THE ACTION OF CHARCOAL ON AQUEOUS SOLUTIONS OF SILVER NITRATE.

by

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The Action of Charcoal on aqueous Solutions of Silver Nitrate.

INTRODUCTION.

It has been known for a considerable time that certain metallic salts in aqueous solution undergo reduction by contact with charcoal [1]. Until recently the charcoals investigated were prepared from complex materials containing hydrogen [2]. Hence it was natural to suppose that the reducing properties of the charcoal might be due simply to the presence of hydrocarbons, or hydrogen, produced by the decomposition of the original substance. Recently, however, Heymann, Salomon, and Kieffer [3] have observed reduction in the case of charcoal prepared by passing carbon tetrachloride vapour over heated mercury. Since this method of preparation excludes the formation of hydrocarbons, or hydrogen, it must be concluded that the carbon itself is involved in the reducing process.

Further investigation is required in order to ascertain the precise manner in which the charcoal acts. In particular it is necessary to know the actual amount of reduction under any given set of conditions. The fact that the determination of the amount of reduction is complicated by the adsorption of the/

the substance undergoing reduction, and of the products of reduction, probably accounts for the lack of essential data. It will be shown that in the case of silver salts, the amount of reduction may be accurately estimated by a simple method.

Hitherto the action of charcoal on silver salts in aqueous solution has not been studied in detail. Morawitz [4] observed that when a solution of silver sulphate, or acetate, was shaken with charcoal, the silver content of the solution decreased rapidly for a short time, and then much more slowly over a long period. It was also found that acid appeared in the solution, and that the tendency of silver to disappear from the solution was more pronounced in the case of the acetate, than in the case of the sulphate. Bartell and Miller [5] have examined the action of ash-free charcoal, prepared from sugar, on solutions of silver nitrate, sulphate, and acetate. They found that sufficiently dilute solutions remained neutral though deprived of the whole of their silver, whereas more concentrated solutions became acid. Ruff, Ebert, and Luft [6] investigated the X-ray spectra obtained with various charcoals after contact with either a neutral solution of silver nitrate or one to which nitric acid had been added. Interference lines, characteristic of metallic silver, were obtained, provided the concentration of acid did not exceed a certain value.

Warlet [7], who also worked with sugar charcoal, has shown that a portion of the salt, in a solution of silver nitrate, is simply adsorbed by the charcoal, and can be recovered by treating the latter with water.

In view of the foregoing, attention in the present work was primarily directed to the influence of (1) concentration of silver nitrate, (2) time of contact between charcoal and solution, (3) acidity of solution, (4) treatment of charcoal, on the amounts of adsorbed silver, reduced silver, and liberated acid. With regard to the charcoal, the effect of treatment with air, oxygen, nitrogen, hydrogen and carbon dioxide, at different temperatures was particularly examined. Measurements of adsorption from solutions of nitric acid, sodium hydroxide, and iodine were made in some instances, in order to elucidate the results obtained with the silver nitrate.

EXPERIMENTAL.

Preparation and Standardisation of Solutions.

A.R. chemicals were used throughout the investigation except in the case of potassium thiocyanate which was, however, of good quality, and free from chloride. All solutions were prepared with good distilled water, and stored in Jena resistance glass bottles. All volumetric apparatus was calibrated; and a rigid procedure adopted for the measuring out of small quantities. The accuracy of delivery of the 0.5 c.c., 1 c.c., and 2 c.c. pipettes, was 0.1%, 0.05%, and 0.05%, respectively.

Nitric acid solutions were standardised with a standard sodium carbonate solution, using phenol red as indicator. Near the end point the solution was boiled vigorously to expel carbon dioxide, after the addition of each drop of acid.

Sodium hydroxide solutions were standardised with nitric acid, using phenol red as indicator.

Iodine, in potassium iodide solution, was standardised with pure arsenious oxide.

Silver nitrate solutions were standardised by Volhard's method, observing the precautions discussed by Kolthoff and Furman*. When not in use, the silver nitrate solutions were kept in the dark; and standardisations made from time to time showed no change in the concentrations.

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* Kolthoff and Furman, "Volumetric Analysis", Vol.1. (1928), 107

Adsorption Procedure.

In all the adsorption experiments, unless otherwise, 10 c.c. of solution and 0.2 gm. of charcoal were thoroughly shaken for 24 hours, at room temperature. The shaking was performed in sealed glass tubes which were fixed radially on a slowly rotating wheel. The tubes which were of soft glass, were rendered as inert as possible by treatment with chromic acid, followed by thorough washing with distilled water, and drying in an oven.

Analysis.

When the shaking was completed, the tubes were unsealed after standing for a moment to allow the solution to drain from the walls, and the charcoal to settle. To prevent any appreciable evaporation, immediately a tube was opened, the solution was decanted through an ashless filter paper, and collected in a tightly stoppered pyrex tube. Portions of filtrate were measured out for analysis as soon as possible. Iodine solutions were filtered through a plug of glass wool, and titrated immediately with sodium thiosulphate.

All titrations were performed in duplicate.

Determination of Liberated Acid.

A solution of silver nitrate becomes acid, on treatment with charcoal. It was found possible to determine accurately the amount of liberated acid, by direct titration with sodium hydroxide, using phenol/

phenol red as indicator. A sharp end point was obtained provided the alkali was added, drop by drop, with constant shaking, to the boiling solution.

The standard silver nitrate solutions showed a slight acidity (roughly proportional to the concentration of silver nitrate) for which the necessary correction was applied.

Determination of Total Adsorption of Silver.

The silver content of the filtrate was determined by Volhard's method. In order to have as large titrations as possible when the concentration of silver in the filtrate was low, the acid and the silver were determined in the same portion of filtrate. After determining the acid as already described, the solution was evaporated almost to dryness, and then warmed with 2 c.c. of concentrated nitric acid, to discharge the colour of the phenol red. The solution was then cooled, and the silver determined in the usual way.

The applicability of the method was verified by blank determinations with known amounts of silver nitrate.

Determination of Reduced Silver.

The charcoal was carefully transferred to the filter paper, and washed several times to remove the bulk of the silver nitrate. To eliminate all the remaining ionic silver, the stem of the filter funnel was closed, and the charcoal/

charcoal covered with a solution of potassium chloride (0.3M.) for thirty minutes. The potassium chloride was then filtered off, and the charcoal washed until free from chloride.

To extract the reduced silver, the charcoal, contained in the filter paper, was heated with nitric acid (approx. 8.0M) for one hour, at 100°. After shaking the mixture to expel dissolved oxides of nitrogen, it was filtered and washed into a porcelain basin, and titrated with potassium thiocyanate in the usual way.

Measurement of Temperatures.

Temperatures above 900° were measured with a Cambridge optical pyrometer, reading to within ± 10° for materials radiating as "black" bodies, such as the walls of a furnace at uniform temperature. The pyrometer might be regarded as a photometer in which, by simply rotating the eyepiece, a beam of monochromatic red light from the hot body was adjusted to equal intensity with a beam of similar light from an incandescent filament through which a constant current was maintained. The pyrometer was standardised by adjusting the filament current until the light emitted was of equal intensity with the light from an amylacetate lamp, burning under carefully regulated conditions. This standardisation was checked by sighting the pyrometer on a Cambridge platinum/

platinum resistance thermometer, heated in an electric furnace. Over the range 900° - 1250°, the readings of the optical pyrometer were consistently higher than those of the platinum resistance thermometer by 15 ± 5°, and the mean values were taken.

The temperature was not read directly during the actual treatment of the charcoal, but the calibration of the furnace temperature against the heating current, showed that the temperature could be reproduced to within 10°. Below is given the data for two calibrations of the high temperature furnace p. 17.

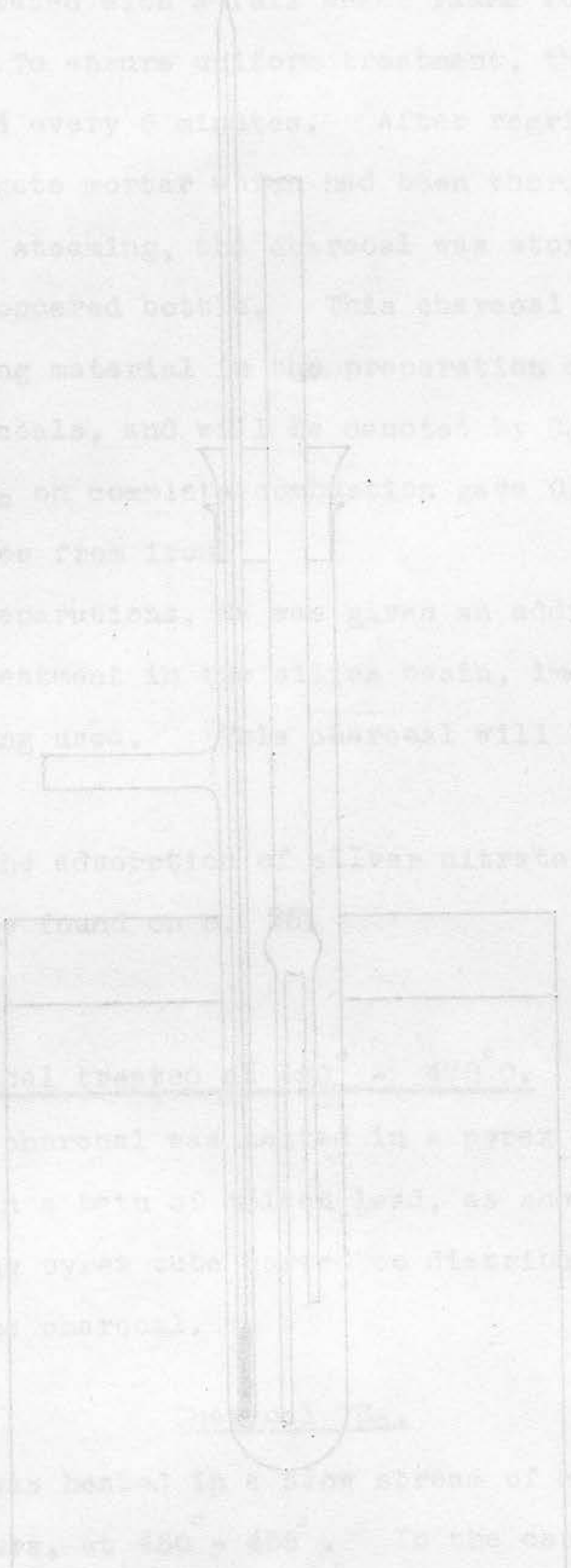
First Calibration		Second Calibration	
Current (amps.)	Temperature (°C.)	Current (amps.)	Temperature (°C.)
3.60	900	3.60	910
4.00	965	4.05	965
4.10	1000	4.15	1010
4.60	1140	4.60	1113
5.10	1250	5.10	1240

For an approximate determination of the temperature of the charcoal heated in a silica basin, with a full Meker flame, a Fe/Ni thermo-couple was used. The thermo-couple was standardised against a platinum resistance thermometer. The temperature of the charcoal varied from 740° to 830°, the bulk of the charcoal being at, approximately, 780°.

Low temperatures, 450° - 470°, were measured with a mercury, in silica glass, thermometer. In this case the bulb of the charcoal was immersed in the charcoal during treatment.

Preparation of Ash Free Sugar Charcoal.

A.R. saccharose was heated, in small portions at a time, in an 8" porcelain basin. A glass plate was placed above the basin to protect it from atmospheric dust. The charring sugar was found to remove the glaze from the basin. To avoid contamination from this source, the first three lots of charcoal were rejected, and the basin was covered with a hard crust of charcoal, about ¼in. thick, which kept the melted sugar from coming in contact with the heated porcelain. When the sugar had been converted into a thick black mass evolving inflammable vapours, the glass cover plate was removed, and the mass ignited, and allowed to burn itself out. The light, flaky charcoal obtained was powdered, placed in a silica basin covered with a loosely fitting lid,/



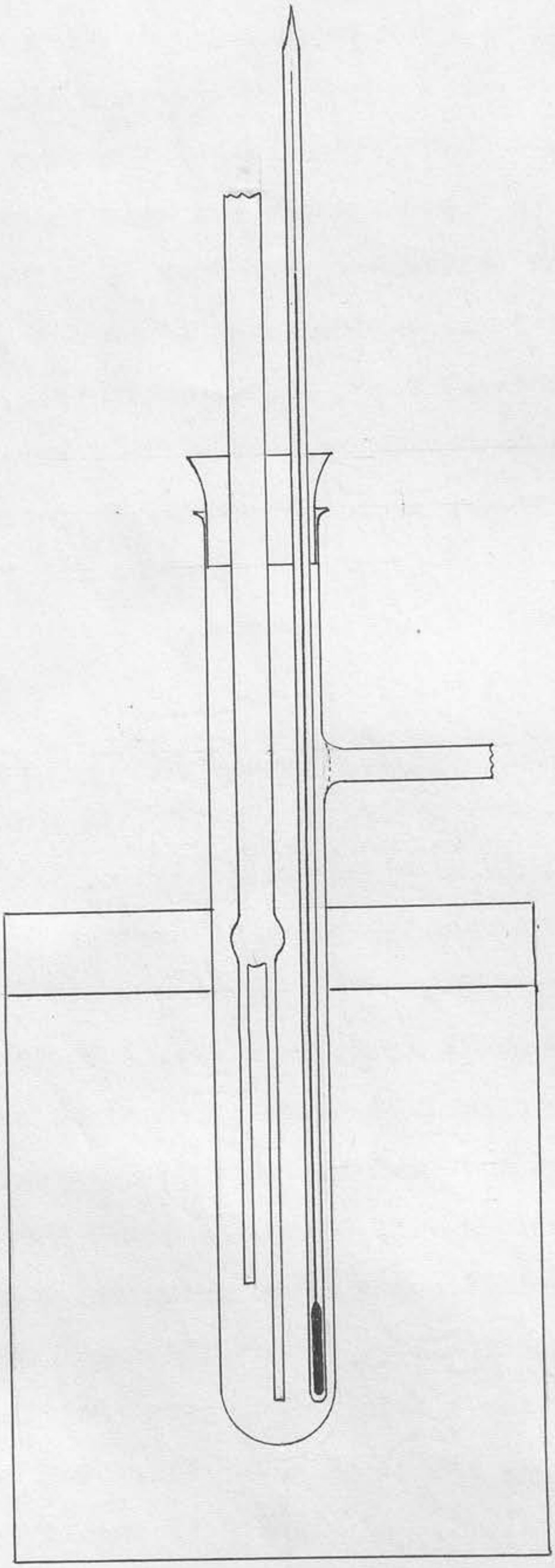


FIG. 1.

lid, and heated with a full Meker flame for 40 minutes. To ensure uniform treatment, the charcoal was stirred every 5 minutes. After regrinding in a smooth agate mortar which had been thoroughly cleaned by steaming, the charcoal was stored in a tightly stoppered bottle. This charcoal served as the starting material in the preparation of all the other charcoals, and will be denoted by C_a. Two grams of C_a on complete combustion gave 0.0004 gm. of ash, free from iron.

