

THE SURFACE REACTION OF CHLORINE
AND ACTIVATED CARBON AT
LOW PRESSURES

*Abstract
at end*

by

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I. INTRODUCTION

The purpose of this brief introduction will be to review the observations already made on the behaviour of chlorine with charcoal and to state the aim of this investigation.

We might list the work done in this field under the following headings; general qualitative observations, activation of charcoal by chlorine, heats of adsorption, formation of carbon tetrachloride and quantitative measurements of isotherms and isobars.

All qualitative observations indicate that something more than ordinary physical adsorption is involved. Berthelot and Petit,⁴ the earliest investigators, found that they could prepare purer charcoal by treating it with chlorine and removing the latter at higher temperatures. Mixer¹⁴ found that even at red heat not all the chlorine was removed though all of it came off at white heat. He believed it combined with the hydrogen in the charcoal and came off as hydrogen chloride.

Ruff, Rimrett and Zeumer¹⁷ found that heating charcoal with chlorine on it at 600° - 800° and keeping the pressure less than 1 mm. removed very little and boiling with ten percent alkali removed none. Alekseevski and Likharev¹ found a considerable part of the chlorine could not be removed by heating in vacuo, boiling with alkalies or electric dialysis. Others who had trouble in removing chlorine from charcoal are Henglein and Orzenkowski.⁸

An increase in the adsorptive power of charcoal after treatment with chlorine and removal of it at high temperatures has been found by several workers. Among them are Winter and Baker,¹⁹ Klar and Müller,¹² Behart and Adams⁶ and Putti and Magli.¹⁵

Keyes and Marshall¹¹ have reported the value of 32,000 calories per mole for the heat of adsorption of chlorine on charcoal at 0° and zero concentration. This value is seven times the heat of vaporization of chlorine and even Berthelot and Guntz's³ value of 13000 cal/mol for pressures up to one atmosphere is three times the heat of vaporization.

Stock¹⁸ claims to have formed carbon tetrachloride by using charcoal and chlorine at 400°C and 2.5 atmospheres and Harris⁷ working at this University obtained a liquid which boiled within a degree of the boiling point of this compound. He used charcoal and chlorine at 560° and about one atmosphere pressure.

Isotherms at relatively high pressures for chlorine and charcoal have been measured by Klar and Müller¹² and Reyersan

and Wishart,¹⁶ and at lower pressures by Arii.² The first found differential heats twice that of chlorine on silica gel, the second hysteresis in desorption and the last, that the pressure dropped slowly over a long period.

Godsen¹⁰ working at this University determined desorption isobars for chlorine from charcoal using the low pressure of 3×10^{-3} and raising his temperature in steps from 20° to 1200°C . He found a large amount desorbed at first then instead of the amount coming off steadily decreasing with rising temperature, it rose to a maximum about 1000° and decreased above that.

The purpose of this investigation is to determine desorption isosteres for varying amounts of chlorine on charcoal in the pressure range 10^{-5} to 10^{-2} mm. of mercury and from -183° to 1200° . From these isosteres, desorption isobars and heats of adsorption will be found and from these more light on the surface reaction of chlorine with charcoal.

II. THEORETICAL CONSIDERATIONS

In this investigation two different adsorption^{FUNCTIONS} are determined - isosteres and isobars. The isosteres are not obtained in the conventional way, that is by adding small increments of the adsorbate and finding pressure and temperature values, but are found by adding a large amount of chlorine, reading the temperatures and pressures (over the somewhat limited range of the gauge used), then removing some chlorine and finding another set of pressure and temperature relationships. The isobars are found directly from the isosteres.

Let us first discuss the isobars and their relationship to the nature of the surface reaction between chlorine and charcoal. If chlorine adsorbs on charcoal in a physical way only, that is if the forces between the chlorine and charcoal are non-specific, then as we raise the temperature, less and less and chlorine will be left on the surface on the adsorbent. In other words the desorption isobar would show a large amount of chlorine coming off at low temperatures and less and less at high temperatures. But if any of the chlorine forms a chemical compound or compounds with the carbon then such would not be the case - assuming that the decomposition temperature range of the carbon-chlorine compounds does not coincide with the range in which the bulk of the physically adsorbed chlorine is evolved. Instead of less and less chlorine coming off as the temperature raised more will be

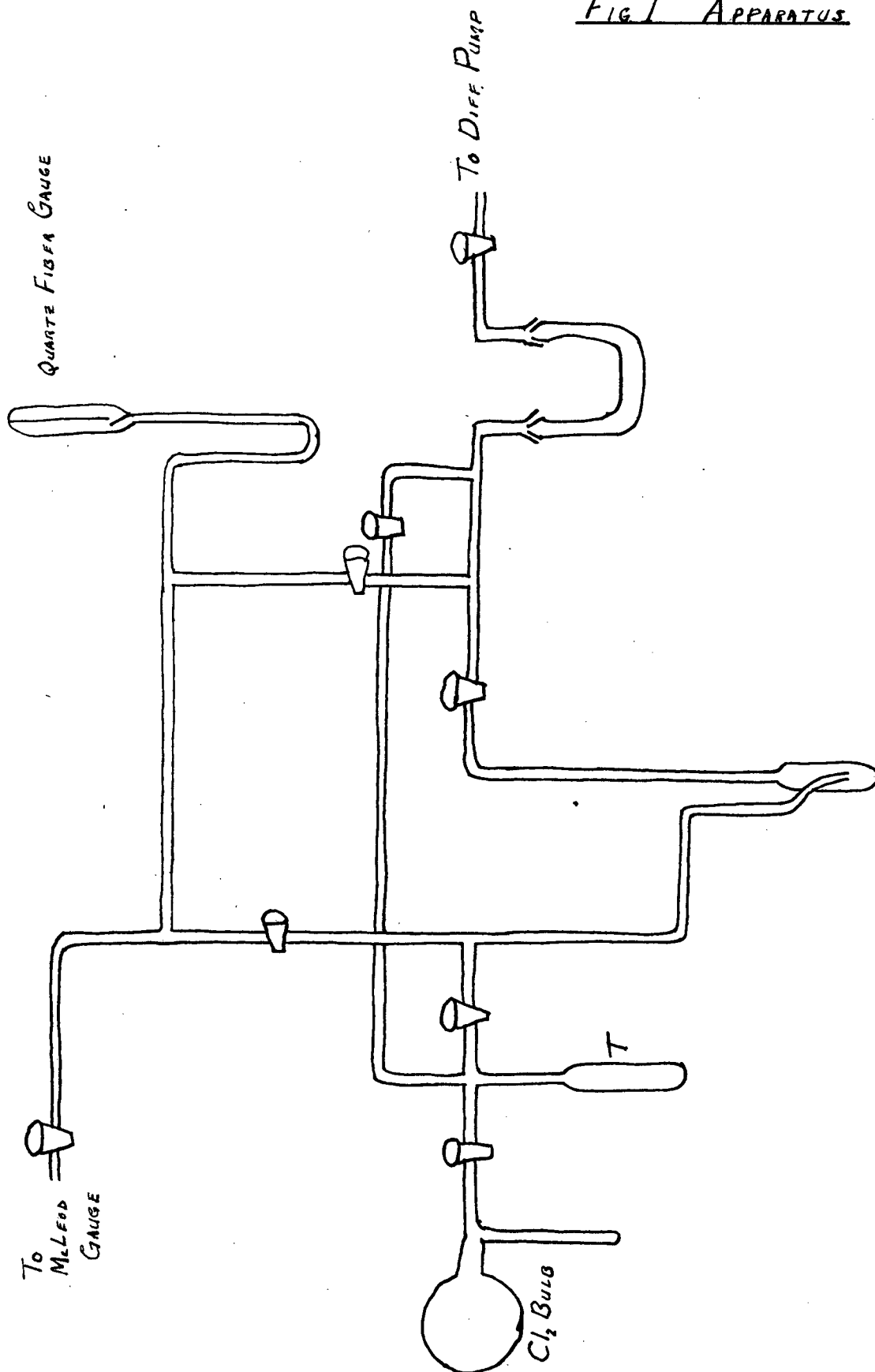
evolved at a higher temperature than a lower. If the desorption isobar shows for example, more chlorine can be removed at the same pressure at 1000° than at 800° or more at 700° than 500° then the chlorine must adsorb to some extent chemically on the charcoal.

