A STUDY OF CONVERSION

In The

MANUFACTURE OF CONTACT SULFURIC ACID

A THESIS

SUBMITTED TO THE FACULTY

of the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING PRACTICE

Submitted By:

Approved By :

June 1, 1927.   ----------------------

INDEX

SUBJECT

The subject of this Thesis

is " A Study of Conversion in

the manufacture of Contact Sulfuric

Acid " at the Merrimac Chemical

Company, South Wilmington, Mass -

achusetts, May 1927 .

AN ACKNOWLEDGEMENT

OBJECT

This investigation was made to
determine the cause of the low overall
conversion (86%) of sulphur to H_2SO_4 in
the " F set " in the contact plant of the
Merrimac Chemical Co, South Wilmington ,
Mass.   It was also desired to determine
the optimum conditions for the most complete
conversion, and to find the maximum theoretical
conversion possible with the present apparatus
and acid production.   Conversion, the effects
of different variables upon conversion, and the
validity of various equations for rates of re-
action and equilibrium of SO_2, O_2, and SO_3
were to be studied.

ABSTRACT

By gas analyses at various points in
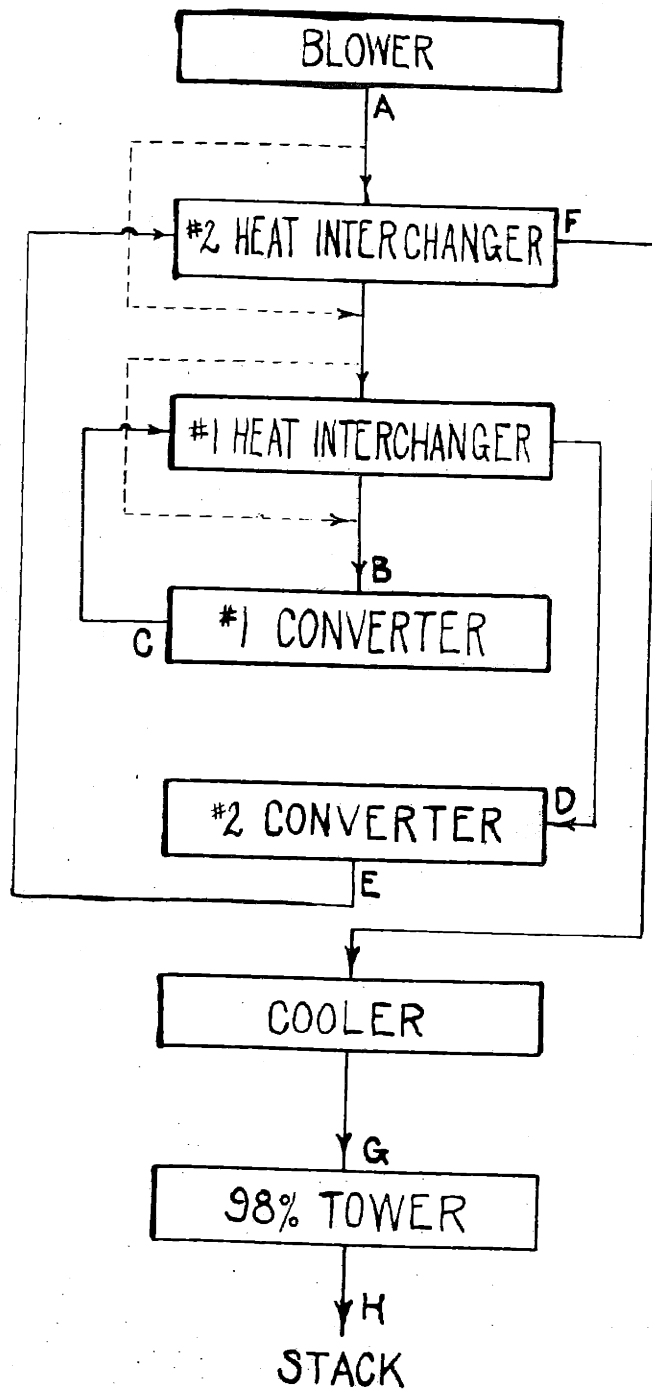the conversion system it was found that the
discrepancy between the conversion calculated
from stack analyses and that from production
figures was due to errors in the former.

By calculation from the rate of reaction
it was found that the present operating conditions
give the optimum conversion and that the best way
to obtain higher conversions would be by revive-
fying the platinum.

INTRODUCTION .

This problem was suggested by the

plant superintendant, Carl Dean, as the

result of a descrepancy between an overall

conversion of 86% , calculated from a sulphur

balance on production figures, and a calculated

conversion of 90% from gas analyses before the

converters and at the stack . The value of

86% is accurate to within 1%. This follows from

the fact that production figures vary but little

from month to month. The hourly fluctuations are

effectively wiped out in long periods of time .

Losses that might account for this descrepancy of

conversions are sulphur losses from trucks, excess

% of sulphur in the acid sold, gas leaks and stack

losses.

PATH OF GAS THRU CONVERTERS

```
                    ┌─────────────────────────┐
                    │         BLOWER          │
                    └─────────────────────────┘
                              │ A
          ┌ ─ ─ ─ ─ ─ ─ ─ ─ ─ ┤
          │    ┌─────────────────────────────┐ F
      ┌──→│──→ │    #2 HEAT INTERCHANGER      │───────┐
      │   └ ─ ─│─ ─ ─ ─ ─ ─ ─ ─ ─→            │       │
      │        └─────────────────────────────┘       │
      │               │                              │
      │         ┌ ─ ─ ─┤                              │
      │     ┌──→│──→┌─────────────────────────────┐  │
      │  ┌──│───┘   │    #1 HEAT INTERCHANGER      │──┼──┐
      │  │  └ ─ ─ ─ │─ ─ ─ ─ ─ ─ ─ ─→             │  │  │
      │  │          └─────────────────────────────┘  │  │
      │  │                 │ B                         │  │
      │  │          ┌─────────────────────────┐       │  │
      │  │  C       │       #1 CONVERTER       │       │  │
      │  └──────────┤                         │       │  │
      │             └─────────────────────────┘       │  │
      │                                               │  │
      │             ┌─────────────────────────┐ D     │  │
      │             │       #2 CONVERTER       │←──────┘  │
      │             └─────────────────────────┘          │
      └──────────────────────┤ E                          │
                             ▼                             │
                    ┌─────────────────────────┐           │
                    │         COOLER           │←──────────┘
                    └─────────────────────────┘
                              │ G
                    ┌─────────────────────────┐
                    │       98% TOWER          │
                    └─────────────────────────┘
                              │ H
                           STACK
```

(INTRODUCTION CONT.)

The converters and the heat interchanger in the "F set" have been installed less than a year. There are two converters, No.1 and No.2, in series. There is no bypass arrangement between the converters, all the gases leaving converter No.1 must go through converter No.2. The hot gases leaving the converters preheat the SO_2 entering the first converter. There are two divisions of the heat interchanger, each of which may be by-passed by the SO_2. The details of arrangement are shown on page --- .

Both converters are similar to those used in the Badische process of making sulphuric acid. The gases enter the top of the converters and react on their way down the plates.

Converter No. 1 is packed from the top to bottom as follows: The filter section consists of one blank plate, followed by four plates of acid washed asbestos. The converter proper has one blank plate, followed by seven plates of platinized asbestos, each plate containing 1020 grams of platinized asbestos (2.117 troy oz. of platinum per plate). The lower part contains 10 plates, each containing 1398 grams of platinized asbestos (2.90 troy oz. of platinum per plate).

Converter No. 2 has a total of 53 plates, 52 of which are packed. There is one blank plate at the top. This is followed by 24 plates, each containing 1398 grams of platinized asbestos per plate. The lower part of this converter contains

28 plates of 1020 grams of platinized asbestos per plate. Seven and one-half percent of each plate is platinized asbestos.

The operator has in his power to control the inlet gas composition of the first converter, and the inlet gas temperatures of both converters. The amount of gas passing thru the converter is constant because the blower is run by a constant speed synchranous motor.

The gas entering the first converter is analysed at a plant control office. Its composition is controlled by admitting secondary air into the combustion chamber after the burner. It takes about twenty minutes for the gas to travel from the sulphur burner to the first converter. This twenty minute log of gas composition between the sulphur burner and the converter made it difficult to regulate the SO_2 content of the gas to a constant value. Over long periods of time the gas composition assumes a constant value, but may vary as much as 1% (from 10.5 to 9.5 %) in 15 minutes. The main factor influencing the gas composition is the rate at which the sulphur is fed to the burner.

The temperatures of the gases entering either converter may be controlled by varying the amount of gas by-passed the heat interchanger. These temperatures vary but little, two or three centigrade degrees in an hour.

An optimum set of conditions has been determined for the maximum conversion by the results of past experience of plant operators. These conditions were determined by "trial and error" methods rather than from theoretical considerations. They are as follows :

Inlet SO_2 composition of No.1 converter = 10.5 %
Inlet temperature of   " "   "   = 400 °C
Inlet temperature of   No. 2   "   = 440 ° C

Work, similar to this investigation, was done on the
"C set" of this same plant two years ago by Wilde, Wang, and
Schaefer. Their report is available at the M.I.T. Practice School
Station at South Wilmington, Mass. Their work may be summarized
in the following manner.

Conversions of SO_2 were computed by means of gas analyses,
using the Reich test for SO_2 content. The results obtained were,
however, not reliable, the calculated conversions being lower
than production figures indicated them.

Next, they tried a "temperature rise" method. This
involved computing conversion from the heat generated by the
reaction $SO_2 + 1/2\ O_2 \relbar\relbar\relbar SO_3$. More accurate conversions were
calculated by this method, and an optimum set of inlet temperatures
determined from an inlet of 9.5% SO_2 gas entering No.1 converter
Their temperatures checked plant experience remarkably well.

In this investigation conversions were calculated from
both gas analyses and temperature methods. An optimum gas comp-
osition entering No.1 converter and optimum inlet gas temperatures
in both converters were calculated from purely theoretical con-
siderations for maximus conversions.

Work has been done of the conversion of SO_2 with platinum
by Knietsch, Bodenstein, Ries, and others. The more reliable data
and equations found in the literature were used in these calculations
A discussion of the theoretical back-ground and the validity of
data found in the literature is given in the "Appendix".

RESULTS

The conversion at the exit of the first converter was experimentally found to be 62.5% and at the exit of the second converter was 84.9% . Analysis indicates the probable existance of a leak within the No.2 heat interchanger. Radiation and Convection heat losses from No. 1 Converter was found to be 3.53% and from No. 2 Converter 11.4% giving an overall loss of 5.61%. There was 164 pounds of SO_2 per hour per pound of platinum. For detailed experimental results see Tabel 3 in Appendix I

The optimum operating conditions derived from theoretical considerations were found to be:

Inlet gas: 10.5% SO_2

Temperature at Entrance No. 1 Converter : 395° C

     "   "   "   No. 2 Converter : 445° C

The platinum mass in No. 2 Converter was found to be 0.438 the activity of the mass in No. 1 Converter.

DISCUSSION OF RESULTS

The conversion of 62.5% at the exit of No. Converter is the average of four determinations taken within a period of eight days and with an average deviation of 0.5% . The Conversion of 84.9% at the exit of No. 2 Converter is the average of eight determinations taken within a period of eight days and with an average deviation of 2.1 % . These conversions, compared with present day practice are low. Such low conversions could be due to:

(1) Excessive gas rate or low weight of platinum

(2) Improper gas composition or temperature

(3) Activity of the contact mass

F.D. Miles on page 126 of his book "Manufacture of Sulfuric Acid (Contact Process)" (1925) gives following ratios of wt of SO_2 per hour to wt. of platinum, for single converters:

Plant	$\dfrac{\text{wt } SO_3 \text{ per hour}}{\text{wt Pt.}}$
U. S. Nav al Proving Grounds	33.1
U. S. Govt. Nitro W. Va.	78.0
Messrs Nobels (South Africa)	45.0

However on page 169 he states that in using two converters as much as 70% of the platinum may be dispensed with and this would greatly increase the above ratio for two converters in series. Therefore 164 lbs. SO_2 per hour per lb. platinum is not the cause of the low conversions.

From purely theoretical considerations taken up in
Appendix II the optimum operating conditions derived, check
remarkably well with present operating practice. Therefore
improper inlet gas composition or temperature is not the cause
of the low conversions.

It is believed by members of the Merrimac Chemical
Company that the activity of this contact mass is very low and
this is indeed a plausible explanation for the low conversions.
Furthermore our results show that the mass in No.2 converter is
less than one half as active as the mass in No. 1 converter.

Plant conversions are based on an analysis made at the
base of one of two stacks through which the gas is exhausted to
the atmosphere. This gas after leaving No.2 converter passes
thru an interchanger, cooler and absorption tower in series before
reaching the stack consequently any variation in gas composition
after leaving the converter should not be credited to it. Production
records over a period of months for this set are about four per
cent less than conversions taken as explained. These production
records check within 1% conversions which were found by analysis
at the exit of No.2 converter during the period of this investigation.

The SO_2 content of the gas leaving the No.2 interchanger
was consistently higher then that leaving the No. 2 Converter.
This indicates the probable existance of a leak within the inter-
changer. No attempt is made to state the magnitude of this
probable leak due to failure to get reasonable checks on the
analyses at the exit of the interchanger, and to lack of agreement

with the leakage calculated from a heat balance.   Inability
to get reasonable checks on the analyses may be due to the location
of the sampling jet which was set in the bottom of the elbow thru
which the gas leaves interchanger.

The heat losses because of the crude manner in which
they were determined are only an approximation. In as much as
errors in these losses have only a slight bearing on the calcula-
tions and results, such a crude method is justifiable.

Due to a mischance in choosing the scales for plotting
the calculations from Reis's equation, the work was not carried to
completion. The predicted rate of reaction was found to be
infinite at 0% conversion. This is very hard to believe, but
the predicted rate falls to a reasonable figure by the time 0.2%
conversion is reached. Even if the rate at conversions of less
than 0.2% is wrong, the error in calculating the time to obtain
ordinary plant conversions is negligible.

The optimum conditions for conversion found by theoretical
calculations check the plant experience almost exactly. The
optimum inlet gas composition is 10.5%, but from inspection of the
curves in plot No.19 it is seen that 9.5 and 10.5 % curves are flat
at their maximums. The 8.5% curve is continuously low, while the
11.5 % curve is peaked giving unsafe ranges. The inlet temperatures
in No.1 converter should be kept in the range of 380-410°C, and
440-460°C in the second converter. In general the inlet temp. of
No. 1 converter should be increased with inlet gas weaker than 10%
and decreased when the inlet gas becomes strong.

CONCLUSIONS

The F set converters are now being operated at the optimum temperatures and inlet gas composition.

Low overall conversion is due to the low activity of the contact mass.

Stack analyses do not give true conversion.

RECOMMENDATIONS

It is recommended (1) that when higher conversion is desired that the contact mass be reactivated, maintaining present operating conditions until this time.

(2) That conversions be based on analyses at the exit of No. 2 converter.

(3) That the advantages of other types of interchangers over the present installation be considered.

(4) That during a shut-down the No.2 interchanger be tested for leakage.

(5) That further theoretical work be done with Reis' equation as a basis.

# APPENDIX I

METHOD OF PROCEDURE:

All the experimental work done in this investigation was completed within ten days. There were thirteen runs made to determine the analysis of the gas at various points in the system. The temperatures at different points were also taken.

Gas analyses consisted of the determination of the SO_2 content present. It was decided that a method proposed by Ries was superior to the ordinary Reich test. Ries analysed synthetic mixtures of SO_2, SO_3, O_2, and N_2, and found that his method of dissolving the gas in KOH and titrating with KIO_3 was in every case more reliable than the Reich test.

Gas analyses were made simultaneously at the various points in the apparatus, A,C,D,E,F,G, and H shown in flow sheet of the converters. Analysis at A checked that made with chromic acid in the control office at the plant, so after the first two runs the blower gas was analysed with chromic acid.

The Ries method for the determination of SO_2 was used at all other points except at "A" . About 1 liter of gas was bubbled thru an absorption train connected to a still sampling tube by means of a mercury seal. The train consisted of an eight inch tube, filled with 60 cc. of 1/10 NaOH thru which gas was bubbled by means of a capillary glass tube, and a 2 1/2 liter graduated aspirator bottle connected by means of a siphan to a similar empty bottle. The apparatus was tested for leaks. The difference in level of the water in the aspirator bottle, read at atmosphuric pressure, measured the O_2 and N_2 passed thru the NaOH. This volume

was approximately 1000 c.c. , and could be measured with an error of not more than 20 cc. giving an accuracy of 2%. The absorbed SO_2 was then washed into an erlenmeyer flask diluted to 100 c.c. with distilled water, the contents made acid with 100 c.c. of 12n HCl and titrated with 1/10 n KIO_3. The normality of HCl during titration was approximately 4.8. The amount of KIO_3 used variated from 2 to 20 c.c. About 10 cc. of C Cl_4 were added before titrating. A deep pink or purple color first appeared in the C Cl_4 layer when the I had been freed, but upon addition of more KIO_3 the I was oxidized to a colorless I Cl which formed the end point of the titration. The equation is as follows:

$$2\ SO_2 + KIO_3 + 2\ HCl \longrightarrow 2\ SO_3 + H_2O + KCl + ICl$$
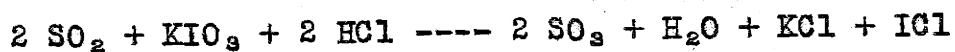
From the amount of SO_2, O_2 and N_2 found in the sample, together with the blower gas analysis; the analysis of the sample was computed.

The KIO_3 was standardized with KI according to the reaction:

$$KIO_3 + 2\ KI + 6\ HCl \longrightarrow 3\ KCl + 3\ H_2O + 3\ I\ Cl$$

(PROCEDURE CONT.)

Temperatures of the gas entering and leaving both converters were measured by means of platinum resistances placed in blind iron tubes at the top and bottom of the converters. These platinum resistances were checked by thermocouples and were found to be correct. It is easy to read the temperatures to the nearest centegrade degree with the platinum resistances. Temperatures of the blower gas were measured by bare mercury thermometers immersed in the gas stream. The temperature of the gas leaving the heat-interchanger was measured by a mercury thermometer placed in an oil well.

Surface temperatures of the converters were determined with mercury thermometers protected by blocks of wook. The bulb was pressed against the converter surface while the block that held the thermometer reduced radiation and convection losses.

The sulphur rate and the amount of sulphur lost in leaving the gas were obtined from plant records.

REFERENCE DATA:

At atmospheric pressure, the heat of formation of SO_2 from SO_2 and O_2 is constant at 22,600 calories per gram mol of SO_3 for the temperature range from 300°C to 660° C.

The heat capacity of SO_2 in calories per gram mol per °C is $7.0 + 0.0071\ T - 0.00000\ 186\ T^2$

The heat capacity of O_2 or N_2 in calories per gram mol per °C is $6.50 + 0.0010\ T$

PLANT DATA

3 % of the sulfur fired is burned to SO_3 and removed in the purification system.

The average sulfur fired per day in the F set is 24,000 lbs.

The normal SO_2 in the blower gas for the F set is 10.5%

In the blower gas, the volume %'s of SO_3, CO_2, and H_2O are negligible.

Weight of platinum in first converter, F.Set = = 43,82 troy oz.

Weight of platinum in second converter, F. Set = = 128.41 troy oz.

EXPERIMENTAL DATA

Standardization of KIO_3 solution.

Blank titration negligible both for standardization and for runs.

1.0059 g. KI	=	29.87 cc. standard solution
0.5500 g. KI	=	16.2 cc.
0.4000 g. KI	=	11.75 cc.
0.2000 g. KI	=	5.8 cc.

Average   1 g. KI   =   29.4 cc.

Table 1

Summarized Experimental Data

May 1927

Run	1	2	3	4	5	6	7	8	9	10	11	12	13
Date May	2	3	3	3	4	4	4	6	9	9	10	11	11
A % SO_2 (chromic)				10.5	12.2	10.1	10.6	8.5	9.5	10.7	10.8	10.6	9.65
Temp °C	17°	12°	19°					27	32.5	32.5	32.5	34	37
c.c. aspirated	760	1110	1090										
Temp gas asp.													
Titration	15.95cc	26.7	25.7										
B Temp °C	402	401	401					401	399.5	399	400	402	401
C Temp °C	582	582	583					580	575	579	580	579	572
c.c. aspirated	640	510	740					920			1690		
Temp gas asp.	20°	21	26					29			23		
Titration	5.3cc		6.5					6.18			15.5		
D Temp °C	441	438	439					435.5	437.5	436	437	446	441
a.c. aspirated								1380			930		
Temp gas asp.								32°			3.5		
Titration								8.92			9.45		

Table 2

Summarized Experimental Data - continued

Run		1	2	3	4	5	6	7	8	9	10	11	12	13
E	Temp °C	496	495.5	497					492	491	493	496	497	499
	c.c. aspirated				1480	1220	1130	860	1170			1010	930	1060
	Temp. gas asp.				41°	35°	35	35	37			35	40	45
	Titration				4.5cc	6.5	3.6	3.0	2.48			4.0	2.2	3.3
F	Temp °C								274	275.5	274	273	265	270
	c.c. aspirated	780	660	950	1000	910	1100	970	1060	875	530	770	340	1110
	Temp. gas asp.	24	23	23	29	26	26	25	28	28	30	25	30	37
	Titration	6.8cc	4.2	6.9	12.5	13.3	5.9	7.8	9.65	11.65	3.1	8.75	5.6	8.4
G	c.c. aspirated							1420	940	1340	1200	460	610	
	Temp. gas asp.							18°	31°	34.5	32	31	34	
	Titration							4.6c.c.		11.15	8.3	2.8	3.0	
H	c.c. aspirated										920		1130	1130
	Temp. gas asp.										2.5		33	36
	Titration										3.2		2.8	2.25

Nomenclature:

The following 6 quantities are each based on 1 gm. mol of total gas (blower gas) entering the first converter:

x =   gm. mols of SO_2 at any point

x_0 =   gm. mols of SO_2 in blower gas

$x_0 - x$ =   gm. mols of SO_3 at any point (This assumes the SO_3 in the blower gas to be 0)

y =   gm. mols of O_2, N_2, and inerts at any point.

a =   gm. mols of O_2 in blower gas.

b =   gm. mols of N_2 and inerts in blower gas.

Note that x, x_0,$- x$, and y are _not_ based on 1 gm. mol of total gas at the point to which they refer.

It is evident that $a + b + x_0 = 1$

Other quantities to be defined are as follows:

ln =   logarithm to the base e

log =   logarithm to the base 10

t =   temperature in °C absolute

θ =   time

$\triangle$ =   increase

P =   partial pressure in atmospheres

e refers to equilibrium

$$K = \frac{(PSO_3)^2}{(PSO_2)_e^2 (PO_2)_e}$$

k is the velocity constant defined by the equation :

$$\frac{dx}{d\theta} = \frac{k\,x^2\left(a - \frac{x_0-x}{2}\right)}{\left(a + b + x_0 - \frac{x_0-x}{2}\right)^3} - \frac{k\,(x_0-x)^2}{K\left(a + b + x_0 - \frac{x_0-x}{2}\right)^2}$$

$$= \frac{k\,x^2\,(a - x_0-x)}{\left(1 - \frac{x_0-x}{2}\right)^3} - \frac{k\,(x_0-x)^2}{K\left(1 - \frac{x_0-x}{2}\right)^2}$$

b' is the velocity constant defined by the equation:

$$\frac{dx}{d\theta} = b'\,x\,(\ln Pe - \ln P) \quad \text{or by}$$

$$= b'\,x\left(\ln \frac{x_0 - x_e}{x_e} - \ln \frac{x_0 - x}{x}\right)$$

$\triangle$ H = heat in calories generated by the formation at atmospheric pressure of 1 gm. mol of SO_3 according to the equation:

$$2\,SO_2 + O_2 \rightarrow 2\,SO_3$$

SAMPLE CALCULATIONS

(A) Standardization.

