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A Kinetic Study of the Intermediates in the Hydrolysis of the Hydroborate Ion

By Francis T. Wang and William L. Jolly*

The stepwise hydrolysis of hydroborate has been studied in cold 88/12 volume per cent methanol/water solutions 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 $BH_2(H_2O)_2^+$ according to the rate equation $-d\ \ln\ [H_2OBH_3]/dt = 0.0015\ sec^{-1} + 0.0016\ H^+\ sec^{-1}\ \underline{M}^{-1}$. The rate data for the hydrolysis of $BH_2(H_2O)_2^+$ solutions at -36° are consistent with the following rapid equilibrium (K = 6.4): $H^+ + H_2OBH_2OH \rightleftarrows BH_2(H_2O)_2^+$. The $BH_2(H_2O)_2^+$ ion is stable toward hydrolysis, whereas its conjugate base hydrolyzes to $H_2OBH(OH)_2$ according to the rate equation $-d\ \ln\ [H_2OBH_2OH]/dt = 0.017\ sec^{-1}$. At -36°, $H_2OBH(OH)_2$ hydrolyzes to $B(OH)_3$ according to the rate equation $-d\ \ln\ [H_2OBH(OH)_2]/dt = 3.3 \times 10^{-4}\ sec^{-1}$.

The species H_2OBH_3, $BH_2(H_2O)_2^+$ and $H_2OBH(OH)_2$ are converted to the anions BH_3OH^-, $BH_2(OH)_2^-$ and $BH(OH)_3^-$, respectively, by the addition of hydroxide. These anions undergo hydrolysis in non-buffered strongly alkaline solutions according to the rate equations $-d\ \ln\ [BH_3OH^-]/dt = 1.8 \times 10^{-4}\ sec^{-1}$ at 20°; $-d\ \ln\ [BH_2(OH)_2^-]/dt = 2.2 \times 10^{-5}\ sec^{-1}$ and $-d\ \ln[BH(OH)_3^-]/dt = 1.1 \times 10^{-3}\ sec^{-1}$ at 0°. The boron-11 nmr spectrum of BH_3OH^- is a 1:3:3:1 quartet, with J_{B-H} = 87 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.

$$BH_4^- + H^+ + 3H_2O \rightarrow B(OH)_3 + 4H_2$$

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2$$

A variety of experimental data have shown that the hydrolysis proceeds in four steps, with the intermediate formation of tri-hydro-, 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°) aqueous or water-alcohol solutions.[5,6] This intermediate is relatively stable in cold acidic solutions, where it is believed to exist as $BH_2(H_2O)_2^+$, but it is unstable toward further hydrolysis in neutral solutions, where it is assumed to exist as H_2OBH_2OH.[7]

The <u>mono</u>hydroboron intermediate has been prepared quantitatively by the reaction of diborane with water-alcohol solutions[5] at -75° and with ice[8] at -80°. The assumed formula of the product of these reactions is $H_2OBH(OH)_2$.[7] Alkaline solutions of the monohydroboron intermediate, presumably containing the ion $BH(OH)_3^-$, have been prepared by the addition of KOH to water-alcohol solutions of $BH_2(H_2O)_2^+$ and $H_2OBH(OH)_2$.[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 have prepared 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 containing the species $BH(OH)_3^-$, $BH_2(OH)_2^-$ or BH_3OH^- were prepared by the addition of excess sodium hydroxide to acidic solutions containing the appropriate intermediates. 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 so that the final ionic strength would be 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 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 either had stopped (in runs with high $[H^+]$) or had become very slow (in runs with low $[H^+]$). The Dry Ice-acetone bath was replaced by another cold acetone bath, the temperature of which was then 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 ± 0.5° 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. Then the volatilized methanol and water were condensed back into the reaction vessel by cooling the later to -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. 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 $BH_2(OH)_2^-$, 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° in the case of $BH_2(OH)_2^-$, and to 20° in the case of BH_3OH^-), and the hydrogen evolution was measured as a function of time. To prepare $BH(OH)_3^-$, a solution containing mainly the dihydroboron species at -78° was warmed to -37 $\pm$ 3° for 40 minutes to allow all the trihydro- and dihydroboron species to hydrolyze. Sodium hydroxide was then added, and the solution was warmed to 0° for the hydrogen evolution measurement. In all runs, after about 80% of the total hydrogen had been evolved, the solutions were heated to 55 $\pm$ 5° for an hour to effect complete decomposition and to allow complete evolution of any dissolved hydrogen. The volatilized methanol and water were condensed back into the reaction vessel at -196°, and the infinite time hydrogen pressures were measured at 0° for $BH_2(OH)_2^-$ and $BH(OH)_3^-$, and at 20° for BH_3OH^-. The sodium hydroxide concentrations were determined by titration with 0.10 M hydrochloric acid, using bromthymol blue was 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 improve the nmr spectrum, the concentration of BH_3OH^- was increased by pumping off 1/3 to 1/2 of the solvent at $-25 \pm 5°$. 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 $NaBH_4$ in the various runs are given in Table I. The hydrogen evolution at -78° was

Table I

The initial concentrations of HCl and $NaBH_4$ 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 $BH_2(H_2O)_2^+$.[5,6] When the resulting solution was then warmed to -36°, further rapid hydrogen evolution occurred. In about 15 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 took place.

$$BH_4^- + H^+ + H_2O \xrightarrow{-78°} H_2OBH_3 + H_2 \qquad (1)$$

$$H_2OBH_3 + H^+ + H_2O \xrightarrow{-78°} BH_2(H_2O)_2^+ + H_2 \qquad (2)$$

$$BH_2(H_2O)_2^+ \xrightarrow{-36°} H_2OBH(OH)_2 + H^+ + H_2 \qquad (3)$$

$$H_2OBH(OH)_2 \xrightarrow{-36°} B(OH)_3 + H_2 \qquad (4)$$

(Evidence for the formulas of the intermediates will be discussed later.)

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

Table II

Hydrogen pressure as a function of time for $[H^+] = 0.110$ 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] $P_\infty = 8.82$ cm.

Table III

Hydrogen pressure as a function of time for $[H^+] = 1.210$ 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] $P_\infty = 13.10$ 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

the expected $\frac{1}{4}P_\infty$, a greater discrepancy being found in the run with the higher hydrogen ion concentration. These discrepancies can be ascribed to premature decomposition of H_2OBH_3, probably caused by 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.[10] 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 the data of all the runs are plotted versus hydrogen ion concentration in Fig. 5. Runs with hydrogen ion concentrations equal to those or runs 1 and 5 were carried out without the addition of LiCl to maintain constant ionic strength; the values of k_2' changed by less than 10%. This result 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 solution[11] and the pressure increase of the hydrogen due to the temperature change. This result indicates that, at the time chosen for the start of the -36° measurements ("zero time"), 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 the subscript zero stands for the zero-time 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 zero time 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

$$(P_\infty - P_o)C = 2[BH_2(H_2O)_2^+]_o + [H_2OBH(OH)_2]_o$$

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

The integrated rate expression[12] can be written as

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

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

By combining the four preceding equations with the relation $[H_2OBH(OH)_2]_o = r[BH_2(H_2O)_2^+]_o$, we obtain

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

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.

Semilogarithmic plots of $(P_\infty - P)$ versus time for runs 1 and 8 at -36° are shown in Fig. 6 and 7. The smooth curves drawn through the points correspond to the computer-calculated values of k_3', k_4' and r. A plot 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 of k_4' was 3.3×10^{-4} sec^{-1} except for run 4 (3.7×10^{-4} sec^{-1}) and runs 7 and 8 (3.5×10^{-4} sec^{-1}). In a separate set of experiments at 0°, k_4' was found to be 4.3, 4.3, 4.6 and 10.5 $\times 10^{-3}$ sec^{-1} at pH 1.00, 0.70, 0.46, and 5.6 respectively. The first three of these pH values were maintained with hydrochloric acid; the last value was maintained by a sodium benzoate-benzoic acid buffer.