The isosteres themselves will show little about the nature of the reaction between chlorine and charcoal. But from them, using the following form of the Clausius-Clapeyron equation, we can calculate the heat of adsorption,

$$\Delta H = \frac{R d \ln p}{d \left(\frac{1}{T} \right)}$$

What should the value of this function be for a chemical reaction at the surface and what value should it have for purely physical adsorption? For the latter there are two values which give an idea of what should be expected. The heat of condensation of chlorine is 4,420 calories and Magnus¹³ reports a heat of 7100 calories for the adsorption of chlorine on silica gel at 10°C. From these figures we might assume any value above 10,000 calories at 10°C would indicate a chemical reaction taking place. The heat of reaction for $2\text{Cl}_2 + \text{C} \rightarrow \text{CCl}_4$ is given as 25,000 calories at 20°C by Badenstein and Gunther⁵ but since all we know about the formula of the compound formed is that it is C_xCl_y this tells us little.

FIG. I APPARATUS



III. APPARATUS, PROCEDURE AND CALIBRATION DATA

A. APPARATUS

The apparatus used is shown in the diagram facing page 6. The McLeod gauge was used for calibrating the quartz fiber gauge and reading the pressures over the charcoal during the outgassing, and the quartz fiber gauge used for measuring the pressure of the chlorine on the charcoal. To set the fiber in this gauge swinging a glass tube with iron sealed in it was pulled from one side to the other with a magnet. The time taken for the fiber to decrease to half amplitude was measured with a microscope with a scale in the eyepiece and a stopwatch. The quartz bulb was specially constructed so that the chlorine which was contained in the bulb B could be admitted to the centre of the charcoal. The U-tube for the potassium was fitted with ground glass joints which were sealed with Picein, a low pressure cement, and the stopcocks were greased with Apiezon. To reduce the chance of a leak all stopcocks in contact with the chlorine at relatively high pressures were mercury seal, vacuum end stopcocks. A platinum resistance furnace with an alundum core was used to heat the charcoal and the temperature was kept at a constant value by a Capacitrol. This instrument which regulated the temperature within $\pm 2^\circ$ has a capacity relay actuated by an electron tube and utilizes a chromel-alumel

thermocouple. The wiring diagram may be found in my B.A. thesis. To find the temperature of the charcoal more accurately another thermocouple in conjunction with a potentiometer was used. A single stage mercury diffusion pump backed by a Cenco Hyvac served to outgas the charcoal and to pull off the chlorine. Lower temperatures than 0°C were obtained by means of liquid oxygen and freezing mixtures of chloroform, ether and toluene. The last mentioned, but a very essential part of the apparatus, was a small nichrome heater to keep the potassium hot enough to react with the chlorine.

B. PROCEDURE AND TECHNIQUES

First the quartz fiber gauge was calibrated using the McLeod gauge and air as primary standards. Mercury vapour was removed from the gauge by immersing the U-tube below it in liquid oxygen. Calibration data for both gauges is given in the next section.

Next the charcoal, which was the same as that used by Godsen, was outgassed thoroughly at 1100°C . Actually it was outgassed for a total of 81 hours, 44 of them at 1100° . The final pressure over the charcoal before admission of the chlorine was 2×10^{-4} mm. at 1100° and less than 5×10^{-5} mm. at 1000° . Before the chlorine was let in all mercury vapour was removed from the bulb and quartz fiber gauge by outgassing for several hours with the U-tube between the pump and the bulb immersed in liquid oxygen. The fact that potassium was always

in the U-tube after this prevented any more mercury vapour getting into the charcoal or gauge.

The chlorine which was admitted to the charcoal came from a tank supplied by the Canadian Industries Limited. In order that the total amount of chlorine going on the charcoal might be known a five hundred millilitre bulb with a stopcock was evacuated, weighed, filled with chlorine and weighed again, and finally sealed on to the apparatus. The chlorine was freed from water vapour by contact with phosphorus pentoxide and from air by condensing it with liquid oxygen and pumping off the residual gas.

The charcoal being outgassed it was heated to 1100° and the chlorine admitted. Then the charcoal was cooled to 560° where it was kept for five hours and then down to -183° at which temperature the pressure went below 10^{-3} mm. To obtain data for the first isostere the quartz bulb and the fiber gauge were shut off from the chlorine bulb and the temperature varied until readings within the limits of the gauge were obtained (10^{-5} - 10^{-2} mm.). For the first isostere, it was necessary to use liquid oxygen and freezing mixtures of chloroform and toluene.

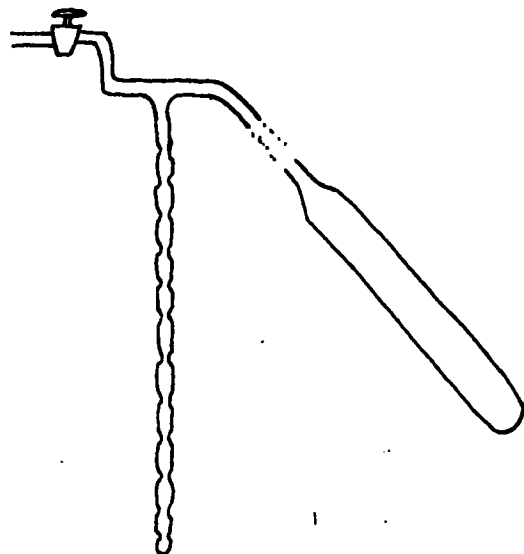
At this point it might be well to describe the U-tube, potassium and analysis technique in some detail. The potassium which was used for collecting the chlorine taken off the charcoal was put in the U-tube in the form of small pellets enclosed in short lengths of 9 or 10 mm. glass tubing. Following a procedure used by Hughes and Poindexter,⁹ the potassium was

cleaned of most of the oil, from the container in which it came, with benzene, then heated in a large tube, sealed at one end and drawn down at the other, until the remaining hydrocarbons were oxidized and the potassium molten. Another similar tube and an apparatus such as

that shown, had been prepared, and the potassium was poured into the other large tube and then this was quickly sealed on to the apparatus.

