THE RATE OF DECOMPOSITION
OF
ETHYL HYPOCHLORITE

Thesis by
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Contents

Introduction

Ethyl hypochlorite, first prepared by Sandemeyer (1) in 1885, is conveniently made in an apparatus like the one described by him (2). The substance is highly unstable, decomposing at room temperature. In direct sunlight the heat of decomposition is sufficient to cause vigerous boiling, soon followed by explosion of the vapors. In dilute carbontetrachloried solution at room temperature, ethyl hypochlorite is relatively stable, since after two to three days, less than ten per cent has decomposed. This decomposition is autocatalytic, since after five days 80 per cent or more of the substance has disappeared (3).

No thorough study has been made of the decomposition of alkyl hypochlorites. Chattaway and Backeberg (4) report that the primary decomposition products of alkyl hypochlorites are the corresponding aldehydes or ketones, and HCl or alkyl chlorides. These reactions may be represented by the following equations:

$$R\text{-}CH_2\text{-}OCl \rightarrow R\text{-}CHO + HCl$$

$$R_2\text{-}CH\text{-}OCl \rightarrow R_2\text{-}CO + HCl$$

$$R_3\text{-}C\text{-}OCl \rightarrow R_2\text{-}CO + R\text{-}Cl$$

Chattaway and Backeberg (5), investigating the chlorination of alcohol, find that ethyl hypochlorite is formed but quickly breaks down in the presence of excess alcohol to give acetaldehyde and HCl. Taylor, MacMullin and Gammal (3) report good yields of ethyl acetate obtained from the decomposition of ethyl hypochlorite. The reactions proposed by them are the following:

$$CH_3\text{-}CH_2\text{-}OCl \longrightarrow CH_3CHO + HCl$$

$$CH_3\text{-}CHO + CH_3\text{-}CH_2OCl \longrightarrow CH_3COOC_2H_5 + HCl$$

Durand and Naves (6) point out that chlorine is also a product of this decomposition, and suggest the following equation for its formation:

$$CH_3CH_2\text{-}OCl + HCl \longrightarrow CH_3CH_2OH + Cl_2$$

The present work was undertaken with a view to determining the mechanism of the decomposition of this extremely interesting substance. Preliminary tests showed that dilute solutions of ethyl hypochlorite (0.1 to 0.3 mols per liter) in dry carbon tetrachloried are quite stable for several hours, if not for several days, at room temperature. When dry HCl gas is dissolved in the carbon tetrachloride, the decomposition takes place at a measurable rate at 40 or 50°C. The photochemical reaction was not investigated; all the work referred to in this paper was done in the dark, or in the presence of weak artificial light. The data obtained in the measurement of the rate of decomposition are given in the experimental part, and in the discussion which follows the attempt is made to picture a mechanism in agreement with the observed facts.

Experimental Part

Preparation of Materials:

The ethyl hypochlorite used in these experiments was prepared by Sandemeyer's method (2) which is briefly the following. Ethyl alcohol is mixed with 50% NaOH in the proportion, 1 mol alcohol to 2 mols NaOH, and enough water is added to produce a clear homogeneous solution. This solution is placed in an inclined glass tube, jacketed with ice water, and closed at its lower end by a stop-cock. When the solution has become cold, chlorine is admitted at a moderate rate until it is no longer rapidly absorbed. This usually requires 20 or 30 minutes, during which time a greenish-yellow layer of the hypochlorite collects above the aqueous phase. The chlorine current is then stopped and the aqueous phase run off through the stopcock. The hypochlorite phase is caught in a separatory funnel containing ice-cold half saturated sodium bicarbonate solution. After gentle agitation for a few seconds the hypochlorite phase is allowed to sink to the bottom, and is immediately drawn off into an ice-cold flask containing a few granules of anhydrous calcium chloried. after gentle agitation for 30 or 40 seconds to remove the water that unavoidably accompanies the hypochlorite, it is pipetted directly into a glass stoppered flask containing the carbon tetrachloried solvent for that run. The volatility of the substance and temperature incertainties made it undesirable to attempt to use the volume as an accurate measure of the amount of material added. Titration of a sample of the solution immediately after mixing served to establish the initial concentration of the hypochlorite.

Carbon tetrachloride was prepared for these runs by drying the commercial CCl_4 over P_2O_5 for several hours with mechanical stirring, decanting the clear liquid into a dry distilling flask and distilling. The middle portion of the distillate was stored in a glass stoppered bottle until required.

Dry hydrogen chloride was dissolved in the carbon tetrachloride for most of the runs. It was prepared according to the conventional method, namely, by running concentrated c. p. hydrochloric acid into the bottom of a tall bottle containing concentrated sulfuric acid. The gas delivered from the bottle was led through a sulfuric acid wash bottle into the carbon tetrachloride to be used for a particular run. About 30 minutes is required to obtain a concentration of about 0.1 mols HCl per liter of solution.

Method of Following Rate:

About 150 c.c. of carbon tetrachloride was placed in a flask connected with the HCl generator and HCl was passed through it until approximately the desired concentration was reached. this solution was kept in a glass stoppered flask during the preparation of ethyl hypochlorite. As soon as this had been added to the flask, the contents were thoroughly mixed. Two 10 c.c. samples were pipetted into iodine flasks containing an excess of KI and a known quantity of standard acid. The remainder of the solution was pipetted into thin walled test tubes, previously drawn out preparatory to sealing. In all except one run, 10 c.c. were placed in each tube. After being sealed off, the tubes were placed in a wire rack and lowered into an oil bath which was kept at a constant temperature by means of a mercury regulator. The manipulations from the addition of the hypochlorite to the carbon tetrachloried, to the placing of the sealed tubes in the thermostat required about fifteen minutes. Preliminary trials indicated that the rate of decomposition at 25° is slow enough to justify the selection of the time of placing the tubes in the thermostat as zero time for that run. At regular intervals one of the samples was withdrawn and analysed.

Analyses were made according to the following proceedure. Standard acid (or distilled water if the acidity of the sample to be analyzed was known to be sufficient) was pipetted into a 500 c.c. conical flask containing a few crystals of KI. A sample tube was then removed from the thermostat, quickly washed with alcohol, placed in the flask and broken with a glass stirring rod. The flask was then stoppered and shaken vigerously for at least 30 seconds. This shaking is necessary to provide sufficient contact between the two phases to complete the liberation of the iodine. The iodine set free was then titrated to a starch end point with N/10 thiosulfate solution. Then a few drops of phenolphthalein indicator were added and the conte contents of the flask titrated to neutrality with standard alkali. Since hydrogen ion does not ehter into the thiosulfate reaction, this alkali titration is a measure of the excess acid in the flask after the liberation of iodine from the KI.

Data:

The following twelve tables summarize the data obtained from twelve runs under different conditions. The first column gives the time in minutes from the instant of placing the sealed samples in the thermostat. The uncertainty in the time recorded (due to variation in the manipulations, as washing, cooling, breaking tube in flask, etc.) is not greater than one minute. The second column gives the millimoles of iodine set free, computed from the thiosulfate titration. It should be noted that one mol of hypochlorite or one mol of chlorine sets free one mol of iodine:

$$EtOCl + 2I^- + H^+ \longrightarrow EtOH + I_2 + Cl^-$$

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

The third column records the millimols of NaOH required to titrate the sample to neutrality following the thiosulfate titration. One must, of course, subtract the number of milliequivalents of acid added initially in order to obtain this value.
In other words, since the liberation of iodine from KI takes place quantitatively only in acid solution, and since one usually is required to add acid to the titration flask before breaking the sample tube in it in order to insure sufficient acidity for this decomposition, one must subtract this acid from the NaOH titration to obtain the value of the "net NaOH".
In the first of the two equations above, hydrogen ion is

used up in the reaction. Assuming that ethyl hypochlorite is the only substance present in the solution which will liberate iodine (see discussion below) one must add to this "net NaOH" the number of millimoles of iodine set free (i.e. the number of millimoles of EtOCl in the sample) in order to obtain values for the quantity of HCl present in the sample at the time of analysis. These values are given in column four, and are in effect the algebraic sum of the values in column two and three.

The data from these tables are presented graphically in figures 1 to 12, where the concentration of EtOCl and of HCl, expressed in mols per liter, are plotted against time.

Table I.

Conditions of Run #1; Thermostat temperature 50°C.

Volume of samples 10.00 c.c.

Time	Millimoles I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	2.179	-0.549	1.630
0	2.177	-0.557	1.620
45	1.661	0.367	2.028
75	1.549	0.578	2.127
105	1.454	0.764	2.218
135	1.401	0.872	2.273
165	1.319	0.999	2.318
195	1.282	1.073	2.355
228	1.235	1.152	2.387
285	1.160	1.237	2.397

Table 2.

Conditions of Run #2: Temperature of thermostat 50°C.
Volume of samples 10.00 c.c.

