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THE RECOVERY OF SULPHURIC ACID IN THE MANUFACTURE OF SODIUM FLUOSILICATE BY USING SODIUM SULPHATE

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Fluosilicic acid, the main by-product in the superphosphate industry, is receiving growing attention from the manufacturers. Sodium Fluosilicate is normally manufactured by treating fluosilicic acid with a solution of common salt, whereby the sodium fluosilicate is precipitated

$$H_2SiF_6 + 2NaCl = Na_2SiF_6 + 2HCl$$

The resulting hydrochloric acid whic is of low concentration and contains a lot of silica in suspension and in solution, has to be neutralized before discharge.

In our factory exists a hydrochloric acid plant which produces this acid by the action of sulphuric acid on common salt, resulting in by-product sodium sulphate. The object of the present work is to investigate the possibility of using this sodium sulphate in the production of sodium fluosilicate according to the reaction :

$$H_2SiF_6 + Na_2SO_4 = Na_2SiF_6 + H_2SO_4$$

whereby the resulting sulphuric acid can be used in the manufacture of superphosphate. Our aim is to obtain an acid with the highest possible content of sulphuric acid and with minimum content of fluosilicic acid, which gives rise to suffocating fumes during mixing with concentrated acid.

The reaction between fluosilicic acid and sodium sulphate solutions has first been studied in the laboratory. Four different concentrations of fluosilicic acid were prepared, which represent the range of available concentrations in the scrubbing plant. Fixed amounts of each concentration (200 mls.) were treated with rising amounts of sodium sulphate solution, the concentration of which were kept constant in all cases. The solutions were well mixed with a mechanical stirrer for 15 minutes and then the fluosilicate was allowed to settle for 1 hour. The specific gravity of the clear solutions was measured together with the temperature. Solutions were filtered and samples taken and analysed for H_2SO_4 and H_2SiF_6.

Tables from 1 to 4 include the results of reaction between sodium sulphate solution of specific gravity 1.153 at 20°C and fluosilicic acid solutions of different concentrations. All experiments were carried out at a temperature of 20°C ± 0.5°C.

Control of the reaction

It has been possible to control the reaction by making use of the relation between the quantity of sulphate added and the specific gravity of the final solution. As can be seen in figure 1, the specific gravity of sulphuric acid solution after precipitation of sodium fluosilicate decreases with an increase in the sodium sulphate used till a minimum value beyond which it starts to rise due to excess sodium sulphate. This minimum value was found to correspond approximately to a mole ratio of 0.9

The four curves in figure 1 represent the changes in specific gravity of the four solutions of fluosilicic acid mentioned in table 1 - 4.

In the process of manufacture, the reaction is carried out in a concrete tank lined from inside with anti-acid bricks. The reaction is controlled by matching the drop in specific gravity of the solutions during the addition of sodium sulphate solution till it reaches the minimum value and starts to rise. As we use the Baumé hydrometers in specific gravity measurements, the specific gravity values given in Fig. 1 are expressed in degrees Baumé, all being measured at a temperature of 20°C.

Conversion to Sulphuric Acid

The effect of amount of sulphate upon the conversion of fluosilicic acid to sulphuric acid, has been studied. The amount of sulphate is expressed as mole ratio of Na_2SO_4/H_2SiF_6, while the percentage conversion is the ratio of sulphuric acid to the total acidity in equivalents per litre in the final solution. Fig.2 represents the relation between the mole ratio and percentage conversion to H_2SO_4 with different concentrations of fluosilicic acid.

The following facts can be drawn from Fig.2

1. The percentage conversion to H_2SO_4 increases with an increase in the mole ratio till a certain value beyond which the increase is very slight compared with the excess sulphate. The curves for the different concentrations are of the same shape.

2. The percentage conversion is affected by the concentration of fluosilicic acid, thus for a mole ratio of 1.0 the percent conversion value is 95 for concentration I, 93.1 for concentration II, about 93.1 for concentration III and about 89 for concentration IV.

It is therefore preferable to use the highest possible concentration of fluosilicic acid, as the conversion value is very low with a concentration of 65 grs/litre.

