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ENCLOSURE (B)

ENCLOSURE (B)1

STUDIES ON THE SYNTHESIS OF $(NH_4)_2S_2O_8$ BY PbO_2 ANODE

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

A 15-20% $(NH_4)_2S_2O_8$ solution is produced with a current efficiency of ca. 80% by decreasing the anode current density, increasing the current concentration*, changing the concentration of $(NH_4)_2SO_4$ and H_2SO_4 in the electrolyte, and adding HF to the electrolyte. On cooling the electrolyted solution to ca. 0°C., $(NH_4)_2S_2O_8$ crystals (purity of 99%) are prepared with a yield of ca. 70%.

I. DETAILED DESCRIPTION

A. Electrolysis of Ammonium Persulfate

Details of the PbO_2 anode and the electrolysis vessel are shown in Figure 1(B)2. Various electrolyte compositions and conditions of electrolysis were tried. In each case, the current efficiency and yield were obtained and recorded. Details of the conditions and results of each experiment are given below.

1. The Effect of Current Density and Addition of Fluorides. In the case of Pt anode, the current density is as high as 100 amp/dm^2, but for PbO_2 anodes this is too high to obtain good current efficiency. The current density in this case must be limited to ca.10-20 amp/dm^2 as may be seen in the following experiment.

The Composition of Electrolyte:

Anode electrolyte: $(NH_4)_2SO_4$, 28gm H_2SO_4, 30gm dissolved in water to 100cc total volume.

Cathode electrolyte: The same composition as anode electrolyte.

Electrolysis Conditions: Volume of anode electrolyte, 100cc current, 2.5 amp; current density of anode, D_A, 5 - 80 amp/dm^2, current concentration in anode electrolyte, C_A, 2.5 amp/100cc; temperature of bath, 15°C; time, 1 hr.

Results are given in Table I(B)1 and are plotted in Figure 2(B)1.

From this data, a current density, D_A, between 5 and 20 Amp/dm^2, appears to be adequate.

2. The Effect of Electrolyte Composition on Yield of $(NH_4)_2S_2O_8$. The relationship between current efficiency and composition of electrolyte was studied in the following tests:

a. The effect of concentration of H_2SO_4. H_2SO_4 is necessary in the electrolyte, but its concentration should not exceed 40% or it will accelerate the decomposition of synthesized $(NH_4)_2S_2O_8$. Results are shown in Table II(B)1

From this data, it appears that the concentration of H_2SO_4 in the electrolyte should be 20-30 gm/cc.

b. The effect of concentration of $(NH_4)_2SO_4$. The concentration of $(NH_4)_2SO_4$ affects the current efficiency remarkably. The results are shown in Table III(B)1.

The $(NH_4)_2SO_4$ saturated solution gives the best yield and the ~~highest current efficiency.~~

c. The effect of the quantity of HF added. Varying the quantity of HF added to the electrolyte, the optimum quantity was determined to be 1.0-1.5gm/100cc. Results are given in Table IV(B)1 and are plotted in Figure 3(B)1.

3. The Effect of Impurities in Electrolyte. When a PbO_2 anode is used, the effect of impurities in the electrolyte is greater than when a Pt anode is used. Hence, pure H_2SO_4, $(NH_4)_2SO_4$, and HF must be used as raw materials. For instance, the electrolyte made from industrial H_2SO_4 gives only a current efficiency of 10% even under the best conditions as described previously. The impurities are assumed to be Fe^{++}, Fe^{+++}, Cu^{++} and other metallic ions.

4. The Effect of Increasing the Quantity of Added HF. From precise measurements, the remarkable rise of anode decomposition voltage by the addition of HF was observed. Therefore, it was attempted to determine the effect of increasing quantities of added HF. The electrolysis conditions of the experiment and a summary of the results were as follows:

Anode Electrolyte (107cc)

$(NH_4)_2SO_4$	61gm
H_2SO_4	9.6gm
HF	5.0gm
H_2O	54.4gm

Cathode Electrolyte

$(NH_4)_2SO_4$ saturated solution 32cc.