The potassium was heated and outgassed and then melted and the apparatus tipped allowing the long tube with the constrictions to be filled with potassium. In order to obtain a charge of potassium for the U-tube a file mark was made at

one of the constrictions and the capsule broken off. This tube was kept in vacuo to prevent oxidation of the exposed potassium. About 10 capsules each around 15 mm. long were obtained from one tube. Once in the U-tube and sealed onto the rest of the apparatus the potassium was outgassed and heated so that it flowed out of the capsule and formed a mirror up the sides of the U-tube. It was found necessary to heat it to around $150^{\circ} - 250^{\circ}\text{C}$ before it would react with the chlorine. The amount of potassium chloride formed was found, by removing the U-tube dissolving the contents in water and analysing for chloride by the Volhard method.



To return to the determination of isosteres, in order to obtain a significant number of, yet not too many isosteres, it was decided to take off enough chlorine each time, so that there would be around 100° temperature difference between the same pressures on the isosteres. To remove the chlorine the charcoal was heated around 100° higher than the highest temperature at which the gauge could be read (9×10^{-2} mm.) and opened to the U-tube but not to the pumps. After the majority of the chlorine had reacted with the potassium and there was no longer any danger of it getting past the U-tube, the charcoal was opened to the pumps, until the pressure became constant over a five to ten minute period. This generally took about half an hour and the pressure reached was about 3×10^{-2} . In the first removal of chlorine, it was condensed out with liquid air in the tube T, and then admitted to the U-tube but this method was not found satisfactory and the above procedure was used in all the other runs. To determine each isostere the charcoal was cooled until the pressure went down to around 10^{-5} and then the temperature raised in $30 - 50^\circ$ intervals until the pressure became 9×10^{-2} . Pressure readings were, of course, taken at each interval. Then the U-tube was removed, a new one put in, more chlorine removed and a new isostere found. The highest temperature reached was 1180°C . Except at -183° , where the pressure continued to drop for 24 hours, equilibrium was reached in about an hour at any given temperature.

C. CALIBRATION DATA

McLeod Gauge

Largest Ratio - 13.00 cm. from etched mark

$$1.054 \times 10^{-3}$$

Smallest Ratio -.93 cm. above etched mark

$$7.57 \times 10^{-5}$$

Volume of Large Bulb and Capillary 516.1 c.c.

Average Cross Section of Capillary (excluding tip)

$$.0361 \text{ cm.}^2$$

Quartz Fiber Gauge.

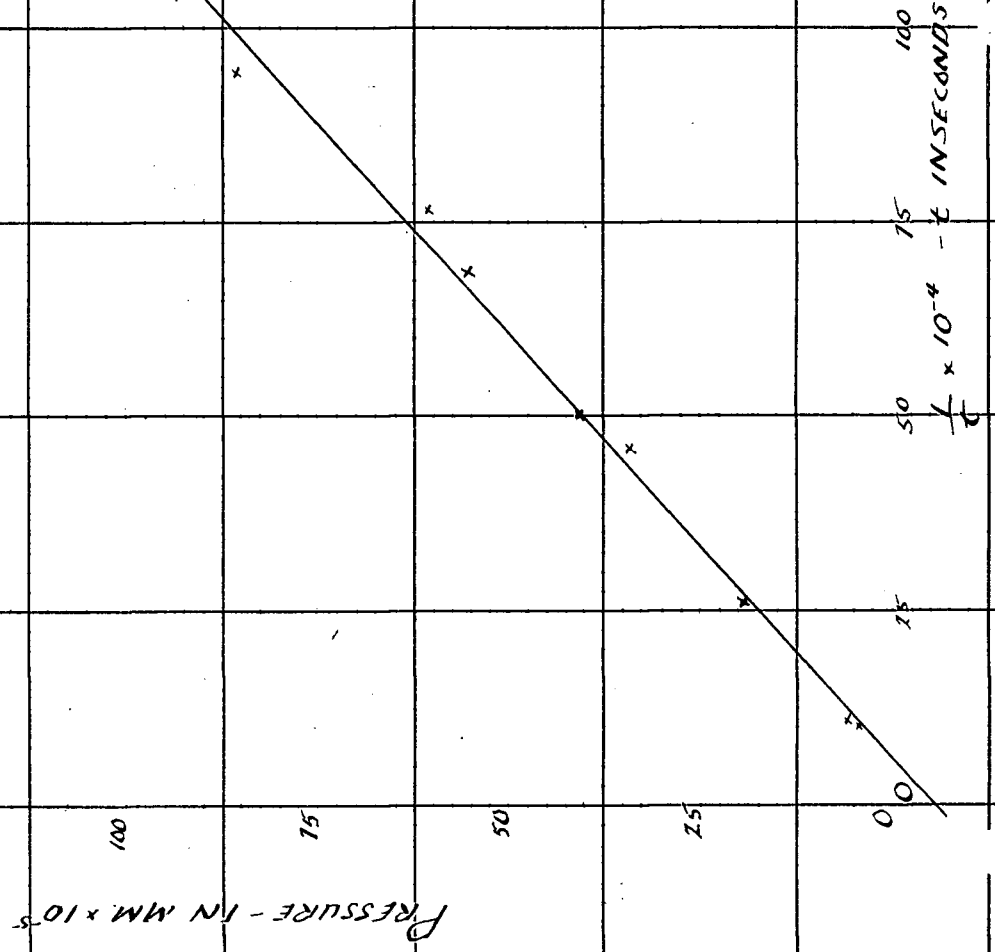
The equation for the quartz fiber gauge is

$$p \sqrt{M} = \frac{c}{\frac{t}{\log \frac{a_1}{a_2}}} - b$$

where p is the pressure, M the molecular weight of the gas, t the time taken for the swinging fiber to drop from amplitude a_1 to amplitude a_2 and c and b are constants for a given gauge and temperature. In our case a_2 was always half a_1 i.e. $\log \frac{a_1}{a_2}$ was a constant so that it simplifies to $p \sqrt{M} = \frac{A}{t} - b$

The calibration curve given in Figure II and the table below were obtained as follows. By using the McLeod gauge and air, values of p and t were found over the range 7×10^{-5} to 1.4×10^{-1} mm. (for air). To convert the pressures for air to those which chlorine would have for the same value of t they were multiplied by $\frac{\sqrt{M_{\text{air}}}}{\sqrt{M_{\text{Cl}_2}}} = \frac{\sqrt{28.96}}{\sqrt{70.91}} = \frac{5.38}{8.42}$

Fig. II
CALIBRATION CURVE
FOR FIBER GAUGE



Then these converted pressures now covering the range 4×10^{-5} to 9×10^{-2} were plotted against the reciprocal of t . Two different scales were used for convenience and accuracy. To find pressures for which t is greater than one minute take its reciprocal and read directly off Figure II and to find pressures for which t is less than 60 seconds read off the following table. These pressures will be of course for chlorine.