The effect of temperature has also been studied. It has been found that the rise in temperature favoured the decomposition of sodium fluosilicate to fluosilicic acid by the action of sulphuric acid, resulting in low conversion values.

Results

It has been possible to recover sulphuric acid from by-product fluosilicic acid in the manufacture of sodium fluosilicate by the application of by-product sodium sulphate in place of sodium chloride.

Concentrations of about 60 grams H_2SO_4 per litre of solution could be obtained, with contents of about 4 grams H_2SiF_6. This acid could be used in the dilution of sulphuric acid for superphosphate manufacture.

The most favourable conditions for the reaction are :-

1. Application of slight excess of sulphate solution beyond the theoretical value (about 1.1 mole ratio)
2. Use of a high concentration of fluosilicic acid (16-18°Bé)
3. Lowering the temperature of reaction as much as possible.

Table I

Fluosilicic acid Sp.Gr.	1.141	°Bé	18.0
H_2SiF_6 grs. per litre	188		
Sodium sulphate solution Sp.Gr.	1.153	°Bé	19.2
Na_2SO_4 grs. per litre	186		

Mls. sulphate solution per 200 mls acid	140	160	180	200	220	240
Mole ratio Na_2SO_4/ H_2SiF_6	0.70	0.80	0.90	1.00	1.10	1.20
Specific gravity of mother liquor °Bé	9.7	9.3	9.2	9.2	9.6	10.1
H_2SO_4 grs./litre	66.17	67.70	67.38	67.50	64.01	63.11
H_2SiF_6 grs./litre	22.49	14.86	9.91	5.24	4.06	3.60
% Conversion to H_2SO_4	81.2	87.0	90.9	95.0	95.9	96.3

Table II

Fluosilicic acid Sp.Gr.	1.100	°Bé	13.2
H_2SiF_6 grs. per litre	132		
Sodium sulphate solution Sp.Gr.	1.153		
Na_2SO_4 grs. per litre	186		

Mls. sulphate solution per 200 mls. acid	100	120	140	160	180
Mole ratio Na_2SO_4 /H_2SiF_6	0.71	0.86	1.00	1.14	1.29
Sp.gr. mother liquor °Bé	8.0	7.7	7.9	8.3	8.7
H_2SO_4 grs. / litre	51.47	53.94	53.61	51.78	49.02
H_2SiF_6 grs. / litre	18.0	9.89	5.85	4.05	3.60
% Conversion to H_2SO_4	80.8	88.9	93.1	95.0	95.2

Table III

Fluosilicic acid Sp.Gr.	1.079	°Bé	10.8
H_2SiF_6 grs. per litre	102.5		
Sodium sulphate solution Sp.Gr.	1.153		
Na_2SO_4 grs. per litre	186		

Mls. sulphate solution per 200 mls. acid	75	90	105	120	135
Mole ratio	0.69	0.83	0.97	1.10	1.24
Sp.Gr. mother liquor °Bé	7.6	7.10	7.1	7.6	8.0
H_2SO_4 grs./litre	42.59	44.41	47.90	46.28	44.12
H_2SiF_6 grs./litre	16.65	10.37	5.26	4.05	3.60
% Conversion to H_2SO_4	79.0	86.3	93.1	94.4	94.70

Table IV

Fluosilicic acid Sp.Gr.	1.051	°Bé	7.0
H_2SiF_6 grs. per litre	65		
Sodium Sulphate solution Sp.Gr.	1.153		
Na_2SO_4 grs. per litre	186		

Mls. sulphate solution per 200 mls acid	50	60	70	80	90	100
Mole ratio	0.72	0.87	1,02	1.16	1.31	1.45
Sp.Gr. mother liquor °Bé	5.8	5.8	6.1	6.4	6.8	7.2
H_2SO_4 grs./litre	31.26	33.38	32.79	32.77	31.24	30.56
H_2SiF_6 grs./litre	12.59	7.66	5.85	4.06	3.60	2.82
% Conversion to H_2SO_4	78.5	86.5	89.2	92.2	92.7	94.1

