A HYDROGEN ELECTRODE STUDY OF THE EFFECT OF VARIATION IN COMPOSITION ON THE EMF OF THE RAYON SPINNING BATH

A THESIS

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I. INTRODUCTION

The Verhave rayon spinning bath, or one of its many modifications, is used in every artificial silk plant that employs the viscose process for making rayon. The formulas used in making up these baths are all empirical and all patented; but, in general, they are aqueous solutions of sulfuric acid, anhydrous sodium sulfate, and hydrated magnesium sulfate. The viscose "syrup" which is forced into the bath to form the filaments of rayon is extremely alkaline with sodium hydroxide, sodium sulfide, and other substances. These react with the acid of the spinning bath and cause it to become "spent", more or less rapidly. A "spent" bath is regenerated by addition of acid and salts, the amounts to be added being determined by analysis.

As far as is known through empirical observation, the efficiency of the spinning bath depends solely upon a property which may be conveniently termed the "acidity". A spent bath is one which is no longer acidic enough to react with all the basic compounds present in the syrup, and which therefore gives an inferior filament; a bath which is too acid will also cause deterioration of the final product.

Since the function of the bath is to convert sodium hydroxide into sodium sulfate and sodium bisulfate by reaction with sulfuric acid, the acidity of the bath varies with change in the percentages of the original components. If this were not true, the bath could not be regenerated by addition of further quantities of these original components.

Also, it is reasonable to suspect that the acidity of the bath, and therefore its efficiency, is directly connected with the pH, if such is measurable.

This study attempts to correlate, by means of the hydrogen electrode, the variation of the pH of the Verhave spinning bath with change in composition in respect to sulfuric acid, sodium sulfate, and magnesium sulfate.

II. THEORETICAL DISCUSSION

The use of the hydrogen - calomel cell for pH measurements, still the standard electrometric method in spite of the growing popularity of the glass electrode, is based on fundamental principles and assumptions which should be outlined carefully here as follows:

If there is set up a galvanic cell of the form

Pt, H_2 (1 atm.), H^+, salt bridge, Hg^+, HgCl (s), Hg(l),

a reaction takes place wherein electrons move through the cell from right to left. This movement creates a difference of potential between the two poles of the cell; and this potential difference may be measured in volts by connecting the poles of the cell to a suitable device, such as a potentiometer.

If we assume that the electromotive force thus measured is caused entirely by the difference of potential between the two electrode surfaces, and neglect any effects of junctions of two solutions of different concentrations, we may, from thermodynamic considerations[1], write

$$E = E_o + \frac{RT}{F} \ln \frac{1}{a_{H^+}} \qquad (1)$$

where E= observed EMF

E_o = electromotive force of the cell when $a_{H^+} = 1$

= electrode potential of the calomel electrode

R = gas constant in joules per degree = 8.316

T = absolute temperature

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[1]See Getman and Daniels, Outlines of Theoretical Chemistry, pp. 431-433;6th ed.; Lewis and Randall, Chemical Thermodynamics, p. 403

F = the faraday = 96,494 coulombs

a_{H^+} = Activity of the hydrogen ions in the solution surrounding the hydrogen electrode

Keeping in mind the limitation of equation (1) imposed by the assumption made above, we may insert the indicated constants, change to common logarithms, and obtain

$$E = E_0 + (.000198T) \log \frac{1}{a_{H^+}} \qquad (2)$$

Since all liquid junction potentials have been neglected in deriving equation (2), it is necessary to reduce these effects to a negligible value before the equation becomes valid. Liquid junction potentials are caused by the difference in rates of migration of the ions in two solutions across their junction. This difference in rates is caused, (in turn), by a difference in the concentrations of the solutions and by a difference in the mobility of the ions those solutions contain. Because potassium ion and chloride ion have very nearly the same mobilities, it is found that interposition of a "salt bridge" of potassium chloride solution between the solution surrounding the hydrogen electrode and that above the calomel reference electrode, tends to minimize the effect of the liquid junction potential. The junction potential has never been completely eliminated, but when the hydrogen ion solution is very dilute, it may be disregarded in ordinary pH measurements when a potassium chloride bridge is used.

When the solution around the hydrogen electrode is concentrated, however, or when the electrolytes it contains are of different valence types, the liquid junction potential becomes more pronounced; and equation (2) is no longer strictly applicable

pH and Hydrogen Ion Activity

The product of the concentrations of hydrogen and hydroxyl ions in any aqueous solution may be written as a constant at any one temperature,

$$C_{H^+} \times C_{OH^-} = K \qquad (3)$$

At 25°C. this constant is very nearly equal to 1×10^{-14},

$$C_{H^+} \times C_{OH^-} = 1 \times 10^{-14}, \text{ so that} \qquad (4)$$

Written in logarithmic form, this equation becomes

$$\log \frac{1}{C_{H^+}} + \log \frac{1}{C_{OH^-}} = 14 \qquad (5)$$

The first term of this expression has been designated as the pH value of the solution under consideration. Substituting this notation, for every solution at 25°C.

$$pH + pOH = 14 \qquad (6)$$

Thus a solution which is exactly neutral has a pH of 7; an acidic solution has a pH below 7; and a basic one, above 7. From mathematical considerations, at least, there is no reason why the pH scale should be limited between values of 0 and 14, as it generally is. A very acid solution might conceivably have a pH of -.5 and a pOH of 14.5, and still agree with the pH equations expressed above.

