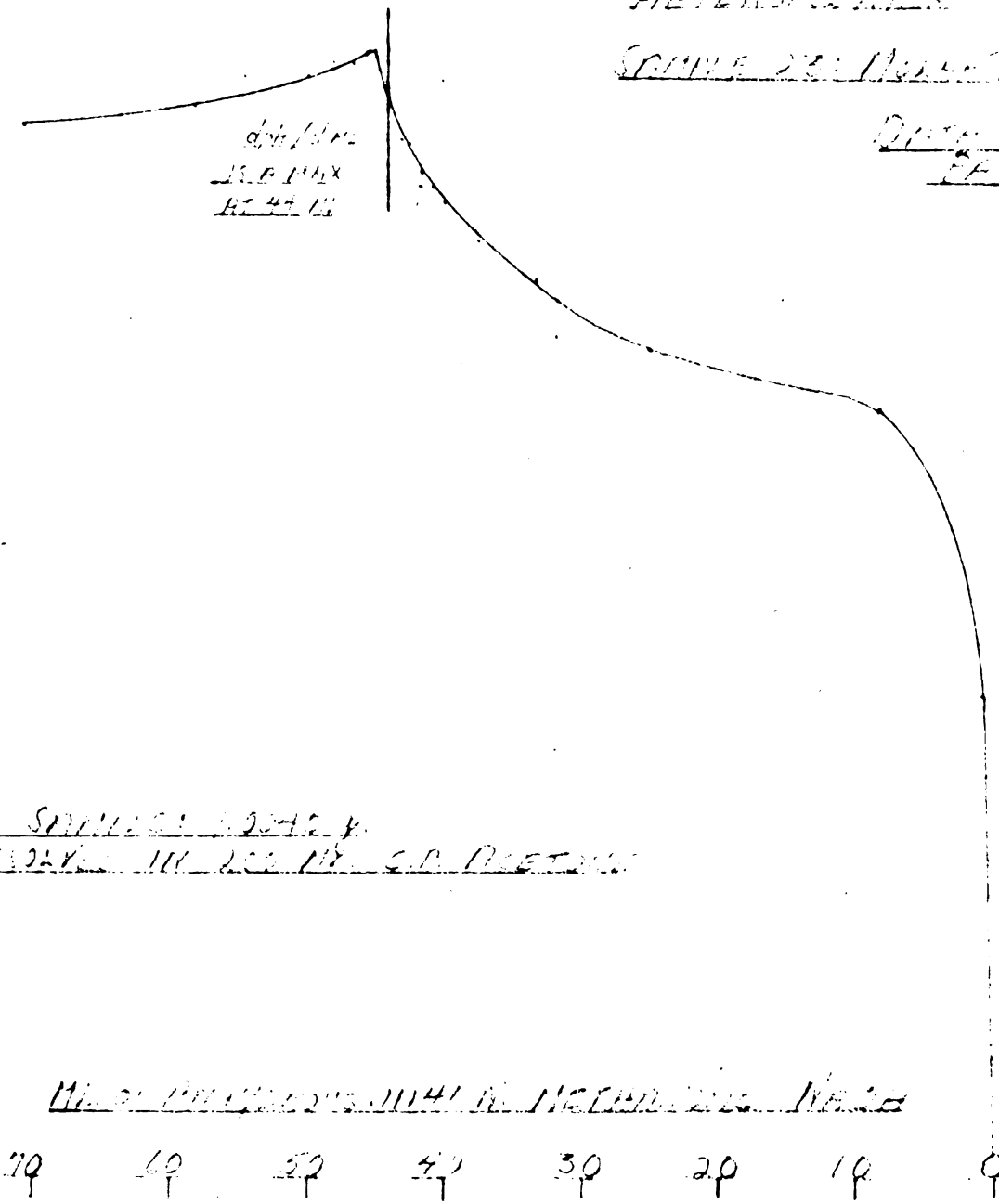


FIGURE 2C

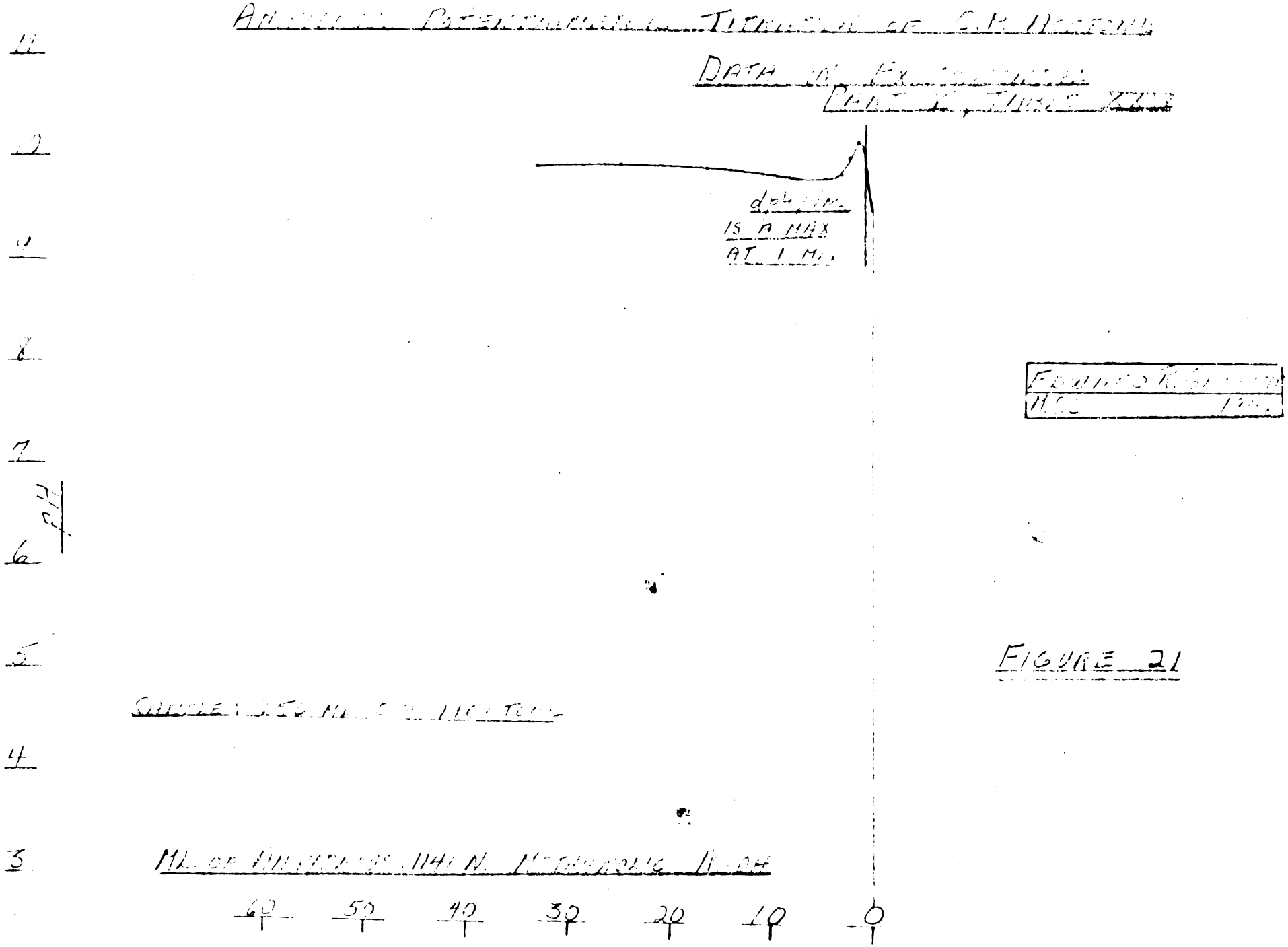
TABLE XXIV

BLANK POTENTIOMETRIC DETERMINATION OF ACETONE

250 ml C.P. acetone was used.

pH of NaOH in abs. methyl alcohol: 10.25

ml. .0949N NaOH	Correction to ml .1141N NaOH	pH
1	.83	9.78
1.2	.998	9.85
1.5	1.25	10.09
2.0	1.66	10.3
3.0	2.49	9.98
4.0	3.32	9.83
6.0	4.98	9.79
10.0	8.3	9.79
20.0	16.62	9.88
30.0	24.9	9.93
40.0	33.22	9.93


d.o.h. min.
IS A MAX
AT 1 MI.
FIGURE 21

PART VI

ELEMENTARY ANALYSIS OF HETEROPOLYMER PRODUCTS FROM DIFFERENT MOLAR RATIO OF REACTANTS

(a) 1:1 (Styrene: Maleic anhydride) molar ratio of reactants: This is the product prepared under Part IV, Study A. Macro quantitative organic analysis.

Sample	Sample weight	CO_2 weight	HOH weight	% C	% HOH
1	.1493g	.3846g	.0700g	70.92	5.25
2	.1365g	.3514g	.0622g	70.2	5.10
			average:	70.57%	5.18%

(b) 3:1 (Styrene: Maleic anhydride) molar ratio of reactants: This is the product prepared under Part IV, Study B. Micro Quantitative methods of organic analysis were used:

Sample	Sample weight	CO_2 weight	HOH weight	% C	% HOH
1	9.655mg	25.434mg	4.591	71.8	5.29
2	9.122mg	23.994mg	4.363	71.7	5.31

DISCUSSION

PART I

COMPARISON OF SOLUTION COPOLYMERIZATION TECHNIQUES

To facilitate the study of the heteropolymer maleic anhydride-styrene, it was necessary to compare several standard procedures[24,25] for preparation of the copolymer by solution polymerization methods using benzoyl peroxide as a catalyst. These procedures demonstrated that benzene (Reaction A) as a reaction medium possessed certain advantages over acetone (Reaction B) in that: a more consistent reaction temperature (80-81°C) was maintained; an insoluble copolymer results which can be readily filtered from the benzene solvent, separating it from the soluble monomers and any byproduct polystyrene. Whereas the copolymer B (acetone solvent) is precipitated by the addition of the non solvent water as a gelatinous, adhesive mass with the pronounced odor of styrene, the copolymer A (benzene solvent) is a granular white powder that is readily washed by benzene and apparently tends not to be solvated with monomers or solvent. Reaction A (benzene solvent) also gave the greater product yield indicating the greater reaction rate and the course of the reaction could be followed visually from the extent of the precipitation.