The values of the constants A and b may be found from the slope and the intercepts of the line in Figure II. The equation for the gauge used here is

$$p \sqrt{M} = \frac{7.73}{t} - 3.86 \times 10^{-4}$$

where t is the time taken to drop to half amplitude.

Values of the pressure for chlorine for values of
 t from 1 - 60 seconds.

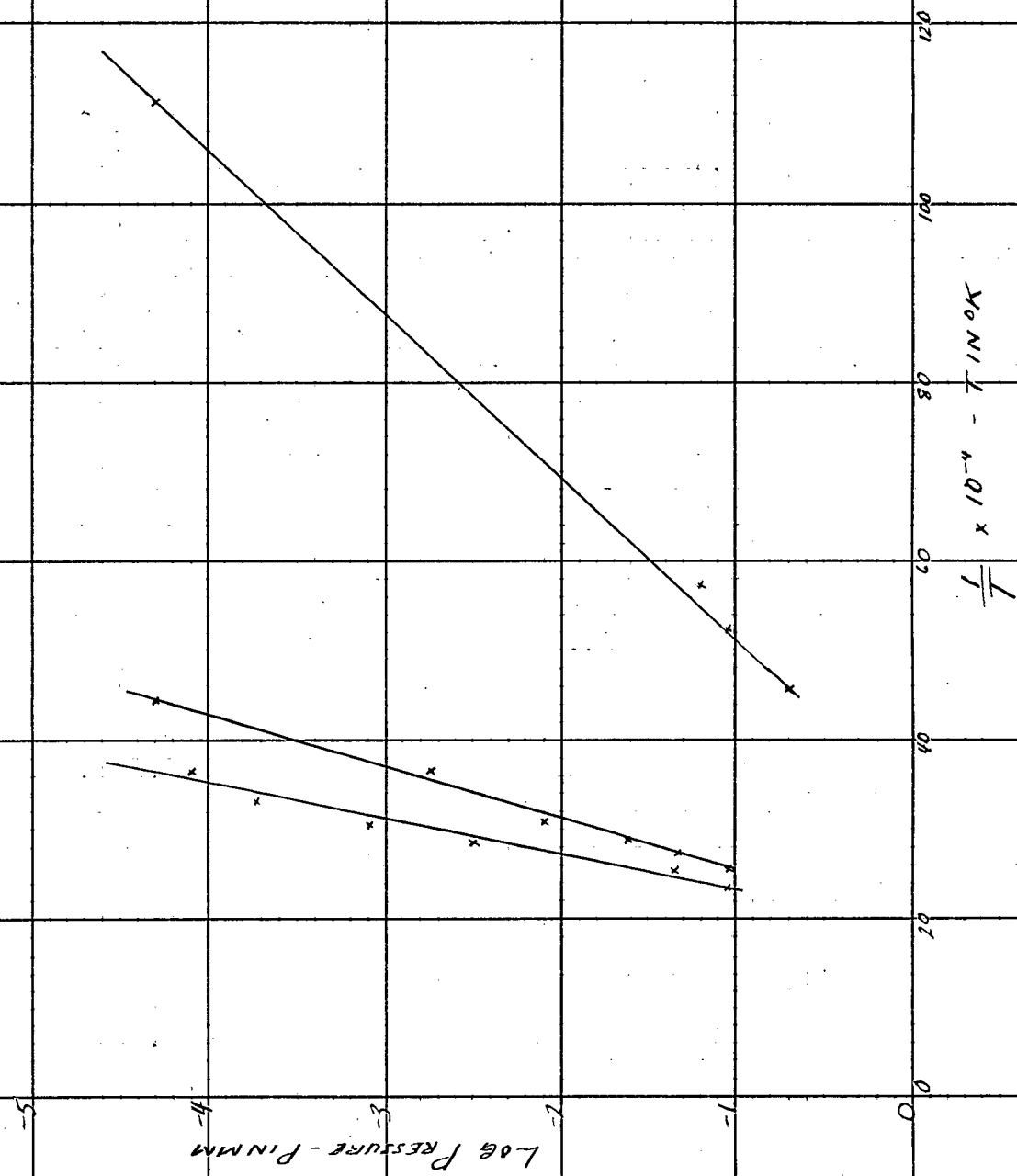
t	$p \times 10^{-3}$	t	$p \times 10^{-3}$	t	$p \times 10^{-3}$
1	91	16	5.8	31	3.0
2	45	17	5.4	32	2.9
3	30	18	5	33	2.8
4	24	19	4.8	34	2.7
5	18	20	4.6	35	2.6
6	15	21	4.4	37	2.5
7	13	22	4.2	38	2.4
8	11	23	4.0	39	2.3
9	10	24	3.8	42	2.2
10	9	25	3.7	45	2.1
11	8	26	3.6	48	2.0

t	$p \times 10^{-3}$	t	$p \times 10^{-3}$	t	$p \times 10^{-3}$
12	7.5	27	3.4	50	1.9
13	7	28	3.3	53	1.8
14	6.5	29	3.2	56	1.7
15	6	30	3.1	59	1.6

Weight of the charcoal in vacuo

19.90 grams.