Equation (2) may be rearranged to give

$$\log \frac{1}{a_{H^+}} = \frac{E - E_o}{.000198\ T} \qquad (7)$$

In dilute solutions of hydrogen ions, it may be assumed that a_{H^+} is equal, or nearly equal, to C_{H^+}. Upon making this substitution, there results the ordinary equation for calculating pH from the electromotive force of a hydrogen-calomel cell.

$$\log \frac{1}{C_{H^+}} = pH = \frac{E - E_o}{.000198\ T} \qquad (8)$$

It must be remembered that equation (8) is derived by making two radical assumptions: that liquid junction potentials are eliminated by the use of a salt bridge, and that hydrogen ion activity is equal to hydrogen ion concentration. Both of these assumptions are permissible in ordinary work, in dilute solutions (up to 0.1M total concentration). What happens when both of the limiting conditions are disregarded by using a very acid solution, containing large amounts of salts of different valence types? Such a solution is furnished by the rayon spinning bath.

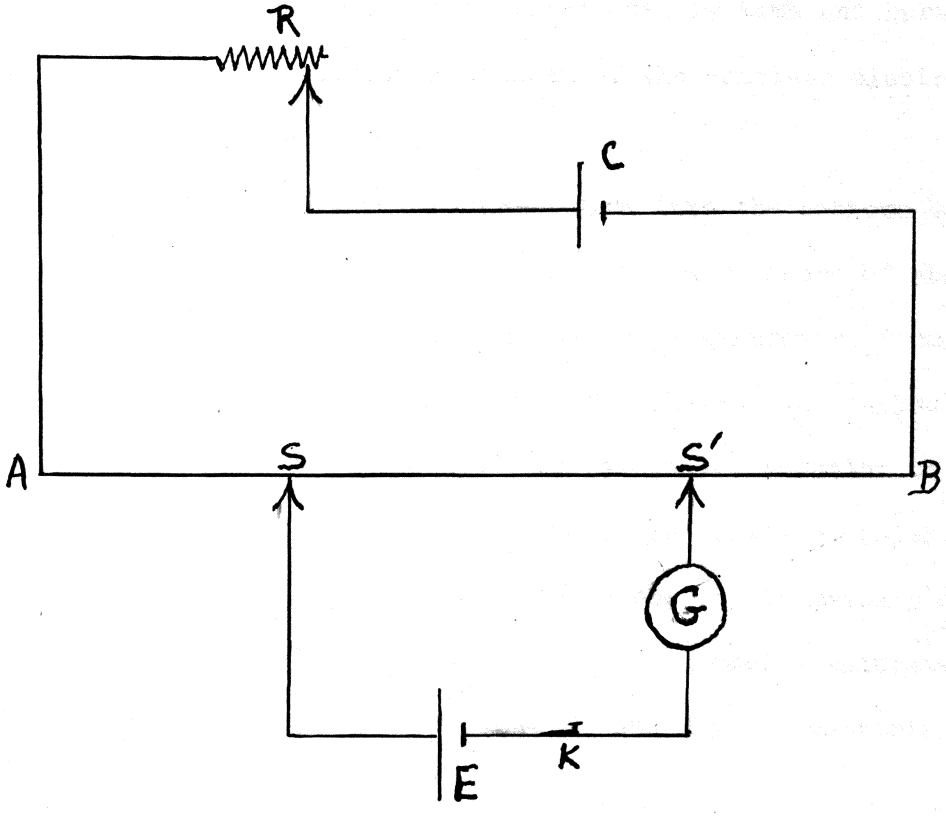
The constant E_o in equation (8) depends upon which of the three types of calomel half-cells is used. The three types are named deci-normal, normal, and saturated, according to the concentration of the potassium chloride solution which is used in making up the half-cell and the salt bridge. The saturated calomel electrode, which was used in this work, has an electromotive force (E_o) of + 0.2458 volts at 25°C.

The Potentiometer

A voltmeter cannot be used to measure the electromotive force developed by the hydrogen-calomel cell because it draws current from the cell and rapidly causes polarization. An ideal device for measuring potential differences with no current flowing is the potentiometer. The essential features of the potentiometer principle are represented in figure 1.

AB is a wire of uniform resistance over its entire length, so that when a current is sent through it from the storage cell C the fall of potential in every unit of length from A to B is exactly the same. AB is graduated in units of length. The cell E whose potential is to be measured is connected, through a galvanometer G, to the wire AB by means of the movable points S and S'. The polarity is reversed, so that the fall of potential caused by the unknown cell is from S' to S. When the circuit is momentarily closed at K, and the distance SS' is adjusted so that there is no deflection of the galvanometer, then the electromotive force of the cell E is exactly balanced by the potential drop from S to S', and is measured by the number of units of length of AB included in the distance SS'.

There remains to be found the fall of potential in AB per unit length. This is done by inserting a standard cell in place of the unknown cell E. If the known potential of the standard cell is, for example, 1.0183 volts, the distance SS' is set to span 1018.3 units of length and the resistance R adjusted until there is no deflection of the galvanometer when the circuit is momentarily closed at K. Then the fall of potential from S to S' is 1.0183 volts and for each scale division of AB it is .001 volt.



AB = slide wire
C = storage cell
E = unknown cell
G = galvanometer
K = key
R = variable resistance
SS' = movable points

Figure 1. Basic Scheme of the Potentiometer Circuit.

III. EXPERIMENTAL

A. Apparatus and Materials

In order to eliminate as much as possible of the liquid junction potential, or at least to render it constant enough to obtain reproducible readings, the flowing liquid junction first used by Lamb and Larson[2] was employed in this investigation. A diagram of the complete electrode system is shown in figure 2.

