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THE BEHAVIOUR OF SULFUR DIOXIDE
OXYGEN, SULFURIC ACID AND WATER
IN AN ELECTROLYTIC CELL.

by

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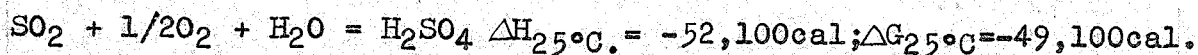
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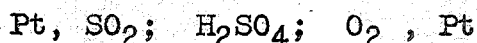
INTRODUCTION

The utilization of the free energy of sulfur dioxide in the form of electrical energy for the production of sulfuric acid is of great industrial importance in the metallurgical and chemical industries where large quantities of waste sulfur dioxide are produced. Hitherto sulfuric acid has been manufactured either by the Chamber process or Contact process. From a consideration of the heat of reaction ΔH and the free energy change ΔG of the reaction:



the possibility of producing sulfuric acid as well as electrical energy in an electrolytic cell is readily visualized.

In the following experiments it was proposed to determine the actual electromotive force of the cell:



at various concentrations of sulfuric acid and at different temperatures.

Hydrates of sulfuric acid are known to exist. Their formation is associated with a large entropy change. In an electrolytic cell the formation of a hydrate would consequently be associated with a correspondingly large potential change. Further, the potential should vary with the nature of the hydrate formed. Hence, it should be

possible to detect the presence and nature of the different sulfuric acid hydrates by means of the aforementioned cell.

HISTORICAL

From the literature it appears that no previous work has been done directly on this problem.

Experiments have been conducted by Messrs. M. de Kay Thompson and N.J. Thompson² and by Messrs. M. de Kay Thompson and A.P. Sullivan³ on the depolarization effects of sulfur dioxide in an electrolytic cell. They showed that it was possible to decrease the polarization at the anode and thus decrease the equilibrium voltage of the cell by the addition of sulfur dioxide. It appeared from their experiments that the polarization was due to the accumulation of free oxygen at the anode. On addition of sulfur dioxide to the anolyte a reaction occurred between this gas and the free oxygen reducing the polarization effects.

Since such a reaction is accompanied by a substantial decrease in free energy it was evident that a cell of the type



should have a definite oxidation-reduction potential.

THEORETICAL CALCULATIONS

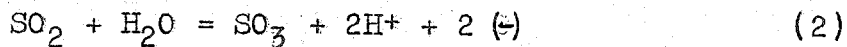
Probable Ionic Mechanism of Cell Reactions.

Anode Reactions:

The sulfur dioxide first dissolves in the sulfuric acid electrolyte and then adsorbs on the surface of the electrode:

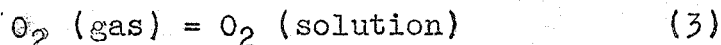


The sulfur dioxide then combines with water as in equation (2)

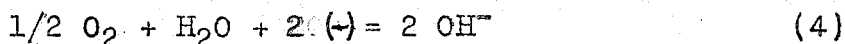


Cathode Reactions:

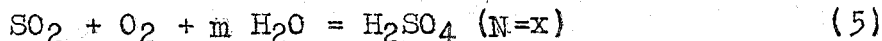
Similarly, oxygen is dissolved in the electrolyte and then adsorbed on the surface of the electrode.



Oxygen combines with water as in equation (4).



Overall Cell Reaction



Thermodynamic Calculations:

Here the following nomenclature has been used.

ΔG = free energy change, calories

ΔH = heat of reaction, calories

ΔP = pressure change, atmospheres.

ΔV = volume change, cubic centimeters.

n = valence

f = Faraday = 96,500

T = temperature, degrees Centigrade.

t = time, hours.

M = mole fraction

N = normality.

X = percent acid

J = conversion factor: 1 cal. = 4.183 joules

1 joule = 9.87 cc.atmospheres.

Variation in E.M.F. with Concentration of Electrolyte.

The number of accurate measurements from which the free energy of dilution of sulfuric acid may be calculated is limited. Tables are available on the free energy of dilution of the acid only for dilute solutions. Insufficient data is known from which to calculate accurately the activity of the ions and hence the free energy of dilution of concentrated solutions. Bronsted⁴ studied the free energy of dilution over a rather wide range of concentrations of sulfuric acid but at temperatures ranging only up to 9°C. Harned and Sturgis⁵ and Lewis and Randall⁶ also studied the free energy of this acid, but over a small range of concentrations.

A satisfactory table of the free energy of dilution at 25°C for concentrations up to .2 mol fraction sulfuric acid has been worked out by Randall and Cushman⁷. Their results which are the free energies ΔG_1 of the reaction:

$$2 \text{H}^+ + \text{SO}_4^{--} + m\text{H}_2\text{O} = \text{H}_2\text{SO}_4(M=X) \quad (6)$$

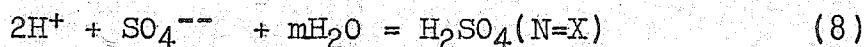
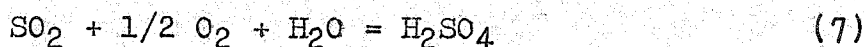
are given in the third column of Table I, and the

corresponding values of mole fraction M and percent acid X in the first and second columns respectively.

