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THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

CULTURAL COMMITTEE
FRANKLIN D. ROOSEVELT
PARIS (8E)
TEL. BALZAC 57-25

CENTRAL OFFICE
44 RUSSELL SQUARE,
LONDON W.C.1
TEL MUSEUM 8927

TO ALL MEMBERS.

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THE CONVERSION STAGE IN THE MANUFACTURE OF SULPHURIC ACID BY THE CONTACT PROCESS.

by G.C. Lowrison and F. Heppenstall,
(Fisons Limited)

SUMMARY

In this paper we have discussed the conversion of sulphur dioxide to sulphur trioxide, considering successively the effects of temperature, pressure and sulphur dioxide concentration on the equilibrium.

Conversion has been dealt with on the basis of the theoretical conversion obtainable using up to four stages of successive cooling and adiabatic heating, and the advantages of the use of quench air as the cooling medium.

This is followed by a consideration of velocity of reaction and the effect on velocity by the use of catalysts. The mechanism of catalysis, the composition and properties of catalysts, and the effects of poisoning, have been considered.

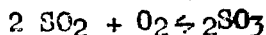
We have calculated the theoretical catalyst placing on the basis of equilibrium being reached in each stage, and have deduced the conditions for maximum utilisation of catalyst.

Finally, we have considered converter design, describing some of the converters which have been and are being used.

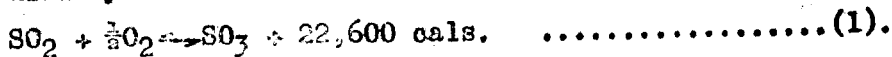
The Conversion Stage in the Manufacture of Sulphuric Acid by the Contact Process.

INTRODUCTION.

The most critical stage in the manufacture of sulphuric acid is the oxidation of sulphur dioxide to sulphur trioxide, basically the reaction is



or as it is more usually written to obtain a single molecule of product



The reaction is reversible and the maximum degree of formation of sulphur trioxide is determined by the equilibrium of this reaction.

The quantitative expression of this equilibrium is derived from the law of mass action discovered by Guldberg and Waage which states that the rate of reaction between substances is proportional to the concentration of the reactants, thus for this reaction the rate of reaction between oxygen and sulphur dioxide is given by

$$r_1 = K_1 [\text{SO}_2] [\text{O}_2]^{\frac{1}{2}}$$

where square brackets indicate concentration of that substance whose symbol is included within them, conversely the rate of reaction proceeding to the decomposition of sulphur trioxide is

$$r_2 = K_2 [\text{SO}_3].$$

At equilibrium these rates are equal

$$r_1 = r_2 \text{ and } K_1 [\text{SO}_2] [\text{O}_2]^{\frac{1}{2}} = K_2 [\text{SO}_3] \text{ or } \frac{K_1}{K_2} = \frac{[\text{SO}_3]}{[\text{SO}_2] [\text{O}_2]^{\frac{1}{2}}}$$

The quotient $\frac{K_1}{K_2}$ of these two constants is equal to another constant,

say K , known as the equilibrium constant of the reaction. From the concept of free energy the following equation can be derived :-

$$-\frac{\Delta G}{T} = R \log_e K \text{ or } 4.576 \log_{10} K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

determined values for which give

$$\log_{10} K_p = \frac{22600}{RT} - 10.68 \dots\dots\dots(2).$$

Where ΔG is the standard free energy change of the reaction, T is the absolute temperature and R is the gas constant, the units all being in the c.g.s. system. This equation may also be written in the form:-

$$R \left(\frac{\log K}{2(1/T)} \right)_P = -\Delta H \dots\dots\dots(3).$$

where ΔH is the standard heat of reaction. It can be used to determine K since $R \log K$ plotted against $\frac{1}{T}$ is a line of slope ΔH , hence K can be determined for any temperature.

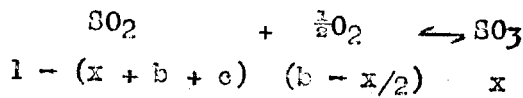
It is obvious that the dimensions of the quantities used in these equations have an important bearing on the value of the equilibrium constant obtained and these must be clearly specified. The result of such a determination is shown in Fig. 1 in which the concentration of the gases was expressed as partial pressures in atmospheres. The equilibrium constant is expressed in these dimensions by the symbol K_p .

As is well known the partial pressures of these gases can only be used in this equation at comparatively low pressures such as one atmosphere and below. If very much higher pressures are used it is necessary to

substitute fugacities for the partial pressures. This will be dealt with more fully later on in the paper.

From such a graph as Fig. 1 the degree of conversion at equilibrium can be calculated at any temperature within the range of the graph from any mixture of sulphur dioxide and oxygen and any unreactive gases. A useful form of the equilibrium equation for such calculations can be derived as follows.

In the reaction let there be a unit number of molecules, b of which oxygen and c are unreactive gases and let x molecules of SO₃ be formed from this mixture. Then the molecular equation becomes:-



Since the partial pressures are proportional to the number of molecules, we can express the appropriate partial pressures as the following fractions of the total pressure P, bearing in mind the c molecules of unreactive gases.

$$SO_2 = \frac{[1 - (x + b + c)] \cdot P}{(1 - x/2)}$$

$$O_2 = \frac{(b - x/2) P}{(1 - x/2)}$$

$$SO_3 = \frac{x}{(1 - x/2)} P.$$

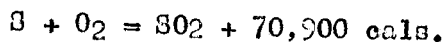
$$\text{Thus } K_p = \frac{x [1 - x/2]^{\frac{1}{2}}}{[1 - (x + b + c)] [b - x/2]^{\frac{1}{2}}} \cdot P^{\frac{1}{2}}$$

$$\text{or } K_p = \frac{x}{[1 - (x + b + c)] \left[\frac{1 - x/2}{(b - x/2) P} \right]^{\frac{1}{2}}} \dots\dots\dots(4).$$

From Fig. 1 at the chosen temperature, K_p can be read and x can be determined from the above equation by trial substitution, graphing the results and interpolating at the appropriate value at K_p.

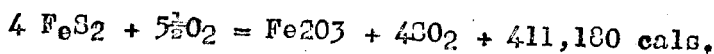
Usually the diluents of sulphur dioxide entering the converter are nitrogen remaining from air used in the combustion of the sulphur bearing materials and excess air. Air is of course the usual source of oxygen in the burning and conversion stages and all subsequent considerations in this paper will be based upon this source of oxygen. We shall also mainly concern ourselves with sulphur as the raw material for SO₂ although we shall make some few references to the use of iron pyrites.

In the sulphur process the formation of sulphur dioxide is in accordance with the following equation:-



Since one molecule of sulphur dioxide is produced from one molecule of oxygen the richest sulphur dioxide gas obtainable from air is that in which all the oxygen in the air has been replaced by an equivalent number of molecules of sulphur dioxide, that is to say a concentration of 21% of sulphur dioxide by volume. Lower concentrations depend upon the quantity of excess air used or upon the presence of combustible materials in the sulphur burning material which consume oxygen without producing sulphur dioxide.

For pyrites of composition FeS₂ the equation for burning is:-



which gives a maximum concentration of 13.2% SO₂.

From the equilibrium equation it is clear that the conversion of sulphur dioxide to sulphur trioxide is favoured by the degree of

concentration of oxygen in the gas mixture and for this reason where pure oxygen is available as a waste material from another process it is fed to the burner with air. The degree of conversion for both sulphur and pyrites from gas of various initial concentrations of SO₂ are shown in Figs. 2 and 3. The reason why there are different conversions for gases of sulphur and pyrites origin is of course due to the fact that in the preparation of sulphur dioxide from pyrites, oxygen has been consumed to make iron oxide leaving more unreactive nitrogen than in the case of sulphur dioxide of sulphur origin. The unreactive gases act as diluents of the sulphur dioxide with a consequent reduction of mass action.

If pure oxygen were used higher conversions would be obtained and any differences in the conversions obtained from sulphur and from pyrites would be solely due to the difference in the partial pressures of the remaining oxygen. It is clear from these graphs that the more the sulphur dioxide is diluted with air (more oxygen) the higher is the conversion at equilibrium. This is the result of the double effect of mass action and of the smaller rise in temperature of the gas mixture consequent upon the heat of reaction from sulphur trioxide produced being dissipated in more diluting gas.

From Figs. 2 and 3 the lower the equilibrium temperature the higher is the conversion. There is, however, a limit to this dilution unless the gas is to be preheated prior to the conversion stage. As will be explained in the later section on the kinetics of the reaction the catalyst has a minimum biting temperature below which it has no effect and in the burning process, if there is more than a certain maximum quantity of dilution air, the temperature of the gas from the burner will be lower than this minimum. The maximum temperatures of gases over a range of dilutions of both sulphur and pyrites origin are shown in Fig. 4. These have been calculated from the specific heat equations:-

$$\text{SO}_2 : 8.12 + 0.006825T - 0.000002103T^2$$

$$\text{O}_2 : 6.13 + 0.00299T - 0.000000806T^2$$

$$\text{N}_2 : 6.30 + 0.001819T - 0.000000345T^2$$

and for iron oxide produced in the pyrites process

$$\text{Fe}_2\text{O}_3 : 24.72 + 0.01604T - \frac{423400}{T^2}$$

in which T is the absolute temperature.

These have been integrated between limits T₁ and T₂ so that they are of the form

$$a(T_1 - T_2) + b/2(T_1^2 - T_2^2) - c/3(T_1^3 - T_2^3)$$

except in the case of Fe₂O₃ which takes the form

$$m(T_1 - T_2) + n/2(T_1^2 - T_2^2) + p \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

a, b, c, m, n and p being of course the constants in the above equations. Since the lower temperature T₂ is known and is the atmospheric temperature (288°K), by multiplying these molal heats by the number of molecules participating and equating the sum of this heat with the heat of reaction, T₁ can be found graphically. The results obtained are shown in the following table:-

Sulphur Gas Temperatures.

% SO ₂	3.5	5.25	10.5	21.0
Temp°C	358	515	952	1702

Pyrites Gas Temperatures.

% SO ₂	3.85	7.7	11.55	15.4
Temp°C	527	940	1282	1577

From these graphs it is seen that for a biting temperature of 415°C the minimum concentration of SO₂ from sulphur is 4.0% and from pyrites 3.1% unless the gases are preheated or as will be mentioned later under 'Quenching' the gases are not diluted at the burner stage but only at conversion stages.

The temperature of the gases fed to the converter are controlled as near the biting temperature as possible since the lower the temperature the higher the equilibrium conversion. Then as conversion takes place in accordance with equation (1) heat is released and the gas mixture rises in temperature in accordance with the appropriate specific heats, the equations for which are given above for sulphur dioxide, oxygen and nitrogen, whilst for SO₃ the equation is:-

$$8.20 + 0.010236T - 0.000003156 T^2.$$

The temperature can rise until the equilibrium conversion is achieved. The progress of this temperature is shown in Fig. 5. These conversions and the corresponding adiabatic temperatures are shown in the following table for initial gas strengths of 14, 10, 8, 7, 6 %SO₂ at the initial temperature of 415°C:-

%SO ₂	14	10	8	7	6	
Adiabatic Temp. °C	636	610	593	580	567	1st Stage
% Conversion	54.0	67.8	76.1	81.6	86.0	

It is not possible to obtain further conversion with these gases unless they are cooled and it is therefore common practice to introduce 2, 3 or 4 stages in the converter, the gases being cooled between stages to the biting temperature of the catalyst. This is also shown in Fig. 5 for a four stage converter with an initial 8% SO₂ gas. The adiabatic temperatures and conversions corresponding with each of the above gas strengths are shown for the 2nd, 3rd and 4th stages with interstage cooling to 415°C prior to entry to the next stage.