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 parts of the -78° runs was markedly decreased by more than a factor of five. Obviously the initial rate of formation of hydrogen in the -78° runs was greater than the rate at which it could escape from solution.

Hydrolysis of $BH_2(H_2O)_2^+$ in 8 M HCl solution. - The hydrolysis of $BH_2(H_2O)_2^+$ in aqueous 8 M HCl solutions in the temperature range -35° to -50° was studied. The reactions can be written as:

$$BH_2(H_2O)_2^+ \xrightarrow{k_3} H_2OBH(OH)_2 + H^+ + H_2$$

$$H_2OBH(OH)_2 \xrightarrow{k_4} B(OH)_3 + H_2$$

From plots of k_3 and k_4 versus 1/T the following activation energies were calculated: for k_3, ΔE_a = 10.7 ± 0.8 kcal/mol ; for k_4, ΔE_a = 11.6 ± 0.9 kcal/mol .

Alkaline Solutions.- A sufficient excess of sodium hydroxide was used in the preparation of the solutions containing BH_3OH^-, $BH_2(OH)_2^-$, and $BH(OH)_3^-$ so that the hydroxide concentration was at least 5 times that of the total boron concentration. For runs between pH 10 and 12, only the piperidine/piperidinium chloride buffer system was found to be suitable. (Other buffer systems were unsuitable because of low solubility in the water-methanol solution, or because of high vapor pressure.)

In strongly alkaline solutions the following net reactions were assumed.

$$BH_3OH^- + 3H_2O \xrightarrow{k_6'} B(OH)_4^- + 3H_2 \qquad (6)$$

$$BH_2(OH)_2^- + 2H_2O \xrightarrow{k_7'} B(OH)_4^- + 2H_2 \qquad (7)$$

$$BH(OH)_3^- + H_2O \xrightarrow{k_8'} B(OH)_4^- + H_2 \qquad (8)$$

(Evidence for the formulas of the species will be discussed later.) The reaction rates were measured using the same techniques used for the acidic solutions.

Data for the hydrolysis of BH_3OH^- at 20° in a solution 0.35 M in sodium hydroxide are given in Table VI. The corresponding plot of $\log(P_\infty - P)$ versus time, shown in Fig. 9, gives a straight line. This indicates that the rate constants for reactions 6, 7 and 8 increase in the order $k_6' < k_7' < k_8'$. If $BH_2(OH)_2^-$ and $BH(OH)_3^-$ had been present in the solution at the time chosen for the start of the measurements at 20°, a sudden increase in the hydrogen pressure would have been observed. It is concluded that at "zero time" $BH_2(OH)_2^-$ and $BH(OH)_3^-$ had already decomposed or had reached secular equilibrium with BH_3OH^-. Values of the pseudo-first-order rate constant k_6' were obtained from the slopes of the lines such as that in Fig. 9. Values of k_6' are 1.7, 1.9, and 1.8×10^{-4} sec^{-1} at pH 13.5, 13.0, and 12.5, respectively. The dependence of k_6' on buffer acid (piperidinium ion) concentration at pH 10 was found to be very slight. The k_6' values 6.5, 8.2, and 7.2×10^{-3} sec^{-1} were determined for piperidinium concentrations 0.1, 0.2, and 0.35 M, respectively. We shall take $k_6' = 6.6 \times 10^{-3}$ at [piperidinium] = 0.

The data for unbuffered strongly alkaline solutions (pH ~13) in which $BH(OH)_3^-$ was the only boron-hydrogen species yielded the following values of k_8': 1.30, 1.10, 1.20 and 0.89×10^{-3} sec^{-1} at 0°. In a buffered solution of pH 10, $k_8' = 9 \times 10^{-3}$ sec^{-1} at 0°.

We were unable to prepare a solution containing $BH_2(OH)_2^-$ uncontaminated with $BH(OH)_3^-$. A plot of $\log(P_\infty - P)$ versus time for a mixture of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ in a solution 0.35 M in NaOH at 0° is shown in Fig. 10. The $BH(OH)_3^-$ hydrolyzes faster than the $BH_2(OH)_2^-$, therefore the hydrolysis of the mixture was treated as two parallel pseudo-first-order reactions. After 3000 seconds, there was essentially no $BH(OH)_3^-$ present (only that in secular equilibrium with the $BH_2(OH)_2^-$) and therefore the curve in Fig. 10 becomes linear, corresponding to the hydrolysis of $BH_2(OH)_2^-$. The expression for $\log(P_\infty - P)$ becomes $\log[BH_2(OH)_2^-]C = \log(P_\infty - P) = \log[BH_2(OH)_2^-]_0C - (k_7't/2.303)$, where C is the factor that converts solution concentration into hydrogen pressure. The linear portion of the curve in Fig. 10 corresponds to $P_\infty - P = [BH_2(OH)_2^-]C = 2.06 \times 10^{-9.1 \times 10^{-5}t}$ cm. The pressure corresponding to $BH(OH)_3^-$ was calculated by difference, $[BH(OH)_3^-]C = P_\infty - P - 2.06 \times 10^{-9.1 \times 10^{-5}t}$. A semi-logarithmic plot of this quantity versus time is shown in Fig. 11; from this plot we obtained k_8'. By such treatment of data for solutions at pH 13.5, 13.3, and 12.8, we obtained the following values for k_7', 2.1, 2.1 and 2.2×10^{-4} sec^{-1}, and the following values for k_8': 1.3, 1.5 and 1.4×10^{-2} sec^{-1}, respectively.

To determine the rate of hydrolysis of a mixture of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ at lower pH, a run at pH 10 was tried. The plot of $\log(P_\infty - P)$ versus time gave one straight line corresponding to a rate constant of 1.4×10^{-2} sec^{-1} for the hydrolysis of $BH(OH)_3^-$. This indicates that at pH 10 the dihydroboron species is rapidly hydrolyzed to $BH(OH)_3^-$. Apparently lowering the pH from 12.8 to 10 makes the rate of hydrolysis of dihydroboron species faster than that of $BH(OH)_3^-$.

The boron-11 nmr spectrum of BH_3OH^- is shown in Fig. 12. In an attempt to obtain a boron-11 nmr spectrum of $BH_2(OH)_2^-$ at -20°± we observed two broad peaks 3.5 ppm apart. The solution was warmed to 60°

for 10 minutes, and the spectrum was again recorded at -20°. Only a singlet, identical to the high-field peak of the original spectrum, was observed. We identified the singlet as sodium borate by substitution.

Discussion

Tetrahydroborate.- 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. This 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^{-3} sec for the hydroborate ion in 0.1 M H^+ at -78°. Indeed, the change of solvent from water too 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 Trihydroboron Species.- The fact that one mole of hydrogen is very rapidly evolved per mole of hydroborate in the acid hydrolysis at -78° and that further hydrogen evolution occurs at a lower, measurable rate suggests the immediate formation of a trihydroboron species. We believe that the trihydroboron species which exists in acid solutions is H_2OBH_3 and that this species is converted to BH_3OH^- by treatment with base. Various types of evidence support these formulations.