Electrolysis Conditions

Current	4 Amp
D_A	10 Amp/dm^2
CA	4 Amp/107cc
Temp	25-30°C
Time	1 hr

Results

$(NH_4)_2S_2O_8$ produced	11.36gm
Concentration of $(NH_4)_2S_2O_8$	10.82gm/100cc
Current Efficiency	66.6%

The current efficiency was augmented exceedingly by the increased quantity of HF. Increasing the quantity of HF five times to 5gm HF/100cc gave a current efficiency of ca. 67%. Further increasing the quantity did not effect appreciably the current efficiency.

5. The Effect of Concentration of H_2SO_4 in Electrolyte Containing an Increased Quantity of HF. Fixing the quantity of HF at 5-6gm/100cc, the effect of various concentrations of H_2SO_4 and $(NH_4)_2SO_4$ on current efficiency was examined. The effect of varying the electrolyte concentration is shown in Table VI(B)1 Figure 4(B)1.

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~~From these data the following electrolyte appears to be the best~~ composition:

100cc electrolyte containing:

$(NH_4)_2SO_4$	58.0gm
H_2SO_4	8.0 - 12.0gm
HF	5.5 - 6.0gm

B. Crystallization of Ammonium Persulfate

By electrolysis, a solution containing 15 - 20% $(NH_4)_2S_2O_8$ is obtained, and when this solution is cooled to ca. 0°C, $(NH_4)_2S_2O_8$ crystals deposit. Typical data pertaining to the crystallization of $(NH_4)_2S_2O_8$ is as follows: A 15.5% $(NH_4)_2S_2O_8$ solution (87.0cc) which contained 13.5gm of $(NH_4)_2S_2O_8$ was cooled to 4°C, and the deposited $(NH_4)_2S_2O_8$ crystals were filtered off from the mother liquor. The yields were as follows:

Weight of wet $(NH_4)_2S_2O_8$ crystals	12.4gm
Purity of wet $(NH_4)_2S_2O_8$ crystals	78.7%
Weight of dry $(NH_4)_2S_2O_8$ crystals	9.7gm (Purity of 99%)
Volume of filtrate	77cc
Concentration of $(NH_4)_2S_2O_8$ in filtrate	5.13%
Weight of $(NH_4)_2S_2O_8$ in filtrate	3.9gm
Yield of $(NH_4)_2S_2O_8$ crystals from electrolyte	71.8%

The filtrate could be electrolyzed again after adjusting its composition.

C. Yields and Operating Difficulties

1. Total Yields. By electrolysis, 16gm of $(NH_4)_2S_2O_8$ in solution are obtained from 100cc of the electrolyte containing $(NH_4)_2SO_4$ 58gm H_2SO_4 8.5gm and HF 6.0gm per 6 ampere-hours and 11.6gm of $(NH_4)_2S_2O_8$ crystals deposit from it on cooling. The total yield is ca. 42%. The mother solution can be separately electrolyzed. The conditions of the process which proved to be best are given in Figure V(B)1.

2. Operating Difficulties

a. HF corrodes the porcelain diaphragm and is consumed gradually, causing the porcelain to interfere with the electrolysis.

b. PbO_2 is slowly attacked by HF, and contaminates the electrolyte considerably. Accordingly, the electrolyte must be filtered before cooling to obtain pure white $(NH_4)_2S_2O_8$ crystals.

II. CONCLUSIONS

For the electrolytic synthesis of $(NH_4)_2S_2O_8$, a PbO_2 anode can be substituted for a Pt anode under the proper conditions.

The addition of HF to the electrolyte presents problems, since the materials for the electrolysis vessels and diaphragms are ordinarily made of porcelain, which is attacked by HF.

When HF is present in the electrolyte, $(NH_4)_2S_2O_8$ must be immediately separated from the solution by cooling.

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PbO_2 is gradually attacked by HF. Therefore, the contaminated electrolyte must be filtered before cooling to obtain stable and pure $(NH_4)_2S_2O_8$ crystals.

The difficulty of regulating the composition of the mother liquor, the problem of materials for the apparatus, and the decomposition of PbO_2 require still further studies before this process can be applied to industry.