%SO ₂	14	10	8	7	6	
Adiabatic Temp. °C	528	493	465	450	437	2nd Stage
% Conversion.	81.7	94.8	97.4	98.2	98.8	
Adiabatic Temp. °C	455	426	417	417.5	416.3	3rd Stage
% Conversion.	91.4	96.5	99.1	99.3	99.4	
Adiabatic Temp. °C	426	422	415	415	415	4th Stage
% Conversion.	94.3	98.8	99.2	99.3	99.4	

It must be emphasised that these are equilibrium conversions and also that they correspond with adiabatic temperatures, in other words they take no account of possible heat losses from the system.

Effect of Pressure on Conversion.

The equilibrium equation (4) applies only to pressures in which the activity of the substances can be taken to be identical to the partial pressure of the gas. At higher pressures this equation has to be modified to include a constant K_f or fugacity co-efficient so that equation (4) correctly reads

$$K_p = K_f \left[\frac{x}{1 - (x + b + c)} \right] \left[\frac{(1 - x/2)}{(b - x/2)P} \right]^{\frac{1}{2}}$$

In accordance with Le Chatelier's principle increase in pressure favours the production of sulphur dioxide since its formation accompanies a reduction in pressure. These co-efficients are shown for various temperatures and pressures in Fig. 6. As an indication of the effect of pressure the following example may be cited for a 7.8% SO₂ pyrites gas, at

one atmosphere and 600°C, the conversion is 30% while the same gas at the same temperature but at a pressure of 100 atmospheres has a conversion of 93%.

Gas Concentration and Pressure: Their Influence on Design.

From the above it is seen that at equilibrium the maximum conversion occurs at the lowest temperature with the lowest gas concentration and at the highest pressure. But in practice the initial plant cost and running costs need to be considered. As low gas concentrations mean large vessels and ducts, and high pressures need thick walled vessels, up to the present time such additional expense cannot be justified. A further disadvantage to dilute gases is that since their temperature from the burner is by comparison low there is a low temperature differential in the heat exchanger and the recovery heat is more expensive. The gas temperature is determined by the biting temperature of the catalyst and consideration must also be given to the maximum temperature the catalyst will tolerate without decomposition or disintegration.

Quenching.

Above it was suggested that a possible method of avoiding the disadvantages of dilute gases from the burner and yet secure the advantages of dilute gases to the converter would be to make concentrated gases in the burner and dilute them down just prior to the conversion stages.

In this way the advantage of both strong and weak gases are obtained in the same plant. A strong gas produced in the burner has a high temperature giving good heat exchange at the waste heat boiler and allows small vessels and ducting. If this is diluted at appropriate stages in the converter with cold air the effect is one of cooling the gases and also of diluting them, both of which steps improve conversion.

In Fig. 7 the effect of successively diluting a 14% gas of sulphur origin is shown. From this diagram it is possible to determine the equilibrium conditions obtained from diluting such a gas so that it corresponds to gases of original SO₂ concentrations of 14, 10, 8, 7 and 6%.

VELOCITY OF REACTION.

All of the above considerations were based upon equilibrium being achieved. The speed at which the reaction proceeds to equilibrium will now be discussed. It is hardly necessary to emphasise that the velocity of the reaction is one of very great practical concern.

The velocity of this particular reaction is highly sensitive to the presence of certain substances which whilst hastening the reaction remain themselves at the end of the reaction unchanged and are called catalysts. We have not been able to discover in the literature the extent of this reaction in the absence of catalysts because, as a matter of fact, the number of substances which act as catalysts are very extensive, even glass has an influence. Norrish and Rideal report, however, that it is not until 305°C that measurable quantities of SO₃ are produced; but this determination was made in glass vessels.

The first observation of what is now called catalytic reaction was made by Sir Humphrey Davy in 1817. He found that a heated platinum wire introduced into various gas mixtures caused an exothermic reaction.

The selection of a catalyst is mainly empirical and many metals and metallic oxides were tried but up to the present time the only two elements adopted industrially to effect oxidation of SO₂ rapidly at temperatures below 500°C have been platinum and vanadium. Iron oxide was used in the Mannheim process but this material is relatively inactive at temperatures below 600°C and at this temperature the maximum theoretical conversion that can be achieved is 60% and it was therefore necessary to have a second conversion stage. In this case platinum was used.

From the literature it is interesting to note that the catalytic effect of palladium and iridium is low compared with platinum. A comparison using in each case 10 grams of mass containing 1.5% of the metal and passing a gas mixture of 1 part SO₂ and 2.5 parts air at the same rate of flow shows:-

T°C	Conversion		
	Platinum	Iridium	Palladium
450	96.2	27.0	0.5
500	89.5	56.7	9.8
550	79.9	67.1	23.4
600	68.8	60.0	27.2
650	47.9	42.8	40.0

The success of a catalyst apart from the advantages of a low kindling temperature is dependent upon the nature of the carrier used. This vehicle must be porous in order to present the greatest possible surface to the gases. It must be capable of withstanding high temperatures and be inert to sulphurous gases. In the case of platinum it must be capable of treatment for recovery of the platinum. These considerations have restricted materials that can be used. Those which have proved successful are asbestos fibre, magnesium sulphate, silica gel and kieselguhr. The first two being used for platinum and the latter two for vanadium.

The common method of making the platinum catalyst was to soak the asbestos in say platinum chloride solution; to remove the platinum, allow it to drain, dry, and fluff it out.

Due to the light nature of this catalyst mass it was necessary for the converters to be down-draughted. The platinised magnesium sulphate mass which was generally used in the Grillo Schroeder process was prepared by spraying platinum chloride on to calcined magnesium sulphate. The platinum content of the mass being approximately 0.3%.

Platinised silica gel which was said to be a much more durable material than either of the other two due to the harder nature of the carrier, consisted of a gel prepared from sodium silicate and hydrochloric acid, this material being dried and sprayed with ammonium chloro-platinate.

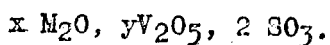
In the early designs of converters the platinum loading was approximately 10 ozs. per ton of acid per day but improved converter design resulted in this being reduced to approximately 4 ozs. of platinum per ton per day.

Although vanadium was advocated for use as a catalyst as early as 1900 it was not until 1915 that it was used on a commercial scale but this early use was apparently unsuccessful due to the disintegration of the carrier causing a high pressure drop across the converter.

Vanadium pentoxide itself is a comparatively poor catalyst and it is only when so called activators are added that high conversions can be achieved.

They are usually compounded with an inert substance of very large superficial area such as Kieselguhr. Manufacturers usually specify very carefully the type of carrier used, for example one given for Kieselguhr is that the density must lie within the range of 130/150 grams per litre and must be sufficiently porous to take up 300/320 grams of water at room temperature without flowing easily.

These activated catalysts fall into a class of composition:-



The metal M in the above formula is usually potassium, sodium being comparatively poor (one authority says it has not more than 60% of the activity of a potassium catalyst) whilst rubidium, caesium and thallium

are successively, and in that order, improvements on potassium.

There is no doubt that a substance of the above general composition is molten at normal conversion temperatures. Topsøe and Nielsen state that the function of these metals is to provide solvents for the vanadium so that a free flowing liquid is produced at the temperature of the reaction. In support of this argument they state that only those metals act as activators which (a) produce low melting point pyro-sulphates, (b) have the ability to absorb SO_3 to decrease their melting point even lower and (c) produce melts of low viscosity. They state that this is further supported by the fact that the catalyst when made is not active until it has been heated in a stream of SO_3 so that pyro-sulphates can be produced. They state that the catalyst functions in the liquid flowing over the surface of the carrier. They have shown that it is possible to obtain similar conversions to those of a conventional catalyst by using a molten catalyst without the carrier circulating this over a packed tower. They claim that this method could form a practical process. The same investigators have made up pellets containing catalyst in an outside annulus and only the carrier in the central core. They have shown that after a very short time of working the catalyst pellet becomes homogeneous.

The ratio of K_2O/V_2O_5 or M_2O/V_2O_5 as is most usual, is found to be important in conferring activity on the catalyst, the higher this ratio the lower the biting temperature of the catalyst. The I.C.I. in a patent show that the following compositions will give optimum velocities at the temperatures indicated:-

Optimum Compositions for Particular Temperatures.

Temp.	380	390	400	410	420	430	440	450	460	470
K_2O/V_2O_5 Ratio.	5.4	5.0	4.5	3.9	3.3	3.1	3.06	3.04	3.03	3.02

and suggest that the catalyst bed could be made up in successive layers of the above compositions so as to achieve maximum velocity of reaction as the conversion proceeds.

Typical compositions of vanadium catalyst in commercial use are:-

V_2O_5	K_2O	Carrier %
9%	10.4%	70% silica Kieselguhr or Cellite
6%	8%	
9.5%	10.0%	
7.1%	9.3%	
8.6%	9.7%	

Iron and manganese are said to improve the activity of the catalyst but Topsøe and Nielsen say that if this is present to a greater extent than 15% to 20% of the molar vanadium present the activity falls off.

Typical methods of preparing the catalyst mass are as follows:-

80/90% vanadic acid containing 12.6 kilos of V_2O_5 is placed in a vessel and made damp with water, 37.4 kilos of 50% caustic potash are added and the mixture warmed in order to dissolve the V_2O_5 , when the solution is complete it is neutralised by the addition of 16 Bc. sulphuric acid until a test sample turns litmus weakly blue. The contents are then made up to 90 litres total volume by the addition of water, 120 kilos of Kieselguhr and 18 kilos of sulphur are added. The vanadic acid suspension is quickly added, followed by 5 to 6 litres of 5% ammonia liquor, and the whole mass mixed for 15 minutes. This mass is then extruded and calcined at a temperature of approximately 300°C.

Another method is stated to be to use a vanadium compound such as

vanadium oxychloride (VOCl_3), vanadium oxalate or ammonium vanadate to which has been added potassium silicate. Then 10% sulphuric acid is added to this mixture so that the pH is below 4, otherwise the silica gel produced is unstable. The whole mass is dried without filtration, calcined and ground.

It is necessary for all vanadium masses to be activated before use. The method of doing this is to heat slowly with hot air until the mass reaches a temperature of 450°C , then to pass a 2% SO_2 gas mixture and raise the temperature to 500°C . The mass can then be used.

POISONING.

The facility of the catalyst to increase the velocity of a reaction is greatly decreased and ultimately completely destroyed by certain substances which are known collectively as poisons, the effect being said to be one of poisoning. Poisoning appears to be of two kinds:-

- (a) That in which the catalyst recovers activity as soon as the poison is removed from the gas stream, and
- (b) That which once present in the catalyst mass cannot be removed except by chemical action, for example by boiling in sulphuric acid.

The former type of poisoning is known as reversible or temporary and the other as irreversible or permanent.

The degree of poisoning is measured by the relative reduction of the velocity constant by a unit weight of poison on unit weight or unit volume of catalyst.

