WAR RESEARCH

CYANOGEN CHLORIDE - PREPARATION, PHYSICAL PROPERTIES, HYDROLYSIS AND SORPTION ON CHARCOAL

A Thesis

by

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(In collaboration with M.R. Foran, M.Sc.)

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INTRODUCTION

The substance cyanogen chloride was first prepared by Berthollet in 1787 by the action of chlorine on hydrocyanic acid. He called it "oxidized prussic acid", but did not apply any formula to it. Gay-Lussac(1) in 1815 made a more complete investigation of this compound, assigning it the formula CNCl from a consideration of its chemical properties. He found that cyanogen chloride could be prepared by reacting moist hydrocyanic acid with chlorine, or by the action of chlorine on dry mercuric cyanide. The physical constants determined by him for cyanogen chloride are not accurate, because his product was impure.

Serullas(2) investigated the preparation of cyanogen chloride and found that moisture facilitated the reaction of chlorine with mercuric cyanide, while sunlight was detrimental to the reaction. His product contained hydrocyanic acid, cyanogen and chlorine. Wurtz, Wöhler, Cahours and Cloez investigated cyanogen chloride, but they employed the reaction of chlorine with hydrocyanic acid or mercuric cyanide, which yielded a product contaminated with hydrocyanic acid and chlorine, and perhaps also cyanogen. The former impurity is especially difficult to remove, and Wurtz believed that a molecular compound corresponding to the formula $2CNCl \cdot HCN$ was formed during the reaction of chlorine with hydrocyanic acid, but Naumann and Vogt showed that no such compound existed. Wurtz removed HCN by treating the CNCl with mercuric oxide. He showed that the product was stable if pure, but if hydrochloric acid and chlorine were present, polymerization to cyanuric chloride, $(CNCl)_3$ occurred.

Langlois(3) employed alkaline cyanides instead of mercuric cyanide, but found that efficient cooling of the reaction vessel was necessary to keep the reaction under control. Hantzsch and Mai(4) modified this procedure by adding potassium cyanide to water saturated with chlorine in an ice bath. Held(5) proposed the addition of zinc sulphate to the potassium cyanide solution in Langlois' method, stating that the mixture was then more stable to the action of chlorine. Mauguin and Simon(6) investigated Held's method, and found that it gave a pure product if the $ZnSO_4$ and KCN were in the proportion corresponding to $Zn(CN)_2 \cdot 2KCN$.

Jennings and Scott(7) in a thorough investigation into the preparation of cyanogen chloride obtained poor yields using Held's method, and proposed a method similar to that of Langlois. Their method is described in detail below.

The structure of cyanogen chloride has been the subject of much controversy. Cyanogen chloride reacts somewhat differently from cyanogen bromide and cyanogen iodide, and the consensus is in favour of the iso-structure

$$Cl \cdot N:C$$

although some investigators believe that two forms exist, the iso-nitrile and nitrile structures. It would be irrelevant here to enter into a discussion of the structure of CNCl. This is discussed at length by Chattaway and Wadmore(8), Grignard(9) and others.

Cyanogen chloride was used as a war gas in October, 1916 by the French. It was employed alone, and also mixed with $AsCl_3$, which was alleged to stabilize it, under the name "Vivrite". It has fair lachrymatory action, and is a very toxic substance, poisoning by cyanogen chloride being similar to that of cyanides, but more severe. Owing to its non-persistent character it was difficult to obtain a lethal concentration in the field. Recent interest in cyanogen chloride has been aroused by the discovery that most service respirators offer very limited protection against this gas when the charcoal contains moisture, that is, under ordinary conditions.

PREPARATION, PURIFICATION AND PHYSICAL PROPERTIES OF CYANOGEN CHLORIDE

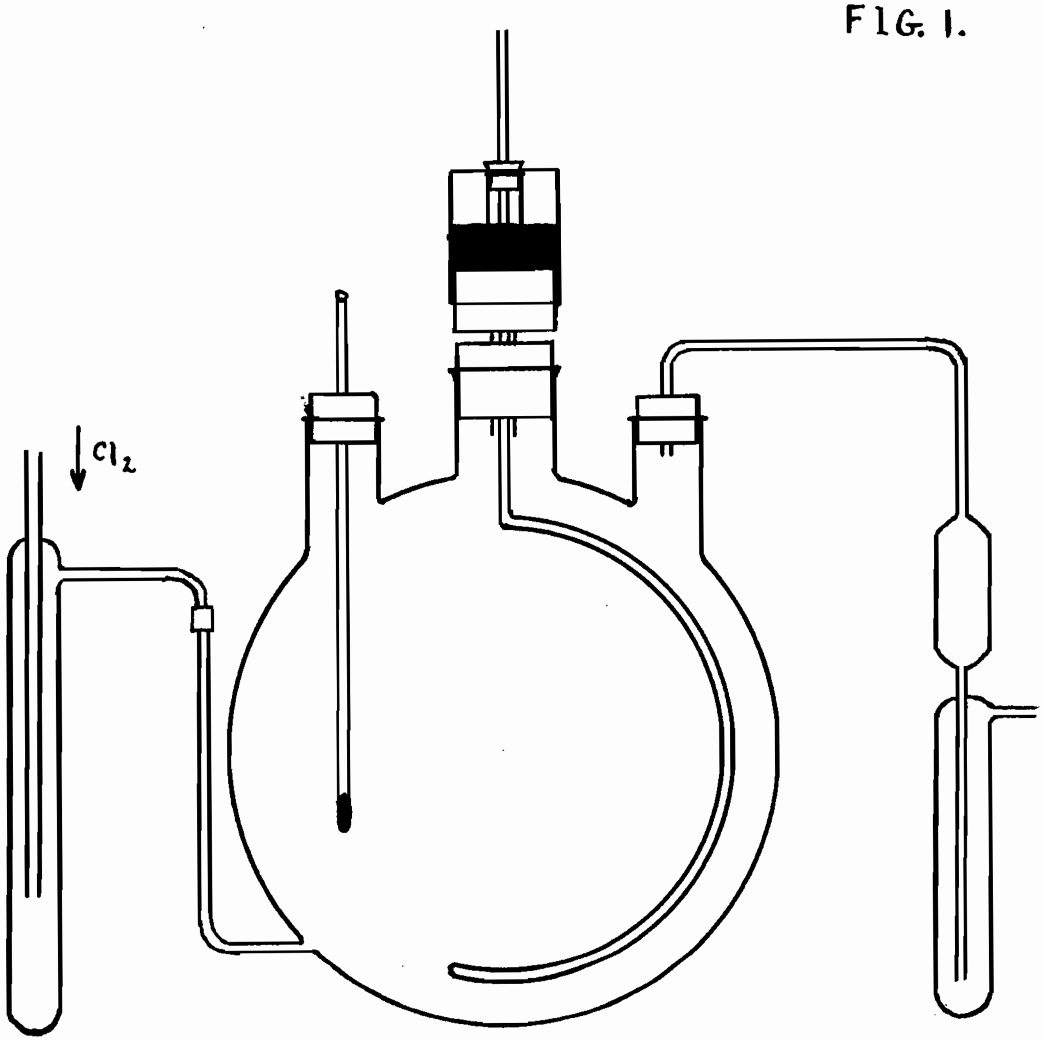
It was desirable for the present studies to have cyanogen chloride of high purity. This was accomplished by preparing the material according to the method of Jennings and Scott(7), with modified subsequent treatment for purification. The method of Held(4) as applied by Zappi(10), and the method of Jennings and Scott were investigated, as they are reported to have given the purest cyanogen chloride. The latter method was found to give a good yield of pure product, provided certain precautions were taken. Efficient cooling and stirring of the reaction mixture were necessary, and care had to be taken that all the sodium cyanide had reacted before the reaction was stopped and distillation begun, otherwise a reaction took place between the sodium cyanide and cyanogen chloride yielding a black solid. Quite often a slight excess of chlorine was added, and any free chlorine in the distillate was removed with mercury. The chief impurity remaining in the cyanogen chloride after distillation and treatment with mercury is carbon tetrachloride, and the percentage of this substance can be reduced to a small amount by passing the CNCl through a fractionating column and by crystallization of the distillate.

Three hundred c.c. of carbon tetrachloride were placed in a one-litre three-necked flask fitted with a thermometer, stirrer with mercury seal, and bubbler containing water. The chlorine delivery tube was joined to the side of the flask, near the bottom. Two hundred grams of Merck's Reagent sodium cyanide were conditioned to approximately 2% moisture by spreading the solid on a piece of paper and sprinkling it uniformly with four c.c. of water from a pipette. The solid was now ground, a small amount at a time in a mortar, and transferred to the reaction vessel, with continuous stirring to prevent formation of lumps. The flask was cooled in a mixture of ice and salt, so that the temperature fell to -3°C. or lower. Chlorine from a chlorine cylinder was then passed through a bubbler containing water or carbon tetrachloride into the reaction vessel at such a rate that the temperature did not rise above 0°C. Soon the reaction mixture became flesh-coloured, and remained this shade until the end-point, when it appeared darker. Chlorine was passed in for eight to twelve hours, the time required depending on the efficiency of cooling. At the end-point, the odour of chlorine could be noticed at the outlet tube, and the temperature of the reaction mixture dropped.

When the reaction was judged to be at an end, a fractionating column and calcium chloride drying tube were fitted to the reaction flask, and the salt-ice mixture was replaced with water at 15 - 20°C. which could be heated near the end of the distillation by an electric light bulb immersed in

APPARATUS FOR THE PREPARATION OF CNCl

FIG. 1.



the water. At first, the fractionating column consisted of a water-jacketed condenser the inner tube of which was packed with a series of glass discs, and about which water at 13° to 14°C. was circulated. In later preparations, a simple tube about eighteen inches long filled with copper gauze was employed with satisfactory results. The gaseous CNCl passed up through the fractionating column, down through the calcium chloride tube, into a trap or large ampoule immersed in an ice-bath, where it condensed. Distillation was stopped when the temperature inside the reaction flask rose to 40°C. If the distillate contained free chlorine, as indicated by a greenish colour, mercury was added to the liquid, and it was shaken occasionally. The purified CNCl was distilled off from the residue.

Various methods of purifying cyanogen chloride were studied. The methods described by Klemenc and Wagner(11) were tried. Fractional distillation at reduced pressure at -78°C. did not remove the last traces of chlorine, and distillation through a suspension of zinc oxide and calcium carbonate caused a lowering of the freezing-point of a fairly pure sample of CNCl, probably as a result of hydrolysis. Chlorine was not removed satisfactorily by arsenic, antimony or zinc metal. Pure cyanogen chloride could be obtained by fractional crystallization of the distillate from the Jennings and Scott method(12).

The water-white liquid was frozen in the trap or ampoule used as a receiver, until it was 80% to 90% solid. The mother liquor was poured off, the solid was remelted, and crystallization repeated until no further rise in the freezing-point occurred. Usually three recrystallizations on redistilled CNCl prepared by the above method were sufficient to give a product better than 99.5% pure.

The purity of the cyanogen chloride was determined by the methods of Mauguin and Simon(6). The first of these involved hydrolysis of cyanogen chloride in an excess of standard NaOH, and back titration with standard H_2SO_4 to a phenolphthalein end-point, care being taken not to make the solution acid.

$$CNCl + 2NaOH \longrightarrow NaCNO + NaCl$$

If a measured excess of H_2SO_4 was then added to the neutral solution, and the solution warmed for some time, the HOCN was converted to $(NH_4)_2SO_4$

$$2HCNO + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + CO_2$$

and the H_2SO_4 could be back titrated with NaOH using methyl red. A third method consisted of titrating the chloride after diluting to 250 c.c. and taking an aliquot part, using 0.05 N $AgNO_3$ with dichlorofluorescein as indicator.

Two methods were employed to get an accurately known sample of CNCl absorbed in NaOH. In the method A, a convenient quantity of liquid CNCl at 0°C. was poured into 50 ml. of 0.5N carbonate-free NaOH cooled to 0°C. The flask and NaOH were weighed before and after adding the CNCl at room temperature and atmospheric pressure. The mixture was allowed to stand at room temperature for an hour or more before back titration with H_2SO_4, to ensure complete hydrolysis of the CNCl.

In method B, the CNCl was placed in little vials made of 6 mm. soft glass tubing. Each of these vials had a solid tip bent at an angle and scratched so that when the stopper was inserted, the vial broke at this point, releasing the CNCl. Liquid CNCl, sealed in a vial, was weighed, cooled to 0° and placed in a flask containing 50 ml. of 0.5N NaOH cooled to 0°C. as before. The weight of the CNCl was determined by collecting the fragments of the vial from the titration flask, drying and weighing them. In Table 1, freezing point and analytical data are given for a series of CNCl samples.

TABLE 1

Freezing Point Data and Purity of CNCl by Chemical Analysis.

				Percentage Purity		
Freezing Point	Sample Weight by Method			(1) by NaOH used	(2) by NH_3 produced	(3) by Cl^- present
-6.90°C	(1)	.5645	A	100.9	-	-
	(2)	.6375	A	100.5	-	-
	(3)	.5517	A	101.0	-	-
-6.92°C	(1)	.4742	A	101.8	-	-
	(2)	.4529	A	100.7	-	-
	(3)	.5062	A	100.2	-	-
-7.25°C	(1)	.4342	A	98.8	-	-
	(2)	.4722	A	99.2	-	-
	(3)	.4527	A	99.3	-	-
-7.32°C	(1)	.6647	B	100.3	-	-
	(2)	.4770	B	96.5	-	-
	(3)	.6970	B	96.2	-	-
-7.00°C	(1)	.6218	A	99.67	-	99.8
	(2)	.5476	A	99.90	-	100.8
-7.00°C	(1)	.6006	B	99.85	99.9	99.4
	(2)	.5758	B	99.10	98.9	99.4
	(3)	.4878	B	99.55	99.5	99.2
-6.92°C	(1)	.8762	A	99.88	-	100.5
	(2)	.7169	A	100.32	-	100.2
-10.50°C	(1)	.6039	A	89.3	-	-
	(2)	.6445	A	88.6	-	-
	(3)	.6134	A	88.1	-	-

The method employed for freezing point determinations was an extension of that used by J.A. Morrison and W.E. Grummitt(13). The apparatus consisted of a small clear dewar to which was sealed a stopcock at the top. The air pressure could be adjusted to give a convenient rate of cooling. This tube was fitted with a stopper through which passed a Beckmann thermometer and a glass ring stirrer driven by an eccentric wheel fitted to a stirring motor. The Beckmann thermometer was compared with two standard thermometers of different ranges calibrated at the P.T.R. The zero points on these were checked with great care. Sufficient cold CNCl was placed in the inner tube to cover the bulb of the thermometer, and the dewar was cooled in an ice-salt mixture at about -12°C. Time and temperature readings were recorded until the freezing-point had been passed. An ice-water bath was then substituted for the ice-salt mixture, and readings were taken as before. The freezing-point could be determined quite accurately from the time-cooling curve, but the melting-point was not well defined, as will be seen from the accompanying curves, figs. 2 and 3.

A further check on the purity of CNCl was made by determining the molal freezing-poing lowering. Into a sealed tube 24.186 gms. of pure CNCl were weighed, the tube was cooled below 0°, and the contents placed in the freezing-point apparatus. The freezing-point was determined as described above. The solid was remelted, 0.7018 gms. of CCl_4 were added, and the freezing-point again determined. A lowering of 0.60°C. for a mol fraction of 0.01117 was found, and the molal freezing-point lowering was calculated to be 3.26°C. Assuming the latent heat of fusion to be constant between -6.92° and 7.52°C., its value is 2650 cal./mole. The entropy of fusion is therefore 9.96 entropy units. From a consideration of the analytical percentage of impurity present in a sample of CNCl, and the molal freezing-point lowering, the molecular weight of the impurity was calculated to be 112. The impurity is probably mainly carbon tetrachloride.

The progress of purification by recrystallization is illustrated in Table 2.

TABLE 2

Purification of CNCl by Fractional Crystallization.

A. Material after removing Cl_2 with Hg and redistilling.

After Crystallization	No. 1	No. 2	No. 3
Freezing Point	-7.73°C	-6.95°C	-6.90°C

B. Mother liquors from crystallizations. *

Crystallizations	1	3	5	6	7
Freezing Point	-10.10°C	-7.45°C	-6.95°C	-6.92°C	-6.92°C

* In this series only about 10% or less of the material was poured off each time.

The vapour pressure of CNCl was measured, using a static method. A trap containing CNCl, and fitted with an Anschutz thermometer was connected to a mercury manometer. The trap was surrounded by a bath at the desired temperature in a dewar flask. The temperature of the bath was measured with one of the standard thermometers used in the freezing-point measurements. Readings were taken over such long periods of time that equilibrium was established between the

CNCl and the bath, and the temperature of the CNCl was taken as that of the bath with only slight error. Observations were made over a period of nearly a week. The data together with those of Klemenc and Wagner are given in Table 3. The latent heat of vaporization was calculated from the Clausius-Clapeyron relation to be 6400 cal./mole.

TABLE 3

Vapour Pressure Data for CNCl

Temperature °C.	Vapour Pressure (mm. of Hg)	
	Present Values	Data of Klemenc and Wagner
-12	-	233
-10	-	265
-8	-	302
-6	342.1	341
-5.6	348.3	-
-4.8	359.1	-
-4.0	-	373
-2.8	396.3	-
-2.0	-	408
0.00	446.8	445
0.00	446.5	-
1.85	483.6	-
2.00	-	484
3.40	515.4	-
4.00	-	527
5.00	558.0	-
6.00	-	573
6.20	581.2	-
7.40	616.5	-
8.00	-	621
9.10	658.3	-
10.00	-	674
10.60	697.3	-
12.00	-	730
12.80	754.8	-
13.00	763.0	-
14.00	-	790
17.82	916.5	-

These data are plotted in fig. 4.