Table I(B)1
EFFECT OF CURRENT DENSITY ON YIELD OF AMONIUM PERSULFATE

	Number						
	1	2	3	4	5	6	7
D_a (Amp/dm^2)	80	60	40	20	15	10	5
$(NH_4)_2S_2O_8$ Produced (gm)	0.22	0.35	0.42	0.62	0.80	0.83	0.81
Current Efficiency (%)	2.1	3.3	4.0	5.8	7.5	7.8	7.6

Table II(B)1
EFFECT OF VARYING CONCENTRATIONS OF H_2SO_4
ON YIELD OF $(NH_4)_2S_2O_8$

No.	$(NH_4)_2SO_4$ sat. sol.	Water	H_2SO_4	$(NH_4)_2SO_4$	Conc. $(NH_4)_2S_2O_8$ (gm/100cc)	Current Efficiency
1	in water	63.7	0	53.7	0.606	9.76
2	in 20% H_2SO_4	57.3	14.3	53.0	2.591	41.74
3	in 30% H_2SO_4	55.1	23.1	49.7	2.809	45.25
4	in 40% H_2SO_4	50.9	33.0	47.6	2.899	46.70
5	in 50% H_2SO_4	43.2	43.2	52.6	2.734	44.04

Note: 1.6gm HF present in all cases

Effect of varying concentration of H_2SO_4 on Yield of $(NH_4)_2S_2O_8$
Anode Electrolyte: Volume, 100cc; Composition is shown below
Cathode Electrolyte: The same as anode electrolyte
Electrolysis Conditions:

Current .... 3.5 Amp
D_A .... 10Amp/dm^2
C_A 3.5Amp/100cc
Temp. .... 25-28°
Time .... 1 hr

Table III(B)1
EFFECT OF VARYING CONCENTRATION
OF $(NH_4)_2SO_4$ ON YIELD OF $(NH_4)_2S_2O_8$

No.	Compositions of Electrolyte 100cc of Each Anode Electrolyte Contains (gm).				Yield and Current Efficiency		
					$(NH_4)_2S_2O_8$		Current efficiency (%)
	Water	H_2SO_4	$(NH_4)_2SO_4$	HF	Produced (gm)	Concen. (gm/100cc)	
1	60.2	15.0	55.5(Sat. Sol)	2.0	14.43	14.43	32.3
2	65.8	16.5	46.1	2.0	12.37	12.37	27.7
3	71.1	17.8	35.6	2.0	9.74	9.74	21.8

Anode Electrolyte: $(NH_4)_2SO_4$ dissolved in 20% H_2SO_4 The composition is given below.
Cathode Electrolyte. $(NH_4)_2SO_4$ saturated solution.
Electrolysis Conditions:
Current .... 3.5Amp.
D_A .... 10Amp/dm^2
C_A 3.5Amp/100cc
Temp. .... 25-30°C
Time .... 3 hr

Table IV(B)1
EFFECT OF VARYING CONCENTATION OF HF ON YIELD OF $(NH_4)_2S_2O_8$

HF(gm)	$(NH_4)_2S_2O_8$ Produced (gm)	Concentration of $(NH_4)_2S_2O_8$ (gm/100cc)	Current Efficiency (%)
1.50	8.02	9.22	34.2
0.75	7.96	9.04	34.0
0.50	8.04	9.24	34.3
0.35	6.28	7.21	26.8
0.25	7.06	8.12	30.2
0.10	5.24	6.02	22.4

Anode Electrolyte: $(NH_4)_2SO_4$ sat'd in 20% H_2SO_4 soln. 90cc.
Cathode Electrolyte: $(NH_4)_2SO_4$ saturated aqueous solution, 30cc
Electrolysis Conditions

Current .... 5.5Amp.
D_A ....10 Amp/dm^2
C_A 5.5Amp/90cc
Temp. .... 25-28°C
Time .... 1 hr

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Table V(B)1
EFFECT OF VARYING ELECTROLYTE CONCENTRATIONS
ON YIELD OF $(NH_4)_2S_2O_8$ (AMMONIUM PERSULFATE)