Because of these facts, all further copolymer preparations were carried out in benzene solvent and these studies are limited to copolymer prepared in that manner.

The solution of weighed polymer samples in acetone and titration with standard alkali to phenolphthalein endpoint yielded inconsistent results and this titration technique was deemed unsatisfactory.

PART II

STUDIES ON THE RATE OF COPOLYMERIZATION

In order to investigate the reproducibility of the copolymerization technique, studies A and B (Experimental, Part II) were conducted to determine reaction rate and to develop quantitative techniques for following the course of the reaction and copolymer properties.

The per cent polymerization data as determined from the extent of polymer precipitation is the more consistent in Study B (see Table 5 and Figure 2) than in Study A (see Table 1 and Figure 1), due to the fact that in the former case the sampling techniques were being perfected and there was a difference in the time of sampling of the several samples listed as being drawn at the same reaction time. This sample time was actually only applicable to the first sample of the pair in Study A. With realization of this fact, it is apparent that the rate of reaction is reproducible within experimental error for the copolymerization with molar ratio of reactants 1:1. The standard induction period is seven minutes.

From kinetic theory, we have for a first order reaction:

(20) $\frac{dX}{dt} = -kt$ where X is the molar concentration of the reactant and k the rate constant. This expression integrates into:

(21) $\log X = -k/2.303\ t + C$

which is in the form of the linear equation:

(22) $\log X = At + C$

where A is the slope of the line determined from the plotting of the time of reaction in seconds as abscissa against log x as ordinate and from which:

(23) $k = -2.303A$

Now, if we assume that the styrene and maleic anhydride enter into the copolymer mole for mole we may consider for the purpose of this discussion that the "monomer" is a styrene-maleic anhydride unit, its molar concentration at any time being the same as the molar concentration of styrene or maleic anhydride. (The assumption of the copolymer composition is 1:1 as a legitimate approximation will be validated further in the discussion.) Using the data compiled in Table 5 (Part II, Study B) we may tabulate the log of the molar concentration of "monomer" vs. the reaction time in seconds as in Table 7.

PART II STUDY B

Table 7

DETERMINATION OF REACTION RATE CONSTANT

Sample	Seconds Time	Weight Unreacted Monomers	Moles Unreacted "monomer"	log ["monomer"]
0	0	47.1470	.2332	-.4774
1	270	47.1450	.2331	-.4776
2	360	47.1455	.2332	-.4774
3	515	45.3554	.2243	-.4943
4	575	44.6011	.2206	-.5017
5	700	42.4323	.2098	-.5235
6	850	39.9335	.1975	-.5496
7	1125	34.5116	.1707	-.6128
8	1225	32.4843	.1607	-.6390
9	1835	22.5834	.1117	-.7970
10	2080	19.3303	.0956	-.8645
11	2780	13.3897	.0662	-1.0241
12	3500	9.8533	.0438	-1.2034
13	3780	10.2309	.0506	-1.1409

METHODS OF CALCULATION: (see data in Table 5, Part II, Study B).

1. 100% - % polymerization = % monomers unreacted.

2. $\frac{\%\text{ monomers unreacted} \cdot \text{initial wt. of monomers}}{\text{Molecular weight of "monomer"}} =$

number of moles of unreacted "monomer"

3. number of moles of unreacted "monomer"/ volume of solution in liters (.7 liter) = molar concentration of unreacted "monomer".

4. Initial wt. of monomers: 47.1470g.
Molecular wt. of m.a.-styrene unit: 202.2.

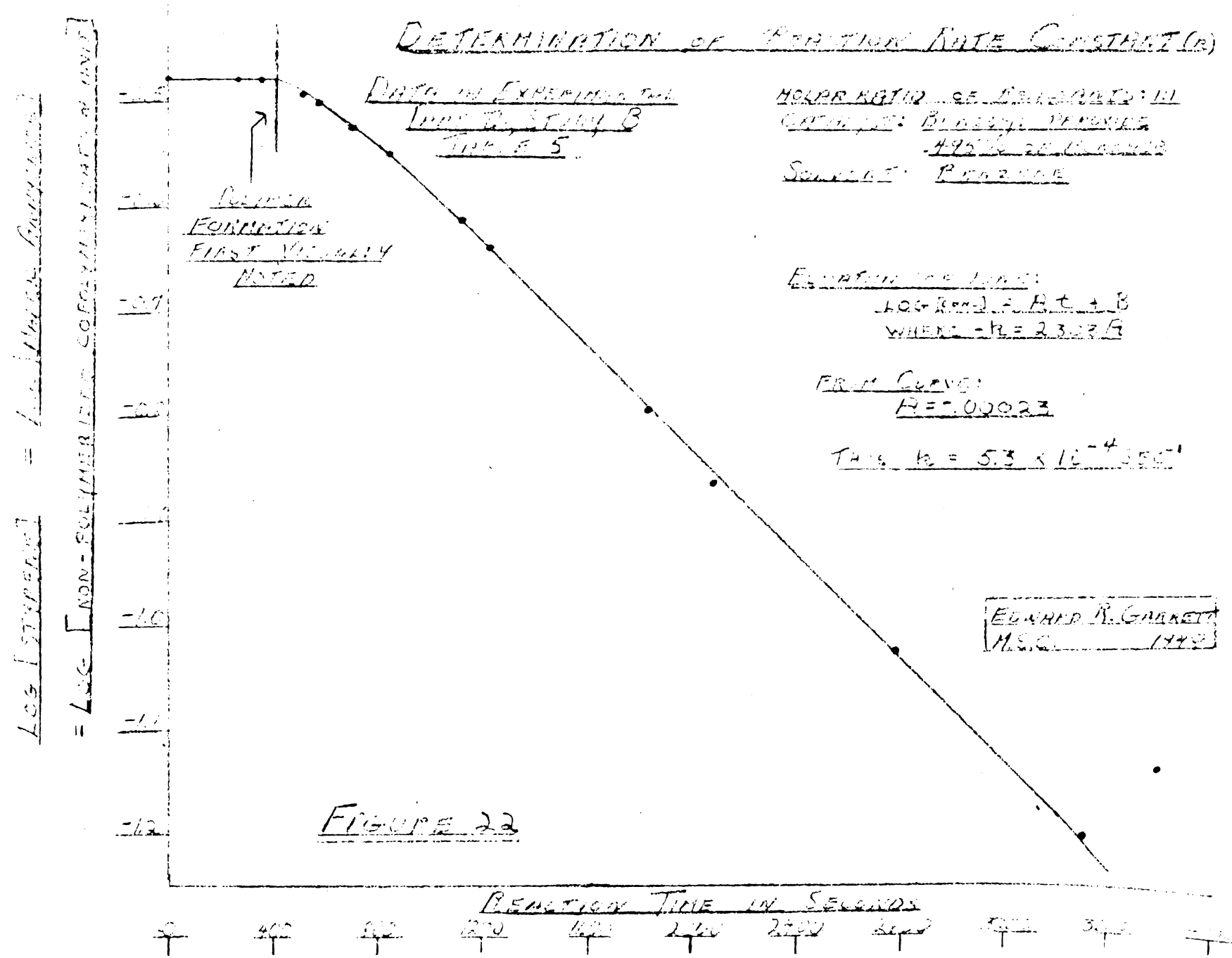

DETERMINATION OF REACTION RATE CONSTANT (k)
DATA IN EXPERIMENTAL LINE B, STUDY B TABLE 5
MOLAR RATIO OF REACTANTS: 1:1
CATALYST: BASIC PYRIDINE
SOLVENT: PYRIDINE
PRECIPITATION FORMATION FIRST VISUALLY NOTED
EQUATION OF LINE:
LOG [CONC] = -kt + B
WHERE -k = 2.303 A
FROM CURVE:
A = .00023
THUS k = 5.3 x 10⁻⁴ SEC⁻¹
EDWARD R. GARRETT
M.S.C. 1952
LOG [CONCENTRATION] = LOG [MOLAR CONCENTRATION OF NON-POLYMERIZED COPOLYMERIZING REACTANTS]
REACTION TIME IN SECONDS
-.5
-.7
-1.0
-1.2
0
400
800
1200
1600
2000
2400
2800
3200

FIGURE 22

The plotting of this data in Figure 22 gives an excellent straight line demonstrating the validity of the data and that the reaction rate is first order with respect to styrene or maleic anhydride under the conditions of the copolymerization. Since the slope (A) of the line is -.00023, we have from equation (23) that the reaction rate constant (k) is $5.3 \cdot 10^{-4}$ sec^{-1}.

We may justify a minimum reaction time of five hours yielding complete copolymerization for all reaction mixtures with molar concentration of "monomer" less than that of the Part II studies (.3333 M in "monomer"), providing they give a 1:1 copolymer composition or the same copolymer composition that resulted from these studies. Consider an initial ["monomer"] of 1/3 at 420 seconds (i.e. 7 minute induction period) and a final ["monomer"] = X at 18000 seconds (5 hours total reaction time). Then we may set up the expression:

$$(24) \quad \int_{1/3}^{X} \frac{dX}{X} = -k \int_{420}^{18000} dt$$

and integrating between the limits:

$$(25) \quad \log 3X = \frac{-(5.3 \cdot 10^{-4})\ (18000 - 420)}{2.303} = -4.05$$

whence X (["monomer"] after five hours of reaction time) is [.00003] and thus the % unreacted "monomer" is .01%. (See Figure 1 for experimental verification.)