(No HCl added to carbon tetrachloride)

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	2.298	-2.331	-0.033
0	2.294	-2.338	-0.044
120	2.283	-2.181	0.102
360	2.279	-2.319	-0.040
1440	2.260	-2.285	-0.025
3020	2.184	-2.079	0.105
4410	2.027	-1.735	0.292
5870	0.5383	----	----
5900	0.4612	1.059	1.520
5920	0.4886	1.023	1.512

Table 3.

Conditions of Run #3: Temperature of thermostat 50°C.

Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.976	-1.264	0.712
0	1.967	-1.281	0.686
30	1.253	0.187	1.440
60	1.142	0.361	1.503
90	1.094	0.406	1.500
120	1.038	0.517	1.555
150	1.006	0.556	1.562
180	0.978	0.592	1.570
270	0.900	0.689	1.589
300	0.887	0.705	1.592
330	0.868	0.737	1.605
360	0.856	0.730	1.586
390	0.830	0.751	1.581

Table 4.

Conditions of Run #4: Temperature of thermostat 50°C.

Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	0.882	-0.147	0.735
0	0.895	-0.162	0.733
30	0.772	-0.069	0.703
60	0.757	0.003	0.760
90	0.753	0.029	0.782
120	0.753	0.045	0.798
180	0.748	0.081	0.829
240	0.724	0.110	0.834
300	0.721	0.136	0.857
360	0.709	0.159	0.868
390	0.703	0.169	0.872
420	0.699	0.180	0.879

Table 5.

Conditions of Run #5: Temperature of thermostat 50°C.
Volume of samples 5.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	3.589	-1.478	2.111
0	3.578	-1.462	2.116
30	1.537	0.452	1.989
50	1.471	0.463	1.934
70	1.375	0.532	1.907
85	1.308	0.584	1.892
100	1.257	0.640	1.897
115	1.286	0.649	1.935
130	1.267	0.647	1.914
145	1.200	0.689	1.889
160	1.174	0.724	1.898
175	1.182	0.732	1.814
190	1.111	0.726	1.837
205	1.138	0.745	1.883

Table 6.

Conditions of Run #6: Temperature of thermostat 40°C.
Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.971	-0.848	1.123
15	1.721	-0.499	1.222
30	1.502	-0.011	1.491
45	1.420	0.157	1.577
60	1.404	0.208	1.612
75	1.375	0.271	1.646
110	1.319	0.366	1.685
140	1.290	0.452	1.742
170	1.253	0.505	1.758
200	1.223	0.553	1.776
260	1.168	0.646	1.814

Table 7.

Conditions of Run #7: Temperature of thermostat 40°C.

Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	2.341	-1.731	0.610
15	1.991	-1.465	0.526
30	2.197	-1.553	0.644
45	2.058	-1.227	0.831
60	1.627	-0.297	1.330
75	1.320	0.338	1.658
90	1.267	0.425	1.692
105	-----	-----	-----
120	1.249	0.404	1.653
150	1.221	0.447	1.668
180	1.201	0.489	1.690

Table 8.

Conditions of Run #8: Temperature of thermostat 40°C.
Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.006	0.258	1.264
15	0.911	0.306	1.217
30	0.923	0.251	1.174
45	0.928	0.270	1.198
75	0.920	0.211	1.131
135	0.892	0.330	1.222
195	0.892	0.385	1.277
345	0.844	0.570	1.414
360	0.843	0.496	1.339
545	0.792	0.587	1.379
560	0.787	0.586	1.373

Table 9.

Conditions of Run #9: Temperature of thermostat 40°C.
Volume of samples 10.00 c.c.

(No ethyl hypochlorite added; chlorine dissolved in CCl_4 to a concentration of 0.10 mols per liter; ethyl alcohol added to a concentration of 0.20 mols per liter).

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.033	0.379	1.412
15	0.910	0.405	1.315
30	0.870	0.429	1.300
45	0.881	0.512	1.393
135	0.757	0.763	1.520
195	0.687	0.902	1.589
225	0.624	0.993	1.617
270	0.616	1.019	1.635
285	0.603	1.047	1.650

Table 10.

Conditions of Run #10: Temperature of thermostat 40°C.
Volume of samples 10.00 c.c.

(Added ethyl alcohol to usual reaction mixture to a concentration of 0.17 moles per liter).

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.826	-1.599	0.227
15	1.786	-1.313	0.473
30	0.939	---	---
45	0.845	0.358	1.203
60	0.821	---	---
75	0.798	0.513	1.311
120	0.680	0.637	1.317
135	0.649	0.671	1.320
165	0.591	0.756	1.347
195	0.558	0.805	1.363
205	0.477	0.905	1.382

Table 11.

Conditions of Run #11: Temperature of thermostat 40°C.
Volume of samples 10.00 c.c.

(No ethyl hypochlorite added; chlorine dissolved to a concentration of 0.181 mols per liter; ethyl alcohol added to a concentration of 0.40 mols per liter).

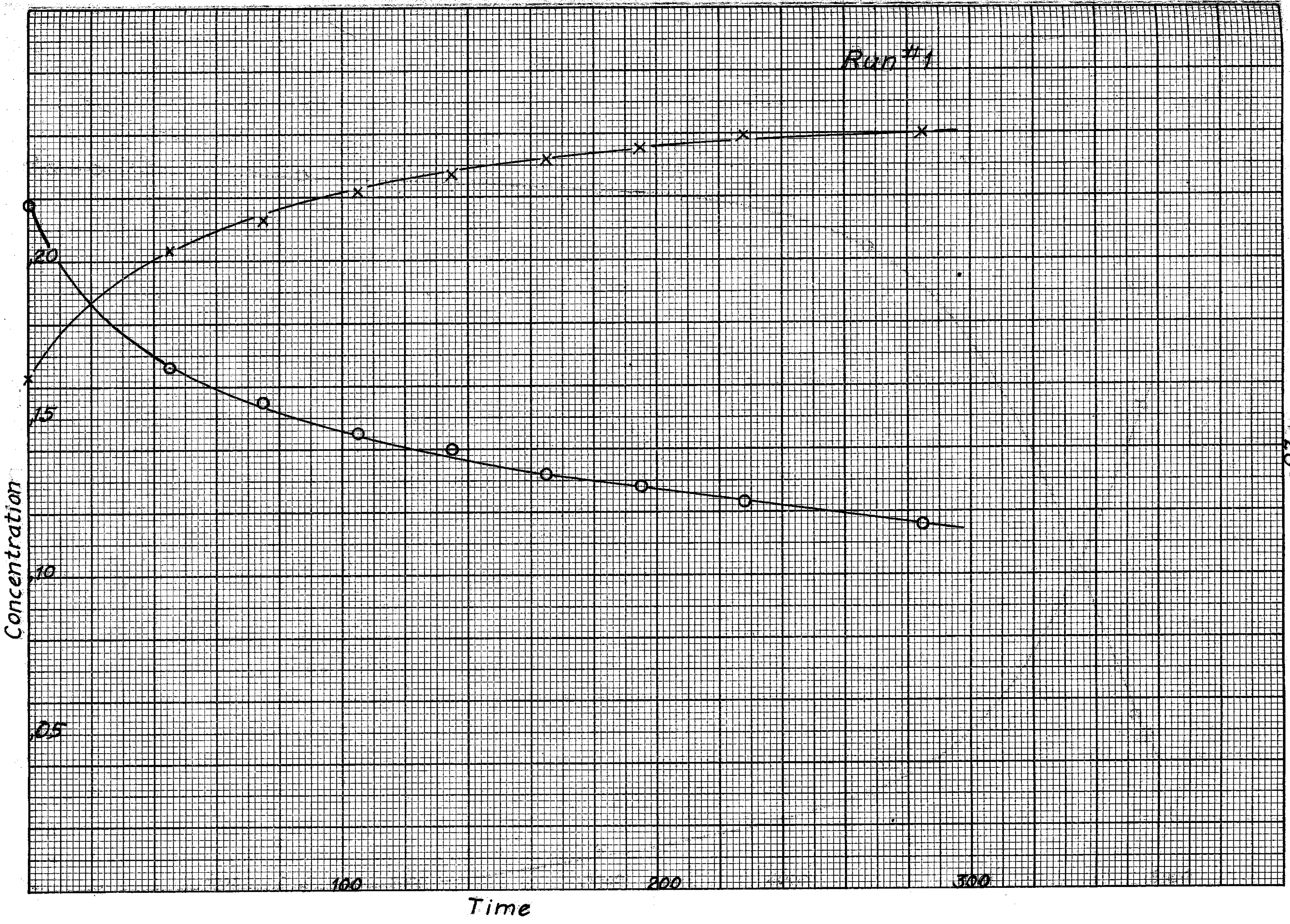
Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.810	0.271	2.081
10	1.533	0.721	2.254
30	1.347	1.069	2.416
45	1.243	1.235	2.478
60	1.153	1.380	2.533
90	0.998	1.610	2.608
120	0.884	1.764	2.648
135	0.817	1.817	2.634
150	0.766	--	--
175	0.694	1.936	2.630

Table 12.

Conditions of Run #12: Temperature of thermostat 40°C.

Volume of samples 10.00 c.c.