In some preparations, Ca was given an additional 30 minutes treatment in the silica basin, immediately before being used. This charcoal will be denoted by C_b.

Data for the adsorption of silver nitrate by C_a, and C_b, will be found on p. 25.

Charcoal treated at $450^\circ - 470^\circ$C.

The charcoal was heated in a pyrex tube immersed in a bath of molten lead, as shown on p.10 A two prong pyrex tube served to distribute the gas through the charcoal.

Charcoal C_c.

C_b was heated in a slow stream of moist air, for 11 hours, at $450^\circ - 455^\circ$. In the case of both C_c and C_d, the amount of combustion was very small.

Air was freed from acid gases and moistened, by bubbling it through dilute sodium hydroxide solution.

Charcoal C_d.

C_b was heated in a slow stream of dry air, for 11 hours, at 460° - 470°.

Air was freed from acid gases with soda lime (1ft.), and dried with phosphorus pentoxide (3ft.).

Charcoal C_e.

C_b was heated in a slow stream of dry hydrogen, for 8 hours, at 455° - 465°.

In the preparation of C_e, and C_f, the hydrogen (from a cylinder) was freed from oxygen with an alkaline solution of pyrogallol, and dried with calcium chloride (4ft.).

Charcoal C_f.

C_b containing 0.5% platinum, was heated in a slow stream of dry hydrogen, for 8 hours, at 455°-465°.

C_b was platinised by shaking 10 grams of charcoal with 50 c.c. of platinum chloride solution (containing 0.01 gm. Pt)., for 12 hours. The charcoal was then washed several times with water, and dried in vacuo at 100°.

Charcoal C_g.

8 gms. of C_a were treated with dry chlorine for 2 hours. Excess chlorine was removed by heating in a stream of hydrogen for 48 hours. Finally, the charcoal was treated with dry oxygen for 3 hours. The/

The loss of weight during activation was 6 gm. The temperature throughout the treatment was 460° - 465°.

Chlorine, hydrogen and oxygen (from cylinders) were dried with sulphuric acid. Before displacing chlorine with hydrogen, and hydrogen with oxygen, the apparatus was cooled to prevent combination of the gases. Hydrogen, after having been passed through the charcoal for 48 hours, still contained a slight trace of hydrogen chloride; 10 c.c. of water shaken with 0.2 gm. of C_g, showed a slight acidity of 8 micromols acid liberated per gm. of C_g. In the oxygen treatment, approximately 60% of the exit gas (CO_2) dissolved in sodium hydroxide; and the remainder burned quietly with a blue flame, and was, therefore, largely carbon monoxide.

Charcoal C_h.

17 gms. of C_a were treated with dry oxygen for 3 hours at 450° - 460°. The amount of combustion was 9 gms.

Oxygen was dried with calcium chloride (4ft.)

Charcoal C_i.

C_a was heated in a stream of dry nitrogen, for 9 hours, at 450° - 470°.

Nitrogen was freed from oxygen with red-hot copper gauze, and alkaline pyrogallol solution, and then dried with calcium chloride (4ft.).

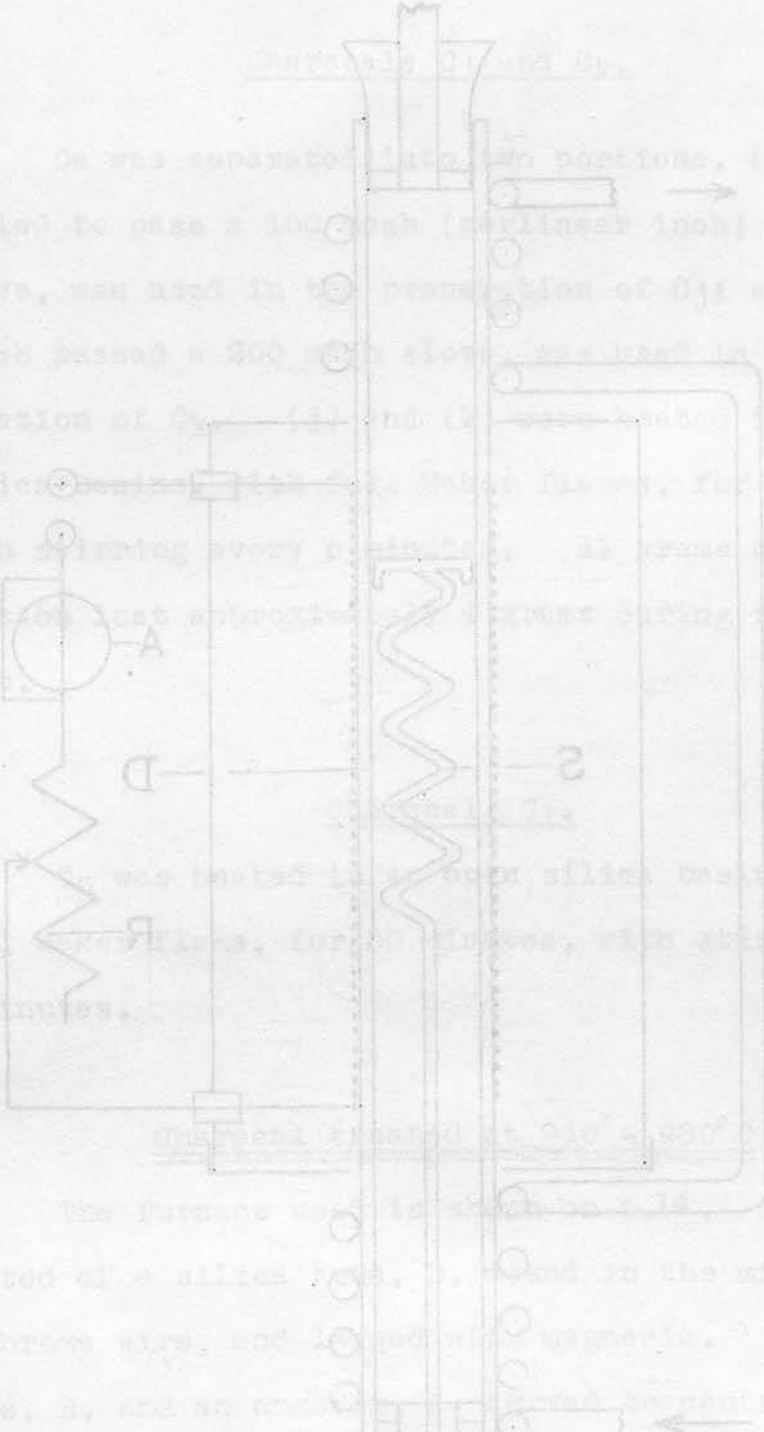


FIG. 2

Charcoal treated at 740° -830°C.

Charcoals C_j and C_k.

Ca was separated into two portions, (j) which failed to pass a 150 mesh (perlinear inch) standard sieve, was used in the preparation of C_j; and (k) which passed a 200 mesh sieve, was used in the preparation of C_k. (j) and (k) were heated in open silica basins, with full Meker flames, for 30 minutes, with stirring every 5 minutes. 11 grams of each portion lost approximately 4 grams during the treatment.

Charcoal C_l.

C_p was heated in an open silica basin, with a full Meker flame, for 30 minutes, with stirring every 5 minutes.

Charcoal treated at 940° - 980° C

The furnace used is shown on p.14. It consisted of a silica tube, D, wound in the middle with nichrome wire, and lagged with magnesia. A resistance, R, and an ammeter, A, served to control the current.

In the preparation of C_m, the charcoal was stirred every 15 minutes by means of the stirrer, S. This consisted of a zig-zag silica rod, one end of which was fixed to a round silica lid which facilitated the introduction/

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In the preparation of C_m, the charcoal was stirred every 15 minutes by means of the stirrer, S. This consisted of a zig-zag silica rod, one end of which was fixed to a round silica lid which facilitated the introduction/

introduction of the charcoal into the furnace, and kept it in the heated zone during treatment; while the other end, which projected into the rubber tubing, was bent to form a small lever which could be turned by twisting the rubber tubing. To prevent overheating of the rubber stoppers, they were faced with asbestos, and the ends of the tube, D, were water cooled.

In the preparation of C_n, C_o, and C_p, the furnace was held in a vertical position, and the silica tube, E, (p.17) containing the charcoal, was introduced. The nitrogen was passed through the charcoal with a two prong silica distributor.

Charcoal C_m.

120 gms. of C_a were treated with dry air, for $4\frac{1}{2}$ hours, at 980°. The amount of combustion was 18 gms.

Air was freed from acid gases with soda lime (1ft.) and dried with calcium chloride (2ft.).

Charcoals C_n and C_p.

C_m (used in the preparation of C_n), and C_b (used in the preparation of C_p) were heated in a slow stream of dry nitrogen for 2 hours, at 900°, and for a further 2 hours, at 945°.

Before heating, air was evacuated from the apparatus, and replaced with nitrogen. Nitrogen

was freed/

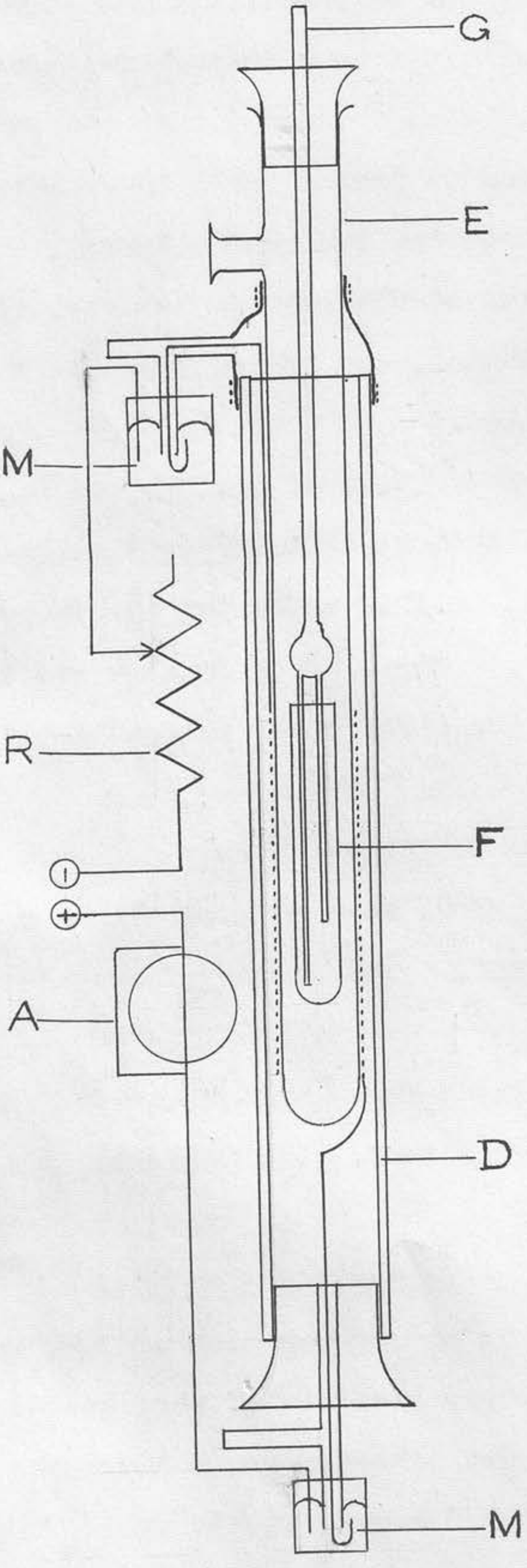

FIG. 3.

freed from oxygen, with hot copper gauze, and a clear alkaline solution of pyrogallol (prepared in an atmosphere of nitrogen), and then dried with calcium chloride (3ft.). At the end of the preparations the pyrogallol solution had darkened only slightly. After leaving the charcoal, the nitrogen was passed through calcium chloride (1ft.), and then through alkaline pyrogallol solution to prevent oxygen from diffusing into the apparatus.

Charcoal C_o.

C_n was treated with intensely dried nitrogen, for 12 days, with occasional heating. After heating the charcoal twice, at 945°, for 2 hours, the furnace fused, and Meker burners were used for further heating (21 hours in all).

Nitrogen was freed from oxygen with hot copper gauze and alkaline pyrogallol solution; and dried with concentrated sulphuric acid (1 ft.) and phosphorus pentoxide (15 ft.). The pyrogallol and the sulphuric acid bubblers were both furnished with two taps, so that they could be refilled every two days.

Charcoal treated at 1000° - 1250° C.

For the treatment of charcoal at and above 1000°, the furnace shown on p.17 was constructed. It consisted of a silica tube, E, wound at the closed end with nichrome wire. To prevent oxidation of the/

the nichrome, tube E was surrounded with another silica tube, D, to form a gas tight jacket which was filled with nitrogen. Two mercury seals, M, formed the terminals of the furnace. The charcoal was contained in the thin walled silica tube, F, which was raised well into the heating zone, by chips of silica placed at the bottom of tube E. Gas was passed into the charcoal through the two prong silica distributor, G. A resistance, R, and an ammeter, A, served to control the heating current.

Charcoal C_q.

C_a was degassed for 4 hours, at 960°, under a pressure of 7 m.m. of mercury, and finally for 1 hour at 1000°, under a pressure of 1 m.m. of mercury.

Charcoal C_r.

C_q was treated with dry air for 2 hours, at 1000°.

There was very little combustion. Air was purified with soda-lime (1 ft.), and dried with phosphorus pentoxide (3 ft.).

Charcoal C_s.

12 gms. of Ca were treated with dry carbon dioxide, for 5 hours, at 1010°. The amount of combustion was 1 gm.

Carbon dioxide, from a Kipp, was freed from hydrogen chloride with water, and dried with calcium chloride (4 ft.).

Charcoal Ct.

C_a was degassed for 1 hour, at 1125°, under a pressure of 1 m.m. of mercury.

Charcoal Cu.

15 gms. of Ct were treated with moist air for 4 hours at 1125°. The amount of combustion was 3 gms.

Air was purified and moistened, by bubbling it through dilute sodium hydroxide solution.

Charcoal C_v.

C_t was treated with moist hydrogen for four hours, at 1125°.

Hydrogen (from a cylinder) was freed from traces of oxygen and moistened, by bubbling through an alkaline solution of pyrogallol.
Before heating, the apparatus was evacuated, and filled with hydrogen.

Charcoal C_w.

C_t was treated with intensely dry nitrogen, for 4 hours at 1125°.

Nitrogen was purified and dried as in the preparation of C_o p. 18.

