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PART I: A KINETIC STUDY OF THE HYDROLYSIS OF SODIUM HYDROBORATE. PART II:
UNFINISHED KINETIC STUDY OF THE HYDROLYSIS OF OCTAHYDROTRIBORATE ION

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HYDROLYSIS OF OCTAHYDROTRIBORATE ION

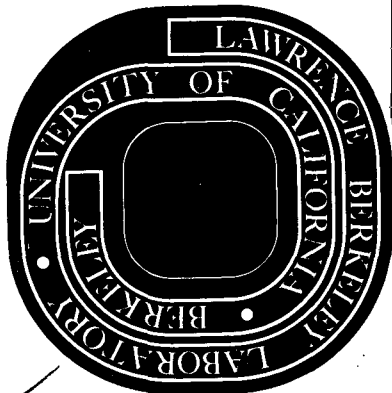
Francis Ting-yuan Wang
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PART I: A KINETIC STUDY OF THE HYDROLYSIS OF SODIUM HYDROBORATE
PART II: UNFINISHED KINETIC STUDY OF THE HYDROLYSIS
OF OCTAHYDROTRIBORATE ION

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ABSTRACT

The stepwise hydrolysis of hydroborate has been studied in a cold 88 vol% methanol/12 vol% water solution, in the hydrogen ion concentration range 0.1-1.1 M. At -78° , BH_4^- rapidly hydrolyzes to H_2OBH_3 , which, in turn, hydrolyzes to $\text{BH}_2(\text{H}_2\text{O})_2^+$ according to the rate equation $-\text{d} \ln[\text{H}_2\text{OBH}_3]/\text{dt} = 0.0015 \text{ sec}^{-1} + 0.0016[\text{H}^+] \text{ sec}^{-1} \text{ M}^{-1}$. The rate data for the hydrolysis of $\text{BH}_2(\text{H}_2\text{O})_2^+$ solutions at -36° are consistent with the following rapid equilibrium ($K = 6.4 \text{ l/mole}$): $\text{H}^+ + \text{H}_2\text{OBH}_2\text{OH}^+ \rightleftharpoons \text{BH}_2(\text{H}_2\text{O})_2^+$. The $\text{BH}_2(\text{H}_2\text{O})_2^+$ ion is stable toward hydrolysis, whereas its conjugate base hydrolyzes to $\text{H}_2\text{OBH}(\text{OH})_2$ according to the rate equation $-\text{d} \ln[\text{H}_2\text{OBH}_2\text{OH}]/\text{dt} = 0.017 \text{ sec}^{-1}$. At -36° , $\text{H}_2\text{OBH}(\text{OH})_2$ hydrolyzes to $\text{B}(\text{OH})_3$ according to the rate equation $-\text{d} \ln[\text{H}_2\text{OBH}(\text{OH})_2]/\text{dt} = 3.3 \times 10^{-4} \text{ sec}^{-1}$.

The species H_2OBH_3 , $\text{BH}_2(\text{H}_2\text{O})_2^+$ and $\text{H}_2\text{OBH}(\text{OH})_2$ are converted to the anions BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$, respectively, by the addition of hydroxide. These anions undergo hydrolysis in non-buffered strongly alkaline solutions according to the rate equations $-\text{d} \ln[\text{BH}_3\text{OH}^-]/\text{dt} = 1.8 \times 10^{-4} \text{ sec}^{-1}$ at 20° ; $-\text{d} \ln[\text{BH}_2(\text{OH})_2^-]/\text{dt} = 2.2 \times 10^{-5} \text{ sec}^{-1}$ and $-\text{d} \ln[\text{BH}(\text{OH})_3^-]/\text{dt} = 1.1 \times 10^{-3} \text{ sec}^{-1}$ at 0° . The hydrolysis rates increase markedly when the pH is reduced to pH 10. The boron-11 nmr spectrum of BH_3OH^- is a 1:3:3:1 quartet, with $J_{\text{B-H}} = 87 \text{ Hz}$, centered

12 ppm unfield from the borate singlet.

The stepwise hydrolysis of the $B_3H_8^-$ has also been studied in the cold methanol-water solution, in the hydrogen ion concentration range 1.0-3.5 M. At -78° , one mole hydrogen per mole of $B_3H_8^-$ was obtained, corresponding to the formation of $B_3H_7OH_2$. However in aqueous 8 M HCl a total of 4.5 moles of hydrogen per mole of $B_3H_8^-$ was obtained at -78° . The reaction mixture, when warmed to room temperature, will give another 4.5 moles of hydrogen.

PART I: A KINETIC STUDY OF THE HYDROLYSIS OF SODIUM HYDROBORATE

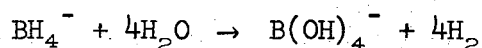
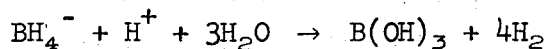
ABSTRACT

The stepwise hydrolysis of hydroborate has been studied in a cold 88 vol% methanol/12 vol% water solution, in the hydrogen ion concentration range 0.1 - 1.1 M. At -78° , BH_4^- rapidly hydrolyzes to H_2OBH_3 , which, in turn, hydrolyzes to $\text{BH}_2(\text{H}_2\text{O})_2^+$ according to the rate equation $-\text{d} \ln [\text{H}_2\text{OBH}_3]/\text{dt} = 0.0015 \text{ sec}^{-1} + 0.0016[\text{H}^+] \text{ sec}^{-1} \text{ M}^{-1}$. The rate data for the hydrolysis of $\text{BH}_2(\text{H}_2\text{O})_2^+$ solutions at -36° are consistent with the following rapid equilibrium ($K = 6.4 \text{ l/mole}$): $\text{H}^+ + \text{H}_2\text{OBH}_2\text{OH} \rightleftharpoons \text{BH}_2(\text{H}_2\text{O})_2^+$. The $\text{BH}_2(\text{H}_2\text{O})_2^+$ ion is stable toward hydrolysis, whereas its conjugate base hydrolyzes to $\text{H}_2\text{OBH}(\text{OH})_2$ according to the rate equation $-\text{d} \ln [\text{H}_2\text{OBH}_2\text{OH}]/\text{dt} = 0.017 \text{ sec}^{-1}$. At -36° , $\text{H}_2\text{OBH}(\text{OH})_2$ hydrolyzes to $\text{B}(\text{OH})_3$ according to the rate equation $-\text{d} \ln [\text{H}_2\text{OBH}(\text{OH})_2]/\text{dt} = 3.3 \times 10^{-4} \text{ sec}^{-1}$.

The species H_2OBH_3 , $\text{BH}_2(\text{H}_2\text{O})_2^+$ and $\text{H}_2\text{OBH}(\text{OH})_2$ are converted to the anions BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$, respectively, by the addition of hydroxide. These anions undergo hydrolysis in non-buffered strongly alkaline solutions according to the rate equations $-\text{d} \ln [\text{BH}_3\text{OH}^-]/\text{dt} = 1.8 \times 10^{-4} \text{ sec}^{-1}$ at 20° ; $-\text{d} \ln [\text{BH}_2(\text{OH})_2^-]/\text{dt} = 2.2 \times 10^{-5} \text{ sec}^{-1}$ and $-\text{d} \ln [\text{BH}(\text{OH})_3^-]/\text{dt} = 1.1 \times 10^{-3} \text{ sec}^{-1}$ at 0° . The hydrolysis rates increase markedly when the pH is reduced to pH 10. The boron-11 nmr spectrum of BH_3OH^- is a 1:3:3:1 quartet, with $J_{\text{B-H}} = 87 \text{ Hz}$, centered 12 ppm upfield from the borate singlet.

INTRODUCTION

The hydroborate ion (otherwise known as borohydride, tetrahydroborate and tetrahydridoborate) undergoes hydrolysis in aqueous solutions to give boric acid below pH 9 and borate above pH 9.



A variety of experimental data have shown that the hydrolysis proceeds in four steps, with the intermediate formation of trihydro-, dihydro-, and monohydroboron species.

The trihydroboron intermediate has been detected in decomposing hydroborate solutions polarographically,^{1,2} by nmr,³ and by trapping with trimethylamine.⁴ In each of these studies, the solution under study was alkaline and the intermediate was probably present principally as the anion BH_3OH^- .

The dihydroboron intermediate has been prepared in essentially quantitative yields by the acid hydrolysis of hydroborate in cold ($< -60^\circ$) aqueous or water-alcohol solutions.^{5,6} This intermediate is relatively stable in cold acidic solutions, where it is believed to exist as $\text{BH}_2(\text{H}_2\text{O})_2^+$, but it is unstable toward further hydrolysis in neutral solutions, where it is assumed to exist as $\text{H}_2\text{OBH}_2\text{OH}$.

The monohydroboron intermediate has been prepared quantitatively by the reaction of diborane with water-alcohol solutions⁵ at -75° and with ice⁷ at -80° . The assumed formula of the product of these

reactions is $\text{H}_2\text{OBH}(\text{OH})_2$.⁸ Alkaline solutions of the monohydroboron intermediate, presumably containing the ion $\text{BH}(\text{OH})_3^-$, have been prepared by the addition of KOH to water-alcohol solutions of $\text{BH}_2(\text{H}_2\text{O})_2^+$ and $\text{H}_2\text{OBH}(\text{OH})_2$.^{5,6}

In the present study we have shown that the kinetics of the four consecutive steps of the acid hydrolysis of hydroborate can be separately studied by appropriate adjustments of the reaction temperatures and the hydrogen ion concentrations. We were able to prepare acidic solutions in which the monohydroboron intermediate was the only boron-hydrogen species present, and solutions in which either the dihydro- or trihydroboron intermediate was the major boron-hydrogen species present. Solutions presumably containing the species $\text{BH}(\text{OH})_3^-$, $\text{BH}_2(\text{OH})_2^-$ or BH_3OH^- were prepared by the addition of sodium hydroxide to such solutions. The kinetics of the hydrolysis of these anions was studied.

EXPERIMENTAL

Material.- Metal Hydrides sodium hydroborate (98%) was used without further purification. The absolute methanol, hydrochloric acid, sodium hydroxide and sodium chloride were all reagent grade.

Procedure.- The apparatus for the kinetic study in acidic solutions is shown in Fig. 1. Methanol was pipetted into the reaction vessel, and sufficient water was added so that, counting the water added later as aqueous HCl, the volume ratio methanol/water was 7.35. The solution was made ca. 10^{-4} M in NaOH, and 15-30 mg of sodium hydroborate was added. Sufficient lithium chloride was added to make the final ionic strength 1.2 M. When the sodium hydroborate was completely dissolved, a fragile bulb containing 7.78 M hydrochloric acid was lowered into the reaction vessel. The amount of acid corresponded to at least 10 times the amount of sodium hydroborate. The solution was then cooled to -78° using a Dry Ice-acetone bath. It was noted that no sodium hydroborate was precipitated. The system was then evacuated, the fragile bulb was broken, the timer was turned on, and the pressure of the evolved hydrogen was measured as a function of time. The increase in the gas volume due to the lowering of the mercury level in the manometer never exceeded 3% of the total volume.

After an hour, the hydrogen evolution stopped (in runs with high $[H^{+}]$) or became very slow (in runs with low $[H^{+}]$). The Dry Ice-acetone bath was replaced by another cold acetone bath, the temperature of which was quickly adjusted to -36° . A second set of pressure measurements

was started. During these measurements, the bath was vigorously stirred, and the temperature, measured with an ammonia vapor pressure thermometer,⁹ was maintained at $-36 \pm 0.5^\circ$ by the occasional addition of powdered Dry Ice. After one and a half hours, the cold bath was removed and the solution was warmed to room temperature to effect complete decomposition and to allow complete evolution of any dissolved hydrogen. Any volatilized methanol and water were condensed back into the reaction vessel at -196° , and the "infinite time" hydrogen pressures were measured after replacing the -78° and -36° baths.

The apparatus for the kinetic study of alkaline solutions is shown in Fig. 2. The initial solvent was the same as that used in the study of acidic solutions. The solution was made ca. 0.03 M in NaOH and 15-50 mg of sodium hydroborate was added. Sufficient sodium chloride was added to make the final ionic strength 0.35 M . When the sodium hydroborate was completely dissolved, a fragile bulb containing 7.78 M hydrochloric acid was lowered into the reaction vessel. The acid was slightly in excess of that required to react with the sodium hydroborate and the 0.03 M sodium hydroxide combined. Another fragile bulb containing a known amount of sodium hydroxide, dissolved in the same solvent, was also lowered into the reaction vessel. (For runs in buffer solutions, sodium hydroxide was replaced by other bases such as piperidine.) The solution was then cooled to -78° using a Dry Ice-acetone bath. The system was evacuated and the fragile bulb containing hydrochloric acid was broken.

To prepare BH_3OH^- , sodium hydroxide (or other bases for making buffer solutions) was added 30 sec after the hydrochloric acid and sodium hydroborate solutions were mixed at -78° . To prepare $\text{BH}_2(\text{OH})_2^-$, sodium hydroxide was added 90 minutes after the initial mixing, at which time hydrolysis of the H_2OBH_3 was complete. The solutions were then warmed to 0° for $\text{BH}_2(\text{OH})_2^-$, or 20° for BH_3OH^- , and the hydrogen evolution was measured as a function of time. To prepare $\text{BH}(\text{OH})_3^-$, a solution containing mainly the dihydroboron species at -78° was warmed to $-37 \pm 3^\circ$ for 40 minutes to allow all the trihydro- and dihydroboron species to hydrolyze. Sodium hydroxide was then added, and the solutions were warmed to 0° for the hydrogen evolution measurements. In all runs, after about 80% of the total hydrogen was evolved, the solutions were heated to $55 \pm 5^\circ$ for an hour to effect complete decomposition and to allow complete evolution of any dissolved hydrogen. Any volatilized methanol and water were condensed back into the reaction vessel at -196° , and the infinite time hydrogen pressures were measured at 0° for $\text{BH}_2(\text{OH})_2^-$ or $\text{BH}(\text{OH})_3^-$, and at 20° for BH_3OH^- . The sodium hydroxide concentrations were determined by titration with 0.10 M hydrochloric acid, using bromthymol blue as indicator. The pH values of buffer solutions were measured with a Radiometer pH meter.

For the boron-11 nmr study of BH_3OH^- , the sample was prepared following the same procedure described for BH_3OH^- solutions, except a 0.2 M sodium hydroborate solution was used. Concentrations higher than 0.2 M are not recommended because the large heat of reaction between hydrochloric acid and hydroborate causes excessive heating of the

solution and decomposition of the H_2OBH_3 . In order to obtain a better nmr spectrum, the concentration of BH_3OH^- was increased by pumping off 1/3 to 1/2 of the solvent at $-25 \pm 5^\circ$. Boron-11 nmr spectra were recorded at -20° on a Varian HA-100 spectrometer equipped with a 32.1-MHz oscillator. A 5 mm sample tube was used.