TABLE I

<u>M</u>	<u>X(%)</u>	<u>ΔG_1(cal)</u>	<u>ΔG_2(k cal)</u>	<u>E(volts)</u>
1.00	100.00	0	-49.1	1.065
.20	57.70	5270	-43.8	.950
.13	44.90	2915	-46.2	1.000
.10	37.70	1645	-47.5	1.030
.08	31.60	702	-48.4	1.048
.065	27.55	-85	-49.2	1.067
.05	22.28	-865	-50.0	1.084
.03	14.42	-2048	-51.1	1.108
.02	10.00	-2735	-51.8	1.122
.01	5.21	-3702	-52.8	1.143
.002	1.08	-5613	-54.7	1.185
.0009	.487	-6547	-55.6	1.204
.00009	.049	-9382	-58.5	1.268

The cell reaction can be divided into two parts as such:



Addition of equations (7) and (8) gives the overall cell reaction. Hence, addition of the free energy of reaction of equations (7) and (8) will give the overall free energy

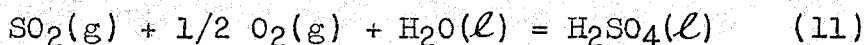
change within the cell. The value of ΔG for equation (7) is obtained from the difference of the free energy of formation of sulfuric acid and the sum of the free energies of formation of sulfur dioxide, water and oxygen. The free energy of formation of $H_2SO_4 = -176,000$ calories⁸, of $SO_2 = -71,740$ calories⁹, of $H_2O = -56,690$ calories¹⁰, of $O_2 = 0$ calories, giving for equation (7) $\Delta G = -49,100$ calories. In equation (8) ΔG is simply the free energy of dilution of sulfuric acid. The calculated values of ΔG_2 for the overall cell reaction (equation 5) are given in the fourth column of Table I.

By simple substitution in to the formula:

$$E = \frac{(\Delta G) (J)}{(n) (f)} \quad (10)$$

the theoretical values of the emf that would be obtained in a completely reversible cell are obtained. The values are given in column 5 of the above table. In Fig. I the values of the emf given in Table I are plotted as ordinates against concentration of sulfuric acid as abscissa. A hypothetical curve was drawn from .2 M to 1 M sulfuric acid, the range of concentration where information on the free energy of dilution was unobtainable.

Variation of E.M.F. with Pressure



Equation (11) indicates a volume change from 1 1/2 moles of gas to zero moles of gas,

$$V = 1.5 \text{ volumes}$$

One mole of gas at N.T.P. = 22,400 cc.

One mole of gas at 20°C and one atm. = 24,050 vv.

$$V = 1.5 \times 24,050$$

$$= 36,075 \text{ cc.}$$

$$1 \text{ joule} = 9.87 \text{ cc. atm.}$$

$$\therefore J = 9.87$$

Apply the formula:

$$\frac{\Delta E}{\Delta P} = \frac{\Delta V}{nfJ} \quad (12)$$

the value $\frac{\Delta E}{\Delta P} = \frac{36,075}{(2)(96,500)(9.87)} = .01892 \text{ volts/atm.}$

is obtained, where $\frac{\Delta E}{\Delta P}$ is the increase in voltage per unit increase in pressure.

DESIGN AND CONSTRUCTION OF THE CELL.

A diagrammatic sketch of the cell is given in Fig.II. It consisted of two stoppered glass vessels, anode and cathode compartments, each containing as electrolyte, sulfuric acid of the same concentration. Through the four holes of each stopper was inserted a gas inlet, a gas outlet, a lead for the electrode and an arm of the sulfuric acid bridge.

At the end of the sulfur dioxide and oxygen inlets were distributors. This gave the entering gas a larger surface area enhancing the saturation process.

Electrical contact was made by two mercury filled glass leads. One end of each lead was sealed to