FIG. III
ISOTHERES #1-3



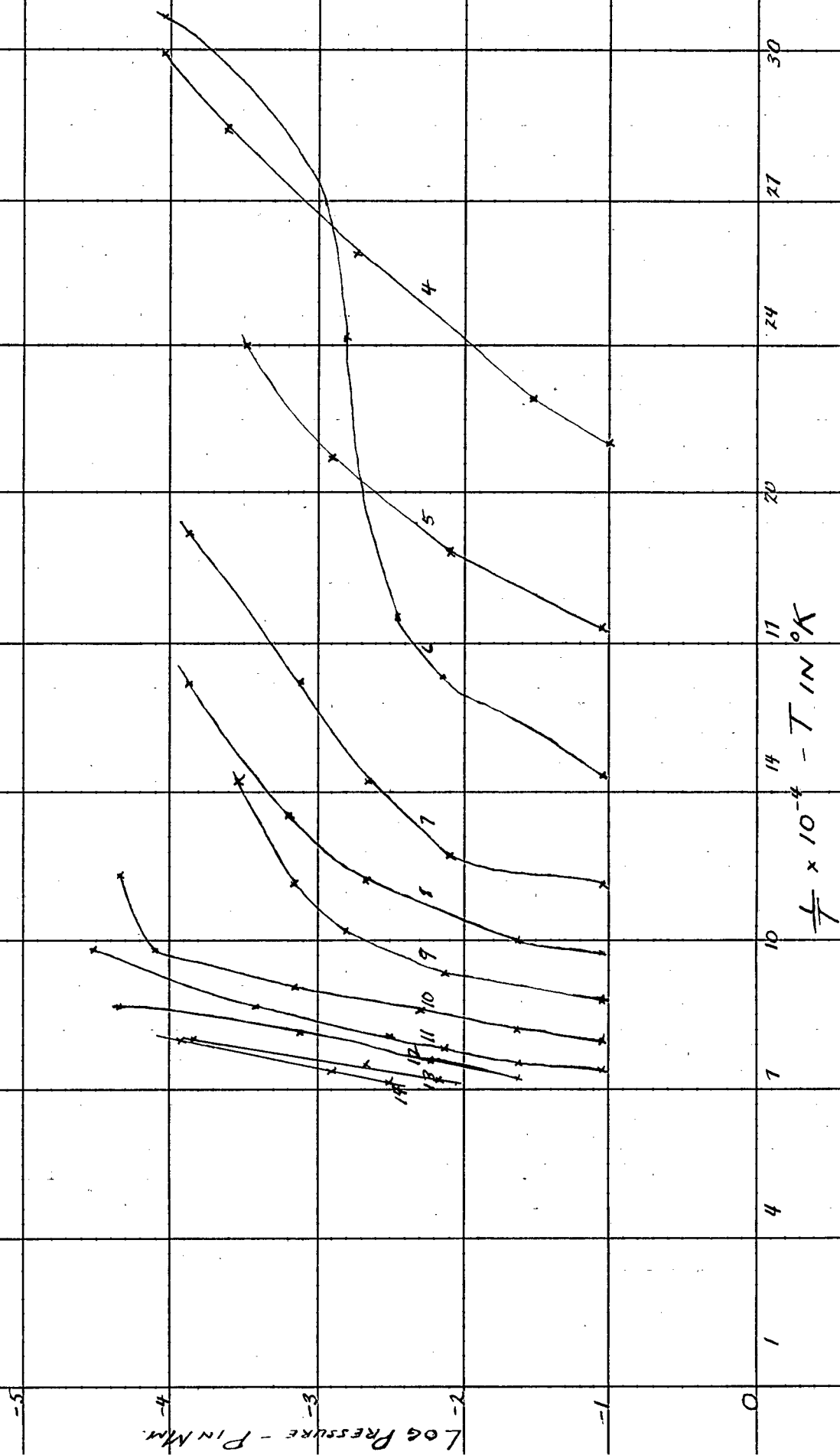
IV. RESULTS

The following table gives all the data obtained in the run, as well as values for the heat of adsorption calculated from the isosteres using the Clausius-Clapeyron equation. To obtain these values of ΔH the logs of the pressure values were plotted against the reciprocals of the corresponding absolute temperatures for each isostere, and the slope of the curve, thus obtained, (taken at the centre of the straight line portion of the curve) found. These curves are shown in Figures III and IV. In the case of isostere No. 6 since there was no straight line portion, no attempt was made to calculate ΔH . y refers to the amount of chlorine on the charcoal for a given isostere, and x refers to the amount of chlorine removed from the charcoal prior to a given isostere. Both are given in micromoles of chlorine per gram of charcoal.

No.	y	x	T°C	P-mm.	ΔH -calories
1	876		-183°	5 x 10 ⁻⁵	2590
			-98°	6 x 10 ⁻²	-183°
			-82°	9 x 10 ⁻²	to -64°
			-64°	2 x 10 ⁻¹	
2	605	271	-47°	5 x 10 ⁻⁵	7830
			0°	1.8 x 10 ⁻³	-47°
			50°	8 x 10 ⁻³	to 118°
			76°	2.4 x 10 ⁻²	
			96°	4.5 x 10 ⁻²	
			118°	9 x 10 ⁻²	
3	533	73.5	0°	8 x 10 ⁻⁵	10,600
			29°	1.7 x 10 ⁻⁴	0°
			57°	7.8 x 10 ⁻⁴	to 153°
			79°	3.2 x 10 ⁻³	
			115°	2.4 x 10 ⁻²	
			153°	9 x 10 ⁻²	