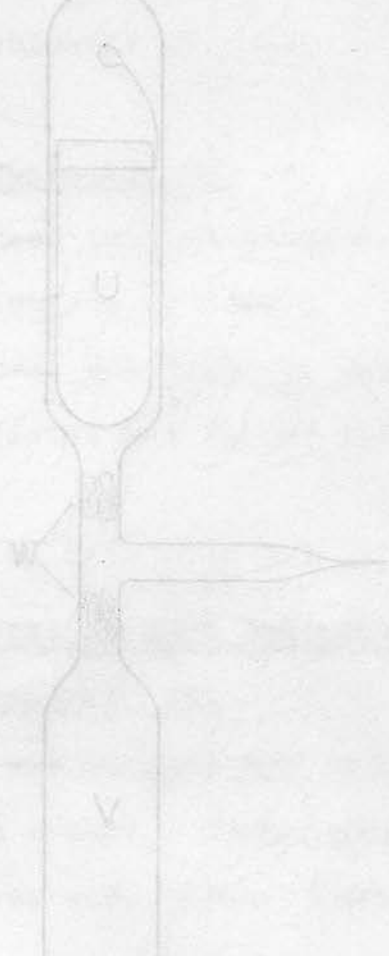

FIG. 4.

Charcoal C_x.

24 gms. of C_a were treated w
8 hours, at 1125°. The amount c
6 gms.

Air was purified with soda-l
dried with calcium chloride (3 ft.

Charcoal C_y.

C_a was introduced into an at
and heated for 35 minutes, at 125(

As silica becomes permeable
1200°, the furnace jacket was fill
dioxide.

Charcoal treated at Room Te

Charcoal C_z.

3.270 gms. C_b was weighed ou
(p.21), and placed in a tube V cont
pentoxide in the lower end. Tube
ated, with the water pump, to 6 m.
sealed off. The cotton wool plug
contamination of the charcoal with
pentoxide.

Decrease in weight after one

Charcoal C_z'.

C_b was placed in a stream of
nitrogen for 1 month.

Charcoal C_x.

24 gms. of C_a were treated with dry air for 8 hours, at 1125°. The amount of combustion was 6 gms.

Air was purified with soda-lime (1 ft.) and dried with calcium chloride (3 ft.).

Charcoal C_y.

C_a was introduced into an atmosphere of CO_2 and heated for 35 minutes, at 1250°.

As silica becomes permeable to gases, above 1200°, the furnace jacket was filled with carbon dioxide.

Charcoal treated at Room Temperature.

Charcoal C_z.

3.270 gms. C_b was weighed out in the tube U (p.21), and placed in a tube V containing phosphorus pentoxide in the lower end. Tube V was then evacuated, with the water pump, to 6 m.m. of mercury, and sealed off. The cotton wool plugs W prevented any contamination of the charcoal with phosphorus pentoxide.

Decrease in weight after one month 0.002 gms.

Charcoal C_z'.

C_b was placed in a stream of intensely dried nitrogen for 1 month.

R E S U L T S.

Adsorption and Reduction of Silver Nitrate.

Table 1.

Charcoal treated at 450° - 470° C.

Charcoal		Initial* $[AgNO_3]$	Final $[AgNO_3]$	A.	B	C
C_c		1.000	-	-	1077	747
		"	-	-	1110	678
		0.2497	0.2148	1760	1018	663
		"	-	-	1064	692
	2 months old	1.000	0.9395	3030	903	720
		"	0.9395	2995	893	683
		"	0.9415	2940	878	742
		"	0.9400	3023	877	725
		0.4986	0.4537	2246	838	686
		0.2497	0.2163	1654	741	607
		"	0.2165	1658	747	612
		"	0.2172	1648	737	602
C_d		1.000	-	-	939	711
		"	-	-	897	696
		0.2497	0.2183	1560	785	596
		"	0.2180	1593	787	600
	2 months old	1.000	0.9438	2821	796	669
		"	0.9433	2820	774	670
		"	0.9460	2705	740	668
		"	0.9460	2743	731	670
		0.2497	0.2197	1501	653	542
		"	0.2197	1522	672	539

* All concentrations are given in mols. per litre. Unless otherwise stated, the adsorption experiments were carried out one or two days after the preparation of the charcoal.

A = Total adsorption of Silver Nitrate, from solution, in micromols per gram of Charcoal.

B = Reduced Silver, in micromols per gram of char.

C = Nitric Acid liberated, " " " " ".

Table 1(Contd.)

Charcoal		Initial [$AgNO_3$]	Final [$AgNO_3$]	A	B	C
C_e	1 day old	1.000	0.9270	3706	1378	1031
		0.4980	0.4390	3000	1389	1092
		0.0992	0.0643	1745	1058	822
	4 days old	1.000	0.9300	3462	1232	951
		0.4986	0.4425	2811	1245	997
		0.2497	0.2061	2211	1100	891
C_f	1 day old	1.000	0.9320	3377	1208	872
		"	0.9320	3488	1224	877
		0.4986	0.4436	2764	1195	925
		0.0992	0.0686	1525	964	670
C_g		1.000	0.9547	2270	703	724
		"	0.9553	2250	703	736
		0.4986	0.4641	1740	689	687
		0.2497	0.2235	1313	600	590
		"	0.2235	1326	618	596
		0.0203	0.0106	481	340	295
C_h		1.000	0.953	2365	880	708
		"	0.955	2270	875	696
		0.4986	0.4631	1786	810	606
		0.2497	0.2213	1417	728	568
		"	0.2213	1390	691	547
		0.0203	0.0109	472	368	215
C_i		1.000	0.9483	2563	1081	792
		"	0.9494	2543	1048	741
		0.4986	0.4580	2048	1036	680
		0.2497	0.2167	1660	900	684
		"	0.2167	1660	900	684
		0.0203	0.0089	570	406	224

Table 2.

Charcoal treated at 740° - 830° C.

Charcoal		Initial $[AgNO_3]$	Final $[AgNO_3]$	A	B	C
Ca	6 months old	0.7504	0.7105	1891	856	580
		"	0.7105	1981	863	591
Cb	1 month old	1.000	0.9503	2520	1101	716
		"	0.9503	2520	1101	716
		0.2497	0.2121	1885	981	688
		"	0.2121	1885	977	688
Cj	2 weeks old	0.9550	0.8937	2923	1088	736
		"	0.8935	2980	1062	707
		0.4803	0.4307	2476	1105	769
		0.2725	0.2338	1915	965	688
		0.0992	0.0743	1247	760	553
		"	0.0747	1228	771	556
		0.0649	0.0432	1072	699	484
		"	0.0435	1070	702	456
		0.0203	0.0073	652	472	256
	8 months old	1.000	0.9455	2717	769	541
		1.000	0.9480	2600	752	547
Ck	2 weeks old	0.9550	0.8876	3373	979	852
		0.9550	0.8856	3457	1038	862
		0.4803	0.4301	2534	1000	830
		0.2402	0.2034	1830	801	654
		0.2725	0.2320	2030	908	717
		0.0992	0.0735	1274	691	558
		"	0.0740	1265	705	596
		0.0649	0.0432	1080	700	496
		0.0203	0.0071	660	462	253
		"	0.0065	680	434	196
	8 months old	1.000	0.9395	3043	735	645
		"	0.9395	3036	731	638
C_1		0.7504	0.7158	1721	503	295
		"	7152	1598	468	291

Table 3.

Charcoal treated at 940° - 980° C.

Charcoal		Initial [$AgNO_3$]	Final [$AgNO_3$]	A	B	C
C_m	4 months old	0.9550	9013	2650	1041	652
		"	8946	2993	-	644
		"	9046	2520	1040	660
		0.4803	4321	2335	1027	647
		"	4368	2184	1049	710
		"	4297	2530	1012	660
		0.2725	2331	1941	910	615
		"	2342	1904	954	595
		0.0992	0.0730	1295	687	509
		"	0.0727	1324	727	491
		0.0649	0.0422	1140	662	416
		0.0203	0.0068	671	443	200
		"	0.0065	680	434	196
	12 months old	2.0	-	-	756	435
		"	-	-	744	438
		0.7504	0.7000	2553	818	537
		"	0.6990	2612	804	539
		0.4986	0.4552	2170	757	509
		"	0.4552	2170	757	493
		0.0992	0.0775	1090	510	350
		0.0992	0.0775	1090	510	356
	Shaken 1 month	0.9550	0.9070	2410	811	293
		"	0.8970	2870	717	397
		0.4803	0.4248	2761	1391	1053
		"	0.4279	2629	1261	883
		"	0.4192	2990	1238	1069
		0.0992	0.0646	1733	1217	949
		"	0.0629	1795	1082	972
		0.0649	0.0341	1524	940	827
	Shaken 24 days	0.0992	0.0647	1738	1266	1025
	Shaken 5 "	0.4803	0.4292	2487	1115	927
	Shaken 4 hrs.	"	0.4402	2010	712	513
	Shaken 10 mins.	"	0.4438	1833	566	371

Table 3 (Contd.)

Charcoal		Initial [$AgNO_3$]	Final [$AgNO_3$]	A	B	C
C_n	0.5gm.& 5c.c.	2.0	-	-	177	39
	" "	"	-	-	177	36
		1.000	0.987	645	-	50
		"	0.983	864	240	54
		0.7504	0.7363	704	224	40
		"	0.7380	624	185	60
		0.4986	0.4912	515	203	43
		"	0.4909	384	148	41
		0.2497	0.2433	315	152	42
		"	0.2430	333	121	41
		0.0992	0.0950	209	104	25
		"	0.0952	199	95	30
		0.0203	0.0181	110	48	8
		"	0.0176	134	62	13
C_o	0.5gm.& 10c.c.	1.000	0.9722	560	241	46
	" "	"	0.9738	524	246	46
	" "	0.2497	0.2317	360	209	49
	" "	"	0.2310	374	231	52
C_p	1.0gm & 10c.c.	1.000	0.9055	945	329	127
	" "	"	0.9128	872	315	118
	" "	0.4986	0.4317	671	323	131
	" "	0.4986	0.4317	671	329	116

Table 4.

Charcoal treated at 1000° - 1250° C.

Charcoal	Initial [$AgNO_3$]	Final [$AgNO_3$]	A	B	C
C_q	1.000	0.9746	1268	674	233
	"	0.9746	1268	709	236
C_r	0.7504	0.7375	641	520	141
	"	0.7375	641	530	137
C_s	1.000	0.9715	1456	766	251
	"	0.9715	1431	731	221
	0.4986	0.4744	1201	675	250
	0.2497	0.2299	997	598	250
	0.0992	0.0839	760	438	192
C_t	1.000	0.9606	1967	548	365
	"	0.9640	1792	548	365
	0.7504	0.7184	1601	597	361
	"	0.7192	1566	604	362
	0.2497	0.2292	1035	501	332
C_u	0.7504	0.7435	345	155	27
	"	0.7444	297	158	27
C_v	0.7504	0.7444	302	126	27
	"	0.7378	290	127	27
C_w	0.7504	0.7382	610	197	59
	"	0.7378	627	198	71
C_x	1.000	0.9806	962	178	90
	"	0.9785	1081	186	92
	0.7504	0.7302	1003	212	80
	"	0.7297	1044	190	78
C_y	1.000	0.9853	737	303	80
	0.2497	0.2414	414	244	83

Table 5.

Charcoal treated at Room Temperature.

Charcoal		Initial [$AgNO_3$]	Final [$AgNO_3$]	A	B	C
C_z		1.000	0.9415	2950	1165	700
		"	0.9418	2929	1164	694
		0.4986	0.4496	2445	1129	768
		0.2497	0.2121	1875	1083	723
		"	0.2120	1887	1093	720
	3 months old	0.2497	0.2161	1669	777	561
		"	0.2160	1685	791	556
C_z'		1.000	0.9453	2726	1054	718
		"	"	2746	1069	730
		0.4986	0.4504	2414	1104	781
		"	"	2398	1119	765
		0.2497	0.2133	1867	1005	709
		"	0.2125	1853	1028	711
	3 months old	0.2497	0.2140	1780	820	620
		"	0.2137	1786	831	617

Adsorption and Reduction of Silver Nitrate Solutions, acidified with Nitric Acid.

Table 6.

Initial $[AgNO_3]$	Final $[AgNO_3]$	Initial $[HNO_3]$	Final $[HNO_3]$	A	B	C	Total Ads. A-C.
0.5000	0.4561	0.4629	0.4401	989	41	-1150	2139
"	0.4833	0.4629	0.4389	829	47	-1192	2021
"	0.4725	0.2314	0.2230	1368	158	- 418	1526
"	0.4826	0.2314	0.2173	864	37	- 700	1564
"	0.4620	0.0925	0.0999	1905	600	365	1540
"	0.4561	0.0486	0.0574	2213	718	445	1768
0.4986	0.4537	-	0.0137	2246	838	686	1560
0.2493	0.2380	0.4629	0.4378	616	20	-1255	1871
"	0.2378	0.4629	0.4378	575	7	-1253	1828
"	0.2215	0.0926	0.0982	1412	599	286	1126
"	0.2222	0.0926	0.0985	1366	606	301	1065
"	0.2332	0.2314	0.2225	805	129	- 447	1252
"	0.2317	0.2314	0.2238	882	181	- 382	1264
"	0.2194	0.0486	0.0562	1499	624	382	1117
0.2497	0.2175	-	0.0118	1648	737	602	1046
0.1249	0.1083	0.4629	0.4549	829	199	- 400	1229
"	0.1175	0.4629	0.4471	379	34	- 789	1168
"	0.1047	0.2314	0.2308	1002	307	- 30	1032
"	0.1056	0.2314	0.2173	955	405	- 10	965
"	0.1044	0.1157	0.1182	1020	498	126	894
"	0.1022	0.0486	0.0543	1145	568	286	859

Adsorption of Nitric Acid.

Table 7.

Charcoal		Initial $[HNO_3]$	Final $[HNO_3]$	Micromols HNO_3 adsorbed per gram of charcoal
C_d	3 months old	0.9257	0.8980	1385
		"	0.9005	1253
C_e	4 days old	0.9257	0.8956	1532
C_f	1 day old	0.9257	0.8852	2046
C_g		0.02032	0.01771	131
C_j	2 months old	0.9257	0.8940	1567
		0.6180	0.5920	1288
		0.4626	0.4394	1122
		0.3080	0.2894	929
		0.0973	0.0860	561
		0.0405	0.0326	391
C_k	2 months old	0.9257	0.8955	1518
		0.6180	0.5904	1387
		0.4626	0.4399	1152
		0.3080	0.2890	959
		0.0973	0.0857	583
		0.0405	0.0326	400
C_m	8 months old	0.9257	0.8968	1448
		0.9257	0.8960	1483
		0.6180	0.5916	1315
		0.4626	0.4397	1115
		0.0973	0.0855	590
		"	0.0850	622
		0.0405	0.0313	461
		0.02032	0.01270	382
		0.00986	0.00348	319
		"	0.00348	314

Table 7 (Contd.)