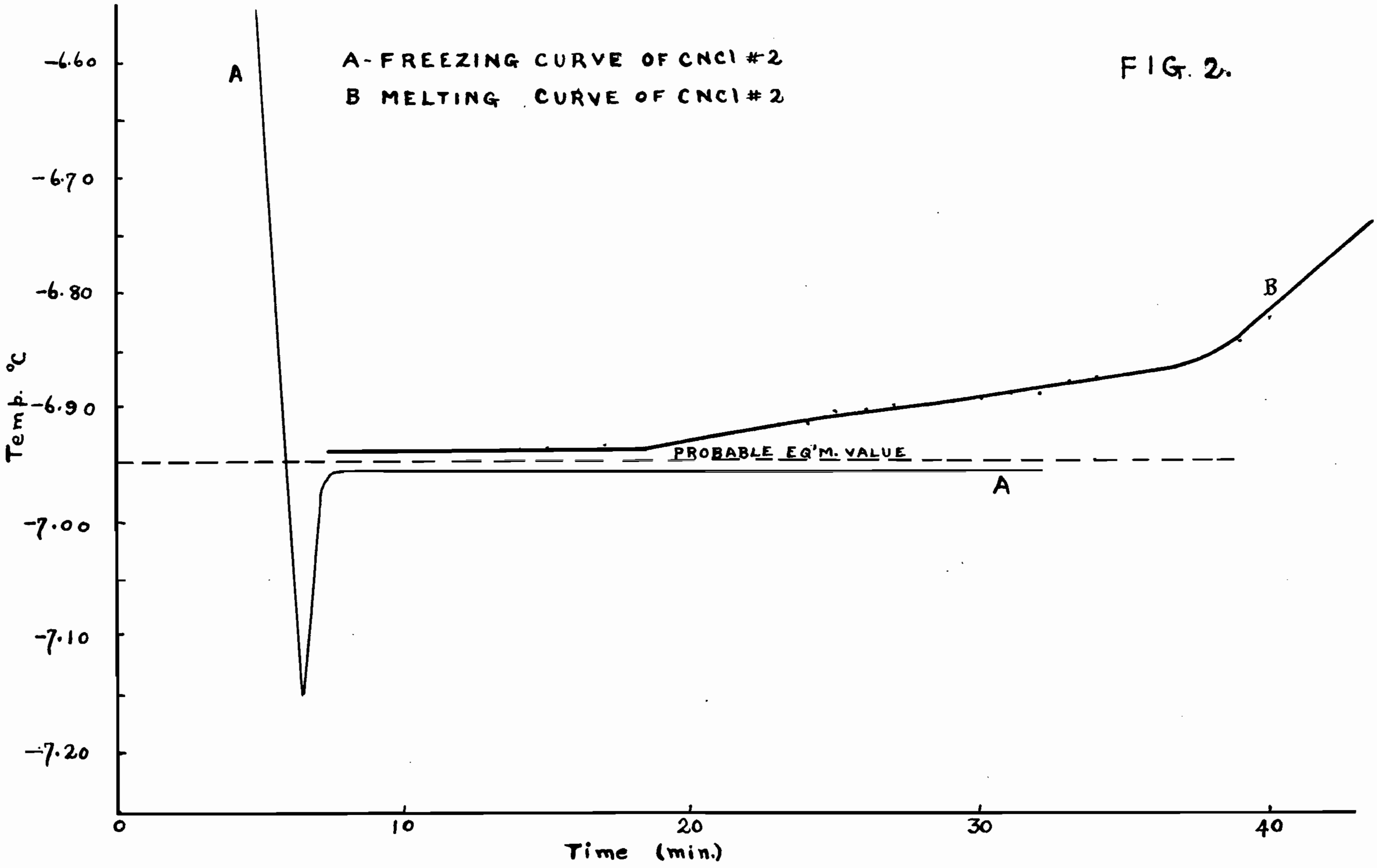


FIG. 2.

A- FREEZING CURVE OF CNCl #2
B MELTING CURVE OF CNCl #2
A
B
A
PROBABLE EQ'M. VALUE
-6.60
-6.70
-6.80
-6.90
-7.00
-7.10
-7.20
Temp. °C
0
10
20
30
40
Time (min.)

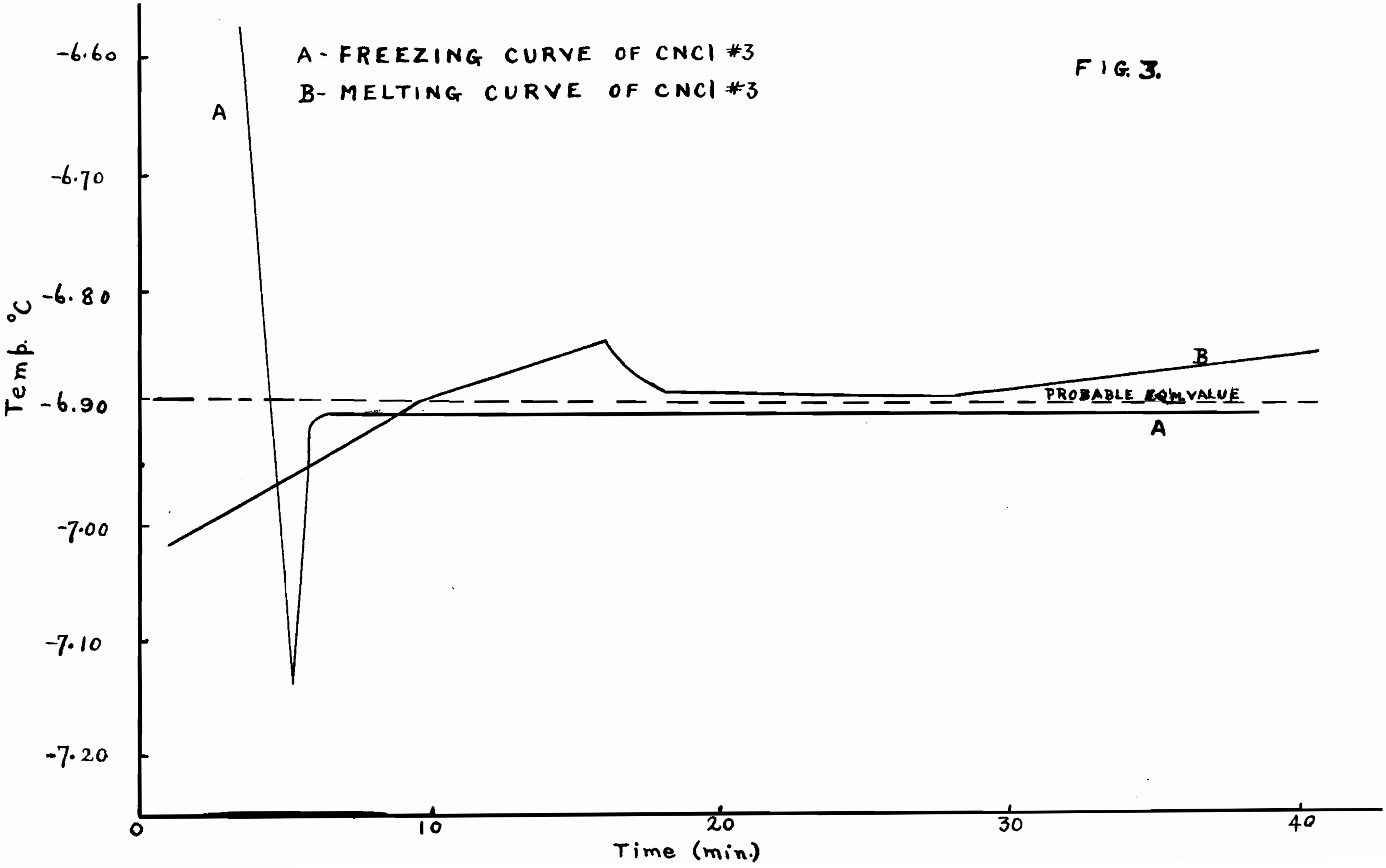

A - FREEZING CURVE OF CNCl #3
B - MELTING CURVE OF CNCl #3
A
B
PROBABLE EQM. VALUE
A
Temp. °C
-6.60
-6.70
-6.80
-6.90
-7.00
-7.10
-7.20
0
10
20
30
40
Time (min.)

FIG. 3.

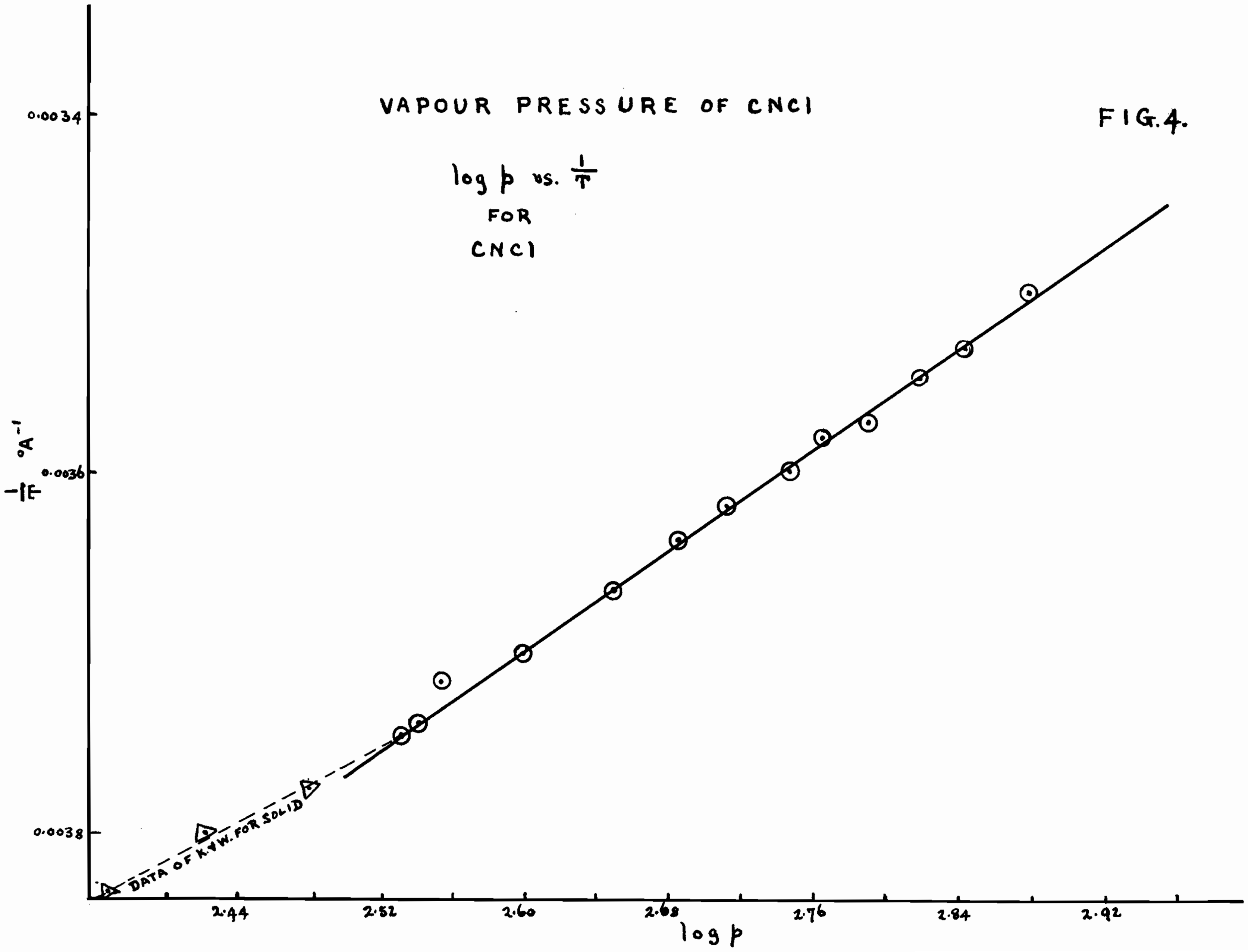


FIG.4.

VAPOUR PRESSURE OF CNCl

log p vs. $\frac{1}{T}$
FOR
CNCl

CONCLUSIONS

Cyanogen chloride may be prepared in good yield by the method of Jennings and Scott. After removal of chlorine with mercury and re-distillation, fractional crystallization provides the most satisfactory method of purification. The methods of Mauguin and Simon provide a means of determining the purity of cyanogen chloride analytically, the chief difficulty being to get an accurately known amount of cyanogen chloride completely absorbed in standard base.

The freezing-point of a sample of cyanogen chloride may be determined with considerable accuracy from the time-cooling curve, and provides an excellent criterion of purity, as the molal freezing-point lowering is large (3.26°C.). The melting-point is ill-defined even under carefully controlled conditions.

Vapour pressure measurements made on a sample of pure CNCl gave values that agree well with those reported by Klemenc and Wagner(11).

PART II

THE HYDROLYSIS OF CYANOGEN CHLORIDE

It was thought desirable to have some information about the kinetics of the hydrolysis of cyanogen chloride before studying the sorption of cyanogen chloride on wet charcoals. Data were available on the reactions of cyanogen bromide and iodide in buffered solutions and in the presence of NaOH, NH_3, methylamines, ethylamines and triethanolamine(14), but a survey of the literature did not reveal any information about the kinetics of the hydrolysis of cyanogen chloride.

Hydrolysis of CNCl takes place in two steps:

$$CNCl + H_2O \longrightarrow HCNO + HCl$$

$$HCNO + H_2O \longrightarrow NH_3 + CO_2$$

In solutions of pH less than 7, hydrolysis of cyanic acid is rapid at ordinary temperatures, and the first reaction is rate determining. Since equivalent quantities of HCl and NH_3 are formed, the pH should not change appreciably during hydrolysis. Hydrolysis of cyanogen chloride (and also of the other halides) is catalysed by OH^- and H^+. In the presence of amines, ammonia and pyridine, very rapid reaction occurs. The reaction of cyanogen chloride with tertiary amines is an example of the von Braun reaction(15). In the presence of NH_3, CNCl reacts to form cyanamid:

$$CNCl + 2NH_3 \longrightarrow NH_2CN + NH_4Cl$$

An aqueous solution of pure cyanogen chloride gives no reaction with aqueous silver nitrate. Hence cyanogen chloride is unionized. Since chloride is formed during hydrolysis, the hydrolysis may be followed by titrating the chloride present. Chloride may be determined very conveniently by titration with $AgNO_3$, using dichlorofluorescein as indicator. The pH should not be less than 4. The initial concentration of CNCl may be determined by one of the methods of Mauguin and Simon described previously. It was thought advisable for preliminary work to study only the hydrolysis in pure water buffered with CO_2, the resulting pH being between 4 and 6, and to find the magnitude of the salt effect. An attempt was made to study the hydrolysis in 0.02N HCl, but reaction occurred so rapidly that no accurate results could be obtained. Rates of hydrolysis were determined over the range of 0°C. to 50°C., and the activation energy calculated.

EXPERIMENTAL PROCEDURE

Distilled water was cooled in an ice bath, and saturated with CO_2 by adding dry ice to the cold water. To approximately 300 ml. of this water sufficient cold liquid CNCl was added to give a solution not stronger than 0.2 M. In most of the work, two concentrations of cyanogen chloride were employed at each temperature. The solutions were always freshly prepared before use. After vigorous shaking, the cyanogen chloride solution was poured into bulbs of 25 to 30 ml. capacity, which were sealed, and placed in a thermostat at the desired temperature. For the 30°, 40° and 50°C. runs, a water thermostat fitted with a stirrer, electric heater and thermoregulator was employed. The heater was operated by a mercury relay described by Black(16). This type of relay was found to be quite reliable, economical, and easily constructed. The thermostat was controlled to about 0.05°C. For the 0°C. run, an ice-water mixture in a dewar flask, and for the 11.1°C. run, acetic acid containing water was employed. The dewar containing this mixture was kept in an ice-box to keep the solid-liquid ratio approximately constant, and the temperature was checked at least once a day. Because of the character of the frozen material, a temperature gradient of two or three tenths of a degree existed between the solid and liquid.

For a study of the salt effect, solutions of CNCl in 0.02 M NH_4Cl and in 0.02 M KNO_3 were prepared. The 0.02 M KNO_3 solution was prepared from water previously saturated with CO_2, but the NH_4Cl solution was unbuffered with CO_2, as the NH_4Cl itself acted as a buffer.

The initial concentration of cyanogen chloride was determined by adding an excess of 0.5N NaOH to a sample of the freshly prepared cyanogen chloride solution, allowing the mixture to stand until hydrolysis was complete, and back-titrating the base with standard H_2SO_4 to a phenolphthalein end-point, as described previously (p. 7). The blank on the water saturated with CO_2 was determined by adding excess base to a sample of the water, and back-titrating with H_2SO_4 as for the CNCl solution. The hydrolysis was followed by titrating the free Cl^- in the samples with 0.03N $AgNO_3$ using dichlorofluorescein as indicator. This method of determining chloride was found to be quite satisfactory if the pH of the solution was greater than 4. A sample of 20 or 25 c.c. of the CNCl solution was withdrawn from a bulb by a pipette attached to a water aspirator, between five and ten drops of a 0.1 per cent solution of sodium dichlorofluorescein were added, and the solution titrated with 0.03N $AgNO_3$ until the suspension of AgCl just became pink. Bulbs removed from the thermostat at the higher temperatures were immediately cooled in ice water before being opened. The time of removal of the bulbs was noted in each case. The concentrations of cyanogen chloride remaining were calculated from the initial CNCl concentrations and the amounts of chloride found in the solution at various times. These data were used in drawing the log $\frac{[\text{CNCl}]\ \text{initial}}{[\text{CNCl}]\ t}$ vs. time curves, and the values of k for the various temperatures were calculated from the slopes of these lines. Finally the Arrhenius line was plotted, and the value of the activation energy determined. The data are given in Tables 4, 5 and 6 and figures 5 to 8.