Time	Millimols I_2 set free	Milliequiv's "net NaOH"	Millimols HCl in sample
0	1.598	-0.474	1.124
15	1.532	-0.396	1.136
30	1.452	-0.238	1.214
45	1.349	-0.050	1.299
60	1.290	0.063	1.353
75	1.185	--	--
90	1.234	0.144	1.378
105	1.177	0.170	1.347
120	1.193	0.209	1.402
165	1.141	0.300	1.441
210	1.062	0.353	1.415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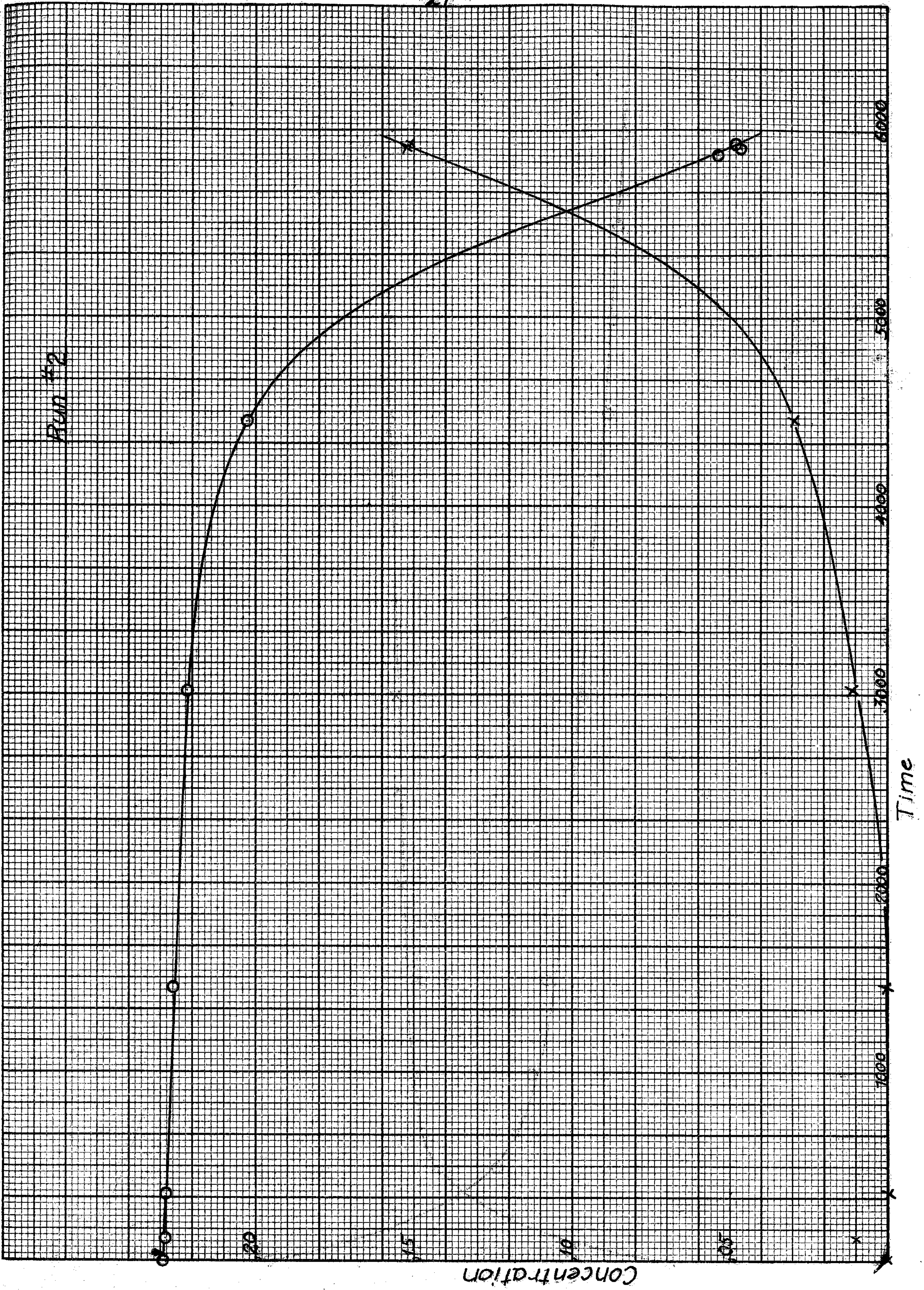
.15
.10
.05
Concentration
100
200
300
Time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5000