In this case, KIO_3 is equivalent to 2 K I

Concentration of standard solution $=$ $\dfrac{gm. \ mols \ K \ I \ O_3}{}$

$$= \frac{1}{(2) \ (166)} \ \bigg| \ \frac{1}{0.0294}$$

$$= \quad 0.1025 \ \text{molal in K I } O_3$$

K I O_3 is equivalent to 2 SO_2

Volume of pure SO_2 under standard conditions equivalent to 1 cc. of standard solution.

$$= \quad (0.1025) \ (0.001) \ (2) \ \bigg| \ \frac{gm. \ mols \ SO_2}{22,400}$$

$$= \quad 4.60 \ cc.$$

(B) % Conversion by gas analysis.

In Run 11, for example, the data are found in Tables 1 and 2 and the results in table 3.

Assume a barometer of 760 mm.

At C, volume of SO_2 at the temperature of the gas aspirated, saturated with water vapor, and at barometric total pressure, equivalent to 1 cc. of standard solution

$$= \quad \frac{(4.60) \ (273 + 23) \ (760)}{(273) \ (760 - 21)} \quad = \quad 5.13 \quad cc$$

Similarly at D and E the volume is 5.49 cc. per cu. of solution

F " 5.19 cc. " " " "

G " 5.35 cc. " cc. " "

Assume no volume due to SO_3 in the gas aspirated

$$y = \frac{(\text{cc. } O_2 \text{ and } N_2 \text{ combined aspirated })}{\text{cc. } SO_2 \text{ absorbed}} x$$

Since $2 SO_2 + O_2 \text{------} 2 SO_3$, the oxygen used is one half the SO_3 formed.

Therefore:

$$y = \text{the original } O_2 \text{ and } N_2 \text{ combined minus } 1/2 \text{ the } SO_3$$

$$= 1 - x_0 - \frac{x_0 - x}{2} = 1 - 1.5 x_0 + 0.5 x$$

and total gm mols at any point $= 1 - \dfrac{x_0 - x}{2}$

Solving the two equations, $x = \dfrac{1 - 1.5 x_0}{\dfrac{cc O_2 \text{ and } N_2}{cc SO_2} - 0.5}$

Also $\% SO_2 = \dfrac{100 x}{1 - \dfrac{x_0 - x}{2}}$

$\%$ conversion $= 100 \left(1 - \dfrac{x}{x_0} \right)$

In Run 11, $x_0 = 0.108$

At C, $x = \dfrac{1 - (1.5)(0.108)}{\dfrac{1690}{(15.5)(5.13)} - 0.5} = 0.0402$

$\% \, SO_2 = \dfrac{(100)(0.0402)}{1 - \dfrac{0.108 - 0.0402}{2}} = 4.17$

$\% \text{ Conversion} = 100 \left(1 - \dfrac{0.0402}{0.108} \right) = 62.8$

Similarly at D, $x = 0.0480$, $\% \, SO_2 = 4.95$, $\% \text{ Conversion} = 55.5$

E, $x = 0.0185$, $\% \, SO_2 = 1.93$, $\% \text{ Conversion} = 82.8$

F, $x = 0.0508$, $\% \, SO_2 = 5.22$, $\% \text{ Conversion} = 53.0$

G, $x = 0.0278$, $\% \, SO_2 = 2.90$, $\% \text{ Conversion} = 74.3$

(C) Leakage of blower gas into converted gas between E and F, that is, within the interchanger between the second converter and the SO_3 cooler.

(1) Calculation by gas analysis for Run 11

Using the values of x at E and F obtained above, we reason that 1 gm. mol of blower gas thru the converters would give 0.0185 mols SO_2 at F 1 gm. mol of blower gas thru the leak, would give 0.108 mols SO_2 at F. Actually, however, part of the blower gas goes thru the converters and part thru the leak.

Let Z = gm. mols thru leak

   1 - Z = gm. mols thru converter

Then $0.108 \, Z + (1-Z) (0.0185) = 0.0508$

$$Z = 0.361 \text{ or } 36.1 \%$$

(2) Calculation by heat balance on the interchanger, Data from tables 1 and 2

      Since, over the temperature range involved, the heat of reaction for the oxidation of SO_2 is constant, the heat capacity of the products is the same as that of the reacting substances. In other words, the heat capacity at any point in the system of the quantity of gas (SO_3, SO_2, O_2, and N_2) resulting from 1 gm. mol of blower gas (SO_2, O_2, and N_2) is the same as that which 1 gm. mol of blower gas would have at the same temperature.

Sensible heat content above 0° C of 1 gm. mol of O_2 or N_2

$$= \int_{273}^{T} (6.5 + 0.001 \, T) \, dT = 6.5T + 0.0005 \, T^2 - 18.2$$

or 220 calories   at   32.5 ° C

     2789 calories   at   400° C

     4097 calories   at   580° C

     3055 calories   a t   437° C

     3499 calories   at   496° C

     1897 calories   at   273° C

Sensible heat content above 0° C of 1 gm. mol of SO_2

$$= \int_{273}^{T} (7.0 + 0.0071\, T - 0.00000186\, T^2)\, dT$$

$$= 7\,T + 0.00355\, T^2 - 0.00000062\, T^3 - 2163$$

or   287 calories   at   32.5 ° C

     3969 calories   at   400 ° C

     6008 calories   at   580 ° C

     4375 calories   at   437 ° C

     5037 calories   at   496 ° C

     2616 Calories   at   273 ° C

Heat content of 1 gm mol blower gas at 32.5 ° C

$$= (0.108)(287) + (0.892)(220) = 227 \text{ calories (A)}$$

or   2917 calories   at   400 ° C   (B)

     4305 calories   at   580 °   (C)

     3197 calories   at   437 °   (D)

     3664 calories   at   496 °   (E)

     1974 calories   at   273 °   (F)

Temporarily assume no leakage, Basis 1 gm. mol of blower gas

$$\text{Input to interchanger} \quad = \quad \overset{A}{227} + \overset{C}{4305} + \overset{E}{3664} = 8196$$

$$\text{Output from interchanger} \quad = \quad \overset{B}{2917} + \overset{D}{3197} + \overset{F}{1974} = 8088 \text{ calories}$$

$$\text{Heat losses} \quad = \quad \left(\frac{8196 - 8088}{8196} \right) (100) = 1.32 \text{ \% of input above } 0° \text{ C.}$$

Temporarily assume no heat losses and a leak of z gm, mols

$$\text{Input to interchanger} \quad = \quad \overset{A}{227} + \overset{C}{4305} (1-Z) + 3664 (1-Z)$$

$$\text{Output from interchanger} = \quad \overset{B}{2917} (1-Z) + 3197 (1-Z) + 1974$$

Equating input to output and solving,

$$Z \quad = \quad 0.0582 \text{ gm. mols}$$

$$\text{or} \quad 5.582 \text{ \%}$$

D.) Heat losses from the converter - Data from Table 4

(1) Radiation , for two parallel planes,

$$\frac{Q\,n}{\theta} = \frac{A\left[\left(\frac{T_1}{100}\right)^4 - \frac{(T_2)^4}{100}\right]}{\frac{1}{P_1\,C} + \frac{1}{P_2 C} - \frac{1}{C}}$$

where $\frac{Q\,n}{\theta}$ is the net loss of heat per unit time from the hotter body, A is the surface area of either body, p_1 and P_2 are the coefficients of relative blackness of the hotter and colder surfaces at the absolute temperatures T_1 and T_2 respectively, and c is the constant 0.162 B.T.U./hr./sq.ft./ $\left(\frac{\circ\,F\,abs}{100}\right)^4$

Assume $P_1 = P_2 = 0.9$ Note that T_1 and T_2 are surface temperatures

The loss by radiation from area No. 1 on the first converter was:

$$\frac{(26.3)\left[\frac{(273+109)^4}{100} - \frac{(273+30)^4}{100}\right](1.8)^4}{\frac{1}{(0.9)(0.162)} \quad \frac{1}{(0.9)(0.162)} \quad \frac{1}{0.162}}$$

$$= 4{,}710 \text{ B.T.U. Per hour.}$$

The heat loss by radiation from No. 1 converter was 17,100 B.T.U./hr

No. 2 converter   19,530 B.T.U./hr

2.(Convection.

Assume h, the coefficient of heat transfer by natural convection to be 0.5 B.T.U./hr./sq.ft./ °F temperature difference between the surface of the converter lagging and the surrounding air.

From area No. 1 on the first converter the heat loss is

$h \, A \triangle t$ or (0.5) (26.3) (109 - 31) (1.8) = 1850 B.t.u./hr.

The heat loss by convection from No. 1 converter was 10.080 B.T.U./hr. No. 2 converter ---------- 11,895 B.T.U./hr.

(3) Total Heat loss

The total heat loss from No. 1 converter was 27,180 B.T.U./hr.

No. 2 converter was 31,425 B.T.U./hr.

The following average values can be used to calculate the heat generated in the converters:

Sulfur burned per day in F set = 24,000 lbs.

Sulfur removed in purification system = 3%

SO_2 in blower gas = 10.5%

Conversion at the outlet to No. 1 converter = 62.5 %

No. 2 converter = 84.9 %

Also, the heat of reaction is 22,600 calories.gm.mol SO_3

Heat generated in No. 1 converter

$$= \frac{24,000}{(24)(32.06)} \left[\frac{1}{0.97} \right] \left[\frac{2}{0.625} \right] \left[\frac{3}{(1.8)(22,600)} \right]$$

= 769,000 B.T.U. per hour

1 = lb. mols S burned per hour
2 = lb. mols S to converters per hour
3 = lb. mols SO_3 formed per hour.

Heat generated in No. 2 Converter

$$= \frac{(\ 0.849 - 0.625\ )}{0.625}\ (\ 769,000\ ) = 276,000 \text{ B.T.U. per hr.}$$

Total Heat loss in No. 1 $= \frac{(\ 27,180\ )}{769,000}\ (\ 100\ ) = 3.53\ \%$

Total Heat Loss in No, 2 $\frac{(\ 31,425\ )}{276,000}\ (100) = 11.4\ \%$

Total Heat loss in bath converters =

$$\frac{(\ 58,605\ )}{1,045,000}\ (100) = 5.61\ \%$$

Discussion of Reference Data: see Appendix 2

Discussion of Calculations:

(B) % Conversion by gas analysis

The error in assuming the barometer to be 760 mm. was negligible. For example, the actual reading one day was 751 mm. and another day 760.8 mm. However, on the former date, a suitable correction was made.

All of the gaseous SO_3 must have been absorbed by the Caustic solution. Some SO_3 escaped in the form of mist, which had no appreciable volume.

(D) Heat losses from the converter.

Since the heat loss was of indirect value only and of minor importance in further calculations, approximations were justifrable.

Two equations were available for computing radiation losses one for the case of two parallel planes, indefinite in extent, and one for a small body completely surrounded by a large body. (Walker, Lewis, and McAdams "Principles of Chemical Engineering " p. 162.). The former equation was more appropriate because the converters were rather closely hemmed in on most sides. The above authors gave 0.9 as an approximate value of p for lagged pipes. This figure was used for both the lagged converters and their surroundings.

The assumption of 0.5 for the coefficient of heat-transfer by convection is entirely reasonable when one considers the empirical equation on p. 147 and the graph on p. 169 of Walker, Lewis & McAdams. The coefficient assumed was less than these references indicate, because the proximity of surrounding objects such as the heat inter-changer and superheater prevented good air circulation.

Table 3

Summarized Experimental Results.

May 1927

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	Aver.	Aver. Duration
Date May	2	3	3	3	4	4	4	6	9	9	10	11	11		11
A % SO$_2$ (Chamber)	9.46	10.5	10.6	10.5	12.2	10.1	10.6	8.5	9.5	10.7	10.8	10.6	9.65		
% SO$_2$ (Iodate)		10.5													
C % SO$_2$	3.78		4.08					3.25			4.17				
% Conversion	61.4		62.8					62.8			62.8			62.5	0.5
D % SO$_2$								3.18			4.95				
% Conversion								63.6			55.5			59.5	4.0
E % SO$_2$				1.54	2.55	1.57	1.70	1.07			1.93	1.20	1.72		
% Conversion				85.9	80.1	85.2	84.7	87.8			82.8	89.3	83.4	84.9	2.1
F % SO$_2$	4.06	2.9	3.32	5.91	6.78	2.50	3.70	4.37	6.27	2.69	5.23	7.82	3.84		
% Conversion	58.3	73.3	69.9	45.2	47.0	76.2	66.2	49.7	34.0	75.9	53.0	27.1	61.4	56.7	13.0
G % SO$_2$									4.12	3.32	2.90	2.38			
% Conversion									57.5	70.2	74.3	78.5		70.1	6.1
H % SO$_2$							1.44			1.60	1.20	1.20	1.00		
% Conversion							87.0			85.7		89.3	90.05	88.0	1.7
Plant % Conversion													90.2		
Leakage by analysis				47.3	41.6	11.2	21.8	43.3			36.1	69.5	25.3	37.0	13.4
" heat balance								.73	.23	3.52	5.82	2.00	2.13	2.41	1.49

Table 4

Heat Losses from Converters

May 1927

Converter #1

average room temp. in vicinity of Converter = 31° C

Area #	Area □	Hot Temp°C	Cold Temp °C	Radiation Loss	Convection Loss
1	26.3	109°	30	4,710	1850
2	45.1	71	23	3,910	1620
3	45.1	74	36	3,310	1740
4	45.1	68	85	−1,820	1500
5	47.1	70	28	3,720	1580
6	47.1	75	40	3,270	1790
				17,100	10,080 Btu/hr
				Total $\frac{Q}{\theta}$ =	27,180 Btu/hr

Converter #2

average room temp in vicinity of Converter = 28°C

Area #	Area □	Hot Temp°C	Cold Temp °C	Radiation Loss	Convection Loss
7	43.5	82	65	1,750	2120
8	45.1	85	68	1,820	2320
9	119.6	75	26.5	10,850	5050
10	47.1	67	28	3,390	1650
11	14.7	85	26	1,720	755
				19,530	11895
				Total $\frac{Q}{\theta}$	31,425 Btu/hr

A P P E N D I X 2

Reference Data: See Appendix 1 and Table 5 and
Plots 1 and 2 following.

Plant Data: See Appendix 1

Nomenclature: See Appendix 1

Table 5

Values for Plot No. 1

$$\sqrt{K} \text{ vs. } \frac{10,000}{T_{Abs}}$$

May 1927.

Temperature °C	Temperature °Ab	$\frac{10,000}{T°_{Abs}}$	$\sqrt{K_p}$
430	703	14.22	231
440	713	14.03	182
460	733	13.64	120
480	753	13.28	79.5
500	773	12.94	53.5
520	793	12.61	36.5
540	813	12.30	26
560	833	12.00	18
580	853	11.72	13.5
600	873	11.45	10
627	900	11.11	6.56
680	953	10.49	3.16

PLOT No 1

$\sqrt{K}$ vs. $\dfrac{10,000}{\text{TEMP IN } ^\circ \text{ABS.}}$

$\dfrac{10,000}{\text{TEMP IN } ^\circ \text{ABS.}}$

$\sqrt{K}$

MAY 1927

PLOT No. 2

Temp	k₁
300°	9,580
350°	45,400
400°	203,500
450°	456,000
500°	649,000
600°	389,000

REACTION RATE CONSTANT k

500,000

300,000

100,000
80,000
60,000

40,000

20,000

10,000
8,000

5,000

2,000

MAY 1927

TEMPERATURE IN °C

300   350   400   450   500   550   600   650
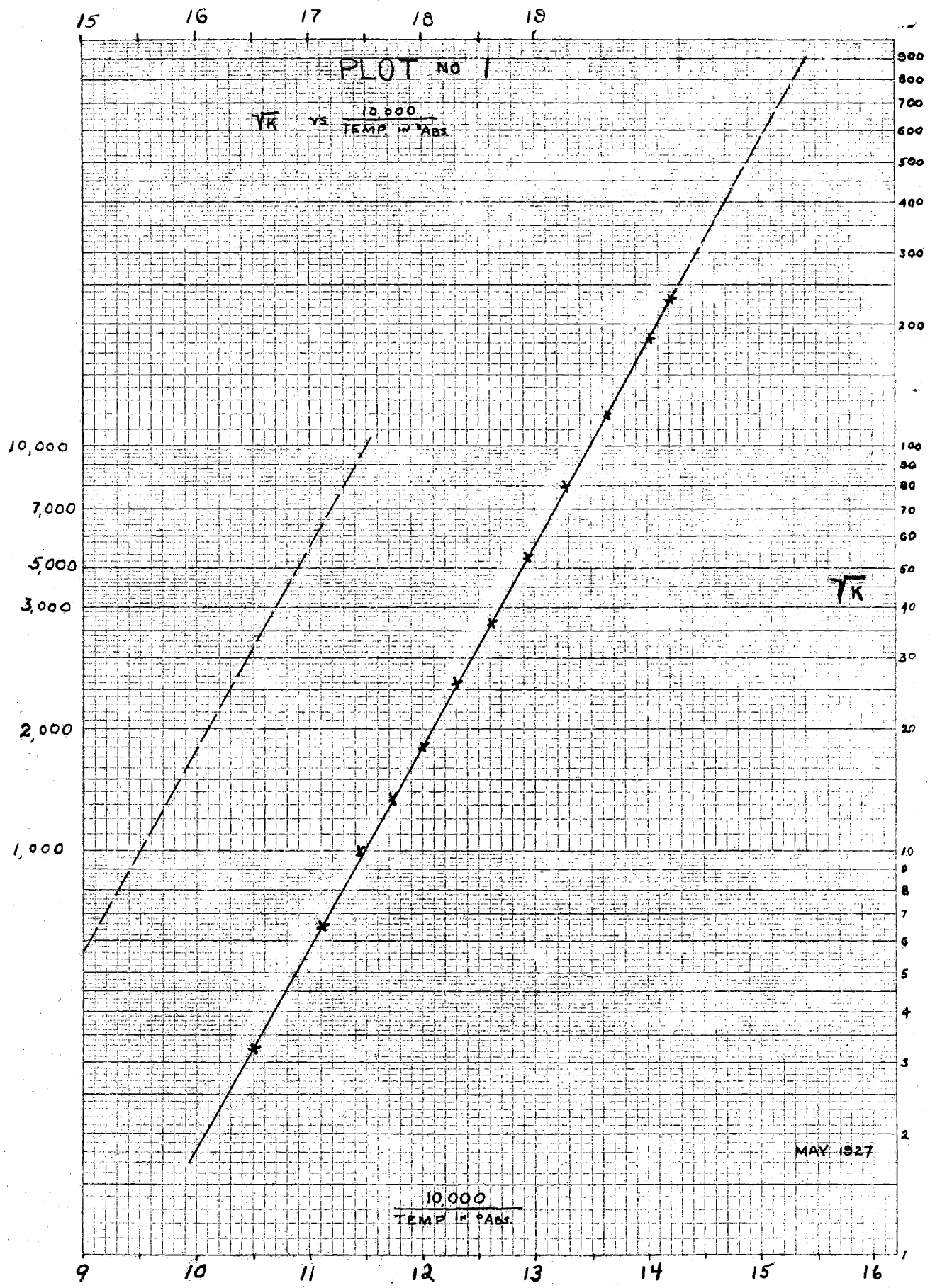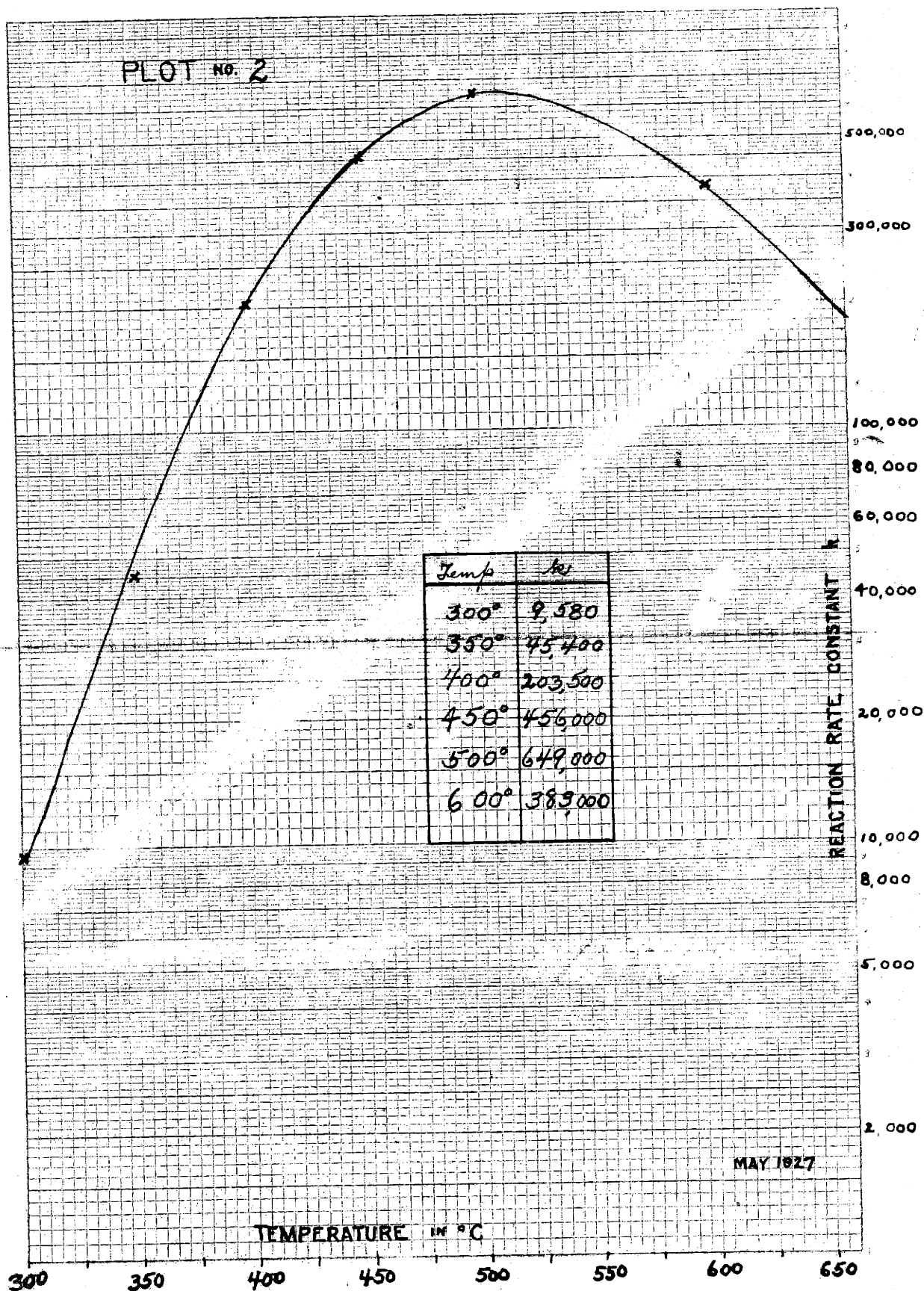
Sample Calculations:

Note that the basis throughout is 1 gm. mol of blower gas.

(A) Heat content of blower gas.

The figures in Table 6 were calculated by the method shown in Appendix 1. (C) (2)

(B) Conversion vs. Temperature.

Assume that the heat loss at any point in the converter is proportional to the rate of conversion.