RESULTS

Acid Solutions.- The initial concentrations of HCl and NaBH₄ in the various runs are given in Table I. The hydrogen evolution at -78° was

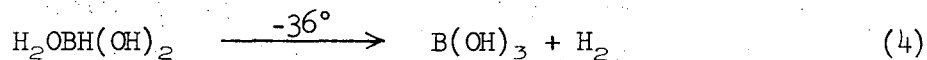
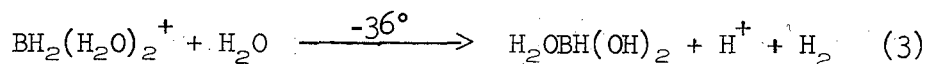
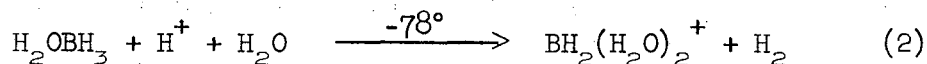
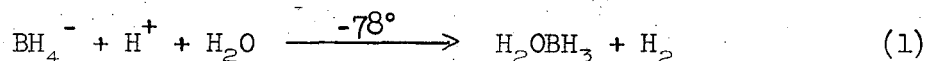
Table I

The initial concentrations of HCl and NaBH₄ at -78°

Run	HCl (M)	NaBH ₄ (M)
1	0.110	0.011
2	0.220	0.014
3	0.330	0.017
4	0.440	0.022
5	0.600	0.028
6	0.700	0.033
7	0.880	0.033
8	1.210	0.039

initially very rapid, and gradually dropped to a negligible rate in about one hour. During this time a total of two moles of hydrogen was evolved per mole of hydroborate, corresponding to the formation of BH₂(H₂O)₂^{5,6}. When the resulting solution was then warmed to -36°, further rapid hydrogen evolution occurred. In about 1.5 hours, the rate became very low, and the total yield of hydrogen almost corresponded to that expected for complete decomposition to boric acid.

Inasmuch as the initial hydrogen ion concentration was always more than 10 times the initial hydroborate concentration (see Table I) the changes in hydrogen ion concentration during the runs were negligible. Therefore the rate data could be interpreted in terms of pseudo-first-order reactions. The following sequence of reactions was assumed.



The pressure data for runs 1 and 8 (for solutions initially 0.110 and 1.210 M in HCl) are given in Tables II and III (the -78° data) and in Tables IV and V (the -36° data). The "infinite time" pressures, P_∞ , correspond to the pressures observed at the indicated temperatures after allowing the solutions to decompose completely.

Tables II and III show that at -78° , one mole of hydrogen per mole of hydroborate was evolved in the first fraction of a minute, and a second mole of hydrogen was evolved in about 45 minutes. Plots of $\log(\frac{1}{2}P_\infty - P)$ versus time are shown in Fig. 3 and 4 for the -78° data of runs 1 and 8 (data from Tables I and II). The values of $(\frac{1}{2}P_\infty - P)$ extrapolated to $t = 0$ from the main portions of the curve are less than the expected $\frac{1}{4}P_\infty$, and a greater discrepancy occurred in the run with the higher hydrogen ion concentration. These discrepancies can

Table II

Hydrogen pressure as a function of time for $[H^+] = 0.110 \text{ M}$ at -78°

Time (sec)	P (cm)	$\frac{1}{2}P_\infty - P^a$ (cm)
0	0	4.41
12	2.28	2.13
38	2.38	2.03
67	2.49	1.92
93	2.57	1.84
128	2.67	1.74
165	2.77	1.64
213	2.89	1.52
270	3.03	1.38
340	3.19	1.22
411	3.31	1.10
462	3.40	1.01
530	3.50	0.91
608	3.61	0.80
690	3.72	0.69
798	3.82	0.59
948	3.93	0.48
1089	4.04	0.37
1269	4.15	0.26
1950	4.36	0.05
4050	4.56	-0.15
8808	4.72	-0.31

^a $P_\infty = 8.82 \text{ cm.}$

Table III

Hydrogen pressure as a function of time for $[H^+] = 1.210 \text{ M}$ at -78°

Time (sec)	P (cm)	$\frac{1}{2}P_\infty - P^a$ (cm)
0	0	6.55
30	4.45	2.10
50	4.65	1.90
72	4.80	1.75
99	4.95	1.60
116	5.06	1.49
133	5.16	1.39
153	5.27	1.28
179	5.37	1.18
203	5.48	1.07
235	5.58	0.97
265	5.68	0.87
300	5.79	0.76
345	5.89	0.66
396	5.99	0.56
457	6.10	0.45
538	6.21	0.34
612	6.30	0.25
2400	6.55	0.00
5100	6.55	0.00

^a $P_\infty = 13.10 \text{ cm.}$

Table IV

Hydrogen pressure as a function of time at -36° (a continuation of the run of Table II)

Time (sec)	P (cm)	$P_{\infty} - P$ (cm)
0	6.92	2.76
31	7.09	2.59
76	7.25	2.43
116	7.35	2.33
193	7.49	2.19
264	7.59	2.09
348	7.67	2.01
498	7.77	1.91
660	7.88	1.80
836	7.98	1.70
1050	8.08	1.60
1239	8.19	1.49
1470	8.29	1.39
1692	8.39	1.29
1950	8.49	1.19
2220	8.60	1.08
2514	8.70	0.98
2877	8.82	0.86
3204	8.90	0.78
3609	9.00	0.68
∞	9.68	0.00

Table V

Hydrogen pressure as a function of time at -36° (a continuation of the run of Table III)

Time (sec)	P (cm)	$P_{\infty} - P$ (cm)
0	8.68	7.32
35	8.79	7.11
68	9.10	6.90
108	9.30	6.70
129	9.40	6.60
167	9.61	6.39
222	9.85	6.15
257	10.03	5.97
309	10.24	5.76
372	10.48	5.52
465	10.82	5.18
510	10.97	5.03
578	11.18	4.82
691	11.50	4.50
828	11.80	4.20
974	12.11	3.89
1106	12.32	3.68
1200	12.48	3.52
1291	12.63	3.37
1588	13.03	2.97
1756	13.24	2.76
1975	13.45	2.55
2325	13.76	2.24
2580	13.96	2.05
2982	14.23	1.77
3195	14.33	1.67
3852	14.69	1.31
4107	14.79	1.21
4605	15.00	1.00
4974	15.10	0.90
∞	16.00	0.00

be explained by premature decomposition of H_2OBH_3 , perhaps as a result of the heat evolved upon mixing the methanol and hydrochloric acid. Because of the extremely rapid evolution of the first mole of hydrogen, we were unable to determine the rate constant for reaction (1). However, we were able to calculate the pseudo-first-order rate constant for reaction (2), k_2' , by measuring the slope of the main portion of the curve. Values of k_2' calculated from data for all the runs are plotted versus hydrogen ion concentration in Fig. 5. Runs 1 and 5 were also carried out without the addition of LiCl to maintain constant ionic strength; the values of k_2' were essentially unchanged. This indicates that the value of k_2' is independent of ionic strength.

When the solutions were warmed from -78° to -36° , the immediate pressure increase was greater than the sum of the increase in vapor pressure of the solution¹⁰ and the pressure increase of the hydrogen due to the temperature change. This result indicated that at the time chosen for the start of the -36° measurements, reaction (3) had already proceeded to a considerable extent. This was especially true at lower hydrogen ion concentrations. At "zero time", the solutions were therefore mixtures of $BH_2(H_2O)_2^+$, $H_2OBH(OH)_2$, and $B(OH)_3$. The first two species were present in a ratio defined as $r = \frac{[H_2OBH(OH)_2]_0}{[BH_2(H_2O)_2^+]_0}$, where subscript zero stands for initial concentration. The presence of boric acid does not affect the calculation of the rate constants k_3' and k_4' . The number of molecules of hydrogen formed during time t is equal to the number of B-H bonds present at time zero minus the

number of B-H bonds present at time t . Using the factor C to convert pressure of hydrogen into the corresponding solution concentration, we write

$$(P_{\infty} - P_0)C = 2[BH_2(H_2O)_2^+]_0 + [H_2OBH(OH)_2]_0$$

$$(P - P_0)C = \{2[BH_2(H_2O)_2^+]_0 + [H_2OBH(OH)_2]_0\} - \{2[BH_2(H_2O)_2^+] + [H_2OBH(OH)_2]\}$$

The integrated rate expression¹¹ can be written as

$$[BH_2(H_2O)_2^+] = [BH_2(H_2O)_2^+]_0 e^{-k_3't}$$

$$[H_2OBH(OH)_2] = \left\{ [H_2OBH(OH)_2]_0 + \frac{k_3'[BH_2(H_2O)_2^+]_0}{k_3' - k_4'} \right\} e^{-k_4't} - \frac{k_3'[BH_2(H_2O)_2^+]_0 e^{-k_3't}}{k_3' - k_4'}$$

By combining the four preceding equations with the relation

$$[H_2OBH(OH)_2]_0 = r[BH_2(H_2O)_2^+]_0, \text{ we obtain}$$

$$(P_{\infty} - P) = \frac{(P_{\infty} - P_0)}{2 + r} \left\{ \left[\frac{k_3' - 2k_4'}{k_3' - k_4'} \right] e^{-k_3't} + \left[r + \frac{k_3'}{k_3' - k_4'} \right] e^{-k_4't} \right\} \quad (5)$$

The parameters k_3' , k_4' and r were evaluated from the data for each -36° run using a least-squares computer program written in FOCAL for a small PDP 8/I computer (see Appendix).

Semilogarithmic plots of $(P_{\infty} - P)$ versus time at -36° for runs 1 and 8 are shown in Fig. 6 and 7. The smooth curves drawn through the points correspond to the calculated values of k_3' , k_4' and r . A plot of

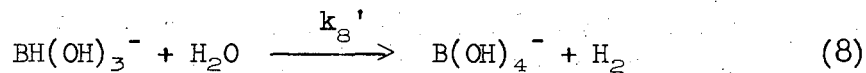
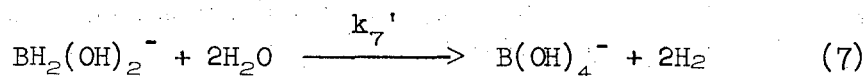
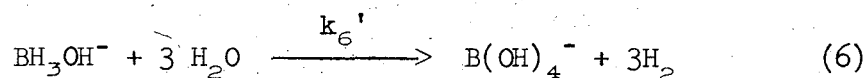
computer-calculated values of k_3' versus hydrogen ion concentration is shown in Fig. 8. The calculated values of k_4' were essentially constant for all the runs. The value was $3.3 \times 10^{-4} \text{ sec}^{-1}$ except for run 4 ($3.7 \times 10^{-4} \text{ sec}^{-1}$) and runs 7 and 8 ($3.5 \times 10^{-4} \text{ sec}^{-1}$). We also studied reaction (4) at 0° and the values of k_4' are 4.3, 4.3, 4.6 and 10.5 ($\times 10^{-3} \text{ sec}^{-1}$) at pH 1.00, 0.70, 0.46 and 5.6 respectively. The latter pH was buffered by an equimolar mixture of sodium benzoate and benzoic acid.

Because of the possibility that the hydrolyzing solutions were supersaturated in hydrogen and that the measured rates were limited by the rate of evolution of gaseous hydrogen from these solutions, we carried out several runs with the stirring rate reduced by more than a factor of 10. The calculated values of k_2' changed by less than 10%, and the values of k_3' and k_4' were essentially unchanged. However, the rate of hydrogen evolution during the first part of the -78° runs was markedly decreased by more than a factor of five. Obviously the initial rate of formation of hydrogen was greater than the rate at which it could escape from solution.

Alkaline Solutions.- The exact concentrations of BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$, and $\text{BH}(\text{OH})_3^-$ were not known, but excess sodium hydroxide was always added so that the final hydroxide concentration was at least 5 times that of the initial sodium hydroborate. For runs between pH 10 and 12, only the piperidine/piperidinium chloride buffer system was found to be suitable (due to low solubility in the water-methanol solution, or

high vapor pressure of other possible compounds). An equimolar mixture of piperidine and piperidinium chloride gives a pH of 10. Below pH 10 the rapid hydrogen evolution prevents accurate measurement.

In non-buffered strongly alkaline solutions the following net reactions are assumed.



The reaction rates were measured in the same way as that used for the acidic solutions. The data for a typical hydrolysis of BH_3OH^- at 20° and 0.35 M in sodium hydroxide are given in Table VI. Plots of $\log(P_\infty - P)$ versus time for the data in Table VI gave a straight line, shown in Fig. 9. This indicates that for the stepwise hydrolysis of BH_3OH^- , the rate increases with each step ($k_8' > k_7' > k_6'$). Assuming that $\text{BH}_2(\text{OH})_2^-$ and BH(OH)_3^- had been present in the solution at -78° , at the time chosen for the start of the measurements at 20° , a sudden increase in the hydrogen pressure should have been observed. It is concluded that a "zero time" $\text{BH}_2(\text{OH})_2^-$ and BH(OH)_3^- were already decomposed. The pseudo-first-order rate constant k_6' was obtained by measuring the slope of the line in Fig. 9. Values of k_6' are 1.7, 1.9, 1.8 and $77 (x 10^{-4} \text{ sec}^{-1})$ at pH 13.5, 13.0, 12.5 and 10.0 respectively.

Table VI

Hydrogen pressure as a function of time
for the hydrolysis of BH_3OH^- at $[\text{OH}^-] = 0.35 \text{ M}$ and 20° .

Time (sec)	P (cm)	$P_\infty - P$ (cm)
0	10.09	4.67
69	10.20	4.56
171	10.30	4.46
398	10.50	4.26
558	10.62	4.14
789	10.81	3.95
969	10.93	3.83
1152	11.03	3.73
1281	11.12	3.64
1458	11.22	3.54
1644	11.33	3.43
1824	11.43	3.33
2025	11.53	3.23
2241	11.64	3.12
2472	11.75	3.01
2655	11.8	2.91
2871	11.96	2.80
3114	12.07	2.69
3366	12.18	2.58
3846	12.38	2.38
4392	12.60	2.16
5214	12.89	1.87
5925	13.13	1.63
6585	13.30	1.46
7398	13.50	1.26
8364	13.69	1.07
9900	13.93	0.83
10920	14.07	0.69
∞	14.76	0

The dependence of reaction rate on piperidinium ion concentration at pH 10 is shown in Fig. 10.

From the solutions containing $\text{BH}(\text{OH})_3^-$ as the only boron-hydrogen species, we obtained the rate constant k_8' at 0° in the same way as k_6' . In non-buffered strongly alkaline solutions, the values of k_8' are 1.30, 1.10, 1.20 and 0.89 ($\times 10^{-3} \text{ sec}^{-1}$) at pH 13.5, 13.4, 13.0 and 12.8, respectively. In a buffered solution of pH 10, $k_8' = 9 \times 10^{-3} \text{ sec}^{-1}$. It was not possible to determine a meaningful dependence of k_8' on piperidinium ion concentration, because the rapid evolution of hydrogen at 0° and pH 10 prevented an accurate measurement.

The species $\text{BH}_2(\text{OH})_2^-$ was always contaminated with $\text{BH}(\text{OH})_3^-$. For a typical run of a mixture of $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ at 0° and 0.35 M in NaOH, a plot of $\log(P_\infty - P)$ versus time is shown in Fig. 11. It can be seen that after 3000 seconds the curve is linear. The linear portion corresponds to the hydrolysis of $\text{BH}_2(\text{OH})_2^-$. The hydrolysis of $\text{BH}_2(\text{OH})_2^-$ is stepwise, with $\text{BH}(\text{OH})_3^-$ hydrolyzing faster than $\text{BH}_2(\text{OH})_2^-$. Therefore we treat the hydrolysis of this mixture as two parallel pseudo-first-order reactions¹² which produce hydrogen. After 3000 seconds, there is essentially no $\text{BH}(\text{OH})_3^-$. The expression for $\log(P_\infty - P)$ becomes $\log[\text{BH}_2(\text{OH})_2^-]_0 C = \log(P_\infty - P) = \log[\text{BH}_2(\text{OH})_2^-]_0 C - (k_7' t / 2.303)$, where C is the factor that converts solution concentration into hydrogen pressure. From the slope and the intercept of the line in Fig. 11, we obtained $[\text{BH}_2(\text{OH})_2^-]_0 C = 2.06 \text{ cm}$, $k_7' = 2.1 \times 10^{-4} \text{ sec}^{-1}$ and $[\text{BH}_2(\text{OH})_2^-] C = 2.06 \times 10^{-9.1 \times 10^{-5} t} \text{ cm}$. The pressure of $[\text{BH}(\text{OH})_3^-] C$ may be calculated by difference, $[\text{BH}(\text{OH})_3^-] C = P_\infty - P - 2.06 \times 10^{-9.1 \times 10^{-5} t}$.