Fig. IV

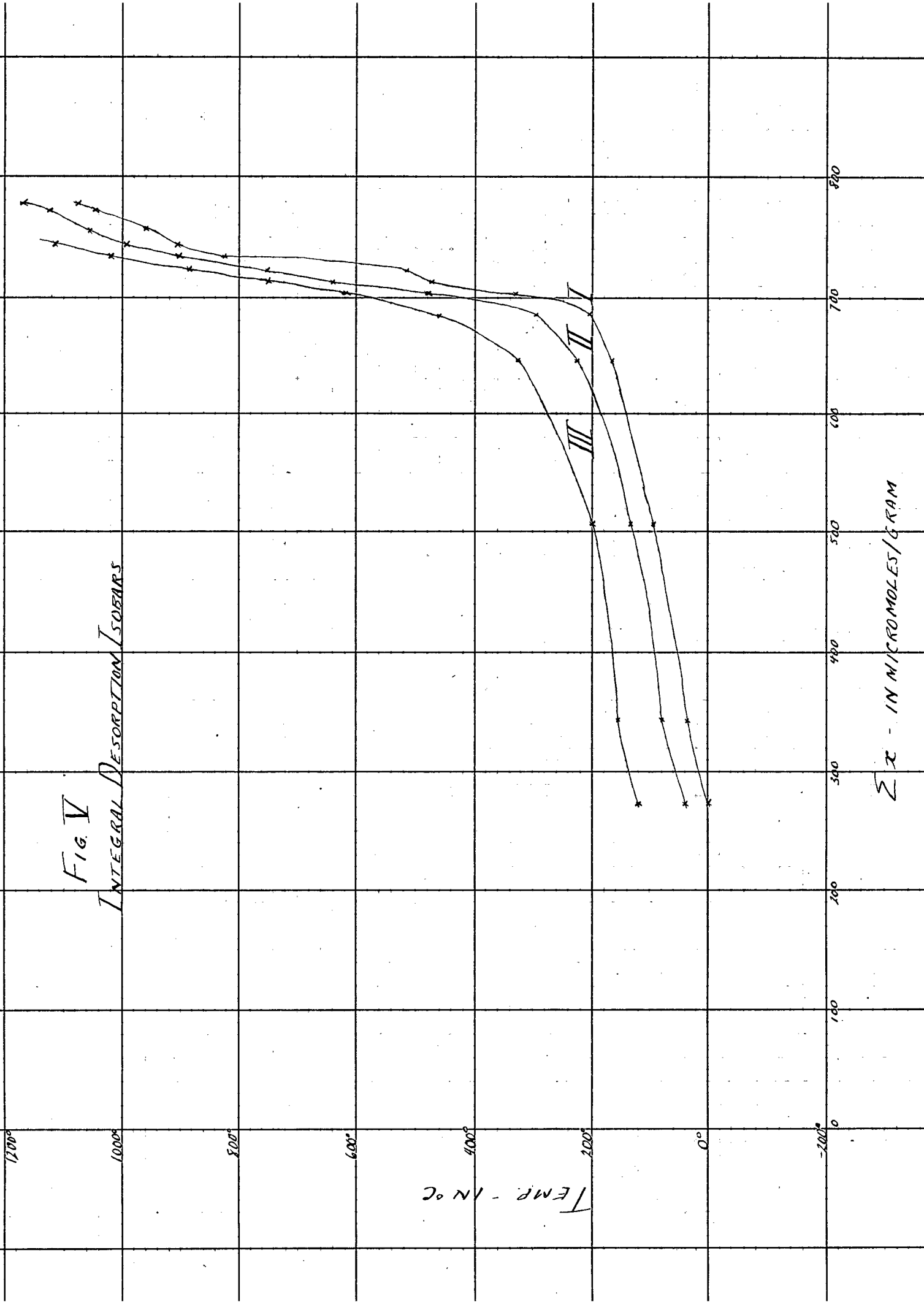
ISOSTERES #4-14



No.	y	x	T°C	P-mm.	ΔH -calories
4	371	162	61°	9 x 10 ⁻⁵	14,100
			81°	1.9 x 10 ⁻⁴	at 81°
			121°	1.7 x 10 ⁻³	21,400
			179°	3 x 10 ⁻²	at 179°
			200°	1 x 10 ⁻¹	
5	232	139	155°	3.2 x 10 ⁻⁴	24,500
			208°	1.26 x 10 ⁻³	at 288°
			263°	8 x 10 ⁻³	
			313°	9 x 10 ⁻²	
6	193	39	152°	9 x 10 ⁻⁵	
			252°	1.6 x 10 ⁻³	
			305°	3.4 x 10 ⁻³	
			357°	7.5 x 10 ⁻³	
			455°	9 x 10 ⁻²	
7	173	20	257°	1.3 x 10 ⁻⁴	11,300
			358°	7.7 x 10 ⁻⁴	257°
			462°	2.2 x 10 ⁻³	to 565°
			565°	8 x 10 ⁻³	
			616°	9 x 10 ⁻²	
8	164	9.5	360°	1.3 x 10 ⁻⁴	26,900
			512°	6.3 x 10 ⁻⁴	612°
			612°	2.1 x 10 ⁻³	to 720°
			720°	2.4 x 10 ⁻²	
			749°	9 x 10 ⁻²	
9	155	8.45	464°	3.1 x 10 ⁻⁴	50,200
			612°	6.8 x 10 ⁻⁴	at 802°
			710°	1.6 x 10 ⁻³	
			802°	7 x 10 ⁻³	
			881°	9 x 10 ⁻²	
10	144	11.2	606°	4.5 x 10 ⁻⁵	68,500
			753°	8 x 10 ⁻⁵	600°
			846°	6.8 x 10 ⁻⁴	to 1017°
			916°	5 x 10 ⁻³	
			978°	2.4 x 10 ⁻²	
			1017°	9 x 10 ⁻²	
11	134	9.9	759°	3 x 10 ⁻⁵	57,500
			903°	3.8 x 10 ⁻⁴	900°
			998°	3.2 x 10 ⁻³	to 1100°
			1045°	7 x 10 ⁻³	
			1099°	2.4 x 10 ⁻²	
			1130°	9 x 10 ⁻²	

Fig. V

INTEGRAL DESORPTION ISOBERS



No.	y	x	T°C	P-mm.	H-calories
12	122	12.3	897°	4.5×10^{-5}	73,500 at 1000°
			990°	7.6×10^{-4}	
			1095°	6×10^{-3}	
			1175°	2.4×10^{-2}	
13	107	15.4	1015°	1.5×10^{-4}	82,300 1000° to 1180°
			1112°	2.1×10^{-3}	
			1178°	6.5×10^{-3}	
14	101	5.6	1020°	1.2×10^{-4}	72,000 1000° to 1180°
			1123°	1.24×10^{-3}	
			1178°	3.2×10^{-3}	

From these isosteres integral desorption isobars were obtained. This was done by plotting the isosteres ($^{\circ}\text{C}$ against $\log p$) and reading off the temperatures on the different isosteres for the same pressure. Three different pressures were used and thus three desorption isobars obtained. The pressure 3×10^{-3} was used by Godsen and the pressure 4.1×10^{-4} by myself in my B.A. thesis. The other pressure was used for comparison purposes. These three integral desorption isobars are plotted in Figure V. By taking the slopes of these three differential desorption isobars were obtained. These are shown in Figures VI - VIII and the values for the integral and differential curves are given in tabular form below. x refers to the amount removed in micromoles per gram, Σx to the total amount of chlorine removed and dx/dT to the slope of the integral curve at that point.

FIG. VI - DIFFERENTIAL

DESORPTION ISOBAR

$P = 4.1 \times 10^{-4}$ MM.