TABLE 4

DATA FOR RATES OF HYDROLYSIS OF CNCl

Time (hrs)	[Cl$^-$] moles/l.	[CNCl] moles/l.	initial log $\frac{[CNCl]}{[CNCl]_t}$	Time (hrs)	[Cl$^-$] moles/l.	[CNCl] moles/l.	initial log $\frac{[CNCl]}{[CNCl]_t}$
	TEMP.0°C.				TEMP.11.1°C.		
0.	0.00000	0.03955	0.0000	0.0	0.0000	0.07806	0.0000
237.	0.00083	0.03872	0.0086	24.4	0.00109	0.07697	0.0091
387.	0.00117	0.3838	0.0128	53.8	0.00139	0.07667	0.0108
525.	0.00149	0.03806	0.0170	67.8	0.00175	0.07631	0.0128
				115.5	0.00282	0.07524	0.0190
				167.3	0.00320	0.07486	0.0211
				212.0	0.00422	0.07384	0.0240
TEMP. 30°C							
0.	0.0000	0.0813	0.0000	0.0	0.0000	0.1845	0.0000
3.25	0.0019	0.0794	0.0103	3.0	0.0047	0.1798	0.0111
20.5	0.0063	0.0750	0.0350	8.5	0.0044	0.1801	0.0105
30.0	0.0084	0.0729	0.0474	13.7	0.0123	0.1722	0.0300
43.9	0.0118	0.0695	0.0681	24.0	0.0174	0.1671	0.0430
52.8	0.0141	0.0672	0.0827	36.7	0.0245	0.1600	0.0619
TEMP. 40°C							
0.	0.0000	0.1413	0.0000	0.0	0.0000	0.0870	0.0000
3.4	0.0053	0.1360	0.0166	3.4	0.0033	0.0837	0.0168
9.6	0.0136	0.1277	0.0439	9.6	0.0083	0.0787	0.0435
13.1	0.0179	0.1234	0.0598	13.1	0.0110	0.0760	0.0587
18.0	0.0247	0.1166	0.0834	18.0	0.0145	0.0725	0.0792
23.5	0.0308	0.1105	0.1067	23.5	0.0183	0.0687	0.1025
	TEMP. 40°C						
0.	0.0000	0.07806	0.0000				
2.2	0.00014	0.07792	0.0008				
4.6	0.00284	0.07522	0.0161				
6.8	0.00489	0.07317	0.0281				
17.5	0.01335	0.06471	0.0814				
TEMP. 50°C							
0.	0.0000	0.1245	0.0000	0.0	0.0000	0.0695	0.0000
1.0	0.0039	0.1206	0.0141	1.0	0.0027	0.0668	0.0172
3.2	0.0114	0.1131	0.0423	3.2	0.0065	0.0630	0.0427
5.5	0.0187	0.1058	0.0709	5.5	0.0116	0.0579	0.0793
9.0	0.0297	0.0948	0.1186	9.0	0.0173	0.0522	0.1243
12.5	0.0395	0.0850	0.1660	12.5	0.0224	0.0471	0.0690
23.5	0.0511	0.0734	0.2297	23.5	0.0368	0.0317	0.3409

TABLE 5

VARIATION OF k WITH TEMPERATURE

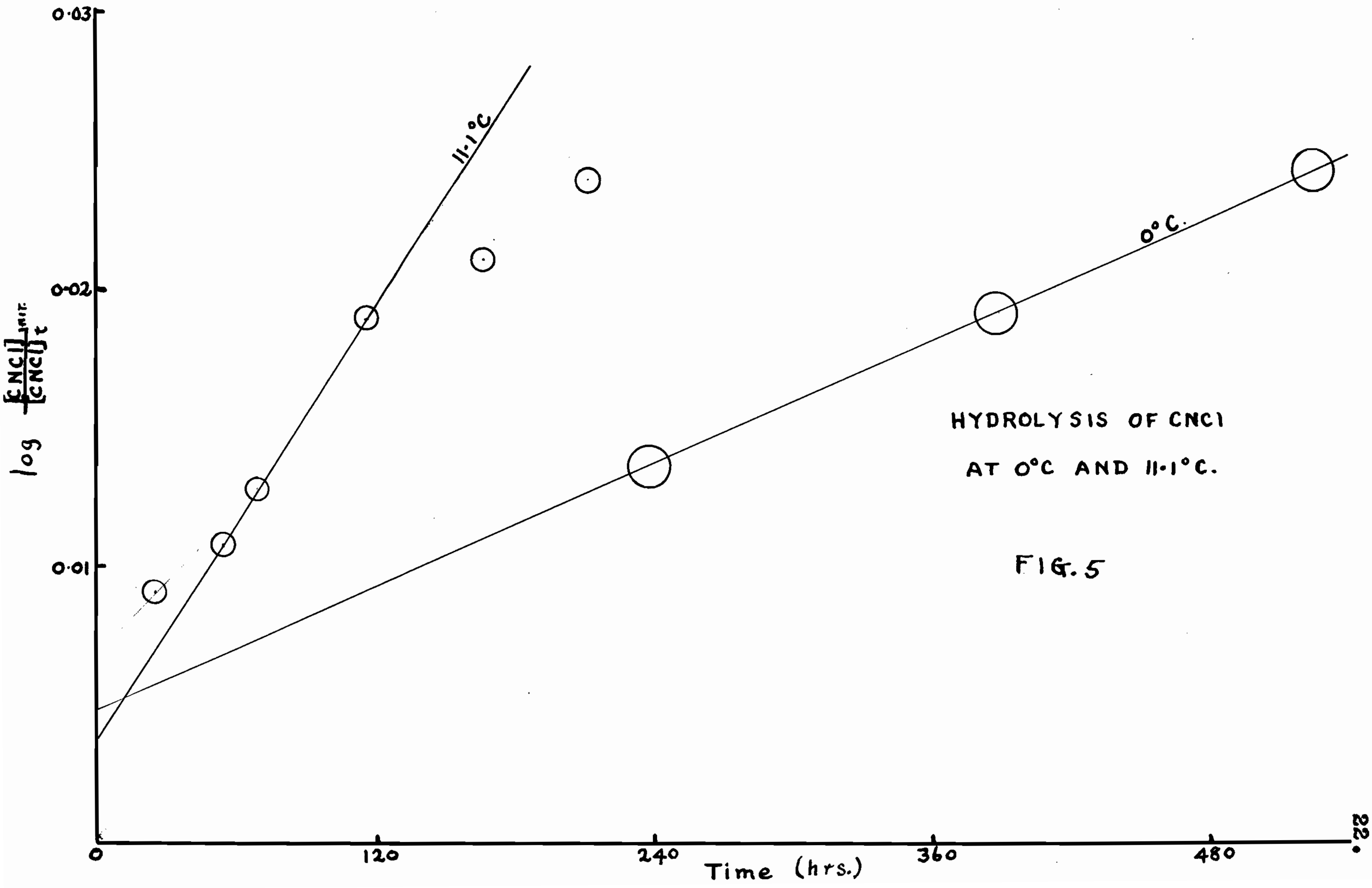
Temp. °A	$1/T_{-1}$ °A	k_{-1} hrs.
323	0.003096	3.130×10^{-2}
313	0.003195	1.151×10^{-2}
303	0.003300	3.585×10^{-3}
284.1	0.00352	3.070×10^{-4}
273	0.003663	8.65×10^{-5}

TABLE 6

EFFECT OF ADDED SALTS ON THE RATE OF CNCl HYDROLYSIS-TEMPERATURE 40°C.

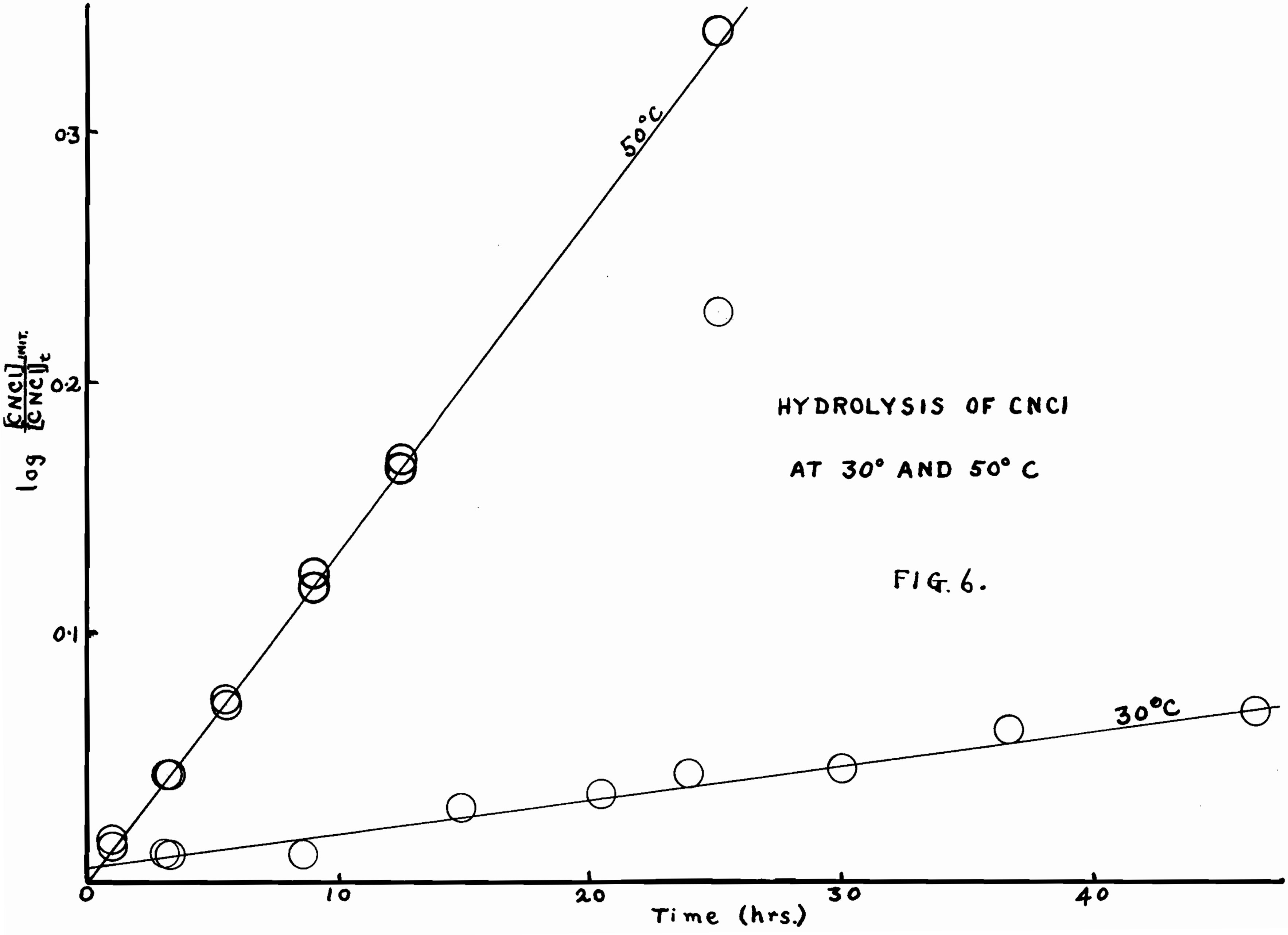
Time (hrs)	$[Cl^-]$* moles/l.	$[CNCl]$ moles/l.	initial $\log \frac{[CNCl]}{[CNCl]_t}$	Time (hrs)	$[Cl^-]$ moles/l.	$[CNCl]$ moles/l.	initial $\log \frac{[CNCl]}{[CNCl]_t}$
	0.01 M	NH_4Cl			0.01 M	KNO_3	
0.0	0.0000	0.1077	0.0000	0.0	0.0000	0.05625	0.0000
3.4	0.0037	0.1040	0.0152	3.4	0.00260	0.05365	0.0205
8.4	0.0089	0.0988	0.0374	6.2	0.00460	0.05165	0.0370
12.6	0.0131	0.0946	0.0563	9.6	0.00664	0.04961	0.0545
				11.4	0.00815	0.04810	0.0679
0.0	0.0000	0.05175	0.0000				
3.0	0.00170	0.05005	0.0146				
5.5	0.00314	0.04861	0.0173				
8.8	0.00481	0.04694	0.0423				
14.8	0.01081	0.04094	0.1018				
20.1	0.01017	0.04158	0.0950				

* Cl^- from hydrolysis of CNCl only.



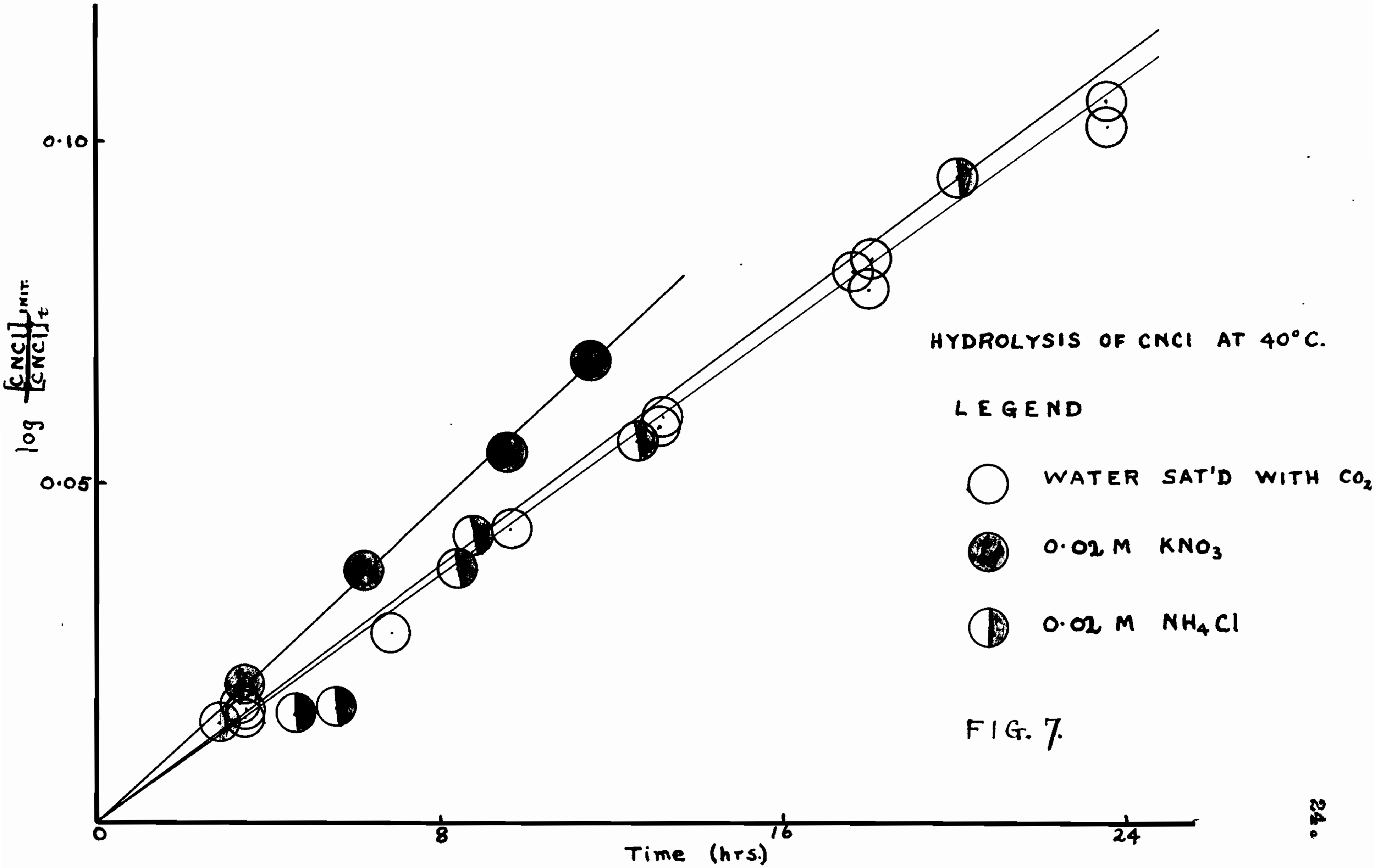
HYDROLYSIS OF CNCl
AT 0°C AND 11·1°C.