The strongest evidence for formation of the BH_3OH^- ion upon adding base to a solution containing H_2OBH_3 is the boron-11 nmr spectrum shown in Figure 13. The 1:3:3:1 quartet is centered 12.0 ppm upfield from the borate singlet, with a coupling constant J_{BH} = 87 Hz. Gardiner and Collat[3] have reported a boron-11 nmr spectrum for BH_3OH^-, with the signal centered 13.9 ppm upfield from the borate singlet and J_{BH} = 82 Hz. Although we were able to observe the proton nmr signal of a solution 0.05 M in BH_4^- at -20°, we were unable to see the proton nmr signal of a 0.2-0.3 M solution of BH_3OH^-. Gardiner and Collat did not observe any proton nmr peaks due to BH_3OH^- in a solution containing both BH_3OH^- and BH_4^- and concluded that the BH_3OH^- spectrum was masked by that of the BH_4^- ion. From our results it seems likely that the proton nmr signal of BH_3OH^- is broadened to the extent of sinking into the background by the ^{11}B quadrupolar relaxation effects.

Gardiner and Collat[2] have reported the rate law for the hydrolysis of BH_3OH^- as

$$-\frac{d\ \ln[BH_3OH^-]}{dt} = k_{HA}[HA] + k_{H^+}[H^+] + k_{H_2O} \quad (9)$$

where [HA] is the concentration of the acid component of the buffer solution and where $k_{H^+} = 7 \pm 3 \times 10^{-6}\ \underline{M}^{-1}\ sec^{-1}$ and $k_{H_2O} = 3.9 \times 10^{-4}\ sec^{-1}$ at 20°. In non-buffered, strongly alkaline solutions (pH 12.5 to 13.5) the right side of Eq. 9 can be approximated as k_{H_2O}. In this pH. range, we found the pH-independent rate constant $k_6' = 1.8 \times 10^{-4}\ sec^{-1}$. The latter value is in fairly good agreement with Gardiner and Collat's k_{H_2O}, particularly in view of the fact that the solvents and ionic strengths were quite different. If we apply Eq. 9 to our kinetic study of the hydrolysis of BH_3OH^- at pH 10, we obtain, using our value of k_6' at [piperidinium ion] = 0, $k_{H^+}[H^+] + k_{H_2O} = 6.6 \times 10^{-3}$ sec^{-1}. Substituting $[H^+] = 10^{-10}$ and $k_{H_2O} = 1.8 \times 10^{-4}$ sec^{-1}, we obtain $k_{H^+} = 6.4 \times 10^7$ M^{-1} sec^{-1}. The latter value is in fair agreement with the k_{H^+} value of Gardiner and Collat.

It is clear that the trihydroboron species in acidic solutions is different from that in alkaline solutions, because the stability toward hydrolysis is markedly increased upon going from acidic to alkaline solution. 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 rate law $-d[H_2OBH_3]/dt = k_{2a}[H_2OBH_3] + k_{2b}[H^+][H_2OBH_3]$, where $k_{2a} = 1.5 \times 10^{-3}$ sec^{-1} and $k_{2b} = 1.6 \times 10^{-3}$ $\underline{M}^{-1}$ sec^{-1} at -78°. The pH-independent rate constant, k_{2a}, is about ten times greater (even at -78°) than the pH-independent rate constant for the hydrolysis of BH_3OH^-, k_{H_2O}, at 20°.

It seems most logical to assume that the change in reactivity upon going from alkaline solution to acidic solution is due to protonation of the oxygen atom of the BH_3OH^- ion to form the neutral H_2OBH_3 species. Indeed the fact that we found k_2' to be independent of ionic strength is supporting evidence for a neutral trihydroboron species in acidic solution.

If we make the plausible assumption that H_2OBH_3 and BH_3OH^- are always in rapid equilibrium,

$$H_2OBH_3 \underset{}{\overset{K_{10}}{\rightleftharpoons}} H^+ + BH_3OH^- \qquad (10)$$

then we can calculate K_{10} from the relation $K_{10} = k_{2a}/k_{H^+}$ if the rate constants k_{H^+} and k_{2a} are known at the same temperature. By using Gardiner and Collat's approximately-evaluated activation energy[2] for k_{H^+} (12 ± 8 kcal/mole), we calculate, for -78°, a lower limit of 4 M^{-1} sec^{-1} and an upper limit of 6×10^6 M^{-1} sec^{-1} for k_{H^+}. Thus we calculate that K_{10} lies between the limits of 2×10^{-10} and 4×10^{-4} at -78°.

The Dihydroboron Species.- At -78°, hydrogen evolution stops, or almost stops, at two moles of hydrogen per mole of hydroborate when $[H^+] \geq 0.5$ M, corresponding to the formation of $BH_2(H_2O)_2^+$. However hydrogen evolution continues past two moles per mole of hydroborate when $[H^+] < 0.5$ M. This result 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 this species is H_2OBH_2OH, the instability of which has been reported previously.[6] We write the following mechanism, in which we assume that $BH_2(H_2O)_2^+$ and H_2OBH_2OH are in rapid equilibrium and that only H_2OBH_2OH undergoes hydrolysis:

$$H^+ + H_2OBH_2OH \overset{K}{\rightleftharpoons} BH_2(H_2O)_2^+$$

$$H_2OBH_2OH \xrightarrow{k_3} H_2OBH(OH)_2 + H_2$$

If we define $[BH_2]$ as the sum of $[H_2OBH_2OH]$ and $[BH_2(H_2O)_2^+]$, then we may write

$$-\frac{d[BH_2]}{dt} = k_3'[BH_2] = k_3[H_2OBH_2OH] = \frac{k_3}{1 + K[H^+]}[BH_2] \qquad (11)$$

By a least-squares fit of the data plotted in Fig. 8 to equation 11, we determined $k_3 = 1.7 \times 10^{-2}$ sec^{-1} and K = 6.4 at -36°. The curve drawn through the points in Fig. 8 was constructed using these values for k_3 and K.

We found that the dihydroboron species in solutions of pH 12.5-13.5 undergoes hydrolysis with a pH-independent rate constant $k_7' = 2.2 \times 10^{-5}$ sec^{-1} at 0°. This rate constant is much lower than k_3 at -36°; clearly a dihydroboron species of much greater stability than H_2OBH_2OH forms upon going to alkaline solutions. We propose that this species is $BH_2(OH)_2^-$, the logical deprotonation production of H_2OBH_2OH.

Mochalov *et al.*[15] have reported the following rate law for the hydrolysis of $BH_2(OH)_2^-$ in the pH interval 9.7-10.7: $-d[BH_2(OH)_2^-]/dt = k[H^+][BH_2(OH)_2^-]$. They found $k = 5 \times 10^5$ $\underline{M}^{-1}$ sec^{-1} at 0° and ionic strength 0.40 $\underline{M}$. These data are at variance with our attempt to measure the hydrolysis of $BH_2(OH)_2^-$ at pH 10, in which we found $-d\ln[BH_2(OH)_2^-]/dt$ to be greater than 10^{-2} sec^{-1} at 0°. By substituting $[H^+] = 10^{-10}$ into the rate law of Mochalov *et al.*, we calculate $-d\ln[BH_2(OH)_2^-]/dt = 5 \times 10^{-5}$ sec^{-1}. We have no explanation for the discrepancy, and Mochalov *et al.* give no experimental details to aid in seeking an explanation.

The Monohydroboron Species.- In both non-buffered strongly acidic solutions and strongly alkaline solutions we observed pH-independent rates of hydrolysis of the monohydroboron species. At 0°, the pseudo-first-order rate constant is 4.4×10^{-3} sec^{-1} in acidic solutions and is 1.0×10^{-3} sec^{-1} in alkaline solutions. Although the rate constants are of similar magnitude, they probably correspond to the hydrolyses of different species. We believe that the species in acidic solutions is $H_2OBH(OH)_2$ and that the species in alkaline solutions is $BH(OH)_3^-$. In buffer solutions of pH 5.6 and 10.0, the rate of hydrolysis of the monohydroboron species was found to be about twice that in acidic solutions. Perhaps this rate increase was due to reaction of $BH(OH)_3^-$ with the acid component of the buffer solution.