Charcoal		Initial $[HNO_3]$	Final $[HNO_3]$	Micromols HNO_3 adsorbed per gram of charcoal
C_m	3 months old	-	-	-
	1.0gm & 20c.c.	0.4629	0.4062	1134
	0.5gm & 30c.c.	0.3086	0.2912	1044
	0.5gm & 25c.c.	0.0973	0.0841	662
	0.124gm & 25c.c.	0.0778	0.0745	666
	0.25gm & 30c.c.	0.0649	0.0600	583
	0.125gm & 20c.c.	0.0487	0.0454	528
	0.3gm & 25c.c.	0.0405	0.0345	496
	0.25gm & 25c.c.	"	0.0381	503
	0.25gm & 25c.c.	"	0.0356	489
	0.12gm & 25c.c.	0.02032	0.0183	430
	0.25gm & 25c.c.	"	0.0162	407
	0.25gm & 25c.c.	0.00986	0.00624	362
	0.122gm & 25c.c.	"	0.00807	369
	0.05gm & 17c.c.	0.00406	0.00313	310
	0.05gm & 15c.c.	0.00203	0.00121	246
C_n		0.9257	0.9183	369
		0.6180	0.6130	250
		0.4626	0.4575	256
		0.3080	0.3034	228
		0.0973	0.0943	153
C_q		0.9257	0.9197	297
		"	0.9197	301
C_s		0.00986	0.00596	195
C_t		0.9257	0.9122	674
		"	0.9120	683
C_x		0.9257	0.9177	400
		"	0.9173	417

Adsorption of Iodine from Potassium Iodide Solution.

Table 8.

Charcoal		Initial $[I_2]$	Final $[I_2]$	Micromols I_2 adsorbed per gram. of char.
C_c	2 months old	0.1016	0.02133	4000
		″	0.02140	4006
C_e	4 days old	0.1016	0.00999	4561
C_t	2 months old	0.1016	0.0622	1948
		″	0.0614	2024
C_v	2 months old	0.1016	0.0924	464
		″	0.0922	476

Adsorption of Sodium Hydroxide.

Table 9.

	Charcoal	Initial [NaOH]	Final [NaOH]	Micromols NaOH adsorbed per gram. of char.
C_d	2 weeks old	0.01067	0.00678	194
C_c	2 weeks old	0.01067	0.00466	300
C_e	1 day old	0.00953	0.00904	25
C_f	1 day old	0.00953	0.00878	38
C_j	1 month old	0.02032	0.01443	118
	" " "	"	0.01422	121
	2 months old	0.01067	0.00817	125
C_k	1 month old	0.02032	0.01331	140
	" " "	"	0.01260	155
	2 months old	0.1067	0.00745	163
C_m	7 months old	0.01067	0.00933	54
	12 " "	0.00953	0.00846	55
C_n		0.01067	0.01014	11
		"	0.01005	12
	1 month old	"	0.1020	8
C_q		0.01067	0.01043	10
		"	0.01059	9
C_x		0.01067	0.01020	24
		"	0.01020	24

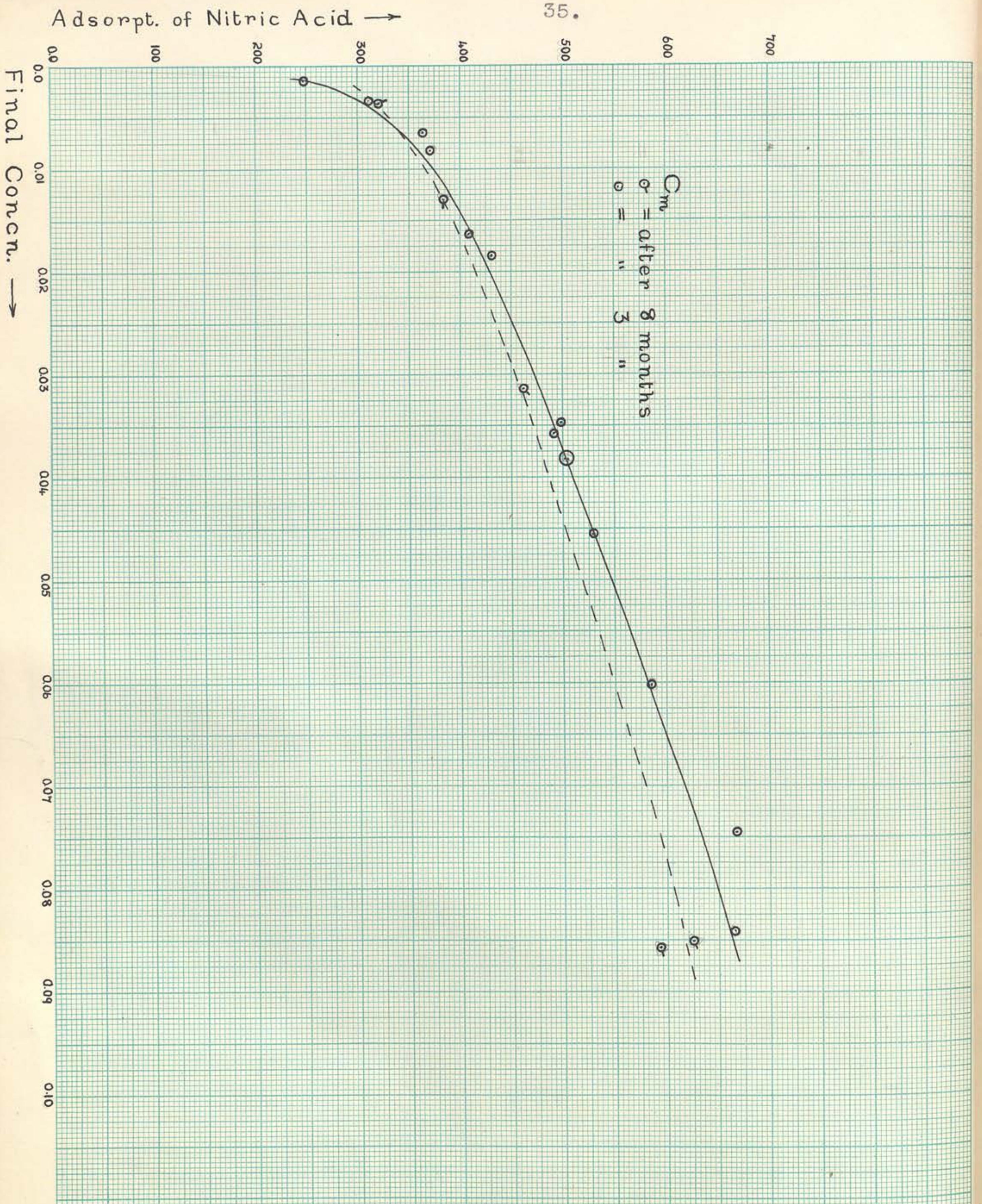
Adsorpt. of Nitric Acid →
0.0
100
200
300
400
500
600
700
Final Concn. →
0.0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
C_m
σ = after 8 months
⊙ = " 3 "

FIG. 15.

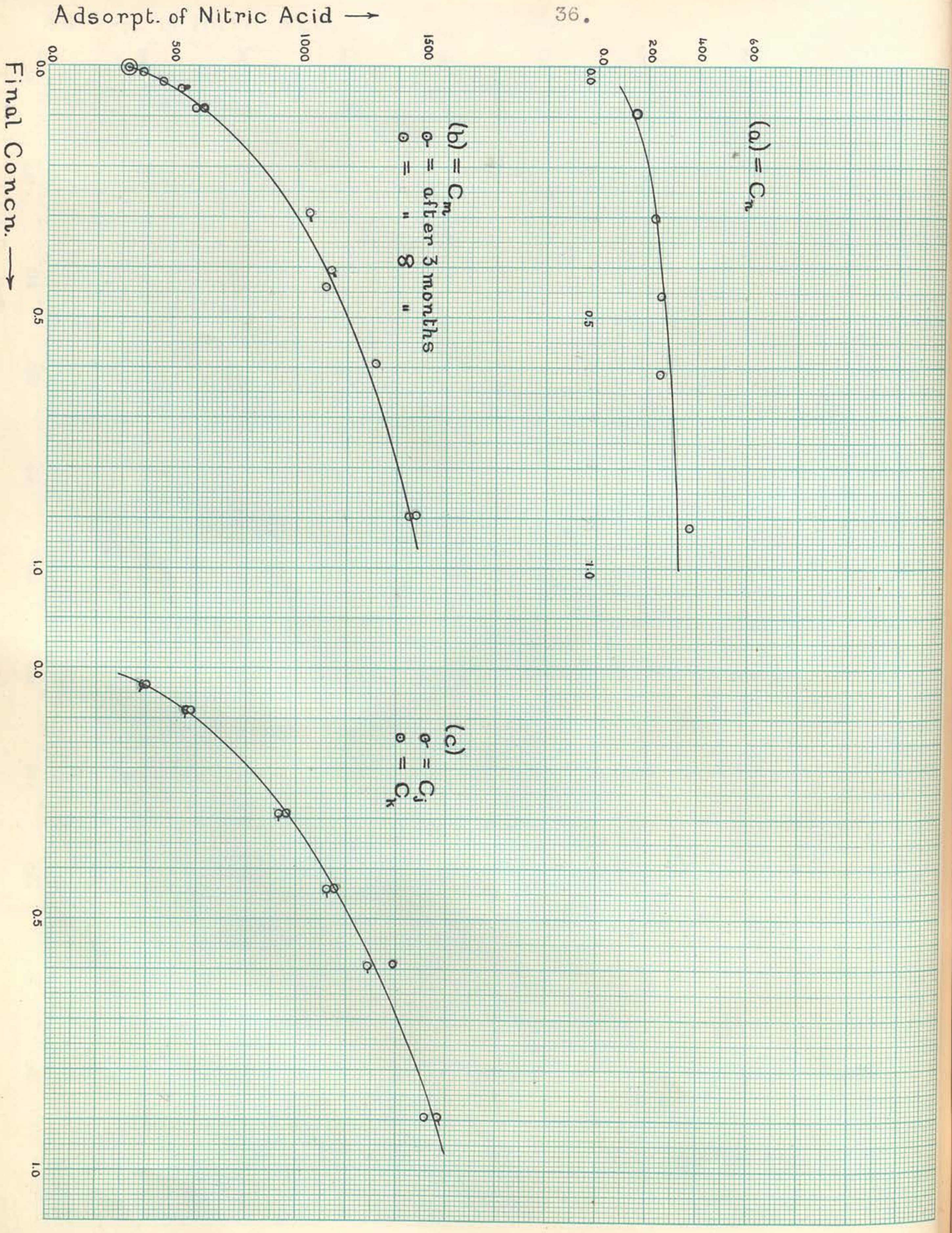
Adsorpt. of Nitric Acid →
Final Concn. →
0.0
500
1000
1500
0.0
200
400
600
0.0
0.5
1.0
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_n
(b) = C_m
⊖ = after 3 months
⊙ = " 8 "
(c)
⊖ = C_j
⊙ = C_k

FIG. 14 (a,b,c)

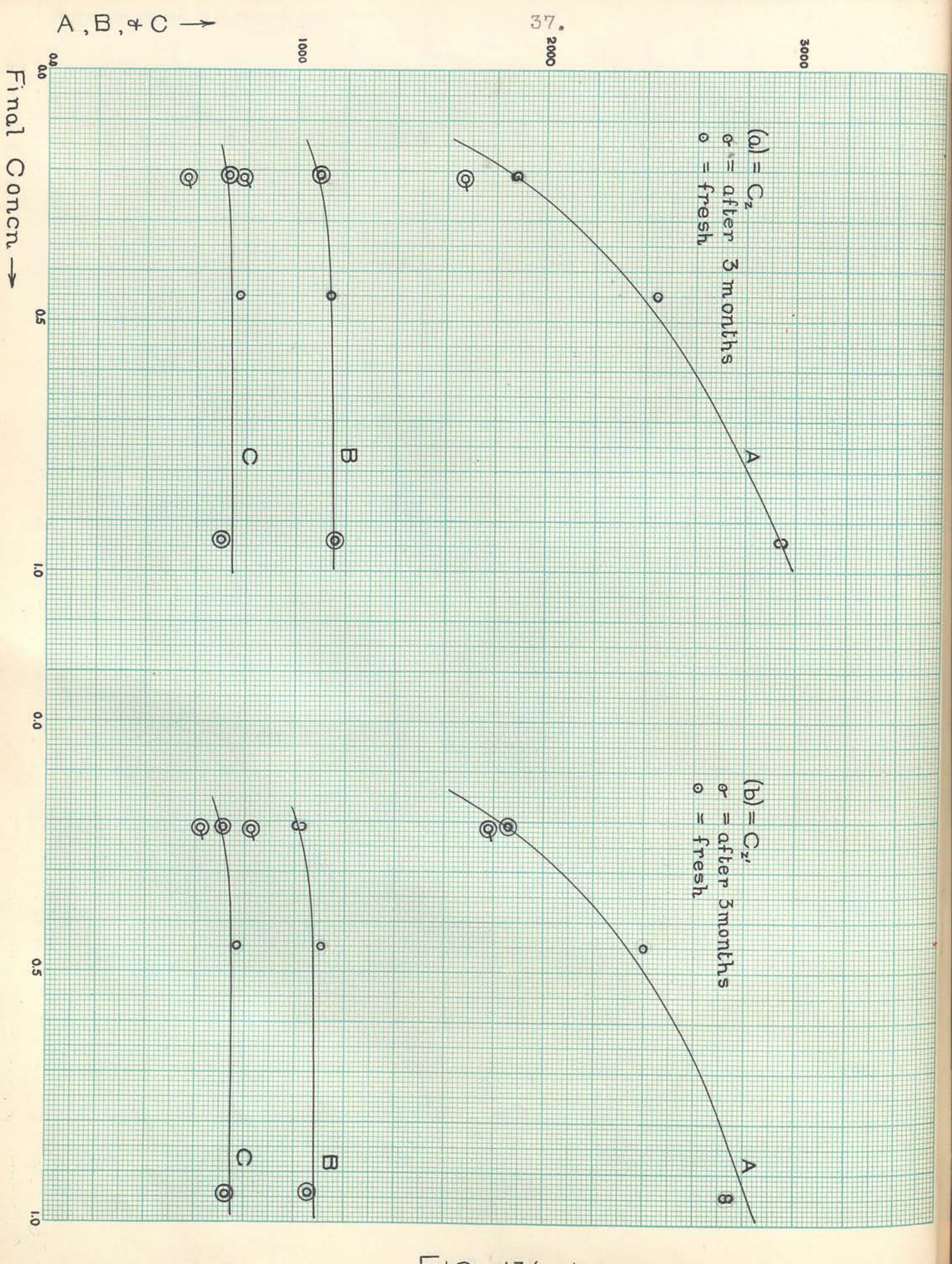
A, B, & C →
0.0
1000
2000
3000
Final Concn →
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_z
⊙ = after 3 months
○ = fresh
A
B
C
(b) = C_z'
⊙ = after 3months
○ = fresh
A
B
C