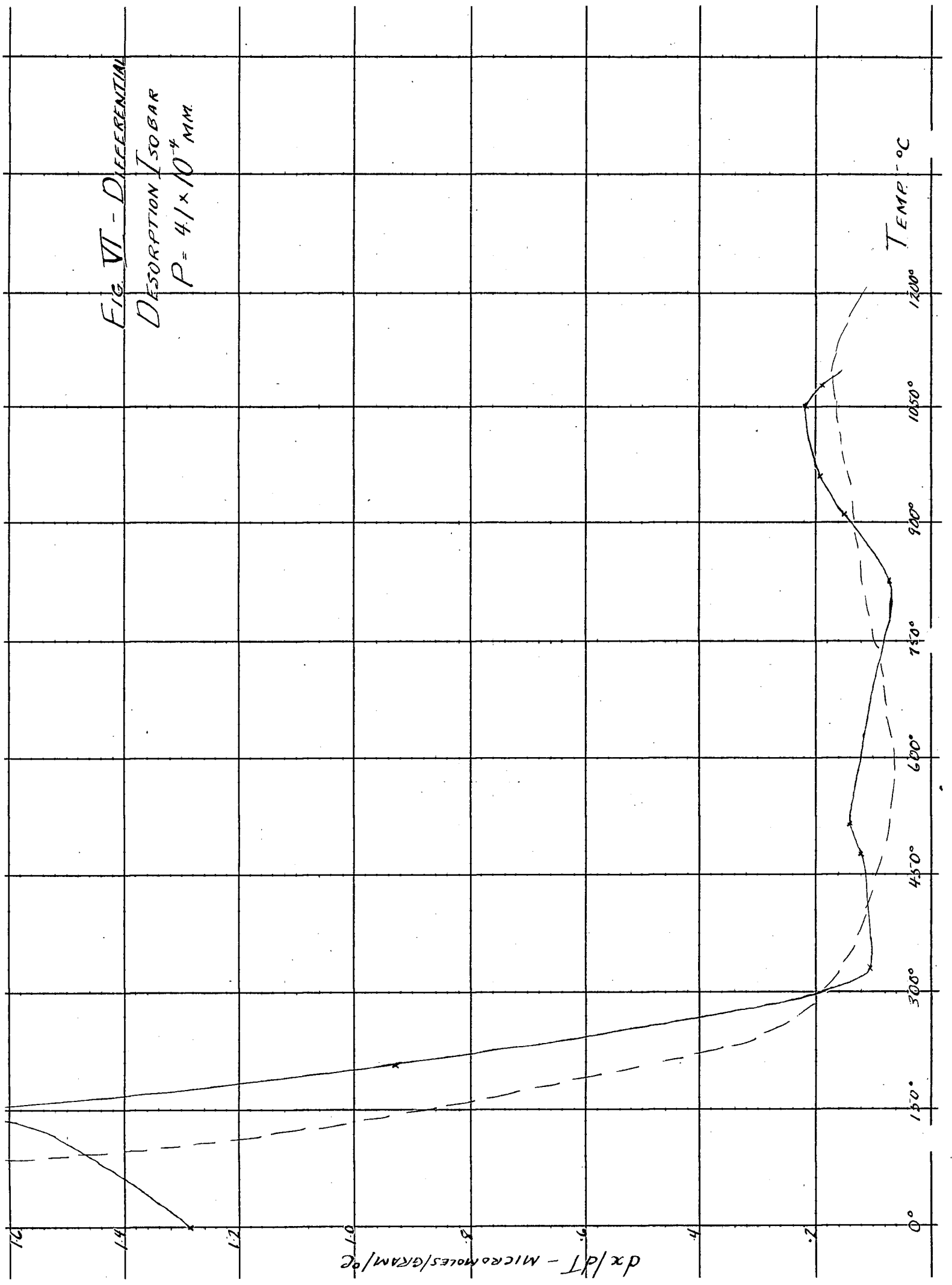


FIG. VII DIFFERENTIAL

DESORPTION ISOBAR $P = 3 \times 10^{-3}$ MM.

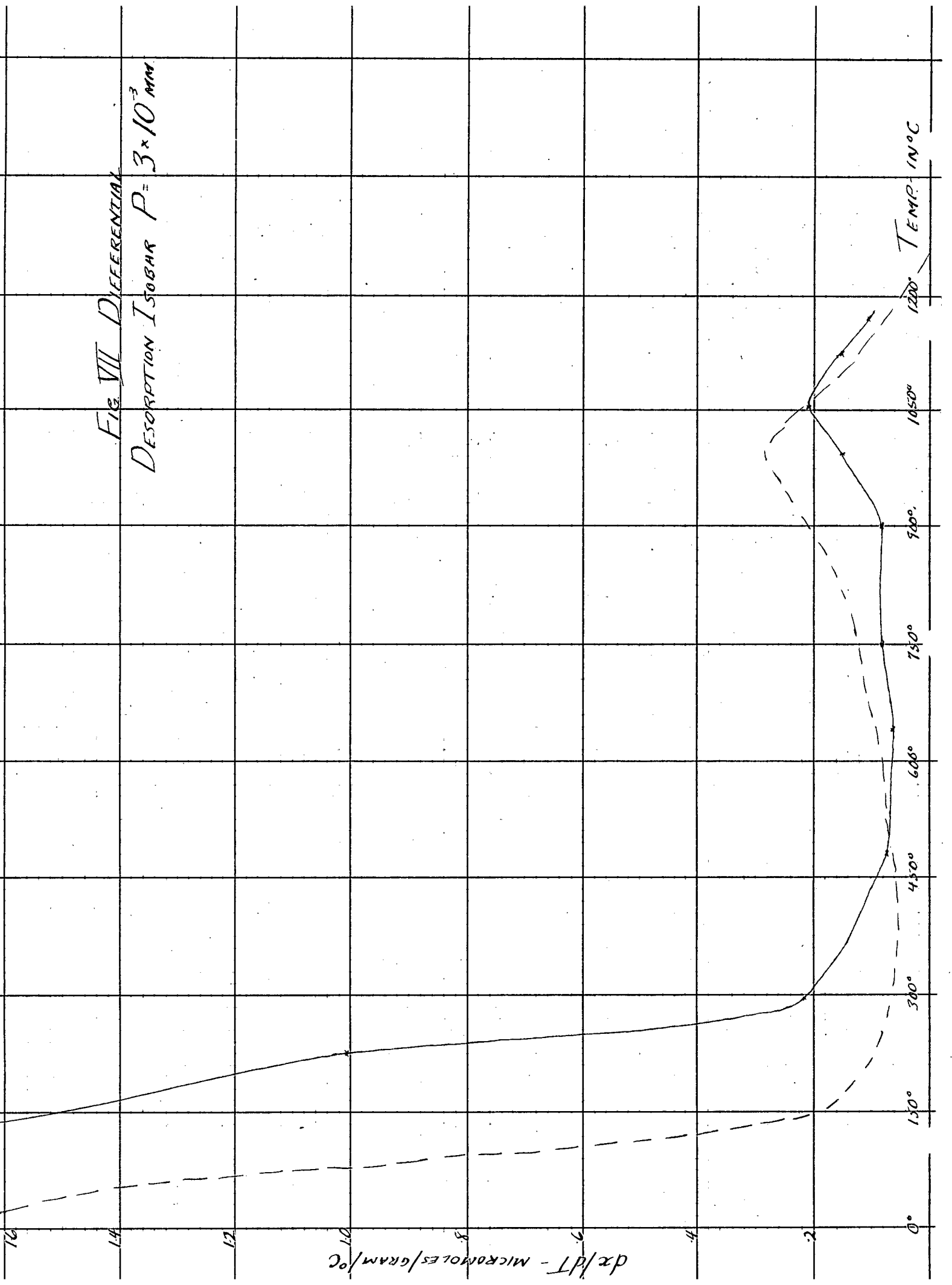


FIG. VIII DIFFERENTIAL
DESORPTION ISOBAR III
 $P = 1 \times 10^{-4}$ MM.