FIG. 5



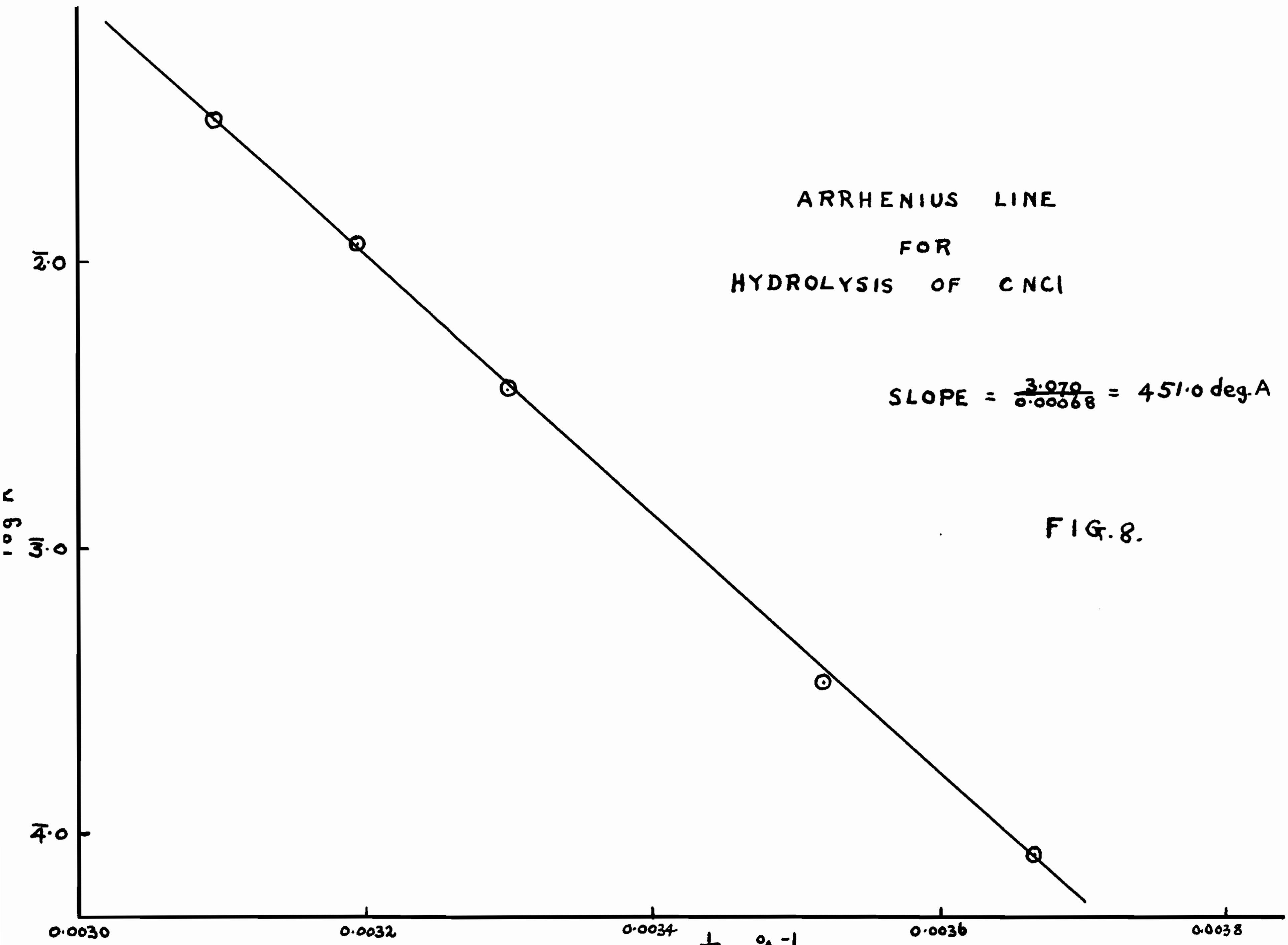
HYDROLYSIS OF CNCl
AT 30° AND 50° C

FIG. 6.



HYDROLYSIS OF CNCl AT 40°C.

FIG. 7.



ARRHENIUS LINE
FOR
HYDROLYSIS OF CNCl

$$\text{SLOPE} = \frac{3.070}{0.00068} = 451.0 \text{ deg.A}$$

FIG. 8.

CONCLUSIONS

The Arrhenius line for the hydrolysis of cyanogen chloride at pH 4 to 6 was found to be a straight line within the experimental error over the range 0° to 50°C. The activation energy for hydrolysis was calculated from the slope of this line to be 20,670 calories per mole. The rate of hydrolysis at 40°C. was only slightly increased in 0.02 M NH_4Cl and in 0.02 M KNO_3.

PART III

THE SORPTION OF CYANOGEN CHLORIDE BY CHARCOAL

Many empirical investigations of the sorption of cyanogen chloride by charcoal have been made during the last few years. This work has been mainly along the lines of testing service respirator canisters, the chief object generally being to determine the service, or breakdown time. Owing to the methods employed and to variation in the experimental conditions only a very incomplete picture of the sorption process has been obtained. A more detailed study is obviously of importance since the empirical tests have shown CNCl to have a short service time on moist charcoals and therefore to be a war gas of menacing aspect.

An apparatus has been constructed in this laboratory which follows the amount of gas sorbed with time, the concentration of toxic gas in the effluent stream and the rise in temperature at two levels in the charcoal bed. Good results have been obtained with this apparatus in the study of the sorption of ammonia and butane by charcoal and slight modification has made it possible to study the sorption of cyanogen chloride.

The results obtained so far in this investigation are of a preliminary nature. Methods of analysing for cyanogen chloride in the effluent stream have been studied and standardized. Sorption on dry charcoal has been studied, but the sorption of cyanogen chloride on wet charcoals, which is of much greater practical importance, remains to be investigated.

STATIC SORPTION

The phenomenon of the sorption of gases and liquids by solids is well known. Extensive investigation has shown that the amount of gas sorbed by a solid is a function of the pressure, expressed by the well-known Freundlich isotherm relation:

$$x = kp^{1/n}$$

where x is the amount of gas sorbed
p is the pressure
and k and n are constants for a given system and a given temperature.

This relation holds only over a limited pressure range. Langmuir assumed that a unimolecular layer of sorbed gas was formed on the sorbent, and postulated a time lag between sorption and re-emission of the gas molecules. From these considerations he derived the formula

$$a = \frac{Kp}{1 + bp}$$

where a is the amount of gas sorbed at a given temperature
p is the pressure
and K and b are constants.

This formula has been verified experimentally. It may be written in simpler forms where the amount of sorption is very large or very small.

In the absence of other factors linear relation between the logarithm of the amount of gas sorbed and the temperature at constant pressure has been found by many investigators. There is a large difference in the amount of gas sorbed for a small temperature change. The mechanism of sorption may change with temperature in some cases.

The amounts of various gases taken up at a given pressure by a given sorbent are approximately in the order of the boiling points or critical temperatures of the sorbates. Sorbents vary greatly in the amounts of a given gas which they can take up, charcoal and silica gel being particularly noted for their marked capacity for sorbing gases. The efficiency of a sorbent frequently depends upon its history, and activation by heating or chemical action has been found possible with many sorbents. The sorption capacity of charcoal depends also upon the source of the charcoal. Heat is evolved during sorption, the amount of heat given off for a given increment of gas sorbed being greater at the beginning of the sorption process than near the end. Sorption occurs rapidly at first, then decreases rather sharply to come to equilibrium which is often reached only after a long period of time. When the sorption of mixtures of gases is studied, it is found that for reversible sorption, the ratio of the amounts of gases sorbed is the same for a given gas mixture and a given sorbent, and is not altered if one gas is added after the other. In other words, gases displace each other from the sorbent, the equilibrium ratio of gases present on the sorbent depending only upon the composition of the gas mixture, other factors being constant.

Two types of sorption may be distinguished: chemisorption and molecular or van der Waals sorption. In the former type molecules or atoms are held to the surface of the sorbent by covalent forces which exist because of the structure of the solid. This type of sorption occurs commonly on metal surfaces, such as tungsten and nickel. Desorption is often difficult, even at very high temperatures. The heat of sorption is high; about three times that for molecular sorption. Langmuir has shown that a unimolecular layer of sorbed gas covers the surface of the sorbent, and that the gas is often sorbed in the atomic state.

Molecular sorption occurs when molecules of gas are held to the sorbent surface by van der Waals, or ordinary intramolecular forces. In the absence of complicating factors, this type of sorption is easily reversible. No decomposition of the sorbate into atoms occurs. Several processes may complicate this type of sorption. In the early stages, true adsorption, involving a unimolecular layer of sorbate, probably occurs. With charcoal and similar porous substances, condensation of the gas to liquid in the capillaries often takes place. Because of the concavity of the meniscus of the liquid in the capillaries, the vapour pressure is low. Water probably exists in the liquid state on charcoal under ordinary conditions. When sorption on such "wet" charcoal occurs, the sorbate may dissolve in, or be hydrolysed by the water present. Catalytic decomposition of the sorbate may be brought about by impregnants on the sorbent.

DYNAMIC SORPTION

Static sorption studies yield results which are of great theoretical importance. However, to evaluate the efficiency of a sorbent, such as charcoal, in removing a toxic gas from an air stream, a dynamic method must be used. The rate of sorption of the toxic gas may depend on either of two factors: (a) rate of diffusion of the gas molecules to the surface of the charcoal or (b) rate of sorption or reaction at the surface of the charcoal. If the former process is rate determining the presence of the "carrier gas" (air) may interfere with sorption. There is also the possibility that desorption of the toxic gas may occur when pure air is passed through the charcoal.

THEORIES OF DYNAMIC SORPTION

Several mathematical theories of dynamic sorption have been developed. Some of these are entirely empirical, while others are based upon rate of diffusion or rate of reaction of the toxic gas as mentioned above. Equations have been derived which express relations between various determinable quantities, and the behaviour of a certain charcoal towards a certain toxic gas under varying conditions of concentration, airflow and bed-length may be predicted if these quantities are known.

There are several quantities and terms which it is convenient to define here before entering into a discussion of the various theories. The most important of these from a practical standpoint is the service, or breakdown time τ. This is the time from the start of the gas flow to the point when an arbitrarily chosen dangerous concentration of toxic gas appears in th effluent stream. This quantity is also somewhat indefinitely defined as the time from the beginning of the gas flow to the point when the charcoal ceases to be 100% efficient in removing the toxic gas from the air stream. For the accurate determination of the service time, the former definition is much more exact, especially when dealing with highly poisonous gases. The critical bed length λ_c is the length of charcoal bed below which immediate penetration of toxic gas occurs. Another term, the "dead length" h is used by some authors, especially Mecklenberg. This is a length of the charcoal bed next the inlet which is visualized as being saturated with toxic gas, the remainder of the charcoal bed being free of gas. It is a mathematical fiction, but it is useful in evaluation of the protective action of sorbents.

Mecklenberg(17) postulated that sorption on charcoal occurred by the mechanism of capillary condensation, and to simplify the mathematical treatment, he assumed all the capillaries to be of uniform length and cross-section. He divided the charcoal bed into three imaginary parts:

(a) a section next the inlet saturated with gas

(b) a "working length", where sorption was occurring

(c) a section which the gas had not reached.

He confined his considerations to the "working length", and employed for the rate of diffusion of toxic gas to the surface the Nernst equation for a heterogeneous reaction,

$$\frac{dc}{dT} = \frac{DF(c-c'')}{\delta} \quad - - - - - - - - - - - \quad 1$$

where c is the partial pressure of gas near the charcoal

c" is the partial pressure of gas in the capillaries

D is the coefficient of diffusion of the toxic gas in air

F is the outer surface of the charcoal grains exposed per c.c.

δ is the thickness of the gas layer sorbed on the charcoal

and T is the time.

He then deduced the following relations:

$$\mathcal{T} = \frac{kQ}{Lc_o}\left(\lambda - h\right) \quad - - - - - - - - - - - - \quad 2$$

$$h = \frac{\delta}{DF}\left(\frac{KQ}{L}\right)^{n-1}\left(\ln\frac{c_o - c''}{c' - c''} - \frac{c_o}{c_o c'}\right) \quad - - \quad 3$$

where h is the dead length

$\mathcal{T}$ is the service time

L is the linear velocity of the air stream

λ is the length of the charcoal bed

Q is the cross-sectional area of the bed

KQ is the portion of the cross-section of the cell not filled with charcoal

c' is the minimum detectable concentration of the gas *

and n is a constant.

Danby, Davoud, Everett, Hinshelwood and Lodge(18) have also treated the problem of dynamic sorption in a theory which will subsequently be referred to as the Hinshelwood theory. According to these authors, the concentration of toxic gas in the effluent air stream increases exponentially with time:

$$c = c_o e^{-\frac{k}{L}} e^{\frac{kbT}{L}} \quad \text{- - - - - - - - -} \quad 4$$

where k is the sorption rate constant

c_o is the initial concentration of toxic gas in the air stream

c is the concentration in the effluent stream

λ is the bed length

T is the time from the start of the gas flow

L is the linear flow rate

and b is the rate of exhaustion of the active centres.

---

* Or, in our consideration, the arbitrarily chosen dangerous concentration of toxic gas.

A simplified treatment by Hinshelwood et al assumes that each successive element of charcoal functions with complete efficiency and then passes completely out of action. Actually, exhaustion is gradual, and a more rigorous treatment takes this fact into account.

Now, since the rate of exhaustion of active centres is directly proportional to the total amount of toxic gas passing, and inversely proportional to the initial number of active centres,

$$b = \frac{c_o L}{N_o} \quad - - - - - - - - - - \quad 5$$

where N_o is the initial number of active centres per c.c.

From equations 4 and 5, the service time for variation in the column length is given by the relation

$$\tau = \frac{N_o}{c_o L}\left(\lambda - \lambda_c\right) \quad - - - - - - \quad 6$$

and if the flowrate is varied, the bed length being kept constant,

$$\tau = \frac{\lambda N_o}{c_o}\left(\frac{1}{L} - \frac{1}{L_c}\right) \quad - - - - - - \quad 7$$

where L_c is the critical flowrate, above which breakdown is instantaneous.

The theory assumes that two zones exist in the charcoal bed; (a) a section of the bed which actively removes toxic gas from the air stream, and (b) a section which is saturated with gas; that is, no active centres are left. Actually, however, saturation of the charcoal is gradual,and sorption often takes place long after the service time has passed. Expressing the decrease in gas concentration through the bed by the partial differential equation

$$-\frac{\partial c}{\partial l} = \frac{1}{L}\left(\frac{\partial x}{\partial T} + \frac{\partial c}{\partial T}\right) \quad \text{- - - - - - - - -} \quad 8$$

where l is distance from the inlet end of the bed to
the point being considered
x is the concentration of gas on the charcoal
and all other quantities are as previously defined

renders the treatment independent of the mechanism or kinetics of sorption. To solve this equation, Hinshelwood et all assume that

$$\frac{\partial x}{\partial T} = kcN \quad \text{- - - - - - - - - - - - -} \quad 9$$

where k is a constant
c is the concentration of toxic gas in the
air stream
and N is the number of active centres per c.c.

The active centres do not retain their activity indefinitely. On the average, each active centre deals with n molecules of gas before becoming inactive. If the number of active centres per c.c. is N_o', then this is equivalent to $nN_o' = N_o$ centres of unit activity per c.c. Neither n nor N_o' is determinable. In this treatment it is also assumed that the sorption process takes place isothermally, and that local changes in the water content of the bed do not alter appreciably the rate of sorption.

From equations 6 and 7,

$$\lambda_c = \frac{L}{N_o k} \ln \frac{c_o}{c'} \qquad \text{----------} \qquad 10$$

where c' is the concentration of toxic gas in the effluent stream at breakdown

$$\text{and } \tau = \frac{1}{kc_o} \quad \ln(e^{kN_o \quad /L} - 1) - \ln(\frac{c_o}{c'} - 1) \qquad \text{---} \qquad 11$$

or, approximately

$$\tau = \frac{1}{kc_o}\left(\frac{kN_o}{L} - \ln \frac{c_o}{c'}\right) \qquad \text{-----------} \qquad 12$$

whence

$$\tau = \frac{N_o}{c_o L}\left(\lambda - \lambda_c\right) \qquad \text{-------------} \qquad 13$$

for variation in bed depth

$$\text{or } \tau = \frac{N_o}{c_o}\left(\frac{1}{L} - \frac{1}{L_c}\right) \qquad \text{-------------} \qquad 14$$

for variation in flowrate

Both treatments give identical expressions for the breakdown time. However, an approximation in the more rigorous treatment has been made which is only valid for $\frac{c_o}{c'} \gg 1$, namely, unity was neglected in comparison with $e^{\frac{kN_o\lambda}{L}}$. When the Hinshelwood theory is applied to conditions near saturation, this approximation cannot be made, since c has nearly the same value as c_o. The distribution of gas through the charcoal bed and the effect of granule size have been discussed in detail in the original report, and will not be considered here. A more complete discussion of the theories of Hinshelwood and of Mecklenberg is given in the theses of Ogilvie(19) and Davis(20).

Lister (21) has extended Hinshelwood's treatment to include the possibility of desorption, and hence the possibility of changes in N_o with changing initial concentration of toxic gas. This makes necessary another parameter, the rate constant for desorption, K. In the case of reversible sorption, if x is the concentration of gas on the charcoal, the value of x at equilibirum will be a function of c_o determined by the condition

$$\frac{\partial x}{\partial T} = - Kx + kc_o(N_o - x) = 0 \quad ------- \quad 15$$

whence $x = N_o$ only when $kc_o \gg K$

The following relations have been taken from Kincaid's summary of Lister's original report(21).

For irreversible sorption

$$\ln\left(\frac{c_o}{c} - 1\right) = \ln e^{\frac{N_ok}{L}} - 1 \quad - kc_oT \doteqdot \frac{N_ok}{L} - kc_oT \quad -- 16$$

and for the reversible case

$$\ln\left(\frac{c_o + N_oKTL}{c} - 1\right) \doteqdot \frac{N_ok}{L} - kc_oT - KT \quad ------ \quad 17$$

The breakdown time is given by the following equations:

Irreversible

$$\tau = \frac{N_o\lambda}{c_oL} - \frac{1}{kc_o}\ln\left(\frac{c_o}{c'} - 1\right) \quad ---------- \quad 18$$

$$\text{whence } \tau c_o = \frac{N_o\lambda}{L} - \frac{1}{k}\ln\left(\frac{c_o}{c'} - 1\right) \quad ---------- \quad 19$$

Reversible

$$\tau c_o = \frac{N_ok}{K/c_o + k}\cdot\frac{\lambda}{L} - \frac{1}{K/c_o + k}\ln\left(\frac{c_o + N_oK \;/L}{c'} - 1\right)$$

$$----- \quad 20$$

The relations for critical thickness are identical with equation 10 for irreversible and reversible sorption.