Morgan[26] proposed that maleic anhydride did not undergo bromine addition alone but did so in styrene mixtures, the amount of bromine addition being equivalent to the amount of styrene and maleic anhydride in the mixture. An attempt was made to apply this principle (Part II, Study A, Table 2) using the direct bromine titration method of Uhlrig and Levin[27] on the unreacted monomer in the sample filtrates. Apparently under the conditions of the bromine titrations, addition to the monomers' ethylenic bonds did not completely occur. From Figure 1, it can be seen that a maximum of 60% of the monomers added bromine. The results are not exceptionally quantitative and the endpoint is a fading one. We may interpret Figure 1 as indicating that maleic anhydride still maintains its non-halogen adding properties even mixed with styrene under the conditions of these titrations and that the bromine addition to styrene was practically complete with some substitution or addition being effected on the maleic anhydride.

In an attempt to correlate relative molecular weight values with extent of reaction, the viscosity method of Staudinger was used[29,30]. As given in Table 3 (Part II, Study A) there is no apparent relation between the viscosities as considered proportional to

time of solution efflux and the extent of the reaction. In fact the deviations between samples are outside the reproducibility possible.

Dissolution of weighed polymer samples in acetone, addition of excess alkali, distilling off the acetone, cooling and back titration with standard acid to phenolphthalein endpoint provided the data in Table 4 (Part II, Study A). As is evidenced from Figure 1 this data is more consistent than the analogous polymer analyses by titration of Part I indicating that these more drastic treatments probably fractured the anhydride linkages of the copolymer to a much greater extent. Yet Figure 1 indicates that copolymer composition is an erratic function of reaction time from the results of these analyses.

In order to estimate the validity of these titrations, the unreacted monomers (Study B) remaining in the sample filtrate were treated as was the copolymer above, after distilling off the benzene. On titrating with standard acid to phenolphthalein endpoint, the data of Table 6 was plotted on Figure 2. Inconsistency of results is more obvious in this Figure. Reproducibility is not apparent and no correlation of copolymer composition with reaction time exists. The huge discrepancies in copolymer com osition as deter-

mined by the two methods, where copolymer analyses in Study A (Figure 1) average 41% m.a. in the copolymer and where by the monomer analysis of Study B (Figure 2) the m.a. in the copolymer averages 73%, readily show that phenolphthalein as a neutralization indicator with copolymers, a common industrial practice[28], is not reliable.

PART III

AQUEOUS POTENTIOMETRIC TITRATIONS OF THE HETEROPOLYMER: MALEIC ANHYDRIDE-STYRENE

As was previously discussed, analysis of heteropolymer composition by aqueous titration to phenolphthalein endpoint was invalid due to the indicator endpoint not coinciding with the pH of acid polymer neutralization. A series of samples from the final product of Study A, Part II (1:1 molar ratio of reactants) were potentiometrically titrated under varying conditions in order to characterize the titration curve of the heteropolymer.

In the plotting of the titration curves the ml. of titer of the several acid and base titrations on the one sample have been calculated and plotted so as to be equivalent to the same normality so that these curves may be properly compared. The zero point on the abscissa is arbitrarily chosen as corresponding to the pH of the solution just prior to the initial titration A. The several curves on each Figure represent the titrations of the same sample in different solution volumes, the decreasing order

of concentration being for curves A, B, C, D, E. In general, the dark vertical line on the graphs represents the point where the pH of the solution is due to the free acid heteropolymer alone in the presence of NaCl that never exceeds .05 molar. At this point any excess acid or base is completely neutralized as computed from the milliliters and normalities of the standard titrating solutions used. For purposes of recognition the tables of potentiometric data are all numbered with roman numerals.

The standard alkali was added to the acetone solution of Sample 1 at a fast enough rate to shock precipitate a portion of the copolymer in the form of hard shreds which did not completely dissolve on the distilling off of the acetone or in the time of heating allowed for the caustic solution of the sample. Thus Figure 3 (data in Table I) does not represent a quantitative amount of sample. This difficulty was avoided in future samples by slow addition of standard alkali with constant stirring to the acetone solution of the copolymer and subsequent adequate heating time to effect complete solution in the aqueous alkali.

From analysis of Figures 3 through 17 it is apparent that a point of inflection exists at a pH of 6.25 where d pH/d ml is a maximum. From

neutralization theory this is recognized as the stoichiometric point of neutralization of a carboxyl and conceivably may represent neutralization of all the carboxyls in the copolymer or merely half of them. If we consider the latter to be the case, we may calculate the amount of maleic anhydride in the sample by considering the amount of titer used between the two stoichiometric points, pH 6.25 and arrowed vertical line, as being equivalent to one half the carboxyls. The results of such calculations are tabulated in Table 8 for some titrations of Part III.

PART III

Table 8

CALCULATION OF MOLAR RATIO OF CO-MONOMERS IN HETEROPOLYMER FROM POTENTIOMETRIC TITRATION CURVES

Sample No.	Fig. No.	Titration	ml. of stoichiometric titer	molar ratio in polymer (m.a.:sty.)	Avg. molar ratio for sample
2	4	A	41.80	.93:1	
		B	39.65	.85:1	
		C	42.50	.96:1	.91:1
3	5	A	42.60	.97:1	
		B	41.60	.92:1	
		C	43.40	.92:1	.94:1
4	6	A	44.75	1.00:1	
		B	43.90	1.07:1	
		C	43.90	1.03:1	
		D	43.90	1.03:1	
		E	43.90	1.03:1	1.03:1
13	10	A	25.0	.92:1	
		B	24.3	.87:1	
		C	24.3	.87:1	
		D	24.3	.87:1	.88:1
14	11	B	27.7	.89:1	
		C	27.7	.89:1	.89:1
				average:	.91:1

The normality of the titer is .1141N.

METHODS OF CALCULATION(for Table 8)

1. (From Figures of the potentiometric curves):
ml. reading from abscissa at free acid hetero-polymer (vertical line) - ml. reading from abscissa at pH 6.25 = ml. of stoichiometric titer for half the carboxyls.
2. ml. of stoichiometric titer • titer normality = millimoles of m.a. unit in the sample.
3. millimoles m.a. unit • .09806 = wt. m.a. units in sample.
4. wt. of sample - wt. m.a. units = wt. styrene units in sample.
5. wt. of styrene units/ .1041 = millimoles styrene units in sample.
6. millimoles m.a. units/ millimoles styrene units = molar ratio in polymer.

The average molar ratio of the samples listed is .91:1. The % Carbon in such a polymer would be:
100 • (m.wt. of total C in .91 m.a. + total C m.wt. in 1 styrene) / (.91 mol. wt. m.a. + mol. wt. styrene) =

$$\frac{43.72 + 96.08}{89.23 + 104.14} \cdot 100 = 72.1\%$$

The % H in such a polymer would be:
100 • (m.wt. of total H in .91 m.a. + total H m.wt. in 1 styrene) / (.91 mol. wt m.a. + mol. wt. styrene) =

$$\frac{1.835 + 8.064}{89.23 + 104.14} \cdot 100 = 5.12\%$$

If the titer actually corresponded to all the carboxyls in the heteropolymer, then we would have one half the number of maleic anhydride units and the molar composition of the copolymer would be .455:1 (m.a.: styrene). The % C in such a polymer would be: 100 • (m. wt. of total C in .455 m.a. + total C m. wt. in 1 styrene) / (m.wt. of .455 m.a. + total m.wt. of 1 styrene) = $\frac{21.82+96.08}{44.7+104.14} \cdot 100 = 79.2\%$

The % H in such a polymer would be:
100 • (m.wt. of total H in .455 m.a. + total H m.wt. in 1 styrene) / (m.wt. of .455 m.a. + total m.wt. of 1 styrene) = $\frac{.917 + 8.064}{44.7 + 104.14} \cdot 100 = 6.04\%$

Macro quantitative analysis of the elements of a copolymer prepared from 1:1 molar ratio of reactants as listed in Part VI conclusively shows that the .91:1 ratio in the copolymer is the correct one and thus we can conclude that the heteropolymer acts as dibasic acid and the above discussed stoichiometric titer corresponds to the neutralization of ½ carboxyls only.

In general, Figures 3 through 17 demonstrate a reasonable coincidence of the titration curves in the buffer regions and a divergence above a pH of 10 and below a pH of 3.3 when the molar concentrations of the heteropolymer vary widely. It is to be expected of weak acids that acidity in the free acid state will

depend on concentration and acidity in the buffer region be relatively independent of it. The secondary carboxyl is apparently so weak that no inflection point could be obtained above a pH of 7 and since the extent of heteropolymer salt hydrolysis would depend on concentration, the divergence above a pH of 10 at different molar concentrations is easily understood. (See Figures 3 and 5).

Figure 3 (Sample 1) obviates the unreliability of phenolphthalein indicator as a means of stoichiometric analysis. The phenolphthalein color change at a pH of 8.2 is well on the buffer portion of the curve corresponding to the second carboxyl neutralization and thus would also give an indefinite and fading endpoint.

In several of the samples (see Figures 4,9,10, 11 and 12) the first acid titration of the alkali dissolved sample gave a stoichiometric titer value in excess of that from subsequent titrations on the same sample; the distinctive point of inflection at a pH of 6.25 was not well apparent. The initial alkali solution of sample 5 (See Figure 7) was allowed to stand exposed to the air for a period of a week and this phenomenon occurred to show that the cause of error in the other first titrations was due to solution of carbon dioxide from the air in the caustic solution of the polymer.

The alkaline solutions of samples 6 and 7 were titrated with standard acid using brom cresol purple as indicator (see Tables VI and VII). Using this indicator with the back titration technique, the calculated stoichiometry of the heteropolymer is valid within 2½%. The stoichiometric titer from potentiometric titrations is approximately 40 ml while 38 ml is the stoichiometric titer for one carboxyl using the indicator.

To the first alkaline solution of samples 8 and 9 were added weighed amounts of maleic anhydride. The resultant curves (Figures 8 and 9) show that the buffer portion of the curves in the lower pH range is similar to that of the heteropolymer acid alone.