4000
3000
2000
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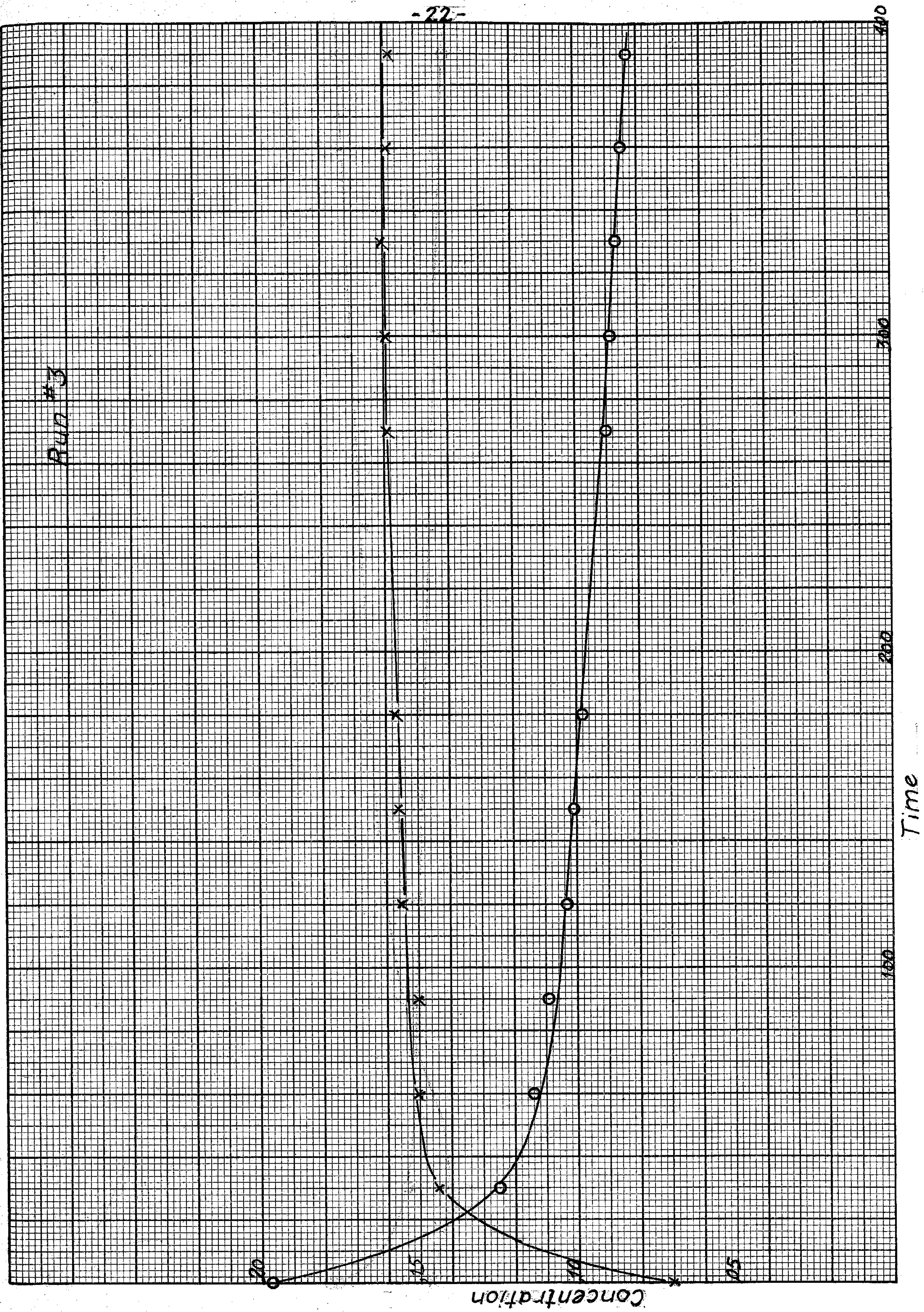
.20
.15
.10
.05
Concentration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Time
Concentration
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15
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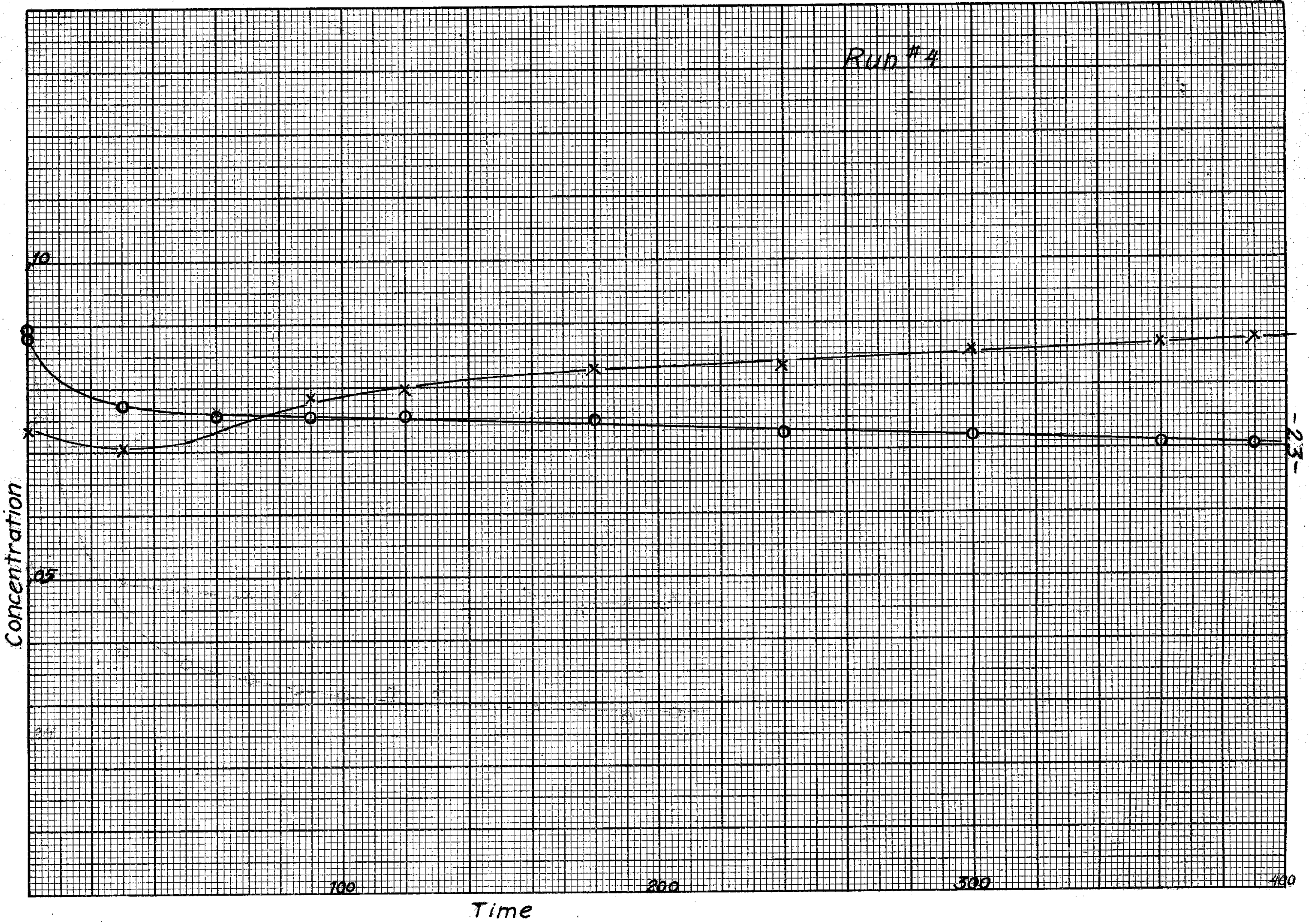
100
200
300
400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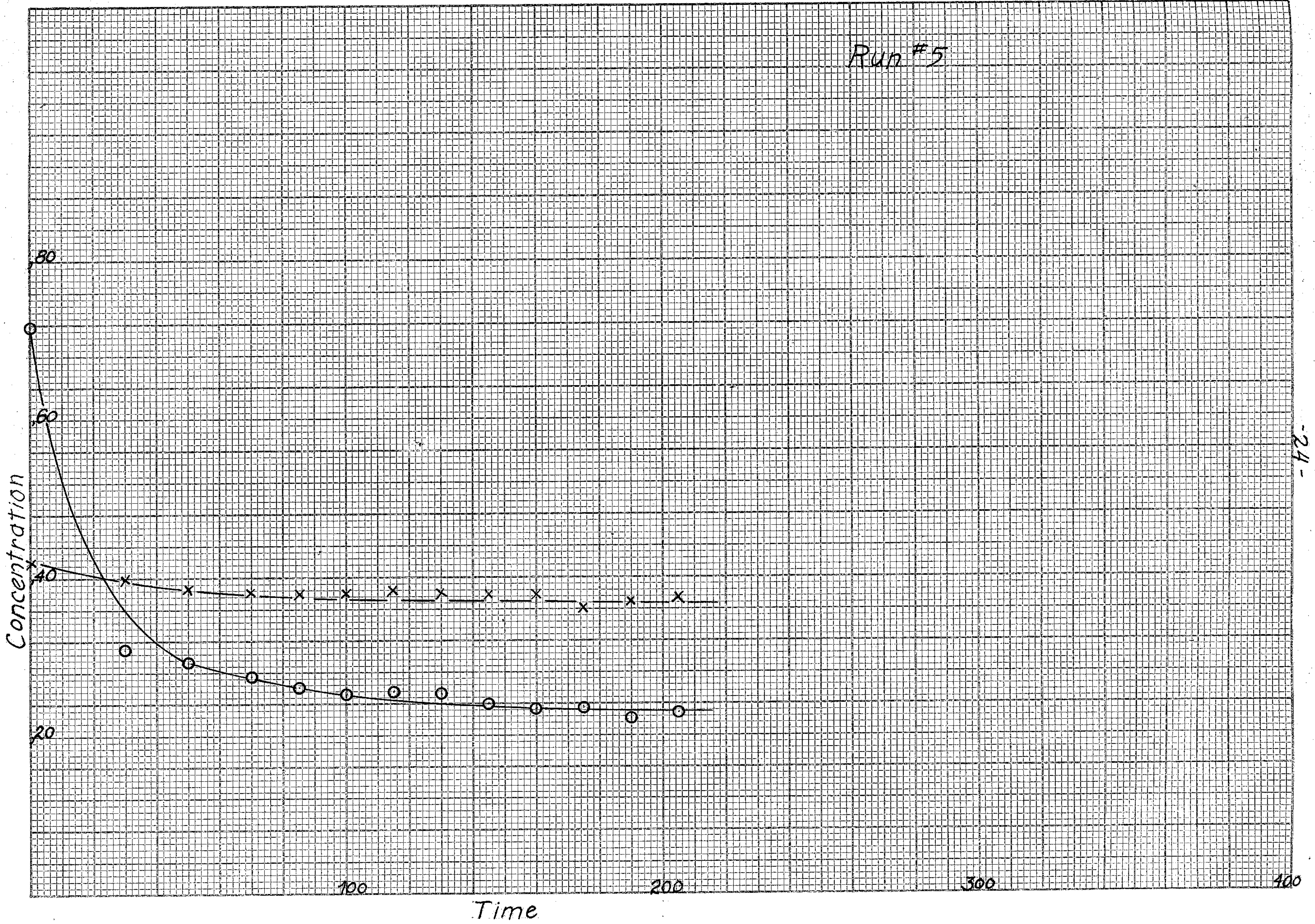
Concentration
100
200
300
400