No.	Composition of Electrolyte (gm)				Yield and Current Efficiency		
					$(NH_4)_2S_2O_8$		Current efficiency (%)
	H_2SO_4	$(NH_4)_2SO_4$	H_2O	HF	Produced (gm)	Concen. (gm/100cc)	
1	2.8	56.5	64.8	5.2	9.96	10.19	58.6
2	8.4	59.1	59.6	5.6	11.25	11.48	66.1
3	11.5	58.0	58.1	5.3	11.00	11.23	64.6
4	14.7	58.3	56.2	5.1	11.96	12.00	68.0
5	18.3	56.4	54.7	5.5	10.48	10.70	61.5

Anode Electrolyte: volume. 100cc
Cathode Electrolyte: $(NH_4)_2SO_4$ saturated solution 32-35cc
Electrolysis Conditions:

Current 4Amp
D_A .... 10Amp/dm^2
C_A 4Amp/100cc
Temp. .... 20-30°C
Time .... 1 hr

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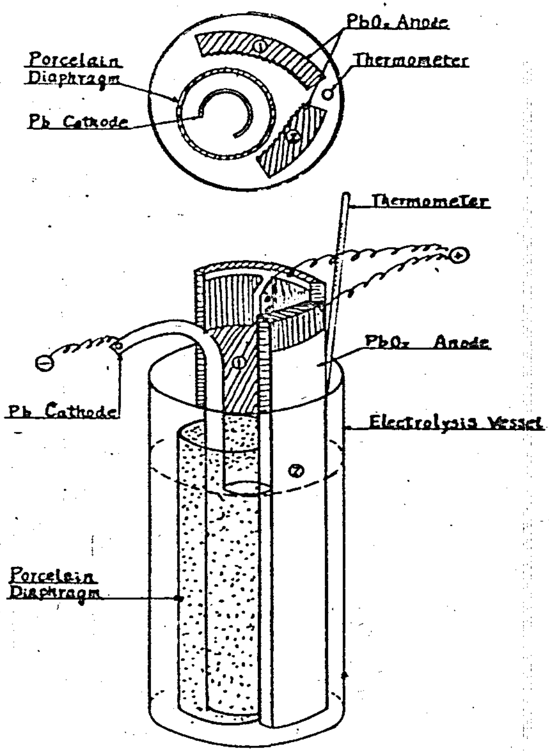

(Dimensions)

- Electrolysis Vessel
  - Internal Diameter — 6.0 cm
  - Height — 12.0 cm
- Porcelain Diaphragm
  - Internal Diameter — 2.8 cm
  - Height — 9.2 cm
  - Thickness — 1.0~1.5 mm
- PbO_2 Anode
  - Height (=Depth of Electrolyte)
    - ① 8.4 cm
    - ② 8.4 cm
  - Width
    - ① 4.3 cm
    - ② 2.2 cm
  - Thickness
    - ① 0.5~1.0 cm
    - ② 0.7~0.9 cm