Analysis of the data for the samples 10, 11 and 12 (see Tables X, XI and XII) show discrepancies between the stoichiometric titers from acid and base titrations that can only be accounted for by erroneous caustic normality. Since a different standard base was only used for these three samples, this conclusion is justified.

PART IV

ANALYSIS OF THE MALEIC ANHYDRIDE-STYRENE HETEROPOLYMERS PREPARED FROM DIFFERENT MOLAR RATIOS OF REACTANTS

Utilizing the benzene solvent copolymerization techniques developed in Part II, three copolymer

products were prepared from different molar ratios of reactants. The potentiometric titrations techniques developed in Part III were then applied to weighed samples of each. Using the methods of calculation of Part III, Table 8, the compositions of these copolymers are tabulated in Table 9. These copolymer products differed from those of Part III in that they were benzene extracted for several weeks and then vacuum dried for a least one week to remove any possibly occluded monomeric maleic anhydride or contaminating polystyrene so that such intense treatment would insure the true copolymer product.

PART IV

Table 9

CALCULATION OF MOLAR RATIO OF CO-MONOMERS IN HETEROPOLYMERS PREPARED FROM DIFFERENT MOLAR RATIOS OF REACTANTS

Sample No.	Fig. No.	Titration	ml. of stoichiometric titer	polymer comp. (m.a.:sty)	Avg. for sample	Avg. for Reactant Ratio
1:1 Molar Ratio of Reactants (m.a.: styrene)						
15	12	A*	-	-		(* exposed to CO_2 of air. ** pH machine off)
		B	48.75	.882:1		
		C	48.75	.882:1	.882:1	
16	13	A	49.25	.899:1		.890:1 (mole fraction m.a. = .471)
		B	49.25	.899:1		
		C	49.25	.899:1	.899:1	
1:3 Molar Ratio of Reactants (m.a.: styrene)						
17	14	A	48.15	.846:1		
		B	47.55	.843:1		
		C	47.55	.843:1	.849:1	
18	15	A**	-	-		.847:1 (mole fraction m.a. = .459)
		B	47.65	.846:1		
		C	47.65	.846:1	.846:1	
3:1 Molar Ratio of Reactants (m.a.: styrene)						
19	16	A	52.15	1.001:1		
		B	51.05	.961:1		
		C	50.10	.928:1	.963:1	
20	17	A	52.15	1.001:1		.975:1 (mole fraction m.a. = .494)
		B	52.15	1.001:1		
		C	51.05	.961:1	.987:1	

It can be noted from Table 9 that the copolymer composition is not greater than 1:1 (m.a.:styrene) notwithstanding the molar ratio of reactants and thus the argument presented under the discussion of Part II as to total polymerization having occurred with a reaction time in excess of five hours is valid in regard to these copolymerizations which were conducted with a total reaction time over 6 hours.

Wall[14] has predicted the instantaneous composition of this heteropolymer prepared from different reactant ratios from a theoretical kinetic study. Alfrey and Lavin[22] have analytically determined the copolymer composition of the first products formed from polymerization with different molar ratios of reactants. For purposes of comparison, these data are tabulated in Table 10.

PART IV

Table 10

COMPARATIVE DATA: MOLE % MONOMER IN REACTION MIXTURE VS MOLE % IN COPOLYMER

Monomers in Reaction Mixture		Composition of Copolymer					
		Alfrey & Lavin[22]		Wall[14]		This Paper	
Mol % m.a.	Mol % sty.	Mol% m.a.	Mol % sty.	Mol % m.a.	Mol % sty.	Mol% m.a.	Mol % sty.
99.9+	.1-	-	-	50	50	-	-
95	5	49.9	50.1	-	-	-	-
75	25	-	-	48.9	51.1	49.4	50.6
50	50	48.9	51.1	47.4	52.6	47.1	52.9
25	75	-	-	44	56	45.9	54.1
16.7	83.3	45.0	55.0	-	-	-	-
9.1	90.9	42.4	57.6	-	-	-	-
5.0	95.0	38.9	61.1	-	-	-	-

It should be realized that the copolymer compositions reported in this paper are not the instantaneous result of a given molar ratio of reactants as with Wall and Alfrey & Lavin, but rather the ultimate product of a total polymerization of a given molar ratio of reactants.

These data are plotted in Figure 23 and show excellent agreement within experimental error. We would expect the curve plotted through the points representing the data of this paper to lie

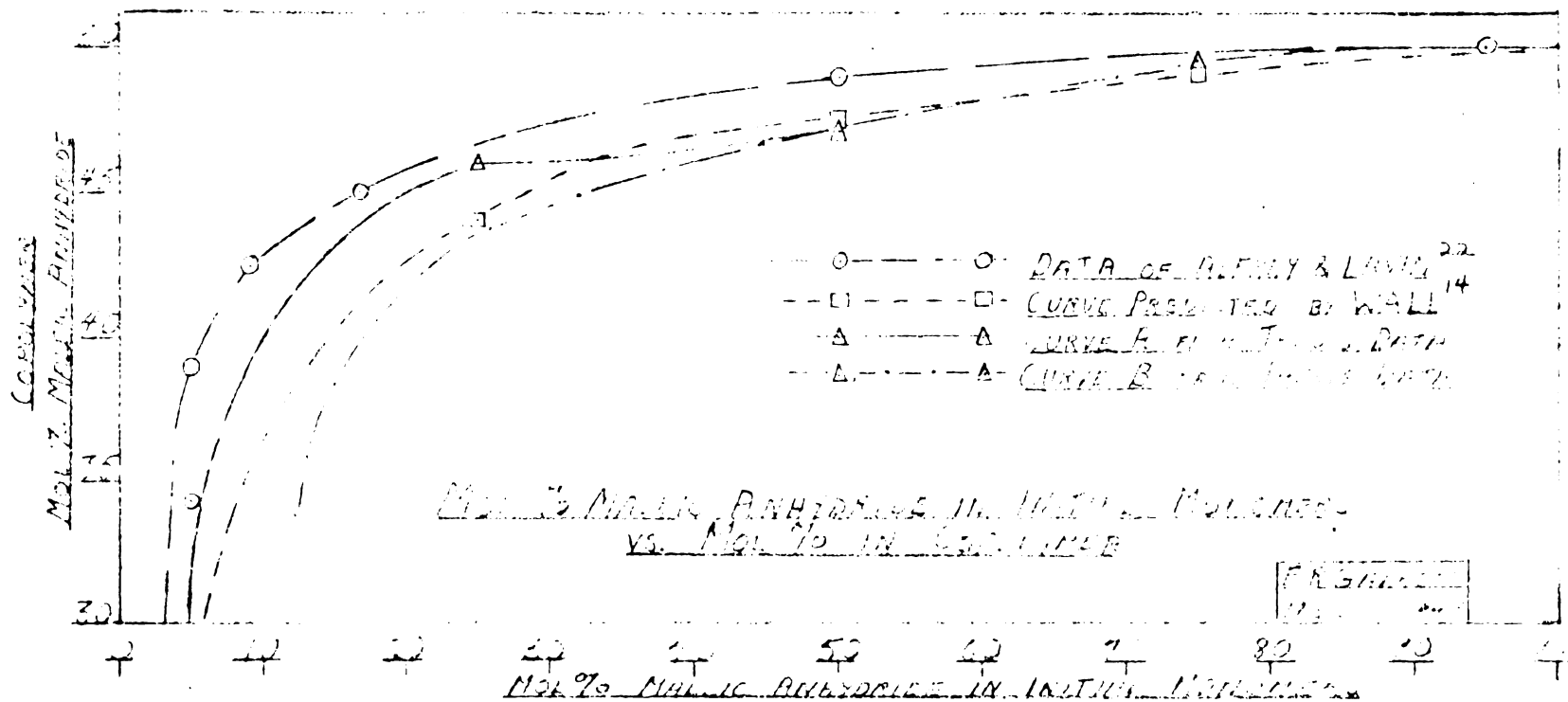

DATA OF A. FRY & LAVIN 22
CURVE PREDICTED BY WALL 14
CURVE A
CURVE B

FIGURE 23

below the curve plotted from the data of Alfrey and Lavin. The smaller the mol percent maleic anhydride in the initial reacting monomers, the greater should be the discrepancy of the two curves which should tend to approach and cross each other as the mol % maleic anhydride increases. The unbroken curve A corresponding to the points of the thesis data represents this comparison. The broken curve B corresponding to the points of the thesis data represents a similar comparison with the theoretical predictions of Wall.

If we define the primary disassociation constant of the free heteropolymer acid as:

$$(26)\quad K_a \text{ (or } K) = \frac{[H^+] \cdot [HMA^-]}{[H_2MA]}$$

where $[H_2MA]$ is the molar concentration of all maleic acid units in the copolymer, $[HMA^-]$ is the molar concentration of all mono-ionized maleic acid units in the copolymer and $[H^+]$ is the molar concentration of hydrogen ions. Then by taking the logarithm of the reciprocals of both sides of this equation we have:

$$(27)\quad \log 1/K = \log 1/[H^+] + \log \frac{[H_2MA]}{[HMA^-]}$$

$$\text{or } (28)\quad pH = pK - \log \frac{[H_2MA]}{[HMA^-]}$$

$$\text{or } (29)\quad pH = pK - \log (1 - \alpha)/\alpha$$

where α is the fraction of mono-ionized maleic

acid units in the Henderson-Hasselbalch equation. If our definition(26) is valid, our potentiometric data should conform to the linear equations (28) and (29). Katchalsky and Spitnik[23] have attempted to apply the Henderson-Hasselbalch equation (29) to potentiometric data from the titrations of the polymeric acids polymethacrylic and polyacrylic and have found it necessary to modify it to the form:

(30) $pH = pK - n \log (1 - \alpha)/\alpha$

as the slope of the lines determined by plotting pH vs log $(1 - \alpha)/\alpha$ for these polymeric acids was not equal to unity.