Let this be α

$$\text{Then } \alpha = \frac{-dK}{K dg}$$

Where K = velocity constant and
 g = weight of poison.

$$\text{Whence } \alpha dg = \frac{-dK}{K}$$

and integration gives $\alpha g = \log_e k + c$

$$\text{or } \alpha = \frac{2.303}{g} \log_{10} \left(\frac{K_1}{K_2} \right)$$

Values of α which have been established are:-

As_2O_3 on platinum at 450°C	$\alpha = 61$ per gram of catalyst
As_2O_3 on platinum at 500°C	$\alpha = 32$ per gram of catalyst
As_2O_3 on $\text{Ba-Sn-V}_2\text{O}_5$	$\alpha = 0.01$ per litre of catalyst
As_2O_3 on $\text{K}_2\text{O-V}_2\text{O}_5$	about same.

It has been stated that the effect on the vanadium catalyst below 550°C reaches a maximum and does not increase with more poison. At temperatures greater than 550°C a volatile compound of As_2O_5 and V_2O_5 is formed which condenses in subsequent catalyst layers.

The effect of arsenic on the activity of a vanadium catalyst is shown in the following example. Suppose in pyrites containing 0.1% As, 75% is volatilised into the SO_2 gas stream. Since pyrites contains about 50% sulphur, from 1 ton of pyrites say 0.50 tons of sulphur are volatilised = 1.53 tons of sulphuric acid containing 0.00075 tons of arsenic = 761 grams or 497 grams/ton of acid. Suppose activity of catalyst reduced by one half

$$\text{or } \frac{K_1}{K_2} = 2$$

$$\text{and } \alpha = 0.01$$

$$\text{then } \alpha = \frac{2.303}{g} \log_{10} \left(\frac{K_1}{K_2} \right)$$

$$\text{or } 0.01 = \frac{2.303}{g} \log_{10}(2) = \frac{2.303 \times 0.3010}{g}$$

$$\text{and } g = \frac{2.303 \times 0.3010}{0.01} = 69.4/\text{litre of catalyst.}$$

Now suppose 1 ton of acid per day needs 200 litres of catalyst.

761 grams of arsenic per day or 200 litres of catalyst will reach this figure for

$$g \text{ in } \frac{69.4 \times 200 \text{ days}}{497} = \underline{\underline{27.9 \text{ days.}}}$$

The effect shown in this calculation is of course in practice much enhanced because the initial layers of catalyst in the first pass are first out of order, therefore the initial stages of conversion are not so far advanced as was allowed in the design and additional duty of conversion is thrown upon subsequent stages in the converter for which cooling facilities have not been provided and the system is therefore thrown completely out of balance with considerable decreased efficiencies.

It will be seen that when producing sulphuric acid from arsenical ores it is necessary to have elaborate gas purification systems.

Both tellurium and selenium poison platinum. Selenium is said only to affect vanadium pentoxide at temperatures less than 400°C and the catalyst recovers its activities by heating at 480/500°. Nothing is known of the effect of tellurium on vanadium.

Carbon monoxide has a deleterious effect upon the reaction in the case of vanadium catalyst because vanadium catalyst unlike platinum does not oxidise carbon monoxide to carbon dioxide and the carbon monoxide reduces the sulphur trioxide formed. Carbon or soot affects both platinum and vanadium because it in fact obscures the surface.

Hydrogen sulphide is said to have no harmful effects on platinum and for a 3% gas no harmful effect was noted on vanadium over 100 hours at both 480 and 425°C. However, it is stated that in the wet catalyst process in which hydrogen sulphide is oxidised directly to water and sulphur dioxide in the burner, this mixture if allowed to pass for several hours and then exchanged for gas of sulphur origin, a lowering of activity is noticed which is only removed by raising the catalyst to a temperature above 500°C.

Although chlorine and hydrochloric acid gas have severe poisoning effects on platinum which is reversible, they have no effect upon vanadium.

Silicon tetrafluoride has a bad effect on platinum due to the formation of silica on the catalyst. It is also said to be harmful to V₂O₅ though whether this is due to the effect on the carrier or upon the catalyst itself has not been stated.

There is an effect which is analogous to temporary poisoning resulting from the use of gases at too low a temperature. The presence of SO₂ at temperatures below 420°C has the effect of reducing the V₂O₅ to V₂O₄ and even to V₂O₃ and thereby reducing the activity of the mass, but this situation can be rectified with the catalyst in situ by blowing through with hot dry air at a temperature of 480/500°C thereby reactivating the mass.

The Mechanism of Catalysis.

In order that a chemical reaction shall proceed it is not only necessary for the change to be accompanied by the release of positive free

energy on a macroscopic scale. It is necessary that microscopically the reacting molecules shall possess sufficient energy to confer upon a complex temporarily produced by their collision and temporary combination the drive necessary to rearrange the energy so as to bring about the disintegration of the complex in the required way.

In other words the molecules themselves must possess a certain energy of activation. This energy of activation is not possessed equally by molecules in the system but is distributed in accordance with the theory of probability in a Gaussian manner.

Therefore although a reaction may result in a positive free energy change it may not possess enough individual molecules with the necessary energy of activation for the reaction to proceed to a measurable extent at a particular temperature.

As the temperature of the system is raised it is usual for the number of molecules possessing at least this required energy of activation to increase; but if the reaction is itself not favoured by an increase in temperature it might well be that as the temperature is approached at which the required number of activated molecules are produced, the required product is unstable.

A catalyst provides a site on which the reacting molecules may be suitably orientated so that the required energy of activation is much less and therefore the reaction can proceed at a much lower temperature.

The extraordinary thing, however, about solid catalysts is that the whole surface of the catalyst is not equally helpful to reaction and in fact the portion of the surface which is effectively being used for the reaction is very small, it might well be 5% or 10% of the whole surface or even smaller.

This observation led to the theory of H. S. Taylor that the surface of the solids of high chemical activity possessed certain "active centres". These active centres have been associated with the heterogeneity of the crystalline surface.

Poisoning is thus the effect of occupying these active centres at the expense of the desired reactants. This theory explains the method by which a small quantity of poison can make ineffective a large quantity of catalyst. This theory also explains the fact that there is a minimum temperature variously called the kindling, ignition or biting temperature of the catalyst, below which the catalyst will not function. For platinum this is usually considered to be 380°C and for vanadium catalyst 415°C. This is the minimum temperature at which an appreciable number of reacting molecules possess sufficient energy to form the compound or chemisorbed complex as it has been called. The catalytic effect is seen to be closely related to the surface of the catalyst exposed to the reactants.

In the particular case of vanadium catalysts, however, the matter is more complicated because the catalysts are said to be in the liquid state when in use. However the greater immunity of vanadium catalysts to poisons might be associated with this fact. That this catalytic reaction is closely associated with surface is supported by the fact that all conditions which give rise to the exposure of greater surface or the greater contact between the individual molecules of the substances and the surface of the catalyst improve the rate of reaction.

We will first deal with the effect of size and shape of the catalyst mass. As has been stated by Adadurov and Gemet the size and shape of catalyst mass determines -

- (1) The ratio of the volume of contact space per unit mass of catalyst
- (2) The contact surface,
- (3) The pressure drop of the system, and
- (4) The degree of erosion of the mass.

Both the void volume and the contact surface are closely allied with the geometrical shape of the catalyst pellets. A tetrahedron has the largest surface per unit volume and a sphere has the smallest surface per unit volume, a cube is the intermediate between these two shapes. However, there is another factor which must be borne in mind and that is the degree of overlapping of the shapes when they are assembled in bulk. Both the tetrahedron and the cube have much overlapping. It is usual to compromise from the point of view of ease of manufacture and maximum surface per unit volume with a cylindrical shape. Hollow rings have been tried but it has been found very difficult to obtain these with sufficient mechanical strength.

With regard to the mass transfer of the reacting gas to the surface of the catalyst, this is achieved in proportion to its turbulence, that is to say it is related to the velocity of flow of the gas. However, this effect is counteracted by the reduced contact time between the gas and the catalyst and therefore there is an optimum flow limit corresponding with a certain gas concentration.

In addition to this problem of mass transfer there is the one of heat transfer with which of course mathematically it is closely related. It is essential of course that the temperature of the catalyst mass shall be kept to a minimum, otherwise the equilibrium conditions achieved on the surface of the catalyst are less favourable than those that are obtained in the body of the gas.

Greater exposure of catalyst surface is of course obtained if the pellets are not in contact, that is to say they are fluidised and certain experiments have recently been reported in which it is stated that between 3 and 4 times the reaction rate is obtained with a fluidised bed compared with a confined bed.

Catalyst Placing.

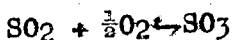
The approach to the problem of catalyst placing can be made along the lines suggested by Hougan and Watson. If r is equal to the rate of reaction in moles converted per gram of catalyst per second W = weight of catalyst in grams, F is equal to the feed rate in grams per second and x is the moles converted per gram of mixture fed, then

$$rdW = Fdx$$

$$\text{and } W = F \int \frac{1}{r} dx.$$

The weight of catalyst can therefore be determined by plotting the reciprocal of the rate of the reaction against the conversion and determining the area under this graph between the limits of conversion being considered.

Calderbank has by adsorption studies shown that the rate of the forward reaction



$$\text{is } r_1 = K_1 P_{SO_2} \cdot P_{O_2}$$

If r_2 is the velocity of the reverse reaction then at equilibrium $r_1 = r_2$ and if r_2 is written in the form

$$r_2 = K_2 \cdot [Y]$$

$$\text{then } K_1 P_{SO_2} \cdot P_{O_2} = K_2 \cdot [Y]$$

$$\text{and } \therefore K_y = \frac{[Y]}{P_{SO_2} \cdot P_{O_2}}; \quad \text{but}$$

$$\frac{K_1}{K_2} = K \text{ the equilibrium constant}$$

$$\text{and } K = \frac{[SO_3]}{[SO_2] \cdot [O_2]^{\frac{1}{2}}}$$

$$[Y] = \frac{[SO_3][O_2]^{\frac{1}{2}}}{[SO_2]^{\frac{3}{2}}}$$

$$r_2 = K_2 \frac{[SO_3][O_2]^{\frac{1}{2}}}{[SO_2]^{\frac{3}{2}}}$$

By plotting the values of K_1 against $\frac{1}{T}$ in accordance with equation (3) the enthalpy change (heat of reaction) is determined from the slope of the graph. Calderbank found

ΔH to be 31,000 cal

and the equation to be

$$\log_e K_1 = \frac{-31,000}{RT} + 12.07 \dots\dots\dots(5)$$

and from (2) $\log_e K_p = \log_e K_1 - \log_e K_2 = \frac{22,600}{RT} - 10.68$

$$\log_e K_2 = -\frac{53,600}{RT} + 22.75 \dots\dots\dots(6)$$

Now the rate of the reaction $r = r_1 - r_2$

$$\text{or } r = K_1 P_{SO_2}^{\frac{1}{2}} \cdot P_{O_2} - \frac{K_2 P_{SO_3} \cdot P_{O_2}^{\frac{1}{2}}}{P_{SO_2}^{\frac{1}{2}}}$$

Values of r have been calculated for the 4 stage conversion of 8% SO_2 gas of sulphur origin assuming equilibrium and the values obtained are shown in the following table:-

Rate of Reaction 8% (Sulphur) SO_2 Gas.							
Temp. °C.	Conversion %	1st Stage			$\times 10^7$ r_1	$\times 10^7$ r_2	$\times 10^7$ r
		$\log_e K_1$	$\log_e K_2$	K_1/K_2			
415	0	-10.57	-16.52	346.7	9.55	0	9.55
418	1.0	-10.48	-16.23	316.2	10.3	0.00036	10.3
420	2.0	-10.41	-16.11	298.5	11.0	0.0021	11.0
422	3.0	-10.34	-16.01	288.4	11.7	0.0035	11.7
426	5.0	-10.22	-15.80	263.0	13.09	0.007	13.08
438	10.0	-9.85	-15.15	199.5	18.11	0.029	18.08
450	15.0	-9.47	-14.52	154.9	25.5	0.084	25.4
462	20.0	-9.12	-13.90	119.1	33.9	0.22	33.7
474	25.6	-8.78	-13.31	92.68	45.7	0.50	45.2
488	31.2	-8.40	-12.64	69.18	61.7	1.23	60.5
501	36.8	-8.06	-12.05	53.7	83.2	2.81	80.4
513	42.4	-7.75	-11.52	43.65	109.6	5.56	104
526	48.0	-7.43	-10.95	33.11	144.5	11.50	133
539	53.6	-7.11	-10.42	27.54	177.8	22.9	154.9
553	59.2	-6.78	-9.86	21.70	224	46.8	175.0
565	64.8	-6.52	-9.39	17.78	266	86.1	180
578	70.4	-6.23	-8.90	14.45	320	167.9	152
587	74.0	-6.05	-8.57	12.45	363	253	110

1st Stage (cont).