A semi-logarithmic plot of it versus time is shown in Fig. 12 from which we obtained k_8' . Values of k_7' , obtained from the mixture, are 2.1, 2.1 and 2.2 ($\times 10^{-5} \text{ sec}^{-1}$); values of k_8' are 1.3, 1.5 and 1.4 ($\times 10^{-3} \text{ sec}^{-1}$) at pH 13.5, 13.3 and 12.8 respectively.

To determine the rate of hydrolysis of the mixture at lower pH, a run at pH 10 was tried. The plot of $\log(P_\infty - P)$ versus time gave one straight line, which represents the hydrolysis of $\text{BH}(\text{OH})_3^-$. This indicates that at pH 10 the dihydroboron species is rapidly hydrolyzed to $\text{BH}(\text{OH})_3^-$. Apparently lowering the pH from 12.8 to 10 makes the rate of hydrolysis of dihydroboron species faster than $\text{BH}(\text{OH})_3^-$.

The boron-11 nmr spectrum of BH_3OH^- is shown in Fig. 13. We also attempted to obtain a boron-11 nmr spectrum of $\text{BH}_2(\text{OH})_2^-$ at -20° . In the initial spectrum, recorded at -20° , a broad doublet was observed; the two peaks were 3.5 ppm apart. The solution was warmed to 60° for 10 minutes and the spectrum was again recorded at -20° . Only a singlet was observed identical to the high field resonance of the original doublet. We identified the singlet as sodium borate using methylborate as external reference.

DISCUSSION

Reaction 1.- Our studies of the effect of stirring speed on reaction (1) showed that the rate of reaction (1) was greater than could be measured by our manometric technique. The result was expected on the basis of extrapolation of the room-temperature data for the acid hydrolysis of hydroborate;¹³ from these data and the measured activation energy one calculates a half-life of 7.7×10^{-8} sec for the hydroborate ion in 0.1 M H^+ at -78° . Indeed, the change of solvent from water to 88 vol% methanol is expected to make the half-life even shorter -- at 25° the methanolysis is ten times faster than the hydrolysis.¹⁴

The hydrolysis of hydroborate ion in acidic solutions at -78° rapidly gave one mole of hydrogen per mole of hydroborate. This suggests the formation of a trihydroboron species. When sodium hydroxide was added 30 seconds after the hydrochloric acids sodium hydroborate solutions were mixed at -78° , this trihydroboron species was stabilized; its boron-11 nmr in strong alkaline solutions (Fig. 13) is a 1:3:3:1 quartet, coupling constant $J_{BH} = 87$ Hz, centered 12.0 ppm upfield from the borate singlet. The reported boron-11 nmr spectrum of BH_3OH^- ³ has $J_{BH} = 82$ Hz and centered 13.9 ppm upfield from borate singlet (obtained with a 19.3 MHz Oscillator). Although we observed the proton nmr signal of 0.05 M hydroborate ion in this solvent at -20° , we were unable to see the proton nmr signal of a 0.2-0.3 M solution of this trihydroboron species. Gardiner and Collat³ did not assign any peaks in the proton nmr to BH_3OH^- and concluded that its spectrum was masked by that of the hydroborate ion that was always present in their system.

Reaction 2. - From Fig. 5 we see that k_2' is a linear function of hydrogen-ion concentration, with a finite value at $[H^+] = 0$. The straight line corresponds to the equation $k_2' = k_{2a} + k_{2b}[H^+]$ and indicates the following two-term rate law $-d[H_2OBH_3]/dt = k_{2a}[H_2OBH_3] + k_{2b}[H^+][H_2OBH_3]$ where $k_{2a} = 0.0015 \text{ sec}^{-1}$ and $k_{2b} = 0.0016 \text{ sec}^{-1} \text{ M}^{-1}$. The value of k_2' is independent of ionic strength.

Gardiner and Collat² have reported the rate law of the hydrolysis of BH_3OH^- as

$$k = k_{HA}[HA] + k_{H^+}[H^+] + k_{H_2O}[H_2O] \quad (9)$$

($[HA]$ is the concentration of the acid component of the buffer solution) with $k_{H^+} = 7 \pm 3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{H_2O} = 7 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 20° . They also reported the dependence of the rate constant on ionic strength, and the activation energy for hydrolysis $\Delta E_{a(H^+)} = 12 \pm 8 \text{ kcal mol}^{-1}$. In non-buffered strongly alkaline solutions (pH 12.5 to 13.5) Eq.(9) can be approximated as $k = k_{H_2O}[H_2O]$. In this pH range, we found the rate constant $k_6' = 1.8 \times 10^{-4} \text{ sec}^{-1}$, independent of pH. By comparison, Gardiner and Collat's rate constant between pH 12.5 and 13.5 is $k = 3.9 \times 10^{-4} \text{ sec}^{-1}$. The agreement is fairly good considering the different ionic strength (0.50 Gardiner and Collat; 0.35 for this work) and different solvent.

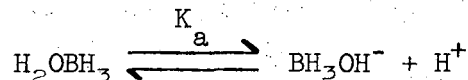
If we apply Eq. 9 to our kinetic study of the hydrolysis of the trihydroboron species in buffer solution of pH 10, we obtain, from the value of k_6' at $[piperidinium \text{ ion}] = 0$ on Fig. 10, $k_6'(H^+)[H^+] +$

$k_6'(\text{H}_2\text{O})[\text{H}_2\text{O}] = 6.6 \times 10^{-3} \text{ sec}^{-1}$. Substituting $[\text{H}^+] = 10^{-10}$ and $k_6'(\text{H}_2\text{O})[\text{H}_2\text{O}] = 1.8 \times 10^{-4} \text{ sec}^{-1}$, we obtain $k_6'(\text{H}^+) = 6.4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ which shows fair agreement with $k_{\text{H}^+} (7 \pm 3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1})$ of Gardiner and Collat.

The dependence of reaction rate on the ionic strength of the trihydroboron species in alkaline solution led Gardiner and Collat to predict a negatively charged species BH_3OH^- . Our studies of the hydrolysis of trihydroboron species were carried out at 20° in strongly alkaline solutions, 98° higher than the studies in acidic solutions (-78°). The term independent of hydrogen ion concentration in strongly alkaline solutions ($1.8 \times 10^{-4} \text{ sec}^{-1}$) is 10 times lower than that in acidic solutions ($1.5 \times 10^{-3} \text{ sec}^{-1}$). If the same trihydroboron species were involved in the two systems, we would expect that the H^+ independent term would be much greater, not 10 times smaller, in the alkaline solutions at 20° than in the acidic solutions at -78° . Therefore we conclude that the trihydroboron species in alkaline solutions is different from that in acidic solutions. Although the rate of hydrolysis of the trihydroboron species in acidic solutions is dependent on hydrogen ion concentration, it is independent of ionic strength. This suggests that the trihydroboron species in acidic solutions is uncharged, and we assign it the formula H_2OBH_3 .

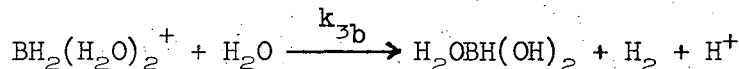
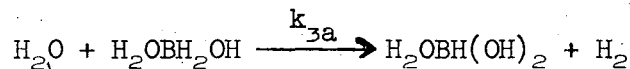
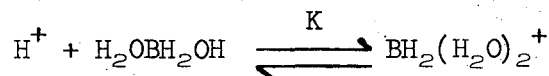
The activation energy for the hydrolysis of BH_3OH^- has been reported² as $\Delta E_{\text{a}(\text{H}^+)} = 12 \pm 8 \text{ kcal mol}^{-1}$ from which we calculated the lower limit (with $\Delta E_{\text{a}(\text{H}^+)} = 20 \text{ kcal mol}^{-1}$) and the upper limit (with $\Delta E_{\text{a}(\text{H}^+)} = 4 \text{ kcal mol}^{-1}$) of the rate constant $k_6'(\text{H}^+)$ at -78° . The values of $k_6'(\text{H}^+)$ are $4.0 \text{ M}^{-1} \text{ sec}^{-1}$ (lower limit) and $6.4 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ (upper limit).

Using these calculated values of k_6' (H^+), we obtained the limits of the dissociation constant of the following reaction at -78° .



$$6 \times 10^{-9} \leq K_a \leq 4 \times 10^{-4}.$$

Reaction 3.- At -78° , hydrogen evolution stops when two moles of hydrogen per mole of hydroborate are obtained when $[H^+] \geq 0.53 \text{ M}$, but does not stop when $[H^+] < 0.53 \text{ M}$. This suggests that there is a species other than $BH_2(H_2O)_2^+$ in existence in acidic solutions at lower hydrogen ion concentrations which is relatively unstable toward hydrolysis. We believe the species is H_2OBH_2OH . The instability of H_2OBH_2OH toward hydrolysis has been reported previously.⁶ The pH dependence of the H_2OBH_2OH concentration suggests that H_2OBH_2OH is in equilibrium with $BH_2(H_2O)_2^+$. From Fig. 6, we see that increasing the hydrogen ion concentration decreases the rate of reaction. We write the following reactions:



If $[H_2OBH_2OH] + [BH_2(H_2O)_2^+] = A$, and $[BH_2(H_2O)_2^+]/[H_2OBH_2OH][H^+] = K$, then $[H_2OBH_2OH] = A/(1 + K[H^+])$ and $[BH_2(H_2O)_2^+] = A[H^+]K/(1 + K[H^+])$.

$$\begin{aligned} \frac{-d[A]}{dt} &= \frac{-d[\text{BH}_2(\text{H}_2\text{O})_2^+]}{dt} - \frac{d[\text{H}_2\text{OBH}_2\text{OH}]}{dt} \\ &= k_{3b}[\text{BH}_2(\text{H}_2\text{O})_2^+] + k_{3a}[\text{H}_2\text{OBH}_2\text{OH}] \\ &= \left\{ \frac{k_{3a} + Kk_{3b}[\text{H}^+]}{1 + K[\text{H}^+]} \right\} A \end{aligned}$$

$$\text{Therefore } k_3' = \frac{k_{3a} + Kk_{3b}[\text{H}^+]}{1 + K[\text{H}^+]} \quad (10)$$

Values of k_{3a} , k_{3b} , and K were calculated by a least-squares fit of the data, and were found to be $k_{3a} = 0.017 \text{ sec}^{-1}$, $k_{3b} = -1.5 \times 10^{-4} \text{ sec}^{-1}$ and $K = 6.4 \text{ l/mol}$. The negative value of k_{3b} is, within experimental error, equal to zero or a small positive number. A calculated curve of k_3' versus $[\text{H}^+]$ was obtained by using $k_{3a} = 0.017 \text{ sec}^{-1}$, $k_{3b} = 0$ and $K = 6.4$. Comparison of this curve with experimental k_3' is shown in Fig. 8. By assigning k_{3b} values in the range $0-3.4 \times 10^{-5} \text{ sec}^{-1}$, while keeping $k_{3a} = 0.017 \text{ sec}^{-1}$ and $K = 6.4 \text{ l/mole}$, we obtained equally good curves, indicating that the approximation of $k_{3b} = 0$ or a small positive number is reasonable.

When $[\text{H}^+]$ becomes sufficiently low Eq. 10 can be approximated as $k_3' = k_{3a}$, corresponding to the hydrolysis of $\text{H}_2\text{OBH}_2\text{OH}$. At -36° $k_{3a} = 0.017 \text{ sec}^{-1}$. We found between pH 12.5 and 13.5 the rate constant $k_7' = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 0° . Since these values are so different, this suggests the dihydroboron species in alkaline solutions is not $\text{H}_2\text{OBH}_2\text{OH}$. The species $\text{BH}_2(\text{H}_2\text{O})^+$ can be converted to an unstable species by lowering hydrogen ion concentration, and we found in alkaline solutions decreasing

the hydrogen ion concentration does not decrease the rate of hydrolysis. Therefore the dihydroboron species in alkaline solutions is not $\text{BH}_2(\text{H}_2\text{O})_2^+$. We believe it to be $\text{BH}_2(\text{OH})_2^-$. The hydrolysis of $\text{BH}_2(\text{OH})_2^-$ at 20° in the pH range of 12.5 and 13.5 was too rapid to be measured.

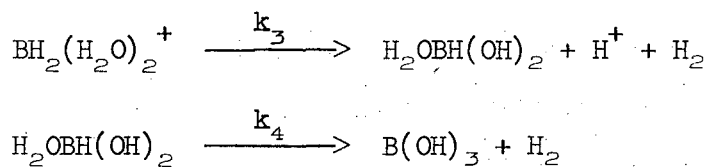
Mochalov et al.¹⁵ have reported a kinetic study of the hydrolysis of $\text{BH}_2(\text{OH})_2^-$ at ionic strength 0.40 and pH between 9.7 and 10.7, the rate equation is $-\text{d}[\text{BH}_2(\text{OH})_2^-]/\text{dt} = k_7[\text{H}^+][\text{BH}_2(\text{OH})_2^-]$ which indicates the essential participation of hydrogen ions. We found, between pH 12.5 and 13.5, the rate of hydrolysis is independent of pH. Their value of k_7 is $0.5 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$ at 0° . Using $[\text{H}^+] = 10^{-10} \text{ M}$ and $k_7 = 0.5 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$, one obtains $-\text{d} \ln[\text{BH}_2(\text{OH})_2^-]/\text{dt} = 0.5 \times 10^{-4} \text{ sec}^{-1}$ and we found it is greater than $0.1 \times 10^{-1} \text{ sec}^{-1}$ at 0° . For the results on the hydrolysis of BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$, the only agreement between our work and Mochalov's is the finding that the more B-H bonds an anion has, the more slowly it undergoes hydrolysis.

Reaction 4.- In both non-buffered strongly acidic solutions and strongly alkaline solutions we observed a pH-independent rate of hydrolysis of the monohydroboron species. At 0° , the pseudo-first-order rate constant is $4.4 \times 10^{-3} \text{ sec}^{-1}$ in acidic solutions and is $1.0 \times 10^{-3} \text{ sec}^{-1}$ in alkaline solutions. This suggests that they are different species. We believe it is $\text{H}_2\text{OBH}(\text{OH})_2$ in acidic solutions and is $\text{BH}(\text{OH})_3^-$ in alkaline solutions. In buffer solutions of pH 5.6 and 10.0, the rate of hydrolysis of monohydroboron species is about twice as fast as that in acidic solutions. This might be explained using the following rate equation,

$$-d \ln[\text{BH}(\text{OH})_3^-]/dt = k_{\text{B}(\text{HA})}[\text{HA}] + k_{\text{B}(\text{H}^+)}[\text{H}^+] + k_{\text{B}(\text{H}_2\text{O})}[\text{H}_2\text{O}] \quad (10)$$

In non-buffered strongly alkaline solutions Eq. (10) can be approximated as $-d \ln[\text{BH}(\text{OH})_3^-]/dt = k_{\text{B}(\text{H}_2\text{O})}[\text{H}_2\text{O}]$ and the rate is independent of pH. In non-buffered strongly acidic solutions Eq. (10) can be approximated as $-d \ln[\text{BH}(\text{OH})_3^-]/dt = k_{\text{B}(\text{H}^+)}[\text{H}^+]$ which is kinetically indistinguishable from the hydrolysis of $\text{H}_2\text{OBH}(\text{OH})_2$. In buffer solutions, when all three terms contribute significantly, a higher rate than that in strongly acidic solutions may be observed. However we were unable to determine the dependence of reaction rate on $[\text{HA}]$, because the evolution of hydrogen was too rapid to measure accurately.