As previously proved, the heat capacity at any point in the system of the quantity of gas resulting from 1 gm. mol of blower gas is the same as that which 1 gm. mol of blower gas would have at the same temperature.

$\triangle$ % Conversion for a given increase in heat content in No. 1 Converter

$$= \frac{1}{(0.01)\,x_0} \cdot \frac{1}{22{,}600} \cdot \frac{1}{1-0.0353} \cdot \text{increase in ht.cont. in cal.}$$

where

- $\dfrac{1}{\text{gm. mols of } SO_2 \text{ formed by 1% conversion}}$
- $\dfrac{1}{\text{calories generated by 1% conversion}}$
- $\dfrac{1}{\text{calories inc. in ht. cont.}}$
- 1% con... increase in ht.cont. in cal.

or for 8.5% SO_2 blower gas $\qquad = \dfrac{\triangle\ \text{heat content}}{18.53}$

9.5% SO_2 $\qquad = \dfrac{\triangle\ \text{heat content}}{20.72}$

10.5 % SO_2 $\qquad = \dfrac{\triangle\ \text{heat content}}{22.80}$

11.5 % SO_2 $\qquad = \dfrac{\triangle\ \text{heat content}}{25.08}$

Similarly for No. 2 converter and 10.5 % SO_2 blower gas,

$$\triangle\ \% \text{ Conversion} = \frac{\triangle\ \text{heat content}}{(.01)(.105)(22{,}600)(1-0.114)}$$

$$= \frac{\triangle\ \text{heat content}}{21.03}$$

The values in Tables 7,8,9, and 10 were obtained by the use of the above equations and table No. 6 of heat contents using the $\triangle$ heat content above the inlet temperature. For example, with an 8.5% blower gas, conversion at 360°C for an inlet of 300° C is

$$\frac{2589 - 2145}{18.53} = 23.96\ \%$$

Tables 7,8,9, and 1a0 are presented graphically on Plots 3,7,11,and 15.

(C) Conversion at Equilibrium.

Table 12 was obtained by reading values from plots 1 & 2.

For example, at 300°C, T=573° and $\dfrac{10,000}{T} = 17.45$

From plot 1, using the upper and left-hand scales, $\sqrt{K} = 9,500$ at 300°C

Similarly at 400°C, $\sqrt{K} = 500$ and $K = 250,000$

Also at 400°C, from Plot 2, $k = 202,000$

$$\frac{k}{K} = \frac{202,000}{250,000} = 0.81$$

Table 11 was calculated from Table 12 as follows:

By definition, $\sqrt{K} = \dfrac{(P_{SO_3})_e}{(P_{SO_2})_e (P_{O_2})_e^{1/2}}$

Where P is the partial pressure in atmospheres

Now it was shown in the calculations for Appendix 1. B that since $2\,SO_2 + O_2 = 2\,SO_3$, the oxygen used is equal to 1/2 of the SO_3 formed.

Assume a total pressure of 1 atmosphere.

	Gm Mols in blower gas	Gm mols in gas at any point	Partial pressure at any point - atm.
SO_2	X_0	X	$\dfrac{X}{1 - \dfrac{x_0 - x}{2}}$
SO_3	o	$X_0 - X$	$\dfrac{X_0 - X}{1 - \dfrac{x_0 - x}{2}}$
O_2	A	$A - \dfrac{X_0 - X}{2}$ y	$\dfrac{A - \dfrac{X_0 - X}{2}}{1 - \dfrac{x_0 - x}{2}}$

Let Xe = mols SO_2 at equilibrium .

$$\sqrt{K} = \frac{(\dfrac{X_0 - Xe}{1 - \dfrac{X}{2} - Xe})}{(\dfrac{\dfrac{Xe}{1 - \dfrac{X_0 - Xe}{2}}})(\dfrac{A - \dfrac{X_0 - Xe}{2}}{1 - \dfrac{X_0 - Xe}{2}})^{1/2}}$$

$$\frac{X_0 - Xe}{Xe} = \sqrt{K} \left(\frac{2 A - X_0 + Xe}{2 - X_0 + Xe}\right)^{1/2}$$

In order to solve for Xe, it is obviously necessary to know A

Assume 3% of sulfur burned to SO_3 and removed in the purification system. Basis, as usual, 1 gm. mol of blower gas.

$$\text{Total sulfur burned} = \frac{X_0}{1 - 0.03} \text{ gm. mols}$$

$$\text{Sulfur burned to } SO_3 = \frac{0.03 X}{0.97} \text{ gm. mols}$$

Since $S + 3/2\ O_2 = SO_3$, O_2 disappearance $= (\dfrac{0.03\ x_0}{0.97})\ (\dfrac{3}{2})$ gm. mol.

$$N_2 = 1 - A - X_0 \text{ gm mols.}$$

$$A = \frac{21}{79} (1 - A - X_0) - X_0 - \frac{(0.03\ X_0)}{0.97} (\frac{3}{2})$$

$$= 0.210 - 1.037\ x_0$$

When X_0 = 0.085, A = 0.1218
           0.095   A = 0.1114
           0.105   A = 0.1011
           0.115   A = 0.0908

Knowing A, Xo , and K, one can solve for Xe by trial or successive approximations.

For example, it is desired to find the % conversion at equilibrium at 520° C for an 8.5% blower gas.

$$\frac{0.085 - X_e}{X_e} = 36.5 \left(\frac{[2][0.1218] - 0.085 + X_e}{2 - 0.085 + X_e} \right)^{1/2}$$

Calling the X_e's on the right hand side of the equation o and solving for X_e, one obtains 0.00739.

Calling the X_e's on the right hand side of the equation 0.00739 and solving for X_e, one obtains, 0.00725 .

Calling the X_e's on the right hand side of the equation 0.00725 and solving for X_e, one obtains 0.00725; thus showing that two approximations are enough in this case.

$$\% \text{ Conversion} = 100 \left(1 - \frac{0.00725}{0.085} \right) = 91.5\%$$

(D) Rate of Reaction:

$$- \frac{d \, C_{SO_2}}{d \, \theta} = k, \, (\, C_{SO_2})^2 \, (\, C_{O_2}) - K_2 \, (\, C_{SO_3})^2$$

$$- \frac{d \, P_{SO_2}}{d \, \theta} = k_3 \, (P_{SO_2})^2 \, (P_{O_2}) - k_4 \, (P \, SO_3)^2$$

Assume a total pressure of 1 atm.

$$- \frac{d \, P \, SO_2}{d\theta} = \frac{d}{d \, \theta} \left(\frac{X}{1 - \frac{X_0 - X}{2}} \right) = \frac{1 - X_0 - \frac{X}{2}}{(1 - \frac{X_0 - X}{2})_2} \quad 1 \approx X$$

Assume $- \frac{d \, P \, SO_2}{d \, \theta} \propto - \frac{d \, x}{d \, \theta}$

$$k_5 = \frac{k \, (P \, SO_2)^2 e \, (P \, O_2)e}{(P \, SO_3)^2_e} = \frac{k}{K}$$

Therefore $-\dfrac{dx}{d\theta} = k \, (P \, SO_2)^2 \, (P \, O_2) - \dfrac{k}{K} \, (P \, SO_3)^2$

$$= k \, x^2 \frac{(A - X - X)}{\left(\dfrac{1 - X_O - X}{2} \right)^3} - \frac{k}{K} \frac{(X_O - X)^2}{\left(\dfrac{1 - X_O - X}{2} \right)^2}$$

k depends upon the weight and activity of the platinim an upon the rate of flow of total gas as well as the temperature. In this case, however we are concerned with only one converter and one rate of flow. Therefore k depends only upon the temperature.

For a gas of a given original composition (A and X_O fixed), at a given temperature (K and k fixed) , and at a given stage in the conversion (x fixed) the net conversion proceeds at a definite rate which can be calculated by substitution in the above equation. The following is an example of the calculations used to obtain Tables 13, 14, 15 and 16.

For an inlet gas of 8.5 % SO_2, X = 0.085 and A = 0.1218

At 640° C, k = 240,000 and $\dfrac{k}{K}$ = 8080

At 40 % conversion, $X_O - X$ = 0.4 X_O = 0.034

$\qquad\qquad\qquad\qquad$ X = 0.085 - 0.034 = 0.051

Under these conditions,

$$-\frac{dx}{d\theta} = \frac{(240,000) \, (0.051)^2 \, (0.1218 - 0.017}{(1 - 0.017)^3} \quad \frac{(80.80)(0.034)^2}{(1 - 0.017)^2}$$

= 68.9 - 9.7 = 59.2 The values obtained in this way are plotted as full lines on plots 4, 8, 12, and 16.

(E) Reaction Rate vs Conversion.

      The dotted curves on Plots 4,8,12, and 16 represent the paths followed by blower gases of the four different inlet compositions and several different inlet temperatures, as they go thru the converter and shows the reaction rate at every point in the conversion. The following example shows how the curve is obtained for 8.5% gas at an inlet temperature of 340°C and how from this curve are found the values in table 17.

      On plot No.3, follow the horizontal lines thru 0, 10, 20, and 30% conversion until they intersect the 360° C slant line. The respective abscissas are 360° C, 384 °C, 40% C, and 433 ° C. On plot 4 follow vertical lines thru these temperatures until they intersect the 0% , 10%, 20% and 30% full curbes respectively. The four intersections give four points on the dotted curve for 360° C. The values of the ordinates at these four points are respectively 61.5, 97.5, 129.5, and 146.5. The respective reciprocals, 0.0163, 0.0103, 0.0077, and 0.0068, can be found in the proper column of Table 17 and plotted on Plot 5.

(F) Time of Contact

      Tables 17 and 18 are graphically represented on plots 5,9,13, and 17. On these plots, the ordinate has an abstract significance only, being $- \dfrac{d\theta}{dx}$. The abscissa is % conversion.

Therefore the area under the curve, above the horizontal axis, and to the right of the 0% conversion line is equal to

$$\int_0^c \left(- \frac{d\theta}{dx} \right) d\% \text{ conversion} \qquad \int_{X_0}^{X_1} \left(- \frac{d\theta}{dx} \right) \left(- dx \right) = \int_0^\theta d\theta = ?\theta$$

Choosing the time at 0% conversion as the reference point, the area above mentioned bounded on the right by a vertical line thru any given % conversion is proportional to the time of contact required to reach that given % conversion.

The areas under the curves out ;to the various % conversions were found by counting the smallest squares and these areas were plotted as abscissas against the % conversion as ordinates in Plots 6,10, 14, and 18. Tables 19 and 20 contain the values for ;these plots. For example, by counting small squares one obtains the follo- wing areas under the 360° C curve ;on Plot 5 (8.5% inlet SO_2) to 0% 0; to 10%, 260; to 20% 435; to 30%, 577; etc. These values form the first part of the 360° C line on Plot 6.

(G) Optimum Inlet Conditions

All the calculations thus far have been on one converter, for one rate of flow gas. Therefore, k has been dependent only on the temperature and, following through, θ is in the same units for all the curves on Plots 6, 10, 14, and 18. Under the circumstances if the time of contact for this particular converter can be found, its performance can be predicted. But from Appendix 1, it is known that with an inlet temperature of 400° C and a blower gas containing 10.5% SO_2, the conversion is 62.5%. Locating this point on Plot 14 gives a time of contact 752 units. Therefore the performance of this converter for this rate of gas flow can be predicted by erecting vertical lines thru 752 time units on Plots 6, 8, 10, and 14 and noting the % conversion at the intersections with the respective inlet temperature curves.

The values at these intersections are presented tabularly and graphically on Plot No. 19, from which it appears that the optimum operating conditions from the point of view of conversion alone, for this converter, at the present rate of gas flow, are 10.5% inlet SO_2 at a temperature of 390-400 $ C to give a conversion of 62.5%.

(H) Second Converter

The calculations for this converter are similar in every respect to those for the first except that the inlet temperatures and times correspond to 62.5% conversion - the optimum for the first converter. It will be noted that the slope of the temperature vs. conversion lines for the second converter (upper left of Plot 11) have a different slope from that in the first converter due to the difference in the % heat loss. Plot 20 is really the magnified lower right hand corner of Plot 12 as far as the full lines are

concerned.   In fact some of the values for 70% and 75% conversion
were used for both plots as may be seen by comparing Tables 15 and
22.

The value of the time for the second converter was
obtained from the results of Appendix I; namely, that 10.5 % gas
at 440 ° C inlet to the second converter gives a total conversion
at the end of the second converter of 84.9%.   θ was found to be
965 units.

The optimum conditions were obtained from plot 22 A
in the same way as for the first converter.

I) <u>Platinum Activity</u>

$$\theta \propto \frac{(\text{weight of platinum})(\text{activity of platinum})}{\text{rate of total gas flow}}$$

Since the rates of gas flow are practically the same,

$$\frac{\theta \text{ first converter}}{\theta \text{ second converter}} = \frac{(43.82)(\text{activity of Platinum})NO.1}{(128.41)(\text{activity of platinum})NO.2}$$

$$= \frac{752}{965}$$

Therefore, $\dfrac{\text{activity of platinum No.2}}{\text{activity of platinum No.1}} = 0.438$

(1) Capacity of the conversion system

$$\frac{\text{wt. } SO_2 \text{ per hr.}}{\text{wt. platinum}} = \frac{24,000}{24} \left| \frac{\text{lbs. S burned/hr}}{0.97} \right| \frac{\text{lbs.S to converter /hr}}{\frac{64}{32}} \left| \frac{\text{lbs. } SO_2 \text{ to conv./hr.}}{\frac{1}{11.81}} \right.$$

$$= 164 .$$

Note that the 11.81 was obtained as follows:

Wt. of platinum $= (43.62 + 128.41)(0.06857)$

$$= 11.81 \text{ avoirdupois pounds}$$

(K) <u>Calculation of Conversion by Temp. Rise Method.</u>

<u>Converter No. 1</u>

The average inlet gas temperature was 401 ° C and the average exit 579 ° C.   From Plot 11, starting with the line beginning at 400 ° C and 0 % conversion and reading up that line until the 579 ° asbcissa is cut, the conversion as read from the scale at the left is 61.0 % .

<u>Converter No. 2</u>

The average inlet gas temperature was 439 ° C while the aferage exit temperature was 495 ° C.   From plot No. 11, starting with the line beginning with 440 ° C and 62.5 % conversion and reading up that line until the 495 ° abscissa is crossed, the conversion after No. 2 converter as read from the scale at the left is 83.0 % .

DISCUSSION OF REFERENCE DATA

(A) Equilibrium constants for the reaction $2 SO_2 + O_2 = 2SO_3$.

These quantities have been determined by Knietsch, by Bodlander and Koppen, and by Bodenstein and Pohl (Z. Electrochem., 1905, 11, 373). A good discussion of their work is found in the "Manufacture of Sulphuric Acid (Contact Process)" by F.D. Miles, 1925, pages 78-81 and 94-101 . Lewis and Randall in their "Thermodynamics," 1923, page 550 agree with Miles that the data of Bodenstein and Pohl are the most accurate and consistent. Their results show that the reaction follows closely the mass action law and the integrated form of the Van't Hoff equation:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Their data can be summarized in the following empirical equation: $\log \sqrt{K} = \dfrac{5186.5}{T} + 0.611 \log T - 6.7497$.

The experimental work was done between 528 ° C and 897 ° C but has been extrapolated by Miles according to the above equation. Table 5 and Plot 1, included with this thesis contain some original and some extrapolated points. They fell so closely on a straight line when $\log \sqrt{K}$ was plotted against $\dfrac{10,000}{T}$ it was considered safe to

extrapolate further.

(B) Heat of reaction at atmospheric pressure for $SO_2 + 1/2 O_2 = SO_3$

Lewis and Randall in their "Thermodynamics," 1923 , page 550 agree with Miles ;in his, "Manufacture of Sulphuric Acid," 1925, page 31 that the best value is 22,600 calories per gram mol of SO_3 as determined by Berthelot thru indirect calorimetric investigation. Reis in his M.I.T. Thesis: " The Thermal Characteristics of Segar cones and a reaction rate study of the contact sulfuric acid process" 1926 found that the heat of reaction as determined by the Van't Hoff equation from the data of Bodenstein and Pohl was about 22,540 calories per gram mol, which checks the former value within the accuracy of Reis's calculations. The fact that this Van't Hoff equation does hold justifies the assumption of constant heat of reaction throughout the temperature range used.

(C) Heat Capacities of the gases in the system

The values for the molal heat capacity of SO_2, O_2, and N_2 were obtained from Lewis and Randall, "Thermodynamics," 1923, page 80.

(D) Rate of reaction.

For the theories of reaction rate see "Discussion of Calculations". Note here, however that the values of Plot 2 were obtained from Knietsch's data by Ries in Connection with his above-mentioned thesis (Pgs. 37-45 & 125) using Bodenstein and Pohl's equation to extrapolate for values of the equilibrium constant. Ries used the following reaction rate equation:

$$ -\frac{dx}{d\theta} = \frac{k x^2 (A - \frac{X_0 - X}{2})}{(a + b + X_0 - \frac{X_0 - X}{2})^a} - \frac{k}{K} \frac{(X_0 - X)}{(a+b+X_0 - \frac{X_0 - X}{2})^a} $$

Note that since Reis used Bodenstein and Pohl's values of K, these values should always be used with his reaction rate constant.

DISCUSSION OF CALCULATIONS

(B) Conversion vs. Temperature

In practice, the temperature at any point in either
converter is very nearly constant. Therefore, one need not know
the heat capacity of the converter in order to obtain a heat balance.
The input in sensible heat of the gas and heat of reaction must be
equal to the output in sensible heat of the gas and heat losses.
Therefore, one can calculate the rise in temperature of the gas due
to it's conversion and follow the corse of the temperature as conver-
sion progresses, provided he knows the heat losses between the desired
points. In the present case, the heat loss could be found for the
converter as a whole, but defied even estimation for the various
shelves on account of the heat flow by radiation within the converter.
Furthermore, the minor nature of the heat loss correction in the
calculation of the temperature rise justified making an assumption;
to wit, that the heat loss at any point is proportional to the rate
of conversion. This seemed fairly reasonable and made the calculations
easier.

As a result of the calculations made from this assumption,
each of the straight lines starting from 0% conversion on Plots 3,7,
11, and 15 represents the progress in conversion and rise in temperature
of the gas entering at a particular temperature and gas composition .
It does not tell us, however, what time or place corresponds to any
given % conversion or temperature.

(C) Conversion at Equilibrium

The assumption of a total pressure equal to 1 atmosphere
is justifiable because :

1. The actual gage pressures in the converters of this
plant vary from a few inches to not more than 40 inches of water.

2. The barometer holds rather closely to 30 inches of
mercury.

3. The fractional error in the desired result (% conversion)
is only about 1/20 of the error in the total pressure.

The assumption of 3% of the S burned to SO_3 is justified
by plant records,

(D) Rate of Reaction

Let us first dispose of the theory of Badenstein regarding
reaction rate. He holds that the net rate of conversion is propor-
tional to the concentration of SO_2 and inversely proportional to the
square root to the concentration of SO_3.

As Reis points out in his thesis, this relation is invalid
because (1) it does not agree any too well with either Bodenstein's
or Reis's data

(2) it was obtained at low temperatures with stationary
gas

(3) it does not allow for the effect of variation in
oxygen present.

(4) it gives an infinite rate at 0% conversion

(5) it gives a zero rate at 100% conversion, not at
equilibrium.

Now we can take up the theory used as the basis for this thesis. One naturally expects the forward rate of a reaction to be proportional to the concentrations of the reacting substances raised to some power depending on the mechanism of the reaction. Thus one would expect some equation of the nature:

$$- \frac{d(C_{SO_2})}{d\theta} \quad k \quad (C_{SO_2})^n \quad (C_{O_2})^n \quad - \quad k_2 \quad (C_{SO_3})^r$$

Reis showed that Knietsch's data could be best explained by giving m in the value 2, $n = 1$, and $r = 2$.

The assumption that $- \frac{dx}{d\theta} \quad - \quad \frac{d \, C_{SO_2}}{d\theta}$ is justifiable on account of the small error involved and is really made necessary by the fact the values of k in Plot 2 were calculated using $- \frac{dx}{d\theta}$.

It will be noted that the units of k are unknown, but this is no disadvantage when only relative values are needed.

It should be noted that this k was obtained at temperatures actually found in converters and with a flowing gas. Furthermore the equation gives a finite rate at 0% conversion and a zero rate at equilibrium. It does not agree with Reis's data so well as his own equation, but does agree within the experimental error with Knietsch's data . Finally it shows that effect of the oxygen concentration.

For Ries's theory of the rate of reaction, see Appendix 3.

(I) Platinum Activity

A valuable reference on the theory used in this thesis
is " Influence of Reaction Rate on Operating Conditions in Contact
Sulphuric Acid Manufacture," J.I.E.C., 17, p. 593, 1925 by W. K.
Lewis and E.D.Ries.   Here it can be found that the specific
reactions rate depends upon the particular platinum. The implicit
assumption of this thesis has been that although this activity may
vary from one mass to another, the ratio of activities is constant
under all variations in operation. Furthermore the time of contact
is proportional to the weight of platinum and inversely proportional
to the rate of total gas flow through the converter.

That is to say, the θ found on Plots 6, 10, 14, 18, etc.
is not an actual time, but an effective time and is proportional to
the quotient,

$$\frac{(\text{weight of platinum})\ (\text{activity of platinum})}{\text{rate of total gas flow}}$$

This gives a means of comparison of platinum masses in actual
operation under entirely dissimilar circumstances.

Table 6

Heat Contents
Units = calories/gram mol above 0°C

May 1927

% SO$_2$	100	0	8.5	9.5	10.5	11.5
% (O$_2$+N$_2$)	0	100	91.5	90.5	89.5	88.5
Temp °C						
300	2896	2077	2145	2154	2162	2170
320	3109	2219	2294	2302	2311	2320
340	3323	2361	2441	2451	2462	2472
360	3534	2503	2589	2599	2609	2618
380	3748	2646	2738	2750	2762	2774
400	3969	2789	2887	2900	2914	2927
420	4188	2933	3037	3050	3064	3078
440	4408	3077	3188	3202	3215	3228
460	4634	3221	3340	3353	3367	3381
480	4858	3367	3493	3507	3522	3537
500	5082	3507	3640	3654	3667	3684
520	5314	3657	3796	3812	3829	3846
540	5545	3803	3948	3966	3985	4004
560	5774	3950	4103	4121	4140	4159
580	6008	4097	4258	4277	4296	4315
600	6241	4244	4412	4432	4452	4472
620	6477	4381	4558	4579	4601	4623
640	6716	4540	4724	4746	4768	4790
660	6954	4688	4879	4903	4926	4949

Table 7
Values for Plot Nos. 3, 7, 11, 15

Conversion vs. Temperature

Converter # 1
May 1927.