Temp. °C.	Conversion %	log _e K	log _e K ₂	K ₁ /K ₂	x10 ⁷ r ₁	x10 ⁷ r ₂	x10 ⁷ r
589	75.0	- 6.00	-8.50	12.16	367.3	284.4	82.9
590	75.5	- 5.98	-8.46	12.02	371	298	73
591	76.0	- 5.96	-8.42	11.75	374.1	314	60.1
<u>2nd Stage.</u>							
415	76.6	-10.57	-16.42	345.9	3.67	0.11	3.56
420	78.7	-10.41	-16.14	306.9	4.07	0.15	3.92
425	80.8	-10.24	-15.85	271.6	4.55	0.22	4.33
430	82.9	-10.09	-15.57	238.8	5.01	0.32	4.69
435	85.0	- 9.94	-15.31	213.8	5.49	0.45	5.04
441	87.1	- 9.75	-14.99	187.5	6.03	0.68	5.35
446	89.2	- 9.60	-14.73	168.3	6.31	0.98	5.33
451	91.3	- 9.45	-14.47	155.2	6.61	1.45	5.16
454	92.5	- 9.35	-14.32	143.2	6.61	1.84	4.77
456	93.4	- 9.30	-14.20	134.0	6.55	2.23	4.32
459	94.5	- 9.23	-14.07	126.5	6.40	2.79	3.61
461	95.4	- 9.15	-13.96	122.5	6.31	3.45	2.84
464	97.0	- 9.07	-13.80	112.7	5.48	5.07	0.41
<u>3rd Stage.</u>							
415	97.4	-10.57	-16.42	346.7	1.135	0.400	0.732
416	97.8	-10.54	-16.35	333.4	1.064	0.471	0.593
417	98.2	-10.51	-16.31	330.4	0.991	0.547	0.444
417.5	98.5	-10.49	-16.26	320.6	0.929	0.619	0.310
418	98.7	-10.48	-16.23	314.1	0.900	0.670	0.270
418.5	98.8	-10.46	-16.20	312.6	0.859	0.736	0.123
<u>4th Stage.</u>							
Negligible improved conversion can be achieved in a fourth stage.							

The following show some of the actual distributions which have been used in practice using vanadium catalyst.

Type of Converter External H.E.	% of Total Mass				Catalyst in litres per ton of acid per day.
	1st Pass	2nd Pass	3rd Pass	4th Pass	
Single Stage	100	-	-	-	
Two Stage	30	70	-	-	180
Three Stage	17	24	59	-	
Four Stage	16	27	27	30	180
	22.3	22.3	22.3	33.1	180
	22	25	25	28	180

Type of Converter Internal H.E.	% of Total Mass			Catalyst in liter per ton of acid per day.
	1st Pass	2nd Pass	3rd Pass	
Single Stage	100	-	-	216
Two Stage	25	75	-	225
Three Stage	13	27	60	230
	23.6	20.6	55.8	206
	23.2	20.8	56.0	206
	16.0	23.0	61.0	268

Those calculated for the 8% gas are as follows:-

Stage	1	2	3	4
Relative Wt. of Catalyst	0.02043	0.06765	0.04334	negligible
% Wt.	15.6	51.4	33.0	-

However the above apply when equilibrium is achieved in each pass and as Fig. 8 shows the graph passes through minima for $\frac{dr}{dT}$ which are of course maxima for r .

More efficient use of catalyst can be made if the conversion does not exceed that corresponding with the maximum rate, with such conditions the placing is:-

Stage	1	2	3	4
Relative Wt. of Catalyst	0.02043	0.0295	0.066	0.0541
% Wt.	12.0	17.3	38.9	31.8

Maximum utilisation of catalyst is achieved by operating continuously at maximum velocities of reaction. Maximum velocity of reaction exists when

$$\frac{dr}{dT} = 0.$$

$$\text{Now } r = r_1 - r_2 = \frac{K_1 P_{O_2} \cdot P_{SO_2}}{P \cdot SO_2^{\frac{3}{2}}} - \frac{K_2 P_{SO_3} \cdot P_{O_2}^{\frac{1}{2}}}{P \cdot SO_2^{\frac{1}{2}}}$$

but both K_1 and K_2 are exponential functions as given in equations (5) and (6)

$$\text{let } K_1 = e^{f_1(T)} \text{ and } K_2 = e^{f_2(T)}$$

$$\text{Then } \frac{dr}{dT} = \frac{f_1^1(T) K_1 \cdot P_{O_2} P_{SO_2}}{P \cdot SO_2^{\frac{3}{2}}} - \frac{f_2^1(T) K_2 P_{SO_3} \cdot P_{O_2}^{\frac{1}{2}}}{P \cdot SO_2^{\frac{1}{2}}}$$

Where $f^1(T)$ indicates the differential derivative of $f(T)$

$$\text{When } \frac{dr}{dT} = 0 \quad \frac{f_1^1(T) \cdot K_1}{f_2^1(T) K_2} = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{\frac{1}{2}}} \dots \dots \dots (7)$$

From equations (5) and (6) it is clear that

$$\frac{f_1^1(T)}{f_2^1(T)} = \frac{-31,000}{RT^2} = \frac{RT^2}{-53,600} = 1 \dots \dots \dots (8)$$

from equation (8)

$$\frac{K_1}{K_2} = \frac{1.73 \cdot P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{\frac{1}{2}}}$$

But $\frac{K_1}{K_2} = \left[\frac{K_p}{K_p} \right]_2$ the equilibrium constant at say a temperature T_2

Whilst $\frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{\frac{1}{2}}} = \left[\frac{K_p}{K_p} \right]_1$, the equilibrium constant corresponding

with this degree of conversion say T_1 .

$$\text{Then } \frac{K_1}{K_2} = \left[\frac{K_p}{K_p} \right]_2 = 1.73 \left[\frac{K_p}{K_p} \right]_1$$

Now from equation (2)

$$\log_e K_p = \frac{22,600}{RT} - 10.68$$

$$\therefore 2.303 \log_{10} \left[\frac{K_p}{K_p} \right]_2 = \frac{22,600}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$= 2.303 \log_{10}(1.73) = 0.548$$

Now $R = 1.99$ calories

$$\text{and } \frac{0.548 \times 1.99}{22,600} = \frac{1}{T_2} - \frac{1}{T_1} = 0.483 \times 10^{-4}$$

$$\text{or } \frac{T_1 - T_2}{T_2 T_1} = 0.483 \times 10^{-4}$$

$$\text{Whence } T_1 = 0.483 \times 10^{-4} T_2 T_1 + T_2$$

$$\text{or } T_2 = \frac{T_1}{1 + 0.483 \times 10^{-4} T_1}$$

Thus in order to achieve maximum velocity the mixture should be kept at a temperature less than that corresponding with its equilibrium temperature in accordance with the above equation.

Ideally, therefore, the mixture of low conversion should be fed into the converter at a high temperature and gradually decreased as conversion proceeds in accordance with the above equation. Certain Internal Heat exchange converters have attempted to follow this principle and will be described later.

Converter Design.

In the early days of converter design very little consideration appears to have been given to the thermal aspects of the reaction. Converters, by comparison with the present day, were small and radiation losses must have been considerable, possibly with advantage to the conversion efficiency.

One of the earlier known types of converter was the Schroeder Grillo which consisted of a C.I. cylinder containing five layers of platinized magnesium sulphate catalyst supported on G.I. grids.

In the original Grillo converter the SO_2 entered at the top, and passed through the various layers of catalyst. No attempt was made to use

the heat of reaction, and it was necessary to preheat the incoming gases to the desired ignition temperature in an external furnace. See Fig. 9(a). A later development of the Grillo converter was the incorporation of annular space around the shell. The SO_2 gas enters the annular space tangentially at the bottom and is forced by means of baffles to take a spiral course upwards, absorbing heat from the hot gases inside the shell, thus giving some degree of temperature control. See Fig. 9(b). In this converter better gas distribution was obtained by downflow which reduced the possibility of channelling, and by the installation of baffle plates between the layers of catalyst. The dimensions of the inner cylinder were approximately 6'-6" inside diameter and 12'-0" high. A converter of these dimensions would contain 2,000/2,500-Lbs. of mass on each shelf with a platinum content of 0.31%. Such a converter would have a capacity of approximately 25 tons H_2SO_4 per day, conversion efficiencies of 92 - 95% being obtained.

Another early type of converter was that employed in the Mannheim system which is the only system using a two stage converter with different catalytic materials. The primary conversion took place in a steel brick lined chamber called an oxide shaft which received the gases direct from the burners. The shaft was charged with burnt iron ore of a particle size of not less than 1". Each 24 hours a proportion of the ore was removed from the bottom of the shaft and replaced with freshly burnt ore, the normal depth of oxide being 8/10-ft. and the gases entering at a temperature of 700° approximately. After leaving this section the gases were cooled, the SO_3 absorbed in conc. H_2SO_4 , the residual gases after preheating to ignition temperature passed into the second stage, consisting of a shaft containing platinized asbestos catalyst. Iron oxide is relatively inactive at temperatures below 600°C , and whilst theoretically a conversion of 60% was possible in the oxide shaft, in practise this seldom exceeded 40%.

One of the early attempts to utilise the heat of reaction, to preheat the cold SO_2 and at the same time give some measure of control on the catalyst temperature and improve the conversion, would appear to be the Badische system, details of which were first published in 1901. This converter was the first to operate on the internal heat exchange principle. The catalyst which was used was platinized asbestos and was contained inside tubes being supported on perforated plates. The cold gas entered at the bottom of the converter, passed upwards around the outside tubes and thence downwards through the converter to leave at the bottom. Originally this converter was designed to take the whole of the gas into converter but a later design incorporated a bypass arrangement giving better temperature control.

Another type of internal heat-exchange converter was that developed by the Tentelow Company. See Fig. 9(c). This converter consisted of a vessel made up into two sections, the upper section contained a perforated plate in which was placed a number of C.I. cones; a layer of catalyst was placed on this perforated plate of such a thickness that the cones projected into the open space above the tray. The cones transmitted heat from the catalyst into the space above this, giving some degree of heat to the incoming gas. The partially converted gas passed into the lower section which contained further catalyst trays. No attempt was made to remove heat from these latter stages. This design of converter would not seem to have been successful as the Tentelow Company later introduced a converter similar to the Badische except that a relatively large void section was incorporated above the tubes in which was installed a perforated distribution plate. The gases acquired some degree of temperature rise by contact with the converter walls.