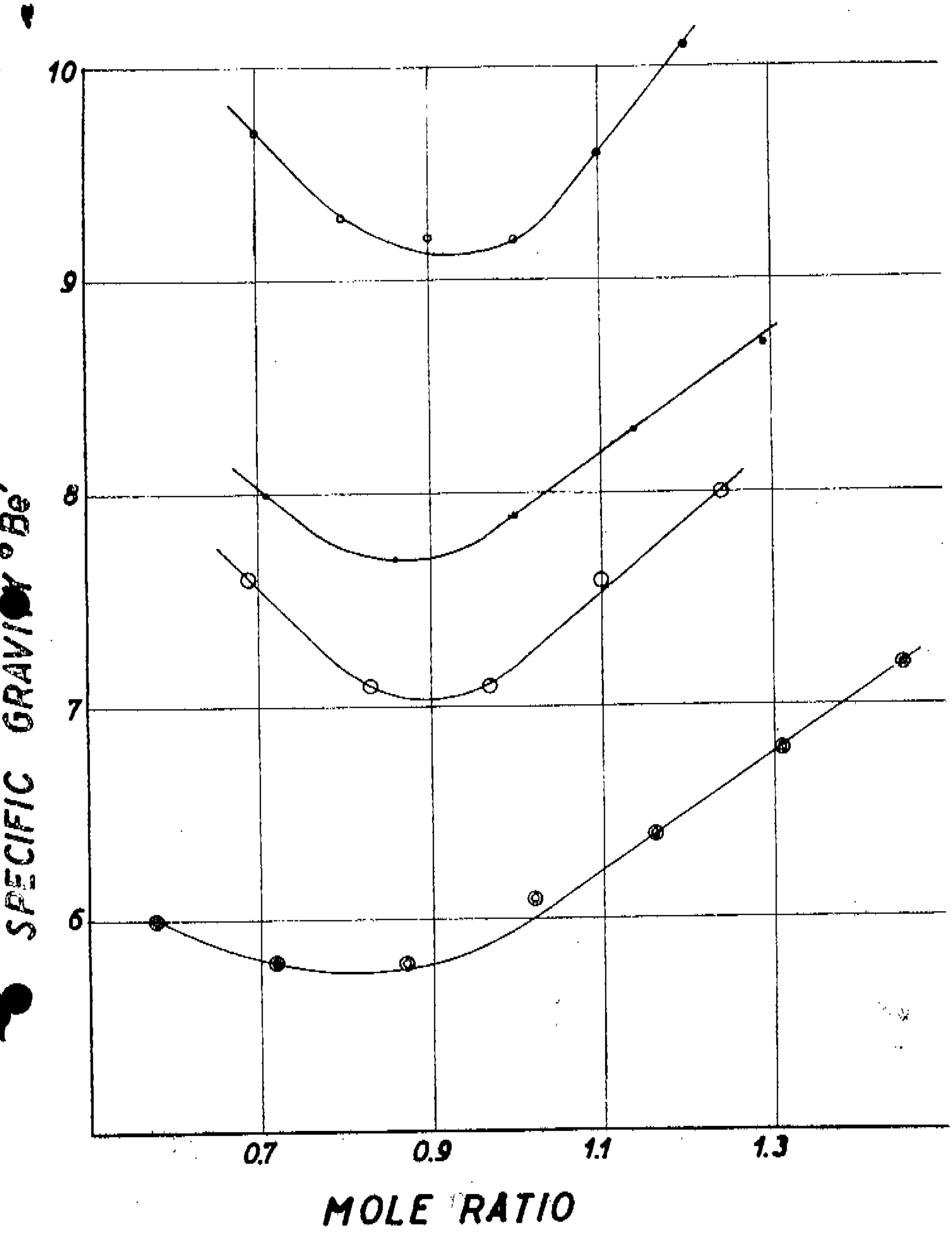

Figure 1

- ∘ refer to Table I
- · refer to Table II
- ○ refer to Table III
- ◉ refer to Table IV