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(10) The kinetics of reaction 1 has been thoroughly studied at higher pH values in the vicinity of room temperature. See the summary in ref. 2.

(11) The vapor pressure was 0.5 ± 0.05 cm at -36° and essentially zero at -78°.

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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. $\mathrm{Log}(\frac{1}{2}P_\infty - P)$ vs. time for the hydrolysis of BH_4^- and H_2OBH_3 at $[H^+] = 0.11$ M and -78°.

Figure 4. $\mathrm{Log}(\frac{1}{2}P_\infty - P)$ vs. time for the hydrolysis of BH_4^- and H_2OBH_3 at $[H^+] = 1.21$ M and -78°.

Figure 5. Values of k_2' as a function of $[H^+]$ for the hydrolysis of H_2OBH_3 in acidic solution.

Figure 6. $\mathrm{Log}(P_\infty - P)$ vs. time for the hydrolysis of the dihydroboron and monohydroboron intermediates for $[H^+] = 0.105$ M at -36°. The curve was calculated from Eq. 5 using the values $k_3' = 0.10\ \mathrm{sec}^{-1}$, $k_4' = 3.3 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $r = 3.2$.

Figure 7. $\mathrm{Log}(P_\infty - P)$ vs. time for the hydrolysis of the dihydroboron and monohydroboron intermediates for $[H^+] = 1.16$ M at -36°. The curve was calculated from Eq. 5 using the values $k_3' = 0.0023\ \mathrm{sec}^{-1}$, $k_4' = 3.5 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $r = 0.39$.

Figure 8. Values of k_3' as a function of $[H^+]$ for the hydrolysis of the dihydroboron intermediates $(BH_2(OH_2)^+$ and $H_2OBH_2OH)$ in acidic solution.

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

Figure 10. $\log(P_\infty - P)$ vs. time for the hydrolysis of a mixture of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ at $[OH^-] = 0.35$ $\underline{M}$ and 0°.

Figure 11. $\log(P_\infty - P - 2.06 \times 10^{-9.1 \times 10^{-5}t})$ vs. time. The function $2.06 \times 10^{-9.1 \times 10^{-5}t}$ is proportional to the concentration of $BH_2(OH)_2^-$ at time t. (The parameters of the latter function were evaluated from the straight-line portion of Fig. 11.)

Figure 12. Boron-11 nmr spectrum of a water-methanol solution of BH_3OH^-. The singlet is due to borate decomposition production; the quartet is due to the BH_3OH^- ion.

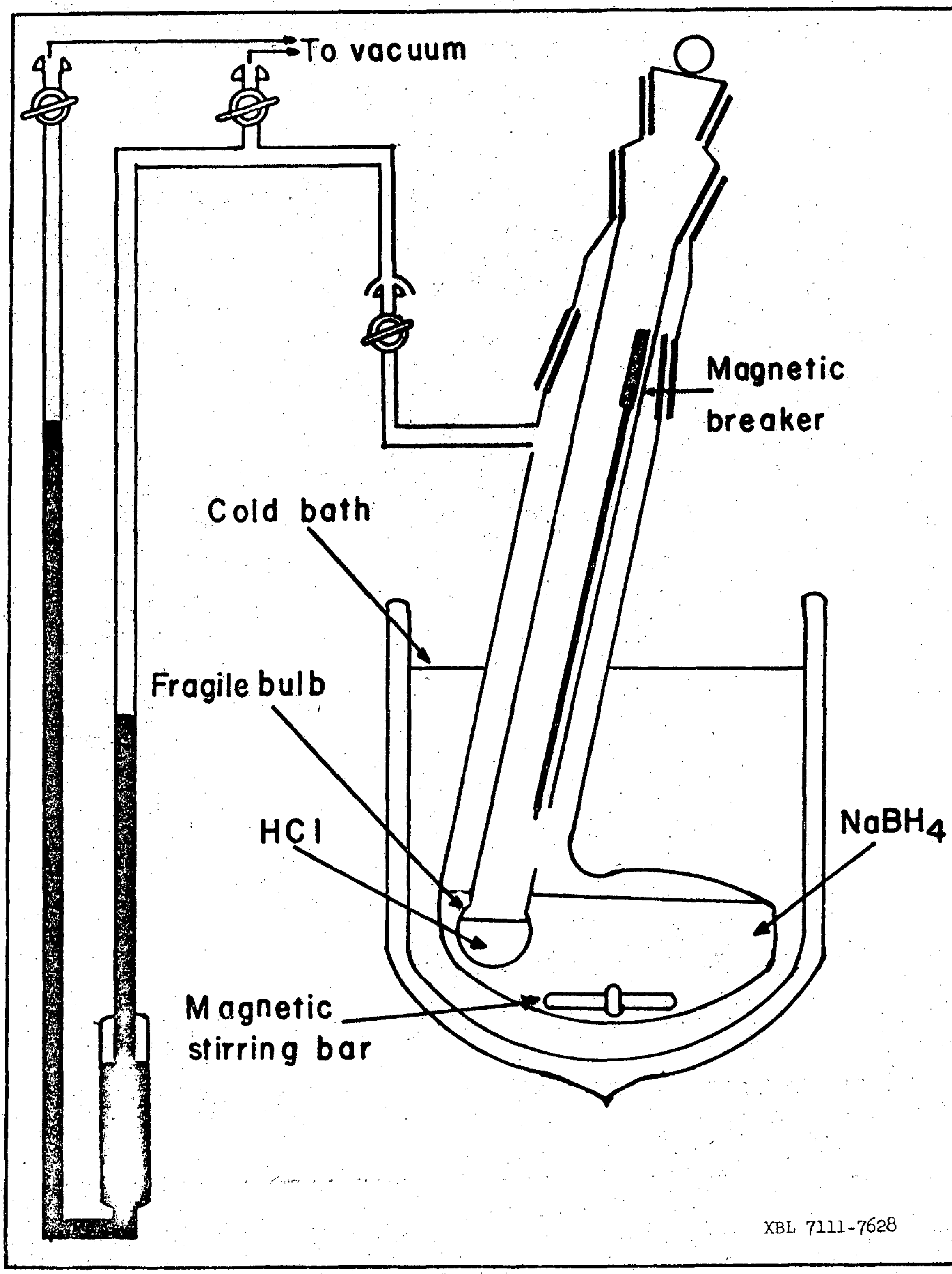
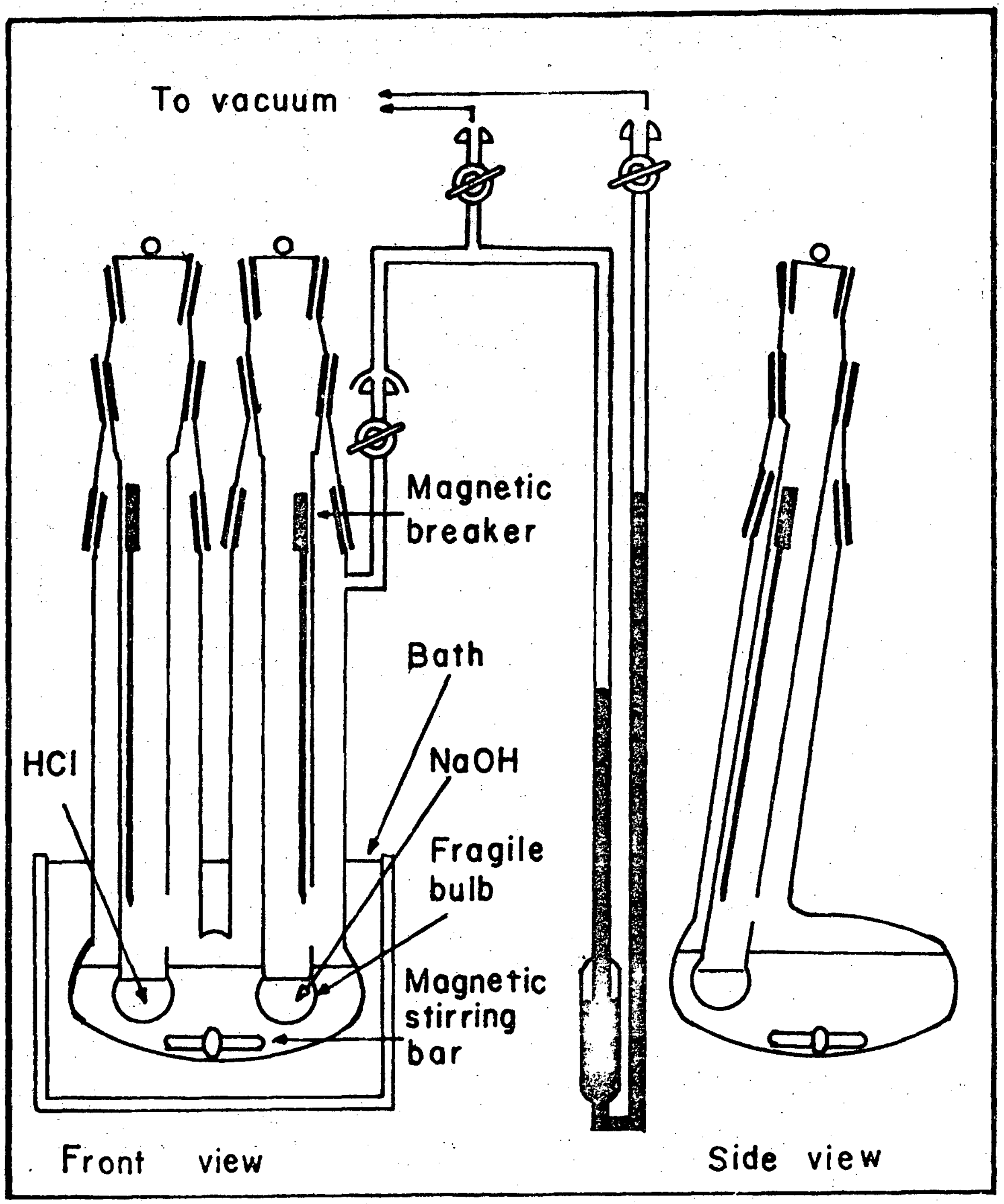