With the early types of internal H.E. converter all the incoming gas was exposed to the whole of the heat exchange surface and with fluctuating gas concentrations accurate temperature control was not possible, and later designs incorporated methods of introducing cold gas at various places in the vessel.

In the early designs of converters for platinum, the loading was approximately 10 ozs. per ton of acid per day. Improved designs resulted in a reduction to approximately 4 ozs. per ton per day. One of the problems associated with the use of platinum was the danger of poisoning by small quantities of arsenical compounds, and it was necessary to have elaborate gas purification systems. Even if not poisoned, platinum suffers a gradual decline in activity, and it is stated that over a 10 year period the whole of the mass would have to be replaced.

Although vanadium was advocated for use as a catalyst as early as 1900 it was not until 1915 that it was introduced on a commercial scale, but it was in the late 1920's before it began to receive worldwide application, and of course has now practically entirely superseded platinum. The early users of vanadium merely replaced the platinum and used the same contact vessels, but as vanadium was a much more durable material it was possible to improve on earlier designs, utilising either internal or external heat exchangers.

Those early designers favouring the internal heat exchange endeavoured to remove the heat of reaction as formed. With external heat exchange advantage can be taken of the increased velocity of reaction at the higher temperatures, thus permitting in a split contact system a conversion in the first stage of approximately 70% using only 50% of the total catalyst, having cooled the gas in the interstage cooler and exposed the gas containing a lesser quantity of SO_2 to a relatively large amount of catalyst giving a relatively longer contact time.

A typical example of an early split contact unit is shown in Fig. 10. It consisted of two vessels fabricated in C.I. of bolted construction, the first vessel containing approximately 30% of the total catalyst in two layers, gas distribution baffles being arranged between the catalyst layers. The second vessel contained the remaining 70% of catalyst in three layers with similar gas distribution baffles. Between the two vessels was an interstage cooler consisting of a tubular heat exchanger using atmospheric air as the cooling medium when burning sulphur or with cold gas when pyrites burning. A further development of the external heat exchange converter was a single vessel of mild steel construction containing four layers of catalyst supported on cast iron grids with cooling between each stage. In the case of sulphur burning the excess heat is recovered in the form of steam. Throughout the development of converters, emphasis has been on the question of gas distribution and recently converters have been designed with the fourth pass split into two layers of catalyst, with the object of improving gas distribution in the final stage. See Fig. 11.

Earlier in the paper the subject of the advantages of cooling by quench air has been discussed and a typical converter designed for quench air is also shown in Fig. 11. The introduction of vanadium catalyst has also permitted considerable development of the internal H.E. converter as with platinum catalyst the high poisoning risk and the difficulties of replacing the mass was a very costly operation. An internal heat exchange converter has a fixed heat exchange surface and for this reason is not so flexible as the external type but it has the advantage of occupying much less floor space. The early designs using vanadium contained the whole of the catalyst inside the tubes but this resulted in a high pressure drop, and so the catalyst layers were divided into the first mass outside the tubes supported on a perforated plate with the top sections of the tubes passing through the first mass. The cool gas entered the lower part of the vessel and circulated outside the tubes passing upwards through the first catalyst layer and then down through the tubes containing the second pass.

The Lurgi internal heat exchange converter tries to utilise the facts discussed above that maximum velocity of reaction is obtained at a temperature somewhat lower than that corresponding with the equilibrium temperature of the mixture. The gas mixture at 320-340°C is fed into the main body of the converter - See Fig. 12 - and passes counter current outside of tubes containing catalyst. The gas then passes through a catalyst bed and then down through the catalyst tubes. In this way maximum temperature is reached at the top of the converter at minimum conversion, and as conversion proceeds the gases are cooled by the surrounding incoming cold gases.

Acknowledgments.

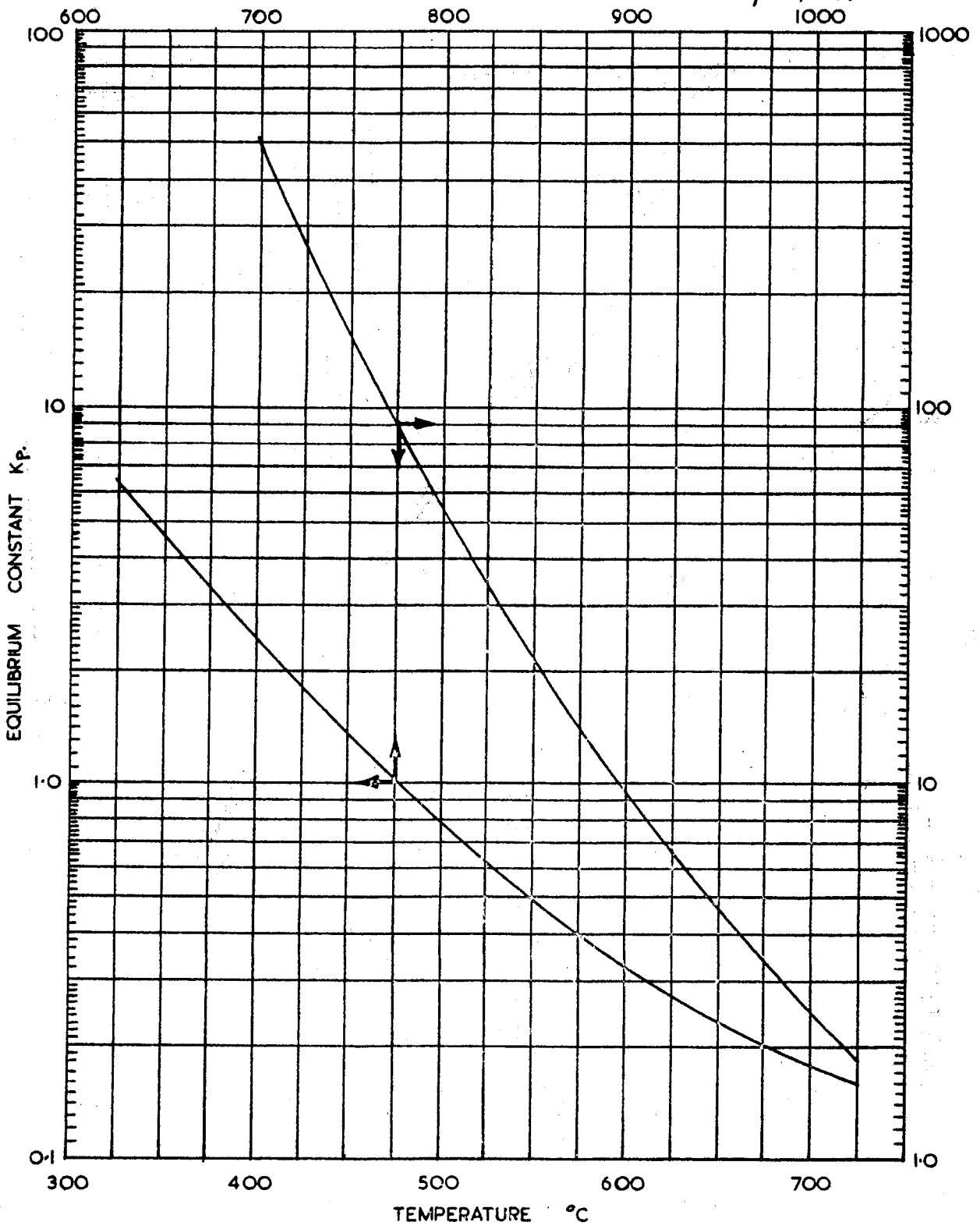
We must first acknowledge great help and inspiration from that most remarkable text book "Chemical Process Principles" by Hougan and Watson, to pay tribute to it would be both impertinent and presumptuous.

We should like to acknowledge the help of Mr. E. E. Bishop of Monsanto Chemical Company for valuable discussion on catalysis, of members of the staff of Messrs. Simon Carves for supplying drawings of converters, of many members of the staff at our Birmingham factory.

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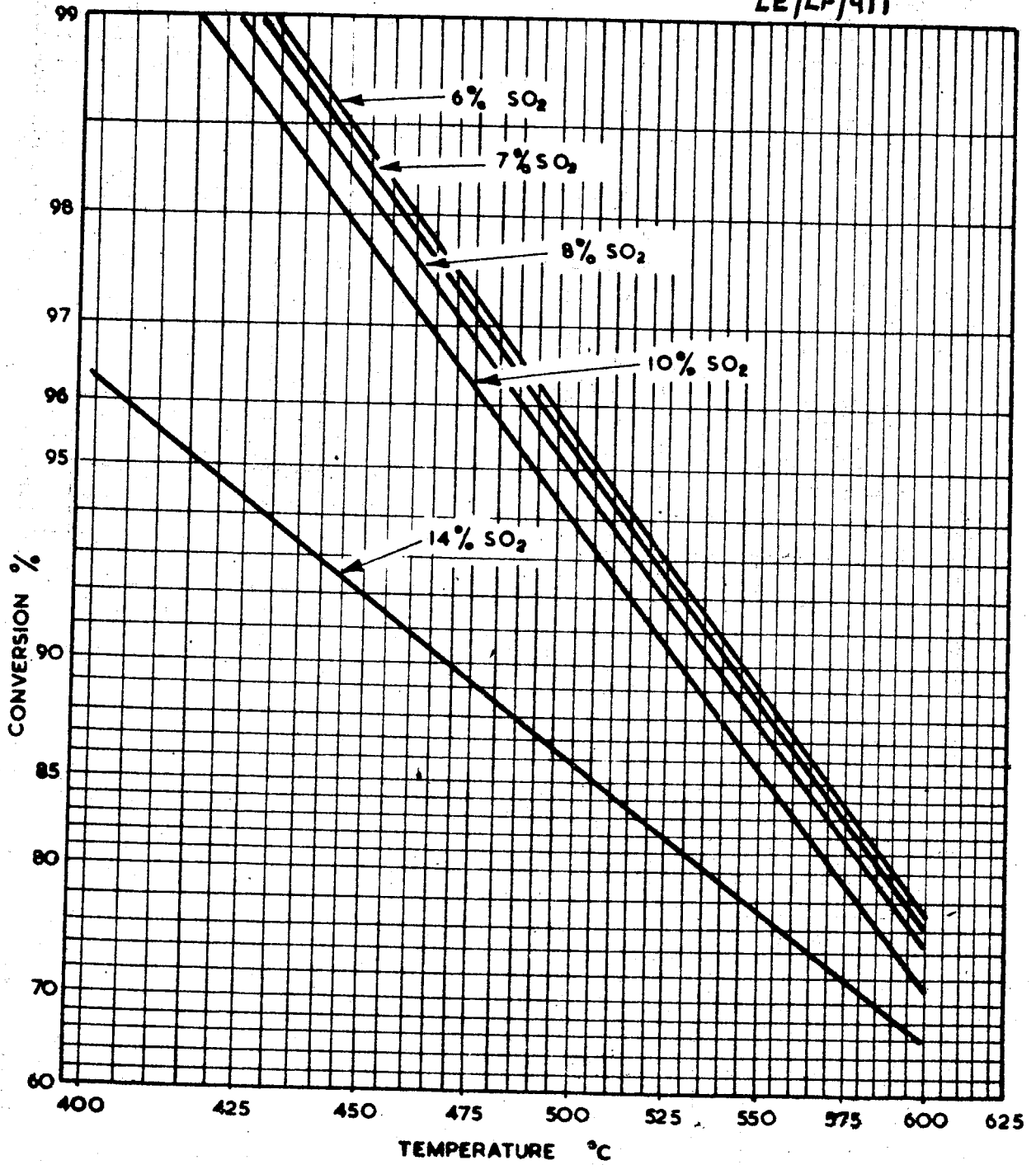
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EQUILIBRIUM CONSTANT FOR REACTION $SO_2 + \frac{1}{2}O_2 = SO_3$

FIG. 1.