The platinized platinum electrode dips into the unknown solution at A, and the hydrogen gas bubbles over it under a pressure of about one atmosphere. The hydrogen was made in a Kipp type generator, from a technical grade of zinc and dilute sulfuric acid. The gas was washed in dilute sodium hydroxide to remove acid, in pyrogallol solution to remove oxygen and other oxidizing agents, and finally in distilled water.

The calomel cell at B was made from electrolytic mercury and electrolytic calomel. The salt bridge, a saturated calomel - saturated potassium chloride solution, extends from B to C, and D is a reservoir of the same solution.

In order to make a sharp liquid-liquid junction at C, the liquid with the smaller specific gravity, in this case potassium chloride solution, must be uppermost. When the junction is to be renewed or freshened, the stopcock in the sidearm is opened and both liquids are allowed to flow out simultaneously; the potassium chloride from the reservoir D and the unknown solution from A through the capillary tube E. When only a few drops have been allowed to flow off, the junction at C is sharp, and the stopcock is closed.

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[2] Lamb and Larson, "The Flowing Junction", J. Am. Chem. Soc., 42, 229, (1920)

. . A Leeds and Northrup No. 7665 potentiometer was used throughout this investigation. The standard cell was a Weston type, 1.01865 volts. The working current was furnished by two single Edison cells in series. The galvanometer was a Leeds and Northrup No. 2420. All leads were of 18 gauge copper wire, insulated.

The chemicals used in making up the spinning bath were as follows:

H_2SO_4, C.P., 93.36% by analysis

Na_2SO_4, C.P. anhydrous

$MgSO_4 \cdot 7H_2O$, U.S.P. Epsom salts

Distilled water

B. Procedure

Several platinum electrodes were made by sealing platinum foil into one end of a Pyrex glass tube and filling the tube with mercury. The platinum tips were thoroughly cleaned and coated with platinum black by connecting two electrodes at a time to a six-volt source of current and immersing them in a chloroplatinic acid solution. The coated electrodes were kept in distilled water until used. Before being used in a spinning bath solution, each electrode was checked in the potentiometer circuit by measuring the EMF developed upon immersing it in a standard potassium acid phthalate solution, pH = 3.85.

Five series of solutions were made up, with varying concentrations of the compounds composing the rayon spinning bath. In every series, the solutions were made by adding sodium sulfate, water, sulfuric acid, and magnesium sulfate, in that order. A complete series was made up, at one time, and the EMF readings made as soon as possible on the whole series of solutions.

Series I. Sodium sulfate, 16%
Magnesium sulfate, 30%
Sulfuric acid, 1 - 12%

Series II. Sodium sulfate, 0 - 16%
Magnesium sulfate, 30%
Sulfuric acid, 9%

Series III. Sodium sulfate, 10 - 19%
Magnesium sulfate, 30%
Sulfuric acid, 6 - 15%

Series IV. Sodium sulfate, 16%
Magnesium sulfate, 0 - 40%
Sulfuric acid, 9%

Series V. Sodium sulfate, 16%
Magnesium sulfate, 24 - 34%
Sulfuric acid, 5 - 15%

In each series, the variations in composition were made from a normal, or standard, composition, as follows:

Sodium sulfate, 16%
Magnesium sulfate, 30%
Sulfuric acid, 9%
Water, 45%

One hundred grams of each solution was made up; each component was weighed to the nearest centigram. The limits of variation of composition in any one series were determined by the solubilities of the salts; that is, EMF readings were not made on baths in which the salts were crystallizing out at temperatures above 45°C.

In making an EMF determination, each solution was heated to about 55°C. and poured into the hydrogen electrode vessel. Hydrogen was bubbled over the electrode, in the solution, until the temperature fell to about 45°C. A sharp liquid junction was made, and a potentiometer reading taken quickly; the junction was renewed and another reading taken immediately. When two such successive readings agreed within 0.2 millivolt, the mean

of the two was recorded as the EMF of the bath.