FIG. 13(a,b)

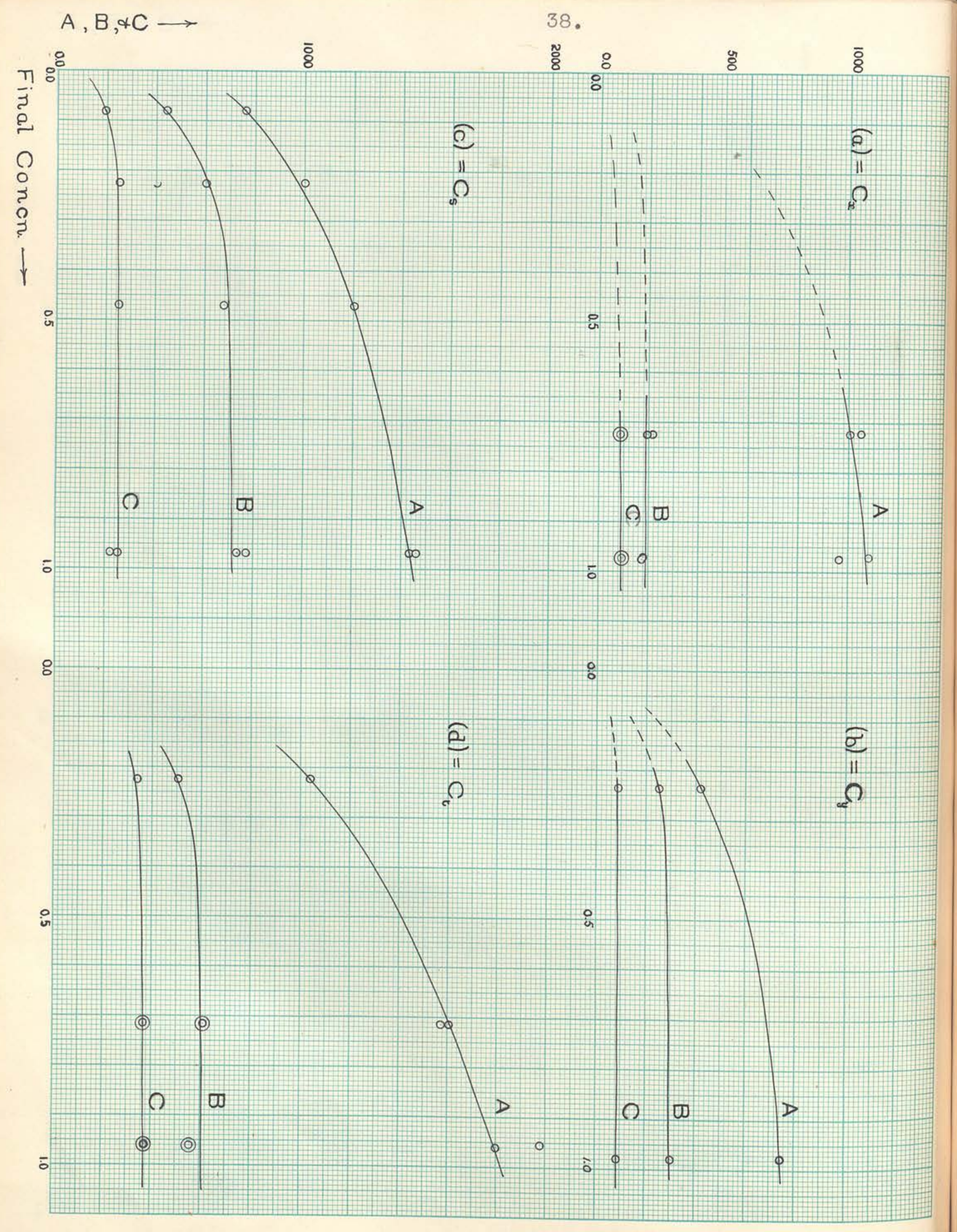
A, B, & C →
Final Concn →
(a) = C_x
(b) = C_y
(c) = C_s
(d) = C_c
0.0
500
1000
0.0
1000
2000
0.0
0.5
1.0
0.0
0.5
1.0
A
B
C
A
B
C
A
B
C
A
B
C

FIG. 12(a,b,c,d)

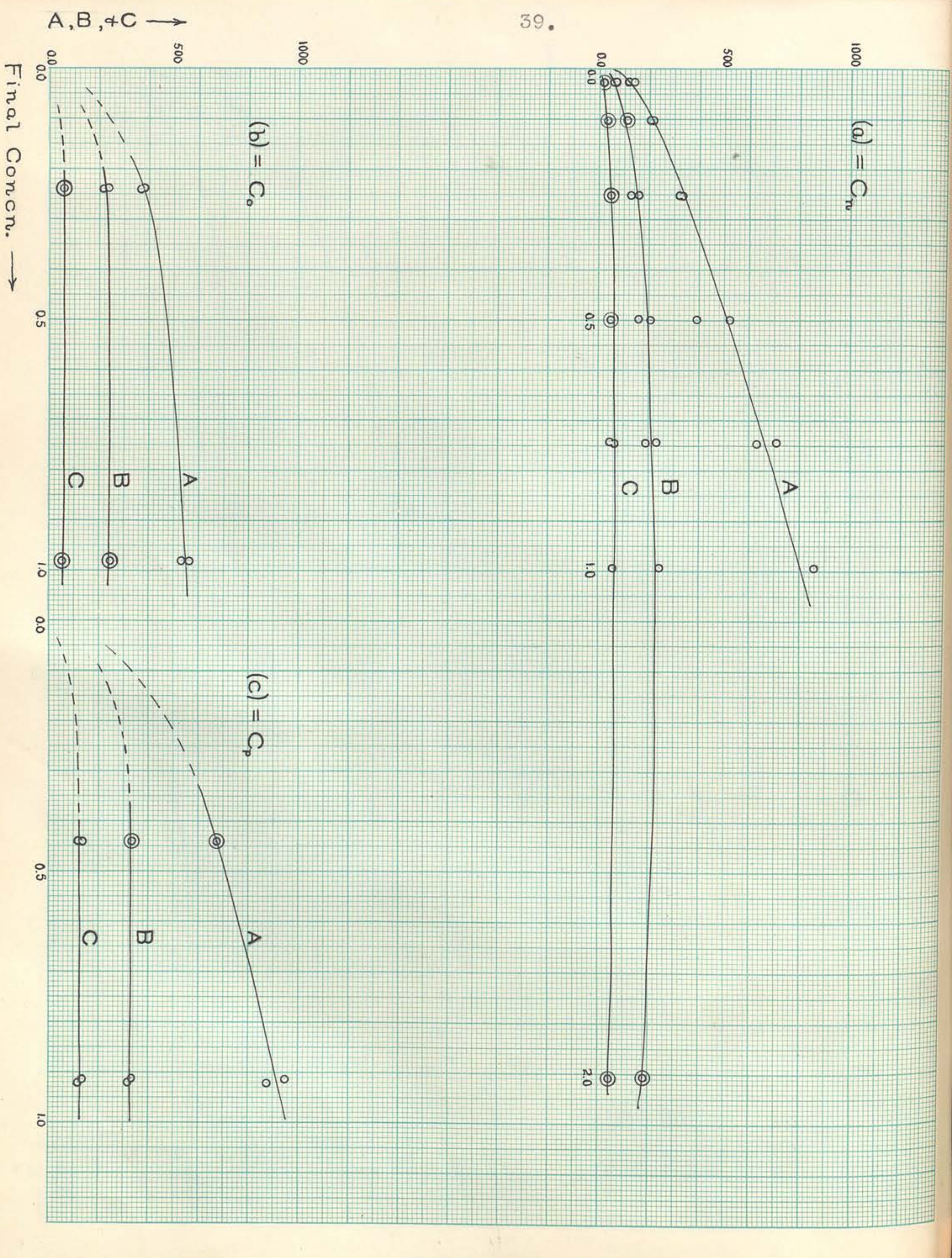
A, B, + C →
Final Concn. →
(a) = C_n
(b) = C_o
(c) = C_p
A
B
C
A
B
C
A
B
C
0.0
500
1000
0.0
500
1000
0.0
0.5
1.0
0.0
0.5
1.0
0.0
0.5
1.0
2.0

FIG. 11(a, b, c)

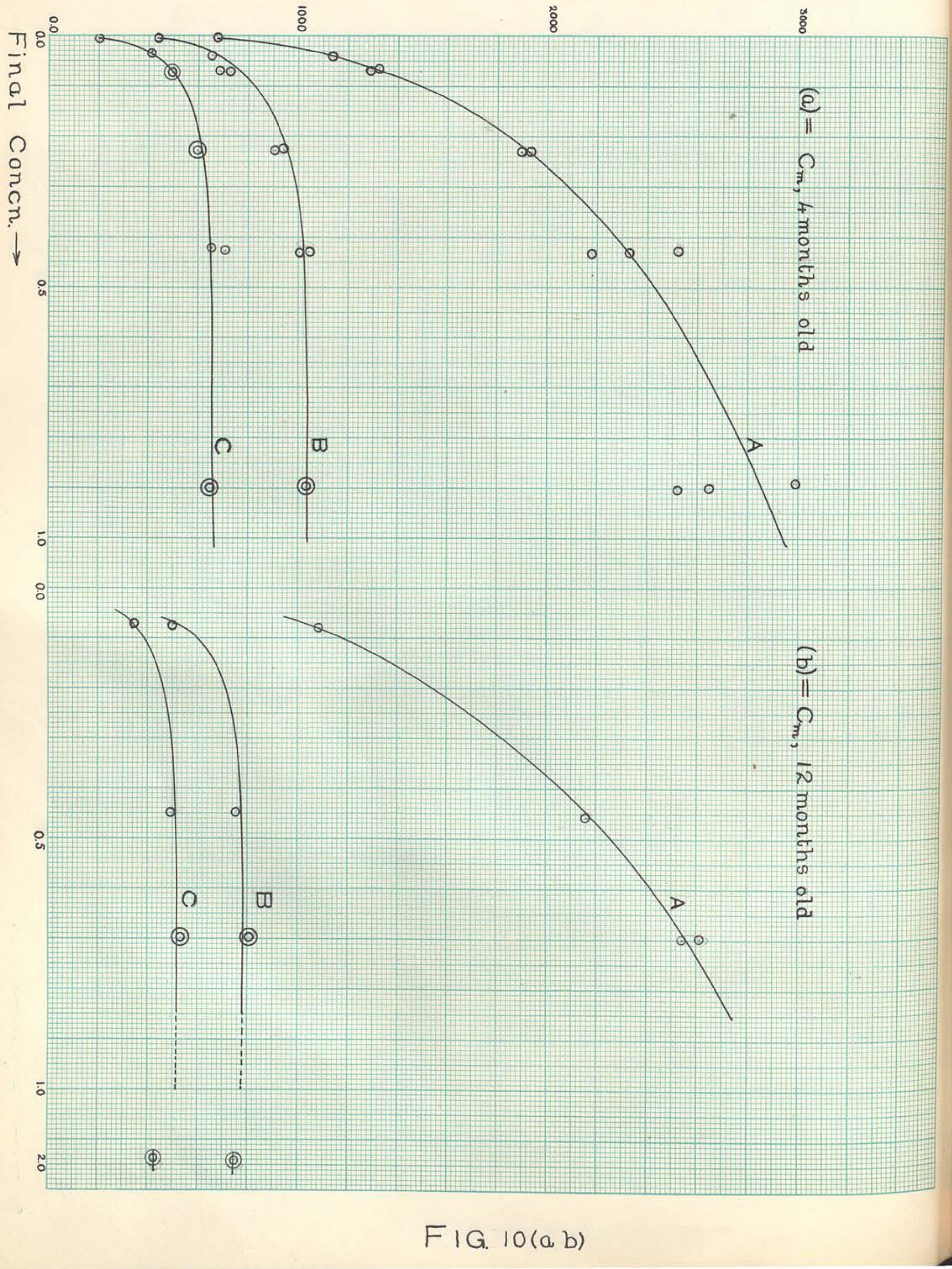
A, B, + C →
Final Concn. →
(a) = C_m, 4 months old
(b) = C_m, 12 months old
A
B
C
A
B
C
0.0
1000
2000
3000
0.0
0.5
1.0
0.0
0.5
1.0
2.0

FIG. 10(a b)

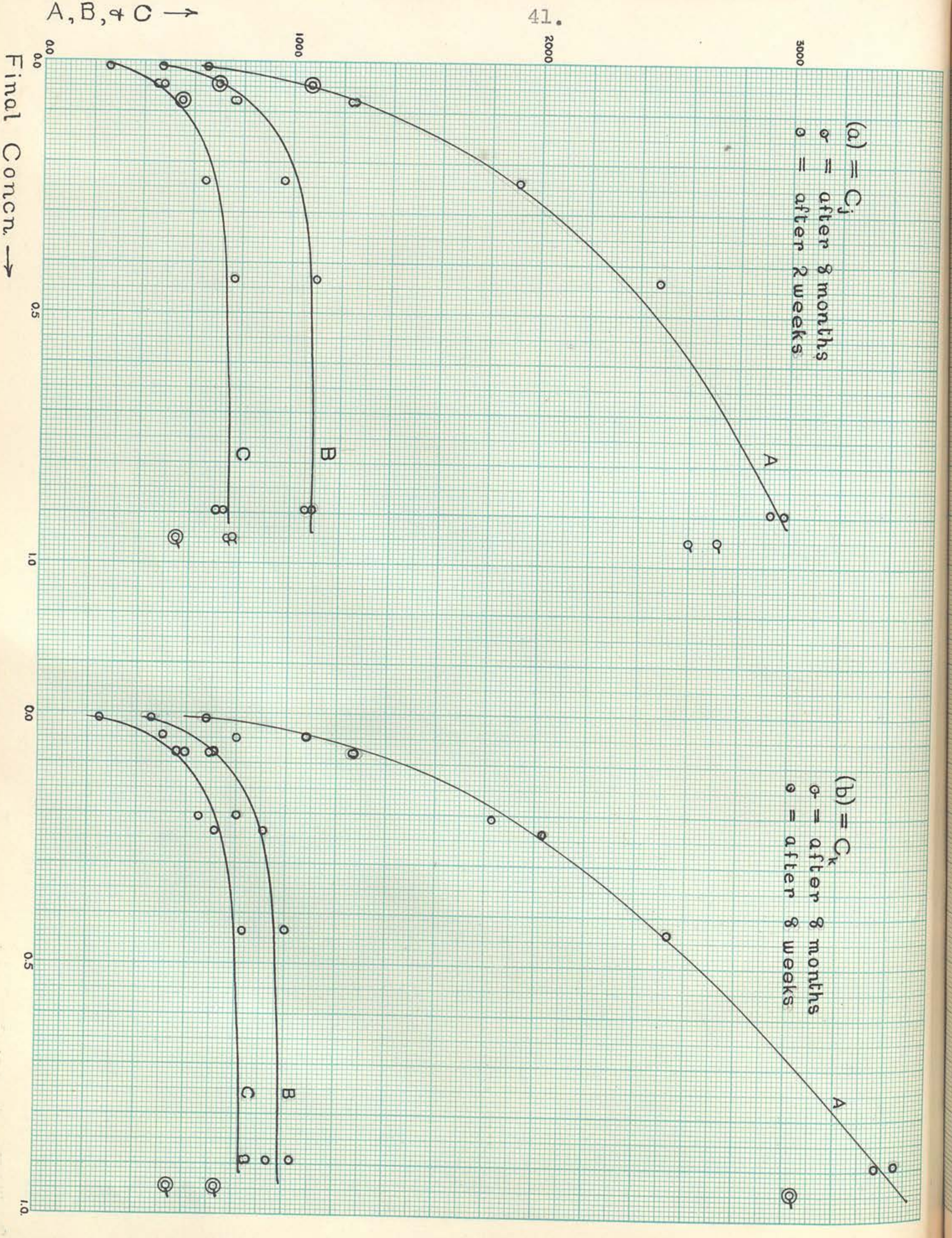
A, B, & C →
Final Concn. →
0.0
1000
2000
3000
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_j
ơ = after 8 months
o = after 2 weeks
A
B
C
(b) = C_k
ơ = after 8 months
o = after 8 weeks
A
B
C