To vacuum
Magnetic breaker
Cold bath
Fragile bulb
HCl
NaBH4
Magnetic stirring bar
XBL 7111-7628

Fig. 1.



XBL 7111-7629

Fig. 2.

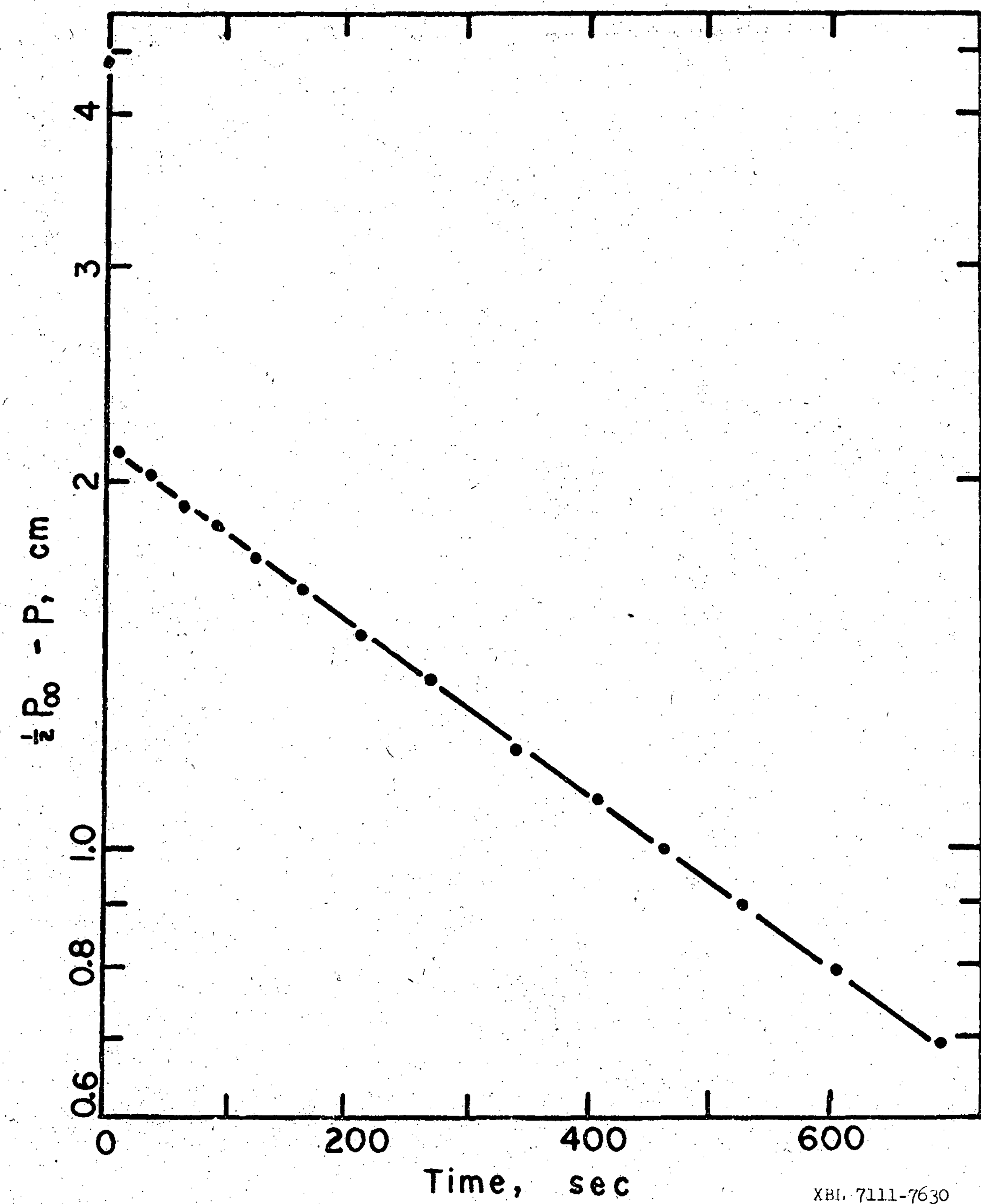
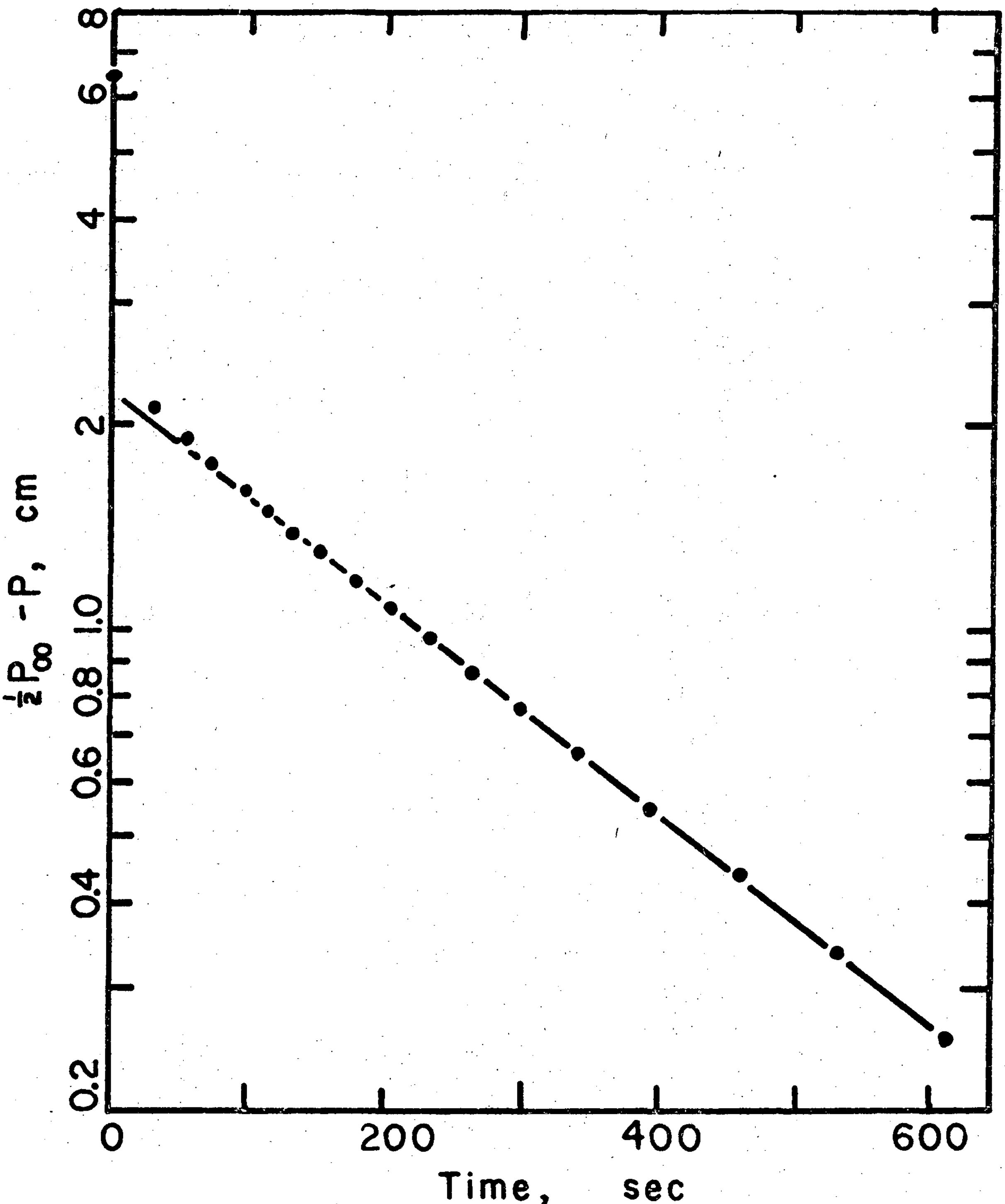