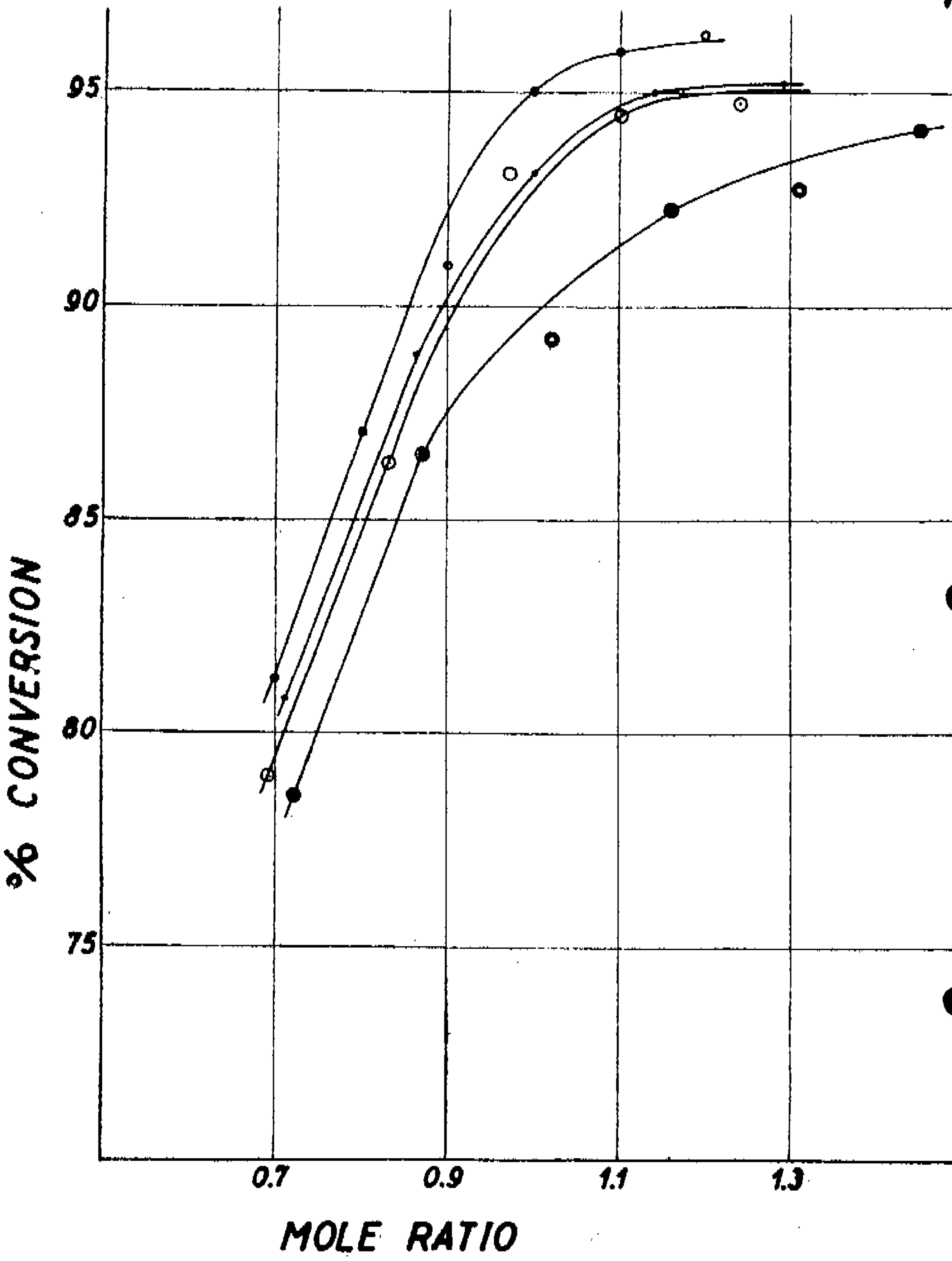

Figure 2

o refer to Table I
• refer to Table II
○ refer to Table III
● refer to Table IV