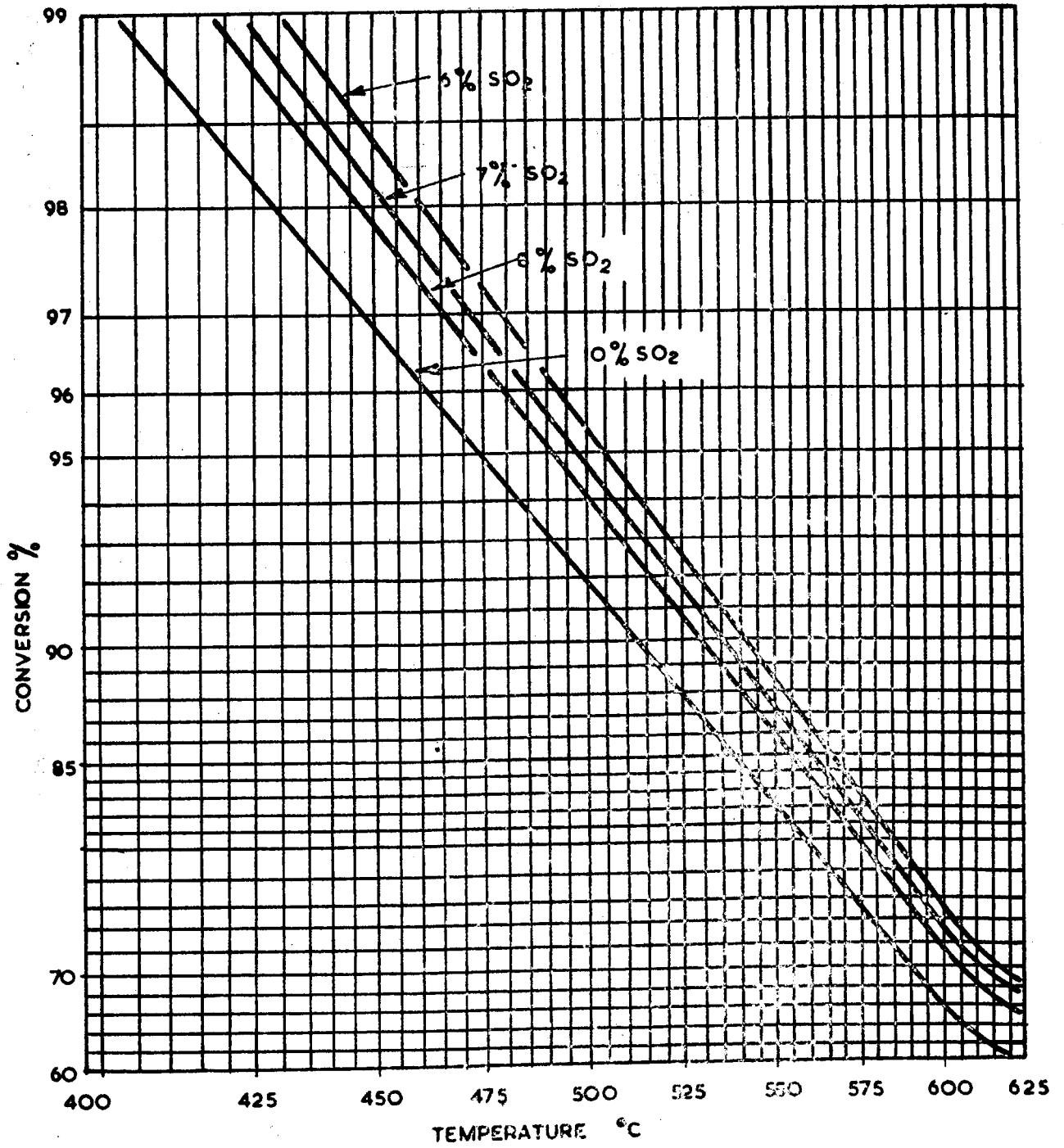
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THEORETICAL CONVERSION OF SULPHUR GAS

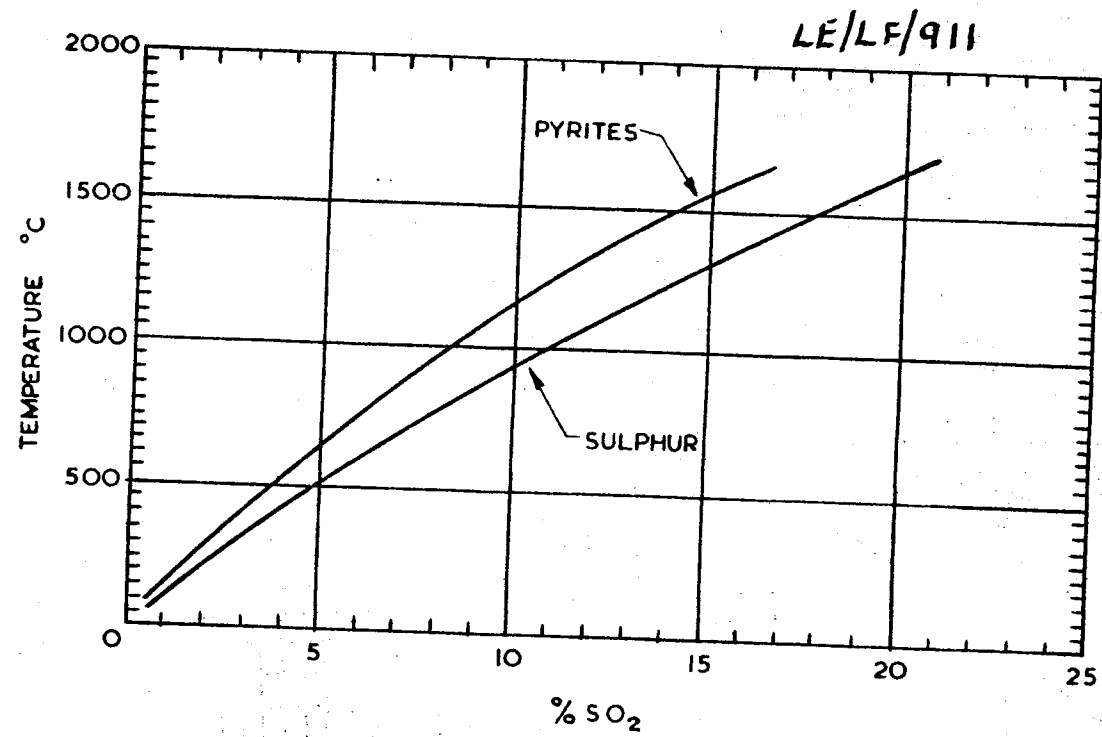
FIG. 2.

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THEORETICAL CONVERSION OF PYRITES GAS

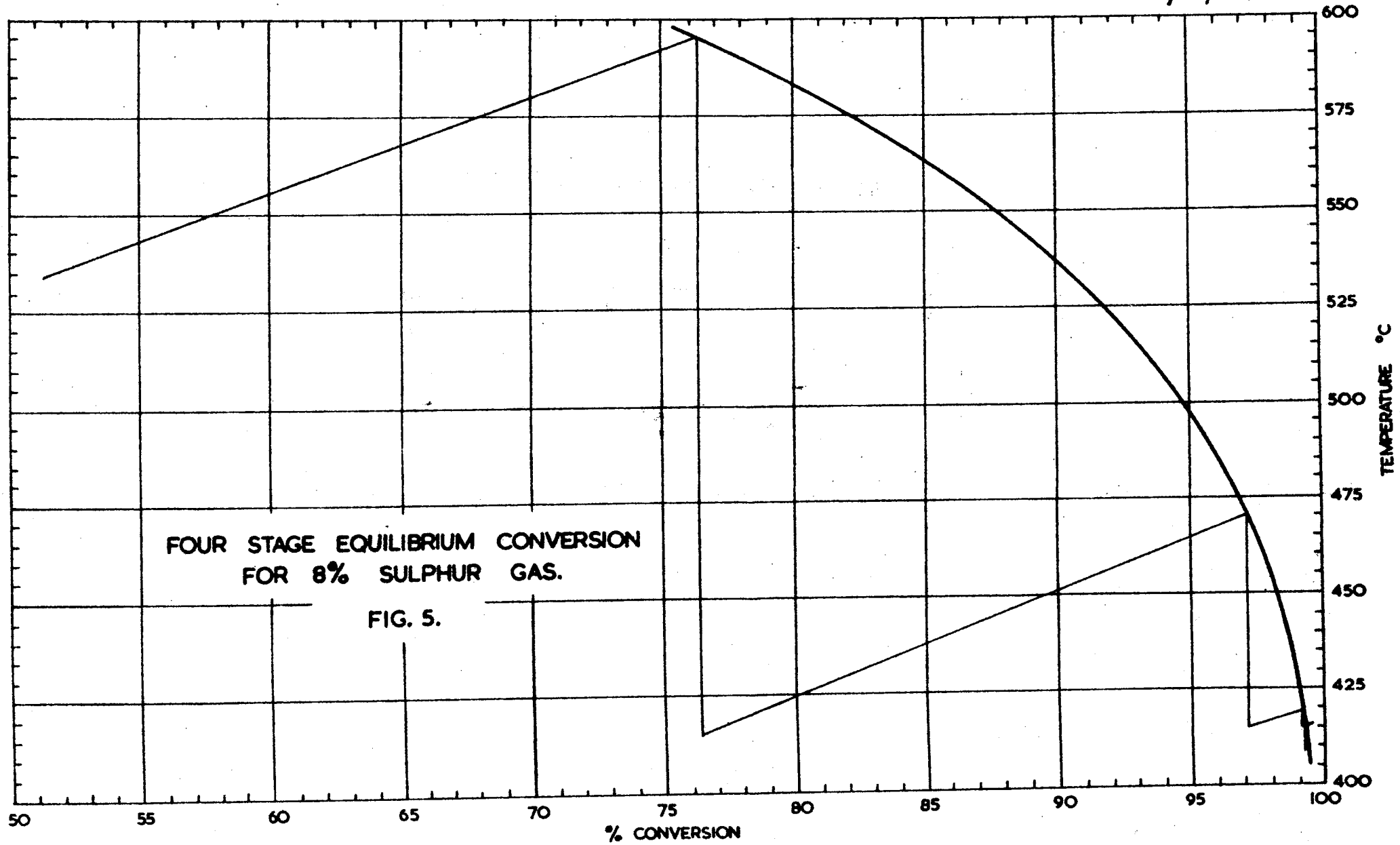
FIG. 3.