PART IV STUDY A

Table 11

TABULATION OF DATA FOR DETERMINATION OF

pK VALUE OF HETEROPOLYMER

Copolymer produced from molar ratio of reactants 1:1 (m.a.: styrene) is of .89:1 composition. From weight of polymer sample (Table XV) and mole fraction of m.a. in copolymer (Table 9) there are .004624 moles of m.a. in the polymer sample.

pH	liters sol'n	[C]	ml. titer added to free acid	[HMA$^-$]	[H_2MA]	log $\frac{1-\alpha}{\alpha}$
5.51	.324	.01428	46	.01349	.00079	1.2320
4.99	.328	.01410	42	.01320	.0009	1.0664
4.79	.331	.01398	39	.01121	.00277	.6071
4.6	.334	.01385	36	.01024	.00361	.4528
4.48	.339	.01365	31	.00870	.00495	.2449
4.30	.345	.01341	25	.00690	.00651	.0253
3.90	.355	.01303	15	.00416	.00887	-.3288
3.50	.362	.01278	8	.00242	.01036	-.6316
3.20	.367	.01261	3	.00142	.01119	-.8965

The representative potentiometric titration data for this table was taken from Table XV, Sample 15, Titration C.

PART IV STUDY B

Table 12

TABULATION OF DATA FOR DETERMINATION OF pK VALUE OF HETEROPOLYMER

Copolymer produced from molar ratio of reactants 1:3 (m.a.: styrene) is of .85:1 composition. From weight of polymer sample (Table XVII) and mole fraction of m.a. in copolymer (Table 9) there are .0045175 moles of m.a. in the polymer sample.

pH	liters soln	[C]	ml. titer added to free acid	[HMA⁻]	[H_2MA]	$\log \frac{1-\alpha}{\alpha}$
3.09	.260	.01738	3	.00185	.01553	-.9240
3.30	.263	.01718	6	.00274	.01444	-.7218
3.61	.267	.01692	10	.00392	.01300	-.5206
3.90	.271	.01667	14	.00519	.01148	-.3447
4.22	.278	.01625	21	.00743	.00882	-.0745
4.38	.283	.01596	26	.00902	.00694	.1138
4.58	.289	.01563	32	.01083	.00480	.3534
4.75	.293	.01542	36	.01200	.00342	.5452
5.1	.298	.01516	41	.01342	.00174	.8872
5.39	.300	.01506	43	.01347	.00109	1.1078
5.85	.302	.01496	45	.01454	.00042	1.5393

The representative potentiometric titration data for this table was taken from Table XVII, Sample 17, Titration B.

PART IV STUDY C

Table 13

TABULATION OF DATA FOR DETERMINATION OF pK VALUE OF HETEROPOLYMER

Copolymer produced from molar ratio of reactants 3:1 (m.a.: styrene) is of .98:1 composition. From weight of polymer sample (Table XIX) and mole fraction of m.a. in copolymer (Table 9) there are .0050401 moles of m.a. in the polymer sample.

pH	liters soln	[C]	ml titer added to free acid	$[HMA^-]$	$[H_2MA]$	$\log \frac{1-\alpha}{\alpha}$
3.39	.257	.01961	4	.00177	.01784	-1.0034
3.61	.261	.01931	8	.00324	.01607	- .6954
3.91	.266	.01895	13	.00489	.01406	- .4587
4.23	.275	.01833	22	.00788	.01045	- .1226
4.39	.281	.01794	28	.00976	.00818	.0861
4.52	.286	.01762	34	.01164	.00598	.2893
4.72	.290	.01738	38	.01281	.00457	.4477
4.88	.293	.01720	41	.01366	.00354	.5865
5.09	.295	.01709	43	.01414	.00295	.6807
5.30	.297	.01697	45	.01471	.00226	.8135
5.61	.299	.01685	47	.01525	.00161	.9765

The representative potentiometric titration data for this table was taken from Table XIX, Sample 19, Titration B.

METHODS OF CALCULATION in Tables 11, 12 and 13.

1. $[C]$ = Total molar concentration of all m.a. units in sample = $\frac{\text{moles m.a. in polymer sample}}{\text{liters of solution}}$

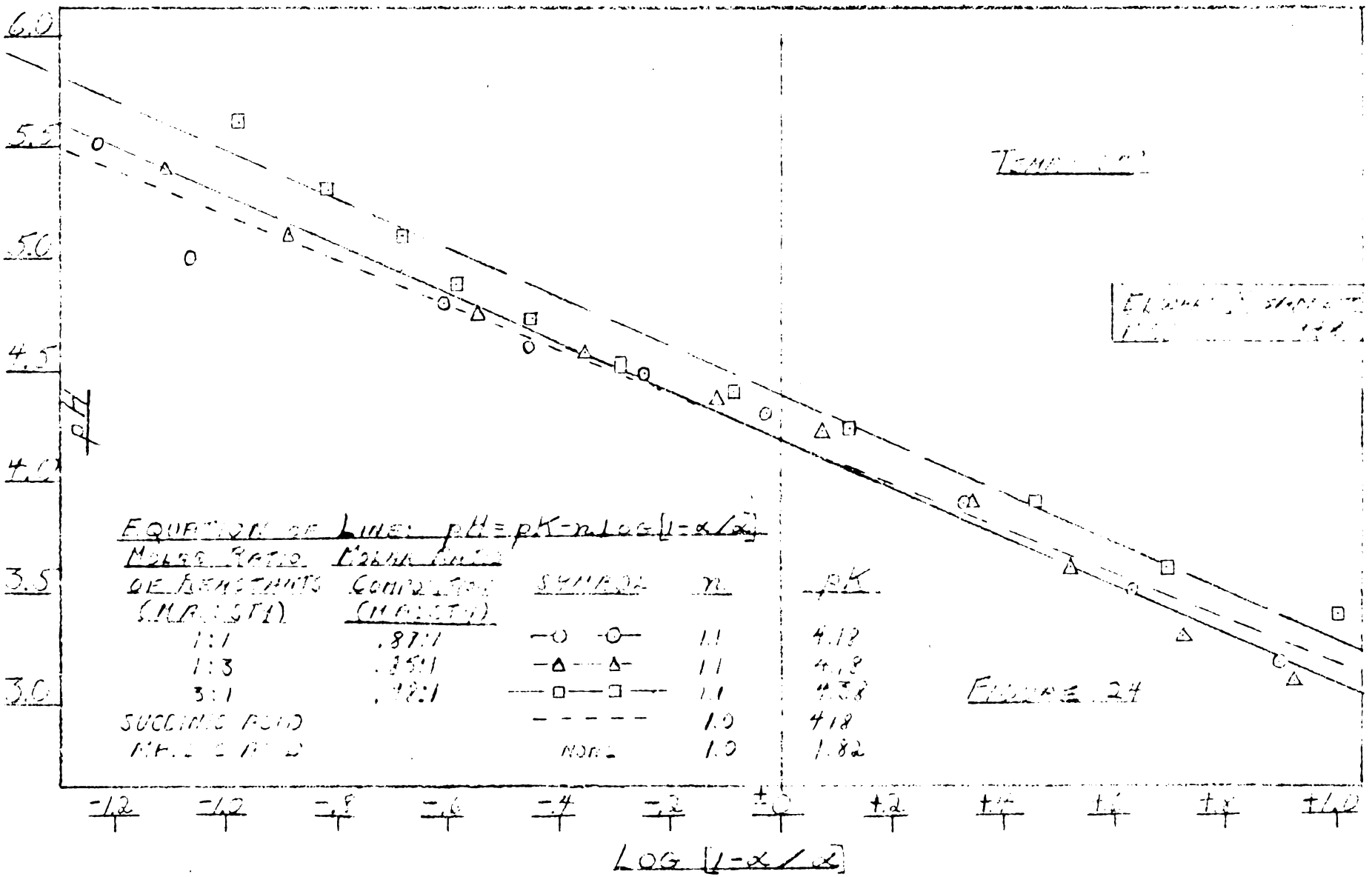
2. $[Na^+HMA^-]$ = molar concentration of the mono salt of m.a. units in heteropolymer = $\frac{\text{ml of alkali titer added to free acid} \cdot \text{norm. of alkali}}{\text{liters of solution}}$

3. $[HMA^-] = 10^{-pH}$ (i.e. $[H^+] = [HMA^-]$ due acid disassociation) $+ [Na^+ HMA^-]$

4. $[C] - [HMA^-] = [H_2MA]$

5. $\log \frac{[HMA^-]}{[H_2MA]} = \log \frac{1-\alpha}{\alpha}$

Determination of pK Values of Mixed Acid-Ethanol Solutions



Equation of Line: $pH = pK - n \log [J - x/x]$

Molar Ratio of Components (Mixture)	Calculated Composition (Mixture)	Symbol	n	pK
1:1	.87:1	—○—○—	1.1	4.18
1:3	.35:1	—△—△—	1.1	4.38
3:1	.98:1	—□—□—	1.1	4.38
Succinic Acid		- - - - -	1.0	4.18
Maleic Acid		None	1.0	1.82

Figure 24

In Tables 11, 12 and 13 are tabulated pH vs $\log \frac{[H_2MA]}{[HMA^-]}$ (i.e. $\log (1-\alpha/\alpha)$ for representative potentiometric data from the three different molar ratios of reactants studied in Part IV. In Figure 24 pH is plotted as the ordinate against $\log (1-\alpha/\alpha)$ as abscissa for the potentiometric titration data from Studies A, B and C. Excellent agreement with the linear nature of equation (30) is obtained and since the possible experimental limits of the slope (n) of the lines drawn through the points are .9 to 1.1, we may take our resultant slope (n) equal to unity in confirmation of equations (28) and (29). These results justify our definition (26) for our heteropolymer acid. Since the intercept of the linear equation (29) is the pK value i.e. when the log function is equal to zero, the pK of the Study A copolymer (1:1 molar ratio of reactants) and the pK of the Study B copolymer (1:3 molar ratio of reactants, m.a.: styrene) are the same within experimental error and equal to 4.18. This latter value is the same as the succinic acid pK for the primary carboxyl's disassociation constant. This item is worthy of note as the copolymerized maleic acid units are actually substituted succinic acids in the copolymer. The pK value of 4.38 for the Study C copolymer (3:1 molar ratio of reactants,

m.a.: styrene) is higher notwithstanding the fact that mole fraction of m.a. in the copolymer molecule is actually the greater.