4
3
2
1.0
0.8
0.6
$\frac{1}{2}P_\infty - P$, cm
0
200
400
600
Time, sec
XBL 7111-7630

Fig. 3.



XBL 7111-7631

Fig. 4.

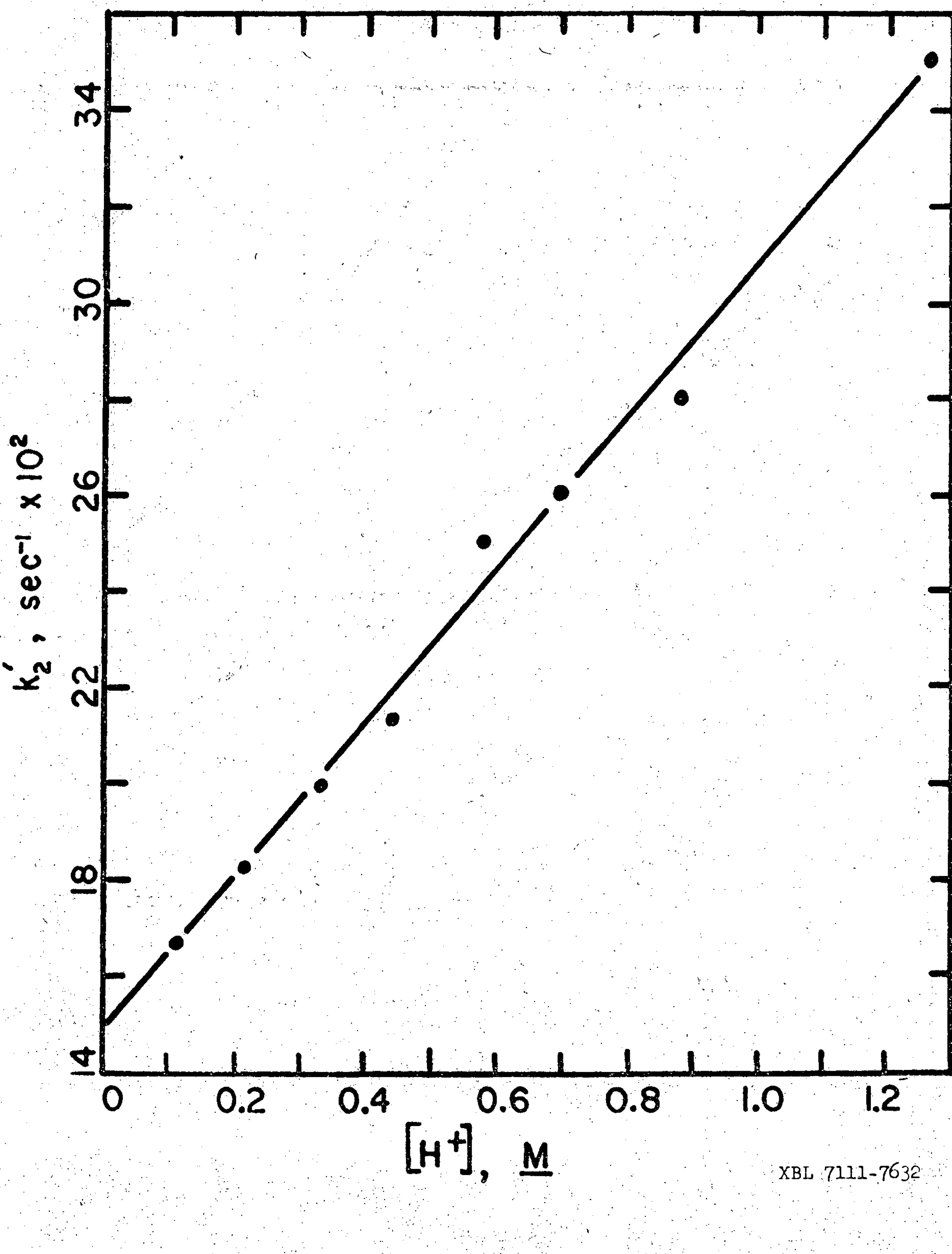


Fig. 5.