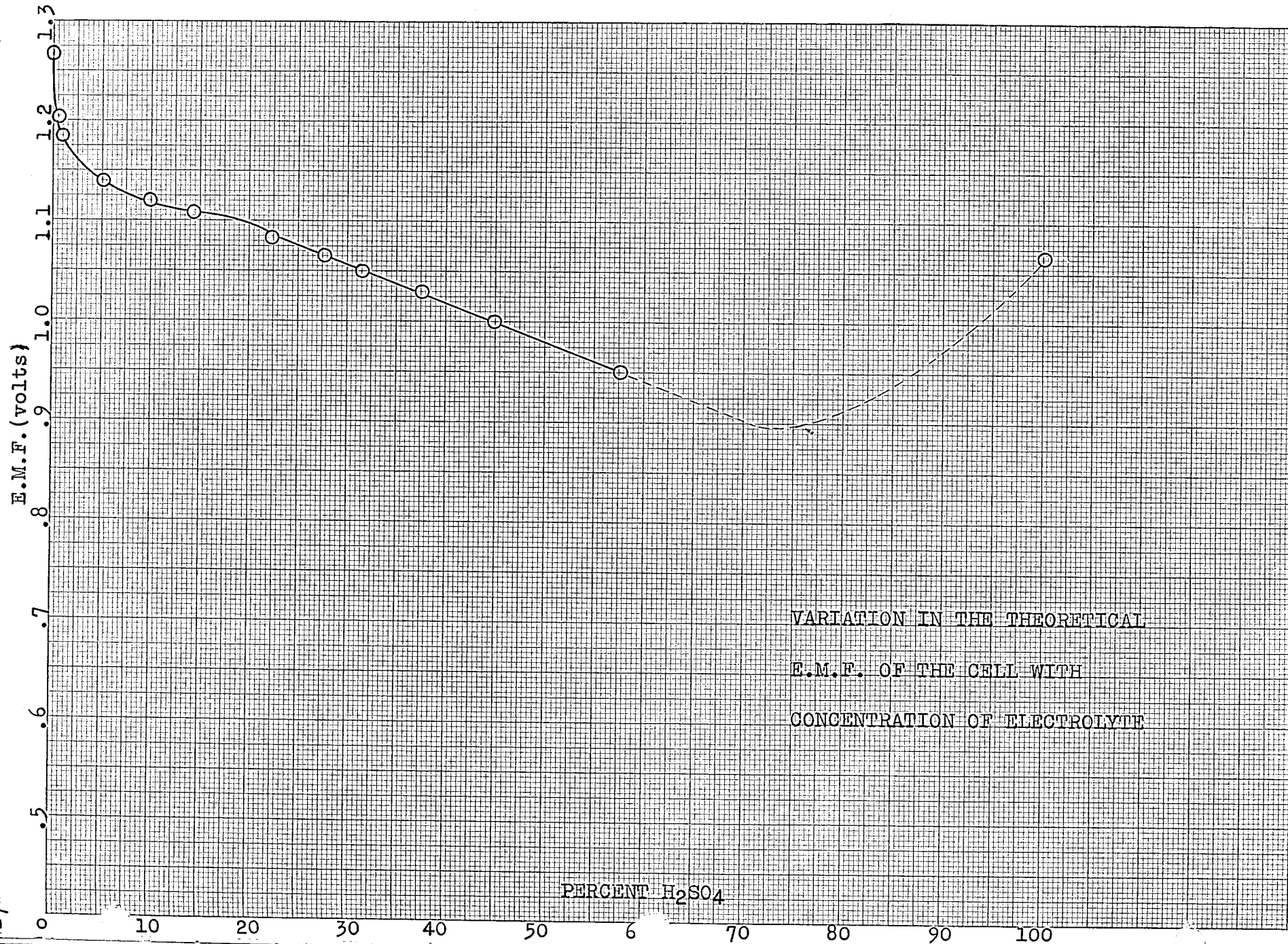
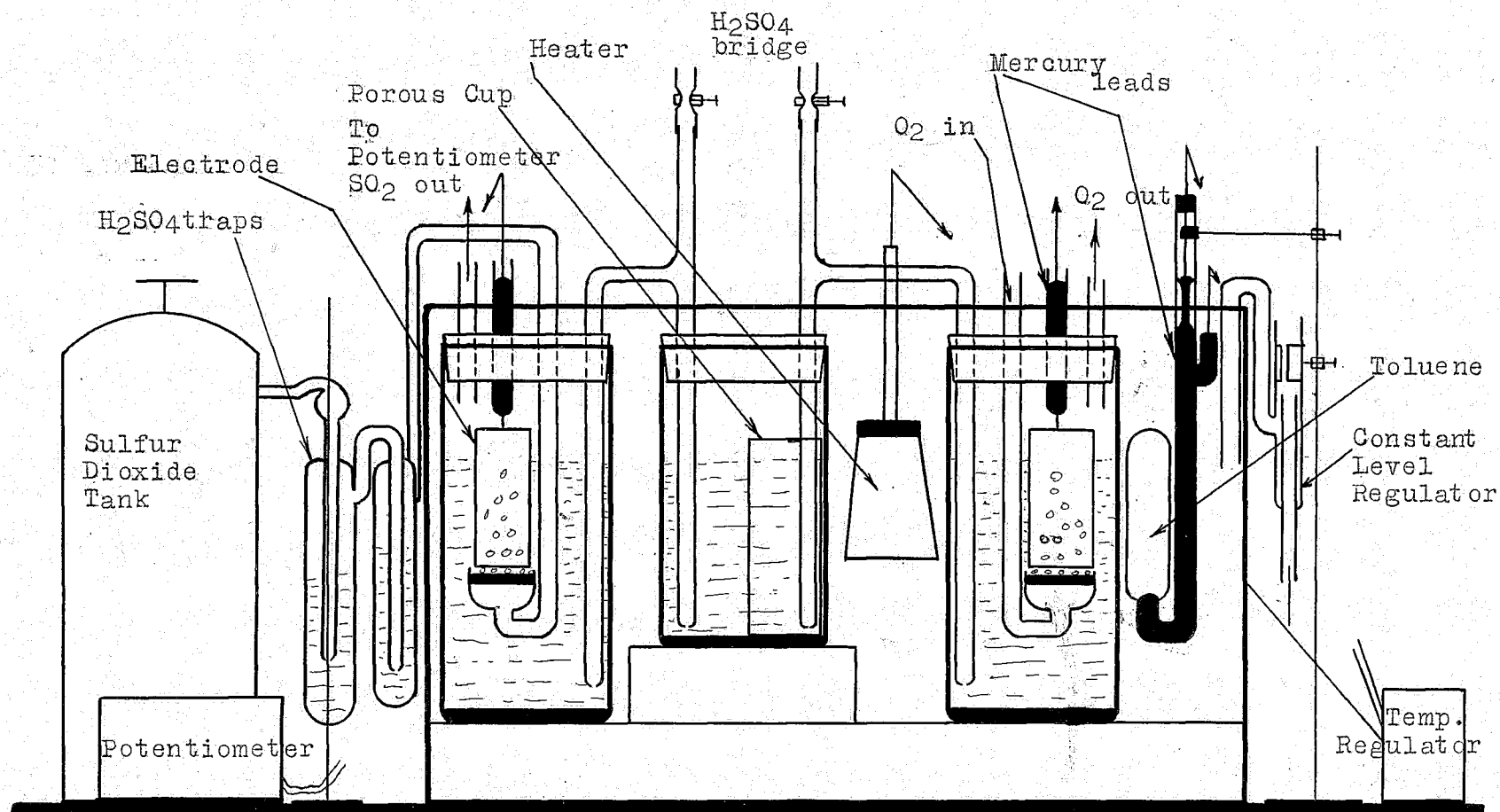


Figure 1



SULFUR DIOXIDE, OXYGEN, SULFURIC ACID CELL

FIGURE 2

the stem of a cylindrical platinized platinum gauze electrode, 2 cm. diameter and 5 cm. high. The potential was read from a potentiometer.

The sulfuric acid bridge consisted of a side arm of capillary tubing from each half cell leading into a third vessel also containing a solution of sulfuric acid.

The whole cell was set in a constant temperature bath provided with a constant level side arm to take care of evaporation. The temperature could be controlled to $\pm .02^{\circ}\text{C.}$ of the desired value.