Inlet SO₂ →	Conversion for inlet of 300°C				Conversion for inlet of 320°C			
	8.5%	9.5%	10.5%	11.5%	8.5%	9.5%	10.5%	11.5%
Temp.								
300	0	0	0	0				
320	8.04	7.15	6.54	5.98	0	0	0	0
340	15.97	14.33	13.15	12.04	7.93	7.18	6.61	6.06
360	23.96	21.48	19.61	17.86	15.92	14.33	13.07	11.88
380	32.00	28.77	26.32	24.09	23.96	21.62	19.78	18.11
400	40.04	36.00	33.00	30.18	32.00	28.85	26.46	24.20
420	48.14	43.25	39.57	36.20	40.10	36.10	33.03	30.22
440	56.3	50.6	46.20	42.2	48.26	43.45	39.66	36.22
460	64.45	57.8	52.8	48.3	56.41	50.65	46.26	42.32
480	72.75	65.3	59.6	54.5	64.71	58.15	53.06	48.52
500	80.7	72.5	66.2	60.5	72.46	65.35	59.66	54.52
520	89.1	80.0	73.1	66.85	81.06	72.85	66.56	60.87
540	97.3	87.5	80.0	73.2	89.26	80.35	73.46	67.22
560		94.9	86.75	79.3	97.56	87.75	80.21	73.32
580			93.60	85.6		95.35	87.06	79.62
600				91.8			93.86	85.82
620				97.9				91.92
640								98.52

Table 8

Values for Plot Nos. 3, 7, 11, 15

Conversion vs. Temperature

Converter #1   May 1927

Inlet $SO_2 \rightarrow$	Conversion for inlet of 340°C				Conversion for inlet of 360°C			
Temp ↓	8.5%	10.5%	9.5%	11.5%	8.5%	9.5%	10.5%	11.5%
340°	0	0	0	0				
360	7.99	6.46	7.15	5.82	0	0	0	0
380	16.03	13.17	14.44	12.05	8.04	7.29	6.71	6.23
400	24.07	19.85	21.67	18.14	16.08	14.52	13.39	12.32
420	32.17	26.42	28.92	24.16	24.18	21.77	19.96	18.34
440	40.33	33.05	36.27	30.16	32.34	29.12	26.59	24.34
460	48.48	39.65	43.47	36.26	40.49	36.32	33.19	30.44
480	56.78	46.45	50.97	42.46	48.79	43.82	39.99	36.64
500	64.73	53.05	58.17	48.46	56.74	51.02	46.59	42.64
520	73.13	59.95	65.67	54.81	65.14	58.52	53.49	48.99
540	81.33	66.85	73.17	61.16	73.34	66.02	60.39	55.34
560	89.63	73.60	80.57	67.26	81.64	73.42	67.14	61.44
580	98.03	80.45	88.17	73.56	90.04	81.02	73.99	67.74
600		87.25	95.57	79.76	98.34	88.42	80.79	73.94
620		93.75		85.86		95.52	86.29	80.04
640				92.46			94.69	86.64
660				98.76				92.94

Table 9

Values for Plot Nos. 3, 7, 11, 15

Conversion vs. Temperature

Converter #1   May 1927.

Inlet SO₂ →	Conversion for inlet of 380°C				Conversion for inlet of 400°C			
Temp	8.5%	9.5%	10.5%	11.5%	8.5%	9.5%	10.5%	11.5%
380	0	0	0	0				
400	8.04	7.23	6.68	6.09	0	0	0	0
420	16.14	14.48	13.25	12.11	8.10	7.25	6.57	6.02
440	24.3	21.83	19.88	18.11	16.26	14.6	13.20	12.02
460	32.45	29.03	26.48	24.21	24.41	21.8	19.8	18.12
480	40.75	36.53	33.28	30.41	32.71	29.3	26.6	24.32
500	48.5	43.73	39.88	36.41	40.46	36.3	33.0	30.12
520	57.1	51.23	46.78	42.76	49.06	44.0	40.1	36.67
540	65.3	58.73	53.68	49.11	57.26	51.5	47.0	43.02
560	73.6	66.13	60.43	55.21	65.56	58.9	53.75	49.12
580	82.0	73.73	67.28	61.51	73.96	66.5	60.6	55.42
600	90.3	81.13	74.08	67.71	82.26	73.9	67.4	61.62
620	98.2	88.23	80.58	73.81	90.16	81.0	73.9	67.72
640		96.23	87.98	80.41	99.06	89.0	81.3	74.32
660			94.88	86.79		96.6	88.2	80.62

Table 10

Values for Plot Nos. 3, 7, 11, 15.

Conversion vs. Temperature

Converter #1   May 1927

Inlet SO_2	Conversion for inlet of 420°C				Conversion for inlet of 440°C			
	8.5%	9.5%	10.5%	11.5%	8.5%	9.5%	10.5%	11.5%
Temp								
420°	0	0	0	0				
440	8.16	7.35	6.63	6.00	0	0	0	0
460	16.31	14.55	13.23	12.1	8.15	7.20	6.6	6.1
480	24.61	22.05	20.03	18.3	16.45	14.70	13.4	12.3
500	32.36	29.05	26.43	24.1	24.20	21.70	19.8	18.1
520	40.96	36.75	33.53	30.65	32.80	29.40	26.9	24.65
540	49.16	44.25	40.43	37.0	41.00	36.90	33.8	31.0
560	57.46	51.65	47.18	43.1	49.30	44.30	40.55	37.1
580	65.86	59.25	54.03	49.4	57.70	51.90	47.40	43.4
600	74.16	66.65	60.83	55.6	66.00	59.30	54.20	49.6
620	82.06	73.75	67.33	61.7	73.9	66.40	60.70	55.7
640	90.96	81.75	74.73	68.3	82.8	74.40	68.10	62.3
660	99.36	89.35	81.63	74.6	91.2	82.00	75.0	68.6

Table 11

Values for Plot Nos. 3, 7, 11, 15.

% Conversion at Equilibrium

May 1927

Inlet gas: % SO_2	8.5	9.5	10.5	11.5
Temp. °C ↓				
460			96.5	
480			94.8	
500			92.5	
520	91.5	90.7	89.6	88.2
540	88.3	87.4	85.9	84.3
560	84.4	83.1	81.5	79.6
580	79.9	78.6	76.9	74.8
600	74.6	73.0	71.2	69.0
620	70.2	67.6	65.6	63.3
640			59.4	

Table 12

Temp °C	$\sqrt{K}$	K	k	$\dfrac{k}{K}$
300	9500		9,000	
320	4800		17,600	
340	2530		36,000	
360	1420		70,000	
380	805		125,000	
400	500	250,000	202,000	.81
420	295	87,030	298,000	3.42
440	183	33,490	402,000	12.00
460	120	14,400	505,000	35.05
480	78.5	6,162	590,000	95.70
500	53	2,809	644,000	229
520	36.5	1,332	640,000	480
540	25.5	650	600,000	923
560	18	324	535,000	1652
580	13.2	174	455,000	2615
600	9.6	92	380,000	4120
620	7.25	52.6	305,000	5790
640	5.45	29.7	240,000	8080
660	4.20	17.6	183,000	10,400

Table 12

Table 13

Values for Plot No 4

$-\frac{dx}{d\theta}$ vs. Temperature

#1 Converter   May 1927

Inlet gas: 8.5% SO_2

% Conversion →	0%	10%	20%	30%	40%	50%	60%	70%	75%
Temp°C ↓									
300°	7.92	6.27	4.85	3.62	2.58	1.74	1.08	0.59	0.40
320	15.5	12.27	9.48	7.08	5.05	3.41	2.12	1.16	0.78
340	31.6	25.1	19.4	14.5	10.34	6.97	4.34	2.36	1.60
360	61.6	48.8	37.7	28.2	20.1	13.56	8.43	4.60	3.12
380	110.	87.1	67.3	50.3	35.9	24.2	15.06	8.21	5.57
400	178.	140.8	108.8	81.3	58.0	39.1	24.3	13.26	9.00
420	262	208	160.4	119.8	85.5	57.7	35.9	19.56	13.27
440	354	281	216.5	161.8	115.4	77.9	48.5	26.4	17.9
460	445	352.	272.	203.	145.	97.8	60.7	33.1	22.1
480		411	318	236.9	169.3	114.	70.7	38.3	25.9
500			346.4	258.8	184.6	124.3	76.9	41.3	27.7
520			344.4	257.2	183.2	123.1	75.7	40.2	26.4
540			322.7	240.7	171.1	114.4	69.8	35.9	22.7
560			287.5	215.9	151.6	100.5	60.0	28.9	16.6
580			244.2	181.3	127.6	83.2	47.6	20.1	9.0
600			203.3	150.1	104.2	65.8	34.5	9.4	
620			162.5	118.7	80.7	48.1	20.9		
640			126.8	91.1	59.2	31.2	6.7		
660			95.5	66.7	40.1	15.8			

Table 14

Values for Plot No. 8

$-\dfrac{dx}{d\theta}$ vs. Temperature

#1 Converter   May 1927

Inlet gas: 9.5% SO_2

% Conversion →	0%	10%	20%	30%	40%	50%	60%	70%	75%
Temp °C ↓									
300°	9.05	7.11	5.45	4.03	2.86	1.92	1.17	0.63	.43
320	17.7	13.9	10.7	7.89	5.6	3.75	2.30	1.24	.84
340	36.2	28.4	21.8	16.1	11.45	7.67	4.7	2.53	1.72
360	70.4	55.3	42.5	31.4	22.25	14.9	9.13	4.92	3.35
380	125.8	98.8	75.9	56.1	39.8	26.6	16.3	8.79	5.98
400	203	159.8	122.5	90.6	64.25	43.0	26.35	14.2	9.66
420	300	236.	180.8	133.6	94.75	63.5	38.9	20.95	14.25
440	404	318	244	180.2	128	85.6	52.5	28.25	19.22
460		399.	306	226	160.7	107.5	65.7	35.3	24.0
480		466.	358	263.9	187.6	125.6	76.7	41.1	27.7
500			389.9	288.3	204.7	136.7	83.2	44.1	29.5
520			387.8	286.6	202.8	135.3	81.8	42.7	28.0
540			363.7	268.2	189.6	125.7	75.05	37.8	23.7
560			323.9	238.6	167.6	110.1	64.1	29.9	16.6
580			275	201.8	140.9	90.7	50.4	19.6	7.5
600			228.8	167.	114.7	71.1	35.4	7.2	
620			182.9	131.9	88.3	51.3	19.9		
640			142.4	100.9	64.3	31.9	3.5		
660			107.2	73.3	42.6	14.4			

Table 15

Values for Plot No 12

$-\dfrac{dx}{d\theta}$ vs. Temperature

#1 Converter   May 1927

Inlet gas: $10.5\% \, SO_2$

% Conversion	0%	10%	20%	30%	40%	50%	60%	70%	75%
Temp °C									
300°	10.04	7.81	5.94	4.35	3.05	2.01	1.22	.64	.43
320	19.60	15.25	11.62	8.51	5.97	3.92	2.38	1.26	.84
340	40.1	31.2	23.8	17.4	12.2	8.03	4.87	2.57	1.72
360	78.0	60.75	46.2	33.9	23.7	15.62	9.47	5.00	3.35
380	139.5	108.5	82.5	60.5	42.4	27.9	16.92	8.93	5.99
400	225.	175.	133.3	97.8	68.5	45.1	27.35	14.42	9.67
420	333.	258	196.8	144.	101	66.5	40.3	21.3	14.3
440	449	348	265.	194.5	136.2	89.6	54.4	28.6	19.2
460	563	438	334	244.5	171.3	112.7	68.2	35.8	24.0
480	658	512	390	286.	200	128.8	79.4	41.5	27.6
500	718	558	425	312	218.1	143.1	86.1	44.6	29.3
520	714	555	423	310	216.1	141.4	84.6	42.9	27.4
540	669	521	396	289	202.3	133.3	77.3	37.4	22.5
560	596	464	352	257	178.5	114.6	65.4	28.6	14.5
580	508	394	299	217.8	149.4	93.9	50.4	17.3	4.2
600	424	330	249	179.8	121.2	72.8	34.0	3.1	
620	340	263	198	141.9	92.8	51.1	16.8		
640	268	207	154.9	108	66.6	30.0	-1.7		
660	204	157.3	116.1	78.	42.8	10.5			

Table 16

Values for Plot No. 16

$$-\frac{dx}{d\theta} \text{ vs. Temperature}$$

#Converter   May 1927

Inlet gas 11.5% SO_2

% Conversion →	0%	10%	20%	30%	40%	50%	60%	70%	75%
Temp °C ↓									
300°	10.8	8.35	6.25	4.52	3.12	2.02	1.19	.61	.40
320	21.1	16.35	12.23	8.84	6.10	3.95	2.33	1.20	.79
340	43.2	33.4	25.	18.1	12.47	8.08	4.77	2.45	1.62
360	84	65	48.7	35.1	24.2	15.72	9.27	4.76	3.15
380	150	116.1	86.9	62.8	43.3	28.1	16.58	8.51	5.63
400	242	187.7	140.4	101.4	69.9	45.4	26.75	13.73	9.09
420	358	277	207.	149.7	103.2	67.0	39.5	20.25	13.4
440	482	373.5	279.5	202.	139.1	90.4	53.2	27.25	18.0
460		469	351	254.	174.7	113.4	66.7	34.1	22.4
480		549	410	295.9	203.8	132.2	77.7	39.4	25.8
500			447	323.2	222.	144	84.1	42.15	27.1
520			445	320.9	220.4	142.2	82.3	40.1	24.9
540			417	299.9	206.	131.6	74.8	34.3	19.5
560				266.5	181.4	114.4	62.4	24.8	10.7
580				225.3	151.7	93.0	46.9	12.5	
600				185.8	122.3	70.8	29.2		
620				146.1	92.7	48.1	10.8		
640				110.5	65.0	25.5			
660				79.0	40.2	4.6			

Table 17

Values for Plot Nos. 5, 9.

$$-\frac{d\theta}{dx} \text{ vs. % Conversion}$$

#1 Converter   May 1927

Inlet gas 8.5% SO_2

Inlet Temp	300°C	320	340	360	380	400	420	440
0% Conv.	.1177	.0645	.0312	.0163	.0091	.0056	.0038	.0028
10%	.0690	.0345	.0179	.0103	.0062	.0044	.0034	.0027
20%	.0370	.0200	.0121	.0077	.0054	.0041	.0035	.0030
30%	.0235	.0140	.0094	.0068	.0052	.0044	.0040	.0038
40%	.0176	.0120	.0090	.0071	.0060	.0055	.0054	.0057
50%	.0164	.0121	.0100	.0087	.0080	.0082	.0088	.0150
60%	.0187	.0154	.0137	.0130	.0136	.0149	.0175	.0227
70%	.0270	.0244	.0244	.0263	.0313	.0416	.0667	.2500
75%	.0385	.0364	.0392	.0454	.0645	.1250	∞	

Inlet gas: 9.5% SO_2

Inlet Temp	300°C	320	340	360	380	400	420	440
0% Conv.	.1111	.0572	.0282	.0140	.0079	.0049	.0033	.0025
10%	.0656	.0274	.0147	.0083	.0054	.0037	.0029	.0024
20%	.0274	.0149	.0093	.0062	.0045	.0035	.0029	.0026
30%	.0172	.0106	.0072	.0054	.0044	.0038	.0035	.0035
40%	.0128	.0092	.0070	.0058	.0051	.0049	.0050	.0055
50%	.0122	.0096	.0082	.0074	.0073	.0078	.0087	.0104
60%	.0149	.0128	.0120	.0125	.0137	.0157	.0200	.0286
70%	.0230	.0227	.0250	.0303	.0400	.0667	.6667	
75%	.0345	.0330	.0455	.0690	.1667			

Table 18

Values for Plot Nos. 13, 17

$$-\frac{d\theta}{dx} \text{ vs. \% Conversion}$$

#1 Converter   May 1927

Inlet gas 10.5% SO_2

	300	320	340	360	380	400	420	440
0% Conv.	.1000	.0513	.0247	.0132	.0072	.0044	.0030	.0022
10%	.0454	.0225	.0122	.0070	.0046	.0032	.0025	.0020
20%	.0215	.0122	.0074	.0051	.0038	.0030	.0026	.0024
30%	.0130	.0082	.0059	.0046	.0038	.0033	.0032	.0033
40%	.0099	.0074	.0059	.0050	.0046	.0046	.0049	.0056
50%	.0099	.0082	.0073	.0070	.0073	.0080	.0093	.0114
60%	.0127	.0116	.0118	.0130	.0149	.0192	.0274	.0526
70%	.0222	.0247	.0299	.0425	.0833			
75%	.0371	.0476	.0833	2.0000				

Inlet gas : 11.5% SO_2

	300	320	340	360	380	400	420	440
0% Conv	.0870	.0455	.0232	.0119	.0067	.0041	.0028	.0021
10%	.0378	.0194	.0105	.0064	.0041	.0030	.0023	.0019
20%	.0172	.0104	.0065	.0045	.0033	.0028	.0024	.0022
30%	.0104	.0070	.0051	.0040	.0034	.0031	.0031	.0033
40%	.0081	.0063	.0052	.0046	.0045	.0047	.0055	.0059
50%	.0085	.0074	.0069	.0070	.0076	.0088	.0109	.0143
60%	.0121	.0120	.0132	.0152	.0196	.0286	.0571	
70%	.0267	.0322	.0513	.1429				
75%	.0588	.1177	∞					

Table 19

Values for Plot Nos. 6, 10

θ vs. % Conversion

(Integrated values of θ from $\frac{d\theta}{dx}$ vs. Conversion plots)

#1 Converter   May 1927

Inlet gas: 8.5% SO_2

Inlet Temp	320°C	340°C	360	380	400	420	440
% Conversion ↓							
10	959	460	260	151	95	71	52
20		753	435	266	179	141	107
30		964	577	370	262	214	173
40			700	479	361	316	266
50			855	611	502	452	414
60				813	718	700	718
65				965	894	921	1027

Inlet gas: 9.5% SO_2

Inlet Temp	320°C	340	360	380	400	420	440
% Conversion ↓							
10	803	385	214	132	85	61	50
20		621	356	230	157	121	100
30		784	469	318	227	183	162
40		924	579	410	310	264	254
50			704	523	433	395	405
60			888	729	662	664	768
65			1040	909	885		

Table 20

Values for Plot Nos. 14, 18

θ vs. % Conversion

(Integrated values of θ from $\frac{d\theta}{dx}$ vs conversion plot.)

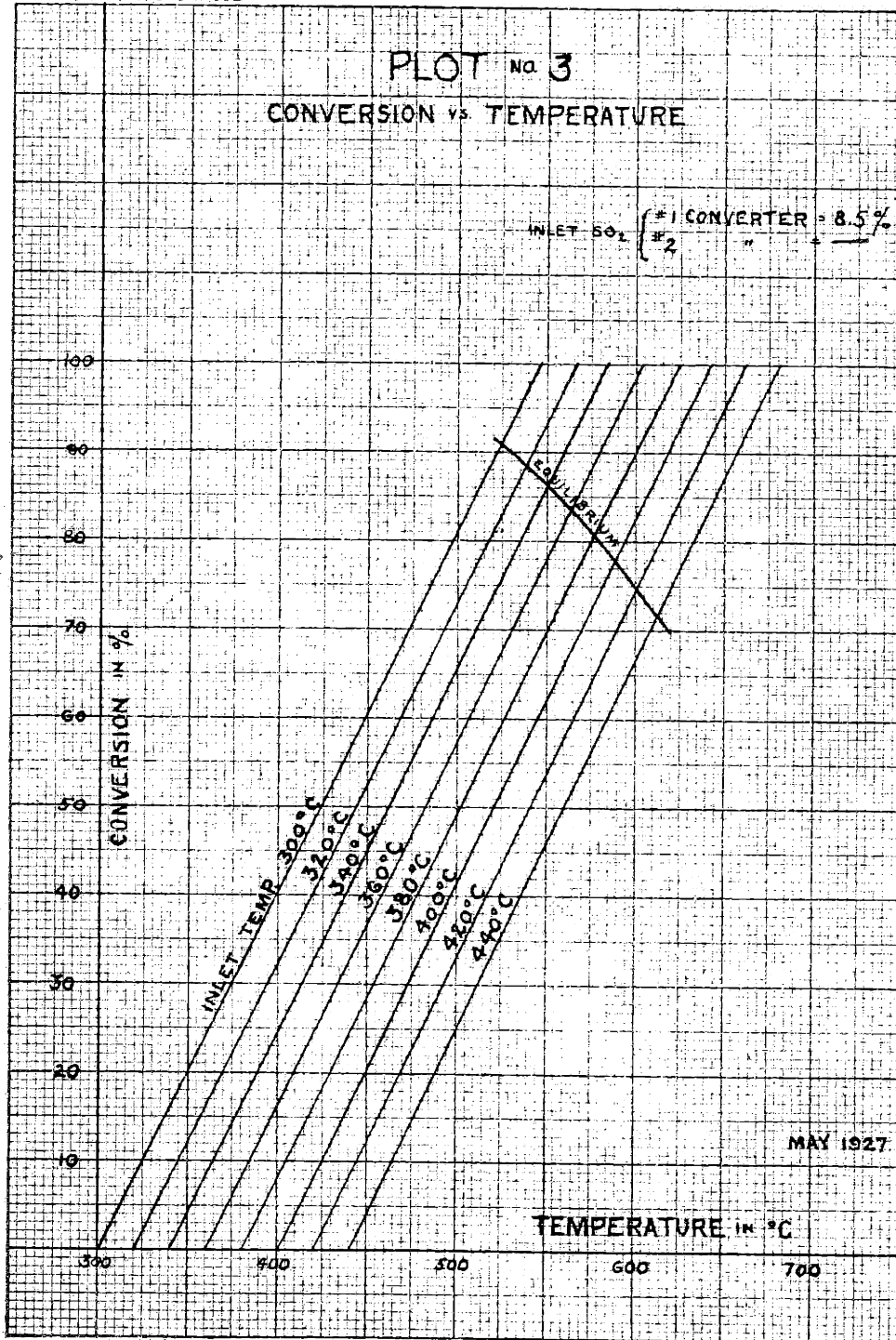#1 Converter   May 1927

Inlet gas: 10.5% SO_2

Inlet Temp	320°C	340	360	380	400	420	440
% Conversion ↓							
10	685	351	183	117	74	52	40
20	1020	540	303	200	134	102	81
30	1220	669	401	275	196	158	136
40		783	494	360	278	237	223
50		912	611	473	297	373	380
60			801	685	646	684	795
65			960	874	921	∞	∞

Inlet gas: 11.5% SO_2

Inlet Temp	320°C	340	360	380	400	420	440
% Conversion ↓							
10	594	313	175	108	69	49	41
20	873	482	284	183	128	96	81
30		595	368	244	187	150	133
40		695	450	319	263	231	217
50		807	565	435	388	378	389
60		999	775	668	679	747	
65			995				