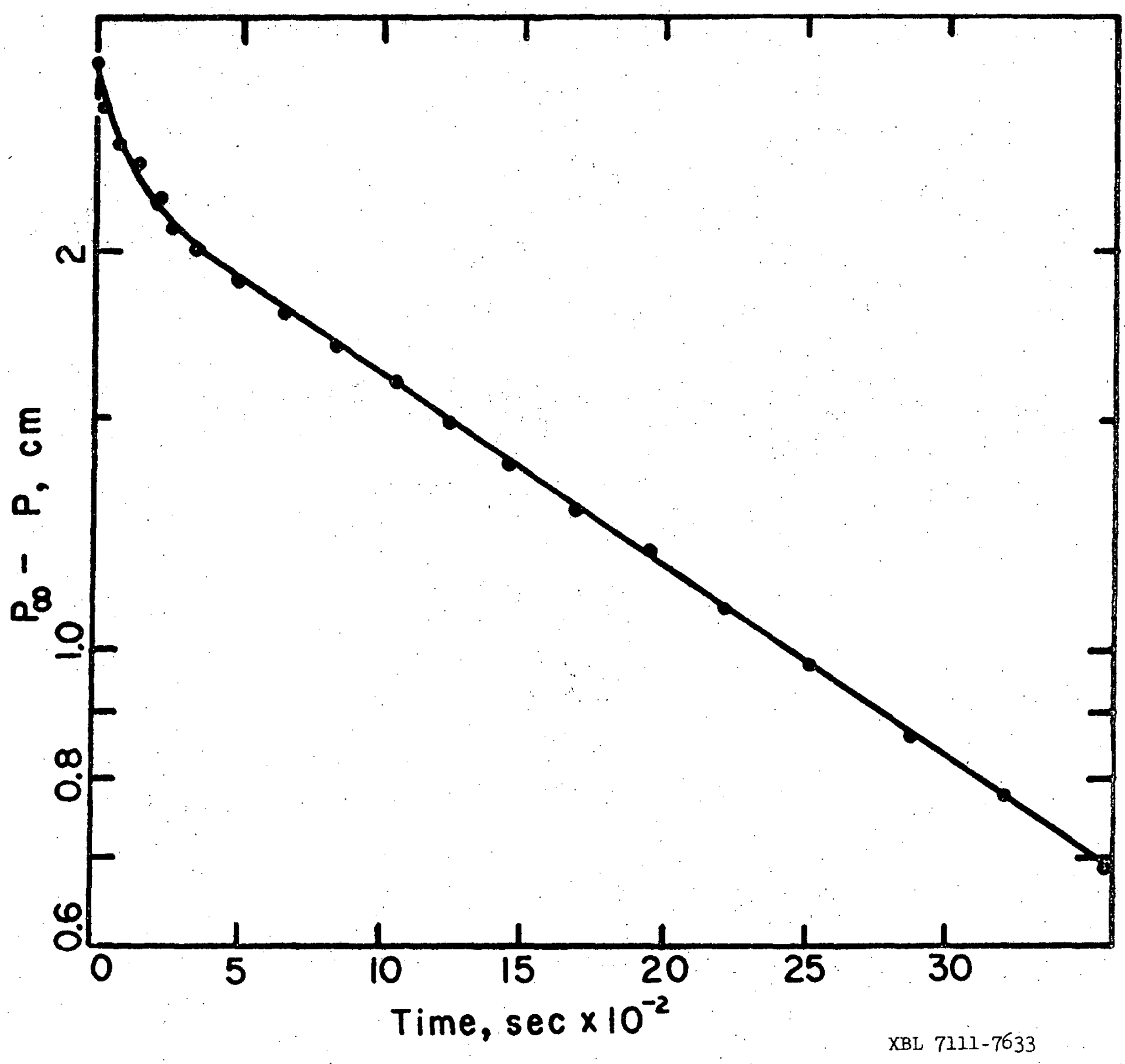
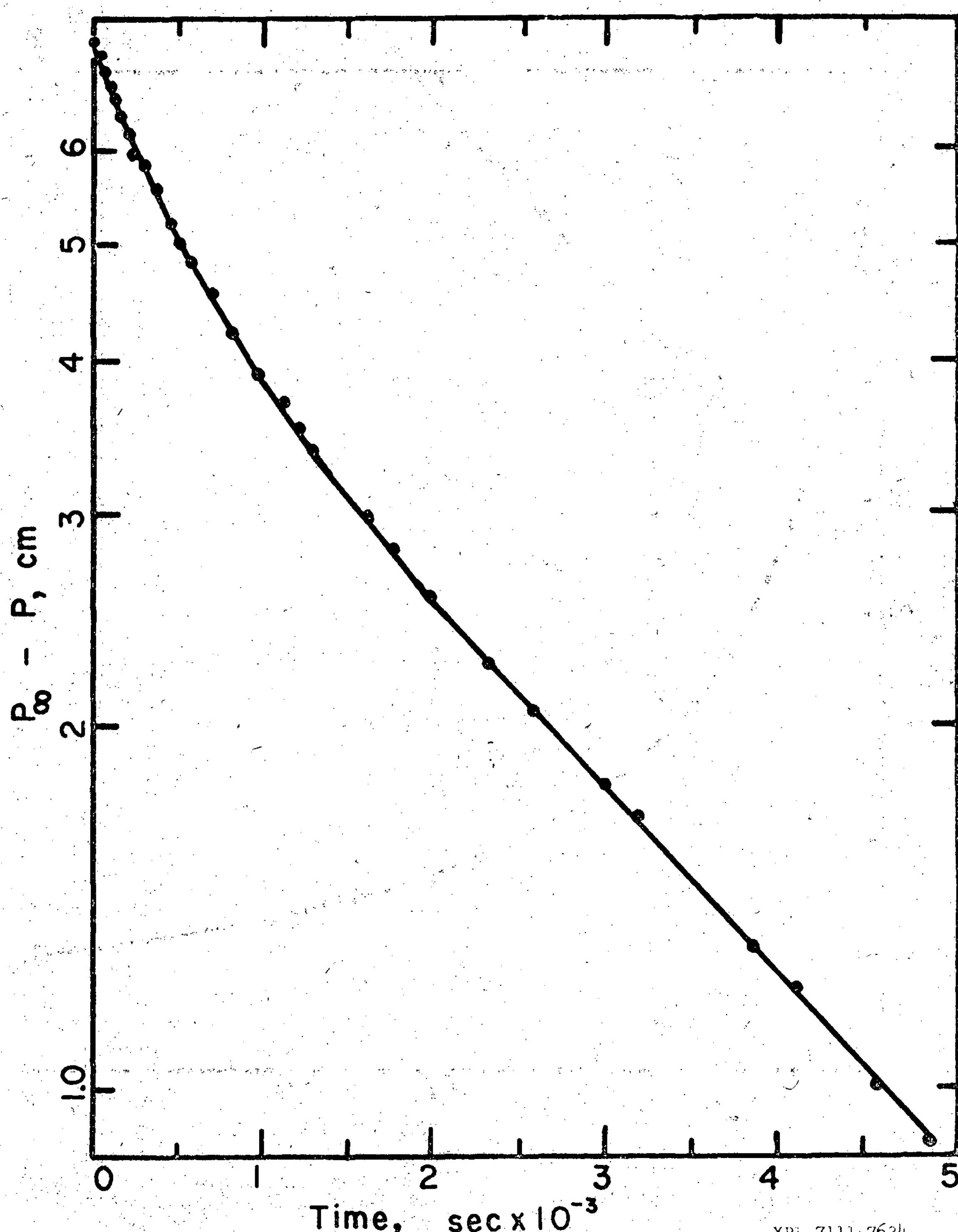
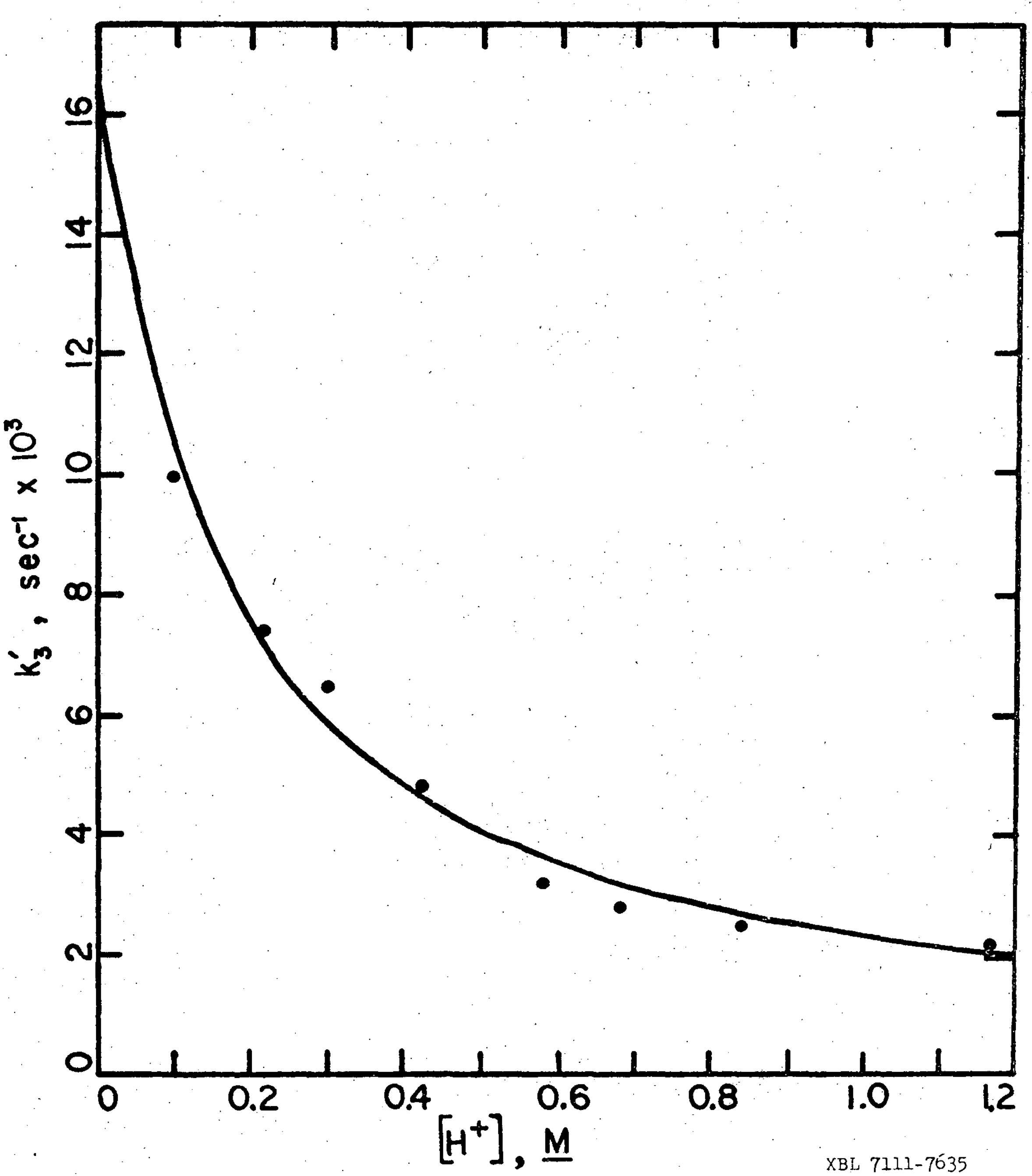