FIG. 9 (a, b)

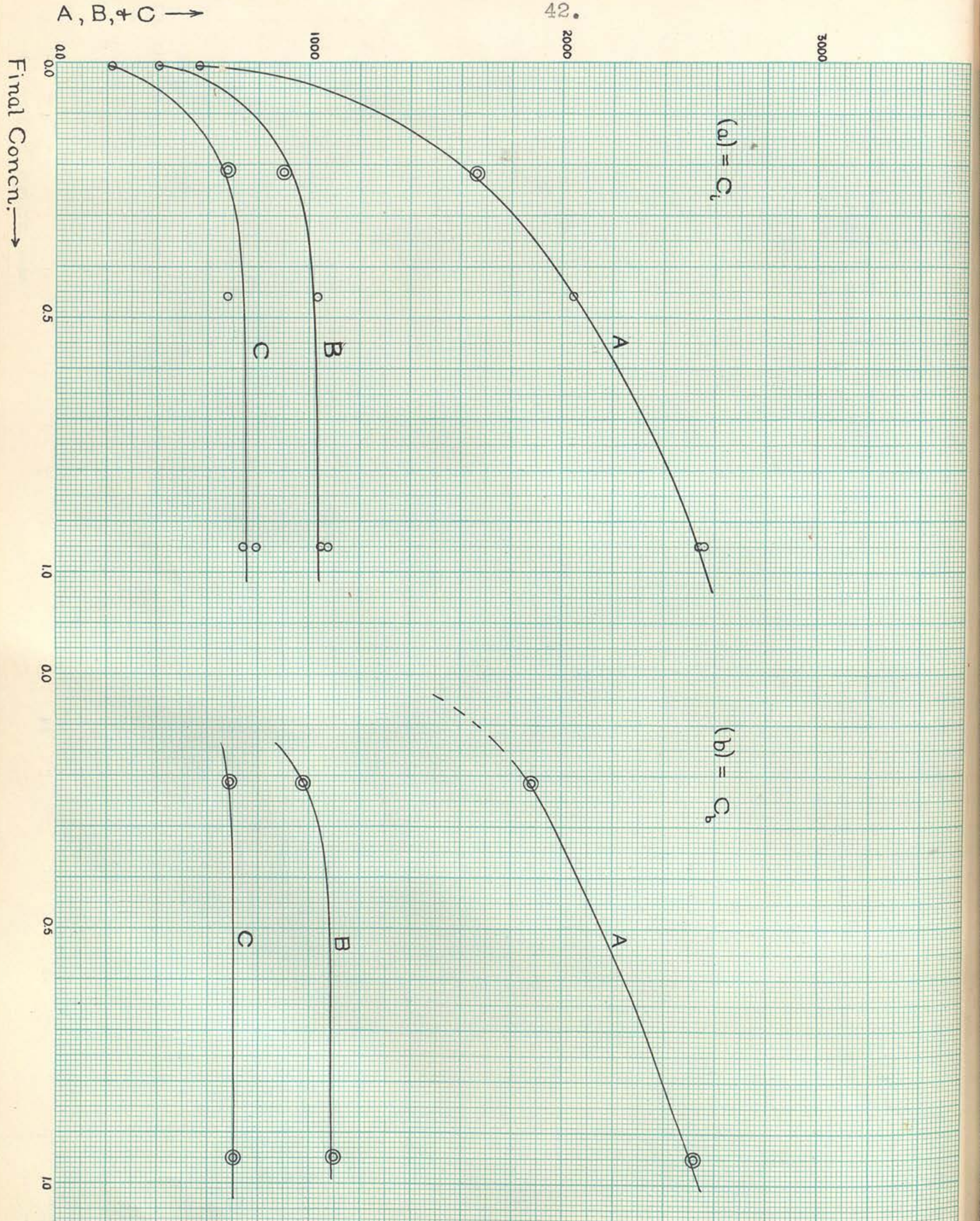
A, B, + C →
Final Concn. →
0.0
1000
2000
3000
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_i
(b) = C_b
A
B
C
A
B
C

FIG. 8(a,b)

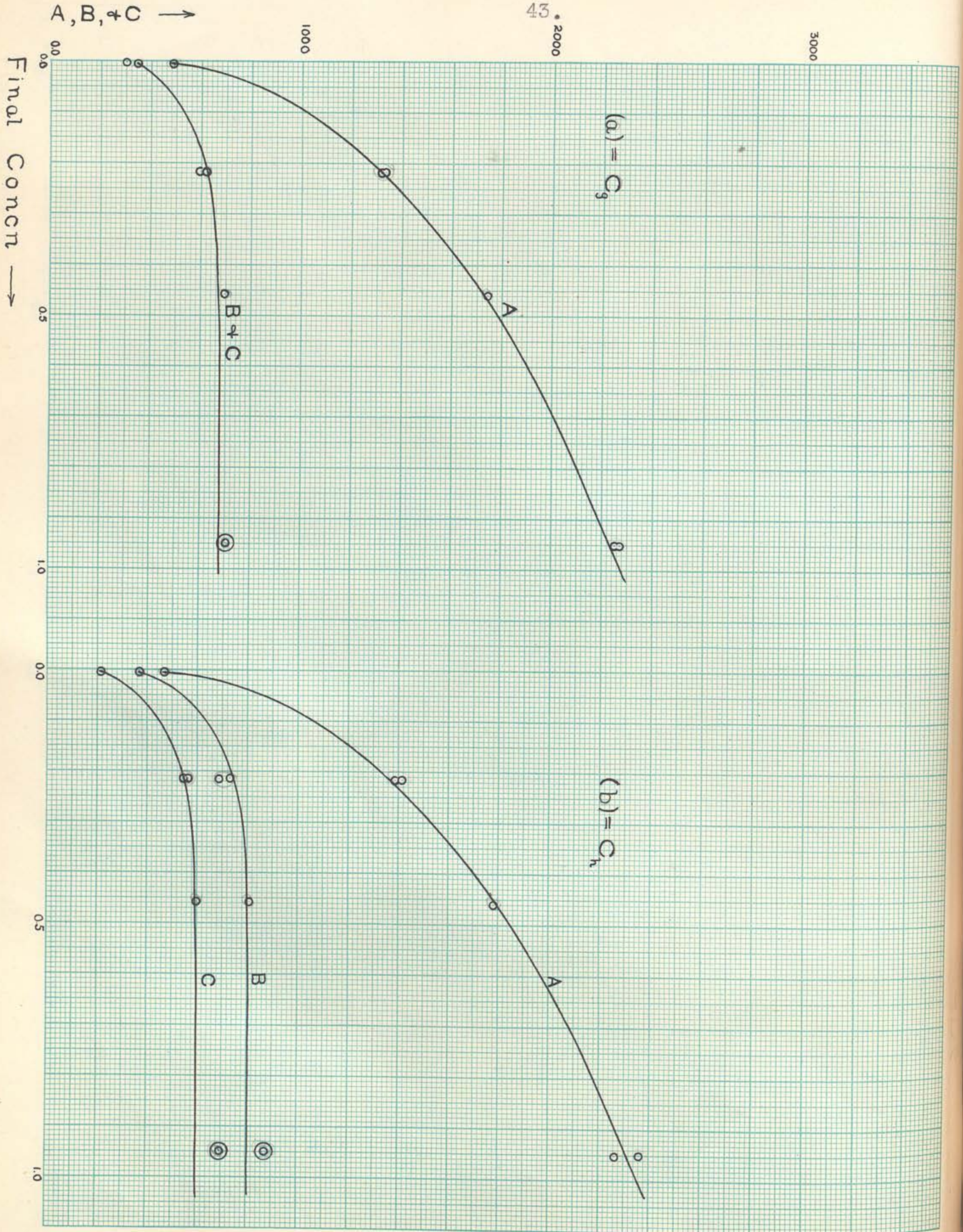
A, B, + C →
0.0
1000
2000
3000
Final Concn →
0.0
0.5
1.0
(a) = C_g
A
B + C
0.0
0.5
1.0
(b) = C_h
A
B
C

FIG. 7 (a,b)

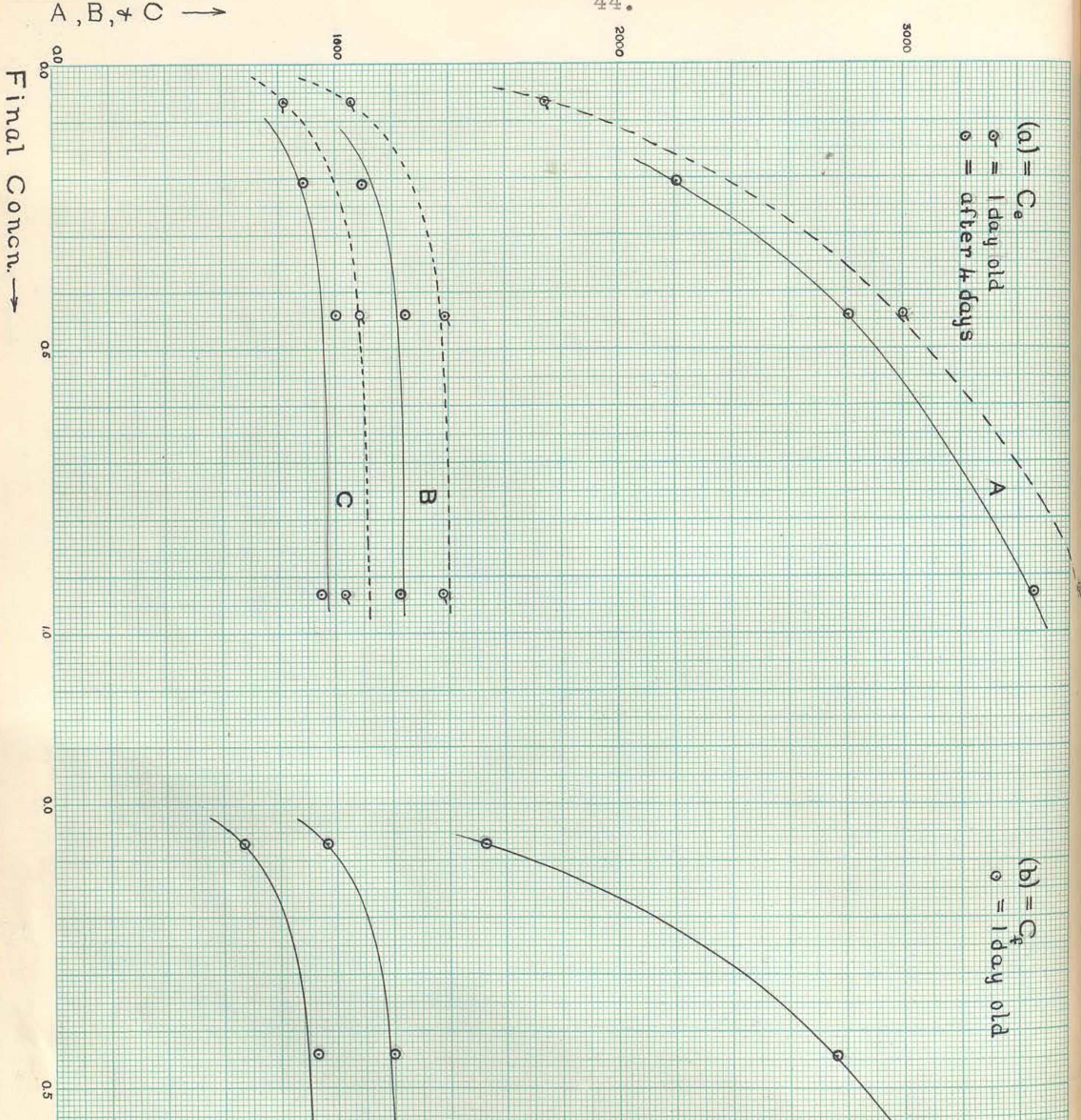
A, B, & C →
0.0
1000
2000
3000
Final Concn. →
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_e
⊙ = 1 day old
⊙ = after 4 days
A
B
C
(b) = C_f
⊙ = 1 day old
A
B
C

FIG 6(a,b).