PLOT №. 3

CONVERSION vs. TEMPERATURE

INLET SO₂ { #1 CONVERTER = 8.5 %
           { #2   "   = 8.5 %

EQUILIBRIUM

INLET TEMP 300°C
320°C
340°C
360°C
380°C
400°C
420°C
440°C

CONVERSION IN %

100
90
80
70
60
50
40
30
20
10

MAY 1927

TEMPERATURE IN °C

300   400   500   600   700

PLOT No 4

#1 CONVERTER

INLET GAS
8.5% SO₂
12.2% O₂
79.3% N₂

MAY 1927
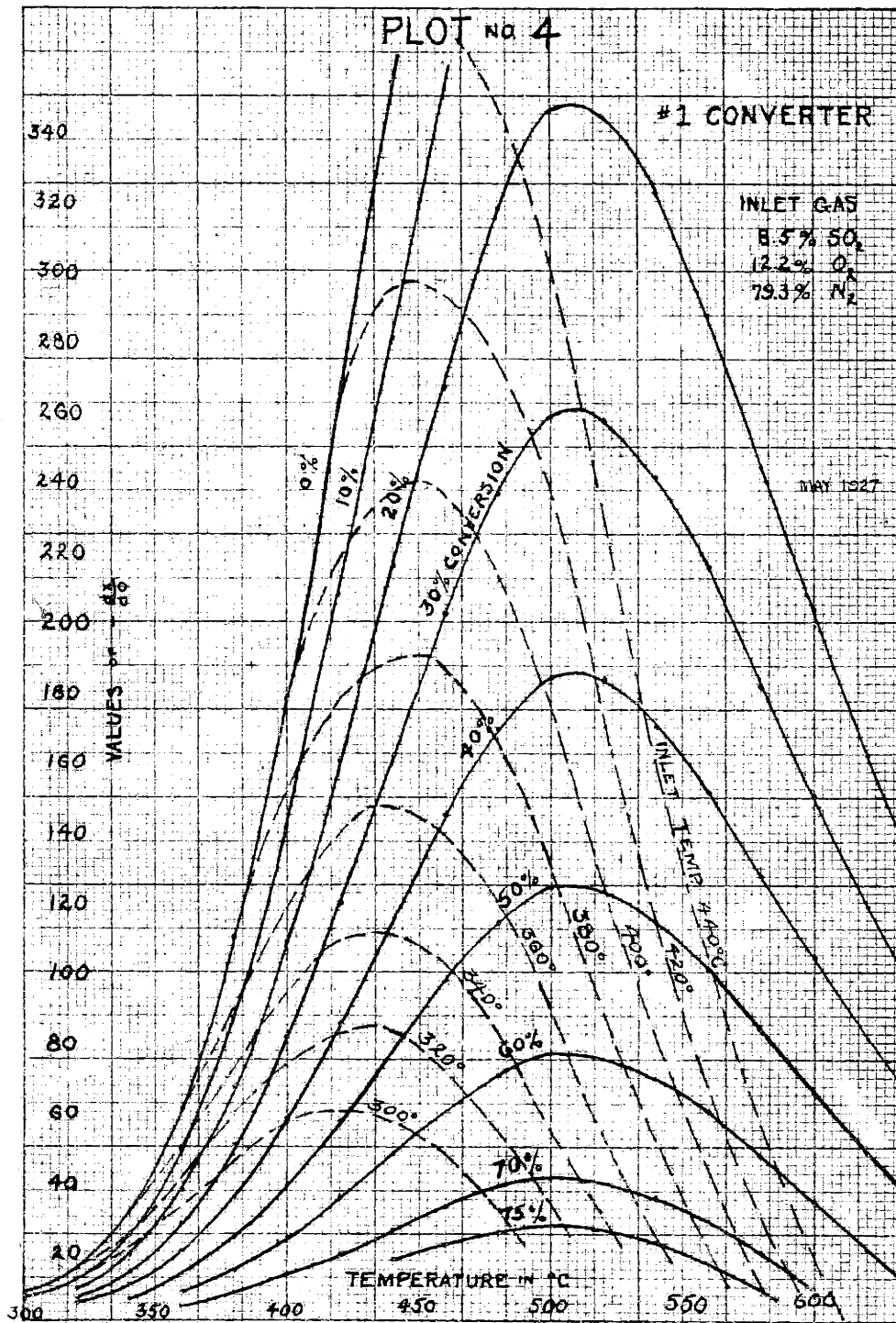
TEMPERATURE IN °C

PLOT NO. 5

#1 CONVERTER

INLET GAS
8.5% SO_2

INLET TEMP. 320°C

340°

360°

380°

400°
420°
440°

VALUES OF $-\frac{d\theta}{dx}$

.06

.05

.04

.03

.02

.01

0   10   20   30   40   50   60   70   80

% CONVERSION

MAY 1927

PLOT No 6

*1 CONVERTER

INLET GAS
8.5% SO₂

% CONVERSION

440°
420°
400°
380°
360°
390°
INLET TEMP 320°C

MAY 1927

TIME UNITS

200   400   600   800   1000
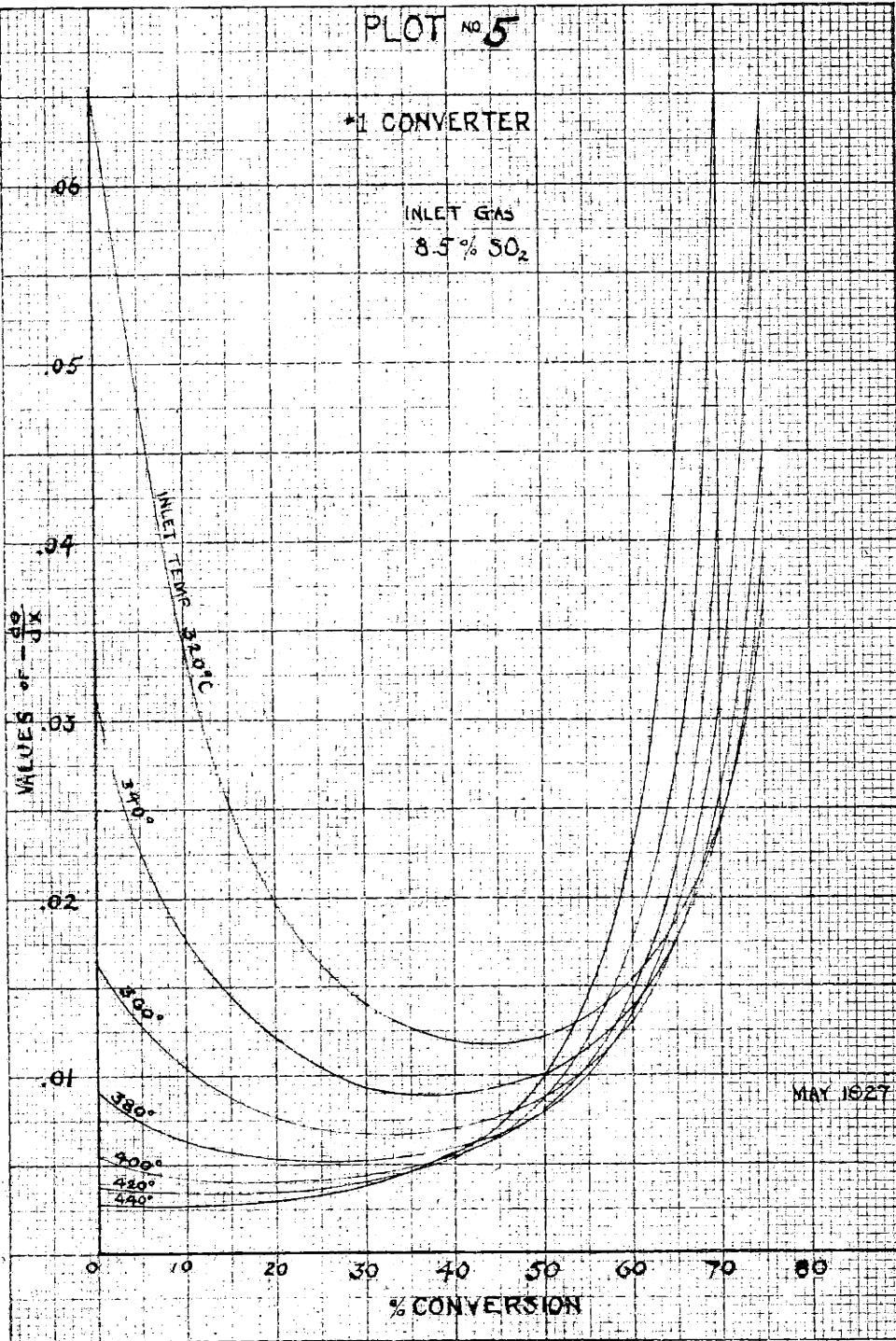
TECHNOLOGY BRANCH
HARVARD COOPERATIVE SOCIETY, CAMBRIDGE
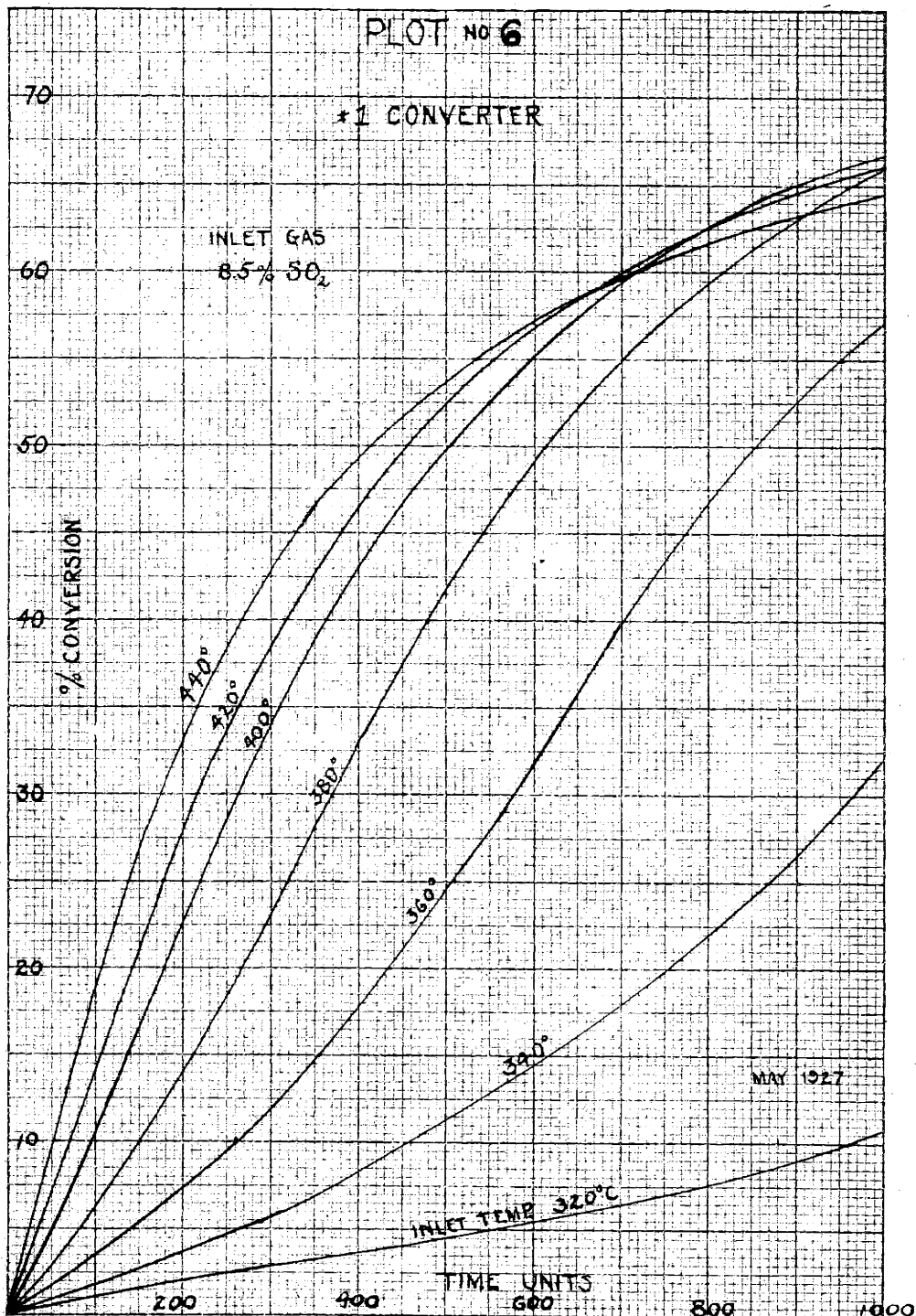
PLOT No 7

CONVERSION vs TEMPERATURE

INLET SO₂ {#1 CONVERTER = 9.5%
{#2 " "

EQUILIBRIUM

CONVERSION IN %

INLET TEMP 300°C
320°
340°
360°
380°
400°
420°
440°

MAY 1927

TEMPERATURE IN °C

300   400   500   600   700

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HARVARD COOPERATIVE SOCIETY, CAMBRIDGE

PLOT No 8

#1 CONVERTER

INLET GAS
8.5% SO₂
11.1% O₂
73.4% N₂

MAY 1927

0%   0%   2.0%   28% CONVERSION   40%   50%   60%   70%   75%

VALUES of $\frac{dy}{d\theta}$

340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20

TEMPERATURE in °C

300   350   400   450   500   550   600

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PLOT No 9

#1 CONVERTER

INLET GAS
9.5% SO_2
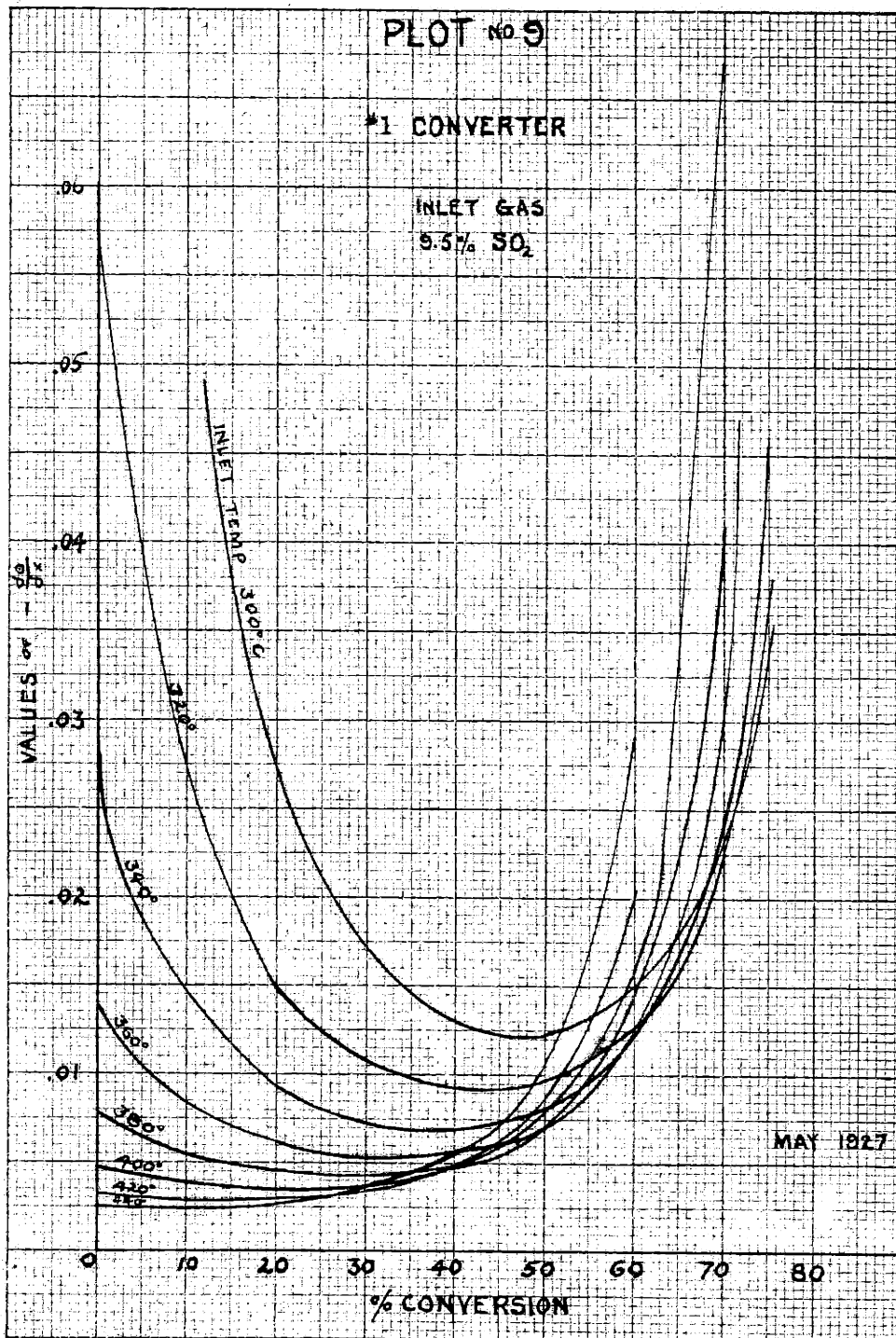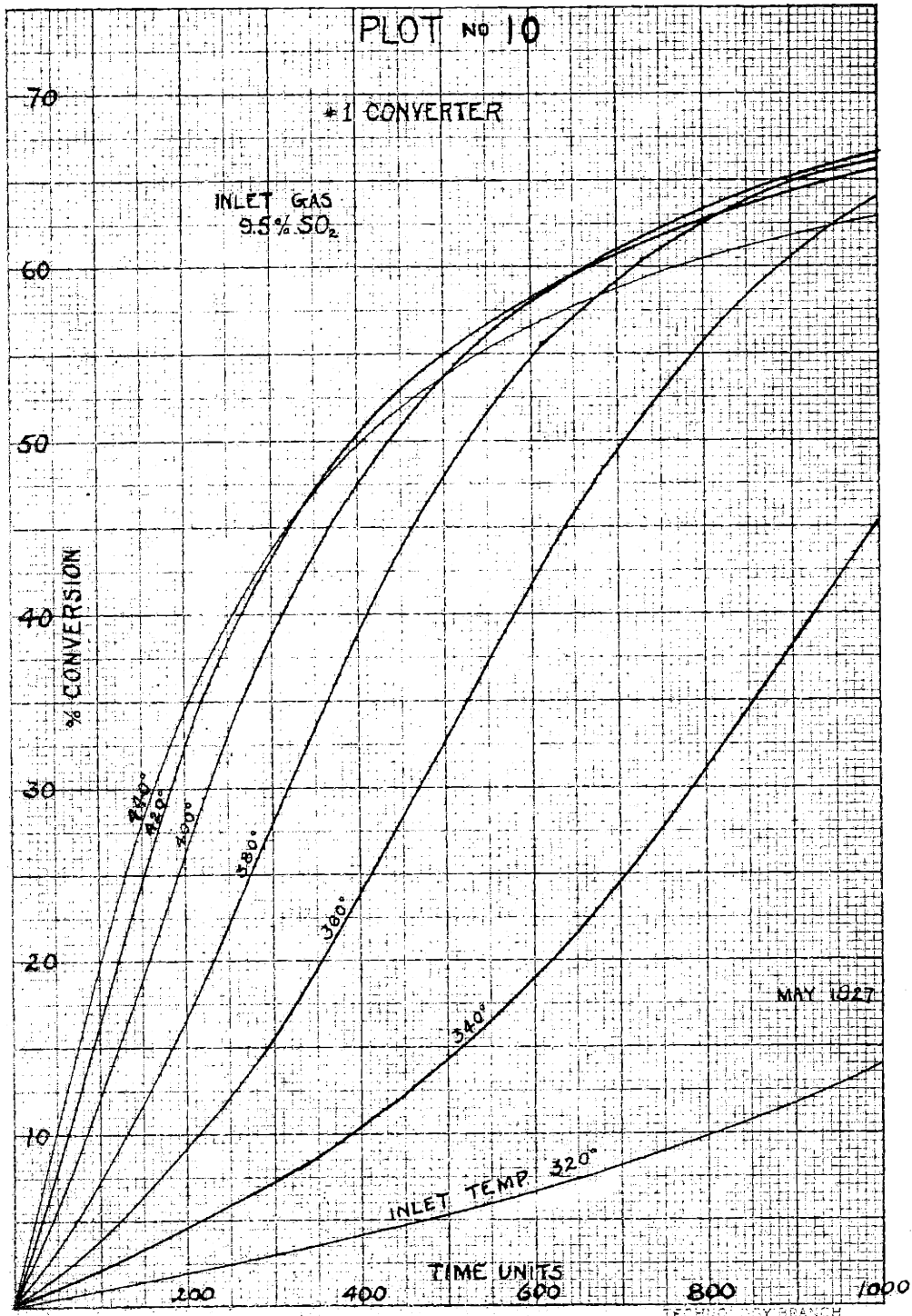
INLET TEMP 300°C

VALUES of $\delta - \frac{d}{dx}$

MAY 1927

% CONVERSION

PLOT № 10

#1 CONVERTER

INLET GAS
9.5% SO₂

% CONVERSION

MAY 1927

INLET TEMP 320°

TIME UNITS

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PLOT No. 11

CONVERSION vs TEMPERATURE

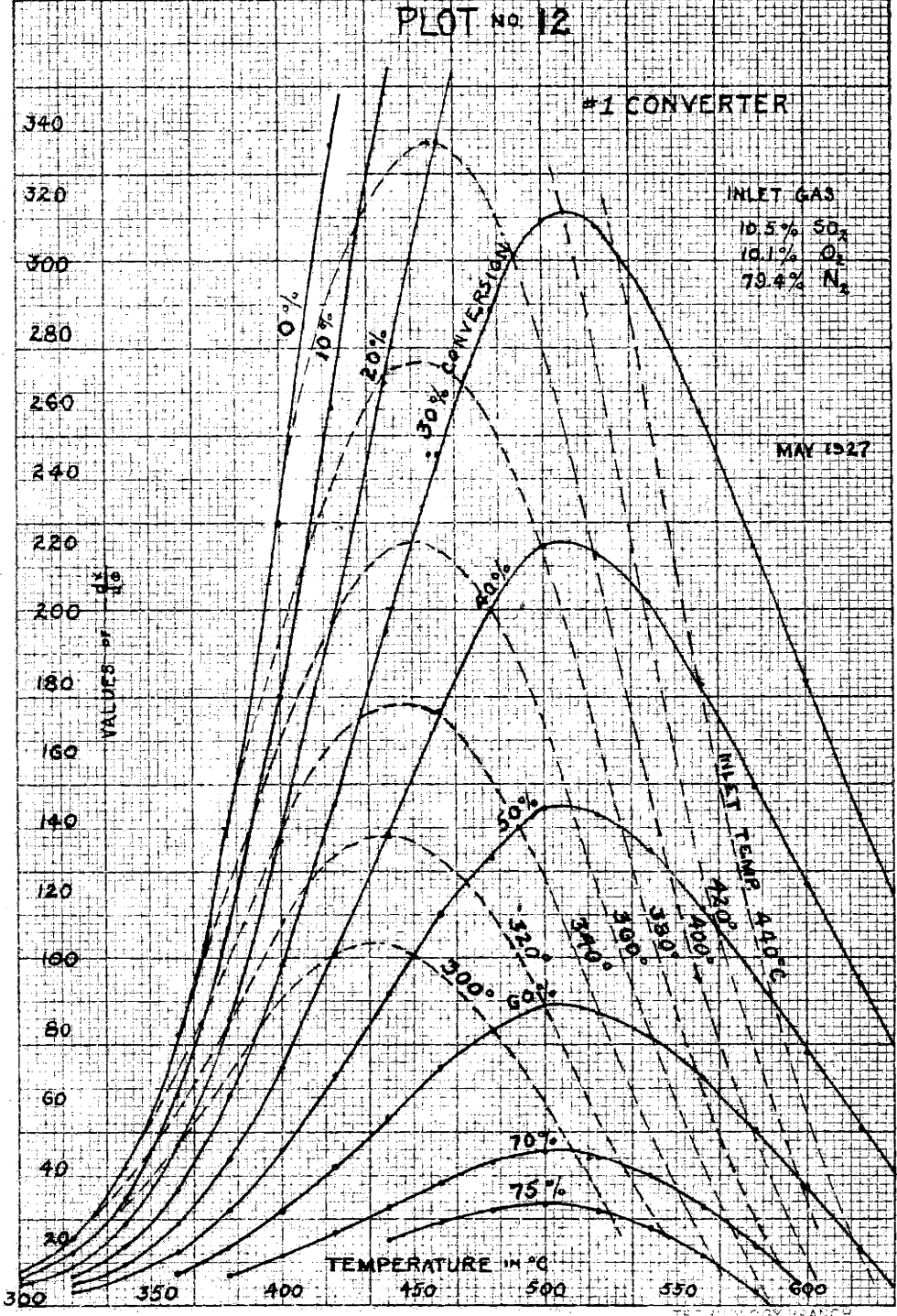INLET SO₂ { #1 CONVERTER = 10.5%
             #2   "   = 62.5%