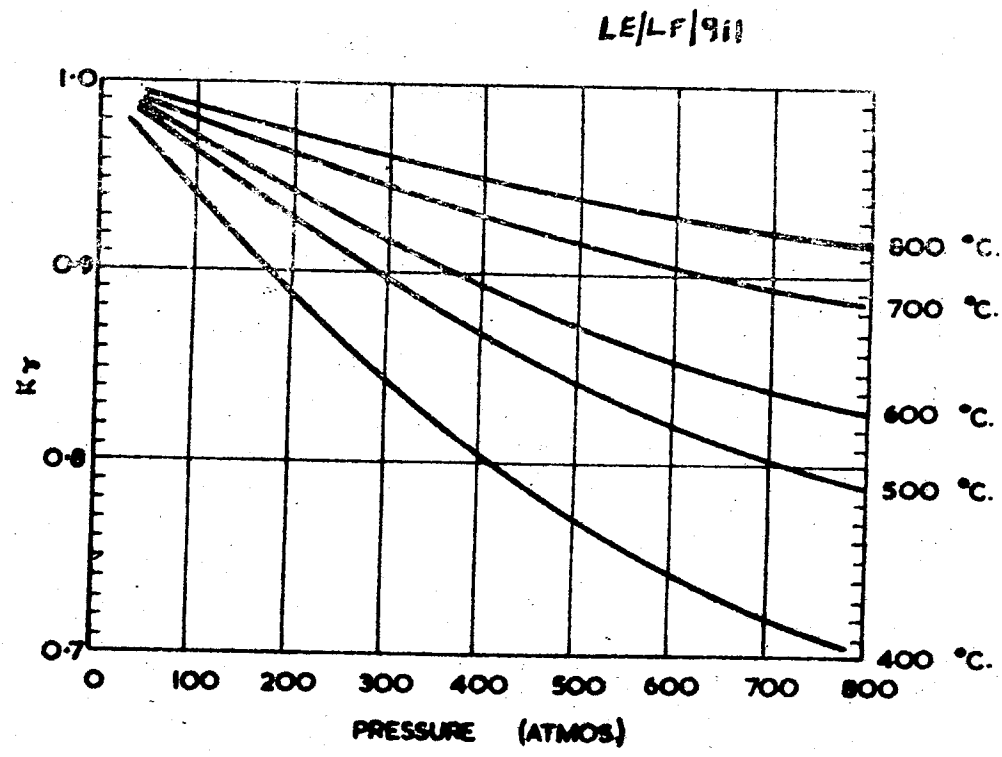


MAXIMUM TEMPERATURE OF GASES LEAVING BURNER.

FIG. 4.

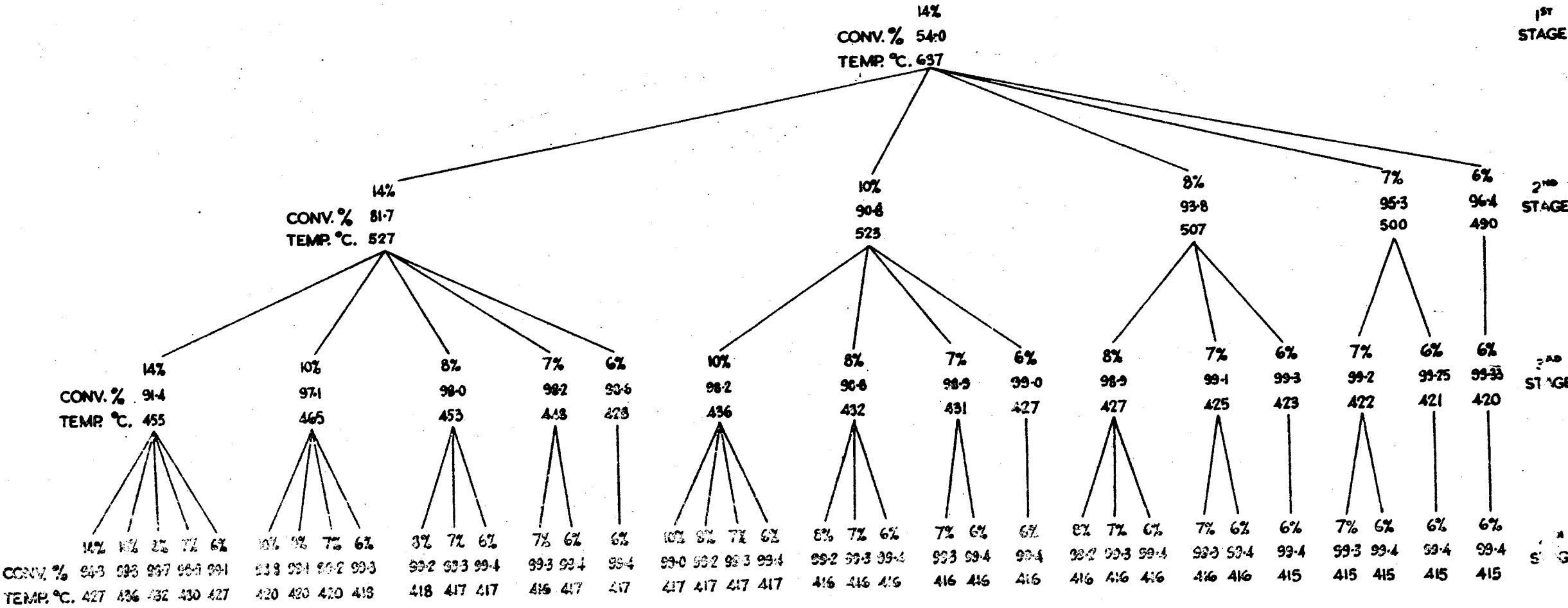
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RATIO OF FUGACITY COEFFICIENTS.

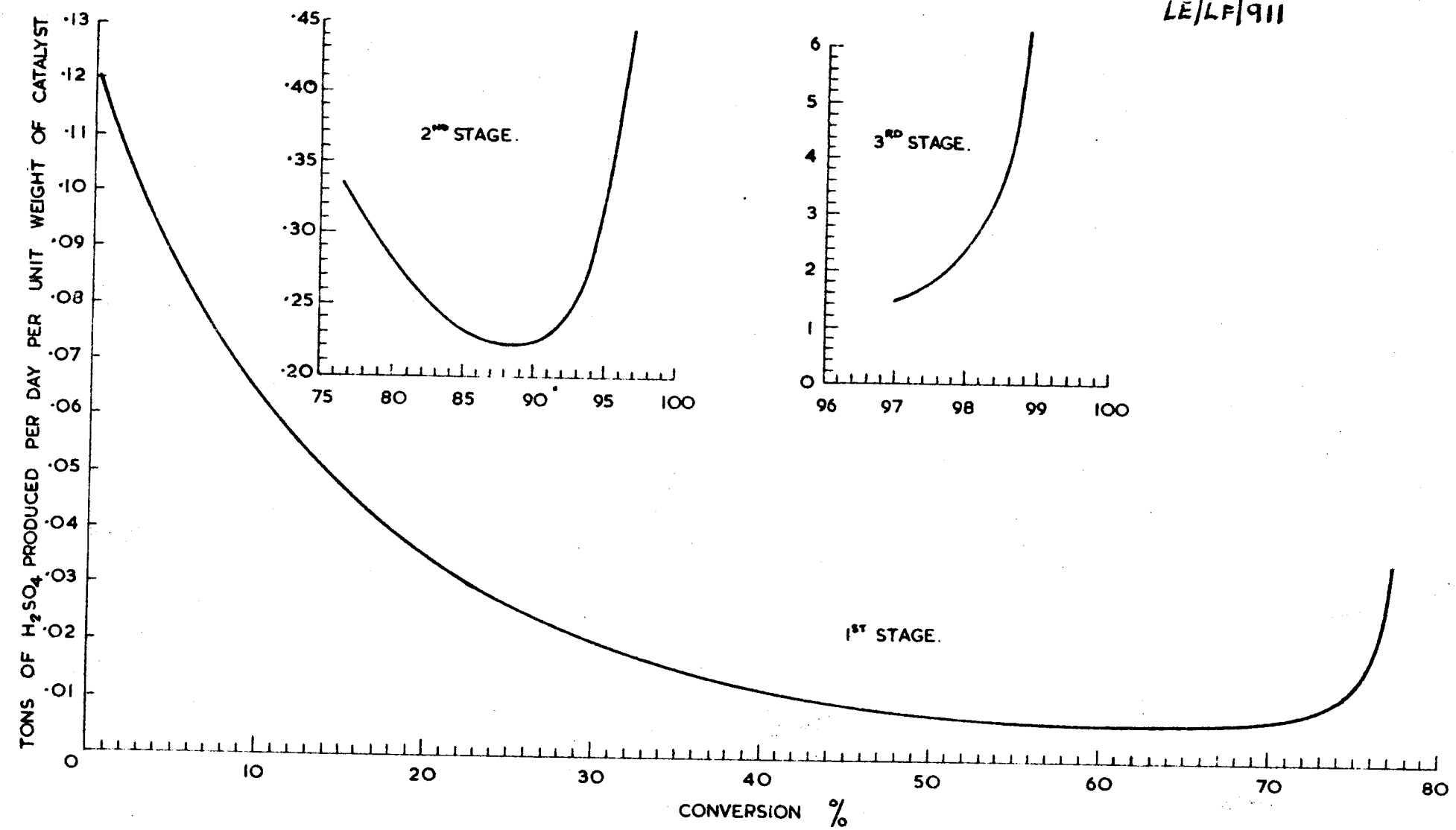
FIG. 6.



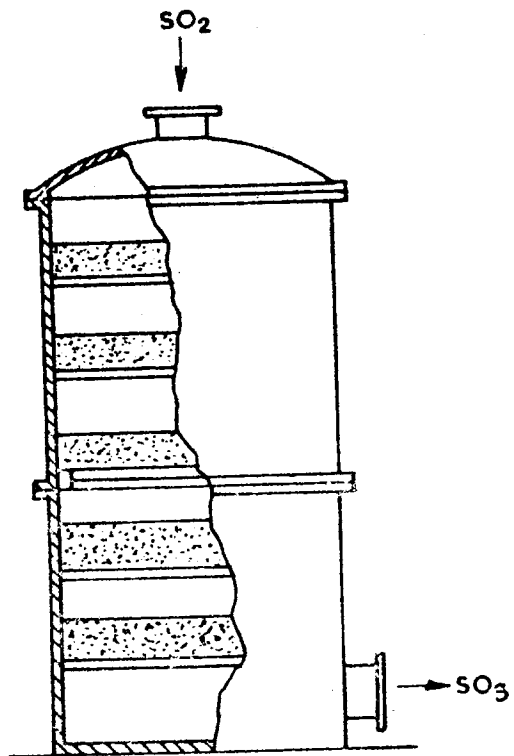
STAGES IN QUENCHING 14% SO₂ SULPHUR GAS
INITIAL TEMPERATURE 415 °C.

FIG. 7.