When the free acid heteropolymer is dissolved in a neutral aqueous medium with no extraneous base present we have in the definition of the primary carboxyl disassociation constant (26):

that (31) $[H^+] = [HMA^-]$ and thus:

(32) $$\frac{1}{[H_2MA] \cdot K} = \frac{1}{[H^+]^2}$$

where in a weak acid $[H_2MA]$ may be equated to the total molar concentration of all m.a. units and taking the logarithm of both sides of the equation, we have:

(33) $2pH = pK + \log 1/[H_2MA] = pK + pMA$

This is a linear equation with the unit slope justified in the above discussion.

Table 14

TABULATION OF 2pH VS pMA BASED ON pH AND VOLUME OF FREE ACID HETEROPOLYMER SAMPLES FOR UNPURIFIED MATERIAL

(Data in Part III)

Sample	Fig.	Table	pH	ml. soln	$10^3 \cdot$ Total moles H_2MA in sample	$[H_2MA] \cdot 10^2$	2pH	Avg. pMA
2	4	II	2.48	138.5	4.7140	3.4040	4.96	1.5309
			2.48	185		2.548	4.96	
			3.00	324		1.455	6.00	1.8372
3	5	III	2.45	139	4.7846	3.442	4.9	1.4985
			2.45	164		2.926		
			2.78	300		1.595	5.56	1.7973
4	6	IV	2.5	139	5.0170	3.609	5.0	1.4785
			2.5	164		3.059		
			2.75	359		1.397	5.50	1.8548
			2.95	619		.811	5.90	2.0910
13	10	XIII	2.74	144	2.7926	1.939	5.48	1.7325
			2.74	158		1.767		
			2.81	233		1.199	5.72	1.9259
			2.81	238		1.173		
14	11	XIV	2.53	144	3.1606	2.195	5.06	1.6776
			2.53	157		2.013		
			2.74	231.5		1.365	5.58	1.8649

Table 15

TABULATION OF 2pH VS pMA BASED ON pH AND VOLUME OF FREE ACID HETEROPOLYMER SAMPLES FOR MATERIAL IN THE PRESENCE OF SODIUM ACID MALEATE & FREE MALEIC ACID

(Data in Part III)

Sample	Fig.	Table	pH	ml soln	$10^3 \cdot$ Total moles H_2MA in sample	$[H_2MA] \cdot 10^2$	2pH	Avg pMA
(A) In the presence of sodium acid maleate								
8	8	VIII	2.72	153	4.74	3.1	5.54	1.5934
			2.72	222		2.1		
9*	9	IX	2.62	171	4.74	2.8	5.34	1.5950
			2.62	206		2.3		
(B) In presence of maleic acid								
8	8	VIII	1.85	184	8.34	4.53	3.70	1.3424
9	9	IX	2.07	185	6.30	3.40	4.14	1.4684

In (B) the total moles of H_2MA in sample now includes the moles of true maleic acid added.

Table 16

TABULATION OF 2pH VS pMA BASED ON pH AND VOLUME OF FREE ACID HETEROPOLYMER SAMPLES FOR PURIFIED MATERIAL PREPARED FROM DIFFERENT MOLAR RATIO OF REACTANTS

(Data in Part IV)

Sample	Reactant Ratio m.a.:sty.	Fig.	Table	pH	ml soln	$10^3 \cdot$ total moles H_2MA in sample	$[H_2MA]_2 \cdot 10^2$	2pH	Avg pMA
15	1:1	12	XV	2.75	217	4.6264	2.132	5.5	1.7028
				2.75	251		1.843		
				3.05	369		1.254	6.1	1.9017
16	1:1	13	XVI	2.98	275	4.6738	1.700	5.96	1.7837
				2.98	293		1.595		
				3.07	411		1.137	6.14	1.9442
17	1:3	14	XVII	2.87	243	4.5315	1.865	5.74	1.7436
				2.87	256		1.770		
				3.04	372		1.218	6.08	1.9143
18	1:3	15	XVIII	2.95	277	4.5220	1.632	5.90	1.7979
				2.95	291		1.554		
				3.07	398		1.136	6.14	1.9446
19	3:1	16	XIX	3.11	238	4.8493	2.042	6.22	1.7036
				3.11	253		1.917		
				3.30	380		1.276	6.60	1.8942
20	3:1	17	XX	3.08	249	4.9142	1.974	6.16	1.7163
				3.08	263		1.869		
				3.20	391		1.257	6.40	1.9006

METHODS OF CALCULATIONS IN TABLES 14, 15 & 16

1. $\frac{\text{Moles } H_2MA \text{ in Sample}}{\text{liters of solution}} = [H_2MA]$

The moles of H_2MA in sample are obtained from the determined copolymer compositions (see Tables 8 and 9) See appropriate table of potentiometric data for liters of solution and weight of sample.

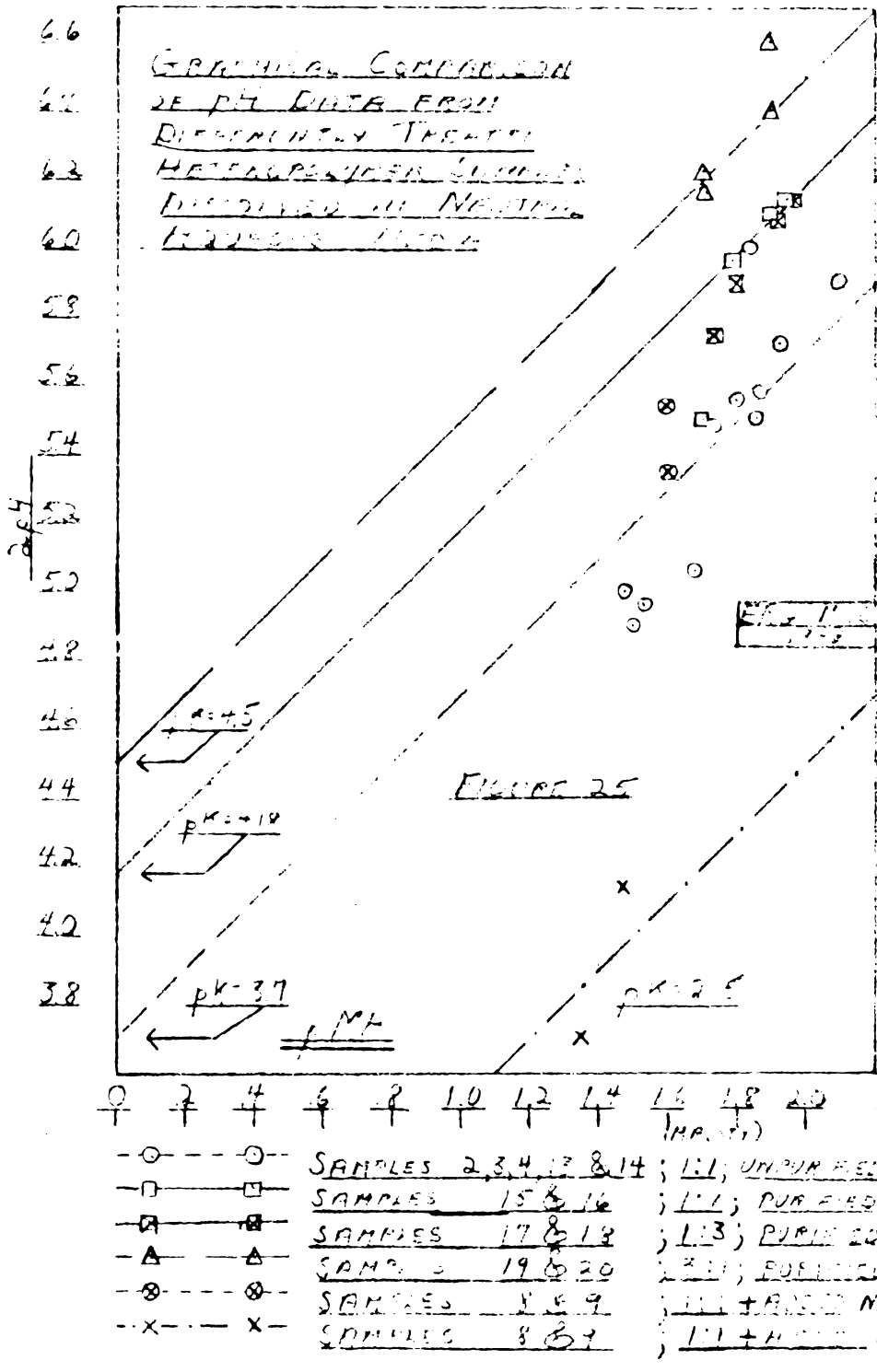
2. In calculations of samples 8, 9 Table 15 (B) the moles of maleic acid added to the solution of the sample is included in the $[H_2MA]$.

3. $pMA = \log \frac{1}{[H_2MA]}$

4. pH of free heteropolymer acid is obtained from vertical line of the appropriate figure.