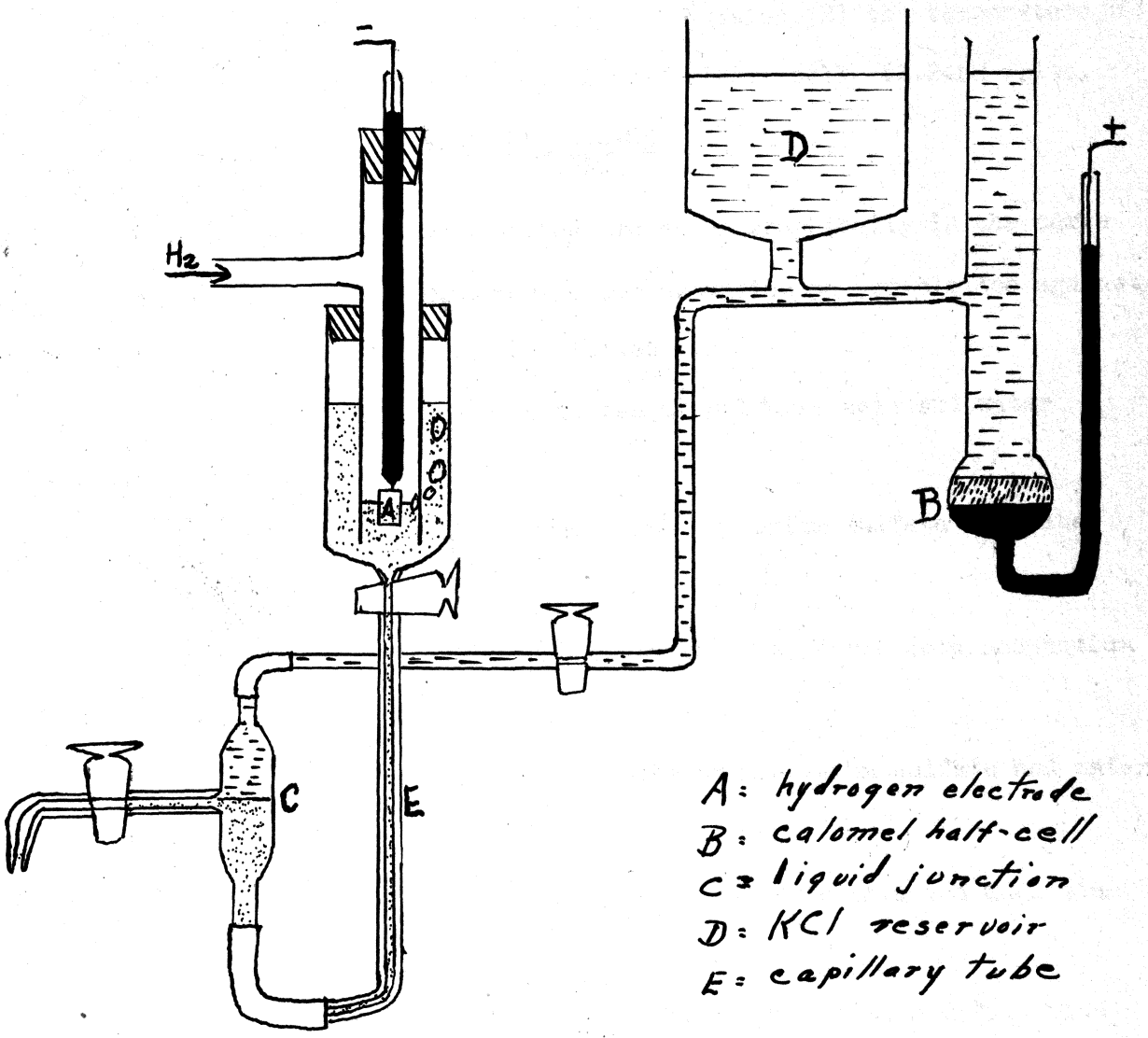


Figure 2. Diagram of Hydrogen - Calomel Cell.

C. Experimental Data

The EMF readings for the solutions in each series are given in tables on the following pages. For each solution, the pH is calculated by the formula obtained by substituting in equation (8) the temperature, 318°A (45°C.), and the potential E_o of the calomel cell, +0.2458 volts.

$$pH = \frac{E - 0.2458}{0.0631}$$

The variations in each series are shown graphically in the curve accompanying each table. EMF and the corresponding pH are plotted against the percentages of the variable constituents.

Table I and Curve I - Percentages of sulfuric acid and water varying simultaneously.

Table II and Curve II - Percentages of sodium sulfate and water varying simultaneously.

Table III and Curve III - Percentages of sulfuric acid and sodium sulfate varying simultaneously.

Table IV and Curve IV - Percentages of magnesium sulfate and water varying simultaneously.

Table V and Curve V - Percentages of sulfuric acid and magnesium sulfate varying simultaneously.

Finally, the results are coordinated in Curves VI and VII. The results from Series I, II, and III, in which the concentration of magnesium sulfate is constant, are plotted together in Curve VI. The data from Series I, IV, and V, in which the concentration of sodium sulfate is constant, are brought together in Curve VII.

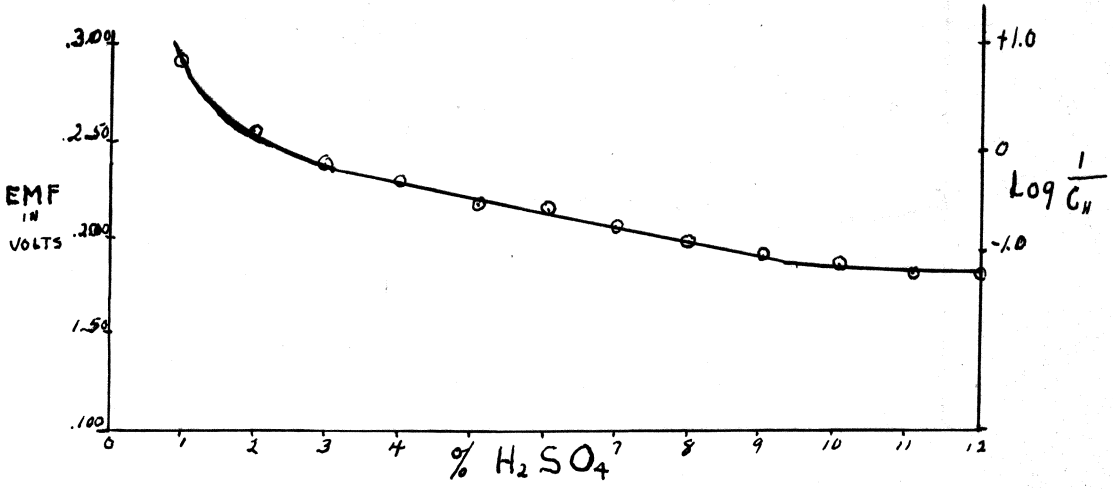
Series I.

Sodium sulfate, 16%; Magnesium sulfate, 30% ; 45° C.