In conclusion may be mentioned the theories of Bohart and Adams, of Bartky and Hestenes(22) and of Wicke(22). Bohart and Adams in 1920 proposed a theory of dynamic sorption which is identical with Hinshelwood's later treatment. They assumed that the rate-controlling step was reaction of the toxic gas with, or sorption on the charcoal, and also that sorption was irreversible. Wicke's treatment concerns sorption and desorption and is based upon diffusion as the rate-controlling factor. Bartky and Hestenes have recently developed a semi-empirical treatment of the data of Dole and Klotz(22). They assume that $\frac{c}{c_o} \rightarrow 1$ at a finite time, rather than when $T \rightarrow \infty$ as assumed in the Hinshelwood treatment. Their differential equation is

$$\frac{\partial N}{\partial T} = -kc\left(1 - \frac{N}{N_o}\right)^{-m}\left(\frac{N}{N_o}\right)^{\eta} \quad \text{- - - - - - - -} \quad 21$$

$$0 < m < 1$$

$$0 < \eta < 1$$

where m and η are empirical constants, and the other symbols have the same significance as in the previous discussion.

To apply this theory, the condition $c_o \tau = \text{const.}$ is necessary but not sufficient.

DISCUSSION OF EXPERIMENTALLY DETERMINABLE QUANTITIES

1. The service time

The theories of Hinshelwood and of Mecklenberg predict a linear relation between service time and bed length. However, Mecklenberg has shown that the linear relation only holds for bed depths greater than a certain minimum length, and this falling off from linearity has been noted by several observers. Lister's theory predicts a linear relation between service time and bed depth for irreversible sorption but not for reversible.

Both the former theories indicate a linear relation between service time and the reciprocal of the flowrate.

Hinshelwood's theory predicts that the service time varies as the reciprocal of the initial concentration for very low concentrations, i.e., τc_0 = const. According to Kincaid, this is only true if $kN_0\lambda/L \gg \ln\left(\frac{c_0}{c'} - 1\right)$. When τc_0 is not constant, it should decrease with increasing initial concentration. In reversible sorption, Lister's theory predicts that τ should increase and reach a constant value as c_0 decreases. This provides a criterion of reversible sorption along with dynamic desorption studies.

2. The dead length and critical length

According to equation 3

$$h \propto v^{1-n}$$

if the flowrate is varied and other variables are kept constant. The value of n is usually about 0.5. From equation 10, the critical length varies directly with the flowrate, and this relation is independent of whether the sorption is reversible or irreversible.

Equation 10 also indicates a linear relation between critical length and the logarithm of the initial concentration.

EXPERIMENTAL

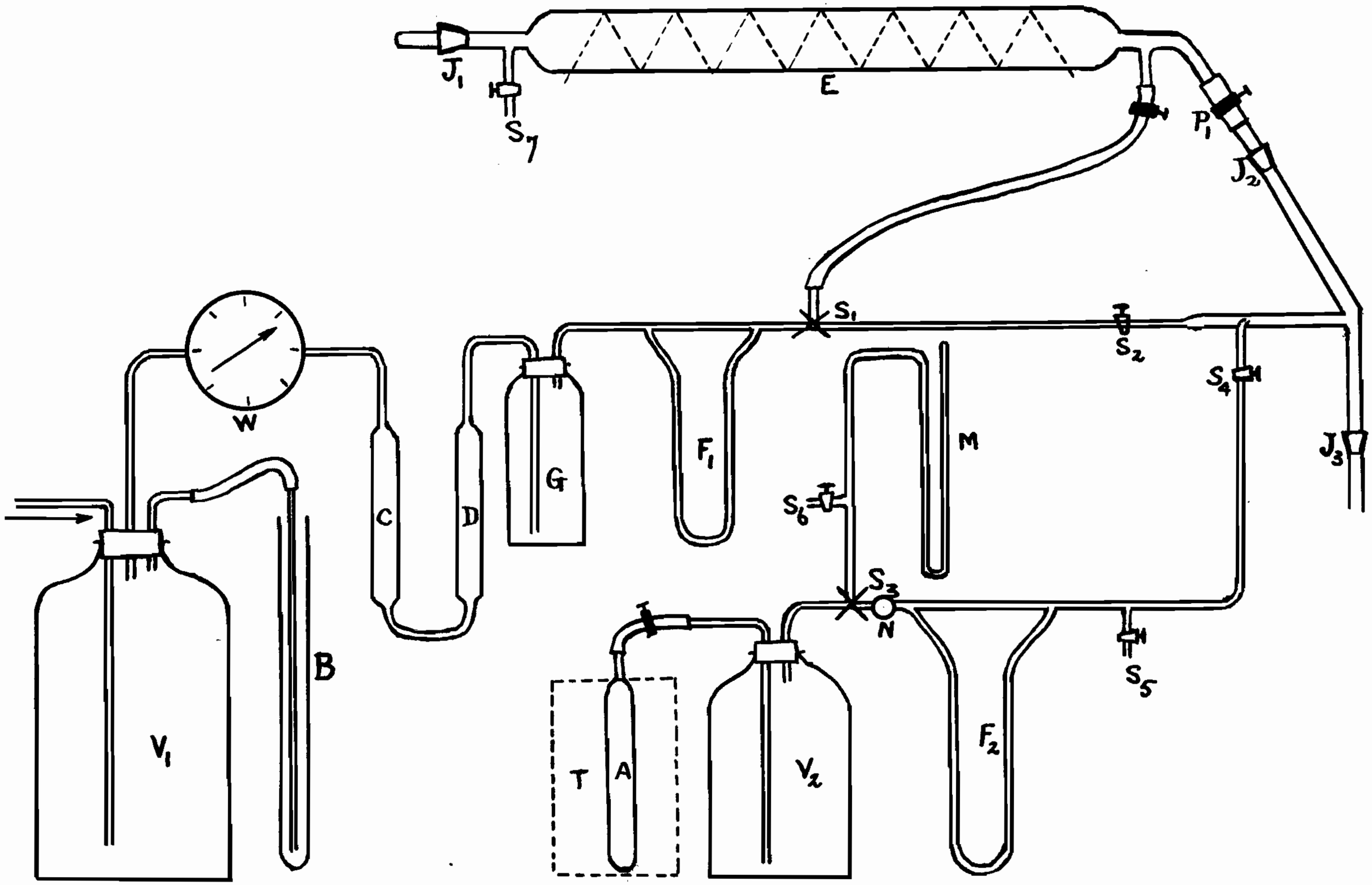
APPARATUS

The apparatus used in this investigation has been described by Pearce(23) and by Ogilvie(19) and Davis(20). A cell which contains the charcoal to be investigated is suspended freely from one arm of an analytical balance, provision being made for the analysis of the effluent stream from the cell. The following description of the various systems applies to fig. 9, which is a simple diagram of the apparatus.

Air was supplied by a Wegner Deka Micro Pump, the outlet of which was attached to a 45-litre ballast volume V_1. The air pressure in the ballast volume was regulated by a water blow-off B. The inlet cock on the pump was turned partly off so that only a small stream of air passed through the blow-off. From the ballast volume the air passed through three calcium chloride tubes C in series to remove water vapour, then through three ascarite tubes D to remove carbon dioxide, and finally through three sulphuric acid bubblers G. By adjusting the concentration of sulphuric acid in these bubblers, air of any desired degree of humidity could be obtained. In this preliminary study dry air was employed, and the bubblers contained concentrated acid. The air flow was measured by means of the wet test meter W, which was filled

SORPTION APPARATUS

FIG 9.



with dibutyl phthalate. The flowrate was adjusted by a capillary flowmeter, containing dibutyl phthalate as the manometer liquid, and the water blow-off. Accurate adjustment of the flow was obtained by moving the air tube on the blow-off up or down. The air stream could be admitted to the conditioner by the three-way stopcock S_1, and to the cell or diverted by the stopcocks S_2 and S_1, the rubber tube being removed from S_1 in the latter case.

The cyanogen chloride was contained in a glass ampoule A, of about 150-c.c. capacity, which was connected to a 10-litre ballast volume V_2 by 8 mm. glass tubing, using as little rubber connecting tubing as possible, since CNCl attacks rubber slowly. To keep the vapour pressure of the cyanogen chloride constant to ensure a constant flowrate, it was necessary to keep the ampoule in a thermostat(T). For this purpose, a large glass beaker, well lagged on the outside, was employed. This contained a coil immersed in water through which tap water at 22°C. circulated. A manometer M served to indicate the pressure of the cyanogen chloride. The flow was adjusted by means of a small steel needle valve N_1 and a capillary flowmeter F_2 containing mercury. Dibutyl phthalate or other organic liquid could not be used as a manometer fluid because of the solubility of CNCl in them. The CNCl could be admitted at will to the air stream by opening the stopcock S_4, or diverted to the waste pipe through the stopcock S_5. The sorbate system was connected to a Hyvac pump through the stopcock S_6 for purposes of evacuation. Any CNCl in the ballast volume was, of course, thoroughly flushed out with air before the system was evacuated.

The conditioner for the charcoal (E) consisted of a pyrex tube about a foot long and two inches in diameter which was wound with nichrome wire and lagged with asbestos. At the upper end there was a ground joint and stopper J, for filling, and an air outlet S_7. The lower end had an air inlet and was connected to the air tube leading to the cell through a short piece of rubber tubing, which could be closed with a pinch clamp P_1, to the ground joint J_2. The temperature of the conditioner was adjusted by a rheostat in the electrical circuit. Dry, carbon dioxide-free air from the purification train was passed through the charcoal during the conditioning process.

The cell (suspended under J_3) was filled with charcoal by opening the screw clamp P_1, raising the conditioner slightly and tapping it. Packing of the charcoal in the cell was always uniform since the charcoal always fell from the same height. No contamination of the charcoal with CO_2 or water vapour could occur.

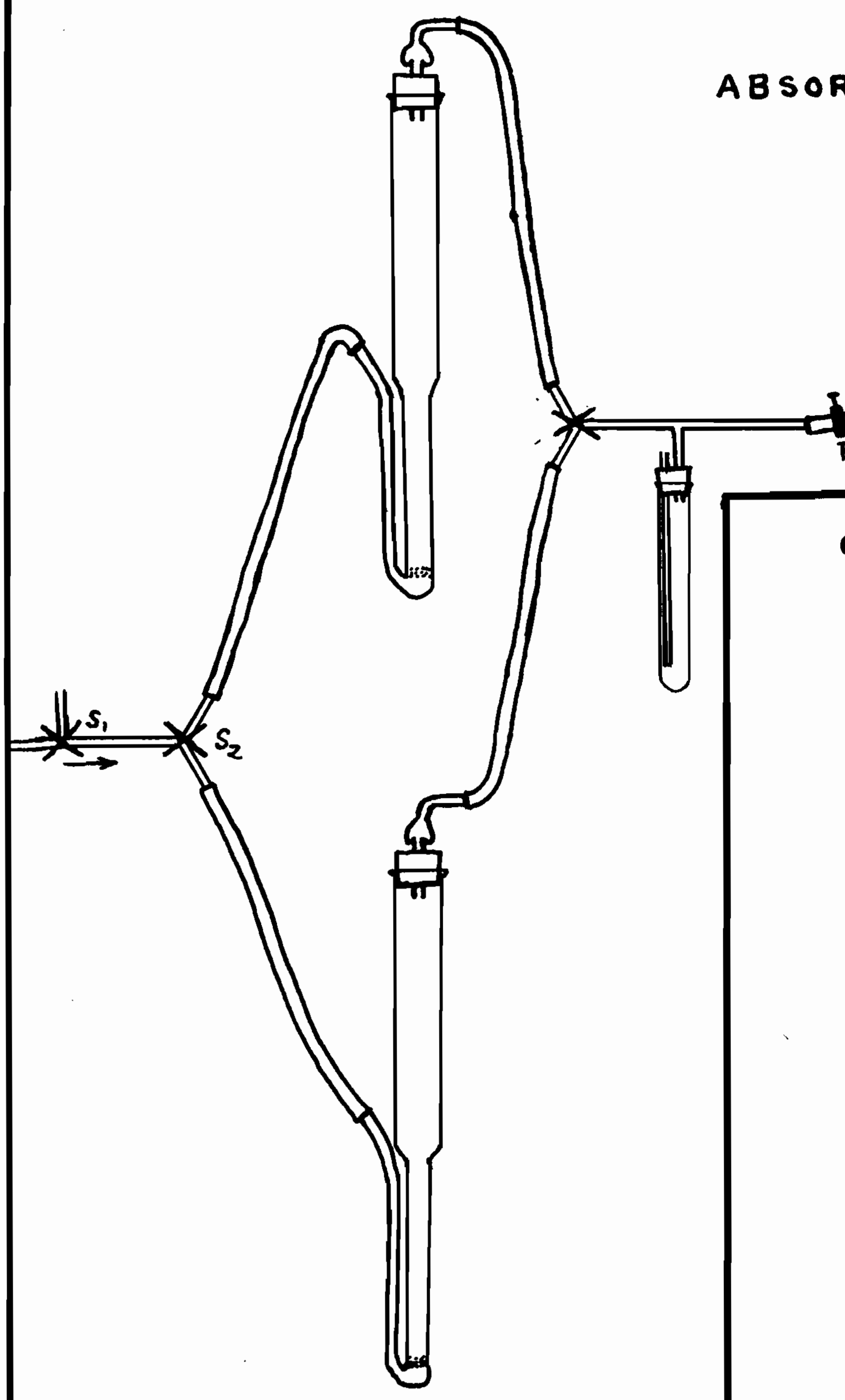
The cell itself consisted of a piece of pyrex tubing 4 cm. inside diameter and 21 cm. long. The top of the tube was fitted with a brass cap sealed to the glass with de Khotinsky cement. Through the centre of this cap was soldered a brass tube 7 cm long and 1.5 cm. in diameter, which extended into the cell. To the lower end of the cell was cemented a narrow brass ring having two projections which fitted into oblique slots in a removable brass cap similar to the one at the top of the cell. By this means an air-tight joint between the cap and the bottom of the cell was secured. A piece of brass tubing of the same dimensions as that at the upper end extended downward from a hole in the centre of this cap. On the inside of the lower cap was soldered a light brass ring about 1 cm. high which just cleared the inside of the tube and to which was attached a circular piece of metal gauze similar to that used as a charcoal support in respirators. This gauze supported the charcoal and allowed free exit to the gas stream. Two small thermal junctions were cemented to this gauze and extended upwards to heights of 1.5 and 2.5 cm. above the gauze near the centre of the cell. They were constructed of copper and constantan, 28 B & S gauge. Connection to the rest of the thermocouple was secured through three pieces of lacquered copper wire, about 40 B & S gauge. Voltage readings were made with a Cambridge unipivot galvanometer.

The cell was suspended through a hole in the bottom of an analytical balance by a light wire support to an arm of the balance. The brass tubes dipped into cups which contained a light hydrocarbon oil having a low viscosity and low vapour pressure, and in which cyanogen chloride was not very soluble. The physical properties of the oil permitted fairly accurate weighing of the cell. A 100-mg. rider was employed. A fixed cell was also constructed, which could be connected directly to the air inlet by a ground joint instead of the oil seal. This cell was found useful in certain instances.

Analysis of the effluent stream presented many difficulties. It was not thought feasible to employ gas sampling methods, and direct absorption of the CNCl in various solutions was resorted to. Sintered glass disc bubblers were used, and the type of tower found most suitable is illustrated in fig. 10. The sintered glass discs were prepared in this laboratory and were of very coarse porosity. A small amount of wetting agent, Aerosol OS, was added to the solutions to produce foaming and thus increase the efficiency of absorption. In the stopper at the top of each tower was fitted a small glass bulb of the form illustrated in fig. 10 in which could be put a drop of capryl alcohol to break the foam if it should rise into the outlet tube. To overcome the back pressure of the sintered glass disc and the column of absorbing liquid, gentle suction was applied by a water aspirator. Adjustment of the suction was secured with an air inlet tube projecting into a tube of phosphoric acid, and fine adjustment with two screw pinch-clamps P_1 and P_2 on the suction line. The suction was adjusted so that no change in the level of the oil in the seals on the cell occurred when the air stream was passed through one of the absorption towers containing the absorbing solution. The effluent stream could be connected to the waste pipe or to either of the bubblers by the stopcocks S_1 and S_2.

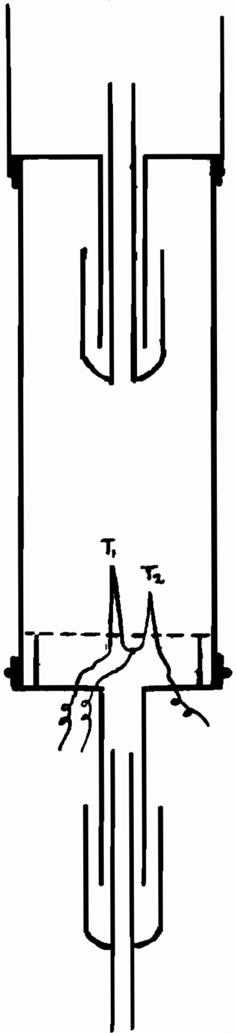
ABSORPTION SYSTEM

FIG. 10



CHARCOAL CELL

FIG. 10A



For the determination of CNCl as thiocyanate, the absorbing solution was 50 c.c. of Na_2S solution (100 gm. of $Na_2S \cdot 9H_2O$ per litre), as recommended by Hinshelwood(24). Cyanogen chloride reacts with Na_2S, yielding thiocyanate.

$$Na_2S + CNCl \longrightarrow NaCNS + NaCl$$

The thiocyanate was determined by Schulek's method(25). This method involves converting the thiocyanate to cyanogen bromide by the action of bromine water, and titrating the iodine liberated from an excess of potassium iodide by the CNBr.

$$NaCNS + Br_2 \longrightarrow CNBr + S + NaBr$$

$$CNBr + 2KI \longrightarrow I_2 + KCN + KBr$$

To the alkaline solution in a glass-stoppered flask 15 c.c. of 40% H_3PO_4 were added, and the mixture boiled for five minutes to drive off the H_2S and coagulate the sulphur produced by the action of the acid on the Na_2S. The flask was then cooled rapidly to room temperature, and bromine water was added until a persistent yellow colour appeared. After half an hour, 2 c.c. of 5% phenol were added to remove the excess bromine, and the flask was shaken vigorously and repeatedly during half an hour. Finally 5 c.c. of 10% KI were added, the flask allowed to stand in the dark for half an hour to two hours, and the liberated iodine was titrated with 0.04N thiosulphate (standardized against CNCl by the above procedure), using starch as indicator. Schulek's method was found to be more accurate and less troublesome than the usual colorimetric method in which ferric thiocyanate is formed by adding $FeCl_3$ to the slightly acidified solution containing thiocyanate and comparing the resulting reddish-brown colour with a standard prepared at the same time as the unknown.