EXPERIMENTAL PROCEDURES.

Variations of the E.M.F. with Concentration of Sulfuric Acid Showing the Existence of Hydrates.

The set up of the cell for each run was as shown in Fig.I. The platinum electrodes were coated with a layer of platinum black deposited electrolytically from a three percent solution of chloroplatinic acid. A current density great enough to produce a moderate evolution of gas was used and the direction of the current reversed every half minute for approximately one hour or until a fine velvety coating of platinum black appeared on the surface of the electrodes.

The sulfur dioxide and oxygen were obtained from pressure tanks. The desired concentration of sulfuric acid for each run was obtained by diluting C.P. 95% acid

with distilled water. The exact strength of the acid in each case was determined by titrating against a standard NaOH solution (approx. 6 N). The sodium hydroxide was standardized against C.P. oxalic acid. Phenolphthalein was used as indicator.

The two half cells were filled about three quarters full with sulfuric acid, the side arms of which dipped into a single intermediate vessel also filled with sulfuric acid to the same level and of the same strength. The electrodes were only partly immersed in the electrolyte about one-quarter remaining above the surface.

All experiments were carried on at 25°C and atmospheric pressure.

After each run the electrodes were removed and degassed by electrolyzing them at approximately 8 amperes in a concentrated solution of sodium hydroxide for one hour, the direction of the current being reversed every ten minutes for the first fifty minutes, then every minute for the last ten minutes. They were finally washed in boiling distilled water for fifteen minutes.

The measurements obtained are given in Table II. The first and second columns give the normality N and the corresponding percent X of the sulfuric acid and the third column, the measured emf. of the cell. Each row represents a new run. The values of the emf. given in the Table are the values obtained after the sulfur dioxide had bubbled through the cell for approximately 24 hours and the

potential had become steady.

TABLE II.

<u>N</u>	<u>X(%)</u>	<u>E (volts)</u>
.93	3.60	.733 ₉
2.70	12.22	.730 ₁
5.11	21.70	.724 ₀
6.26	26.82	.677 ₄
8.50	33.30	.673 ₁
10.70	40.10	.671 ₀
12.40	44.97	.668 ₄
14.14	49.65	.666 ₂
16.71	56.04	.664 ₀
17.30	57.44	.660 ₀
18.00	59.13	.630 ₄
18.47	60.17	.605 ₅
20.71	63.75	.590 ₅
24.00	69.46	.589 ₇
25.30	74.35	.574 ₁
26.50	76.68	.572 ₀
27.50	78.49	.572 ₀
28.90	81.14	.574 ₁
29.89	83.02	.547 ₅
30.60	84.40	.526 ₂
31.70	86.45	.522 ₀
36.80	97.70	.522 ₅