Hydrolysis of $\text{BH}_2(\text{H}_2\text{O})_2^+$ in 8 M HCl solution. - The hydrolysis of $\text{BH}_2(\text{H}_2\text{O})_2^+$ in aqueous 8 M HCl solutions at a temperature range from -35° to -50° was also studied. The reactions can be written as:



Values of k_3 and k_4 were obtained in the same way as k_3' and k_4' from Eq. 5. Plots of k_3 and k_4 versus $1/T$ are shown in Fig. 14 from which the following activation energies were calculated: for k_3 , $\Delta E_{a3}^\ddagger = 10.7 \pm 0.8 \text{ kcal mole}^{-1}$; for k_4 , $\Delta E_{a4}^\ddagger = 11.6 \pm 0.9 \text{ kcal mole}^{-1}$.

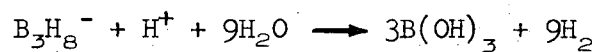
PART II: UNFINISHED KINETIC STUDY OF THE HYDROLYSIS
OF OCTAHYDROTRIBORATE ION

ABSTRACT

The stepwise hydrolysis of the $B_3H_8^-$ has also been studied in the cold methanol-water solution, in the hydrogen ion concentration range 1.0-3.5 M. At -78° , one mole hydrogen per mole of $B_3H_8^-$ was obtained, corresponding to the formation of $B_3H_7OH_2$. However in aqueous 8 M HCl a total of 4.5 moles of hydrogen per mole of $B_3H_8^-$ was obtained at -78° . The reaction mixture, when warmed to room temperature, will give another 4.5 moles of hydrogen.

INTRODUCTION

The octahydrotriborate ion undergoes hydrolysis at room temperature in aqueous acidic solution to give boric acid and hydrogen:



The study of the kinetics of stepwise hydrolysis of hydroborate between -78° and -35° led us to investigate the hydrolysis of B_3H_8^- at lower temperatures to see if stepwise hydrolysis occurs. Only the potassium salt was used for this study because it is soluble in methanol-water solutions at low temperature and is non-hygroscopic.

EXPERIMENTAL

Material.- Sodium octahydrotriborate in the form of the trisdioxane complex was prepared by the literature procedure.¹⁶ Potassium octahydrotriborate was prepared by the addition of concentrated KOH solution to a nearly saturated NaB_3H_8 solution. The potassium octahydrotriborate was then precipitated. Potassium hydroxide is insoluble in THF and can be easily separated from KB_3H_8 .

The potassium octahydrotriborate was then precipitated from the THF solution by the addition of dioxane. The potassium salt was isolated by evaporating an aqueous solution to dryness and then vacuum drying the solid at 100° .¹⁷ The hydrogen analysis showed it is 97% pure. Tetramethylammonium octahydrotriborate, supplied by Alfa Inorganic Inc., was used without further purification. Other compounds were all reagent grade.

Procedure.- The apparatus used is shown in Fig. 1. The solvent of 88 vol% methanol 12 vol% water was pipetted into the reaction vessel, and a known amount of HCl, dissolved in the same solvent, was added. Sufficient lithium chloride was added to make the final ionic strength 3.5 M.

A fragile bulb, containing 35-55 mg KB_3H_8 in 2 ml of solvent, was lowered into the reaction vessel. The solution was then cooled to -78° using a Dry Ice-acetone bath, whereupon no KB_3H_8 precipitated inside the fragile bulb. The system was then evacuated, the fragile bulb was broken, the timer was turned on, and the pressure of the evolved

hydrogen was measured as a function of time. The total amount of hydrogen evolved at -78° was then measured.

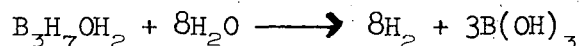
The same procedure was used for the runs in aqueous 8 M HCl solutions. At -78° , after 6 hours the hydrogen evolution had essentially ceased and the amount of H_2 was measured. The Dry Ice-acetone bath was then replaced by another cold acetone bath of the desired temperature (-49.4° , -43.5° , -38.4° , and -35.6°). A second reaction vessel, containing a solution of $BH_2(H_2O)_2^{5,6}$ in 8 M HCl, was also placed in this bath. Each reaction vessel was connected to a manometer and the hydrogen evolved measured as a function of time. During these measurements, the bath was vigorously stirred and the temperature, measured with an ammonia vapor pressure thermometer,⁹ was maintained in a range of $\pm 0.5^{\circ}$ by the occasional addition of Dry Ice. After a few hours, the cold bath was removed and the solution was warmed to room temperature to effect complete decomposition and to allow complete evolution of any dissolved hydrogen. Any volatilized HCl and water were condensed back into the reaction vessel at -196° , and the "infinite time" hydrogen pressure was measured after replacing the cold bath.

RESULTS AND DISCUSSION

Methanol-water solution.- At -78° , the hydrolysis of KB_3H_8 yielded one mole of hydrogen per mole of B_3H_8^- ; typical ratios of the moles of hydrogen evolved per mole of B_3H_8^- consumed were: 1.09 (at $[\text{H}^+] = 3.4 \text{ M}$), 1.03 ($[\text{H}^+] = 2.9 \text{ M}$), 1.06 ($[\text{H}^+] = 2.0 \text{ M}$) and 1.07 ($[\text{H}^+] = 0.9 \text{ M}$). This corresponds to the formation of $\text{B}_3\text{H}_7\cdot\text{OH}_2$ which is a very stable species in acidic solution ($[\text{H}^+] \leq 3.4 \text{ M}$) at -78° .

For all runs the hydrogen ion concentration is always a few hundred times that of KB_3H_8 ; therefore the rate data could be interpreted in terms of pseudo-first-order reaction. The rate data from a typical run of the -78° hydrolysis of KB_3H_8 at $[\text{H}^+] = 3.5 \text{ M}$ is shown in Table VII. A plot of $\log(P_{\infty} - P)$ versus time for the data of Table VII is shown in Fig. 15. (Here P_{∞} corresponds to the pressure of one mole of hydrogen per mole of KB_3H_8 at -78° .) Between hydrogen ion concentration range 1.0-3.5 M we were unable to determine a meaningful dependence of the hydrolysis rate on $[\text{H}^+]$, because at the lower hydrogen ion concentration ($[\text{H}^+] = 1.0$ and 2.0 M) the large quantity of LiCl present prevented rapid stirring of the solution, and it was not possible to measure accurately the hydrogen evolution. This reaction should be investigated again in a hydrogen ion concentration range between 0.1 and 1.0 M.

When the $\text{B}_3\text{H}_7\text{OH}_2$ solutions were warmed to -40° , complete hydrolysis was observed:



The stable compound $\text{B}_3\text{H}_7\text{OH}_2$ formed at -78° should prove a useful intermediate in the preparation of other B_3H_7 adducts.

Table VII

Hydrogen pressure as a function of time for the hydrolysis of KB_3H_8 at $[\text{H}^+] = 3.5 \text{ M}$ and -78°

Time (sec)	P (cm)	$P_\infty - P$ (cm)
0	0	1.26
18	0.22	1.04
48	0.43	0.83
60	0.53	0.73
78	0.64	0.62
96	0.74	0.52
120	0.74	0.42
144	0.94	0.32
192	1.04	0.22
246	1.14	0.11
402	1.25	
4000	1.26	

In a separate experiment, a large excess of cold 8 M HCl was added to a beaker containing a mixture of $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ and methanol-water solvent. After three hours a cold solution of sodium hydroxide was added to see if the $\text{B}_3\text{H}_7\text{OH}_2$ formed would be stabilized in alkaline solution. The reaction mixture was warmed to room temperature and a boron-11 nmr spectrum was recorded. The spectrum is identical to that of a mixture of hydroborate and borate. This reaction may be worth a more careful study, for example using KB_3H_8 and the apparatus in Fig. 2 which would allow the hydrogen evolution to be followed.

Aqueous 8 M HCl. - At -78° , 1.05 moles of hydrogen per mole of KB_3H_8 were evolved within 70 sec. in the hydrolysis of KB_3H_8 , corresponding to the formation of $\text{B}_3\text{H}_7\text{OH}_2$. This further hydrolyzes at -78° to give a total of 4.5 moles of hydrogen in 5 hours and an unknown state of boron-hydrogen intermediate which when warmed to room temperature will give another 4.5 moles of hydrogen to the complete hydrolysis of B_3H_8^- .



The rates of hydrolysis of the unknown boron-hydrogen intermediates at -49.4° , -43.5° , -38.4° and -35.6° were compared with those of $\text{BH}_2(\text{H}_2\text{O})_2^+$ solution. A typical run at -35.6° is shown in Fig. 16. The different initial slopes of the two plots indicate that if the unknown mixture contains $\text{BH}_2(\text{OH})_2^+$, it is not the only species present. However it is apparent that the hydrolysis involves $\text{H}_2\text{OBH}(\text{OH})_2$ immediately before the formation of boric acid.

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Figure Captions

- Figure 1. The apparatus for the kinetic study in acidic solutions.
- Figure 2. The apparatus for the kinetic study in alkaline solutions.
- Figure 3. $\text{Log}(\frac{1}{2}P_{\infty} - P)$ vs. time for the hydrolysis of BH_4^- and H_2OBH_3 at $[\text{H}^+] = 0.11 \text{ M}$ and -78° .
- Figure 4. $\text{Log}(\frac{1}{2}P_{\infty} - P)$ vs. time for the hydrolysis of BH_4^- and H_2DBH_3 at $[\text{H}^+] = 1.21 \text{ M}$ and -78° .
- Figure 5. Values of k_2' as a function of $[\text{H}^+]$ for the hydrolysis of H_2OBH_3 in acidic solution.
- Figure 6. $\text{Log}(P_{\infty} - P)$ vs. time for the hydrolysis of the dihydroboron and monohydroboron intermediates for $[\text{H}^+] = 0.105 \text{ M}$ at -36° . The curve was calculated from Eq. 5 using the values $k_3' = 0.10 \text{ sec}^{-1}$, $k_4' = 3.3 \times 10^{-4} \text{ sec}^{-1}$ and $r = 3.2$.
- Figure 7. $\text{Log}(P_{\infty} - P)$ vs. time for the hydrolysis of the dihydroboron and monohydroboron intermediates for $[\text{H}^+] = 1.16 \text{ M}$ at -36° . The curve was calculated from Eq. 5 using the values $k_3' = 0.0023 \text{ sec}^{-1}$, $k_4' = 3.5 \times 10^{-4} \text{ sec}^{-1}$ and $r = 0.39$.
- Figure 8. Values of k_3' as a function of $[\text{H}^+]$ for the hydrolysis of the dihydroboron intermediates $(\text{BH}_2(\text{OH})_2)^+$ and $\text{H}_2\text{OBH}_2\text{OH}$ in acidic solution.

Figure 9. $\text{Log}(P_\infty - P)$ vs. time for the hydrolysis of BH_3OH^- at $[\text{OH}^-] = 0.35 \text{ M}$ and 20° .

Figure 10. Values of k_6' as a function of the piperidinium ion concentration.

Figure 11. $\text{Log}(P_\infty - P)$ vs. time for the hydrolysis of a mixture of $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ at $[\text{OH}^-] = 0.35 \text{ M}$ and 0° .

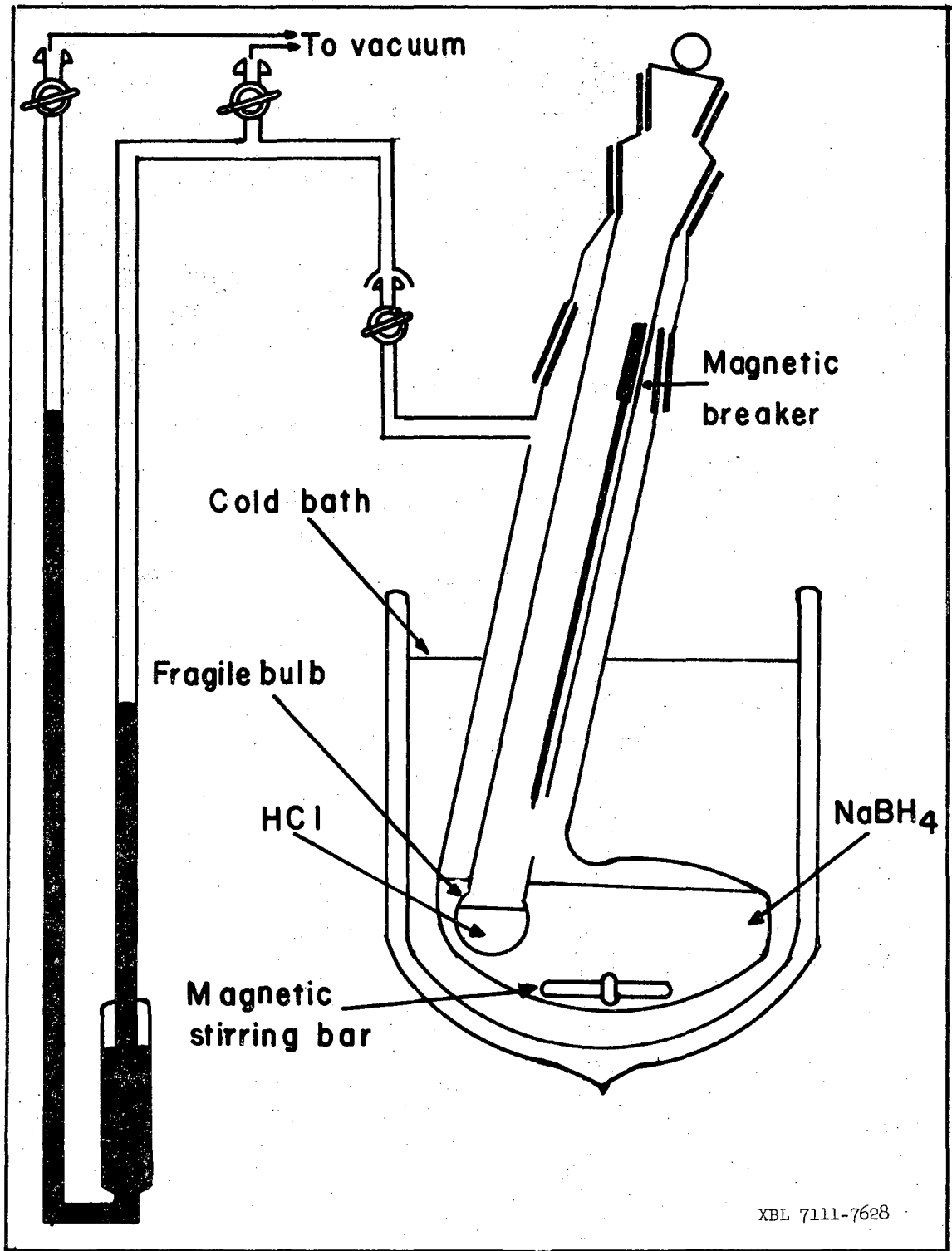
Figure 12. $\text{Log}(P_\infty - P - 2.06 \times 10^{-9.1 \times 10^{-5} t})$ vs. time. The function $2.06 \times 10^{-9.1 \times 10^{-5} t}$ is proportional to the concentration of $\text{BH}_2(\text{OH})_2^-$ at time t . (The parameters of the latter function were evaluated from the straight-line portion of Fig. 11).