PbO_2 ANODE

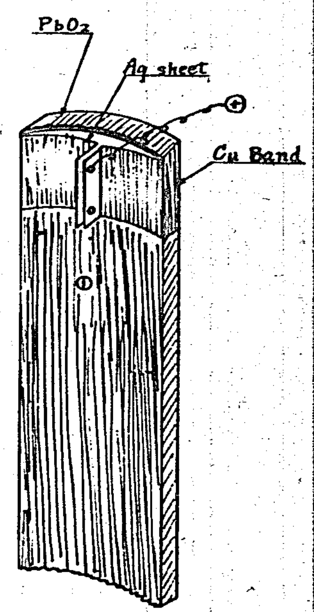

Figure 1(B)1
DRAWING OF ELECTROLYSIS VESSEL AND PbO_2 ANODE

ENCLOSURE (B)1

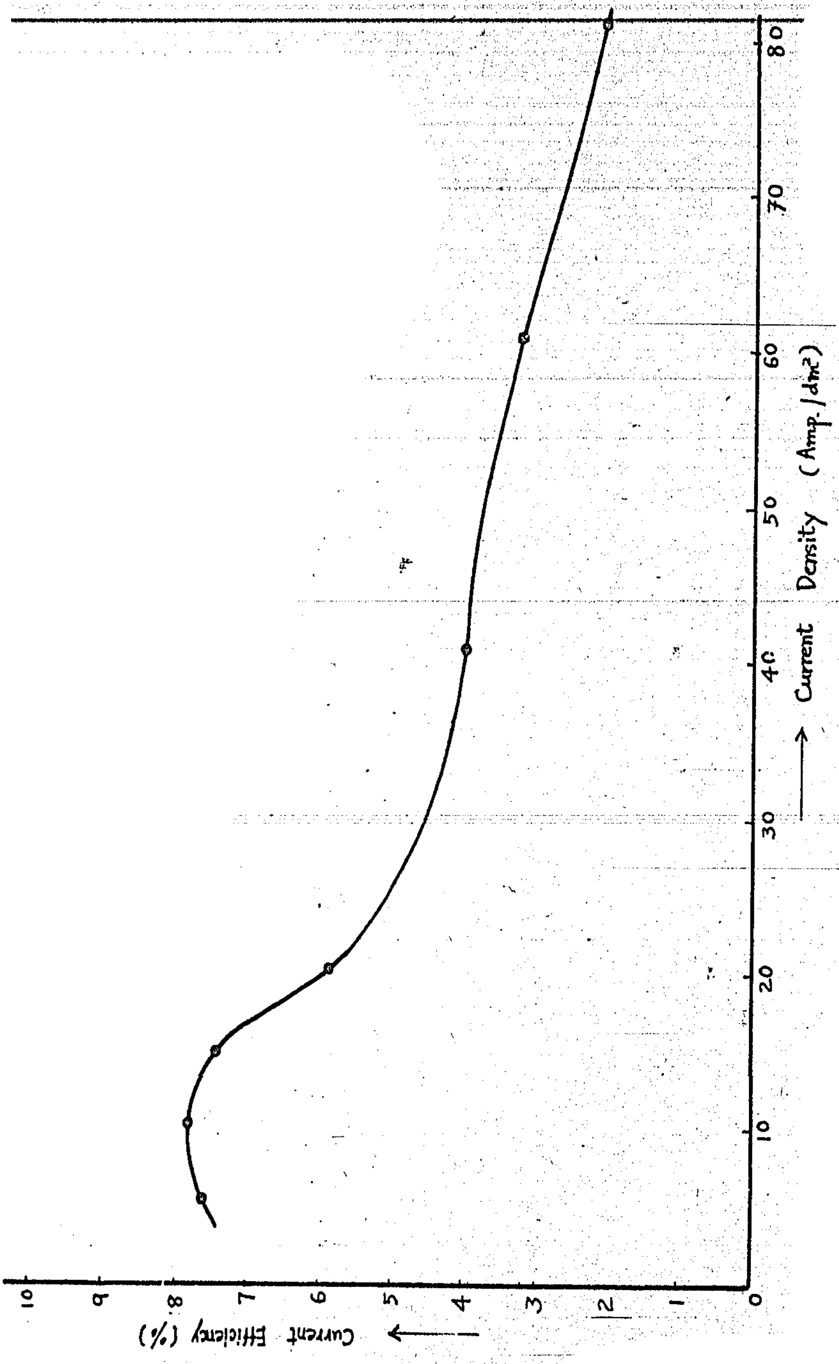

Figure 2(B)1
CORRELATION CURVE BETWEEN