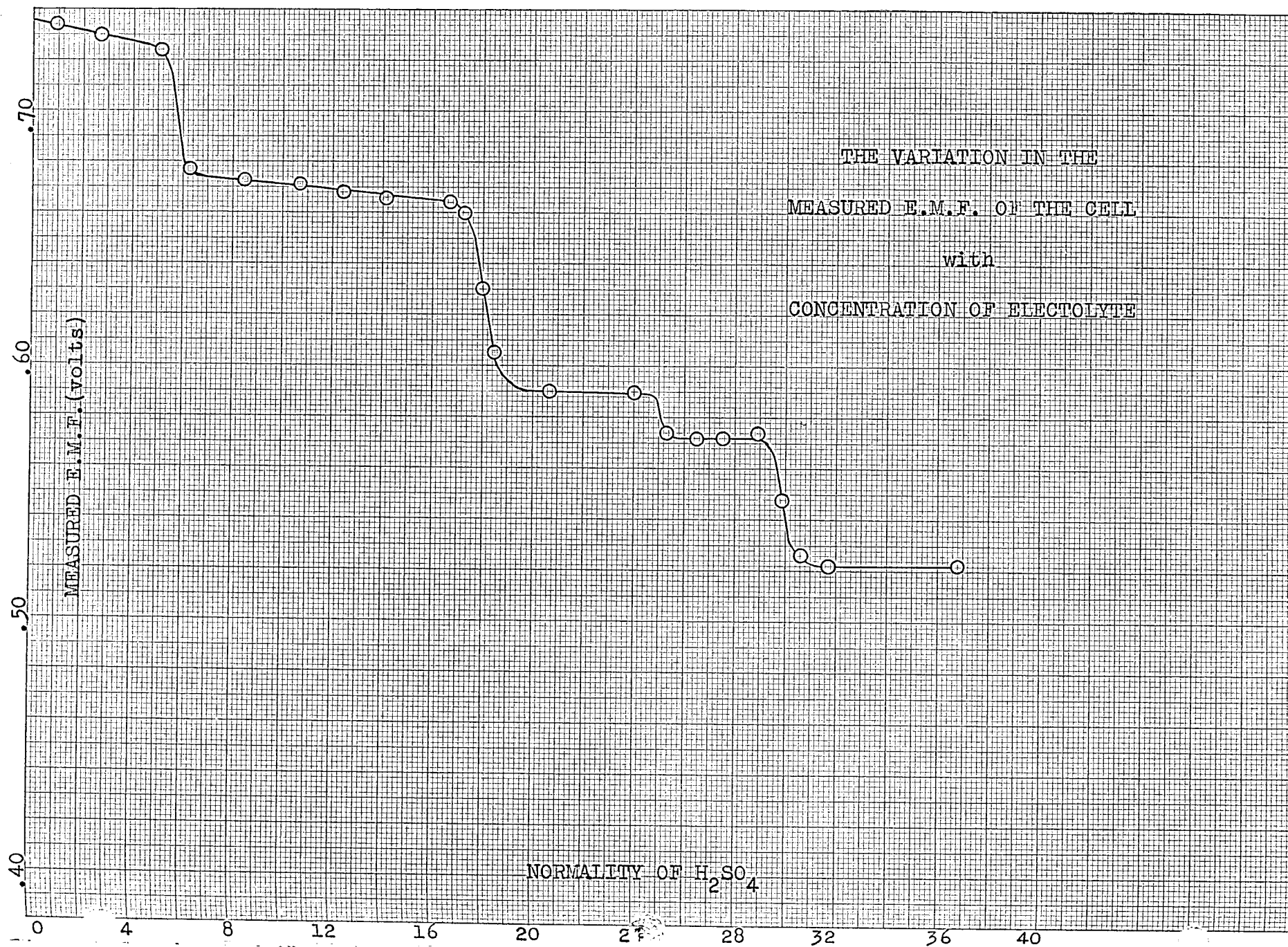


Figure 3

In Fig.III the values of the emf given in Table II are plotted as ordinate. The abscissa is the normality and the corresponding percent acid. The experimental results fall on a stepwise curve. Each of the four steps corresponds on the abscissa to a hydrate of sulfuric acid. The first step at 30.7 N (84.48%) corresponds to $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; the second at 24.6 N (73.13%) to $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; the third at 17.3 N (57.56%) to $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; the fourth at 5.04N (21.40%) to $\text{H}_2\text{SO}_4 \cdot 20 \text{ H}_2\text{O}$. It may also be noted that the slope of each plateau or flat portion of the curve from 36.8 N to 0 N acid increases slightly.

The formation of a hydrate is associated with a comparatively large free energy change and entropy change. From the formula $\Delta G = -nFE$ it necessarily follows that the formation of a hydrate in an electrolytic cell would be associated with a large change in potential. Conversely, the presence of the stepwise increases in potential presumes a large increase in free energy or decrease in the irreversibility (entropy) and hence, substantially indicates the existence of the four hydrates $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 20 \text{ H}_2\text{O}$ at 25°C and atmospheric pressure.

Other experimenters have shown evidence for the existence of three of these hydrates by other means.

Pickering¹³ obtained the hydrate $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ by fusion methods.

Giron¹⁴ found the hydrate $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ by solidifying mixtures