Figure 13. Boron-11 nmr spectrum of a water-methanol solution of BH_3OH^- . The singlet is due to borate decomposition product; the quartet is due to the BH_3OH^- ion.

Figure 14. $\text{Log } k_3$ and $\text{log } k_4$ vs. $1/T$ for 8 M HCl . The starting solutions contained pure $\text{BH}_2(\text{OH}_2)_2^+$.

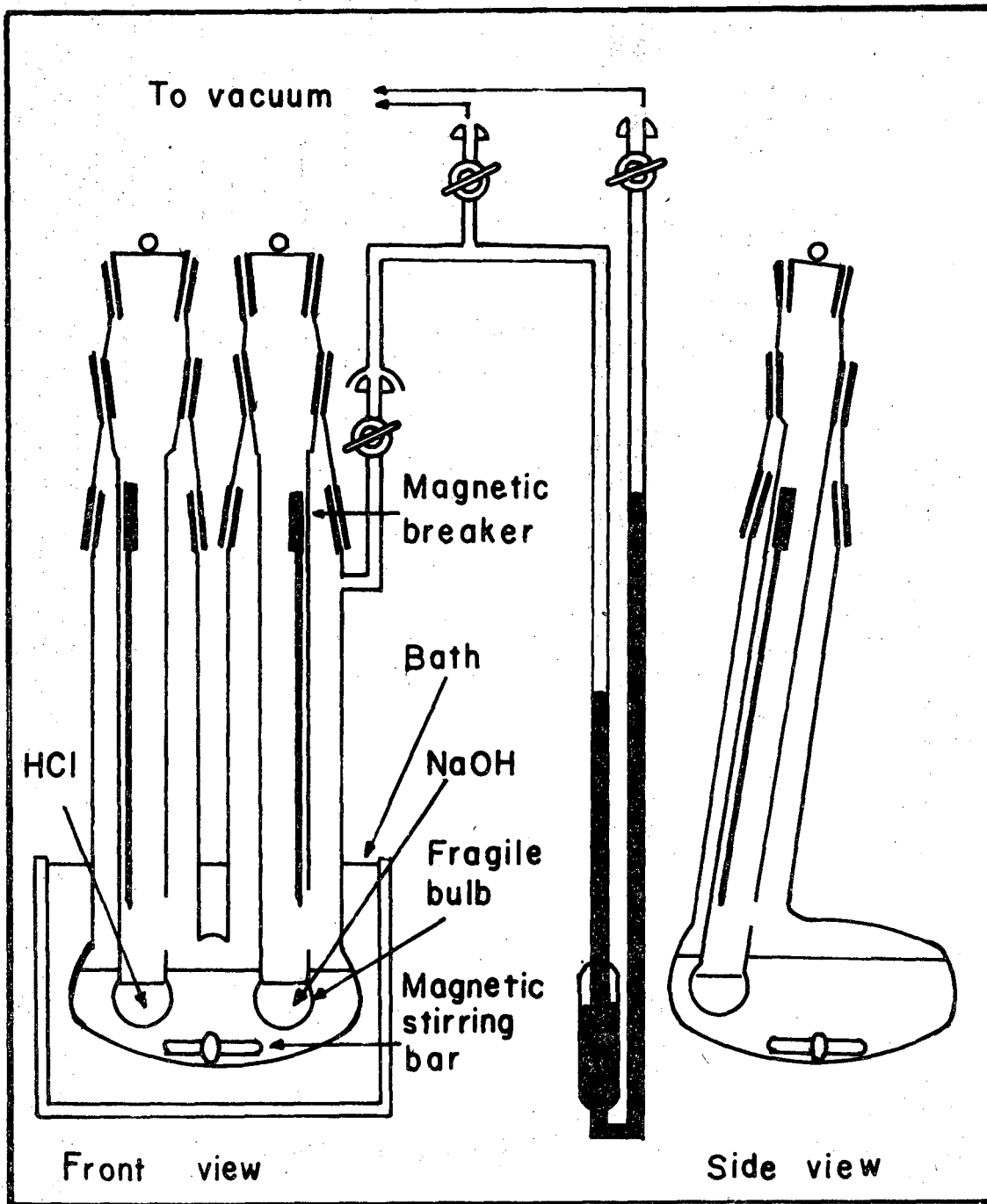
Figure 15. $\text{Log}(P_\infty - 0)$ vs. time for the hydrolysis of KB_3H_8 at $[\text{H}^+] = 3.5 \text{ M}$ and -78° .

Figure 16. Comparison of the hydrolysis of $\text{BH}_2(\text{OH})_2^+$ in 8 M HCl (\blacktriangle) with the unknown boron-hydrogen intermediate in 8 M HCl (\bullet) at -35.6° .



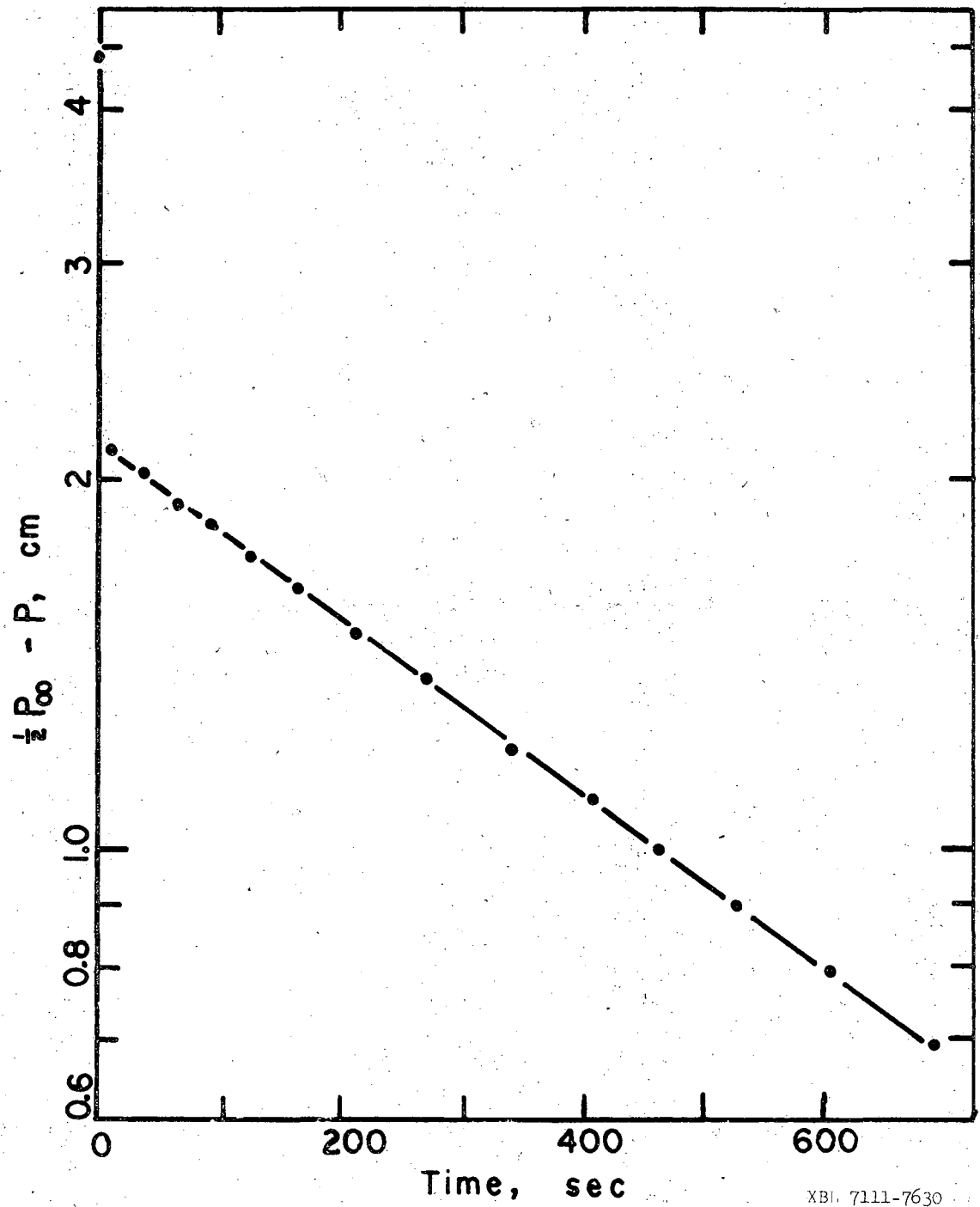
XBL 7111-7628

Figure 1



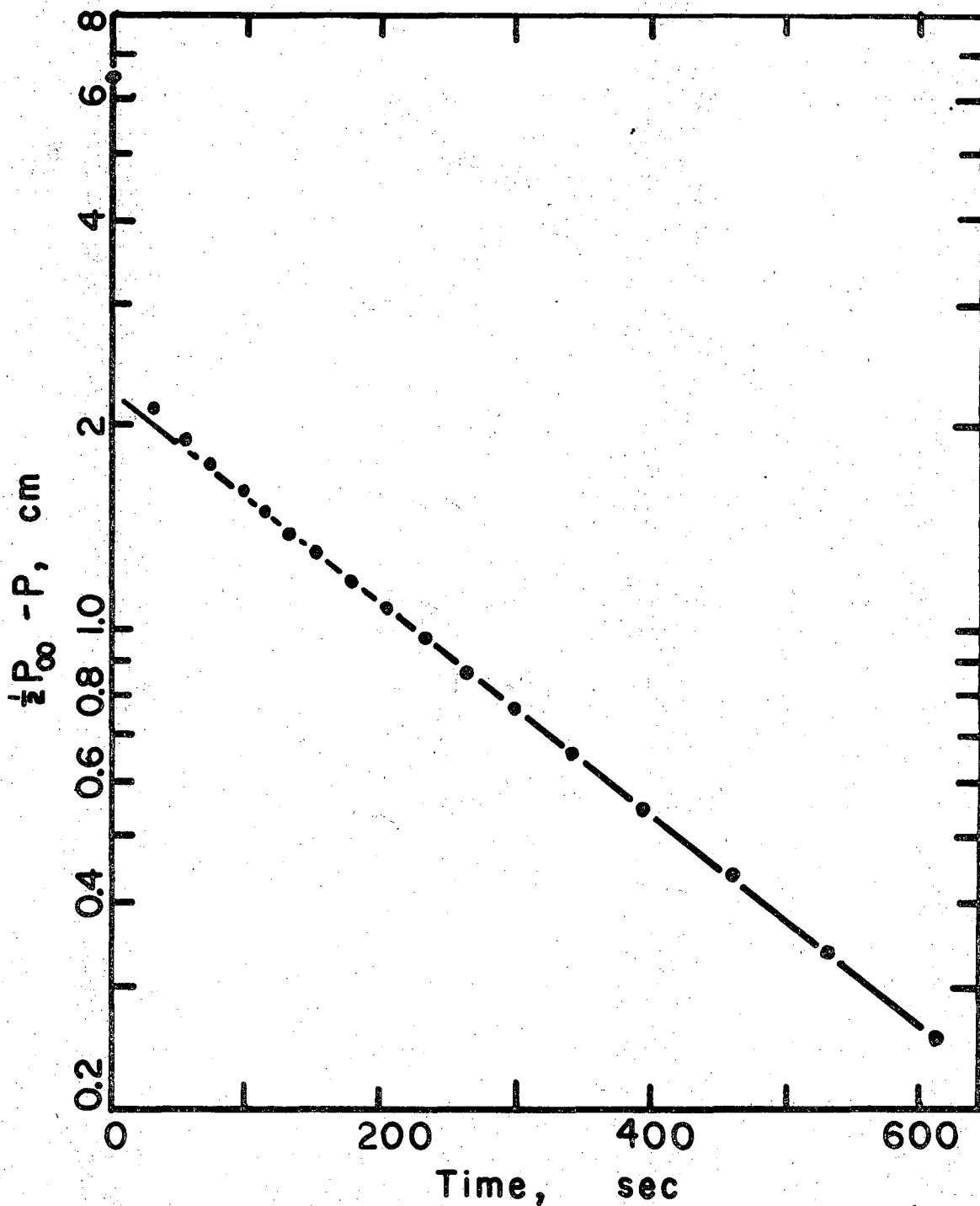
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Figure 2



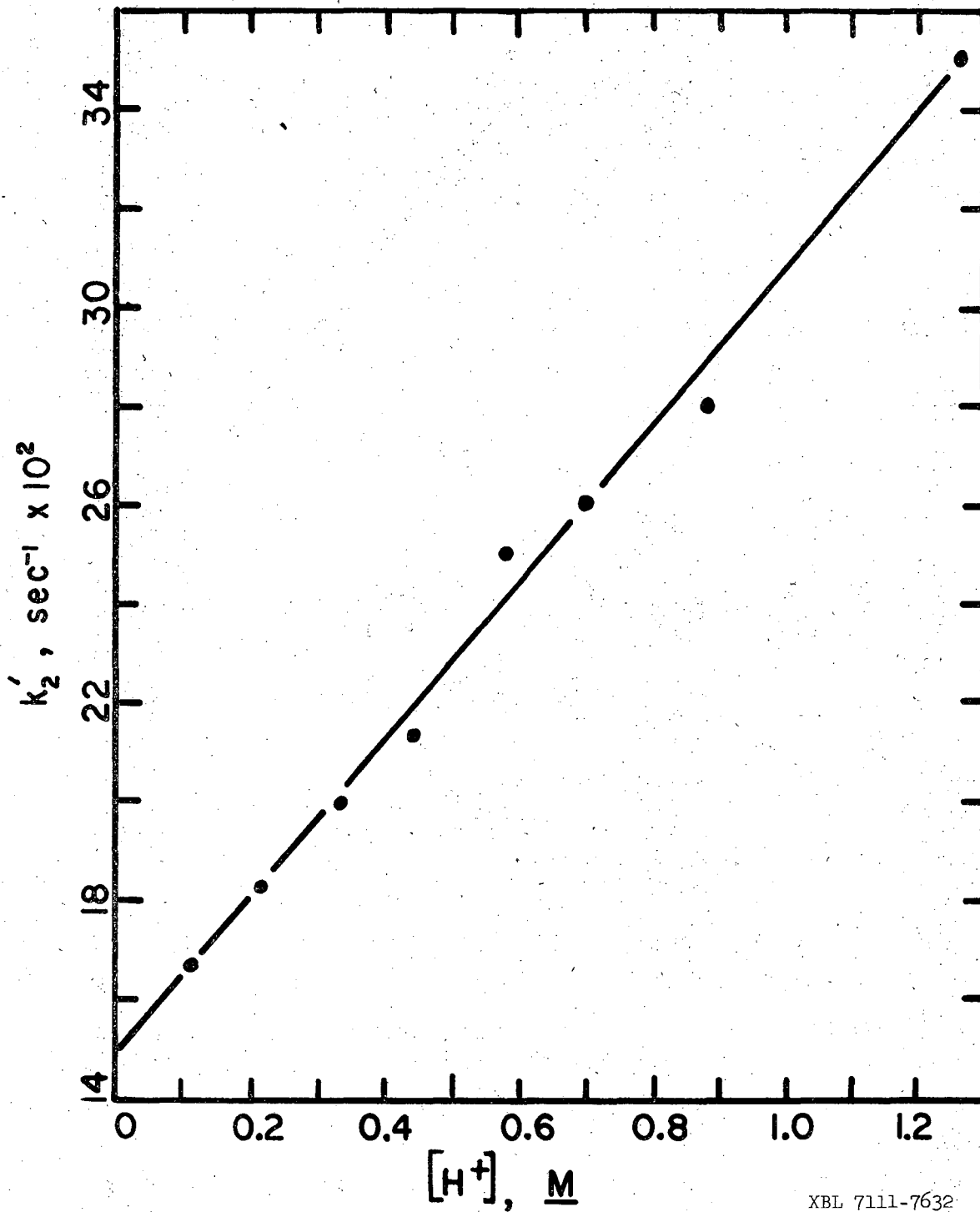
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Figure 3