Table I

% H_2SO_4	% H_2O	EMF in volts	pH (calculated)
1	53	0.2954	0.835
2	52	0.2742	0.450
3	51	0.2632	0.276
4	50	0.2570	0.177
5	49	0.2424	-0.054
6	48	0.2330	-0.203
7	47	0.2250	-0.330
8	46	0.2126	-0.536
9	45	0.2120	-0.535
10	44	0.1991	-0.752
11	43	0.1945	-0.850
12	42	0.1920	-0.878

Curve I



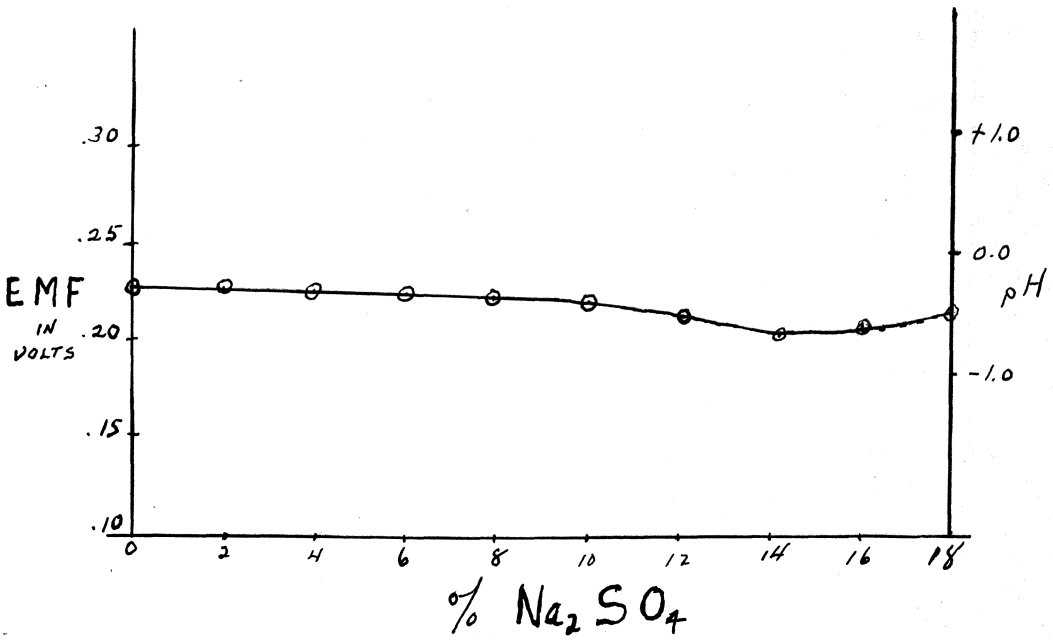
Series II.

Sulfuric acid, 9%; Magnesium sulfate, 30%; 45° C.

Table II

$\%Na_2SO_4$	$\%H_2O$	EMF in volts	pH (calculated)
0	61	0.2283	-0.277
2	59	0.2270	-0.298
4	57	0.2250	-0.330
6	55	0.2225	-0.369
8	53	0.2180	-0.441
10	51	0.2141	-0.502
12	49	0.2117	-0.540
14	47	0.2146	-0.494
16	45	0.2162	-0.469

Curve II



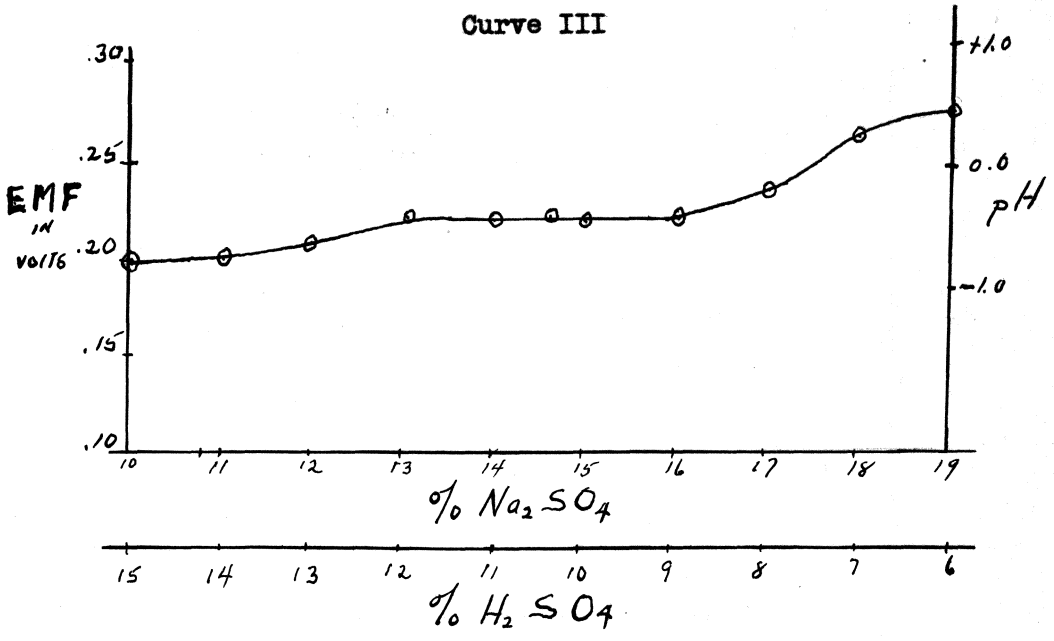
Series III.

Water, 45%; Magnesium sulfate, 30% ; 45° C.