Time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Concentration
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40
20
Time
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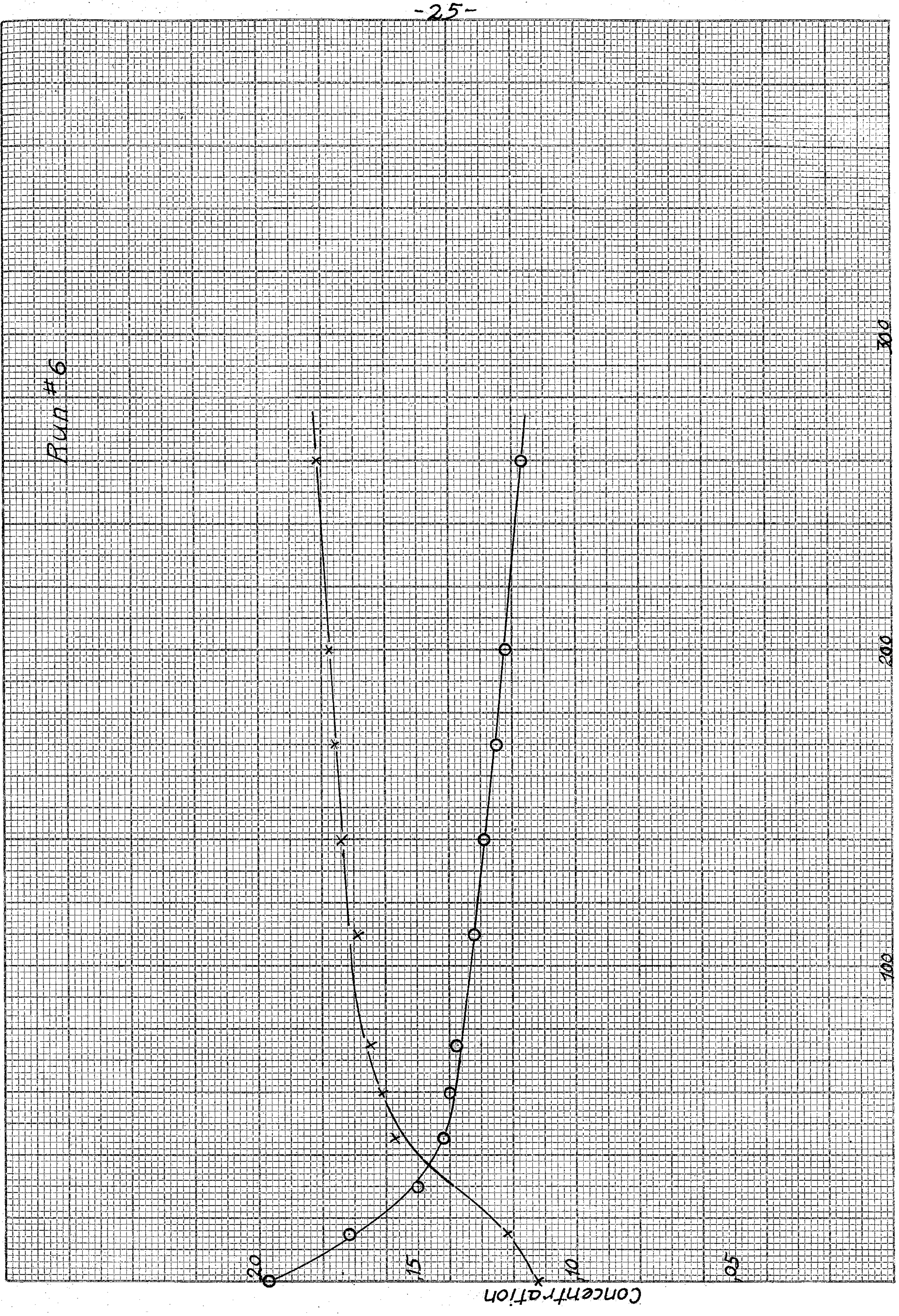
200
300
400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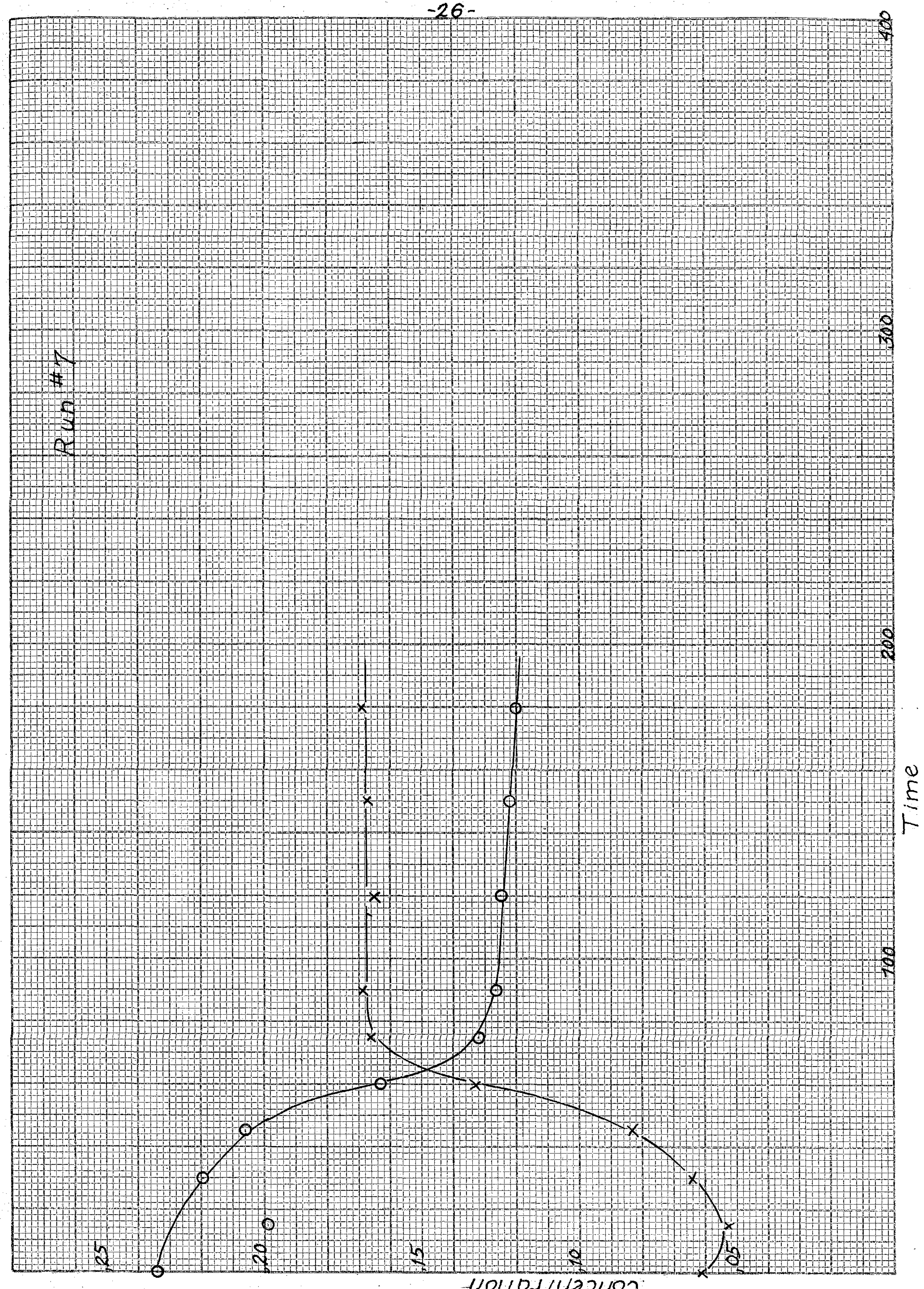
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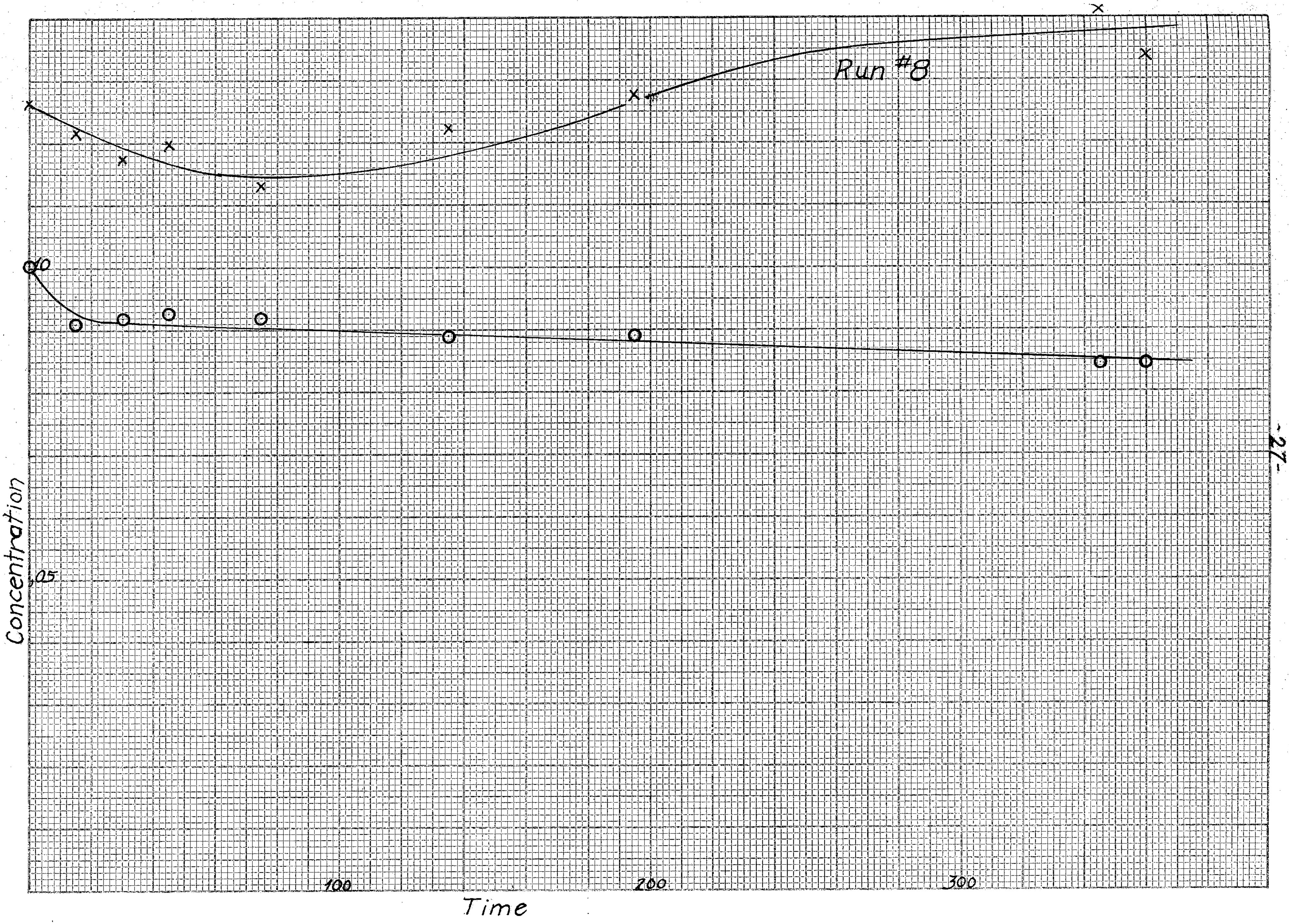
200
300
400
Time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Concentration