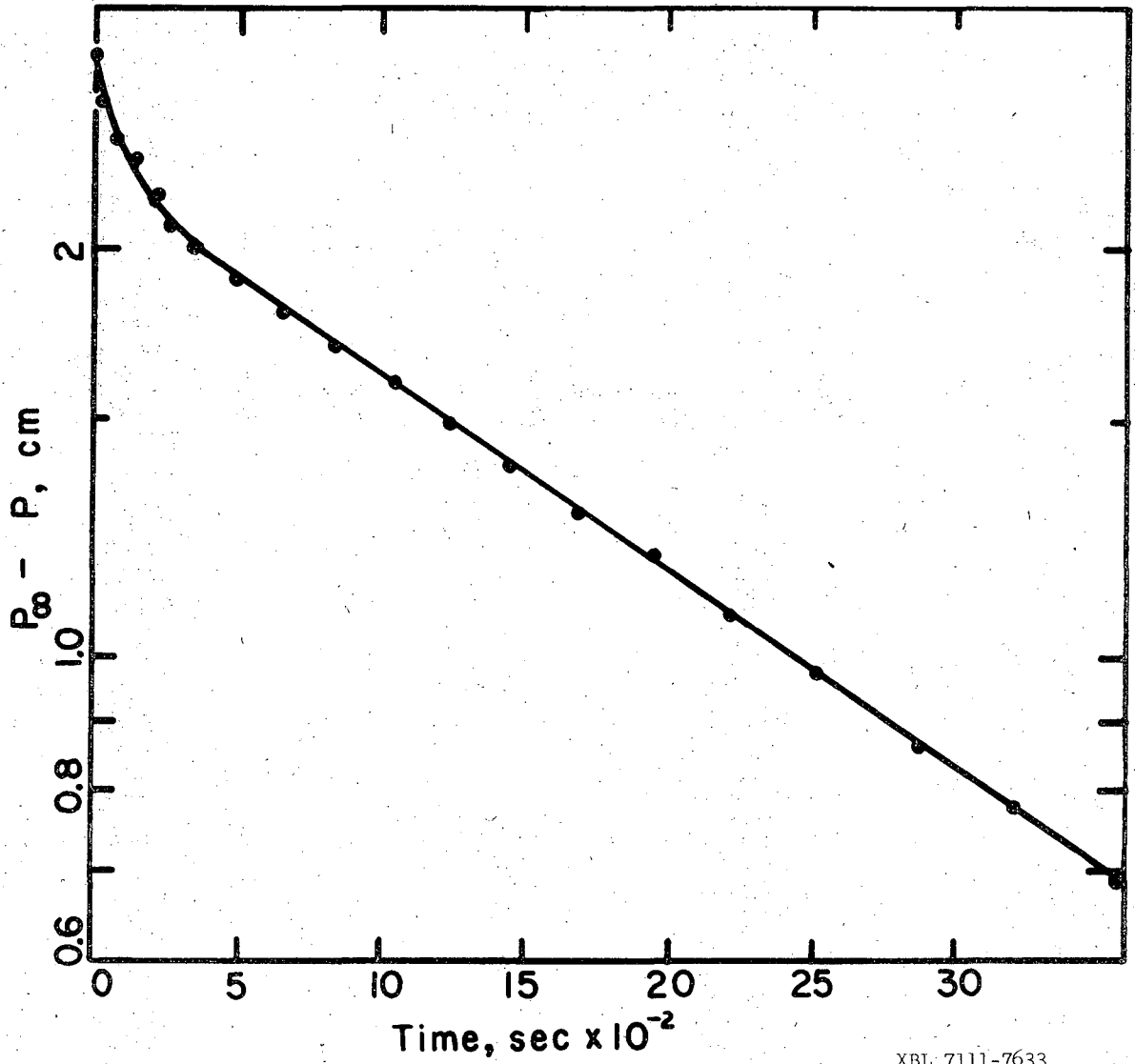
XBL 7111-7631

Figure 4



XBL 7111-7632

Figure 5



XBL 7111-7633

Figure 6

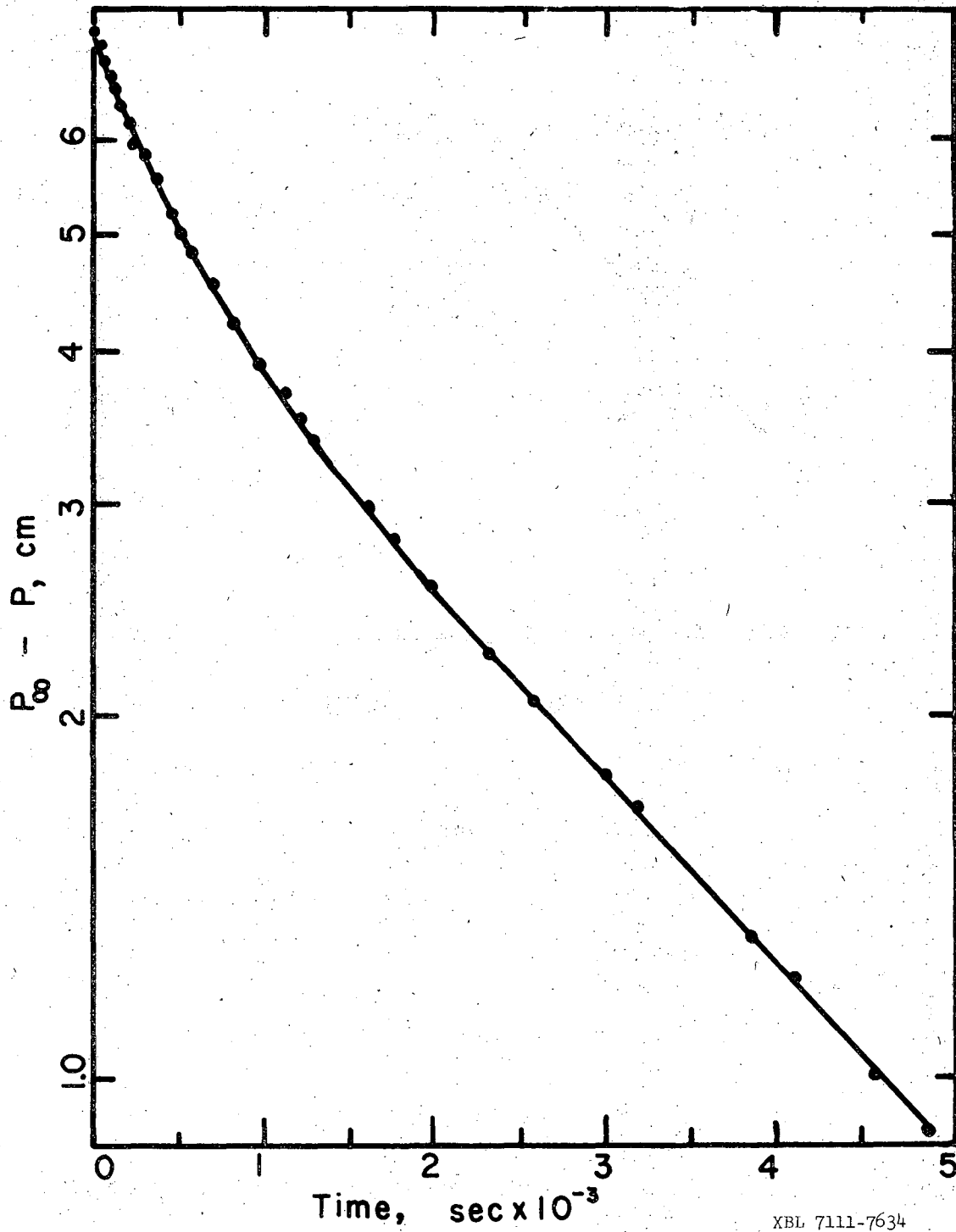
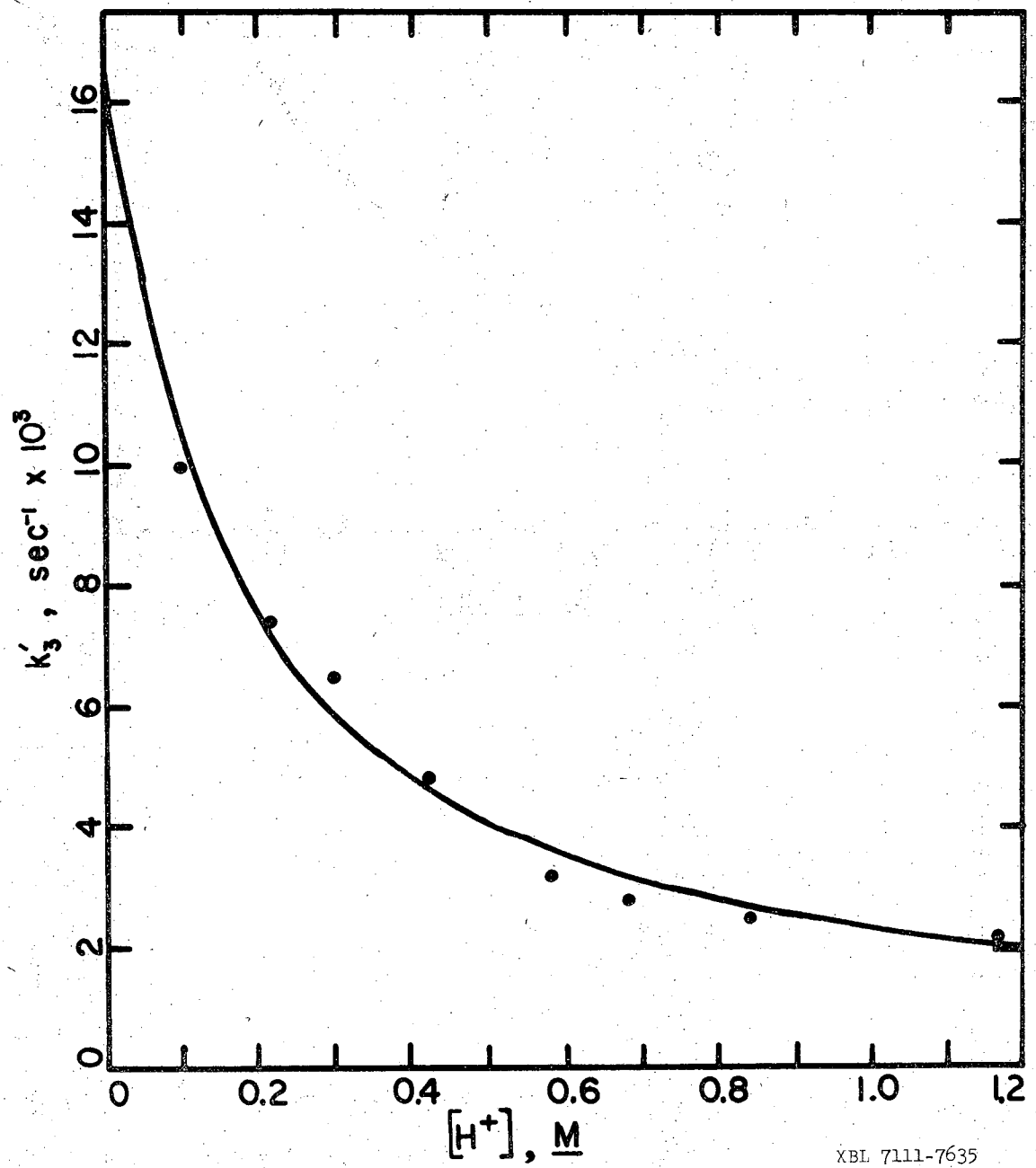