CONVERSION IN %

INLET TEMP 380°C 400° 420° 440° 460° 480°

EQUILIBRIUM

INLET TEMP 300°C 320° 340° 360° 380° 400° 420° 440°

TEMPERATURE IN °C

300   400   500   600   700

MAY 1927

TECHNOLOGY BRANCH
HARVARD COOPERATIVE SOCIETY, CAMBRIDGE
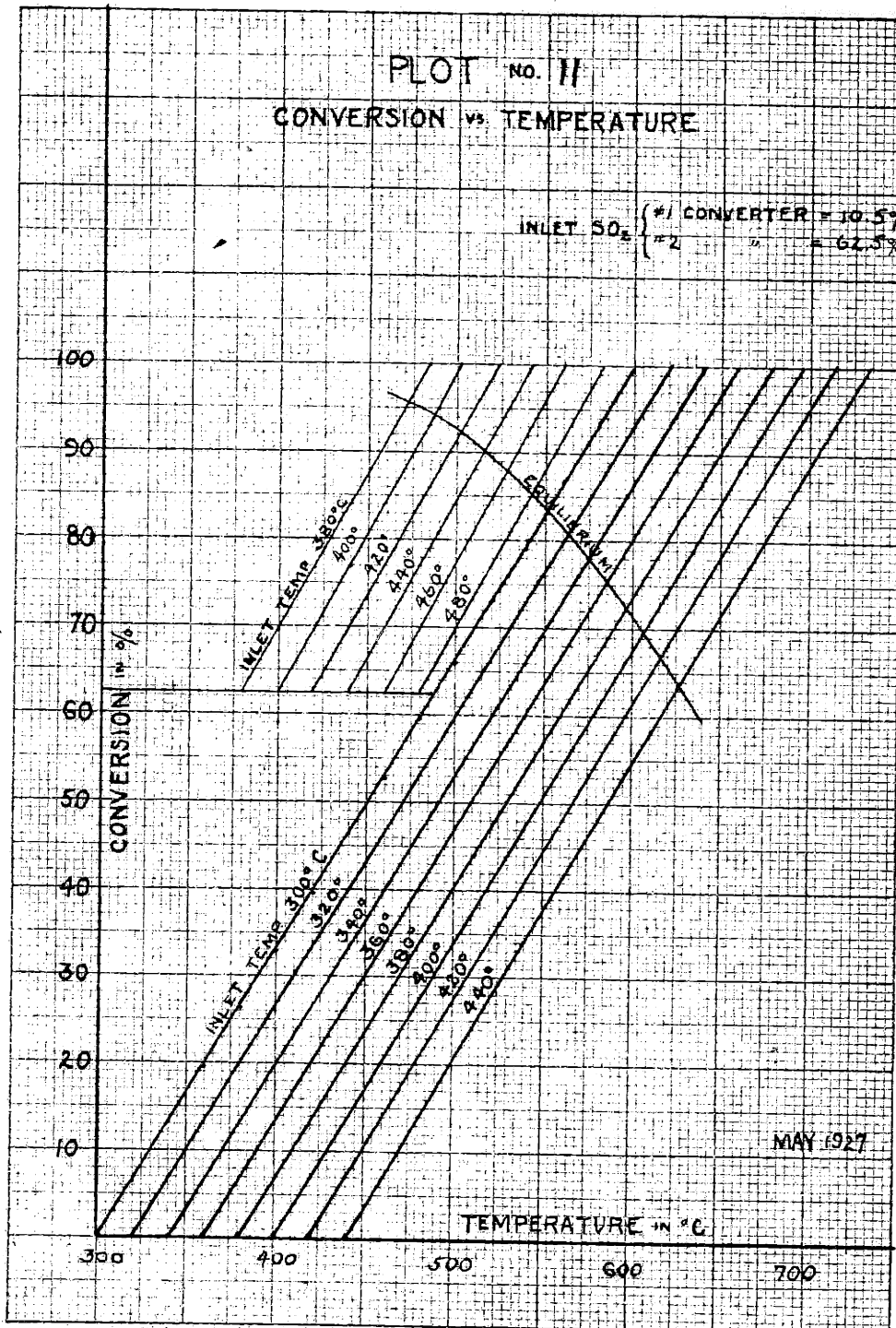
PLOT No. 12

#1 CONVERTER

INLET GAS
10.5% SO₂
10.1% O₂
79.4% N₂

MAY 1927

TEMPERATURE IN °C

PLOT No. 13

#1 CONVERTER

INLET GAS
10.5 % SO_2

VALUES OF $-\frac{d\theta}{dx}$

INLET TEMP. 320°C
340
360°
380°
400°
420°
440°

MAY 1927

% CONVERSION

.06 .05 .04 .03 .02 .01

0 10 20 30 40 50 60 70 80
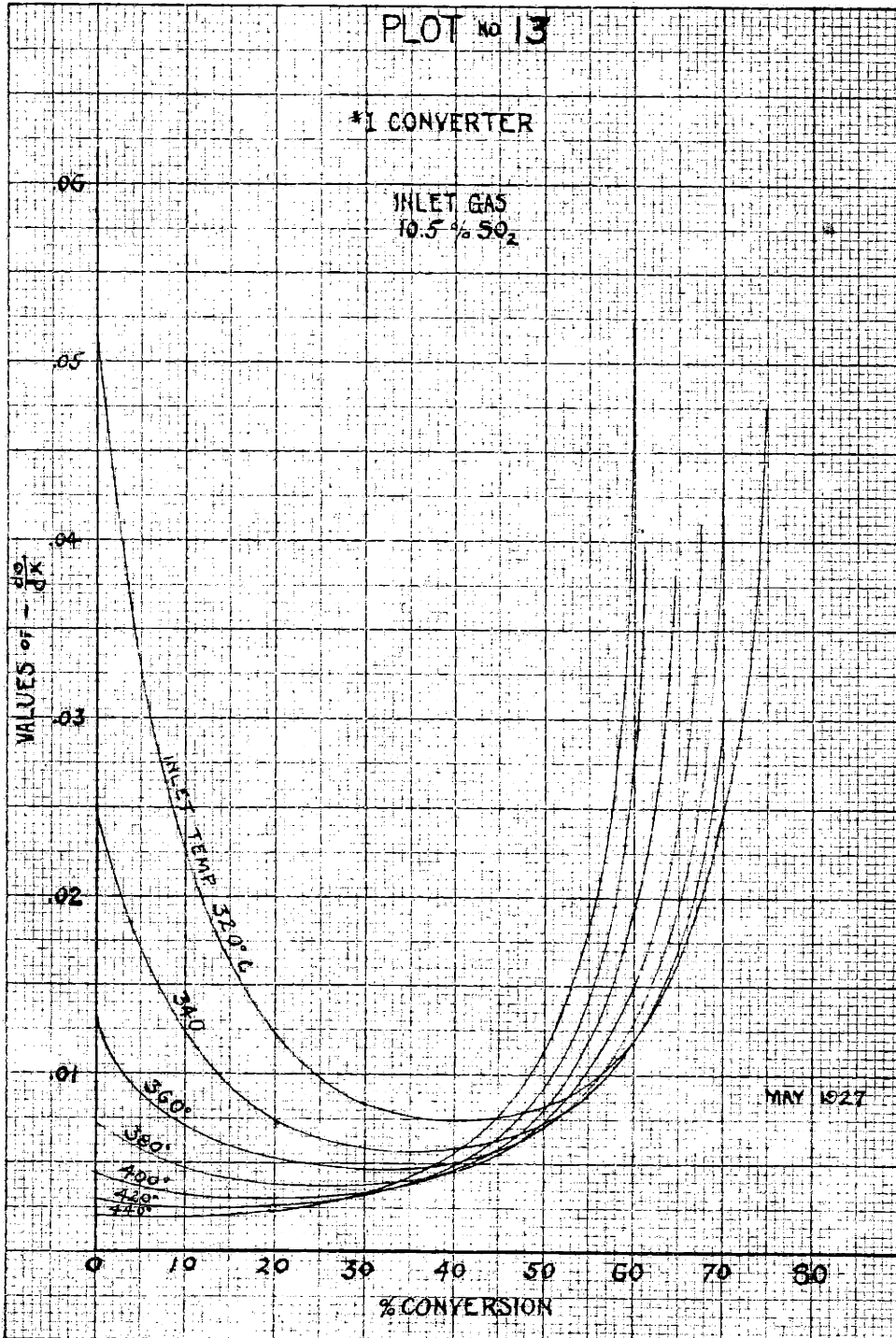
PLOT NO. 14

#1 CONVERTER

INLET GAS
10.5% SO₂

% CONVERSION

MAY 1927

440°
420°
400°
380°
360°
340°
INLET TEMP 320°C

70
60
50
40
30
20
10

TIME UNITS

200   400   600   800   1000
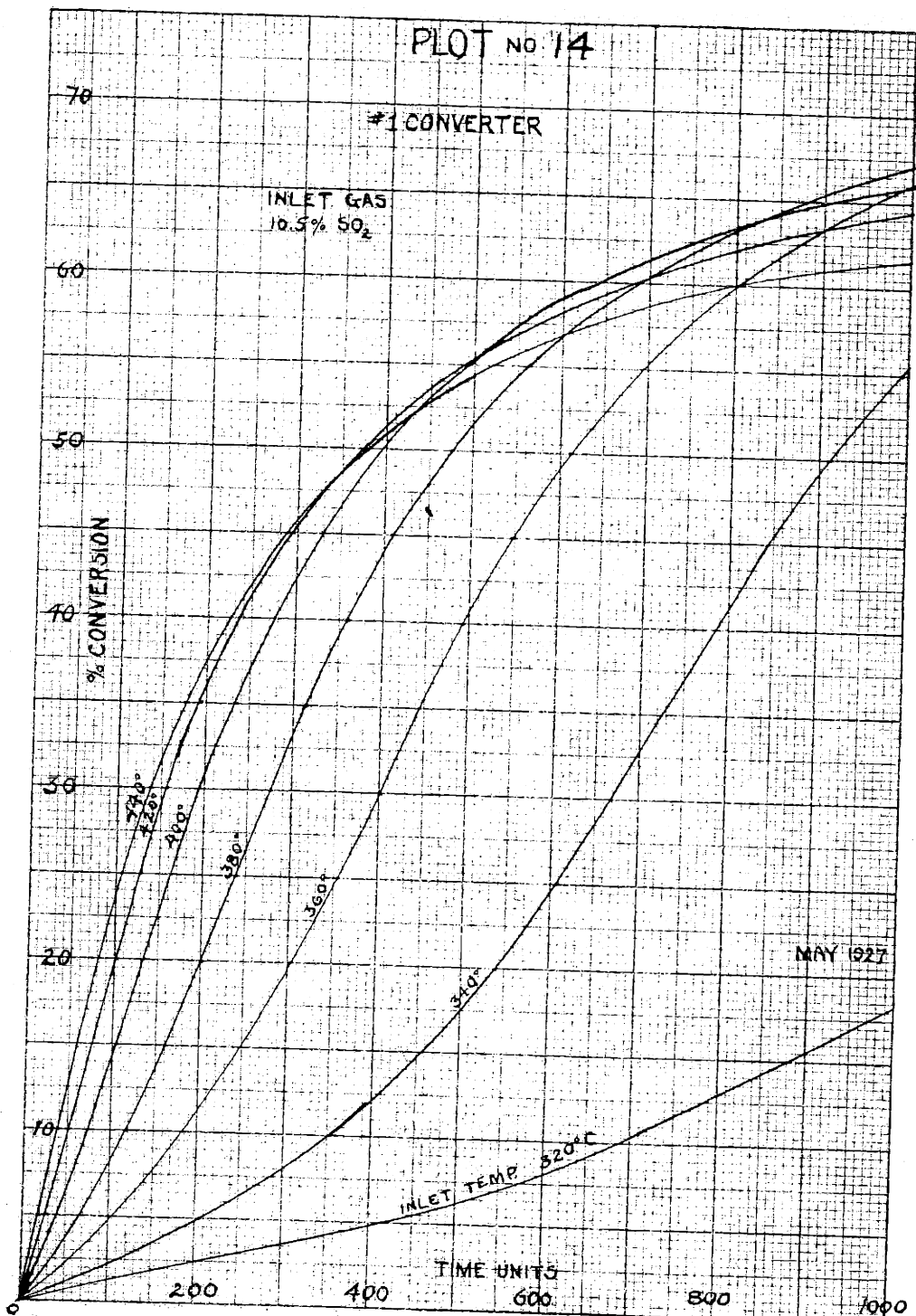
PLOT No. 15

CONVERSION vs TEMPERATURE

INLET SO₂ { #1 CONVERTER = 11.5%
{ #2

CONVERSION IN %

INLET TEMP. 300°C
320°
340°
360°
380°
400°
420°
440°

EQUILIBRIUM

TEMPERATURE IN °C

300   400   500   600   700

MAY 1947

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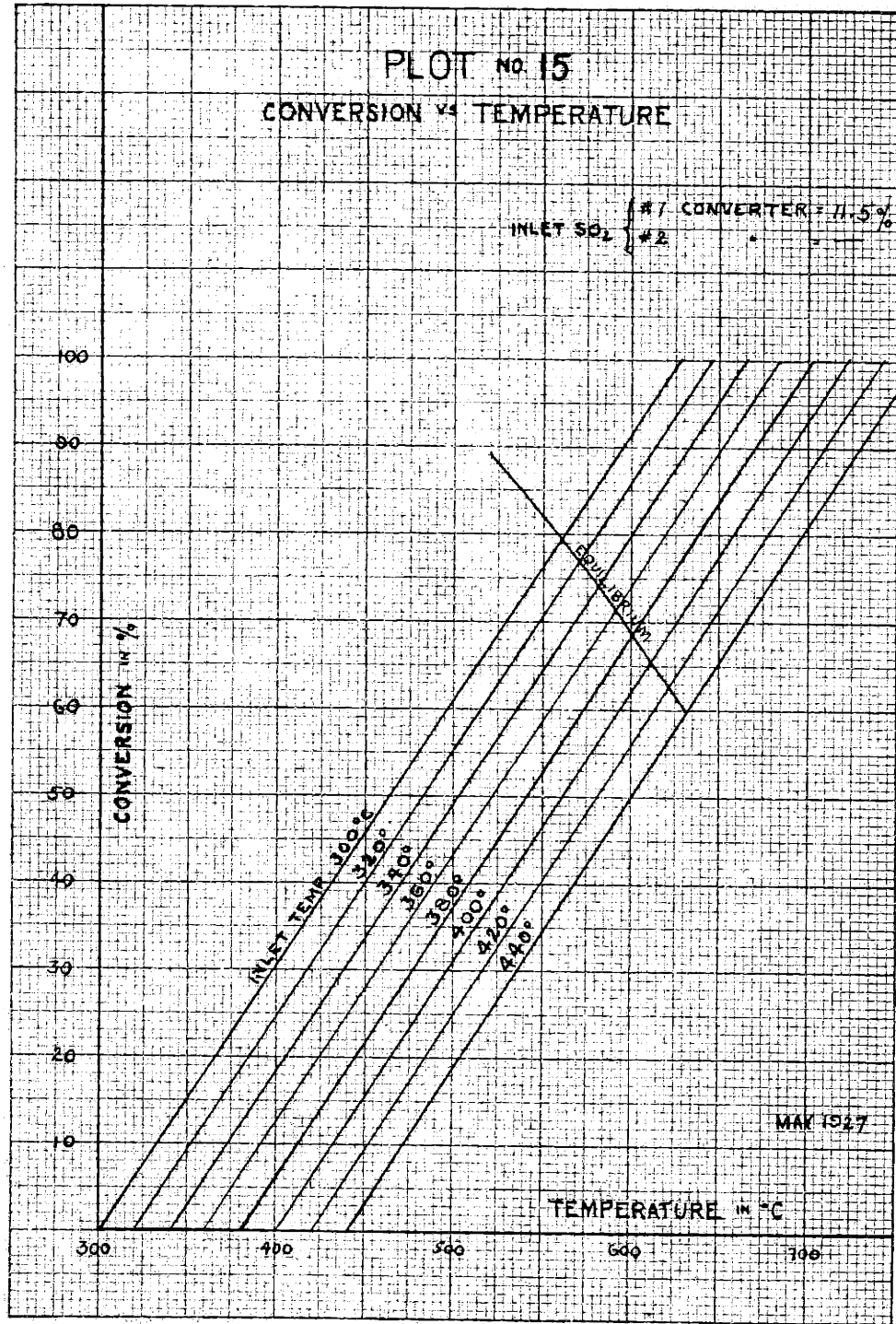
PLOT No. 16

#1 CONVERTER

INLET GAS
11.5% SO₂
8.1% O₂
79.4% N₂

MAY 1927

TEMPERATURE in °C

VALUES OF $\frac{dx}{dq}$

0%
10%
20%
30% CONVERSION
40%
50%
60%
70%
75%

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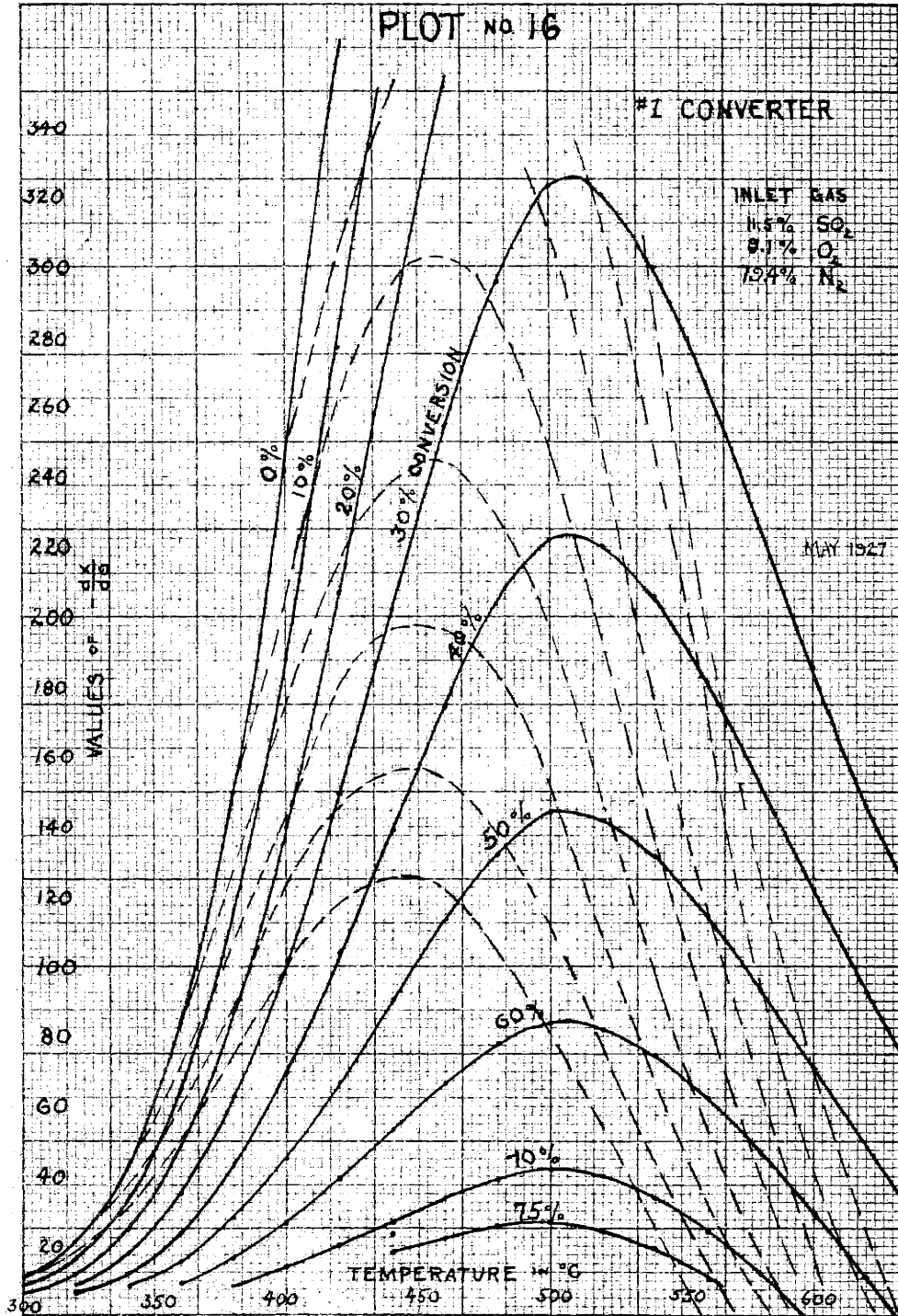
PLOT No. 17

#1 CONVERTER

INLET GAS
11.5 % SO₂
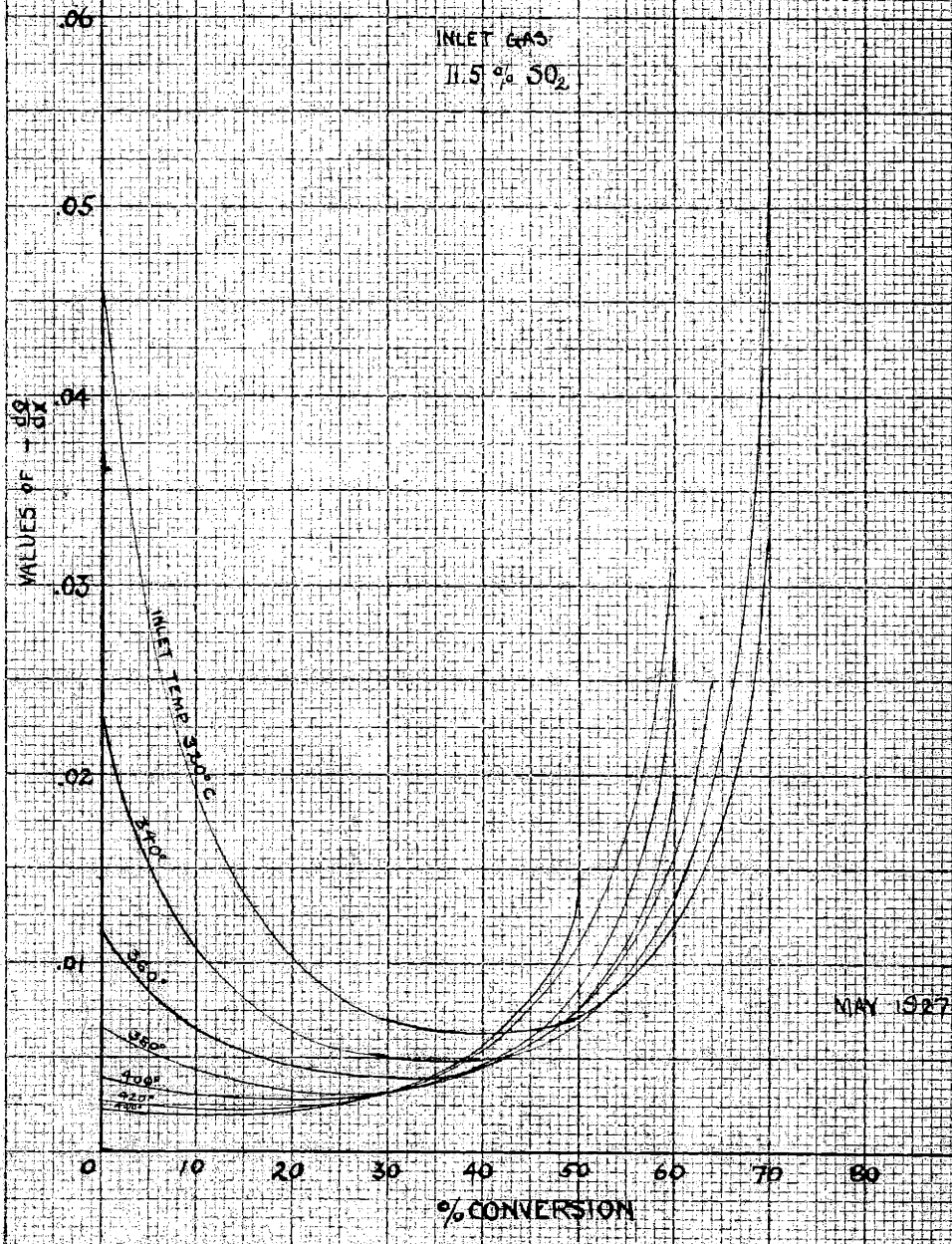
VALUES OF $+\frac{d\theta}{dx}$

INLET TEMP 320° C.