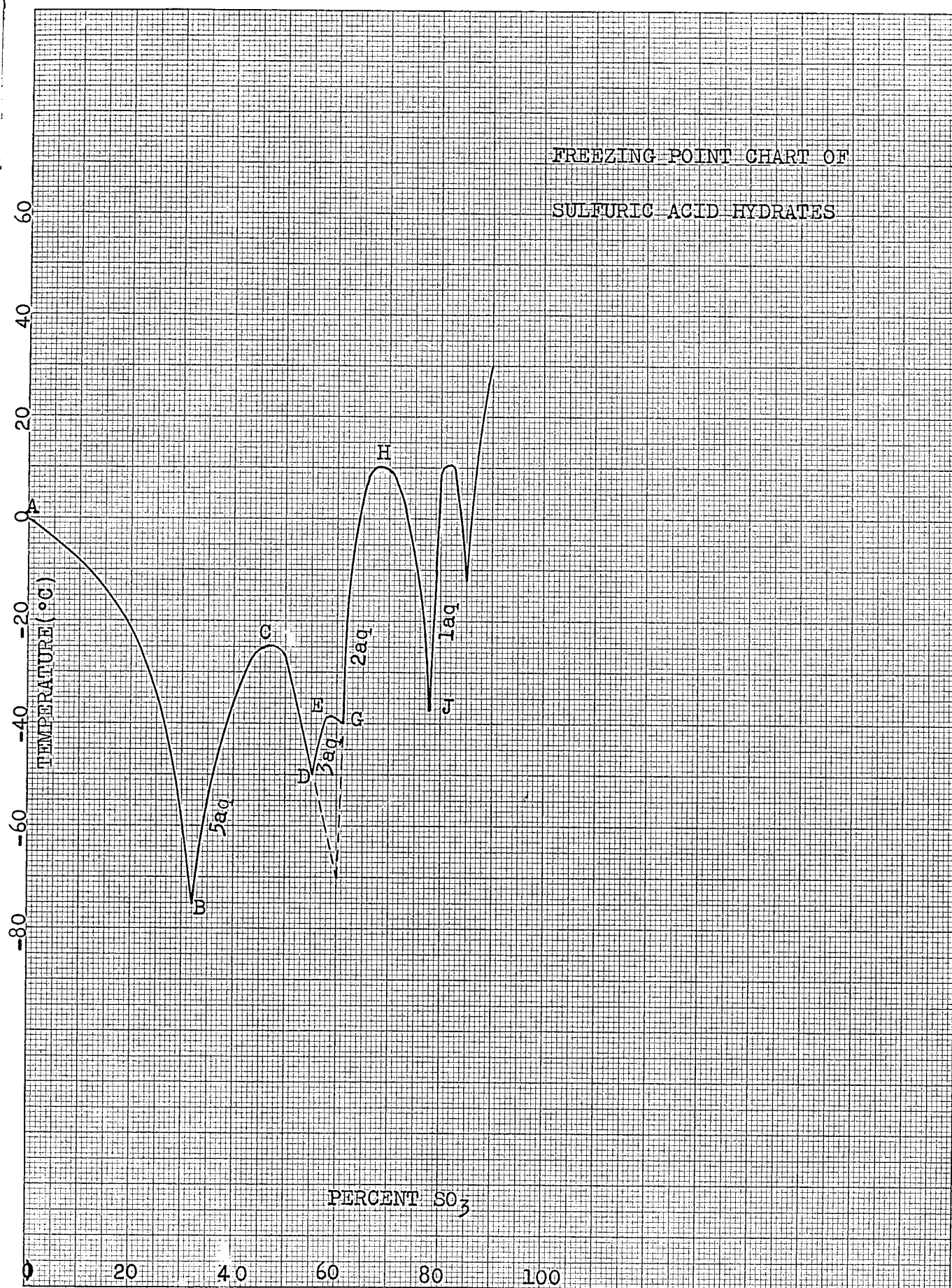


Figure 4

containing from 68 to 70% of the acid. Donk¹⁵ obtained crystalline sulfuric acid monohydrate $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ by freezing methods. Bourgoin¹⁶ indicated the presence of $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ from observations on electrolysing dilute vitriol. The graph given in Abegg's Handbuch der Anorganischen Chemie, IV, 472 (1927) and reproduced in Fig. IV covers all of the hydrates found by the freezing point method. B, D and G are the cryohydrate points and C, E and H the melting points of the hydrates $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ respectively. From B to C, D to E and G to H these respective hydrates solidify out. The existence of $\text{H}_2\text{SO}_4\cdot 20\text{H}_2\text{O}$ is not indicated in the graph. Water supposedly solidified out from A to B. Probably on much closer examination another cryohydrate point and melting point between A and B would have been detected representing $\text{H}_2\text{SO}_4\cdot 20\text{H}_2\text{O}$. Since in such a hydrate it would be difficult to detect the H_2SO_4 in the combined state it may have been overlooked.

The electrolytic method of the writer gives evidence that these hydrates are also stable in solution up to at least 25°C as well as at their freezing points.

It may be of interest to note the large irreversibility or unavailable work content of this cell by comparing the reversible emf of the cell as calculated from free energies (Table I, Fig. I) with the actual measured values obtained from this cell (Table II, Fig. III). In addition, the calculated emf values do not show this step-

wise phenomenon. This may be explained by the fact that the calculated values of the free energy are actually overall values in which the free energy of formation of the hydrate is only one factor.

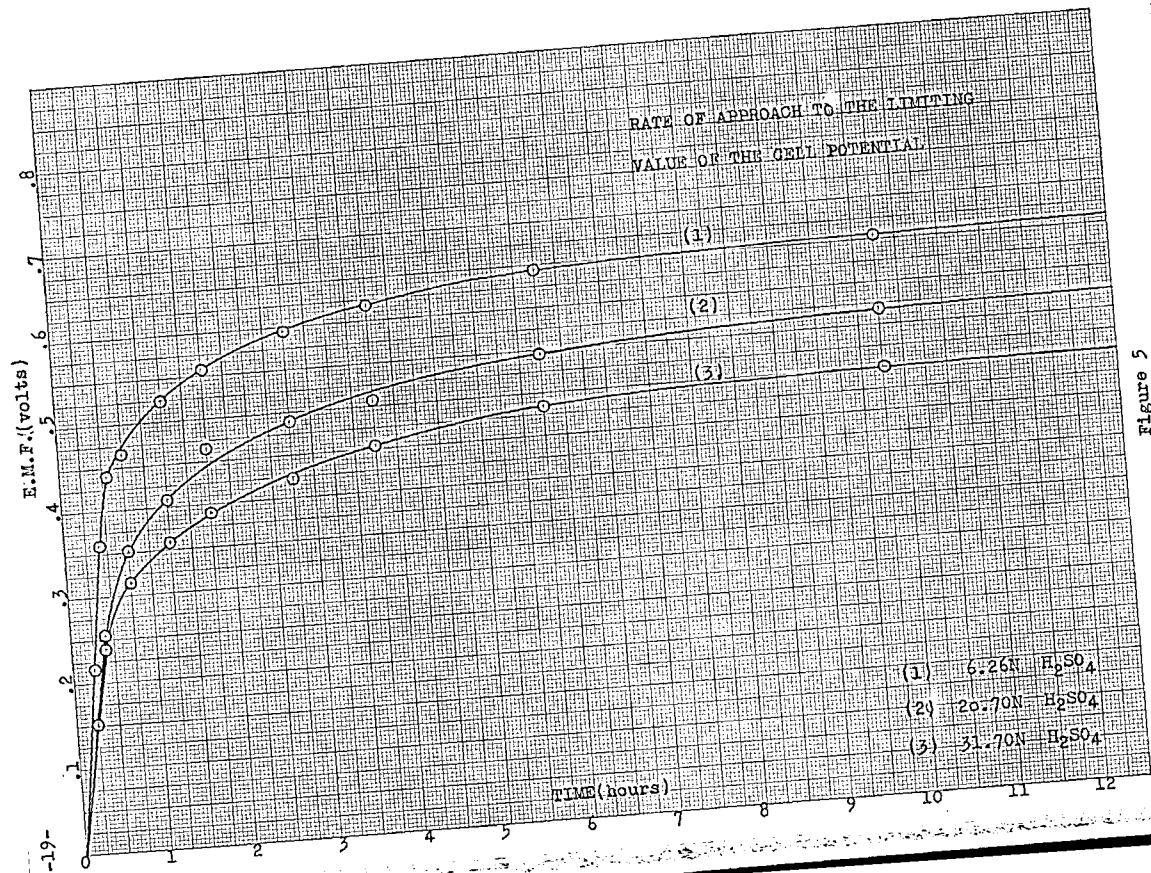
Rate of Approach to the Limiting Value of the E.M.F.

The limiting values of the emf given in Table II are the values obtained after the sulfur dioxide had bubbled through the cell for several hours and the values had become steady. That is to say, a steady state was not approached immediately but required 24 to 30 hours.

Measurements were made of emf with time for several concentrations of sulfuric acid. The measurements for three concentrations are given in Table III. The first column gives the time, the second, third and fourth give the emf measured with 6.26 N, 20.7 N and 31.7 N acid respectively and the fifth the rate of change of emf $\frac{dE}{dt}$ for 6.26 N acid.