Figure 7



XBL 7111-7635

Figure 8

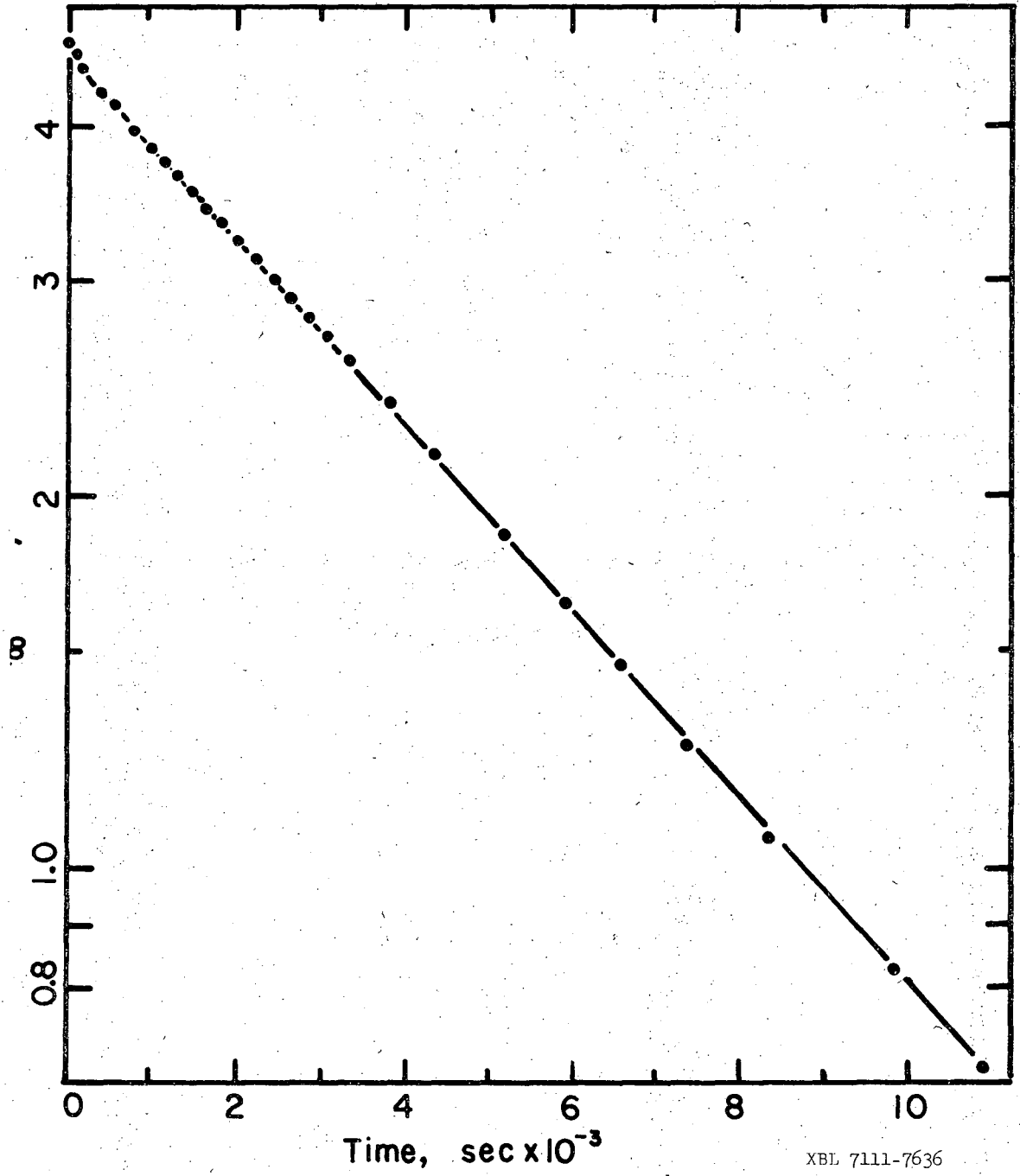
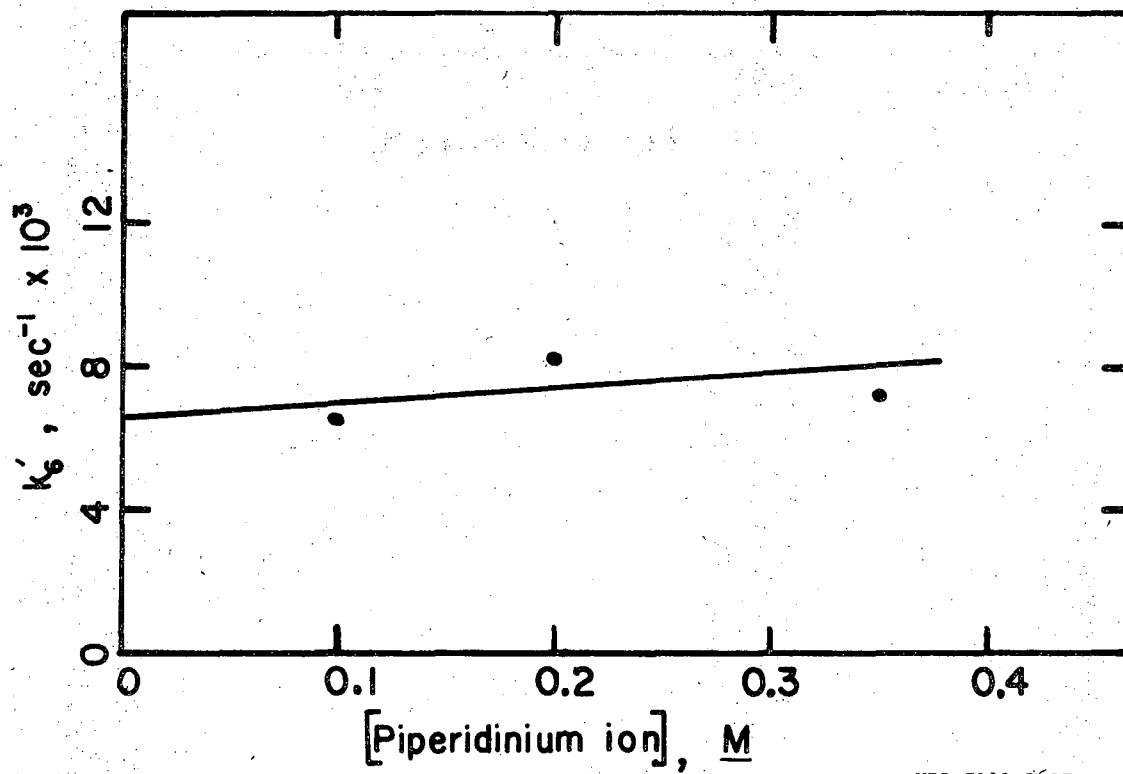
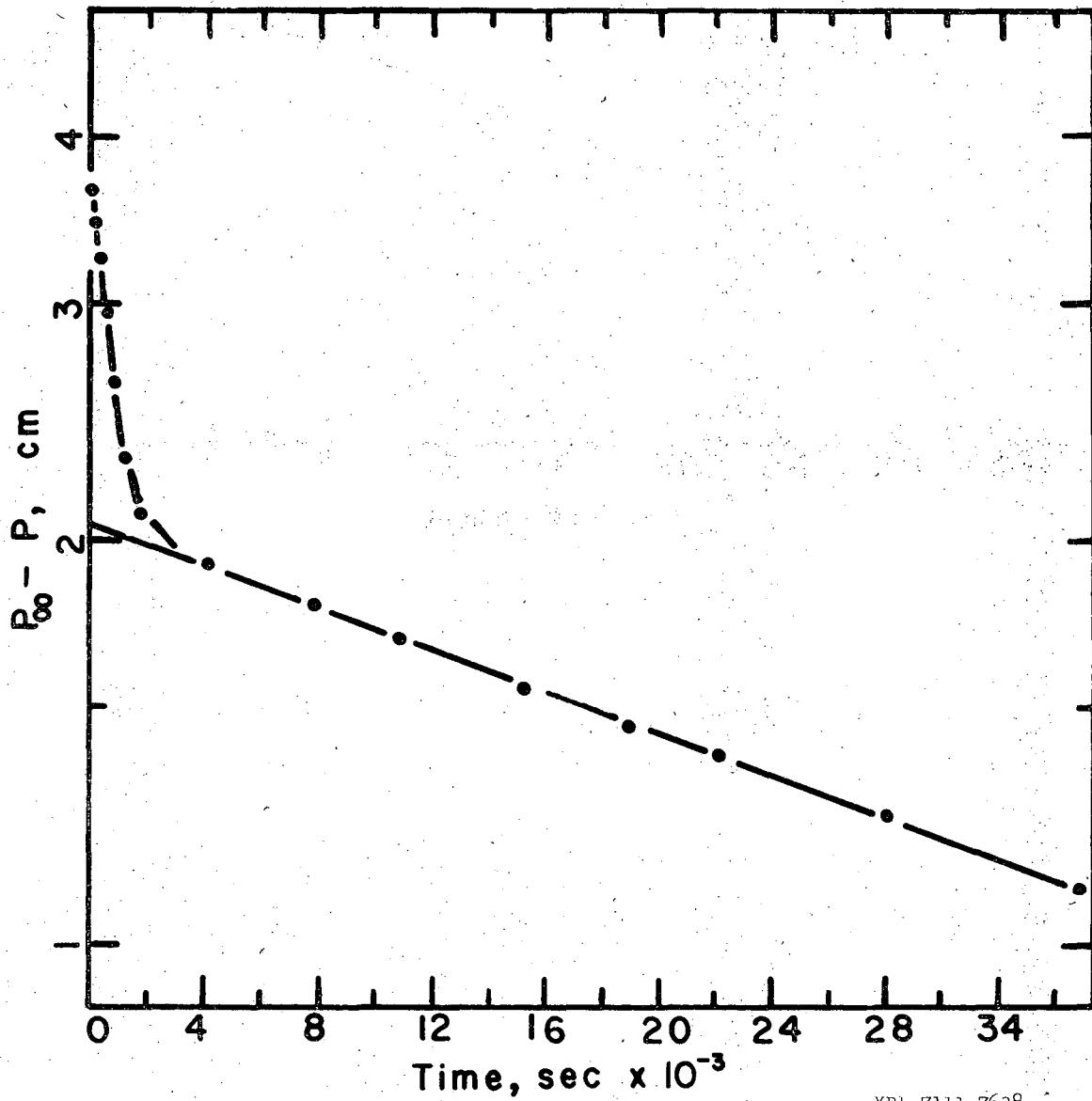


Figure 9



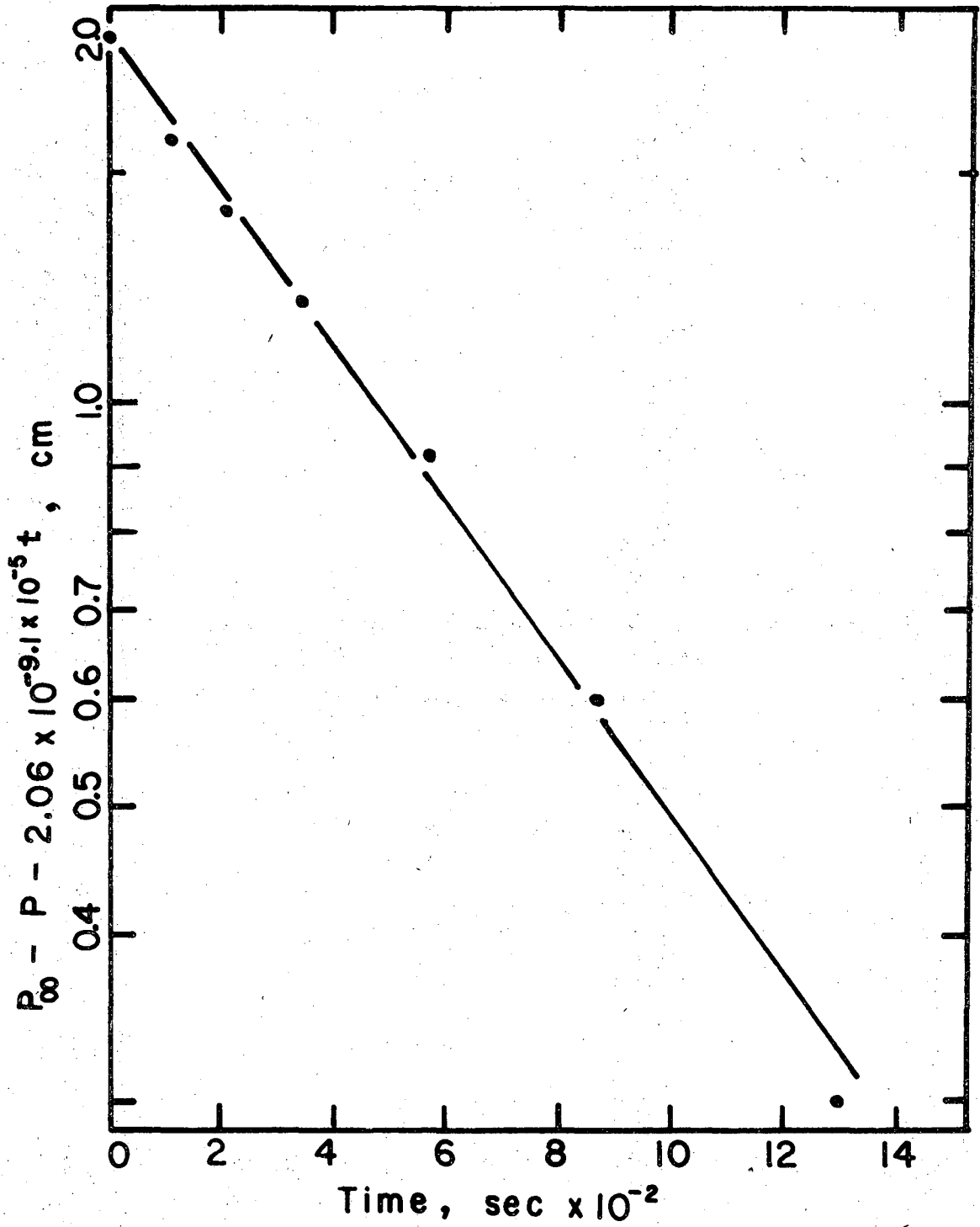
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Figure 10