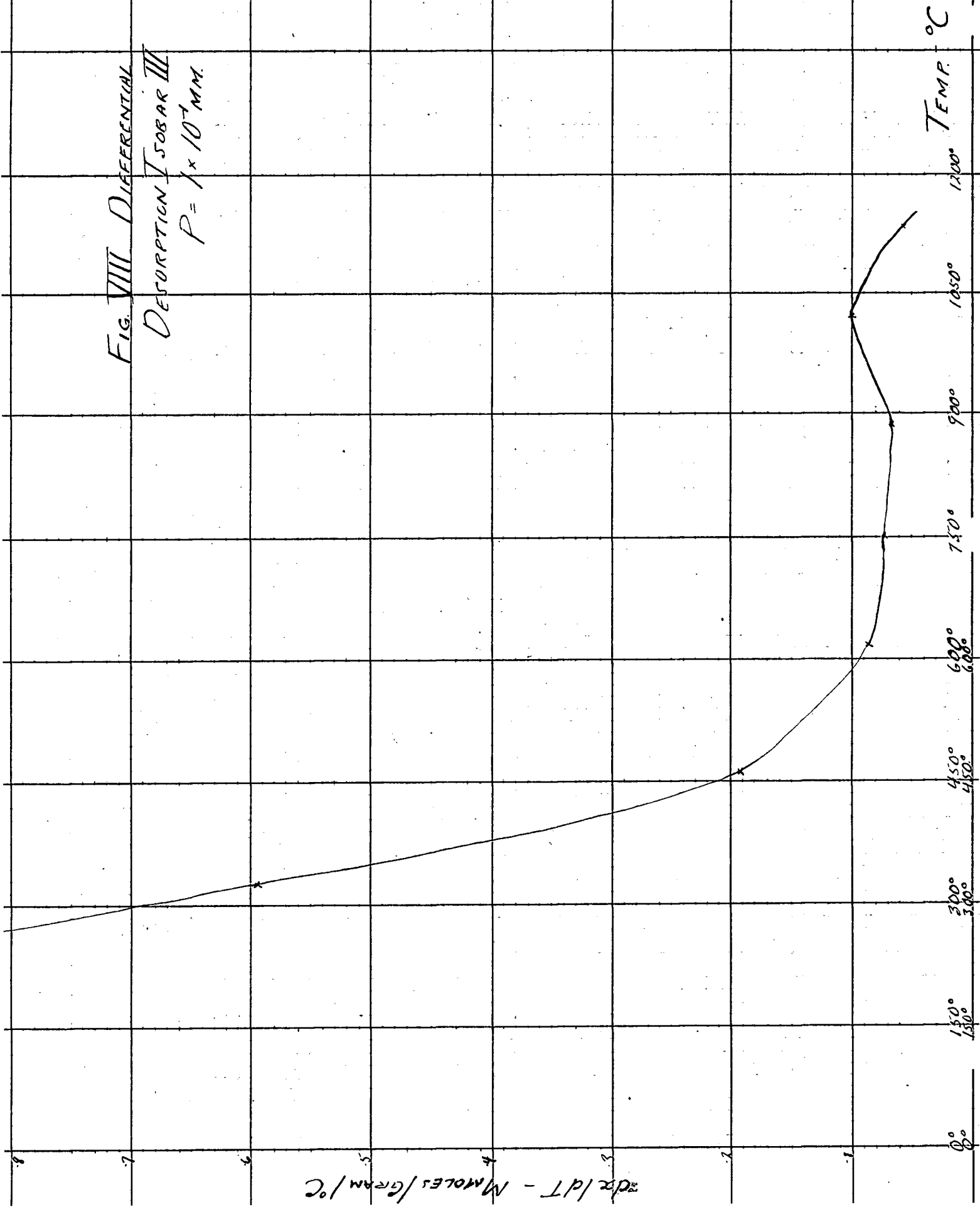


Table for Figure VI

Pressure = 4.1×10^{-4} mm.

T°C	x	Ex	dx/dT
-2°	271	271	1.285
38°	73.5	344.5	3.00
92°	162	506.5	2.44
170°	139	646.5	1.66
205°	39	684.5	.93
330°	20	704.5	.102
475°	9.5	714	.120
515°	8.5	722.5	.14
825°	11	733.5	.07
910°	10	743.5	.15
960°	12.3	755.5	.194
1050°	15.4	770.5	.222
1075°	5.6	776	.192

Table for Figure VII

Pressure = 3×10^{-3} mm.

T°C	x	Ex	dx/dT
40°	271	271	1.46
80°	73.5	344.5	2.80
130°	162	506.5	2.50
225°	139	646.5	1.03
295°	39	684.5	.216
480°	20	704.5	.0741
640°	9.5	714	.0655
750°	8.5	722.5	.0824
900°	11	733.5	.082
995°	10	743.5	.152
X1055°	12.3	755.5	.211
1125°	15.4	770.5	.15
1170°	5.6	776	.104

Table for Figure VIII

Pressure = 1×10^{-1} mm.

T°C	x	Ex	dx/dT
120°	271	271	.97
155°	73.5	344.5	6.83
200°	162	506.5	1.55
325°	139	646.5	.595
460°	39	684.5	.192
620°	20	704.5	.0875
750°	9.5	714	.0705
885°	8.5	722.5	.067
1020°	11	733.5	.100
1135°	10	743.5	.0595

The broken line on Figure VI is the one obtained in my B.A. thesis and the broken line on Figure VII was obtained by Godson.

V. DISCUSSION OF RESULTS AND CONCLUSIONS

The values^{OF} the heat of adsorption obtained from the isosteres are in many cases quite inaccurate and only the most general sort of conclusions can be drawn from them. The small values obtained in the first three isotherms are probably due to the fact that true equilibrium was not established. The large values at high temperatures though, would seem to indicate three things. First chlorine does react chemically with the surface of charcoal at low pressures. Second that the heat of adsorption increases with decreasing concentration and finally this heat increases with increasing temperature.

The three differential desorption isobars obtained all indicate that the bulk of the physically adsorbed chlorine comes off in the range $40^{\circ} - 160^{\circ}\text{C}$ and that the optimum temperature for desorption of the chemical surface complex is 1050° . The qualitative agreement of these results with Godson's would seem to indicate that little doubt can be held regarding the chemical reaction of chlorine with the surface of activated carbon.

The extreme stability of this compound is shown by the fact that some chlorine is still on the charcoal after the pressure has been reduced to 3×10^{-3} at 1180° . Just how much is impossible to say for although the total amount of chlorine initially put on the charcoal was known, some of the chlorine may have come off as a carbon complex or even carbon tetrachloride and may not have been picked up by the potassium.

VI. ABSTRACT

The nature of the surface reaction of chlorine with activated carbon was investigated in the following way. A measured amount of chlorine was admitted to outgassed charcoal and pressure and temperature readings taken over the pressure range 10^{-5} - 10^{-2} mm. Chlorine was removed in increments until a series of isosteres were obtained in the temperature range -183° to 1180°C . From these functions desorption isobars and heats of adsorption were calculated. Conclusions were drawn from the values of these as to the nature of the surface reaction of the chlorine and activated carbon.

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