Table III

% H_2SO_4	% Na_2SO_4	EMF in volts	pH (calculated)
15	10	0.2005	-0.718
14	11	0.2052	-0.643
13	12	0.2160	-0.472
12	13	0.2202	-0.406
11	14	0.2200	-0.409
10.5	14.5	0.2215	-0.385
10	15	0.2190	-0.425
9	16	0.2200	-0.409
8	17	0.2362	-0.152
7	18	0.2610	0.241
6	19	0.2662	0.323

Curve III



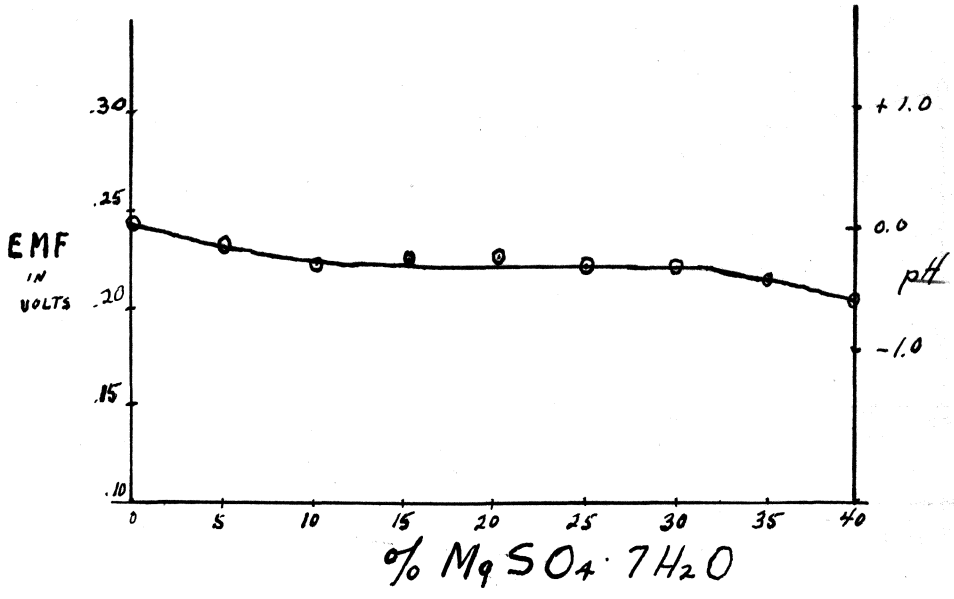
Series IV

Sulfuric acid, 9%; Sodium sulfate, 16%; 45° C.

Table IV

% $MgSO_4 \cdot 7H_2O$	% H_2O	EMF in volts	pH (calculated)
0	75	0.2456	0.000
5	70	0.2442	-0.025
10	65	0.2293	-0.261
15	60	0.2316	-0.225
20	55	0.2325	-0.211
25	50	0.2296	-0.257
30	45	0.2292	-0.263
35	40	0.2228	-0.364
40	35	0.2170	-0.456

Curve IV



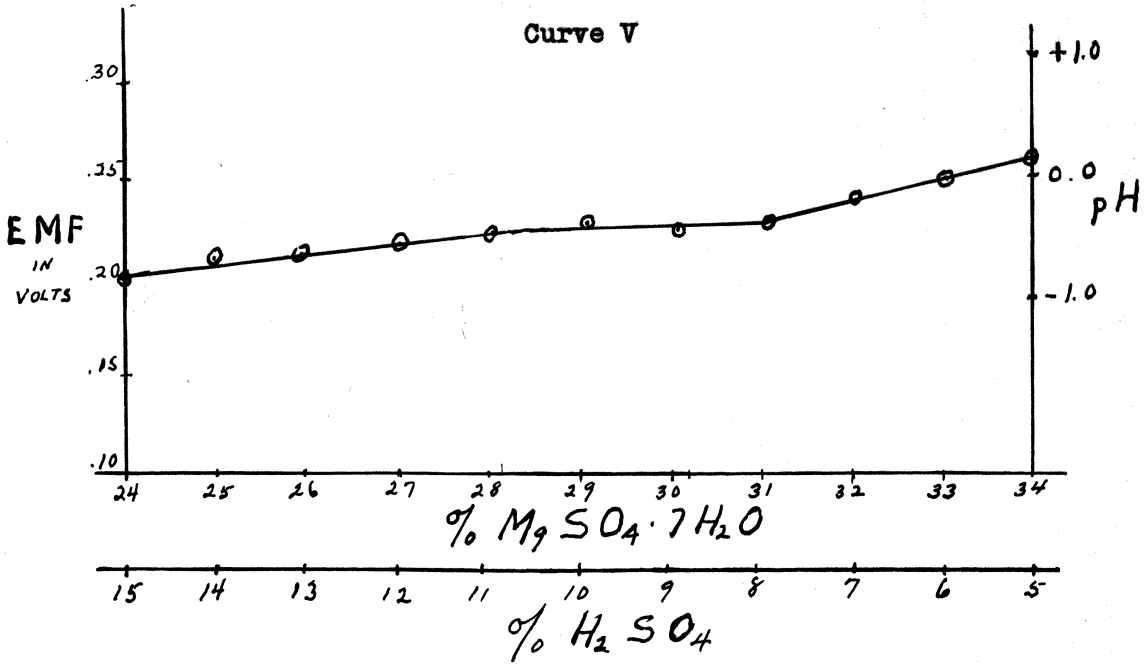
Series V.