XRI. 7111-7638

Figure 11



XBL 7111-7639

Figure 12

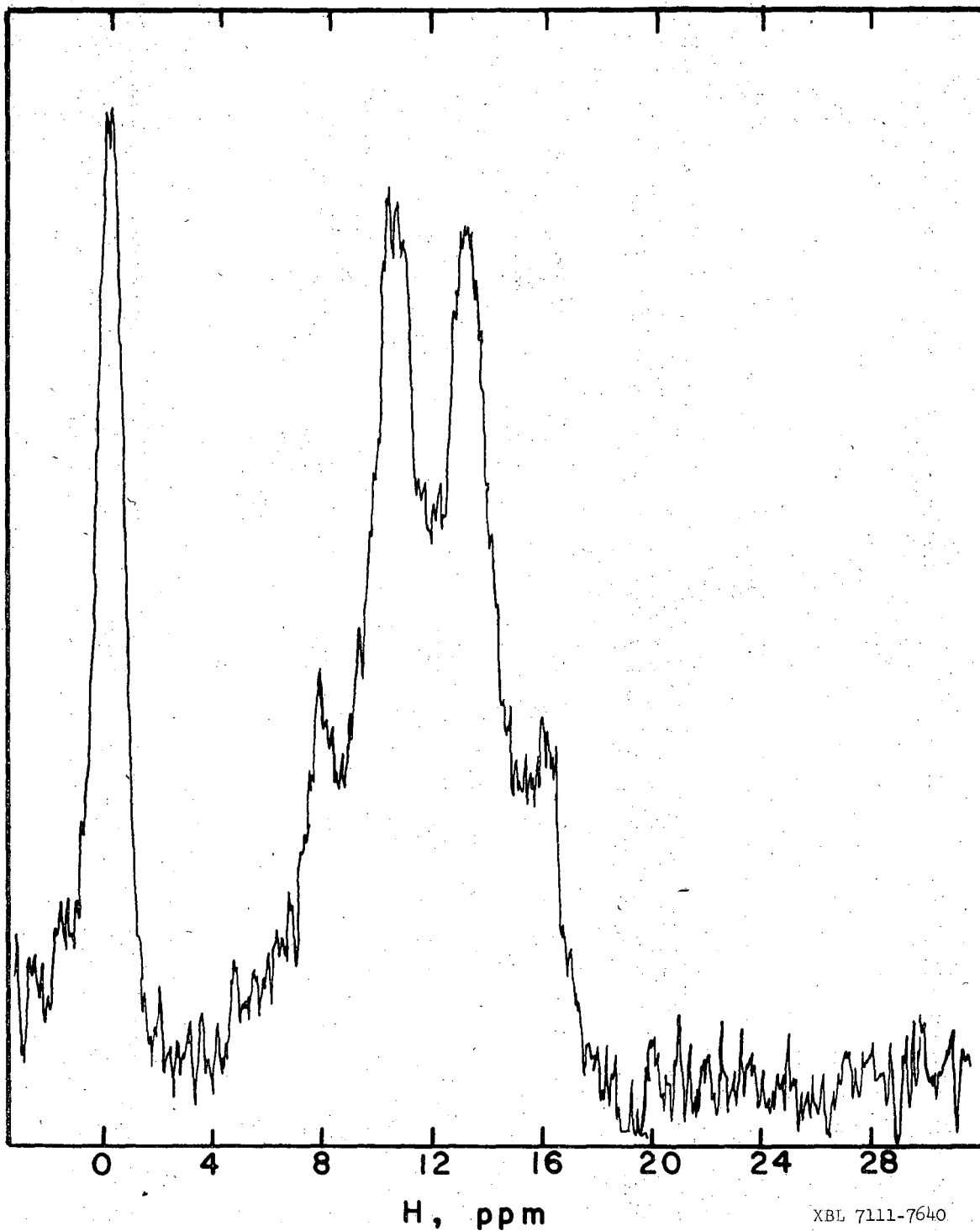
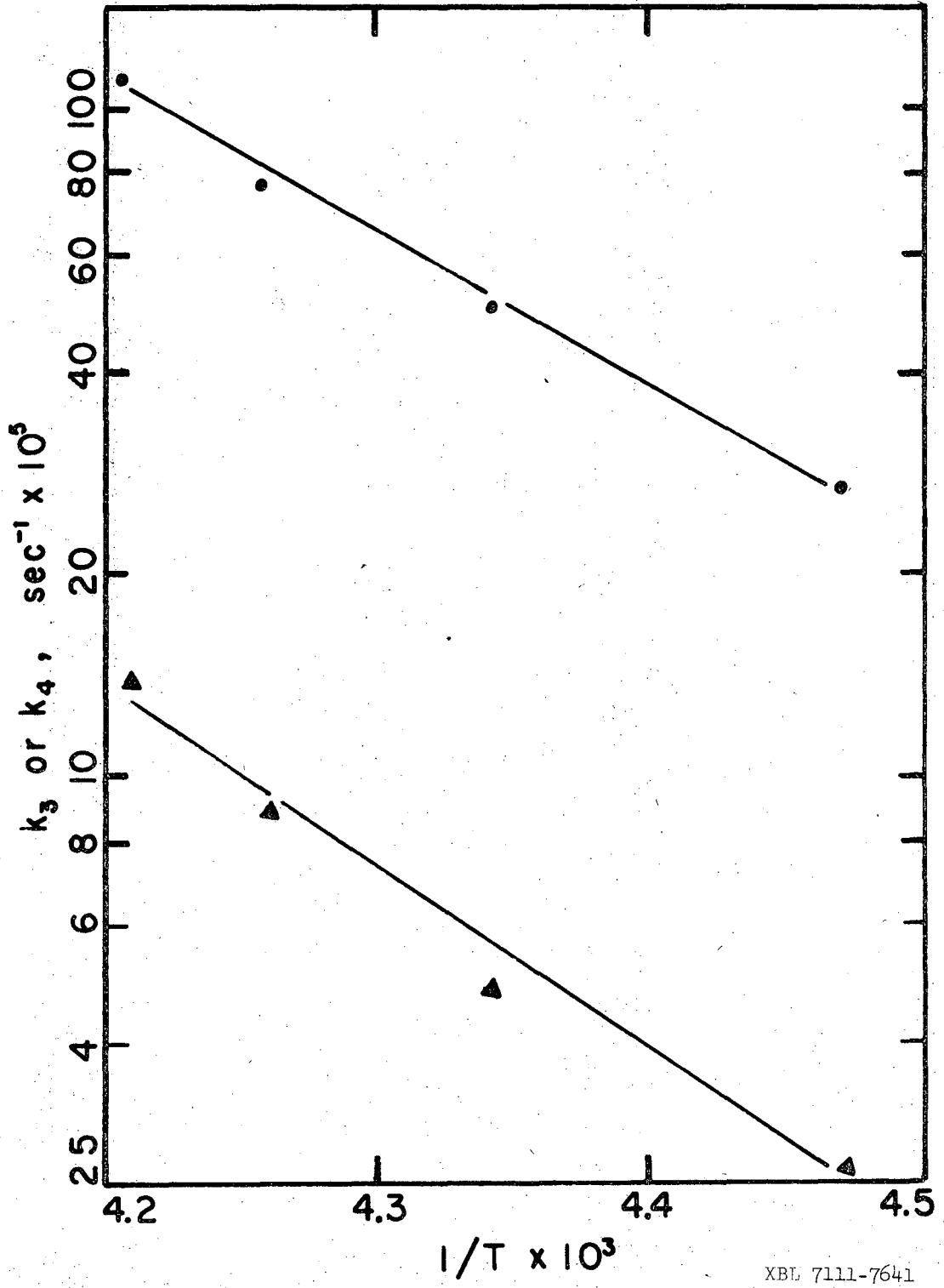
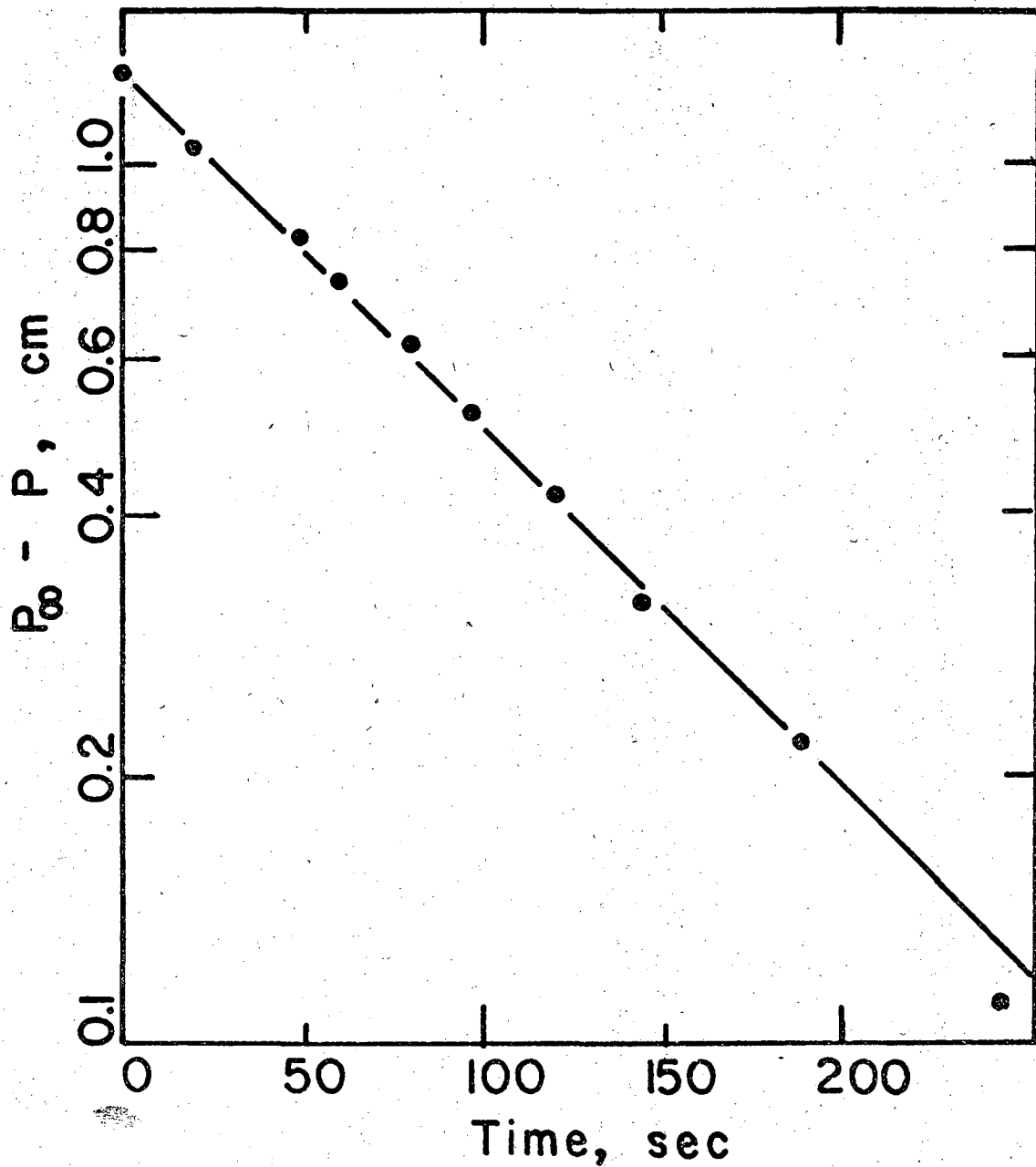


Figure 13



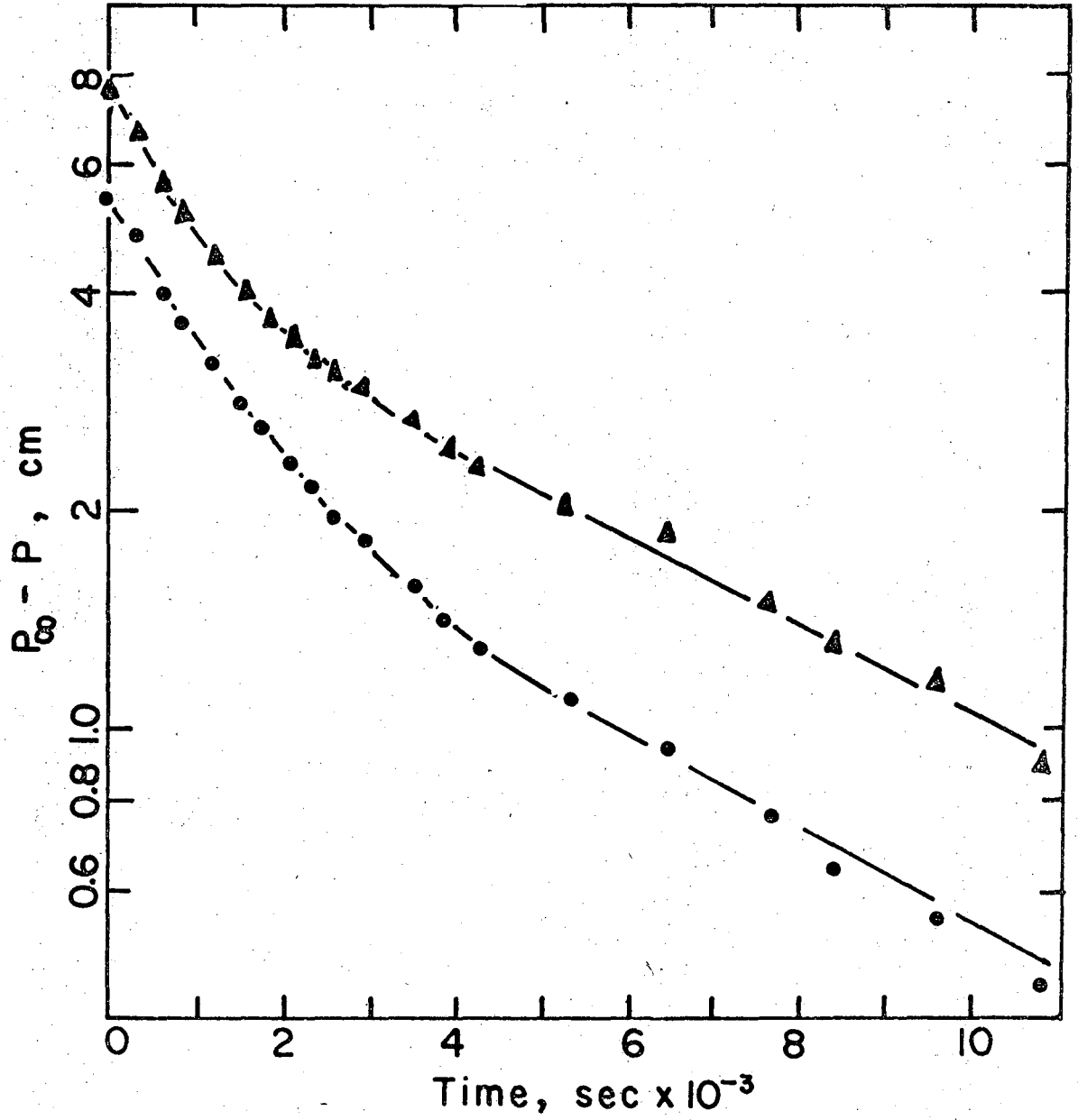
XBL 7111-7641

Figure 14



XBL 7111-7642

Figure 15



XBL 7111-7643

Figure 16

APPENDIX

C-8K FOCAL @1969

```
01.05 TYPE %8.05, "KINETICS LEAST SQUARES", !
01.10 ASK "NO. OF POINTS ", NO,!
01.12 SET J= NO-1
01.13 FOR I=0,J;T %2,I+1," ",%8.05;A "T",T(I)," Y",Y(I),!
01.15 ASK "TRIAL"," H2 INF",H2," K1",K1," K2",K2,!
01.16 ASK " GAMMA", G, !
01.19 SET L=3
01.20 SET S1=1.E+10
01.29 SET S=0
01.30 FOR J=0,2; FOR K=0,3; SET A(J+L*K)=0
01.35 FOR I=0,NO-1; DO 2.0
01.36 T "SUM OF SQUARES ", S, !
01.40 IF ( FABS(S-S1) - 1.E-5 ) 1.9, 1.9,1.5
01.50 SET S1=S
01.51 DO 10
01.52 SET G=G+X(0)
01.54 SET K1=K1+X(1); SET K2=K2+X(2)
01.55 GOTO 1.29
01.90 FOR I=0,NO-1; DO 3
01.91 T !, "K1",K1, " K2", K2,!
01.92 TYPE " GAMMA ", G, !
01.95 QUIT

02.01 SET B1=K1/2; SET B2=K1-K2; SET B3=B1-K2
02.02 SET B4=B2*B2; SET B5=K1-2*K2; SET B6=K2/2
02.03 SET B7=B1/B2
02.05 SET C1=FEXP(-K1*T(I)); SET C2=FEXP(-K2*T(I))
02.06 SET C3=(B1-K2)/B2; SET C3=C3*T(I)
02.07 SET C4=2+G
02.08 SET D1=((B3/B2)*C1+(B7+G/2)*C2)/C4
02.09 SET D1=C2/2-D1
02.10 SET D2=(B6/B4-C3)*C1-(B6/B4)*C2
02.15 SET D3=- (B7/B2)*C1-((B7+G/2)*T(I)-B7/B2)*C2
02.20 SET Y1=((B1-K2)/B2)*C1 + (B7+G/2)*C2
02.50 SET D2=H2*D2
02.52 SET D3=H2*D3
02.54 SET Y1=H2*Y1
02.60 SET D1=((2*H2)/C4)*D1
02.62 SET D2=(2/C4)*D2
02.64 SET D3=(2/C4)*D3
02.66 SET Y1=(2/C4)*Y1
02.89 SET DI= Y(I) - Y1
02.90 SET A(0)=A(0)+D1*DI
02.91 SET A(3)=A(3)+D1*D2; SET A(1)=A(3)
02.92 SET A(6)=A(6)+D1*D3; SET A(2)=A(6)
02.93 SET A(9)=A(9)+D1*DI
02.94 SET A(10)=A(10)+D2*DI
02.95 SET A(11)=A(11)+D3*DI
02.96 SET A(4)=A(4)+D2*D2
02.97 SET A(7)=A(7)+D2*D3; SET A(5)=A(7)
02.98 SET A(8)=A(8)+D3*D3
02.99 SET S= S+ DI*DI
```

```
03.10 DO 2
03.20 T T(I), " ", Y(I), " ", YI, !
03.30 RETURN
```

```
10.05 C SOLVE MATRIX EQ AX=B
10.10 SET N=L-1; S I=-1; FOR K=0,N; SET R(K)=K+1
10.14 SET M= 1.E-6
10.16 FOR J=0,N; FOR K=0,N; DO 11.0
10.17 SET R(P)=0
10.18 FOR K=0,L; SET A( P+L*K) = A(P+L*K)/M
10.20 FOR J=0,N; DO 12.0
10.22 SET I= I+1
10.23 IF (I-N) 10.14, 10.26, 10.14
10.26 FOR J=0,N; FOR K=0,N; DO 13.0
10.28 FOR K=0,N; TYPE !, %2, "X(" K,") ", %8.05, X(K)
10.29 TYPE !!; RETURN
```

```
11.05 IF ( R[J] ) 0, 11.3, 11.1
11.10 IF ( FABS< A[J+L*K] >-FABS[ M ] ) 11.3;
11.20 SET M= A( J+L*K )
11.22 SET P=J; SET Q=K
11.30 RETURN
```

```
12.10 IF ( J-P ) 12.2, 12.4 , 12.2
12.20 SET D=A(J+L*Q)
12.30 FOR K=0,L; SET A(J+L*K)=A(J+L*K)-A(P+L*K)*D
12.40 RETURN
```

```
13.10 IF (1.0E-6 -FABS[ A<J+L*K> ] ) 13.20; RETURN
13.20 SET X(K) = A(J+L*L) ; RETURN
```

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