% CONVERSION

MAY 1927

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PLOT №18

#1 CONVERTER

INLET GAS
11.5% SO₂

% CONVERSION

TIME UNITS

MAY 1927

INLET TEMP 370°C

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PLOT № 19

1 CONVERTER

INLET SO$_2$	8.5%	9.5	10.5	11.5
TEMP				
340	20.0	28.0	37.2	45.3
360	43.5	51.8	58.0	59.4
380	57.4	61.1	62.0	62.0
400	61.2	62.2	62.5	61.4
420	61.4	61.8	61.3	60.0
440	60.7	59.7	59.5	56.8
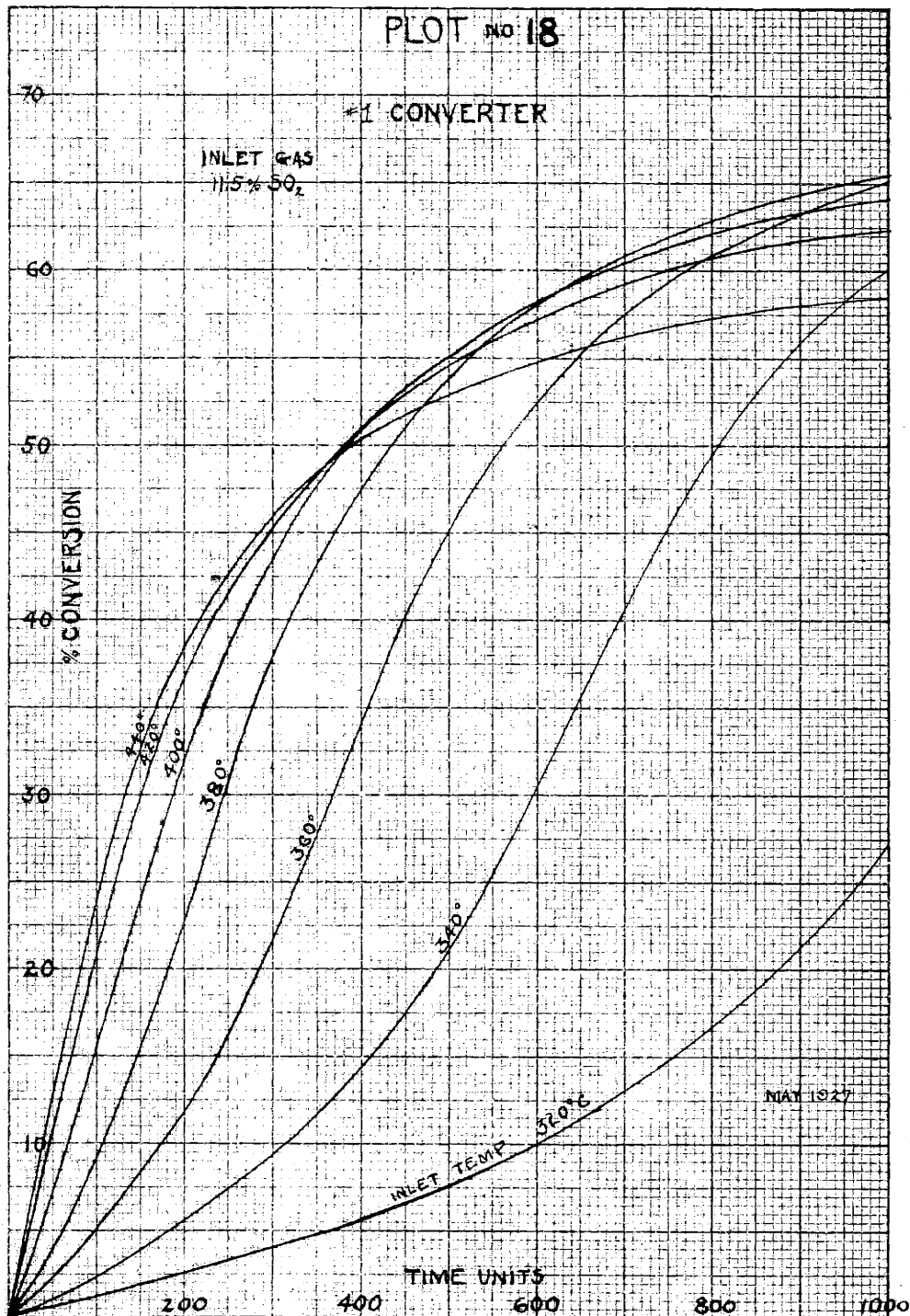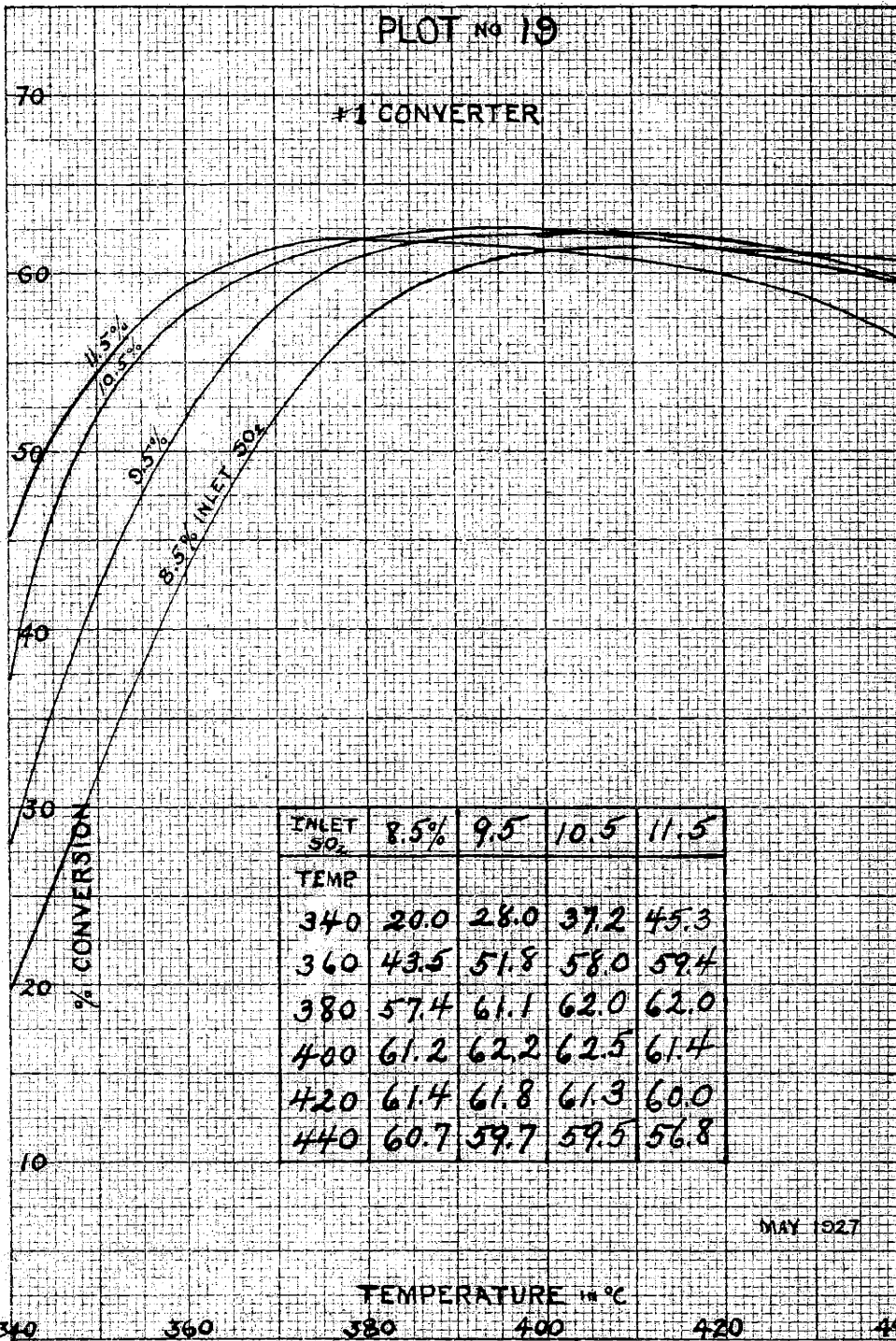
MAY 1927

TEMPERATURE in °C

Table 21

Values for Plot No. 11

% Conversion vs Temperature

#2 Converter

May 1927

Inlet Temp →	380°C	400	420	440	460	480
Temp °C						
380	62.5					
400	69.7	62.5				
420	76.9	69.7	62.5			
440	84.0	76.8	69.6	62.5		
460	90.3	83.1	75.9	68.8	62.5	
480	98.6	91.4	84.2	77.1	70.8	62.5
500		99.2	92.0	84.9	78.6	70.3
520			98.8	91.7	85.4	77.1
540				99.1	92.8	84.5
560					100.2	91.9

Table 22

Converter #2
Values for Plot Nos. 20
$-\dfrac{dx}{d\theta}$ vs Temperature

May 1927

% Conversion	62.5	70	75	80	85	90	95
Temp °C							
380	14.7	8.93	5.99	3.7	2.0	0.9	0.2
400	23.7	14.42	9.67	6.0	3.2	1.4	0.3
420	35.0	21.3	14.3	8.8	4.8	2.0	0.5
440	47.1	28.6	19.2	11.8	6.4	2.7	0.5
460	59.1	35.8	24.0	14.7	7.8	3.2	0.4
480	68.9	41.5	27.6	16.8	8.7	3.1	
500	74.5	44.6	29.3	17.3	8.4	2.1	
520	73.0	42.9	27.4	15.3	5.9		
540	66.3	37.4	22.5	10.7	1.6		
560	55.3	28.6	14.5	3.2			

Values for Plot No. 21
$-\dfrac{d\theta}{dx}$ vs % Conversion

Inlet Temp.	380°C	400	420	440	460	480
% Conversion						
62.5	.068	.042	.029	.021	.017	.015
70	.069	.046	.035	.028	.024	.022
75	.078	.057	.045	.038	.035	.035
80	.101	.077	.064	.058	.059	.071
85	.153	.125	.114	.120	.170	.833
90	.322	.312	.408	10.000		
95	4.000					

Table 23

Values for Plot No. 22

θ vs % Conversion

(Integrated values of θ from $\frac{d\theta}{dx}$ vs conversion plots)

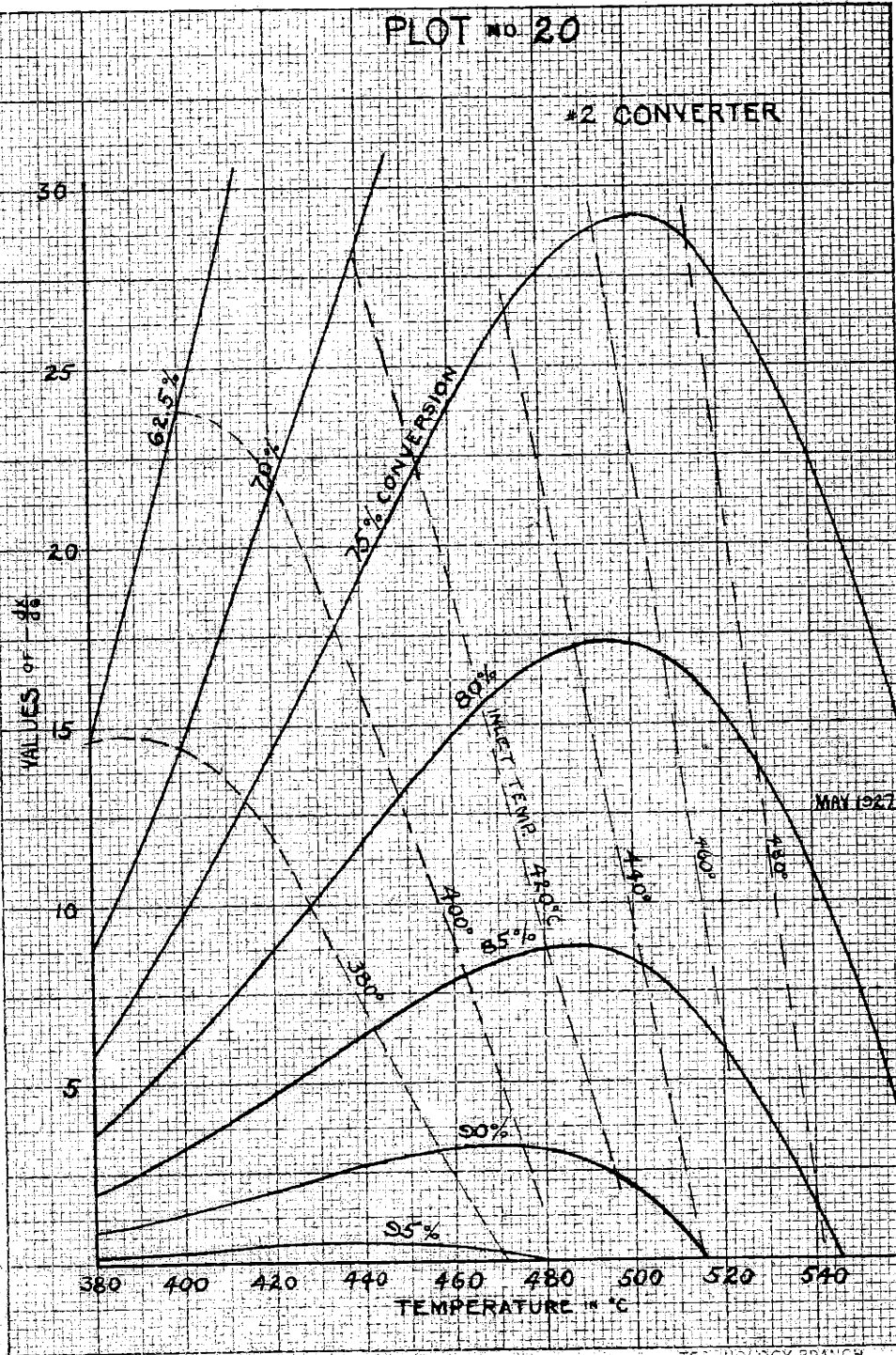#2 Converter   May 1927

Inlet Temp	380°C	400	420	440	460	480
% Conversion						
65	167	105	74	55	45	40
67.5	334	211	151	113	94	85
70	504	322	234	178	150	135
72.5	680	442	326	252	214	194
75	867	575	430	338	291	270
77.5	1073	727	549	441	388	373
80	1328	904	693	568	517	521
82.5		1117	873	741	698	759
85		1387	1113	987	992	1018

PLOT № 20

#2 CONVERTER
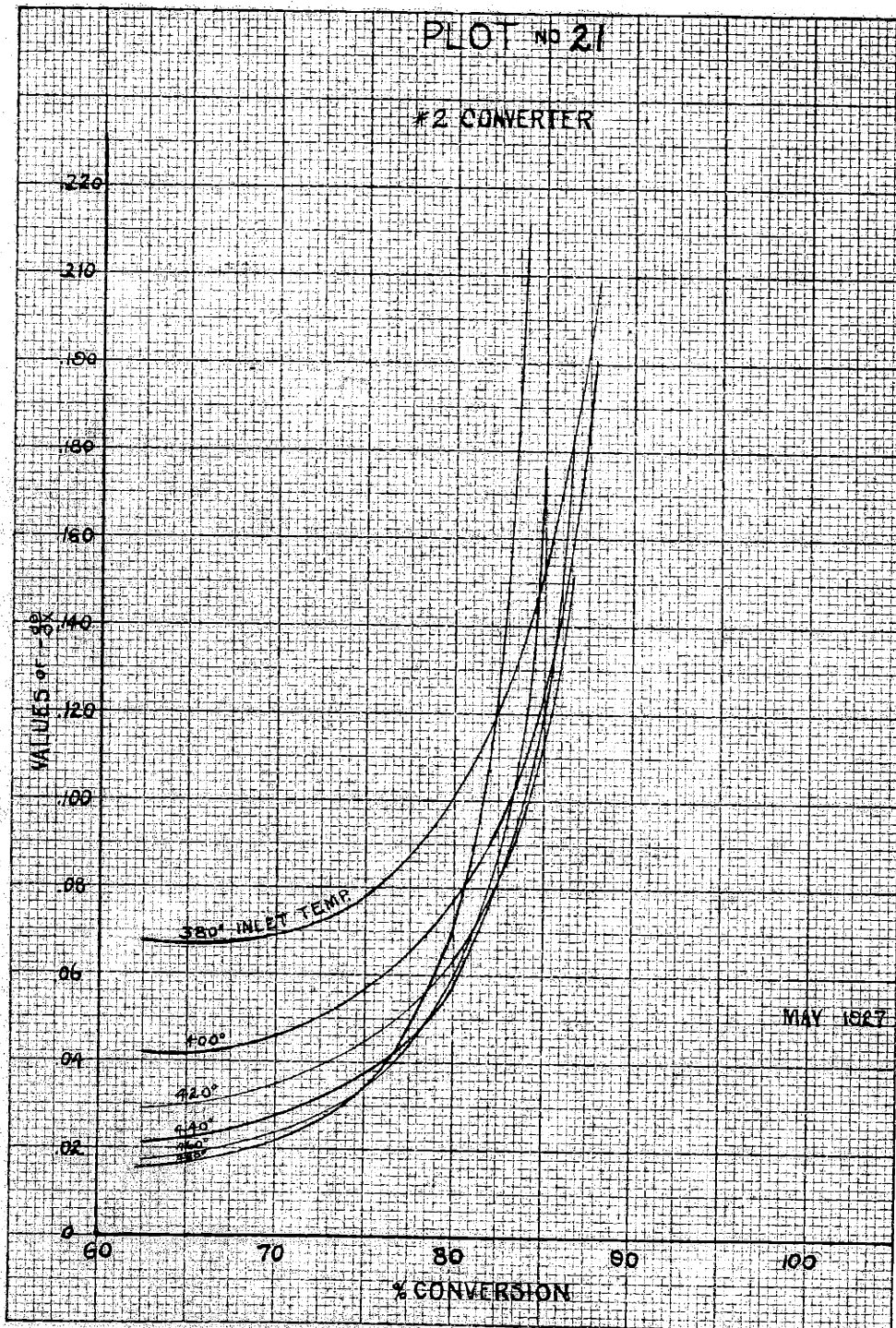
MAY 1927

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PLOT № 21

#2 CONVERTER

VALUES OF $\frac{dX}{3X}$

380° INLET TEMP.

400°

420°

440°
460°
480°

MAY 1927

% CONVERSION

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HARVARD COOPERATIVE SOCIETY, CAMBRIDGE

PLOT № 22

#2 CONVERTER

% CONVERSION

INLET TEMP 380°C

480°
460°
440°
420°
400°

TIME UNITS

200   400   600   800   1000

95
90
85
80
75
70
65
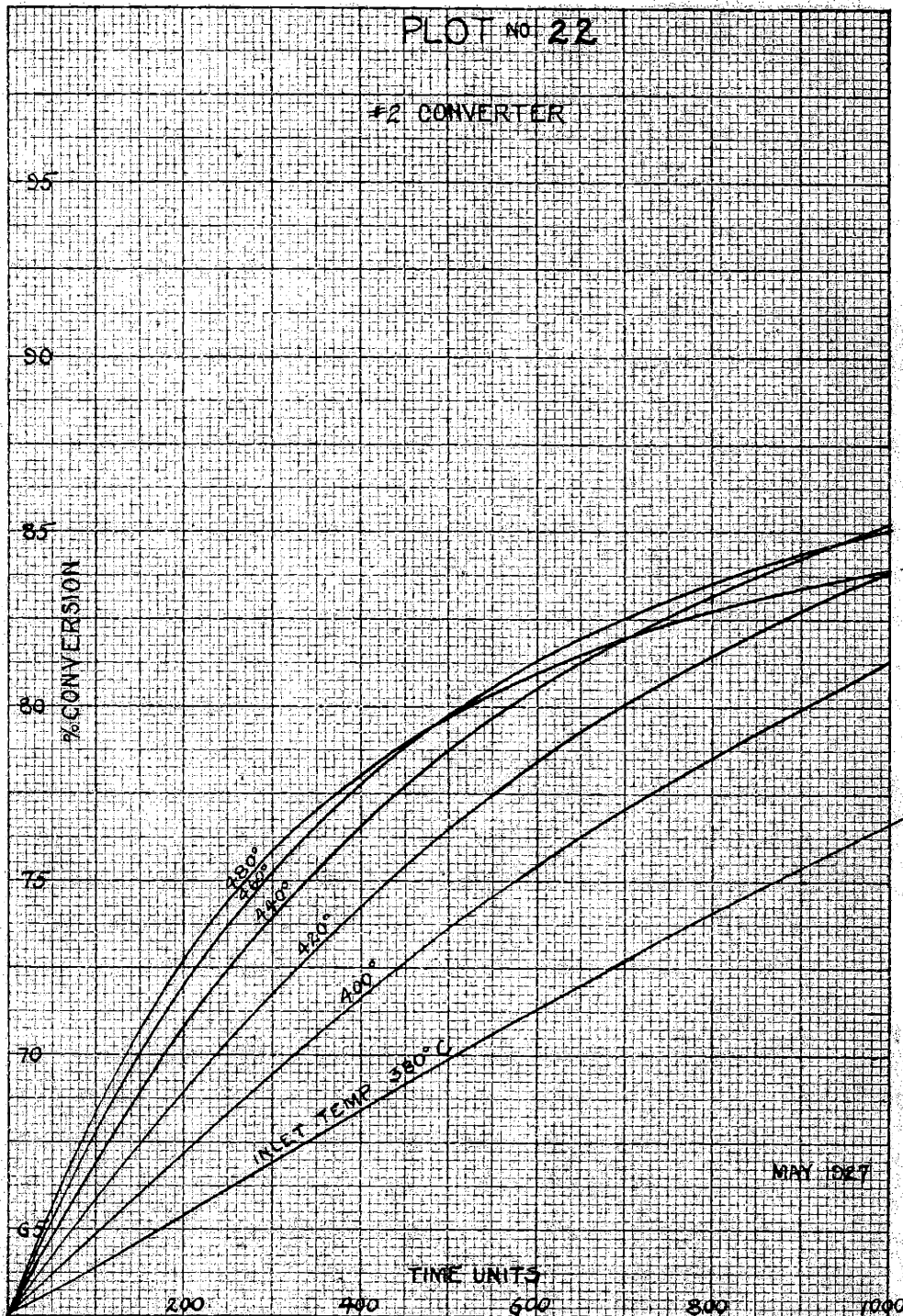
MAY 1927

TECHNOLOGY BRANCH
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PLOT No 22 A