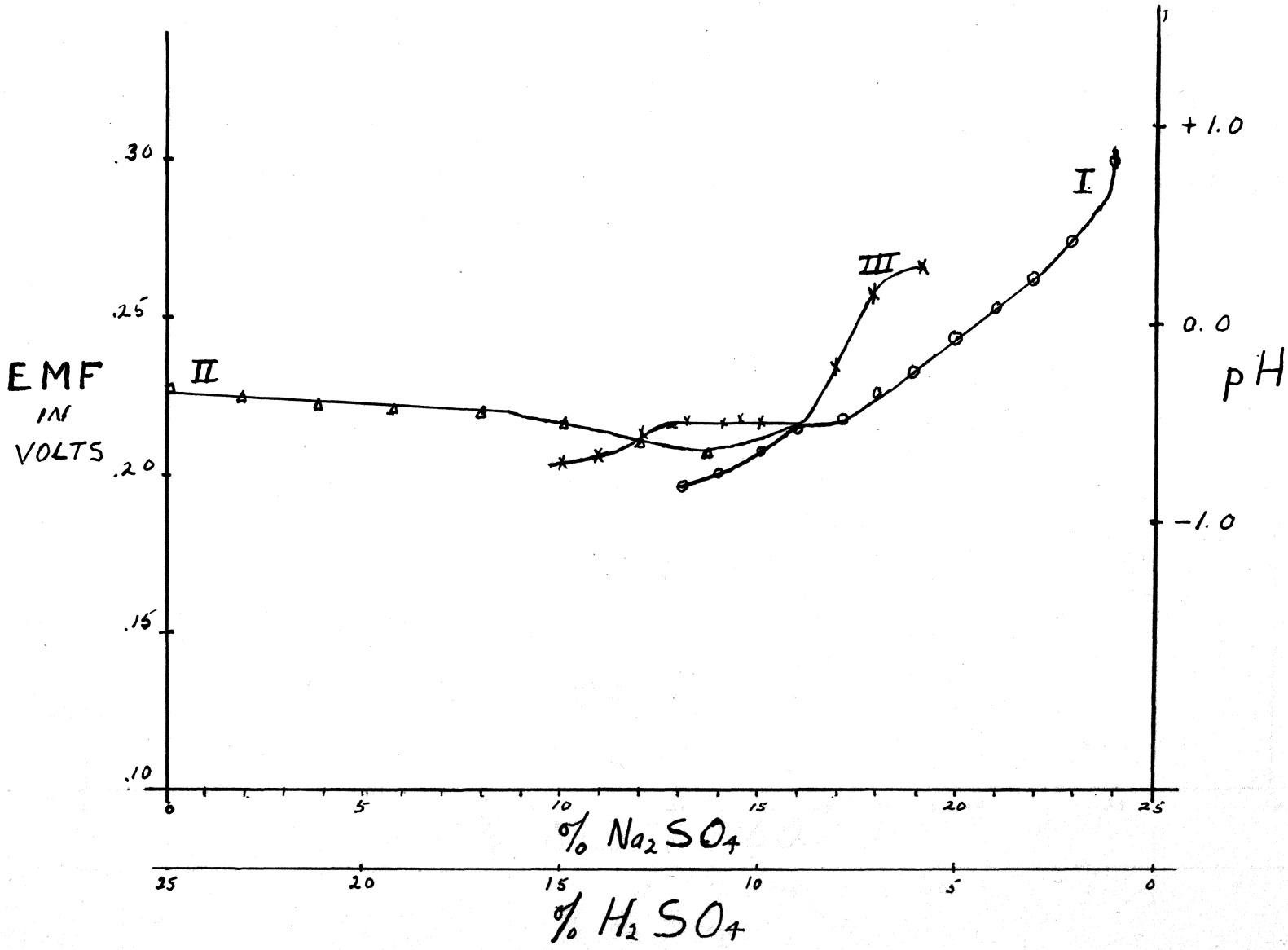
Water, 45%; Sodium sulfate, 16%; 45° C.