It was also desirable to have a method of analysing for one of the possible decomposition products of CNCl, and determination of total chloride was chosen as the most suitable procedure. Absorption of the CNCl in the effluent stream in cold 0.5N NaOH and titration of chloride gave poor checks. No better results were obtained when 2N NaOH was employed, but when the CNCl was absorbed in hot (about 80°C) NaOH, the chloride analyses checked quite well, and also agreed with thiocyanate determinations on samples taken in Na_2S solution at the same time. This seemed to indicate that failure of absorption occurred in cold 0.5N NaOH owing to the slowness of the hydrolysis reaction. Finally, a procedure was evolved and standardized in which 0.5N NaOH containing 25 c.c. of Reagent grade pyridine per litre was used as the absorbing medium. It is well known that cyanogen chloride reacts with pyridine itself, forming a reddish compound. It was found that the pyridine-base solution became slightly yellow in the presence of CNCl, the yellow colour fading slightly on standing, and disappearing when excess acid was added. The reactions which occur are not known. This absorbing solution foamed easily, only a trace of Aerosol OS being necessary to stabilize the foam. Probably a high concentration of pyridine existed in the foam films, owing to the surface-active character of pyridine.

After absorption of the effluent CNCl in 50 c.c. of the pyridine-NaOH solution described above, 5 c.c. of concentrated nitric acid were added, and the mixture allowed to stand for ten hours or more. The chloride was titrated with 0.05N mercuric nitrate solution, using sodium nitroprusside as indicator. For each 10 c.c. of solution being titrated, 0.1 c.c. of 10% sodium nitroprusside was used. This method was found to be very rapid and accurate, and is more sensitive than titration with silver nitrate. The solution must be acid, but the concentration of acid does not have to be adjusted. The method depends upon the formation of practically unionized $HgCl_2$, and an indicator which shows the presence of mercuric ion is employed. In the presence of sodium nitroprusside, a turbidity appears at the end point due to the formation of highly insoluble mercuric nitroprusside. There is a small indicator blank of approximately 0.17 c.c. which is not constant, but varies with the concentration of $HgCl_2$. This blank was neglected in the larger titrations, as it is well within the experimental error.

A saturated alcoholic solution of diphenylcarbazide was also employed as indicator, but when used in aqueous solution under the above conditions, the indicator blank was constant and about 0.5 ml. Apparently it is more sensitive when the titration is carried out in alcoholic solution. Diphenylcarbazide gives a violet colour at the end-point.

Another method for the determination of CNCl, which involves absorption in 0.5N NaOH in 50% methanol and titration of the Cl^- is under investigation, and appears to give favourable results.

PROCEDURE

A supply of conditioned charcoal was kept in the conditioner. This charcoal was conditioned at 150°C. in a current of dry, CO_2-free air for twelve hours, and air was allowed to circulate for an additional twelve hours after the current was turned off. The conditioner was shut off from the atmosphere by closing the air inlet and outlet. Enough charcoal was conditioned at one time for several runs.

The airflow and the CNCl flow were adjusted at the desired values with the help of the flowmeters, and the oil seals on the charcoal cell were conditioned by passing the air-CNCl stream through the empty cell for about two hours. Several determinations of the influent concentration were made by passing the gas mixture through absorbing solutions for known periods of time. The CNCl flow was diverted to the waste pipe, and the empty cell was weighed after having been flushed out with a small amount of pure air. The air flow was deflected to the waste pipe, and charcoal was dropped into the cell to the desired depth. The cell containing the charcoal was then weighed without air flowing, and then with air flowing. The time was noted, the CNCl stream was turned into the cell again, and time, weight and temperature readings were taken at appropriate time intervals. One or two samples of the effluent stream were taken before the expected break time, and several more between the break time and saturation, the time at which sampling was begun and ended being noted. The sampling interval was chosen to give a convenient quantity of CNCl for determination, the interval being calculated from the influent CNCl flowrate and the change in weight of the cell with time. The wet test meter was read at the beginning of the run, and several times during the run. The CNCl and air flowmeters were read occasionally, and the temperature of the air stream, back pressure due to the purification train and barometric pressure were recorded. A few desorption studies were also made. When saturation was attained, the CNCl flow was shut off, the time noted, and weight readings were taken while pure air was passing through the charcoal. Occasional samples of the effluent stream were also taken.

The weight readings were accurate to 0.002 gm. in most cases. The overall experimental error was about 5%. Variations in the CNCl flow, errors in time of sampling, and variation in room temperature because of the necessity of having good ventilation accounted for at least part of this error.

The materials employed in this investigation were

Charcoal,	Canadian SB (unimpregnated) Canadian S.B.T., silver impregnated
Cyanogen chloride,	Prepared and purified as described in Part I.

Because of the large number of observations made during a run, complete data for each run are not recorded here, but a typical data sheet follows, to illustrate the essential observations made during a run.

TYPICAL DATA SHEET

N.B. These data have been condensed for the sake of clarity.

Run 15

Airflow: 6.24 l./min. CNCl flow: 68 mg/min.
= 4.96 c.c./min./cm.^{2}

Atmospheric pressure: 751 mm. Hg. Air pressure: 2.58 in. Hg.
(65 mm. Hg.)

Temperature of air: 82.5°F. (28°C.)

Depth of charcoal bed (measured) 3.0 cm.
(calculated) 3.1 cm.

Cross-section of bed: 12.57 cm.^{2}

Weight of charcoal plus cell (air flowing): 29.496 gm.
(still): 29.411 gm.

Weight of cell (air flowing): 8.906
(still): 8.906

Weight of charcoal: 20.505

Final weight (charcoal plus cell): 35.710

CNCl sorbed: 6.214

Air meter readings:

Initial 760.92 cu. ft.
860.63

99.71 cu. ft. Time: 441 min.

$$\text{Air rate} = \frac{99.71}{441} \times 28.3 \times \frac{273}{301} \times \frac{816}{760} = 6.24 \text{ l./min.}$$

Time min.	Cell Weight gm.	Gain in Weight gm.	T_1 °C	T_2 °C
0	29.496	0.000	21.6	21.9
2.3	29.596	0.100	24.2	23.4
4.55	29.760	0.264	29.2	23.8
18.23	30.650	1.154	38.2	30.5
20.91	30.840	1.344	39.2	31.8
23.12	30.978	1.482		
28.00	31.198	1.702	39.8	34.0
32.26	31.600	2.104	39.3	34.6
37.19	31.920	2.424	39.0	35.5
40.20	32.120	2.624	38.1	35.8
43.13	32.300	2.804		
47.59	32.600	3.204	36.8	36.2
54.12	32.992	3.490	35.2	36.0
60.50	33.327	3.831	33.9	34.9
65.26	33.580	4.084	32.7	34.3
72.00	33.881	4.385		
80.50	34.168	4.672		
83.59	34.268	4.772	29.5	30.3
90.00	34.432	4.936	28.3	29.0
103.33	34.695	5.199	26.3	27.0
112.41	34.835	5.339	25.6	26.1
120	34.944	5.448	25.6	25.5
130	35.033	5.537		
138	35.100	5.604		
150	35.176	5.680	23.4	24.5
162	35.241	5.745	23.6	23.8
171	35.269	5.773	23.6	23.8
182	35.299	5.803		
236	35.395	5.899	23.0	23.3
276	35.430	5.934	23.0	23.3
412	35.695	6.199	22.2	22.5
439	35.705	6.209	22.3	22.7
499	35.710	6.214	21.8	22.0

Analytical data for the effluent stream

Sample	Time in min.	Mg. CNCl/min.	Mg. CNCl/cu.m./min.
M	19-20	0.09	14.4
O	46-48	16.9	1430
P	81-82	32.6	5230
R	182-183	55.5	8910

RESULTS AND DISCUSSION

Analytical Methods

As stated on pp. 47 and 48, the CNCl in the effluent stream from the charcoal cell was determined as thiocyanate and as chloride. The CNCl concentration data, unless otherwise stated, were obtained from the thiocyanate determinations. In Table 7 and fig. 11 a comparison of the results of the two methods is given for run 12. Thiocyanate values appear to be slightly higher than chloride for low concentrations, but both methods check well. The experimental error in sampling is quite large, and is generally not less than 2%.

Sorption Data

A summary of the data obtained from the runs made is given in Table 8. For each run data were obtained for the weight of CNCl sorbed at different times, and for effluent concentrations. When the initial concentration of CNCl was not too low, temperature measurements were also made. Runs were carried out over a range of bed depths, air flowrates and CNCl flowrates. To obtain a complete picture of the variation in the different quantities as the variables λ, L and c_o were altered one at a time would require approximately eighty runs for a single charcoal. Since it was not the purpose of this investigation to provide experimental evidence to prove or disprove the theories of dynamic sorption, no such extensive investigation has been made.

TABLE 7

Comparison of Chloride and Thiocyanate Analyses of Effluent Stream, Run 12

Time (min.)	Thiocyanate mg. CNCl	 mg/min/m^3	Chloride mg. CNCl	 mg/min/m^3
185-195	0.025	3.9		
196-207			0.019	3.0
345-355			0.10	15.8
355-365	0.153	24.2		
438-444			1.55	245.
444-450	1.70	269.		
557-563			4.32	684.
563-568	4.46	706.		
855-860			5.61	889.
860-865	6.68	1050.		
865-870			5.87	930.
874-879	6.94	1100.		
879-884			6.40	1010.
884-889	6.64	1050.		

EFFLUENT CNCl - TIME CURVES

(RUNS 12, 17 AND 18)

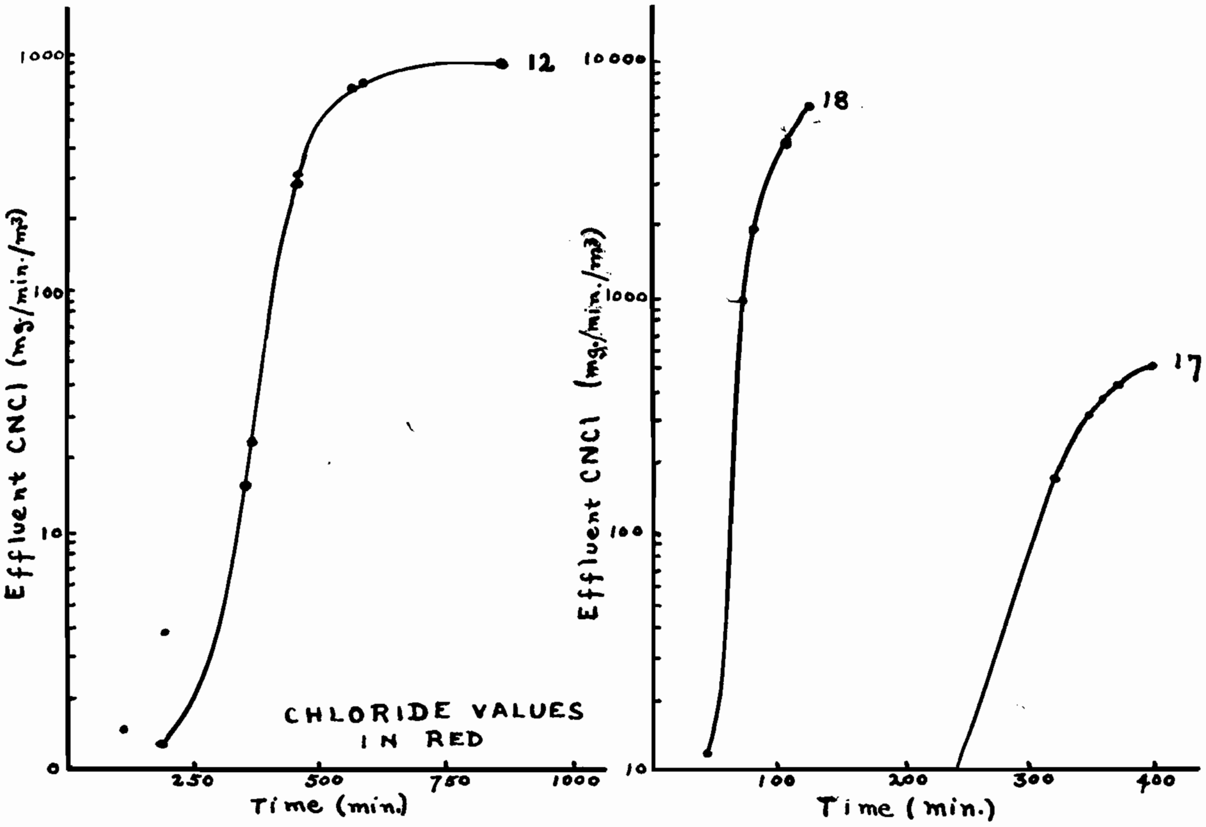


FIG. 11.

TABLE 8

Summary of Sorption Data for CNCl

Run No.	Bed Depth (cm.)	Air flow ml/cm^2/min	CNCl flow mg/min.	CNCl conc. mg/l.	Service Time By Analysis min.	Service Time From Sorption Curve min.	Total Wt. Sorbed gms.
Canadian S.B.T. Charcoal							
1	5.19	413	68	13	77	95	10.03
2	5.11	381	68	14.1	60	100	9.24
3	4.75	395	68	13.7	67	97	10.00
4	5.13	379	44	9.2	117	145	8.63
6	4.07	381	69	14.3	36(Cl$^-$)	75	6.47
7	3.12	362	68	14.9	27	58	5.3
8	4.13	131	20	12.1	320	360	3.06
9	3.30	378	14	2.9	175	215	2.92
10	2.82	382	23.5	4.9	60	120	3.68
11	4.04	509	24.5	3.8	105	135	5.11
12	4.98	502	6.6	1.0	350	440	3.47
13	4.92	313	69.	17.5	90	115	10.75
14	4.77	497	68.	10.8	80	90	9.85
15	3.12	496	68.	10.9	30	55	6.2
16	5.01	501	1.6	0.25	850	850	2.2
S.B. Charcoal (unimpregnated)							
17	5.02	483	5.7	0.93	250	300	2.757
18	5.03	490	66.5	10.8	46	70	7.895

Weight sorbed-time curves

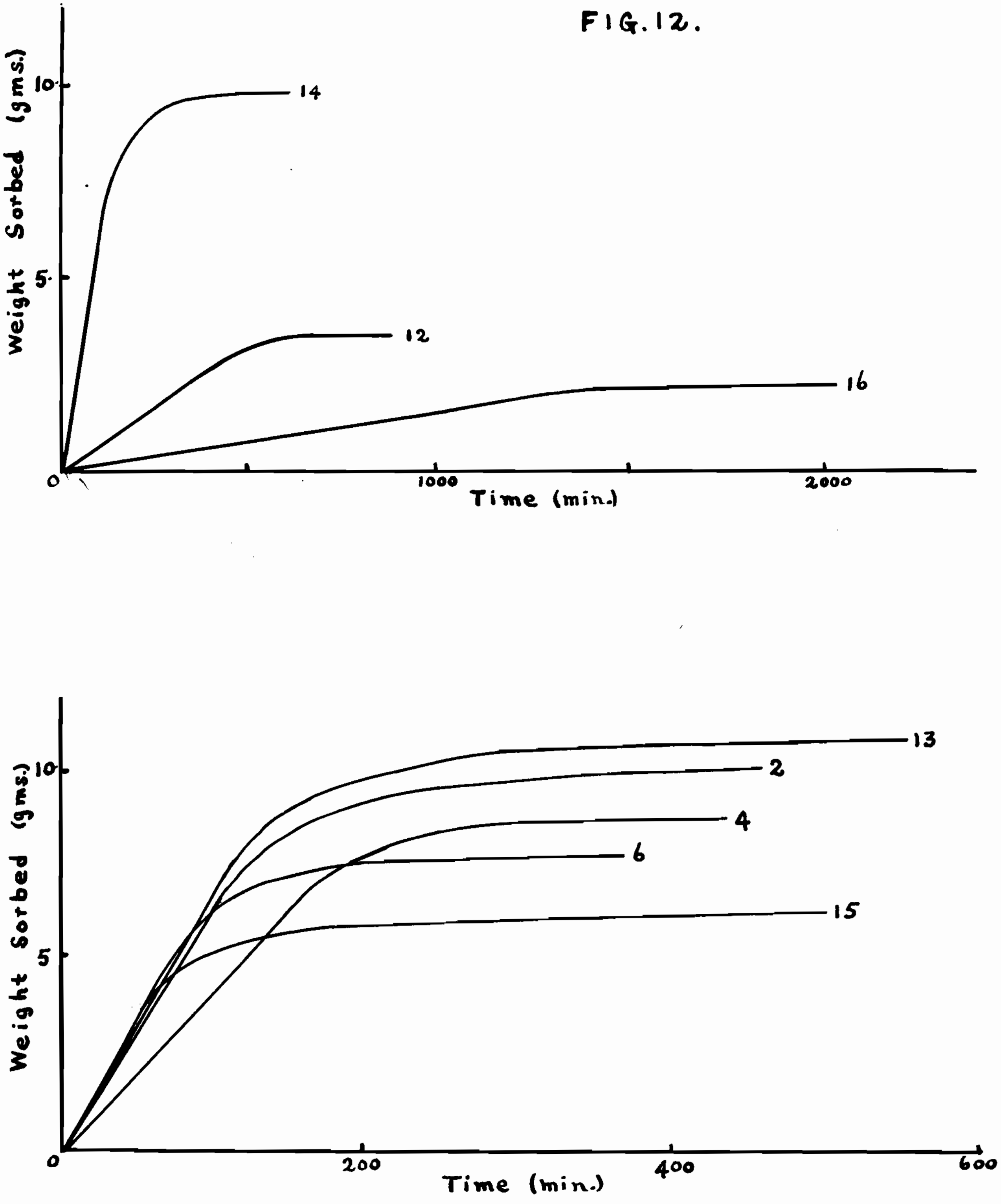
The shape of the sorption isotherms is shown in figs. 12 and 13. The rate of sorption is constant over the first part of the curve, and then decreases, until finally equilibrium is reached. This equilibrium was attained quite readily, and a small change in the CNCl flowrate at saturation immediately made itself apparent in a change in the weight of the cell.