In Tables 14, 15 and 16 we have tabulated 2pH vs. pMA as determined from the pH and volume of the solutions of free heteropolymer acid, which data comes from the potentiometric titration tables. The data from these tables is plotted in Figure 25 with 2pH as the ordinate and pMA as the abscissa. Thus on the basis of equation (33) only one point is theoretically necessary to graph the linear function by drawing a line through the point with a slope of unity. For purposes of ascertaining the validity of the data, several points are plotted for each sample

Equation of Curve: $2pH - pK = 1.14$



set and a focal point chosen to determine the drawn line and it can be readily seen from the figure that the data for a particular set of samples gives consistent agreement with equation (33). The conclusions drawn from Figure 24 are substantiated by Figure 25 in that the pK value of 1:1 and 1:3 copolymers (molar ratio of reactants; m.a.: styrene) is 4.18 and the pK value from the 3:1 copolymer is decidedly higher (4.5). It may seem contradictory that the weaker heteropolymer acid (3:1) is the richer in maleic acid composition and to afford further comparison the data for samples 2,3,4, 13 and 14 were tabulated in Table 14 and plotted in the figure. These polymer samples did not undergo any extensive purification treatment to remove contaminating monomers and it can be presumed that they may possess a slight excess of occluded monomeric maleic anhydride. The variations in the extent of such occlusions may be surmised by the greater inconsistency of this data with the linear plot of equation (33) through a focal point. The samples 8 and 9 tabulated in Table 15 B had known amounts of maleic anhydride monomer added and this monomer was treated as actual m.a. in the copolymer in the tabulation for the purpose of comparative plotting in Figure 25. Thus it is obvious that occluded maleic acid increases the sample acidity and lowers that pK value. The data

of Table 15A when plotted in the figure also show that when the primary carboxyl of the occluded maleic acid monomer is neutralized the free heteropolymer acid will have the ostensible pK value in the presence of monosodium maleate that it would have in the absence of monosodium maleate.

PART V

ANHYDROUS POTENTIOMETRIC TITRATIONS OF ANHYDRIDE HETEROPOLYMER WITH METHANOLIC CAUSTIC

Moran and Siegel[32] have shown that in anhydrous solutions organic anhydrides form the mono-ester of primary alcohols with the speed of an ionic reaction and that titration of the anhydride with alcoholic alkali in acetone solvent gives the stoichiometric value for one carboxyl. The data of Tables XXI, XXII and XXIII for samples 21, 22 and 23 represents an attempt to apply this principle to a polymeric anhydride. From their respective potentiometric titration curves in Figures 18, 19 and 20 it will be noted that d pH/ d ml (rate of change of pH with milliliters of titer) occurs at a maximum during the methanolic alkali titration until a peak pH is reached, from which point the pH slowly decreases to a constant reading. Considering this rate of change maximum as a stoichiometric point for neutralization of one half the potential carboxyls of the anhydride units of the heteropolymer we have the tabulations of Table 17

which demonstrate that the heteropolymer composition (ma.a: styrene) is .93:1 by this method.

PART V

Table 17

CALCULATION OF MALEIC ANHYDRIDE-STYRENE RATIO IN THE HETEROPOLYMER BASED ON POTENTIOMETRIC TITRATIONS IN NON AQUEOUS MEDIA (ACETONE) WITH ALCOHOLIC NaOH

Ml. of .1141N methanolic NaOH used to neutralize a monocarboxyl of all anhydride units is calculated from inflection point where dpH/ dml is a maximum.

Sample	Table	Fig.	ml. of .1141N NaOH	Net ml	weight sample grams	Ratio m.a.: sty. in polymer
21	XXI	18	43	42	1.0062	.90:1
22	XXII	19	43	42	1.0020	.93:1
23	XXIII	20	44	43	1.0040	.97:1
Acetone Blank	XXIV	21	1			
					average:	.93:1

This .93:1 result agrees well with the copolymer product compositions tabulated in Table 8 for Samples 2,3,4 whose average is .94:1. Those polymer samples were from the same lot as these used in the anhydrous titrations. It is demonstrated that the methods of anhydrous potentiometric titrations are applicable to heteropolymers and give data equal to that of aqueous

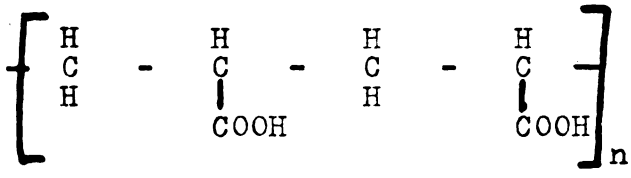
titrations. It provides the clinching argument for the dibasic nature of the copolymer. Due to the fact that the copolymer precipitates during the titration and adsorbs phenolphthalein indicator, the indicator method is not too valid with these anhydrous titrations.

GENERAL DISCUSSION

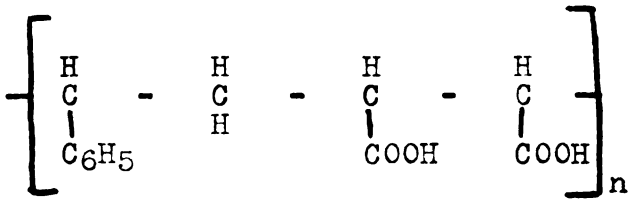
The similarity of the acid units in the heteropolymer to individual succinic acid molecules goes beyond the coincidence of pK values in that the potentiometric curves exhibit no point of inflection for the neutralization of the second carboxyl. This lack of inflection point is characteristic of the titration curve for succinic acid. In contrast to Katchalsky and Spitnik's[23] polymeric acids (polyacrylic and polymethacrylic) the calculated pK values are independent of polymer concentration in the ranges investigated, as would be expected of the monomolecular succinic acid. Introduction of an empirical factor "n" into the Henderson-Hasselbalch equation is not necessary in our heteropolymer as it was with these other polymeric acids since the intercession of at least one ethyl benzene molecule between substituted succinic acids apparently allows each substituted succinic, for all practical purposes, to act independently of another. The greater pK value, or

weaker acid characteristics, for the heteropolymer prepared from a molar excess of maleic anhydride is not readily understood. Perhaps different mechanisms of termination provide different end groups in the polymer molecule when styrene is in molar insufficiency since the latter may possibly react with the polymer radical whereas maleic anhydride cannot do so in excess of a 1:1 molar composition of the copolymer.

To fully clarify this phenomenon it is suggested that future work be carried out on the potentiometric analysis of other polymeric acids. Katchalsky and Spitnik[23] have studied polyacrylic acid:

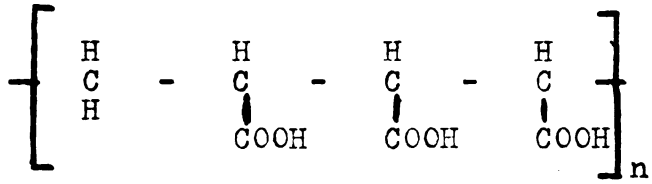


with carboxyls alternating with methylene groups. This paper treats a linear molecule:



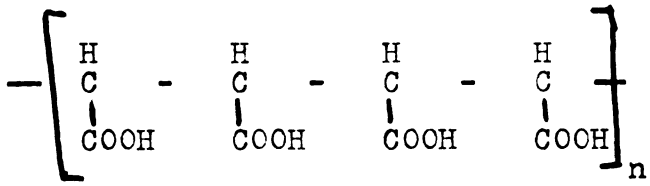
with pairs of carboxyls alternating with a substituted ethylene.

For a fully "homologous" series, we may study the copolymer of acrylic acid (using ester or nitrile as starting material) and maleic acid (using the anhydride as starting material):



This provides a linear molecule with three carboxyls alternating with a methylene.

Polymaleic acid[21] would be the ultimate of the "homologous" series:



From the previous detailed discussion, we may conclude that the pK value of the heteropolymer for most intermediate molar ratios of reactants is independent of polymer size. This confirms the observations of Katchalsky and Spitnik on their polymeric acids. The copolymer compositions determined in this thesis for differing molar ratios of reactants confirm the data of Alfrey and Lavin and the theoretical predictions of Wall in that with increased reactant maleic anhydride, the copolymer constitution tends to approach 1:1. With lessening amounts of maleic anhydride, the copolymer constitution has a predominance of styrene units. This situation is readily comprehended in the light of the concept first proposed by Bartlett and Nozacki[21] and recently embellished by Mayo, Lewis, Walling et al[16,18,20]. The polymerizing unit in these types of "alternating" copolymers (i.e. heteropolymers) is a polar "radical-ion" or resonant complex formed from

a stoichiometric ratio of the co-monomers i.e. 1:1 and that it is this complex which actually acts as the monomeric unit. Since maleic anhydride itself will not readily copolymerize whereas styrene will, it is to be expected that the molar ratio in the polymer composition can never exceed 1:1 (m.a.: styrene). This concept readily serves as a mechanical model for the mathematical predictions of Wall[14] based on Mayo and Lewis' differential equations[12] of copolymerization.

The application of anhydrous potentiometric titrations of heteropolymer with alcoholic alkali indicates that monoesterification of the anhydride units of the heteropolymer readily occurs. This affords an easy method of preparation of hemi-esterified maleic anhydride-styrene heteropolymer that may possess desirable properties.

Specific properties of the maleic anhydride-styrene heteropolymer have also been characterized. The polymer is alkali soluble and the free acid polymer is soluble in water alone. It provides excellent buffering action in the acid range 3.5 - 4.5 pH and lathers well, possessing dispersive properties that indicate its possible use as a feasible detergent in acid pH's, i.e. the unusual phenomenon of an acidic soap. The polymer is very

readily soluble in acetone both in the free acid and anhydride form. On refluxing with absolute methyl alcohol with the probable formation of the di-ester, it forms a compound readily soluble in methanol. The free acid heteropolymer is soluble in acetone and water mixtures of all compositions. However addition of alkali will precipitate out the partial heteropolymer acid salt which will again dissolve on distilling off the acetone. Subsequent addition of acetone will again precipitate the salt but freeing of the heteropolymer acid by strong acid will again make it miscible with acetone-water mixtures.

In the studies of Part III samples, special note was taken of the pH values when precipitation of the heteropolymer first appeared and disappeared. The former values are the more valid since equilibrium is more easily achieved under the conditions of precipitation than under those of dissolution. These pH's for the different titrations are tabulated in Table 18 and show that the pH of polymer precipitation for a 1:1 molar ratio of reactants heteropolymer is independent of heteropolymer concentration.