Table V

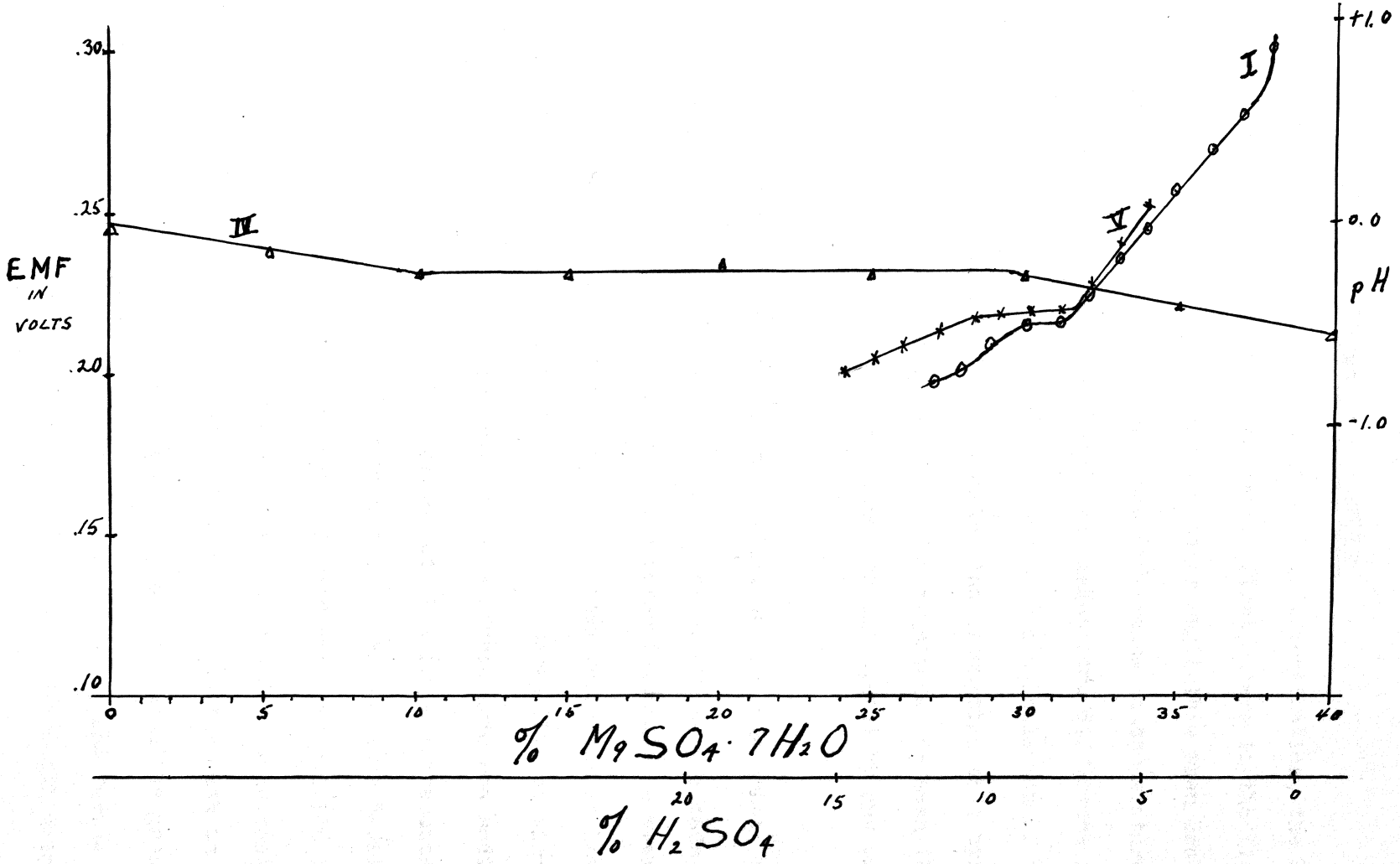
% $MgSO_4.7H_2O$	$\%H_2SO_4$	EMF in volts	pH (calculated)
24	15	0.2058	-0.634
25	14	0.2140	-0.504
26	13	0.2130	-0.520
27	12	0.2192	-0.421
28	11	0.2240	-0.345
29	10	0.2263	-0.309
30	9	0.2225	-0.369
31	8	0.2292	-0.260
32	7	0.2381	-0.122
33	6	0.2457	0.000
34	5	0.2573	0.182

Curve V





Curve VI. Comparison of Series I, II, and III.



Curve VII. Comparison of Series I, IV, and V.

IV. DISCUSSION OF RESULTS

Under the experimental conditions of this investigation, the EMF readings are subject to two sources of error. First, there is the liquid junction potential, which is impossible to render negligible when dealing with concentrated solutions; and second, the difference in temperature between the spinning bath and the calomel cell makes some difference in the reading. A third source of error is added when a calculation of pH is attempted from these EMF readings - namely, the assumption that hydrogen ion activity is equal to concentration. The magnitude, or even the relative weight, of any of these errors cannot be calculated by any present methods.

However, since the concentrations are all of the same order; since the temperature difference was constant; and since readings were made with a flowing junction so that the liquid junction potential would be nearly constant - it may be assumed that the values obtained represent at least relative pH values. On this assumption, a study of Curve III, obtained by varying simultaneously the concentrations of sulfuric acid and sodium sulfate, is interesting. If the flat portion of this curve represents a series of solutions of different concentrations, but of the same "acidity", then a spinning bath solution made up with 12% sulfuric acid and 13% sodium sulfate would spin the viscose syrup as well as the standard bath containing 9% acid and 16% sulfate. Moreover, since the acid in the bath is converted to sulfates during the spinning process, the bath with the greater acid content would have a longer life than the usual bath, and during use would change in concentration along the flat portion of Curve III without changing in "acidity".

The greatest buffering action of sodium sulfate on sulfuric acid should theoretically occur when the molal concentrations of the two are equal, since they react mol for mol to form sodium bisulfate. This point occurs about midway of the flat portion of Curve III, at 10.2% acid and 14.8% sodium sulfate.

Variation of sulfuric acid concentration alone produces the effect, in Curve I, that is to be expected. The pH falls off rapidly at first with increasing concentration, then levels off near the point where the salts begin to come out of solution. Variation of sodium sulfate concentration alone produces very little effect. A comparison of the results obtained by varying sulfuric acid, then sodium sulfate, then both together, is given in Curve VI. The same comparison, varying magnesium sulfate instead of sodium sulfate,is given in Curve VII. The effects in this case are much less marked.

It should be of interest to study the quality of the rayon produced upon spinning with the solutions of varying concentrations as used in this study. Especially is this true of those baths represented by the flat portion of Curve III. Further work in this investigation should also include a comparison of the EMF readings obtained with a hydrogen-calomel cell and with a glass electrode.

V. CONCLUSIONS

The electromotive force of various compositions of the Verhave Rayon spinning bath, as measured on the hydrogen electrode, gives some negative pH values when substituted in the usual equation for obtaining pH from EMF. It is extremely doubtful that the hydrogen electrode measures pH, with solutions of such high concentration.

Changes in concentration of sulfuric acid produce more marked variations in EMF than do changes in concentration of sodium sulfate and magnesium sulfate.

Several spinning bath solutions, of different composition with respect to sulfuric acid and sodium sulfate, are found to have the same EMF. Any one of these baths should give the same quality of rayon, and the one with the highest concentration of acid should be the most efficient.

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