#2 CONVERTER
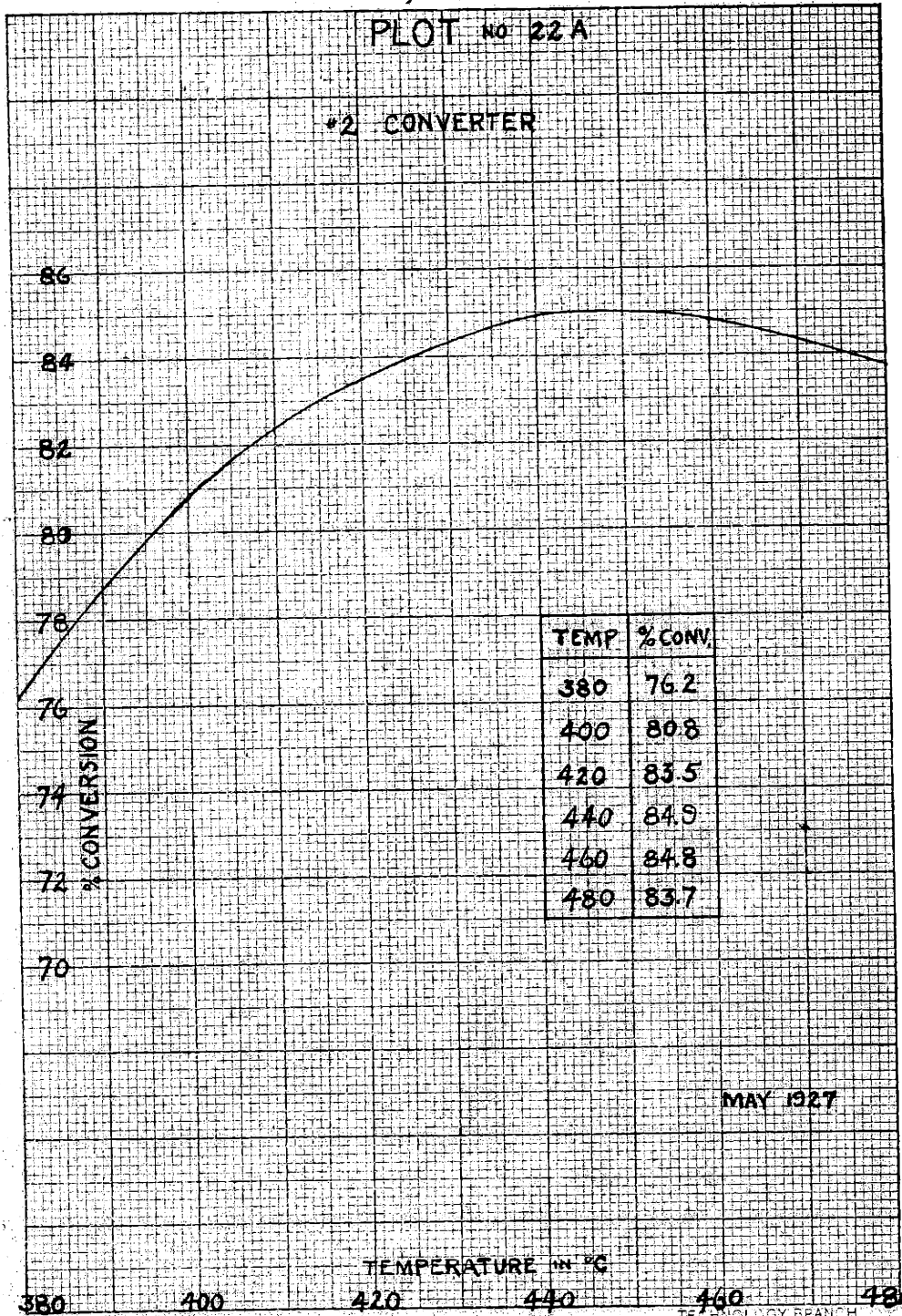
TEMP	% CONV.
380	76.2
400	80.8
420	83.5
440	84.9
460	84.8
480	83.7

MAY 1927

% CONVERSION

TEMPERATURE IN °C

APPENDIX 3

PLOT NO 23

TEMPERATURE IN °C

E.D. RIES' REACTION RATE CONSTANT

Temp	k
400°	.0380
420°	.0865
435°	.106
450°	.145

MAY 1927
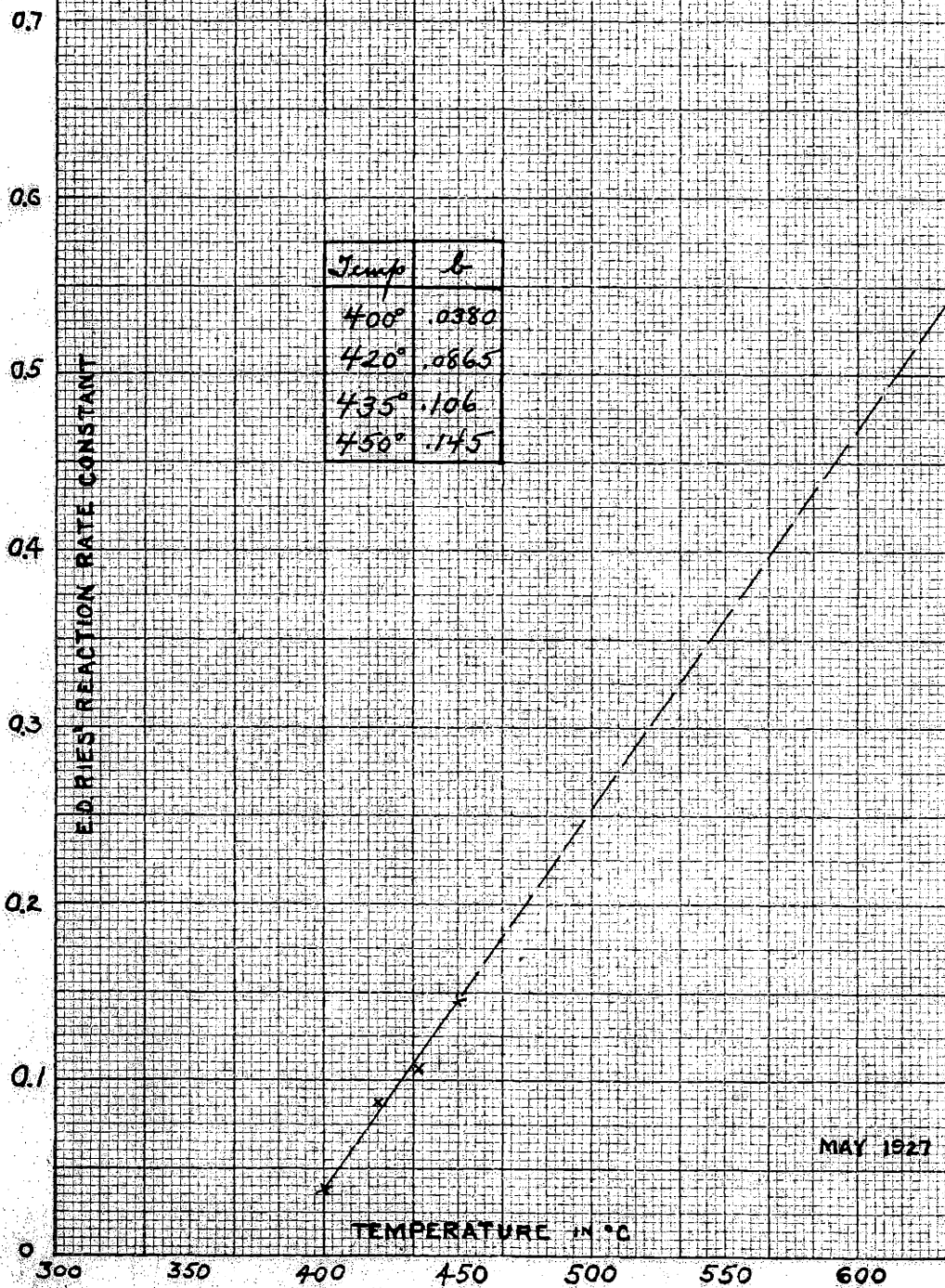
SAMPLE CALCULATIONS

(A) For the variation of temperature with conversion, see Appendix 2, which is equally applicable here.   Since in this appendix, only 10.5 % SO_2 is considered, Plot 11 is the one to be used.

(B) Reaction rate. According to Reis in his thesis (previously cited) the net speed of the reaction

$$2 SO_2 \pm O_2 = 2 SO_3$$

is given by the equation:

$$- \frac{dx}{d\theta} = b' x (\ln e - \ln)$$

$$= b' x (\ln \frac{X_0 - X_e}{X_e} - \ln \frac{X_0 - X}{X})$$

For the variation of b' with the temperature, see Plot 23, which had to be extrapolated thru the high temperature range.

To obtain the reaction rate for a given blower gas (X o fixed), at a given temperature (b' fixed), and after a given conversion has taken place (x fixed), one need only substitute the proper values in the above equation.

Let us find, for example, the reaction rate for a 10.5% blower gas at 440° C and 30% conversion.

DISCUSSION OF CALCULATIONS

(B) Reaction Rate. Reis's equation suffers from the theoretical disadvantage of predicting infinite reaction velocity at 0% conversion. Practically speaking, however, the rate seems abnormally high only below about 2 % conversion and this has little effect on Plots 25 and 26 when high conversions are being considered.

It has the theoretical and practical advantage or predicting 0 rate at equilibrium. It also takes into account (very slightly) the effect of initial % O_2, because this influences Xe. Furthermore, the data was obtained with a flowing gas at temperatures actually used in the contact process. The equation does not accurately interpret Knietsch's data, but does interpret Bodnstein's data and Reis's data more accurately than either of the other two equations discussed in Appendix 1 (D) Since these investigators worked chronologically in the order given above, Bodenstein claims to have profited by Knietsch's mistakes and Ries by those of both the others. Thus Ries's data should be the best and his equation the best.

Table 24

Values for Plot No. 24

$$\frac{dx}{d\theta} \text{ vs. Temperature}$$

Assuming Reis' equation valid

#1 Converter   Inlet gas: 10.5% SO_2 May 1927

% Conversion → Temp °C ↓	0.2	2	10	20	30	40	50	60	70	75
400	.0417	.0338	.0249	.0195	.0156	.0123	.0094	.0069	.0046	.0036
420	.0848	.0673	.049	.0379	.0301	.0235	.0179	.0129	.0086	.0066
440	.1238	.0973	.0695	.0533	.0418	.0323	.0243	.0173	.0113	.0086
460		.1239	.087	.0660	.0512	.0391	.0291	.0204	.0130	.0097
480		.1469	.1012	.0756	.0580	.0438	.0320	.0220	.0136	.0099
500			.113	.0831	.0627	.0466	.0335	.0224	.0133	.0094
520			.1221	.0882	.0656	.0479	.0335	.0218	.0122	.0082
540			.1288	.0912	.0665	.0474	.0323	.0201	.0103	.0064
560			.133	.0923	.0657	.0456	.0298	.0173	.0077	.0039
580			.137	.0927	.0644	.0432	.0269	.0144	.0048	.0012
600			.1373	.0902	.0605	.0387	.0222	.0098	.0008	
620			.1376	.0873	.0563	.0339	.0174	.0052		

Table 25

Values for Plot No. 25
$-\frac{d\theta}{dx}$ vs. % Conversion
Assuming Reis' equation Valid

Converter #1   Inlet gas: 10.5% SO_2 May 1927

Inlet Temp	400°C	420	440
% Conversion			
0	0	0	0
0.2	23.4	11.8	8.0
2	22.2	13.0	9.5
10	16.6	12.9	10.7
20	15.2	13.3	12.1
30	16.6	15.6	15.1
40	20.8	21.1	21.7
50	31.5	34.6	39.7
60	68.5	95.3	
70			
75			

Table 26

Values for Plot No. 26

θ *vs* % *Conversion*

assuming Reis equation valid
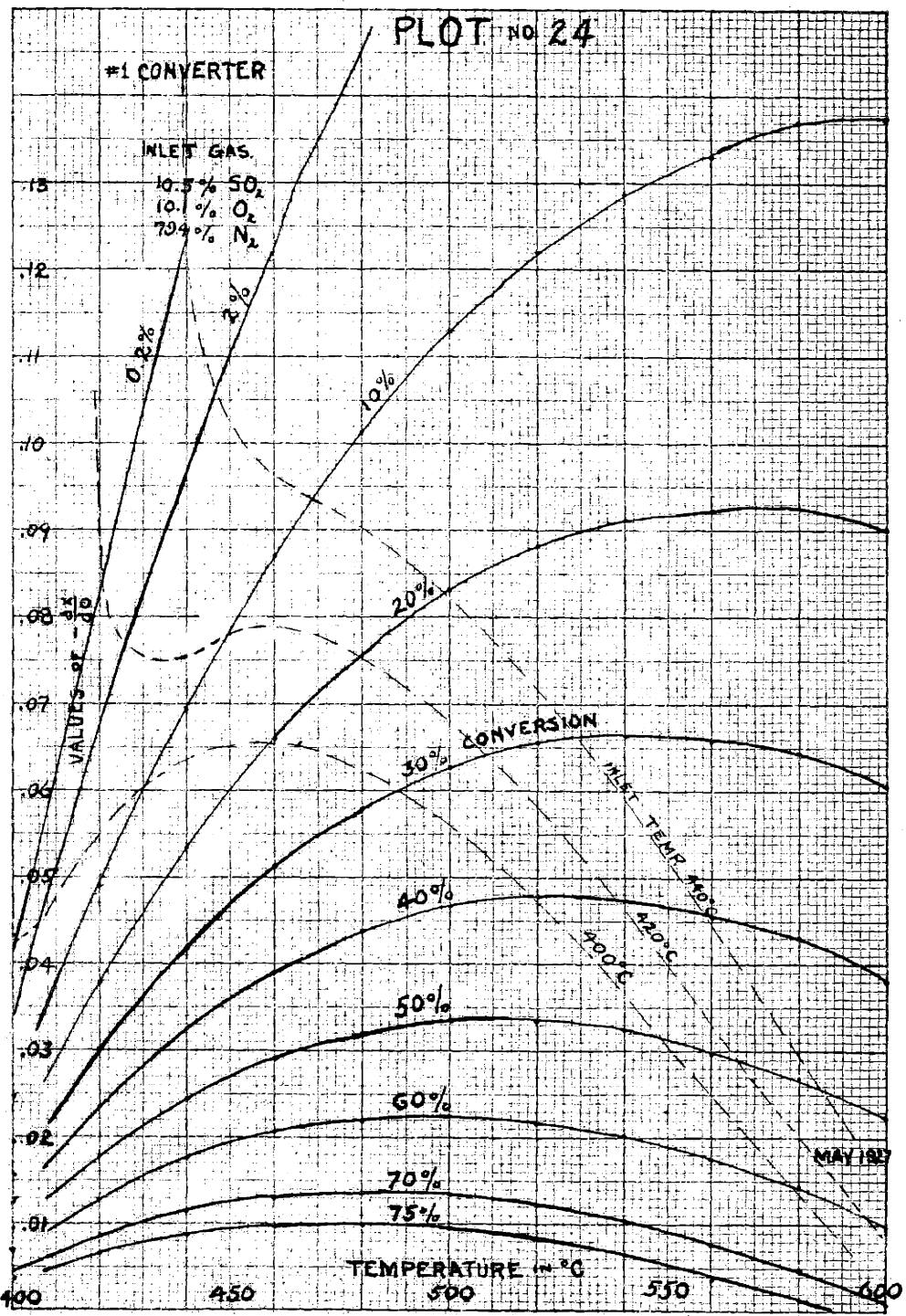
(Integrated values of θ from $\frac{d\theta}{dx}$ vs. conversion plots)

Converter #1   Inlet gas : 10.5% SO_2 May 1927

Inlet Temp °C	400	420	440
% Conversion ↓			
5	216	127	95
10	398	256	202
15	557	383	312
20	708	513	429
25	860	650	555
30	1020	799	697
35	1193	967	862
40	1388	1164	1063
45	1618	1404	1318
50	1902	1706	1656
55	2261	2121	
60	2787		

PLOT No 24

#1 CONVERTER

INLET GAS.
10.5 % SO₂
10.1 % O₂
79.4 % N₂

PLOT no. 25

1 CONVERTER.

INLET GAS
10.5% SO₂
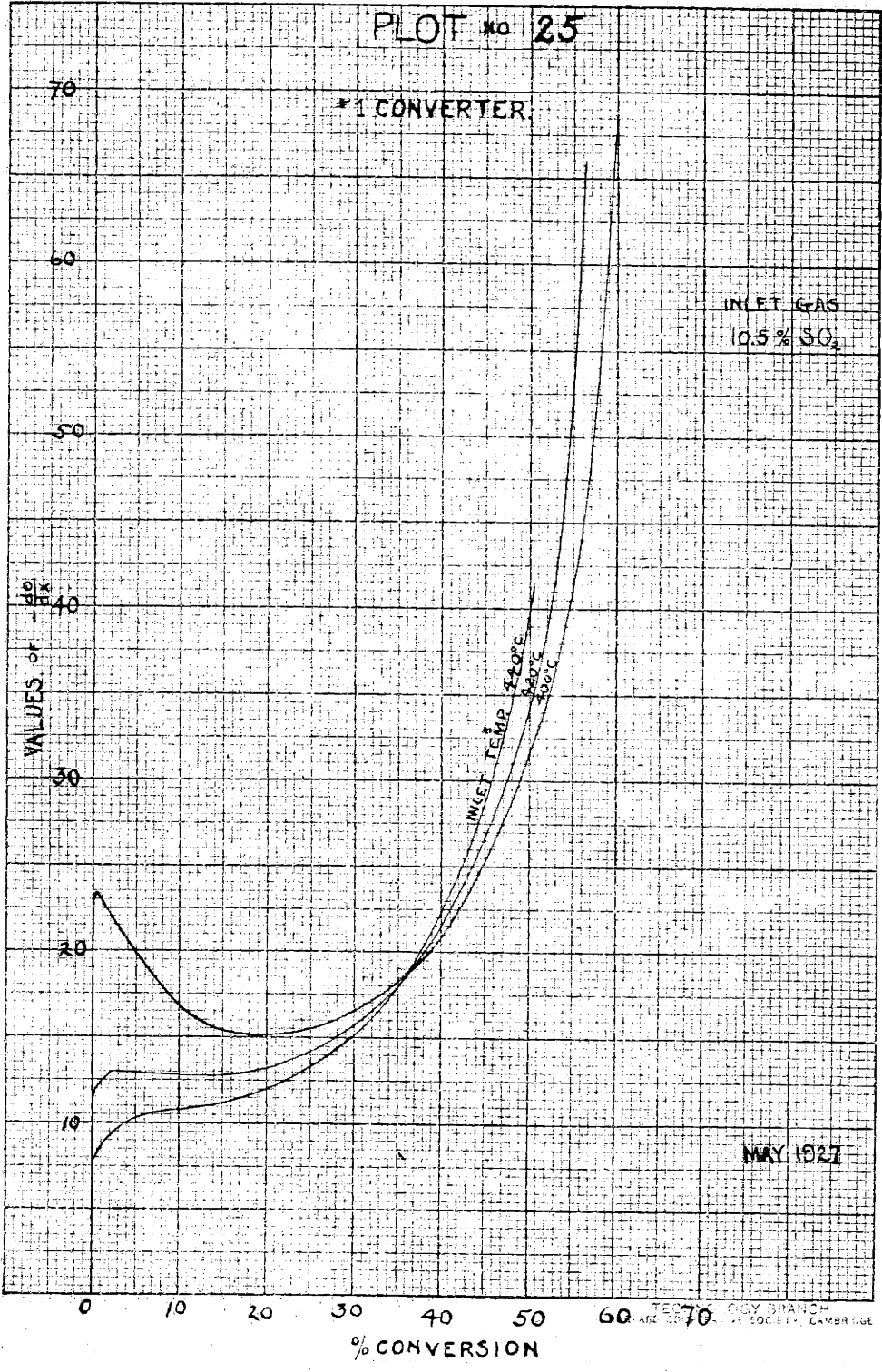
VALUES OF $-\frac{d\theta}{dx}$

INLET TEMP. 420°C / 440°C / 400°C

% CONVERSION

MAY 1927

PLOT № 26

#1 CONVERTER

INLET GAS
10.5% SO_2

% CONVERSION

440°
420°
INLET TEMP 400°C

MAY 1927

TIME UNITS
600   1200   1800   2400   3000
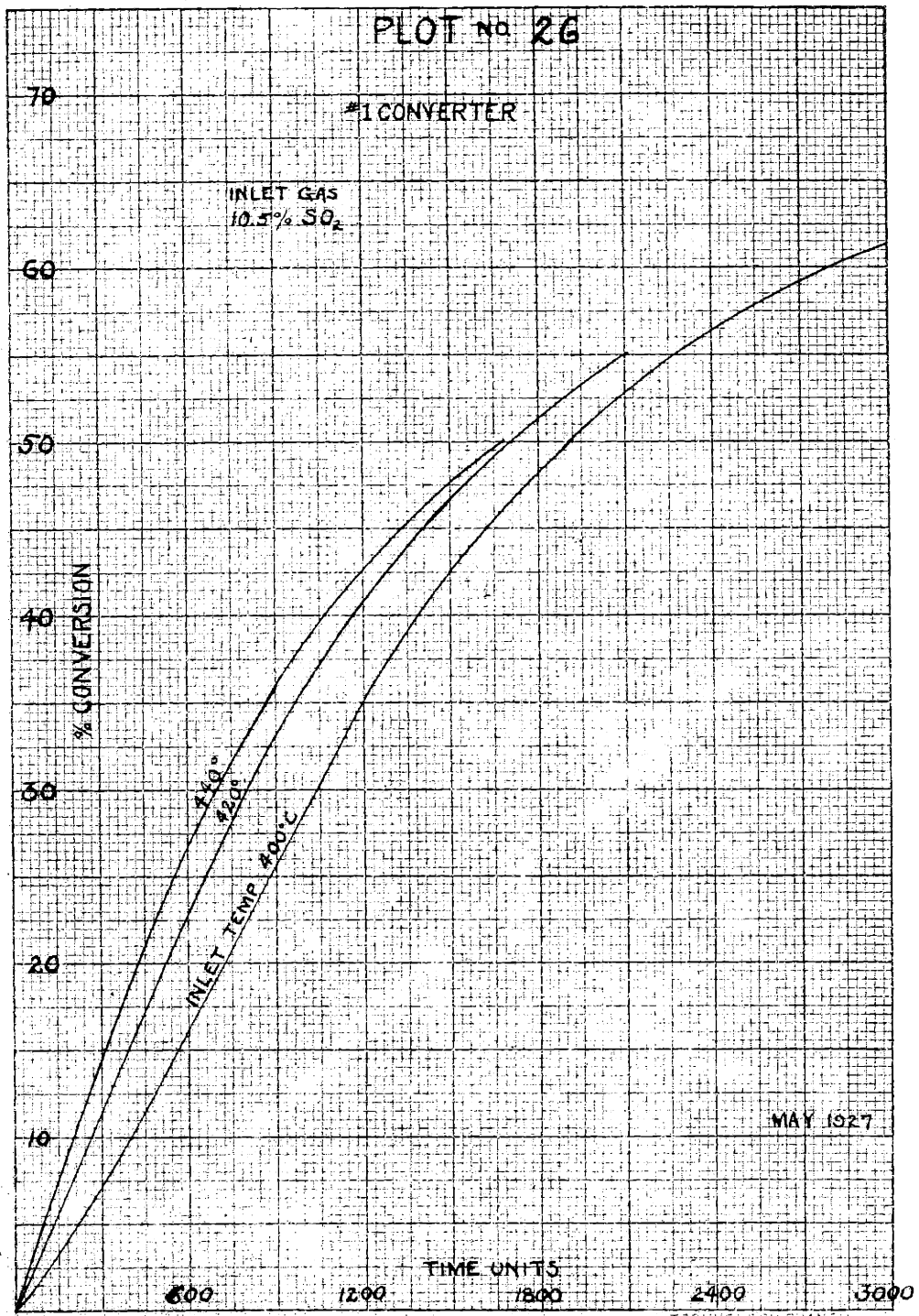
TECHNOLOGY BRANCH
HARVARD COOPERATIVE SOCIETY, CAMBRIDGE

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