TABLE III

<u>t</u>		<u>E(6.26N)</u>	<u>E(20.7N)</u>	<u>E(31.7N)</u>	<u>$\frac{dE(6.26N)}{dt}$</u>
<u>hours</u>	<u>mins.</u>	<u>volts</u>	<u>volts</u>	<u>volts</u>	<u>volts/hour.</u>
	0	0	0	0	.872
	15	.217	.150	.156	.868
	25	.360	.255	.240	.858
	30				.533
	34	.440			
	40				.191
	45	.465	.352	.315	
1	00				.104
1	15	.525	.410	.359	
1	30				.066
1	45	.558	.465	.380	
2	15				.038
2	45	.596	.489	.424	
3	15				.022
3	45	.618	.508	.453	
4	45				.013
5	45	.644	.547	.486	
7	45				.003
9	45	.655	.569	.499	
13	15				.001
20	45	.675			
21	45				.0009
22	45	.6768	.590 ₅	.521 ₆	
34	45				.00002
46	45	.6774	.590 ₅	.522 ₀	



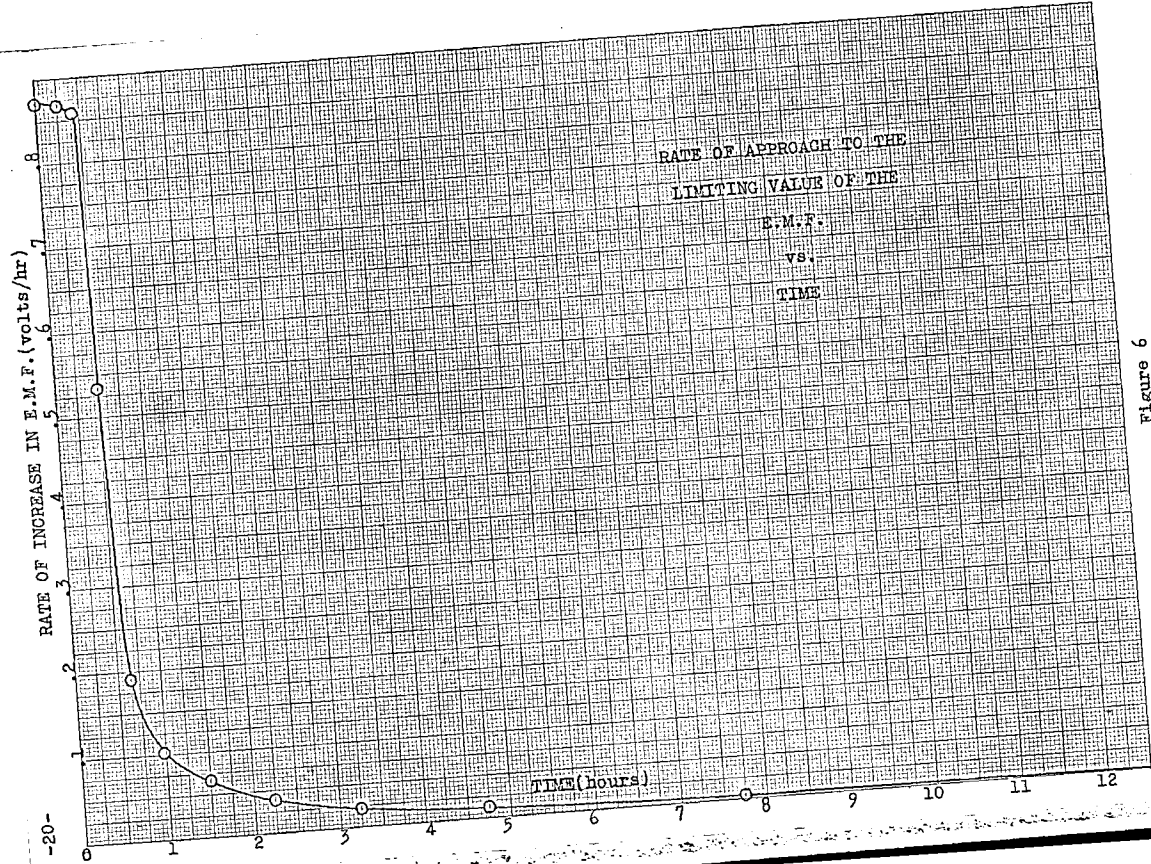


Figure 6

In Figures V and VI the values of the emf and the rate of change of emf respectively are plotted as ordinates against time as abscissa. It was deduced from a comparison of the results that the rate of change of emf with time varied only slightly over large ranges of concentration as long as the rate of introduction of sulfur dioxide into the cell was consistent for the different concentrations. From a close examination of the curves it was assumed that the absorbitivity of the electrodes was very high at first, approaching a straight line relationship but decreased rapidly as the electrodes approached saturation.

Figures V and VI give only a qualitative picture since the rate of introduction of sulfur dioxide varies the clope of the straight line portion of the curves although leaving the general shape the same.

Effect of the Rate of Sulfur Dioxide and Oxygen into the
Cell on the Limiting E.M.F.

Although the rate at which equilibrium is attained is affected somewhat by the rate of sulfur dioxide into the cell the absolute value of the emf after a limiting condition is reached, is almost independent of the rate. For example, on increasing the rate of sulfur dioxide into the cell from 120 bubbles per minute to over 240 bubbles per minute, the limiting value of the emf (after several hours) changed from .724₀ to .725₁. This value returned to .724₁ on decreasing the rate back to 120 bubbles per minute. Decreasing the rate still further to 20 bubbles per minute, cut the emf to .723₀.

which returned to .724₀ on increasing the rate back to 120 bubbles per minute.