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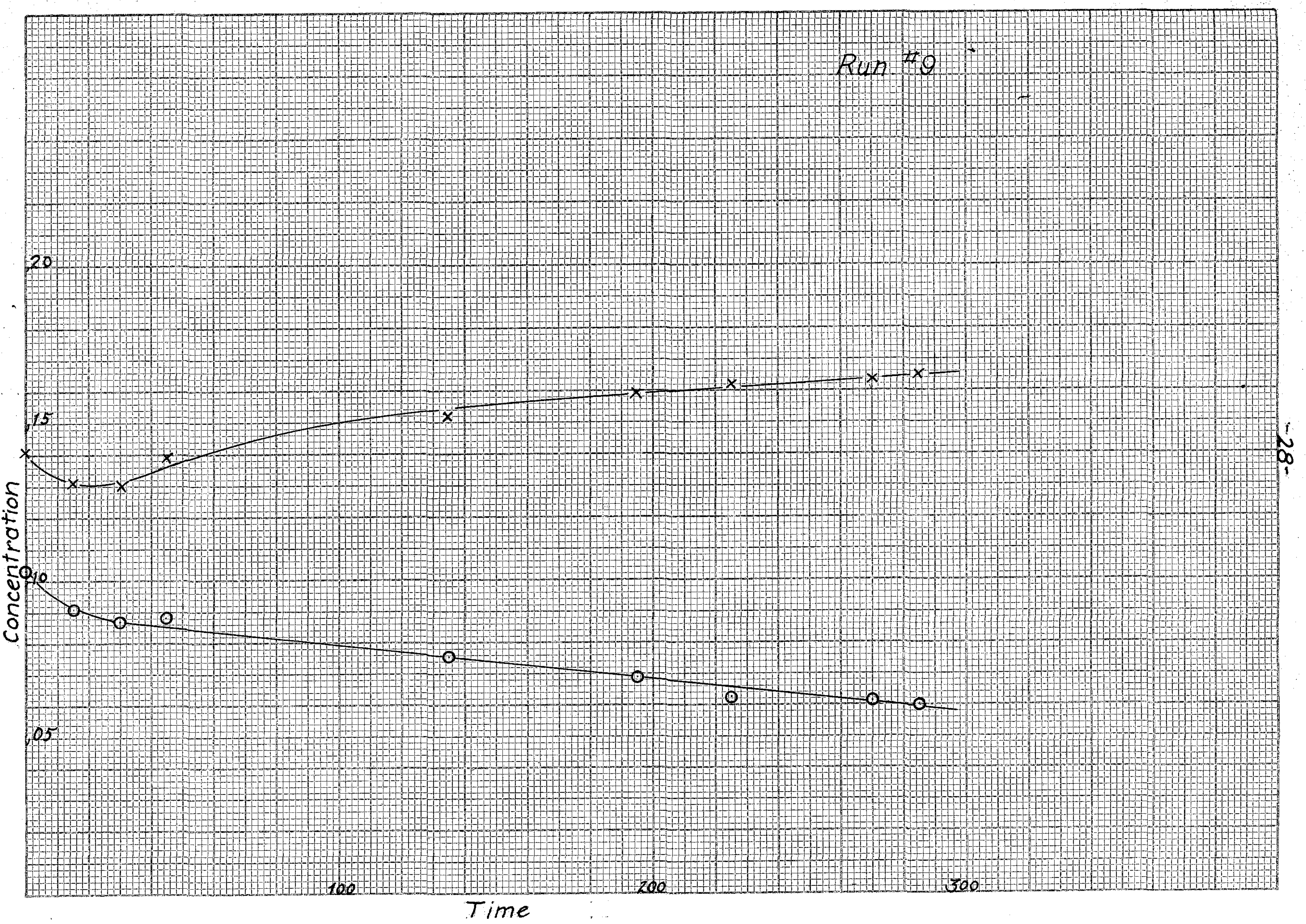
200
300
Time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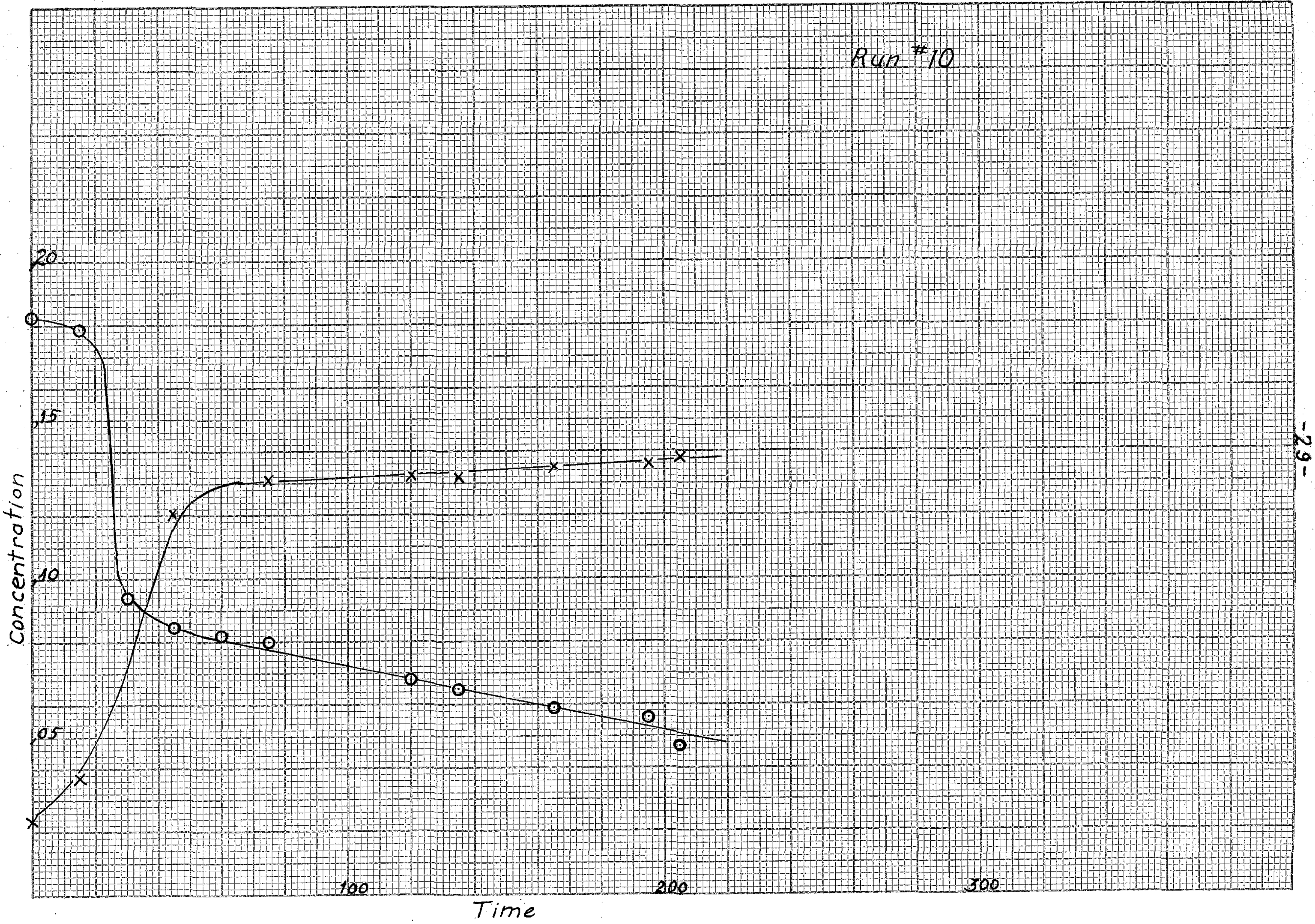
Time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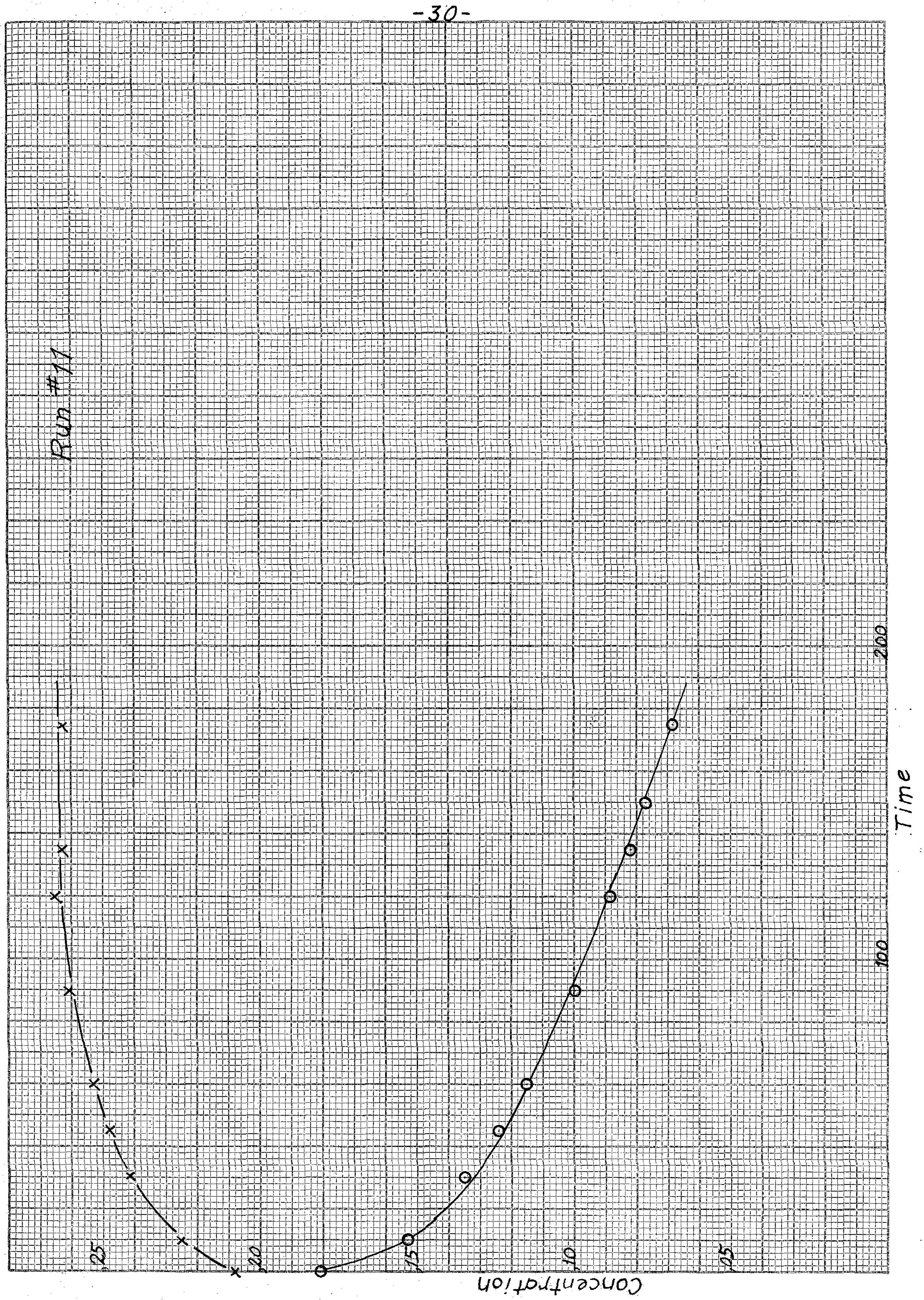
Time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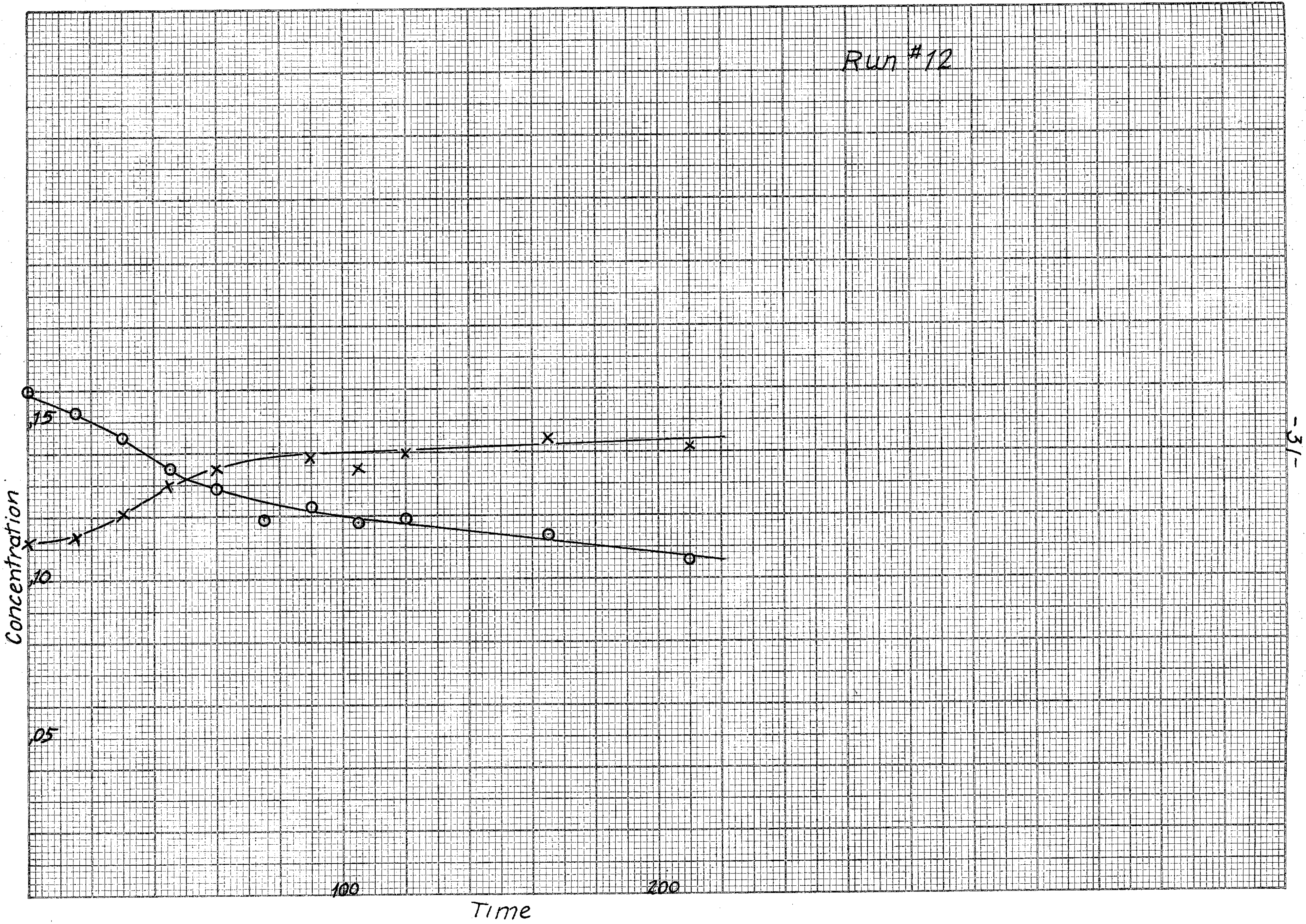
200
Time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.05
Concentration
100
200
Time