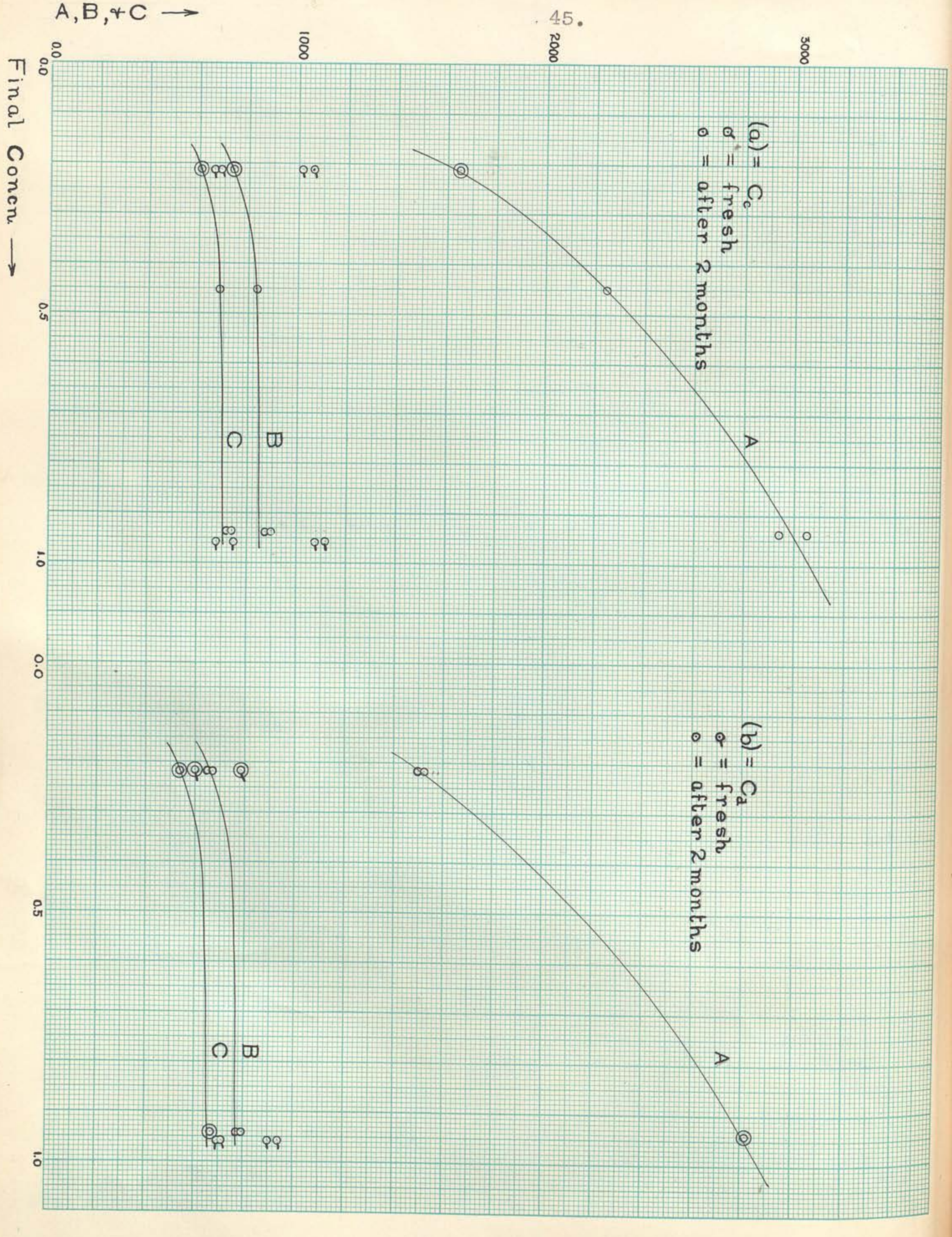
A, B, + C →
Final Concn →
0.0
1000
2000
3000
0.0
0.5
1.0
0.0
0.5
1.0
(a) = C_c
σ = fresh
⊙ = after 2 months
A
B
C
(b) = C_a
σ = fresh
⊙ = after 2 months
A
B
C

FIG. 5(a,b)

DISCUSSION.

1. Estimation of Amount of Reduction.

At the outset of the research it appeared probable that the silver would be present on the surface of the charcoal in one or more of three forms, viz;- silver nitrate, silver hydroxide, and metallic silver. Hence the principle adopted in estimating the amount of reduction was to convert any silver present as nitrate or hydroxide into silver chloride, and then dissolve out the metal. The actual procedure (see p. 6) consisted in treating the charcoal with potassium chloride solution, removing excess potassium chloride by washing, and then extracting the metallic silver from the charcoal with nitric acid, followed by washing. It will be seen that the reliability of the method depended on the following conditions -- (1) complete conversion of the unreduced adsorbed silver into silver chloride, (ii) complete elimination of the excess of potassium chloride, (iii) complete removal of metallic silver from the charcoal, (iv) insolubility of silver chloride in the nitric acid, (v) absence of action between the potassium chloride and the metallic silver.

The solubility of silver chloride in concentrated nitric acid [8] is exceedingly small (1 part in 100,000 parts of nitric acid)., so that (iv) was satisfied.

Pure silver wire was covered with .3M potassium chloride for 18 hours; the solution was then filtered off, and the potassium chloride converted into sulphate; the solution obtained was free of silver, so that (v) was satisfied.

It has been shown by Miller[I5] that adsorbed nitric acid, which could not be removed from charcoal by washing, was completely removed by treatment with sodium hydroxide solution and, therefore, it seemed highly probable that all the unreduced silver would be precipitated by potassium chloride solution. It is shown below that the precipitation of silver chloride was complete in 30 minutes, and also that the metallic silver extracted with nitric acid was the same whether the charcoal was treated with approximately .01M or .3M potassium chloride. Hence condition (1) was proved.

Failure of either or both (ii) and (iii) would have resulted in the amount of silver extracted with nitric acid being less than the actual amount of reduced silver. The following experiment showed that (ii) and (iii) were satisfied.

About .2 gm. of charcoal, C_c was shaken for 24 hours with 10 c.c. of 0.2497M silver nitrate. Instead of first separating the charcoal from the solution, as was usually done, 10 c.c. of 0.2593M potassium chloride were added, the solution filtered off, and the concentration of potassium chloride in the filtrate estimated by Mohr's method, the liberated acid having been neutralised with sodium hydroxide. In this way the amount of unprecipitated silver was obtained. The values for this, in two independent experiments, were found to be 743, and 757 micromols silver per gram of charcoal. The charcoal was further washed, and extracted with nitric acid in the usual way, and the extracted silver found to be 721 and 748. The agreement of these figures with those obtained above, indicated that (ii) and (iii) were fulfilled, and incidentally, that there was no adsorption of potassium chloride by the charcoal.

In the foregoing experiments the analyses were performed 30 minutes after the addition of the potassium chloride. Figures were also obtained for experiments of exactly the same nature except that the charcoal was left in contact with the potassium chloride for 18 hours.

In this case the unprecipitated silver amounted to 760 and 765, while the silver extracted with nitric acid was 737 and 753, figures which agreed with those obtained above. Further, the amounts of silver extracted in three experiments after treating the charcoal with .3M potassium chloride were 741, 747 and 737 (see p.23). Hence (1) was verified. The results also showed that .3M potassium chloride had no action on silver in 30 minutes, further confirming (iv).

In agreement with Warlet [7] it was found that silver was desorbed on treating the charcoal with water. After percolation of water through the charcoal for 18 hours the desorption appeared to be complete, and extraction of the charcoal with ammonium hydroxide did not remove any silver. On treating finally with nitric acid, a further quantity of A_g was removed from the charcoal. Actually, it was found that all the adsorbed silver could be recovered by treatment with water and acid, providing further confirmation of (iii).

The following experiments were obtained in some experiments with charcoal Cm.

/.

Total Adsorption of Silver (A) (micromols per gm. of char.)	Total Silver Recovered (micromols per gm. of char).
1738	1650
1833	1912
2010	2086.

It thus appeared that part of the adsorbed silver was soluble in water (and could be precipitated as chloride), while the remainder was insoluble in water, and ammonium hydroxide, but soluble in nitric acid. That the latter portion contained any constituent other than metal itself seems very improbable.

With charcoals which gave a large reduction of silver nitrate, a relatively large quantity of white metallic looking particles was clearly visible after shaking the charcoal for 24 hours with silver nitrate. A large proportion of the particles (about 50%) could be separated by floating off the charcoal. The particles were insoluble in ammonium hydroxide but dissolved completely in nitric acid (8M). It is probable that a more efficient method of separation would have shown that the bulk of the reduced silver had separated from the charcoal. Hence, assuming that all the reduced silver comes off the charcoal, the silver /

Table 10.

Initial $[AgNO_3]$	Period of Shaking.	A.	B.	A-B
0.0992	24 hours	1295	687	608
	"	1324	727	597
	24 days	1738	1266	472
	1 month	1733	1217	516
	"	1795	(1082)	(713)
0.4803	10 mins.	1833	566	1267
	4 hours	2010	712	1298
	24 "	2335	1027	1308
	"	2184	1049	1135
	"	2530	1021	1517
	5 days	2487	1115	1372
	1 month	2761	1391	1370
	"		1261	1368
	"		1238	(1752)

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silver actually adsorbed (and which can be desorbed) at any time is equal to the difference between,(A) the total adsorption of silver from solution, and (B), the reduced silver (see p. 23)*

The above experiments show that Warlet's[7] assumption that the undesorbed silver is present as silver hydroxide, is incorrect.

2. The Mechanism of Reduction.

It is well known that a charcoal surface is of a composite nature. For the explanation of the results obtained in the present investigation, it was found necessary and sufficient to assume that the carbon atoms at the charcoal surface were of two different types, viz;- (a) atoms whose residual valencies were completely satisfied by chemisorption with oxygen and, therefore, adsorbed little or no silver nitrate, or nitric acid; and (b) atoms which were not covered with a chemisorbed layer, and were therefore free to adsorb nitric acid, and to adsorb and reduce silver nitrate.

*Henceforth the term adsorbed silver nitrate will be used to denote the quantity (A - B).

Influence of Time, and Silver Nitrate Concentration.

In the great majority of the experiments, the charcoal was shaken with the silver nitrate solution for 24 hours. It will be seen that the graphs (Figs. 5-13) obtained under these conditions were all of the same type. While the total amount of silver adsorbed (A), increased rapidly with increasing concentration of silver nitrate, the amount of reduced silver (B), and acid liberated (c), increased more slowly, and became practically constant for concentrations greater than about 0.4 M. The question arose as to whether the observed constant value of the reduction represented the limit of the reducing capacity of the charcoal. Some experiments were, therefore, carried out to ascertain the influence of time of shaking upon the amount of reduction. The results shown in Table 10 were obtained with charcoal, C_m (see p.26). The last column of the above table shows that the amount of silver nitrate was independent of the period of shaking, being substantially the same whether measured after 10 minutes or one month. In contrast with the very rapid rate of adsorption of the silver nitrate, was the rate of reduction. Thus, with 0.4803 M silver nitrate, the reduction in 24 hours was about twice as great as that in 10 minutes. At both concentrations the reduction continued/

continued to increase after 24 hours, but within a month had reached a maximum value of about 1260 micromols in both cases. The slow adsorption of silver from solutions of silver sulphate, and silver acetate, by charcoal, was observed by Morøwitz,[4] and may well have been due to slow reduction. ⌈a

To explain the above results, the following hypothesis was advanced. The silver nitrate was rapidly adsorbed on the surface carbon atoms which possessed the reducing property, the amount of silver nitrate adsorbed varying with the concentration of the solution. The reduction then commenced, the rate of reduction falling as the more active reducing centres were used up. The reduction was pictured to occur thus;

$$(C)AgNO_3 + H_2O = (COH) + \underset{\downarrow}{Ag} + HNO_3.$$

After reduction the silver atom left the charcoal surface (see p.50) while the carbon atom, which had acquired a positive charge, combined with a hydroxyl ion furnished by the water. It was assumed that the carbon atom was not oxidised so completely as the carbon atoms which held chemisorbed oxygen, and still possessed sufficient residual valency to adsorb another molecule of silver nitrate, without, however, reducing it, thus keeping the amount of adsorbed silver nitrate unchanged./

The assumption that a reducing centre would reduce only one molecule of silver nitrate is supported by the fact that the reduction of mercuric chloride stops at mercurous chloride.[6] Heymann [9] found that platinium, adsorbed by charcoal, at room temperature, from a solution of platinic chloride, could be recovered by washing with hydrochloric acid, and he concluded that the platinic chloride was hydrolytically adsorbed as platinic hydroxide. Above 100° this was reduced by the charcoal to platinium. There is no reason to assume that the reduction of silver nitrate was preceded by hydrolytic adsorption. On the one hand, the platinic chloride was already hydrolysed [10] in the solution, whereas the silver nitrate [11] was not; while, on the other hand, the conditions favourable to hydrolytic adsorption of silver nitrate on the reducing surface, viz; low adsorption of nitric acid, and high adsorption of silver - were absent (see Table 6).

According to the above hypothesis, the concentration at which the reduction reaches a maximum should be that concentration at which the silver nitrate just completely covered the reducing surface. Since the reduction was not complete in 24 hours, the adsorbed silver nitrate (A - B) should be somewhat greater than the reduction. The figures shown in Table 11 for the reduction and adsorption at/

Table 11.

Charcoal	$AgNO_3$ reduced (B)	$AgNO_3$ ads.(A-B)
C_c	920	1300
C_d	850	1200
C_e 1 day old	1360	1550
4 days "	1220	1500
C_f	1180	1500
C_g	660	980
C_h	800	900
C_i	1000	960
C_j	1080	1200
C_k	960	1500
C_l	1060	1000
C_m 4 mths.old	1010	1260
12 " "	980	1280
C_n	180	260
C_o	230	240
C_p	300	340
C_s	680	460
C_t	580	720
C_y	280	280
C_z	1120	1170
$C_z{}^1$	1080	1200

at a concentration of 0.4 M (values read from graphs) show that this was almost invariably the case.
On the other hand, the figure for the adsorbed silver nitrate should correspond to the maximum reduction attained after shaking the charcoal with silver nitrate for a month. It will be seen that this was the case with charcoal C_m, which gave an adsorption of 1260 micromols after 24 hours, and a reduction of 1296 (average, see Table 10) micromols after 1 month.

At concentrations greater than about 0.4 M, the total adsorption continued to increase, probably, due to the building up of a layer of silver nitrate more than one molecule thick. This is supported by the fact that Langmuir's equation (plotting $1/[AgNO_3]$ v $1/(A-B)$), applied to the adsorption of silver nitrate, gave curves which were convex towards the axis, $1/(A-B)$. Ruff, Ebert, and Luft,[6] from X-ray analysis of the adsorbed layer, concluded that metallic salts could exist on charcoal in a layer more than one molecule thick.

At concentrations less than about 0.4 M, the amount of reduction became greater than the adsorbed silver nitrate, and, in the case of C_m, after 1 month,/

month, had reached approximately the same value as that obtained at the higher concentration. This is easily explained. Although the reducing surface would be only partially covered with silver nitrate, the fact that the adsorption of the silver nitrate was reversible, (see p.49) allowed the silver nitrate to come in contact with all the reducing centres.