Oxygen acted differently. Increasing the rate from 60 bubbles per minute to 4 times that value, caused the limiting value of the emf to drop from .724₀ to .723₁ while increasing the rate to well over 8 times caused the emf to drop down to .720₁. On decreasing the rate back to 60 bubbles per minute, the emf went up to .723₆ while shutting off the O₂ inlet caused no perceptible change. Hence, it can be assumed that at low rates the emf is independent of the rate while at greater rates, oxygen has a polarizing effect.

Variation of E.M.F. with Temperature.

Measurements were made using 5.27 N acid at temperatures ranging from 15°C. to 45°C. The measurements are given in Table IV.

TABLE IV.

<u>T (°C.)</u>	<u>E (volts)</u>
15	.740 ₀
25	.723 ₀
35	.693 ₄
45	.629 ₇

In Fig.VII the values of the emf from Table IV are plotted as ordinates against temperature as abscissa. The results fall on a smooth curve. An asymptotic curve approaching $E = .755$, seems to result on extrapolation, to lower temperatures.

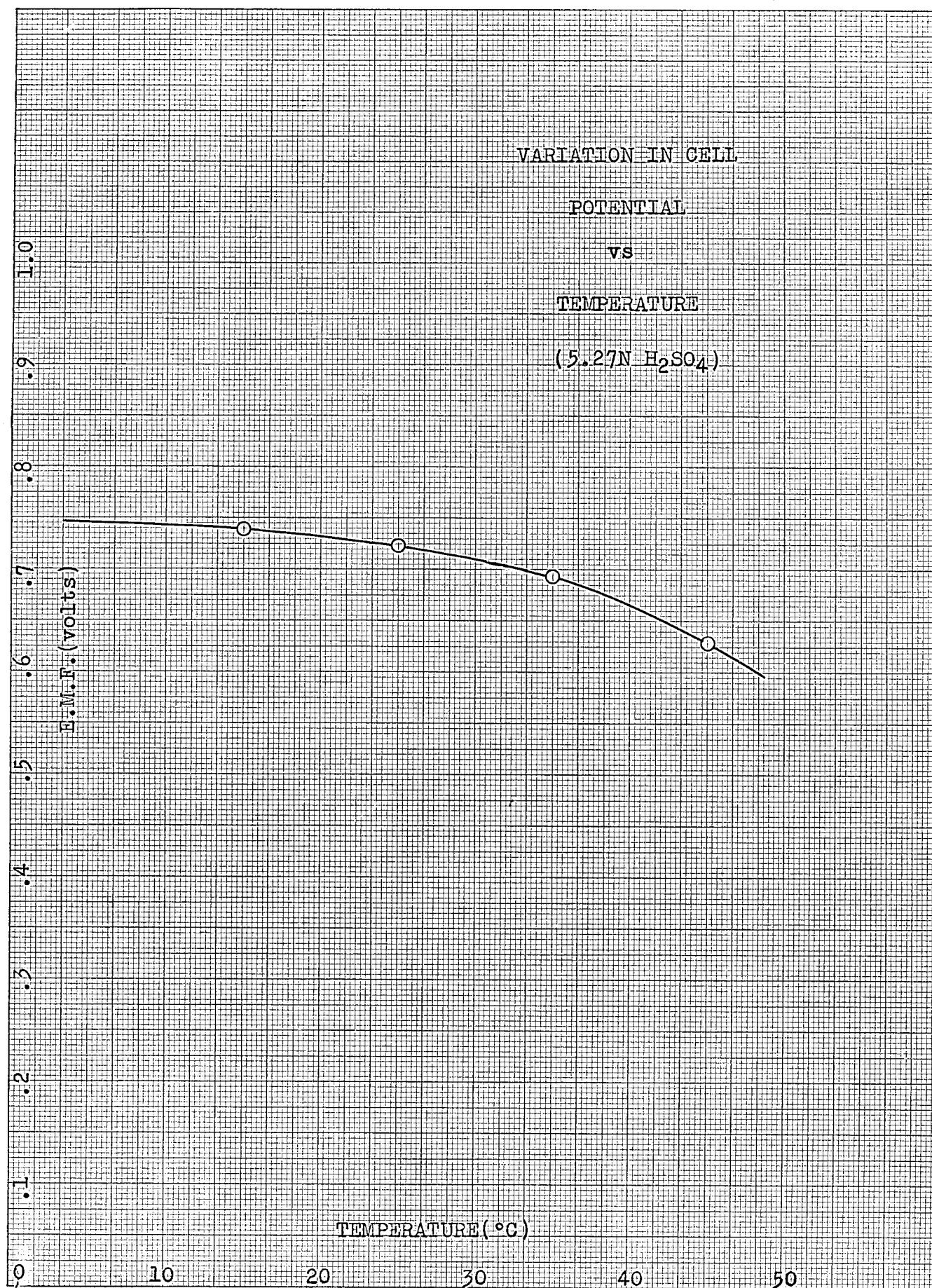


Figure 7

CONCLUSION

It was shown from the experiments conducted throughout this research that the utilization of the free energy of sulfur dioxide in the form of electrical energy has considerable possibilities.

Platinized platinum electrodes alone were used throughout the investigation. Although they gave good results it should be possible to decrease the irreversibility and approach the theoretical emf as calculated from free energies more closely with more reversible electrodes¹⁷. Certain possibilities are the use of platinum black on an asbestos carrier, iridium black on platinum or lead electrodes.

A further study into the stepwise phenomenon of Fig.III may unveil some conclusive facts regarding the hydrate formation already proposed and lay the basis for a theoretical explanation of this phenomenon as well as a more thorough knowledge of sulfuric acid itself. A suggestion would be to study each half cell separately against a standard cell, such as the hydrogen electrode.

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17. Wyld, W., Sulfuric Acid and Sulfur Dioxide.

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