Table 18

pH OF INITIAL POLYMER PRECIPITATION & DISAPPEARANCE

(Data from Part III)

Sample	Titration	pH ppt. first noted	pH ppt. disappears
1	A	2.4	
	B		2.6
2	A	2.2	
	B		2.4
	C	2.4	
3	A	2.15	
	B		2.4
	C	2.15	
4	A	2.15	
	B		2.5
	C	2.15	
	D		2.5
	E	2.25	
8	A	2.2	
9	A	2.25	
	B		2.7
10	A	2.18	
	B		2.5
	C	2.1	
11	A	2.3	
	B		
	C	2.2	
12	A	2.2	
	C	2.13	
13	A	2.13	

The data from samples 8 and 9 also show that occluded or additional monomolecular maleic anhydride does not affect the pH of precipitation. Analysis of the Remarks in the corresponding potentiometric titration tables (for example, see Table II, sample 2, Titration C) shows that increased precipitation occurs only with lessening pH. For weak monomolecular acids, however, it would be expected that the greatest amount of precipitation in an acid pH would occur at one value if sufficient time for equilibrium is allowed even with the further addition of strong acid. This phenomenon is directly attributable to the buffering effect of the precipitating weak acid on the solution. Allowing more than sufficient equilibrium times, this phenomenon of precipitation at constant pH did not occur with the heteropolymer acid. Now, from our definition of the primary disassociation constant (26) of the heteropolymer acid we have:

$$(34)\quad \frac{K}{[H^+]} = \frac{[HMA^-]}{[H_2MA]} = \frac{10^{-4.2}}{10^{-2.2}} = 10^{-2} = 1:100$$

Thus we may consider that on a probability basis only one out of every hundred carboxyls in the heteropolymer can be ionized when precipitation initially occurs. If we disregard a proportionality factor dependent on chain length and consider for the purposes of this discussion that it takes one ionized carboxyl

per polymer molecule to hold that molecule in solution, it is obvious that on a probability distribution of ionized carboxyls that more of the smaller polymer molecules would tend to be in the uncharged portion that tends to precipitate. Thus the smaller polymer molecules would tend to precipitate first and it may be estimated on the basis of the above calculated ratio that the approximate molecular weight of the fraction of polymer molecules that first precipitate is 100 • (m.wt. of unit or 200) = 20,000. If total precipitation is considered to be effected at a pH of 1.5 a similar calculation gives the approximate molecular weight of the finally precipitated fraction i.e. the very last portion to precipitate as 40,000.

In this regard, it is interesting to note that Bartlett and Nozacki[21] have determined the molecular weight of the copolymer allyl acetate-maleic anhydride as produced by benzoyl peroxide catalysis as averaging 40,000. The copolymer is similar in nature to the one of this paper in that it tends to a 1:1 molar ratio of copolymer composition. Future work may show exact correlation between molecular fractions precipitated at various pH's and their molecular weight. It may also provide a method of molecular fractionation of carboxyl-containing high polymers and shed light on the general theory of electrolytes.

CONCLUSIONS

1. The rate of copolymerization of a 1:1 molar ratio of maleic anhydride and styrene in refluxing benzene when catalyzed by .495% (of monomer weight) benzoyl peroxide is first order with respect to styrene, maleic anhydride or a homopolymerizing "radical-ion" complex where $k = 53 \cdot 10^{-4}$ sec^{-1}. The copolymerizations can be duplicated.
2. Half the carboxyls of the free acid heteropolymer are neutralized at a pH of 6.25. Thus phenolphthalein is an unreliable indicator for neutralization whereas brom cresol purple gives a stoichiometric approximation of $2\frac{1}{2}$%. A quantitative analytical method for copolymer com osition is provided by potentiometric titration.
3. Mono esters of heteropolymer acids can be easily formed by addition of primary alcohols to the heteropolymer anhydride in acetone solvent. Thus anhydrous potentiometric titrations with methanolic NaOH provide a good analytical method of determining the maleic anhydride content of the copolymer.
4. The heteropolymer acid conforms to the Henderson-Hasselbalch equation: $pH = pK - \log \frac{1-\alpha}{\alpha}$ with no slope other than unity being necessary to introduce into the linear equation.

5. The theoretical predictions of Wall and the data of Alfrey and Lavin on copolymer composition resulting from different molar ratios of reactants are confirmed. A 1:1 (m.a.: styrene) molar ratio of reactants yield a .89:1 heteropolymer molar composition; a 1:3 ratio yield a .85:1 polymer; and 3:1 ratio yields a .98:1 polymer.
6. The heteropolymers prepared from a 1:1 and a 1:3 molar ratio of reactants (m.a.: styrene) give titration curves and pK_1 value (4.18) coincidental with succinic acid, one of the recurring units of the copolymer. Heteropolymers formed from increasing amounts of maleic anhydride tend to have higher pK_1 values viz: The product of a 3:1 (m.a.:styrene) molar ratio of reactants has a pK_1 of 4.4.
7. Heteropolymer acid with greater number of maleic acid units composition has less acidic properties than a mixture of a heteropolymer composed of a lesser number of such units and pure maleic acid.
8. Secondary carboxyls of the heteropolymer are very weak acids and their salts readily hydrolizable. There is no inflection point in the titration curve of the secondary carboxyl.
9. The pH of initial precipitation of the acid heteropolymer is 2.2. On the basis of a theoretical development, the approximate molecular weight of the portion precipitating at a pH of 2.2 is predicted to be 20,000.

LITERATURE CITED

1. Wagner-Jauregg,T., Ber., 63, 3213 (1930).

2. Voss,A. and Dickhauser,E., German patents:
   540,101 (1930); 544,366 (1932)
   C.A., 26 1813 (1932).
   British Patent 376,479 (1931)
   U.S. Patent 2,047,398 (1936).

3. Arnold, H.W., Brubaker, M.M. and Dorough,G.L.,
   U.S. Patent 2,300,356 (1942).

4. E.I. du Pont, British Patent 549,682 (1942).

5. Gerhart, H.L., U.S. Patent 2,297,351 (1943).

6. Van Nelsen, U.S. Patent 2,297,039 (1943).

7. Swan,D.R., U.S. Patent 2,299,189 (1943).

8. Stoops,W.N. and Denison, W.A.,
   U.S. Patent 2.324,740 (1944).

9. D'alelio, G., U.S. Patent 2,340,110 (1944).

10. Halbig,P., Matthias,F. and Treibs,A.,
    U.S. Patent 2,344,085 (1944).

11. Wall,F.T., J. Am. Chem. Soc., 63, 1862 (1941).

12. Mayo, F.R., and Lewis, F.M., J. Am. Chem. Soc.,
    66, 1594 (1944).

13. Norrish, R.G.W., and Brookman, E.F., Proc. Roy.
    Soc., (London) 171A, 147 (1939).

14. Wall,F.T., J. Am. Chem. Soc., 66, 2050 (1944).

15. Lewis, F.M., Walling,C., et al, J. Am. Chem.
    Soc. 70, 1519 (1948).

16. Mayo, F.R., Lewis, F.M., and Walling,C., J. Am.
    Chem. Soc. 70, 1529 (1948).

17. Lewis, F.M., and Mayo, F.R., J.Am. Chem. Soc. 70,
    1533 (1948).

18. Walling,C., Briggs, E.R., Wolfstirn,K.B. and Mayo,
    F.R., J.Am.Chem. Soc. 70, 1537 (1948).

19. Lewis, F.M., and Mayo,F.R. Ind. Eng. Chem.,Anal.Ed.
    17, 134 (1945)

20. Walling,C., Seymour,D. and Wolfstirn,K.B., J.Am.Chem. Soc. 70, 1544 (1948).

21. Bartlett,P.D., and Nozacki,K., J. Am. Chem. Soc., 68, 1495 (1946).

22. Alfrey,T., and Lavin,E., J. Am. Chem. Soc., 67, 2044 (1945).

23. Katchalsky,A., and Spitnik,P., J. Poly Sci, II, 432 (1947).

24. D'Alelio,G.F. "Experimental Plastics & Synthetic Resins", J.Wiley & Sons, Inc. N.Y. 1943 Expt.66, Part B, Pg 113,(1943)

25. Guile,R.L., and Huston,R.C., "Revised Lab. Manual of Synthetic Plastics and Resinous Materials", 1944, Expt. 44, Pg 94.

26. Morgan, H.D., B.S. Thesis, Michigan State College (1943)

27. Uhlrig,K., and Levin,H., Ind. Eng. Chem., Anal.Ed., 13, 90 (1941).

28. Simonds, H.R. and Ellis,C., "Handbook of Plastics", D.Van Nostrand Co., Inc., N.Y. (1943) pg. 742-755.

29. Staudinger, H. and Hauer,W., "Die Hochmolekularen Organischen Verbindungen", Springer, Berlin 1932 p.1179.

30. Yang, P.T., M.S. Thesis, Michigan State College (1947).

31. Mihina,J.S., M.S. Thesis, Michigan State College (1948)

32. Moran,M.K., and Siegel, E.F., J. Am. Chem. Soc. 69, 1457 (1947).

ABSTRACT

Application of the method of continuous variations to benzene solutions of para substituted styrenes with maleic anhydride proves the formation of a 1:1 complex, heretofore surmised, and indicates further interaction of the complex with styrene in at least two observable cases (p-chlorostyrene and styrene).

Generally applicable methods have been developed to prove the simultaneous existence and composition of several complexes in solution when the method of continuous variations fails. These methods have been applied.

Constants have been evaluated on the basis of these theories allowing the prediction of the optical density of such complexes at all wave lengths (complexes of maleic anhydride with styrene, p-chlorostyrene, p-methylstyrene, p-methoxystyrene and p-dimethylaminostyrene.

True equilibrium and Beer's law have been demonstrated for the instantaneous formation of the complexes. Comparison of solutions of the same concentration in the substituted styrene and anhydride to spectrophotometrically compare complex stability is not warranted.

The kinetics of the interaction of p-dimethylaminostyrene and p-methoxystyrene with maleic anhydride have been studied and interpreted. It has been shown that other complexes are formed. The observed kinetics have been correlated with structure and alternating tendencies in copolymerization.

CHEMISTRY DEPT.
T541
G239 Garrett 206042

Garrett
Studies on the heteropolymer: maleic anhydride-styrene.