Discussion

Reactions:

The reactions taking place in this system are by no means apparent. Preliminary experiments at 25°C. showed that the rate of disappearance of oxidizing substances from the carbon tetrachloride solution is more rapid in the presence of dissolved HCl. A comparison of Run #2 with say Run #1 shows this difference. The work of other investigators on dthyl hypochlorite and related substances indicate that in may undergo decomposition in several ways. We will consider in the following paragraphs some of the rea reactions that may take place.

Chattaway and Backeberg (4) have prepared a series of alkyl hypochlorites. They find that the n-propyl, i-propyl, n-butyl and i-butyl hypochlorites are very unstable, and keep only a short time even at ice temperatures. The tert-butyl and tert-amyl hypochlorites are relatively stable, and can be kept at room temperature in the dark. The preparation of a hypochlorite from benzyl alcohol was attempted, but apparently the substance is so unstable that it decomposes almost as fast as it is formed, to give benzaldehyde. The chief decomposition products of the oth other hypochlorites are indicated by the following equations:

$$R\text{-}CH_2OCl \longrightarrow R\text{-}CHO + HCl$$

$$R_2\text{-}CHOCl \longrightarrow R_2\text{-}CO + HCl$$

$$R_3\text{-}COCl \longrightarrow R_2\text{-}CO + R\text{-}Cl$$

Taylor, MacMullin, and Gammal (3) report 80 to 90% yields of ethyl acetate, obtained from the decomposition of ethyl hypochlorite, for which they postulate the following reactions.

1. $EtOCl \longrightarrow CH_3CHO + HCl$

2. $CH_3CHO + EtOCl \longrightarrow EtOAc + HCl$

Durand and Naves (6) point out that ethyl hypochlorite reacts with HCl to regenerate the alcohol and chlorine. This reaction, under the proper conditions, can be violent.

3. $EtOCl + HCl \longrightarrow EtOH + Cl_2$

The evidence of Chattaway and Backeberg (5) indicates that the reverse of this reaction takes place when chlorine is passed into alcohol.

None of the above reactions have been reported as taking place in a system strictly analogous to the one under consideration, namely, in dilute carbon tetrachloride solution.