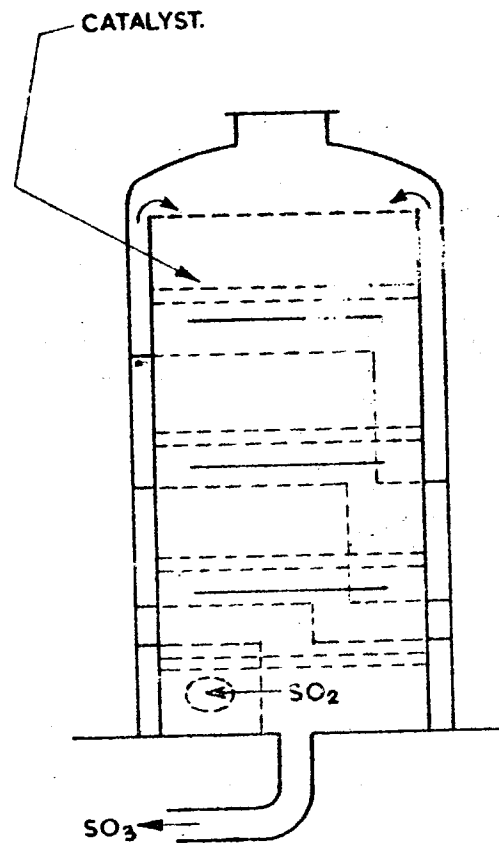
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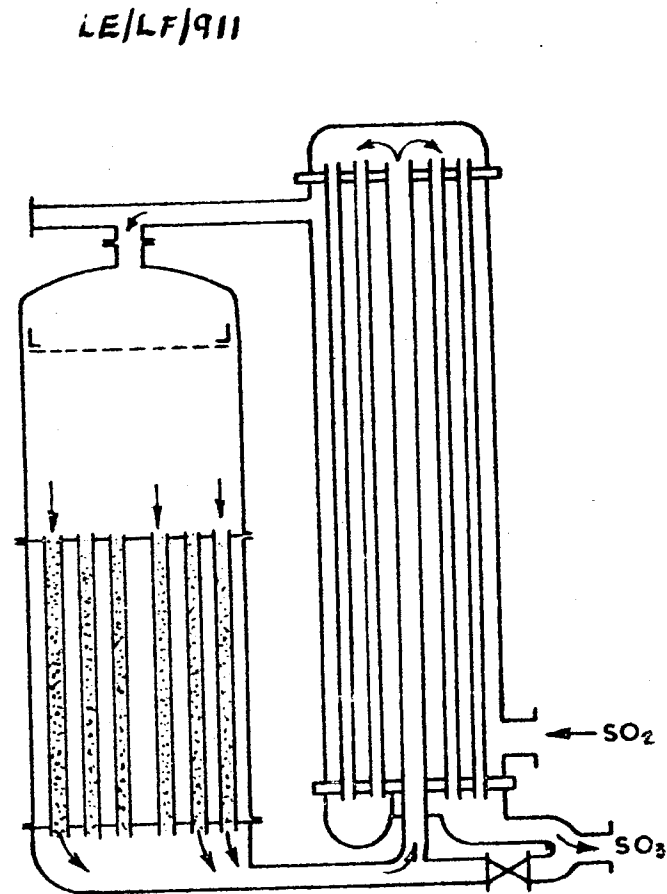
THEORETICAL CATALYST DISTRIBUTION RATIO FOR EQUILIBRIUM CONDITIONS
IN THREE STAGE CONVERSION OF 8% SULPHUR GAS.



OLD PATTERN
GRILLO CONVERTER.
(a)

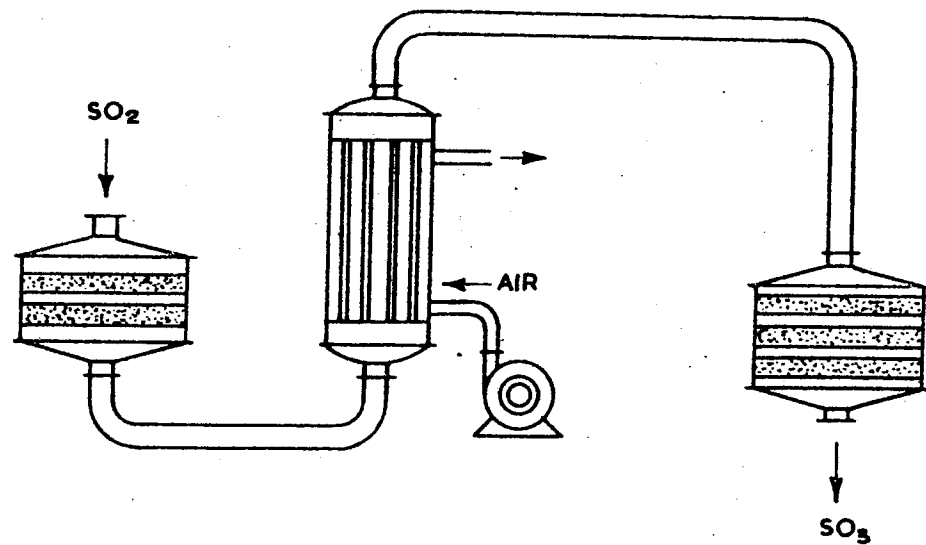


REGENERATIVE
GRILLO CONVERTER.
(b)



TENTELW CONVERTER
& HEAT EXCHANGER.
(c)

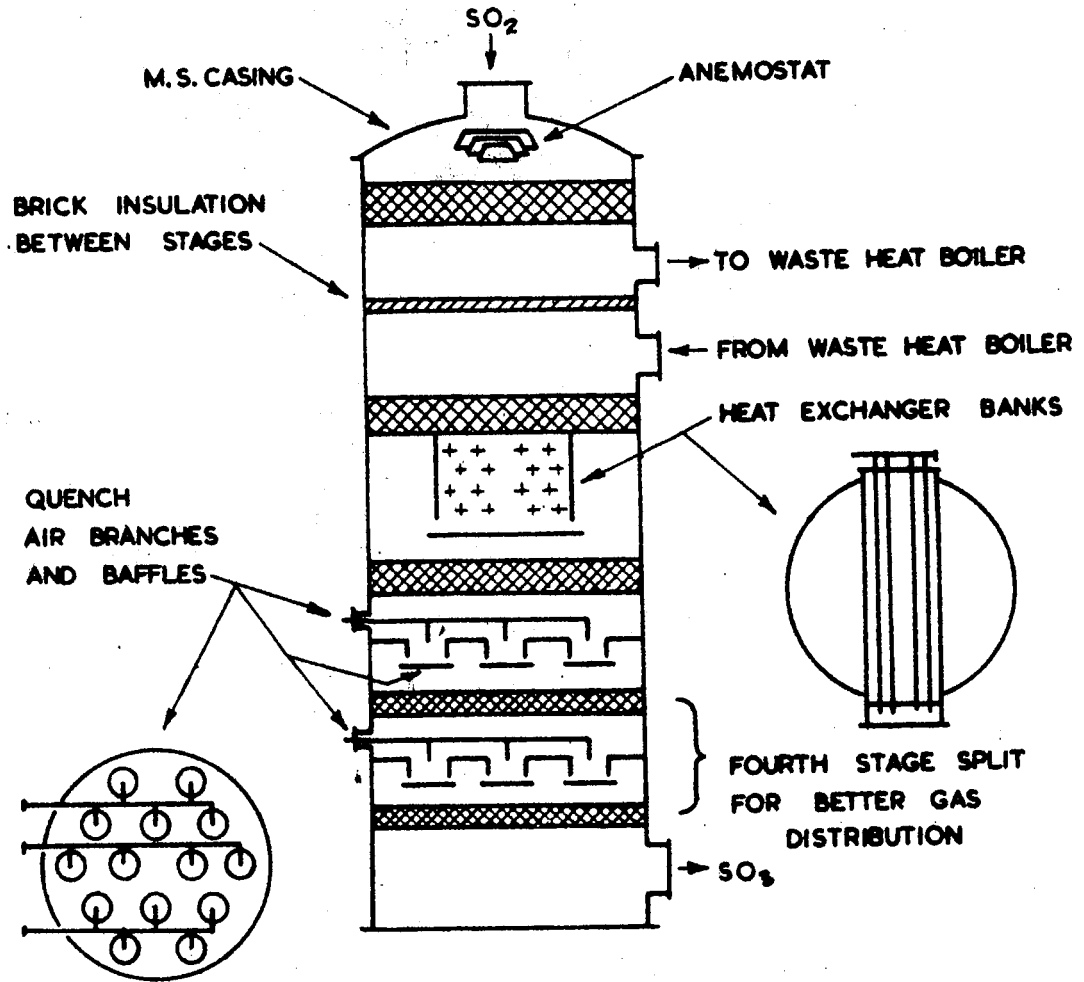
FIG. 9.



TWO STAGE CONVERSION WITH INTERMEDIATE AIR BLOWN COOLER.

FIG. 10.

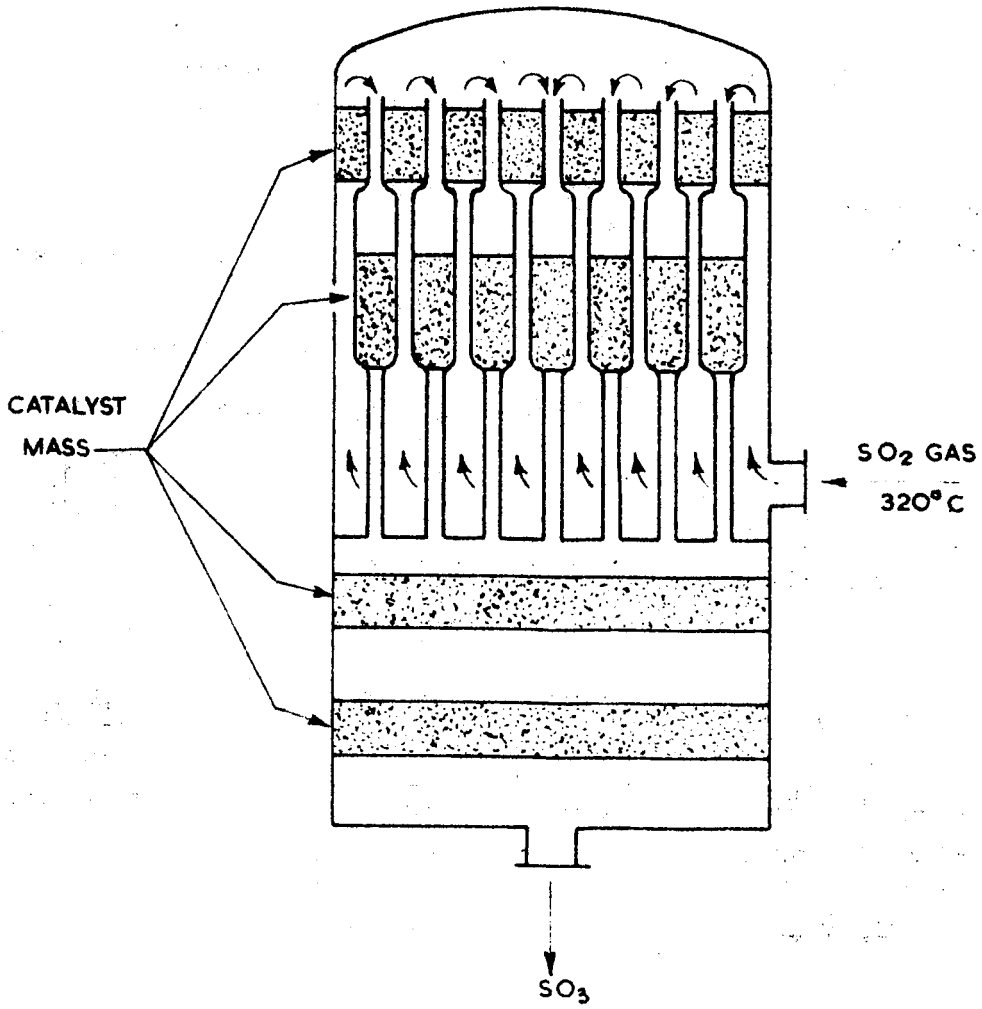
LE/LF/911



DEVELOPMENTS IN THE FOUR STAGE CONVERTER.

FIG. II.

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INTERNAL HEAT EXCHANGE CONVERTER.

FIG. 12.