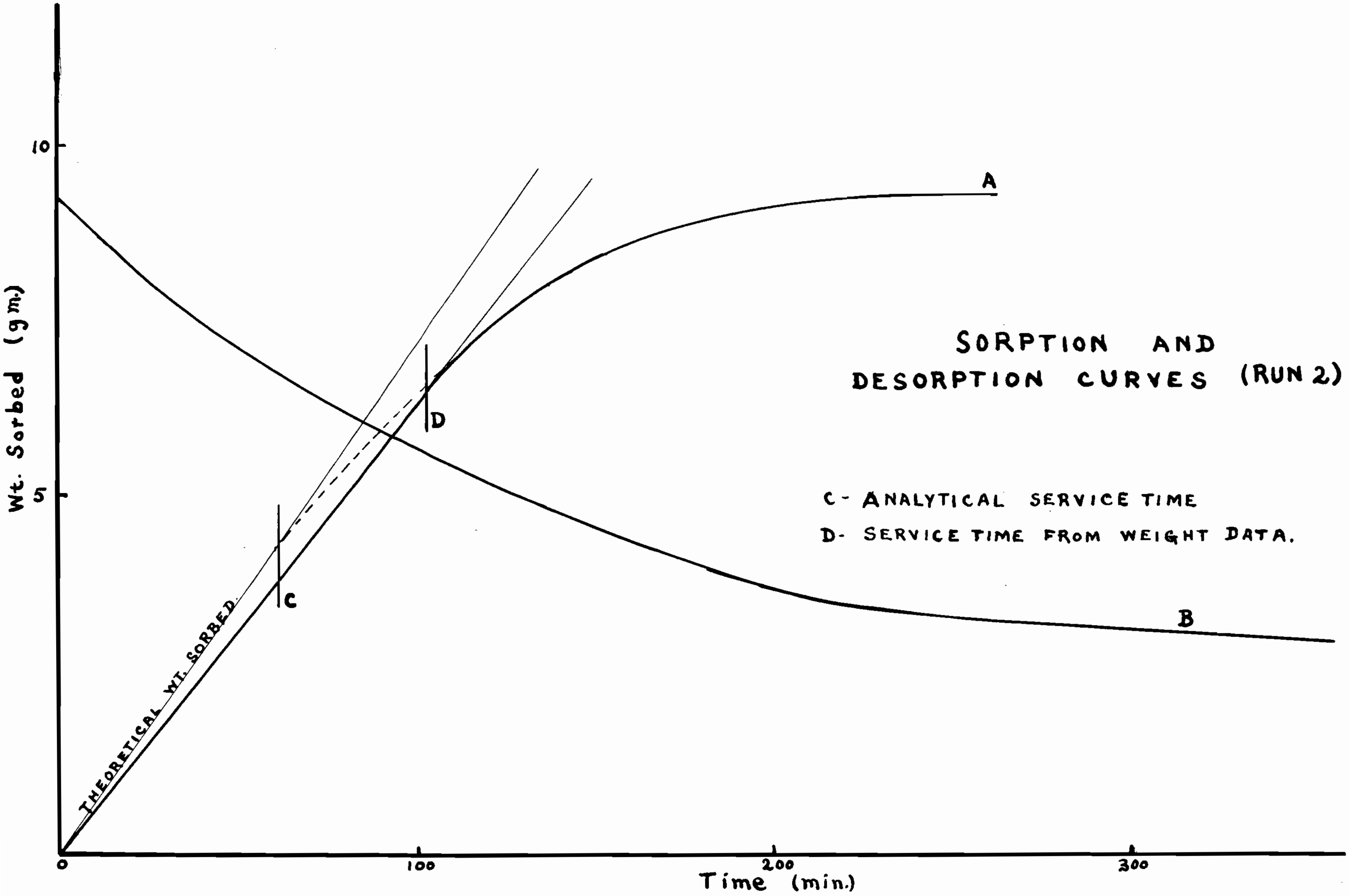
This apparently easily reversible equilibrium at saturation was quite different from the behaviour during desorption. When pure air was passed over charcoal saturated with CNCl, desorption took place readily at first, the rate of desorption falling off continuously with time, as illustrated in fig. 13. Finally a point was reached where the rate of desorption became very small, although several grams of CNCl remained on the charcoal. In run 2, for example, 2.61 gm. of CNCl were still present on the charcoal after approximately thirteen hours, the decrease in weight during the last seven hours being only 0.16 gm. Some static sorption studies might, perhaps, offer an explanation for this behaviour. Two different types of sorption may occur simultaneously: a small proportion of the CNCl being held strongly perhaps by true unimolecular adsorption, and the remainder of the CNCl sorbed through capillary condensation. The possibility of polymerization of the CNCl on the charcoal to cyanuric chloride must not be overlooked.

WEIGHT SORBED – TIME CURVES

(NUMBERS REFER TO RUNS)

FIG. 12.



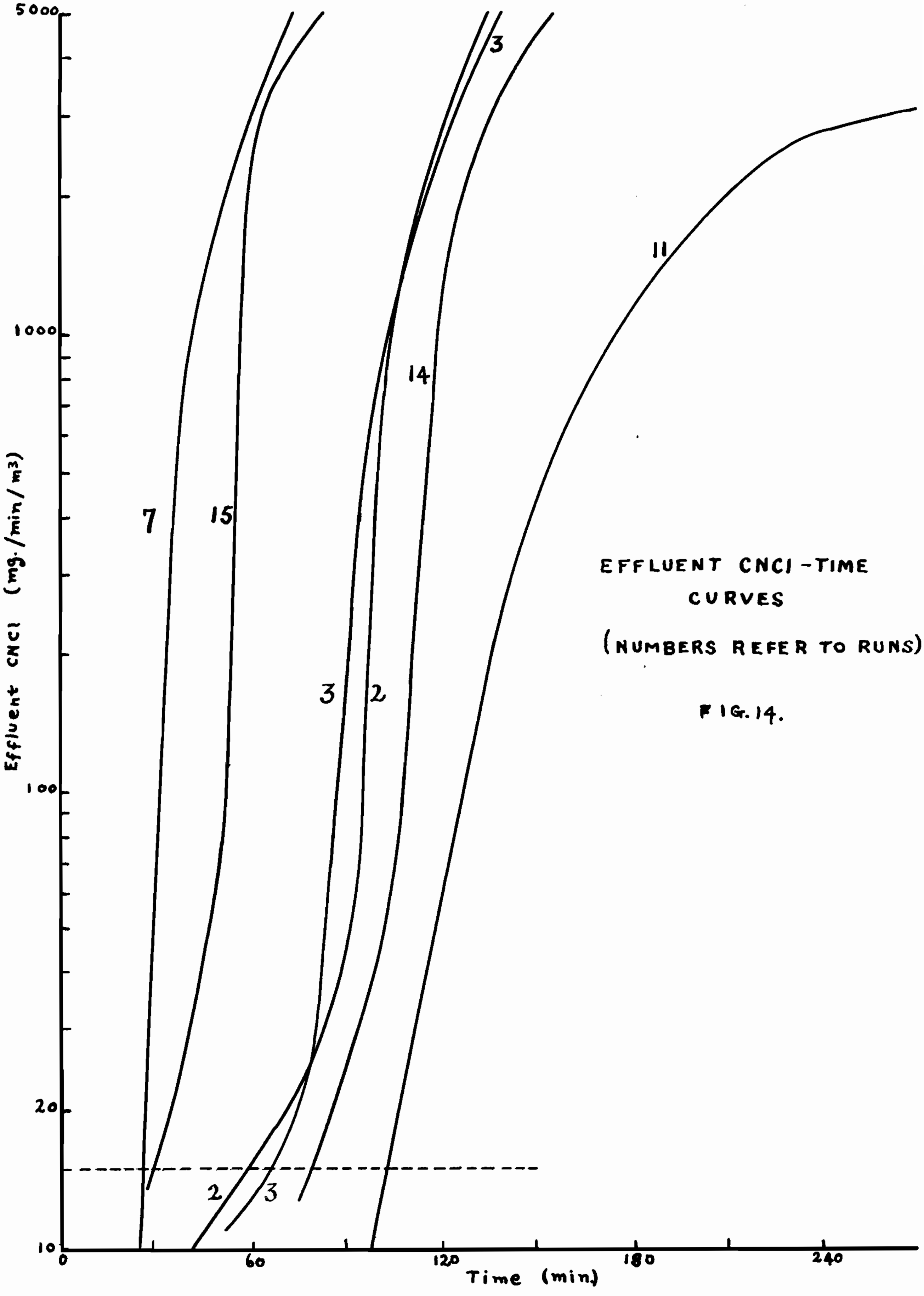


SORPTION AND DESORPTION CURVES (RUN 2)

Effluent concentration curves

The effluent concentration curves were plotted on a semi-logarithmic scale so that the entire range of concentrations could be shown in a satisfactory manner. The service times were obtained from these curves by determining the points at which a horizontal line at the concentration 15 mg. per cu. metre (the physiologically determined break concentration) cut the curves. The first few samples taken during a run tended to give high results for the CNCl concentration because of the absorption of CNCl by the rubber connecting tubes when high concentrations were passed through them, and its emission at low concentrations. Sometimes the concentration in early samples exceeded 15 mg per cu. metre but this value decreased to the correct one after one or two samples were taken. Loss of CNCl from the lower oil seal on the cell also accounted for part of this error.

According to the theory of Hinshelwood et al, the concentration of CNCl in the effluent stream should increase exponentially with time after breakdown. The effluent concentration-time curves plotted on a semi-logarithmic scale are in general linear over an interval past the break concentration, but begin to bend towards the time axis some time before saturation is attained. Examples of these curves are given in figs. 11 and 14.



EFFLUENT CNCl -TIME CURVES

(NUMBERS REFER TO RUNS)

FIG. 14.

The Service Time

The service time was obtained by two methods: (a) by analysing the effluent stream and determining the time at which a concentration of 15 mg./cu.m. was reached, as described above, and (b) by determining the point on the weight sorbed vs. time curve where the rate of sorption began to fall off, i.e., the point at which the charcoal ceased to be 100% efficient in removing CNCl from the air stream. A comparison of the service time obtained by these two methods is given in Table 8. It will be seen that the latter method gives higher values than the former except when the CNCl flowrate is small. The discrepancy is much greater than the error in estimating the point at which the sorption isotherm deviates from a straight line.

If the increase of weight of the charcoal with time as determined from the CNCl flowrate is plotted with the sorption isotherm, as in fig. 13, it is seen that the slope of the linear part of the sorption curve is smaller than the calculated slope. This behaviour was noted by Ogilvie and Davis(19, 20), and they attributed it to the desorption of air. Analytical results for the effluent CNCl concentration indicate that the loss of CNCl from the charcoal before the service time is not great enough to account for the discrepancy between the theoretical and actual rate of increase in weight of the charcoal, so that displacement of air from the charcoal by the CNCl offers the only logical explanation of the phenomenon. The sorption of air during the desorption of CNCl, and the converse phenomenon of the desorption of air during the sorption of CNCl are clearly shown in Table 9.

The desorption of air accounts in part for the difference in the values of the service time as determined by analysis from the weight sorbed-time curve. Referring to curve A of fig. 13, if the curved portion of the isotherm is extrapolated back to touch the calculated weight-time line, the service-time D thus obtained agrees well with the analytically determined service-time C. This extrapolation is, of course, very inaccurate, and is intended only to give a qualitative indication of the reason for the discrepancy in the service-time values.

Service times were plotted against initial concentrations (c_o) and against $\frac{1}{c_o}$ for three runs in which the bed depth and airflow were constant. The theory of Hinshelwood et al predicts that τc_o = const., that is, a plot of τ against c_o gives a rectangular hyperbola. As will be seen from fig. 15, the behaviour of CNCl approximates to this relation over the range of concentrations studied. Three points are not sufficient to determine the shape of this curve with any degree of accuracy, and determinations over a greater range of concentrations might yield valuable information. The plot of τ vs. $\frac{1}{c_o}$ (fig. 16) is not a straight line, but bends towards the $\frac{1}{c_o}$ axis at high concentrations. According to Lister's theory, if sorption is reversible, this line should become horizontal at very low concentrations, that is, τ increases to reach a constant value as c_o decreases. More runs at lower concentrations should offer evidence in favour of, or against this theory.

TABLE 9

The Desorption of Air by CNCl and the Desorption of CNCl by Air.

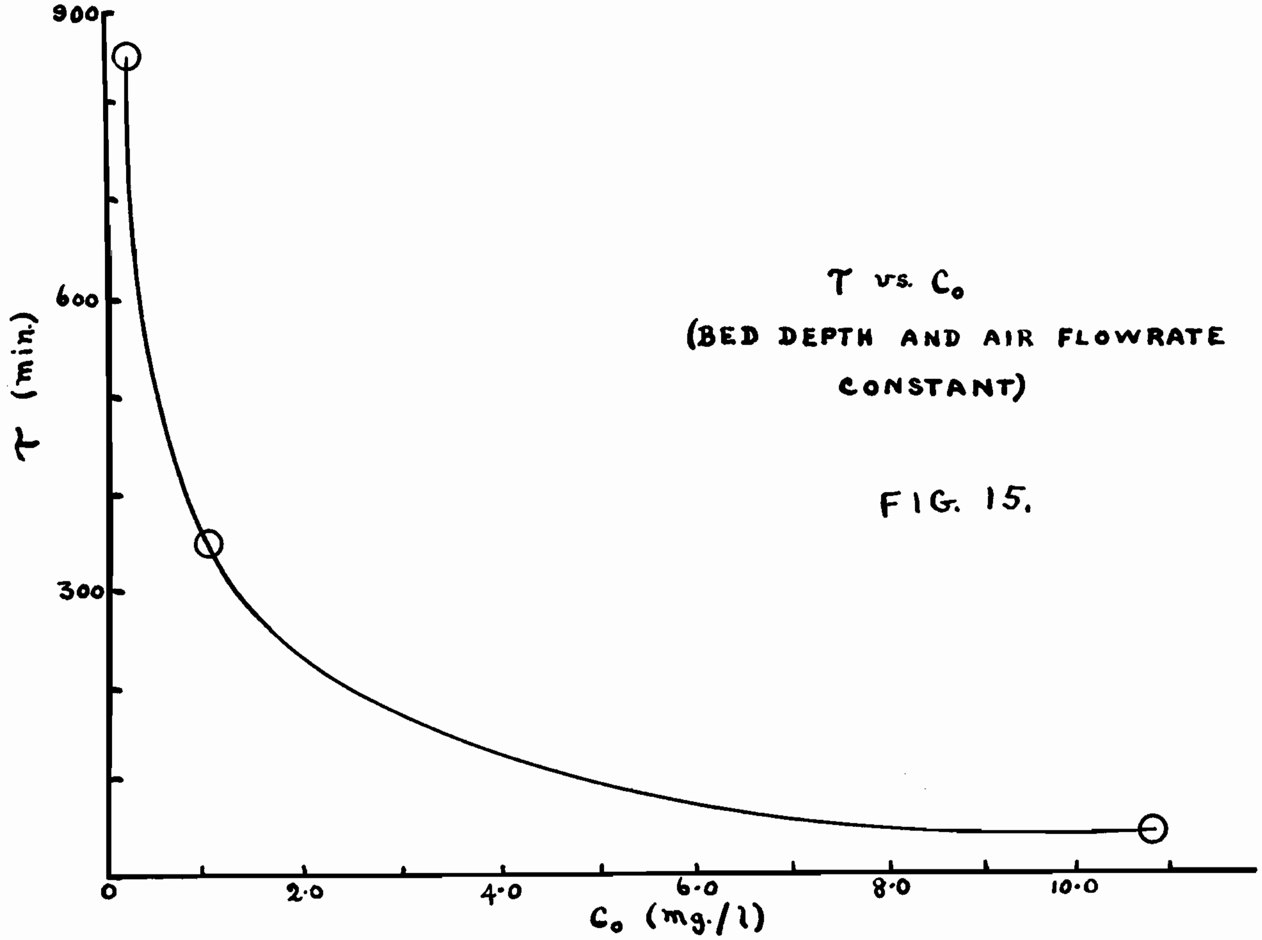
	Sorption of CNCl				Desorption of CNCl		
Run No.	Rate of increase of cell wt. before break mg./min.	Influent CNCl rate mg./min.	Effluent CNCl rate mg./min.	Time min.	Time min.	Effluent CNCl rate mg./min.	Rate of decrease of cell wt. mg./min.
2	63.6	68.	0.06	45	154	12.8	14.0
12	6.6	6.6	0.03	130	13	6.3	6.5
					242	5.0	4.0
					470	2.2	1.9