The purpose of the present paper is to set up a tentative mechanism which accounts in a qualitative if not in a quantitative way for the data obtained. This mechanism will then form a convenient point of departure for additional experimental work. In attempting to work out a mechanism accounting for the observed facts, it is more satisfying to consider only those reactions known to take place than to set up a series of hypothetical reactions for which there is no evidence. Such a tentative mechanism is developed in the following pages. While its quantitative agreement leaves much to be desired, it has the recommendation that the deviations can to some extent be explained, and no new hypothetical reactions had to be introduced.

In all the reactions considered above, one mol of HCl is produced for every mol of EtOCl decomposed. Even if areaction 3 above takes place to completion, the subsequent disappearance of Cl_2 would be expected to liberate an equivalent quantity of HCl. A casual inspection of the tables or curves will show that this amount of HCl was seldom found. In the case of most of the runs, the discrepancy is not large enough to become of major importance. In the case of Run #5, where the initial EtOCl concentration is about five times that of most of the other runs, there is little or no HCl formed in the decomposition. Apparently, to investigate the reactions by which EtOCl disappears without forming equivalent amounts of HCl, it will be necessary to work an high EtOCl concentrations.

Reaction Rate Constants:

In the expression for the rate of reaction

$$-dc/dt = k F(c,d)$$

c is the concentration of oxidizing substances and d that of HCl at the time t, as determined by titration. In order to determine the way in which the reaction rate depends upon the two variables c and d, we can assume various functions and evaluate the expression, solving for k. The constancy of k with varying values of c and d (i.e. from run to run) is the test that whould select the proper form of the function of the reaction. The constant k can be evaluated from the above equation in the form of the definite integral, using the experimental data for any pair of points in a run. However, the formation of the integral necessarily involves the stoichiometric relationship between c and d. As was mentioned above, the increase in d is not identical with the decrease in c, and apparently their relationships vary from run to run. A better way of testing the constancy of k involves the graphical determination of the slope of the curve. With reasonable care its value can be obtained with less that 10% error. The values of c and d to substitute in the function are read off the curves at the point where the tangent is taken. in this way, different functions of c and d of the form $c^{L}d^{n}$ were tried. m and n were varied separately, being given the values 1/2, 1, 3/2, 2, etc. Of sixteen forms tried, seven of the functions gave about the same constancy in k; for the other nine, k varied over a much wider range.

Another method of attack is the following. If between any two runs at the same temperature, the value of either c or d is the same while the value of the other variable is different in the two runs, one can determine roughly from a consideration of the concentrations and rates involved the manner in which the rate changes with one of the variables. However, the results of these comparisons were not decisive, partly at least because enough really comparable runs were not available.

Mechanism:

The following set of equations represents the most satisfactory mechanism that has been worked out up to the present time.

$$\text{I.}\quad EtOCl + HCl \rightleftharpoons EtOH + Cl_2$$

$$\text{II.}\quad EtOCl + EtOH \longrightarrow CH_3CHO + EtOH + HCl$$

~~III. EtOCl CH_3CHO~~

III. EtOCl + CH_3CHO ⟶ EtOAc + HCl

In Run#2 we see that EtOCl alone does not react at an appreciable rate, but that the products of some slow reaction serve to accellerate the decomposition. According to the equilibrium reaction (I.) HCl is necessary to the formation of EtOH which in turn is necessary for the further decomposition of EtOCl. Also, the presence of excess alcohol or aldehyde should speed the reaction. No runs were made with aldehyde added. Runs #9,10, and 11 all contain excess alcohol. As inspection of the curves shows, the slopes are appreciably greater than runs at the same temperature and comparable concentrations not containing any added alcohol. (Compare #9 and #8, or #10 and #12)

Up to thes point, no assumptions regarding the above series of reactions other than those implied in simply writing them out have been made. Reaction I. can have any reasonable value for its equilibrium constant, and the equilibrium may be attained slowly or rapidly. The relative rates of reactions II II. and III. are of no immediate importance to the above considerations.

Before specific reaction rate constants can be calculated it is necessary to make assumptions regarding the above reactions. First, we will assume that reaction I. is rapid and reversible. This assumption implies that reactions II. and III. are the rate controling factors. For their rates, we can write the expressions:

$$-dc/dt = k_2(EtOCl)(EtOH) + k_3(EtOCl)(CH_3CHO)$$

In the absence of data on the concentration of aldehyde, we cannot calculate k_3. However, if we assume that after the initial stages of the reaction are over, a more or less steady state with respect to aldehyde concentration is attained,

$$k_2(EtOCl)(EtOH) = k_3(EtOCl)(CH_3CHO)$$

and

$$-dc/dt = 2k_2(EtOCl)(EtOH)$$

Substituting for (EtOCl) its value in the equilibrium expression

$$\frac{(EtOH)(Cl_2)}{(EtOCl)(HCl)} = K$$

The rate expression becomes

$$-dc/dt = \frac{2k_2}{K} \cdot \frac{(EtOH)^2(Cl_2)}{(HCl)}$$

or

$$-dc/dt = k(EtOH)^2(Cl_2) / (HCl)$$

In the runs in which the starting material was EtOCl, with no added alcohol, the value of the Cl_2 concentration equals the concentration of alcohol. Since the iodine titration cannot distinguish between Cl_2 and EtOCl, the curve plotted represents actually the sum of EtOCl and Cl_2. A further assumption must be made before it is possible to use the analytical data for the purpose of calculating rate constants, namely, that the equilibrium in reaction I is so far to the right that the consideration of the iodine titration as a measure of the Cl_2 concentration introduces no appreciable error. The accompanying table shows the calculation of the rate constants under the above

Table of Reaction Rate Constants:

Run #	Time (min)	Temp (°C)	Slope (s)	Conc HCl (d)	Conc Cl$_2$	c^3 x 10^5	Conc EtOH	k (= sd/(EtOH)^{2}c)
---	----	----	x 10^5	mols/liter	(c) (m/l)	-----	-----	x 10^5
1	285	50	8.5	0.1237	0.1160	156	c	6.74
1	228	50	12.8	0.1152	0.1235	188	c	7.81
1.	135	50	22.0	0.0872	0.1401	275	c	6.97
3	360	50	3.75	0.0750	0.0856	62.5	c	4.38
3	270	50	6.3	0.0689	0.0900	72.9	c	5.49
3	150	50	12.5	0.0556	0.1006	102	c	6.81
4	240	50	1.50	0.0110	0.0724	38.0	c	4.34
5	190	50	25.0	0.1452	0.2222	1100	c	3.30
5	145	50	30.8	0.1578	0.2400	1580	c	3.07
5	885	50	50.5	0.1168	0.2616	1780	c	3.31
6	260	40	10.8	0.0646	0.1168	259	c	4.56
6	140	40	11.5	0.0452	0.1290	214	c	2.38
6	60	40	21.0	0.0208	0.1404	276	c	1.58
7	180	40	7.0	0.0489	0.1201	173	c	1.98
8	545	40	2.00	0.0587	0.0792	49.8	c	2.36
9	270	40	10.0	0.1019	0.0616	23.4	0.1616	0.635
10	135	40	19.0	0.0670	0.0649	27.4	0.2349	0.356
11	175	40	31.6	0.1956	0.0694	33.4	0.2884	1.05
11	90	40	44.5	0.1610	0.0998	99.5	0.3188	0.706
11	45	40	63.0	0.1235	0.1243	193	0.3433	0.530
12	165	40	6.3	0.0300	0.1141	148	c	1.27

assumptions. The slopes of the curves given in the table were obtained graphically. The agreement is not very satisfactory. For example, the rate constants of Runs #9, 10, and 11 are all somewhat low. However, the variations in the conditions of the different runs are considerable, and one can expect that factors negligible in one run will exert an appreciable influence in a another.

While it is possible to account for the larger deviations observed by considering the changes in the conditions of the runs, and the effect one would expect these changes to have on the relation between the velocities in reactions II and III, or in the position of the equilibrium in reaction I, speculation of this sort has no special significance for the present purpose. It is clear that there are too many inter-related reactions to permit a sound quantitative treatment of this system without further information. The most profitable line for additional work on this problem seems to be the separate study of reactions 2 and 3. This might yield data that would be quite useful in clarifying not only this problem, but also the more general one of the mechanism of chlorine substitution.

Temperature Coefficient:

The temperature coefficient of reactions are usually reported as the ratio of the reaction rate constants at T 10 and T °C:

$$Q_{10} = k_{t+10} / k_t$$

Temperature coefficients have been found to vary for different reactions from about 1.8 to 4.5. The mechanism proposed here gives a temperature coefficient within this range; about 2.3 if we omit the constants for Runs #9, 10, and 11. If these constants are included, the value of Q_{10} becomes about 3.5.

Summary

Data has been submitted showing the rate of disappearance of oxidizing substances from carbon tetrachloride solutions. Similar data is submitted for solutions of alcohol and chlorine. A tentative mechanism has been submitted which explains, qualitatively at least, the facts observed. This mechanism has the recommendation that it includes no purely hypothetical reactions.

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