In the case of 0.955 M silver nitrate, however, it was observed that the amount of reduced silver decreased from 1040 micromols (average, 24 hours) to 764 micromols (average, 1 month). The evidence showed that the liberated acid dissolved some of the coarse silver. On the one hand, the quantity of the latter visibly decreased, and on the other, acid disappeared from the solution equivalent in amount to the decrease in reduced silver (p.26). Thus

Table 12

	After 24 hours	After 1 month	Decrease
Reduced Silver (B)	1041 1040	811 717	
	Mean 1040	764	276
Liberated Acid (C)	652 644 660	293 397	
	Mean 652	345	307

It is difficult to account for the resolution of the silver, as the concentration of nitric acid in the solution was so low (less than.01 M)[12] It was thought, at first, that it was due to the reduction of the nitric acid to nitrous acid by the charcoal, but it is difficult to see how the amount of reduction could be greater at high concentrations of silver nitrate. A possible explanation was that the silver nitrate contained a minute quantity of some polyvalent ion, e.g., copper, which catalysed the solution of the silver,[13] and that only at high concentrations of silver nitrate was the amount of impurity sufficient to exert any appreciable action on the silver. In agreement with this explanation it was found (see Fig. 10b.) that with 2.0 M silver nitrate; the reduction had fallen somewhat below the maximum value, even in 24 hours.

Adsorption of Silver Nitrate, Nitric Acid, and Iodine.

In Table 13 the adsorption of silver nitrate, nitric acid, and iodine, by various charcoals, are compared.

It will be seen that there was a distinct parallelism between the results. The changes in adsorption of silver nitrate, nitric acid, and iodine, from charcoal to charcoal, were approximately proportional to one another.

Table 13.

Charcoal	Adsorption per gram of charcoal.		
	Silver Nitrate (micromols).	Nitric Acid (micromols)	Iodine. (Micromols)
C_f	1990	2046	-
C_j	1790	1567	-
C_e	1950	1532	4561
C_k	1920	1518	-
C_c	1810	-	4003
C_m	1771	1466	-
C_d	1740	1319	-
C_t	983	679	1986
C_x	873	409	-
C_q	576*	299	-
C_n	460	320	-
C_v	170	-	470

Initial Concn. of Iodine = 0.1016 M.

Initial Concn. of Nitric Acid=0.9257 M.

Final Concn. of Silver Nitrate=0.72 M except * = 0.975 M.

This can be explained by assuming that the adsorption in all three cases occured on the same part of the charcoal surface, viz; the carbon atoms which were not already covered with chemisorbed atoms or molecules.

The adsorption curve for nitric acid on C_m, at low concentrations (Fig.15), showed a sudden change in direction at a concentration of about 0.005 M. This effect was presumably due to the irreversible adsorption of part of the adsorbed nitric acid, which was observed by Miller [15]. The nitric acid adsorption curves for C_j, and C_k (Fig. 14 (b)), showed that the amount of adsorption was little affected by the fineness of the charcoal particles.

Influence of Nitric Acid.

The results obtained for the adsorption of silver nitrate and nitric acid, by charcoal C_c, from acid solutions of silver nitrate, are given in Table 6. Although the values of A, B, and C, in duplicate experiments, were not always in very good agreement, the values for the total adsorption of nitric acid and silver nitrate, (A-C), agreed closely. Further, as is shown in Table 14, the total adsorption/

adsorption in acid solutions did not differ greatly from the total adsorption from an originally neutral silver nitrate at the same equivalent molar concentration.
These results are in agreement with the assumption (see p.61) that the same part of the charcoal surface was largely responsible for the adsorption of both silver nitrate, and nitric acid.

Table 6 also shows that, at a given concentration of silver nitrate, the reduction decreased with increasing concentration of nitric acid, until, at about 0.45 M, it had become very small.
That the decreased reduction was not due merely to the resolution of the reduced metal, is shown by the results of Ruff, Ebert, and Luft [6]. These investigators found that the reduction of auric chloride by purified "supernorit" charcoal, was inhibited when the concentration of hydrochloric acid was greater than 1.0 M. In this case the metal could not redissolve in the acid, hence, the inhibition of the reduction must have been due to the preferential adsorption of hydrochloric acid on the reducing surface.

/

Table 14.

see Table 6				see Fig. 5a.	
(I) Final [$AgNO_3$]	(II) Final [HNO_3]	(I) (II)	(A - C)	Final [$AgNO_3$]	(A - C)
0.4561	0.4401	0.8962	2139	0.91	2240
0.4833	0.4389	0.9222	2021		
0.4725	0.2230	0.6955	1526	0.69	1960
0.4826	0.2173	0.6999	1564		
0.2380	0.4378	0.6758	1871		
0.2378	0.4378	0.6756	1828		
0.4620	0.0999	0.5619	1540	0.56	1750
0.1083	0.4549	0.5632	1229		
0.1175	0.4471	0.5646	1108		
0.4561	0.0574	0.5135	1768	0.51	1670
0.2332	0.2225	0.4557	1250	0.46	1570
0.2317	0.2238	0.4555	1260		
0.1047	0.2308	0.3355	1032	0.31	1300
0.1056	0.2312	0.3368	965		
0.2215	0.0982	0.3197	1126		
0.2222	0.0985	0.3207	1065		
0.2194	0.0562	0.2756	1117	0.28	1200
0.1044	0.1182	0.2226	894	0.22	1040

	A	B	C	B-C
	829	199	-400	599
	379	134	-789	823
Difference	450	165	389	224
	1368	158	-418	576
	864	37	-700	737
Difference	504	121	318	161

If we examine the duplicate experiments which were not in good agreement (see above), it will be seen that the results are more in agreement with the above conclusion. Decreased reduction, due to solution of silver, would decrease the acid in solution (C), by 165, and 121, respectively, and the total adsorption of silver (A), by the same amount. Decreased reduction, due to increased adsorption of nitric acid (224,161) on the reducing surface, before reduction has occurred, would decrease the adsorbed silver nitrate by an approximately equal amount, and the reduced silver by a somewhat smaller amount (see p.55), hence, the total adsorption (A) would be decreased by approximately 448, and 322, respectively (i.e. twice 224, and 161).

Ageing of the Charcoal.

In many cases the action of the various charcoals on silver nitrate was re-examined after the charcoal had been kept for some time. It will be seen from Table 15, that the amount of reduced silver (B) was always considerably less at the end of the period of ageing (11) than at the beginning(1), whereas the adsorption of silver nitrate remained constant, or, more generally increased slightly.

In the above cases the charcoals were kept in stoppered tubes, in the presence of air, during the period of ageing. Now charcoal, C_Z, was prepared by keeping a sample of C_b in an evacuated vessel for one month. At the end of this period the reducing action of C_Z was determined, and also that of a second portion of C_b which had been stored in the usual way, for the same length of time. As the following data show, the reduction produced by C_Z was definitely higher than that brought about by C_b.

Initial [$AgNO_3$]	Reduction by	
	C_b	C_Z
0.0992	981 997	1083 1093
1.000	1101 1101	1165 1164

Table 15.

Char.	Initial [$AgNO_3$]	Period of ageing	$AgNO_3$ adsorbed (A-B)		Reduction (B)	
			(I)	(II)	(I)	(II)
C_d	0.2497	2 mths.	771	849	786	662
C_j	1.000	$7\frac{1}{2}$ "	1910	1900	1090	760
C_k	"	"	2510	2680	990	720
C_m	0.0992	8 "	603	580	707	510
C_z	0.2497	3 "	793	893	1088	784
$C_z{}^1$	"	3 "	843	958	1017	825

King and Lawson[14] found that the amount of water vapour adsorbed by charcoal, which they associate with the chemisorbed oxygen layer, increased by exposure of the charcoal to air.

Lowry and Hulett[16], found that oxygen was slowly adsorbed at room temperature, and was not recoverable except at higher temperature, as carbon monoxide, and carbon dioxide. It seemed likely, therefore, that the loss of reducing power on ageing, was caused by partial oxidation of the more active reducing centres which decreased the reduction without affecting the adsorbing surface. The fact that the adsorption of nitric acid showed very little change on ageing of the charcoal (see Fig.15), supported the view that the adsorbing capacity of the surface was unchanged.

Charcoals treated at 450° - 470°.

Table 16.

Charcoal		Treatment	Reduct.(B) Final Conc.=.7M.
Before Treat.	After Treat.		
C_b(B=1080)	C_c	moist air	1090
	C_d	dry air	920
	C_e(1 day)	" H_2	1400
	" (4 days)		1240
C_b Pt.	C_f(1 day)	" "	1200
C_a	C_g	Cl_2, H_2, O_2	680
(B=1101)	C_h	dry O_2	800
	C_i	" N_2	1030.

Charcoals treated at 940° - 980°

Table 17.

Charcoal		Treatment	Reduct.(B) Final Conc.=.7M.
Before Treat.	After Treat.		
C_a(B=1101)	C_m(4 mths)	dry air, 4 hrs.	1040.
C_m	C_n	" N_2, 4 "	220
C_n	C_o	" N_2, 12 days	240
C_b(B=1080)	C_p	" N_2, 4 hrs.	330.

Compare C_1 (= C_p, heated in air, ½ hr.) B= 488.

Adsorption of Sodium Hydroxide (see Table 9).

In agreement with other investigators (e.g. King), it was found that the adsorption of sodium hydroxide, by charcoals activated with air, decreased as the temperature of activation was increased. The maximum adsorption was obtained with moist air[14], at 450° - 470°, (see C_c). Contrary to King [14], however, no trace of oxalic acid could be extracted from the charcoal (C_c), with water. No relation appeared to exist between the adsorbing power of a charcoal for sodium hydroxide, and its reducing capacity. This was to be expected, since the amount of adsorption of sodium hydroxide appears to depend more on the nature of the oxide layer than on its size.

Charcoals treated at 450° - 470° (see Table 16).

Charcoals C_c and C_d.

The reduction produced by C_c was greater than that produced by Cd, and may have been caused by the hydrogen formed by the decomposition of the moisture, by the charcoal.

Charcoals Ce and C_f.

Treatment with hydrogen greatly increased the reduction, probably as a result of the physical adsorption of hydrogen by the charcoal. The rapid decrease in reduction/

reduction, and the higher value of the reduction, in the case of C_e, was probably due to the catalytic combustion of the hydrogen, at the surface of the charcoal, which would be greatest in the case of C_f [19].

Charcoal, C_h.

In the preparation of C_h, the charcoal was treated with oxygen until about 50% of it had been burned. The enlargement of surface, resulting from combustion [18], had little effect on the reduction. Hence, it appeared that the combustion had also increased the fraction of the total surface covered with the oxide layer.

Charcoal, C_g.

The reduction produced by C_g was less than that by Ch, and this could be accounted for on the greater amount of combustion (75%) in the case of C_g. Hence the chlorine treatment alone did not lower the reduction, but may have increased it. This showed that the reduction was not caused by physically adsorbed hydrogen or hydrocarbons.[6] Chemisorbed hydrogen, if present, may not be removed by the chlorine, but it is not likely to be the cause of the reduction, as Barrer [20] has shown/

shown that the chemisorbed hydrogen is held very strongly on the charcoal. It will be seen from Fig. 7a, that all the acid formed during reduction, appeared in the solution. This was due to the fact that the hydrogen treatment did not remove all the hydrochloric acid (see p.13), which reacted with the silver nitrate, and liberated nitric acid.

Charcoal C_i.

Nitrogen treatment increased the reduction, probably, as a result of the removal of hydrocarbons from the reducing surface.

Charcoals treated at Room Temperature.

Charcoal C_z' (see fig. 13).

Treatment with cold intensely dried nitrogen had no effect on the reduction.

Charcoal C_z.

Charcoal C_z has already been discussed (see p.65).

Charcoal treated at 740° - 830° (see Fig. 9(a,b).

Charcoals, C_j and C_k.

The reduction in both cases increased, although the amount of combustion was considerable (ca. 36%). It appeared, therefore, that the effect of increased surface of the charcoal exceeded that of increased chemisorption of oxygen.

Charcoals treated at 1000° - 1250°.

Table 18.

Charcoal		Treatment	Reduct.(B) Final Concn. =.7M.
Before Treat.	After Treat.		
C_a	C_q	degas 4 hrs, 960°. " 1 hr. 1000°.	692
C_a	C_t	" 1 hr. 1125°.	560
C_q	C_r	air, 2 hrs. 1000°.	525*
C_a	C_s	CO_2, 5 hrs. 1010°.	700
C_t	C_u	air,(moist)4 hrs,1125°.	157
C_t	C_v	H_2(moist),4 hrs, 1125°.	127
C_t	C_w	N_2, 4 hrs, 1125°.	198
C_a	C_x	air, 8 hrs, 1125°.	201*
C_a	C_y	CO_2, ½ hr. 1250°.	300

*Final Concn. $AgNO_3$ = 0.98 M.

The nitrogen present probably hindered the formation of the oxide layer.

Charcoals treated at 940° - 980° (see Table 3).

Charcoal, C_m.

C_m was very similiar to C_j (cf. figs. 9a and 10a) and the same remarks apply to it.

Charcoals C_n, C_p and C_o.

Treatment of Cm, and C_p, with nitrogen produced a striking decrease in the reduction. The reducing capacity of Cp was partially restored by heating it in air at 740° - 830°. It seemed likely, therefore, that the effect was due to chemisorption of nitrogen. The reducing capacity of C_p was very slightly greater than that of C_n, which showed that very little desorption of the nitrogen occurred when the charcoal, C_n, was heated at 740° - 830°. Syrkin and Potapow [17] have also obtained evidence of the chemisorption of nitrogen on charcoal, at high temperatures.

Charcoals treated at 1000° - 1250°.

It will be seen from Table 18_m that the reducing capacity of the charcoal became less, and less, dependent on the nature of the gas used, as the temperature of treatment rose. Graphitisation appeared to be the controlling factor.

Barrer [20] has shown that charcoal was exceedingly stable at 930°, but commenced to graphitise above 1000°, with the decomposition of the surface compounds. Almost complete graphitisation was obtained after heating for several days at 1000°, or for some hours at 1100°. It seemed likely, therefore, that heating the charcoal to a much higher temperature (see C_y), would yield a carbon surface, free from surface compounds.

Hence, the appreciable reducing capacity of charcoal, C_y furnished additional evidence that the charcoal itself was responsible for the reduction[3].

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SUMMARY.

1. A method has been devised for estimating the amount of reduced silver, formed by the action of pure sugar charcoal on silver nitrate solutions,

2. Determinations have been made of (1) adsorption of silver, and (2) reduced silver, and (3) the acid liberated.

3. The influence of the following factors has been investigated;-

    (1). Concentration of silver nitrate.

    (2). Acidity of the solutions.

    (3). Period of contact of the charcoal with the silver nitrate.

    (4). Treatment with air, oxygen, nitrogen, hydrogen, and carbon dioxide, at different temperatures.

4. Determinations of the adsorption of (1) nitric acid, (2) sodium hydroxide, and (3) iodine, have been made in the case of certain of the charcoals.

5. A hypothesis has been advanced to correlate the results obtained.

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