TABLE 10

Variation of Service Time with Initial Concentration

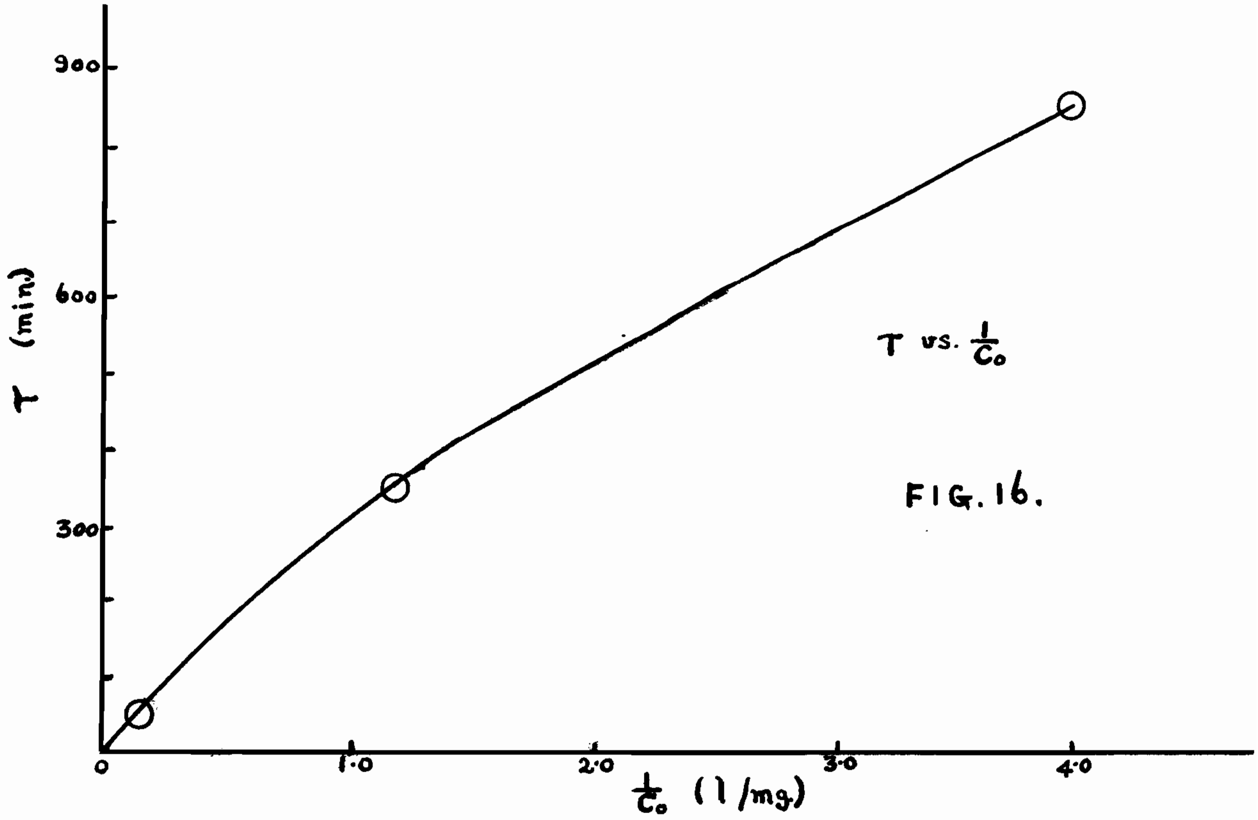
Bed depth 5 cm. Air flowrate 500 c.c./min./cm.^{2}

Run No.	Initial CNCl Concentration c_o mg./l.	$\frac{1}{c_o}$ l./mg.	Service time min.
16	0.25	4.00	850
12	1.03	0.97	350
14	10.8	0.09	80



τ vs. C_o
(BED DEPTH AND AIR FLOWRATE CONSTANT)

FIG. 15.



τ vs. $\frac{1}{C_o}$

FIG. 16.

The service time may be visualized as the time when a definite concentration gradient is set up through the charcoal bed. Between service time and saturation, this concentration gradient moves upward through the bed with constant velocity. It might be expected then that some relation exists between the weight of charcoal sorbed per gram ($\frac{x}{m}$) at the service time and the initial concentration for a given bed depth similar to that between $\frac{x}{m}$ at saturation and the initial concentration. In the former case, the $\frac{x}{m}$ would represent an average value, since the CNCl concentration varies continuously through the length of the bed. Data are given in Table 11 for three runs, and the shape of the $\frac{x}{m}$ vs. c_o curves is shown in fig. 17. Curves A and B appear to be similar in shape, but the latter curve flattens out before the former.

Temperature-Time Data

Temperature-time curves are given in fig. 18 for two representative runs. The lower curves represent the temperature of the lower junction in the cell. The maximum in the upper curve occurs a short time before breakdown, and serves as a good indication of its approach. The maximum in the lower curve occurs at, or slightly after breakdown. The rise in temperature of the charcoal bed during sorption should decrease the service time, since a rise in temperature decreases the amount of sorption. The theories of dynamic sorption assume isothermal sorption occurs, but this is only true when the

TABLE 11

Weight of CNCl Sorbed per Gram of Charcoal at Service Time and at Saturation

Bed depth 5 cm. Air flow 500 c.c./min./cm.^{2}

Run No.	Initial CNCl conc. c_0 mg./l.	Total wt. CNCl Sorbed gms.	Wt. CNCl sorbed at Service Time gms.	Wt. Charcoal gms.	$\frac{x}{m}$ At Saturation	$\frac{x}{m}$ At Service Time
16	0.25	2.20	1.32	32.896	0.062	0.040
12	1.03	3.47	2.30	32.708	0.106	0.070
14	10.8	9.85	5.25	31.306	0.314	0.167

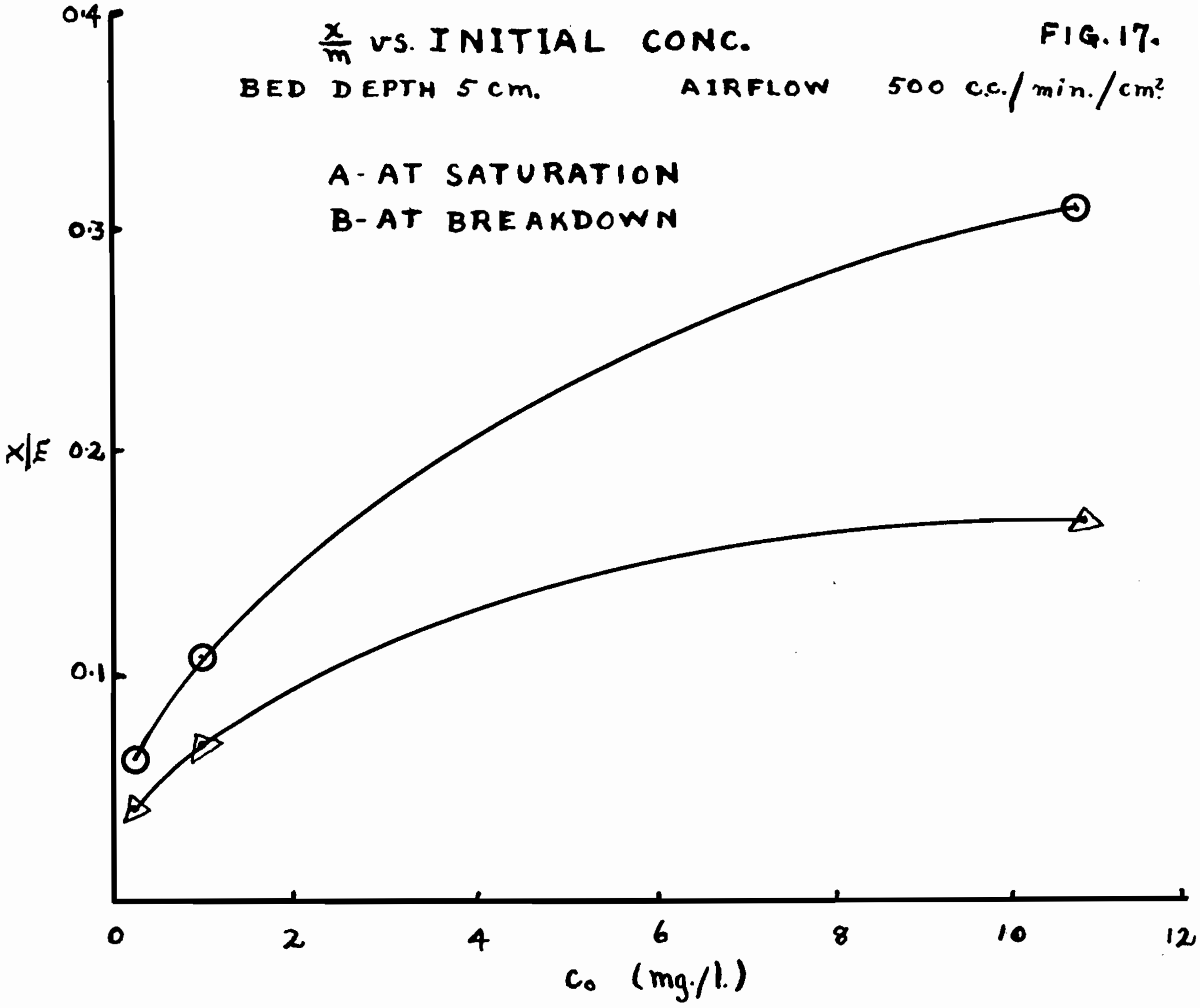

$\frac{x}{m}$ vs. INITIAL CONC.
BED DEPTH 5 cm.
AIRFLOW 500 c.c./min./cm²
A - AT SATURATION
B - AT BREAKDOWN
0.4
0.3
x/E 0.2
0.1
0
2
4
6
8
10
12
C_0 (mg./l.)

FIG. 17.

concentration of sorbate is low or when the airflow is large. The lowering of the temperature of the charcoal bed during desorption has been noticed, but no extensive observations on this phenomenon have been made.

Behaviour of different charcoals

The variation of service time and total weight sorbed with silver-impregnated and unimpregnated charcoals under similar experimental conditions is illustrated in Table 12. The CNCl service time is shorter for the unimpregnated charcoal at both high and low concentrations than for the silver-impregnated, and the weight of CNCl taken up at equilibrium is greater for the latter charcoal than for the former.

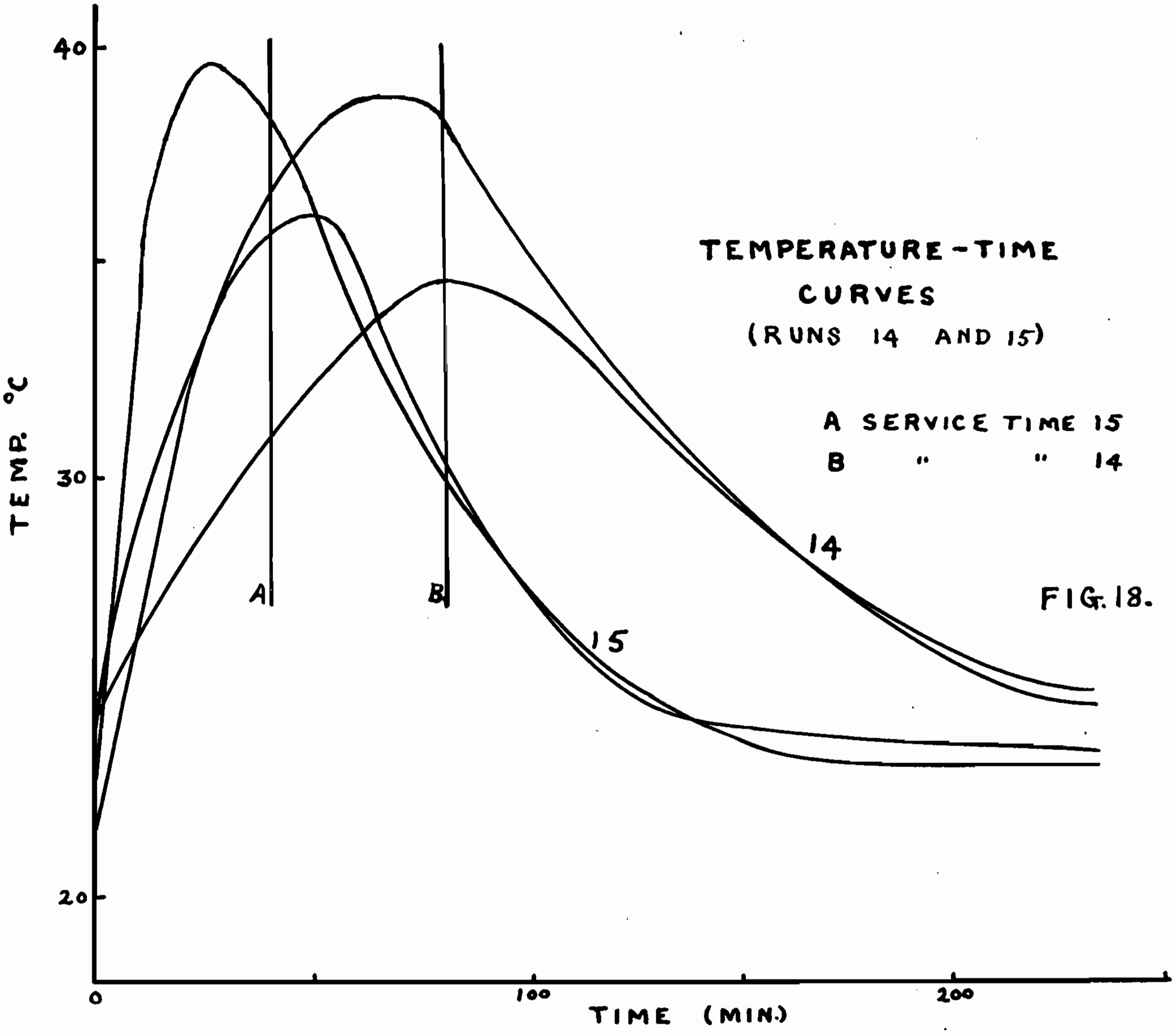

TEMPERATURE-TIME
CURVES
(RUNS 14 AND 15)
A SERVICE TIME 15
B " " 14
TEMP. °C
40
30
20
0
100
200
TIME (MIN.)
A
B
14
15

FIG. 18.

TABLE 12

Comparison of Unimpregnated and Impregnated Charcoals

Bed depth 5 cm. Air flow 495±10 c.c./min/cm.^{2}

	Initial CNCl conc. c_o mg./l.	Service Time min.	Total wt.CNCl at saturation gm.
Charcoal S.B.T. (Ag impreg.) (Volume Activity 20.2)	1.03	350	3.47
	10.8	80	9.85
Charcoal S.B. (Unimpreg.) (Volume Activity 17.7)	0.95	250	2.76
	9.27	46	7.90

CONCLUSIONS

The dynamic sorption of CNCl by dry charcoal has been studied over a range of concentrations, air flowrates and bed depths. Weight sorbed-time and effluent concentration-time curves have been obtained, and service times determined for various conditions. In addition, the temperature rise at two levels of the charcoal bed has been followed with thermocouples.

The sorption of CNCl on dry charcoal has been shown to be partially reversible. At saturation, equilibrium is shifted very readily by a small change in the CNCl flowrate. During desorption, the rate of removal of CNCl decreases steadily until it reaches a small value, part of the CNCl being held very tightly by the charcoal. No explanation of this behaviour is offered, but the possibility of the existence of two types of sorption operating simultaneously, or the polymerization of the cyanogen chloride on the charcoal to cyanuric chloride has been suggested.

The desorption of air during the sorption of CNCl and the converse process of sorption of air during desorption of CNCl has been demonstrated, and hence service times and CNCl flowrates determined from weight sorbed-time curves are not accurate unless the CNCl concentration is small (about 1 mg. per litre).

The effluent CNCl concentration has been shown to increase approximately exponentially with time over an interval past breakdown, as predicted by the theory of Hinshelwood et al.

The product τc_0 was found to be essentially constant over the range of concentrations studied. No conclusions as to the validity of Lister's theory when applied to the sorption of CNCl can be drawn owing to lack of data at low concentrations.

The results described above must be regarded as preliminary to a great deal of work yet to be done. The effect of various charcoal impregnants and the effect of moisture on the charcoal are now under investigation using the apparatus described previously.

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SUMMARY

Cyanogen Chloride - Preparation, Physical Properties, Hydrolysis and Sorption on Charcoal

Cyanogen chloride of high purity has been prepared by fractional crystallization of the product obtained by the method of Jennings and Scott. Freezing point and vapour pressure measurements have been made on the pure substance.

The hydrolysis of cyanogen chloride in aqueous solution at pH 4 to 6 has been studied over the range 0°C to 50°C. The rate of hydrolysis was found to be independent of the CNCl concentration. The activation energy calculated from initial rates is 20,670 cal./mole.

The dynamic sorption of cyanogen chloride on dry charcoal has been studied at bed lengths from three to five centimetres, and CNCl concentrations of 0.3 to 11 mg. per litre. The sorption process has been found partially reversible, and the desorption of CNCl has been demonstrated. The weight sorbed-time curves are linear for part of their length, and flatten out at saturation. During desorption, the rate of loss of CNCl decreases continuously to a small value, part of the sorbed CNCl being held very tightly. Service times determined from the sorption isotherms have been found to agree poorly with those determined analytically, and this discrepancy has been explained by the desorption of air. The product of the service time and

initial concentration was essentially constant over the range of concentrations studied, a small deviation occurring at the higher concentrations. The behaviour of CNCl on dry charcoal appears to be in accordance with the theory of Hinshelwood et al.

M.Sc Chemistry

Donald Edward Douglas

War Research

Cyanogen Chloride - Preparation, Physical Properties, Hydrolysis and Sorption on Charcoal.

Cyanogen chloride of high purity has been prepared by fractional crystallization, and some physical constants have been determined.

The hydrolysis of cyanogen chloride in aqueous solution at pH 4 to 6 has been studied from 0° to 50°C. The activation energy is 20,670 cal./mole.

The dynamic sorption of cyanogen chloride on dry charcoal has been studied. Sorption has been found to be partially reversible, and desorption of air by cyanogen chloride has been demonstrated. The product of the service time and initial concentration was found to be essentially constant over the range of concentrations studied, in accordance with the theory of Hinshelwood et al.