CURRENT DENSITY AND CURRENT EFFICIENCY

ENCLOSURE (B)1

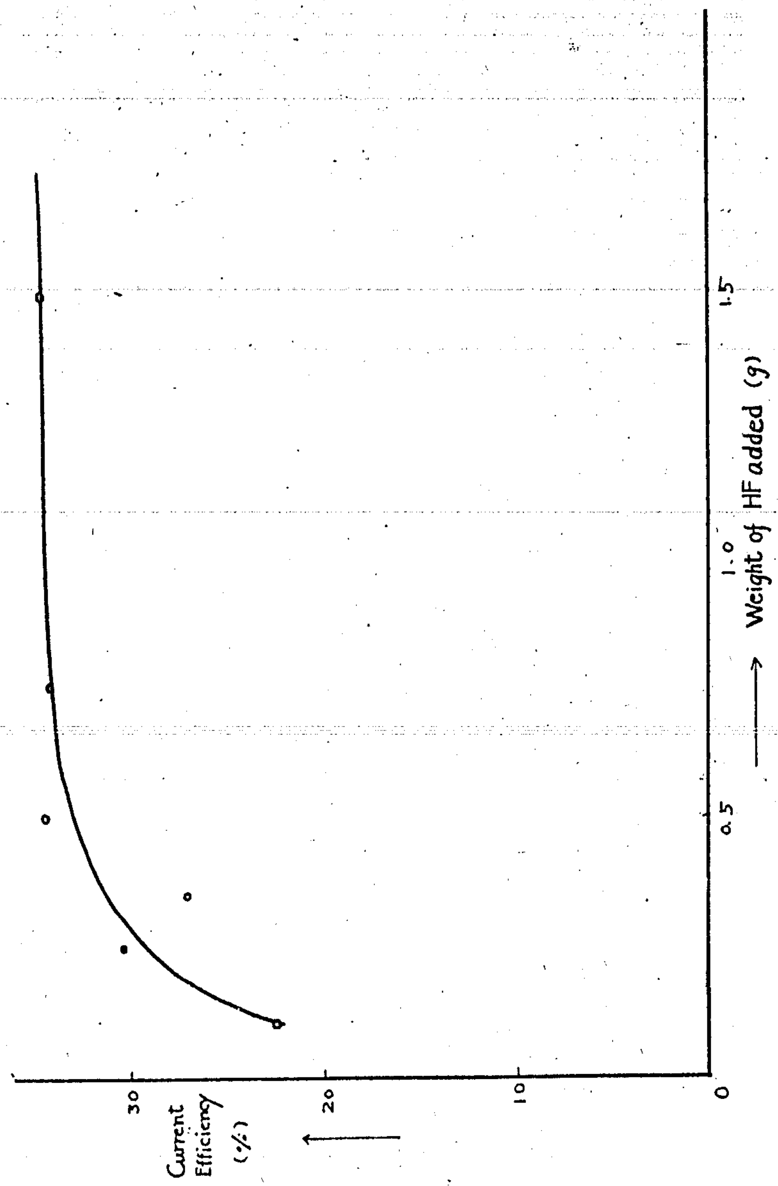

Figure 3(E)1
CORRELATION CURVE BETWEEN
THE QUANTITY OF ADDED HF AND CURRENT EFFICIENCY

ENCLOSURE (B)1

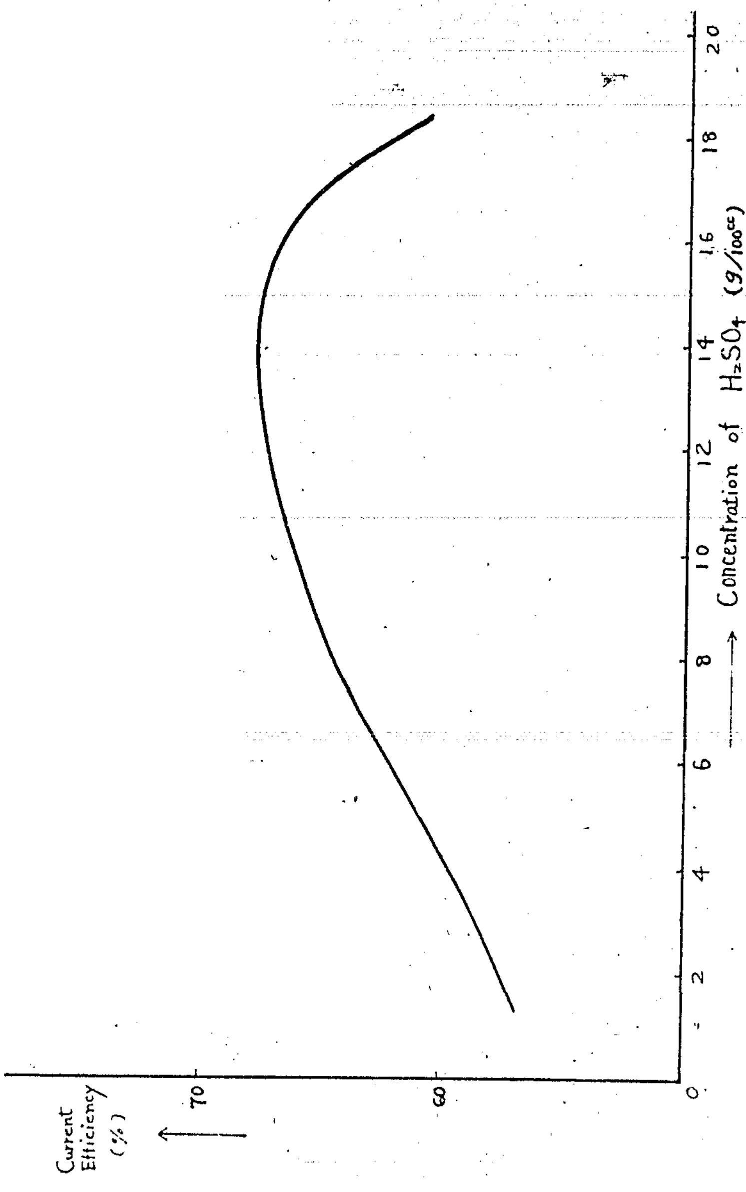

Figure 4(B)1
CORRELATION CURVE BETWEEN
THE CONCENTRATION OF H_2SO_4 AND CURRENT EFFICIENCY

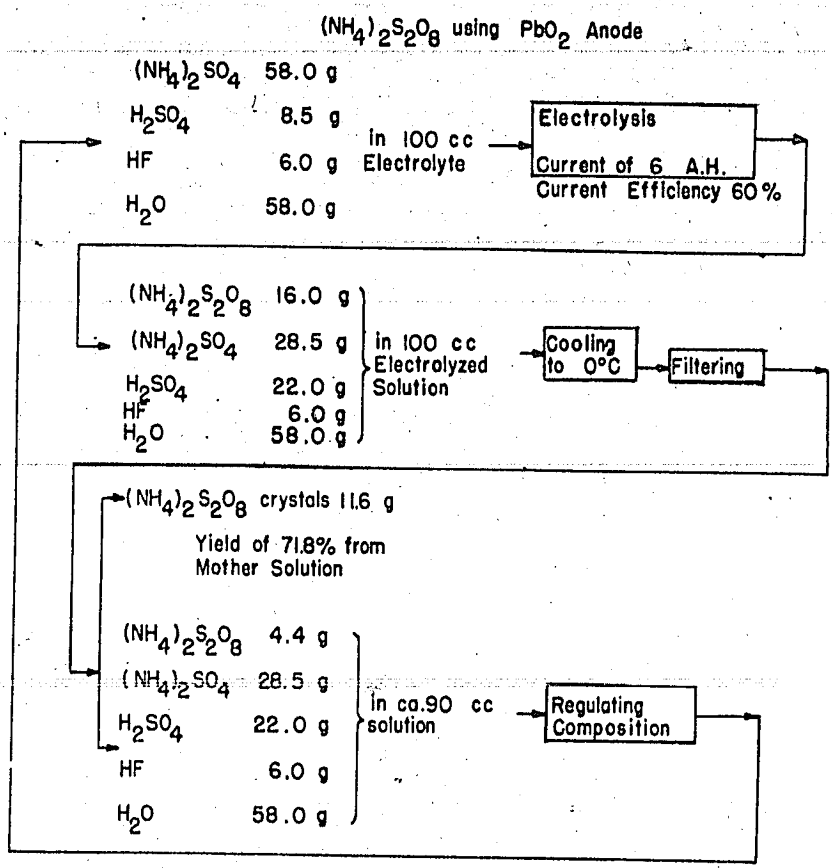

Figure 5(B)1

OPTIMUM CONDITIONS FOR PREPARATION OF $(NH_4)_2S_2O_8$ USING PbO_2 ANODE