2
1.0
0.8
0.6
$P_\infty - P$, cm
0
5
10
15
20
25
30
Time, sec $\times 10^{-2}$
XBL 7111-7633

Fig. 6.



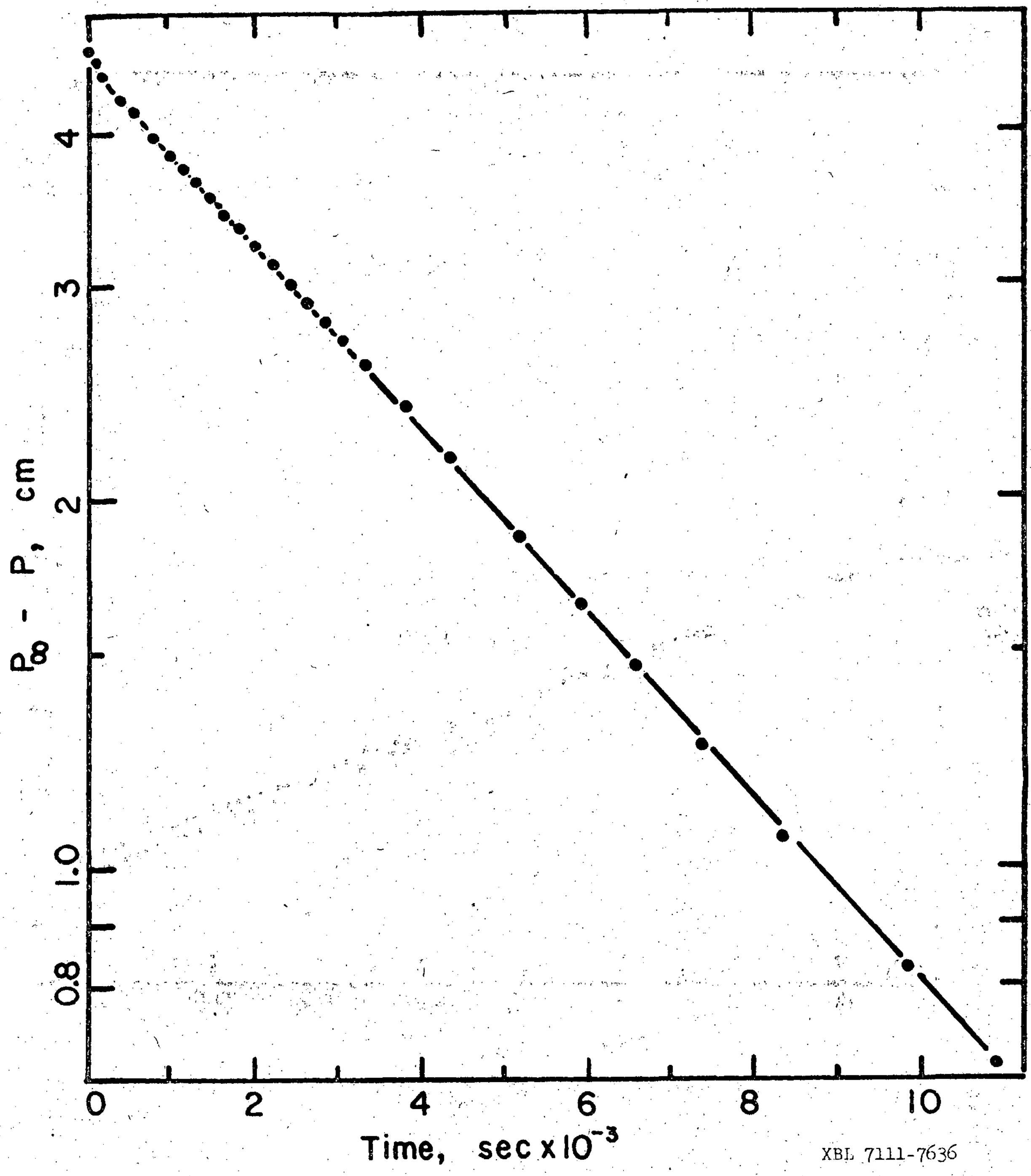
XBL 7111-7634

Fig. 7.



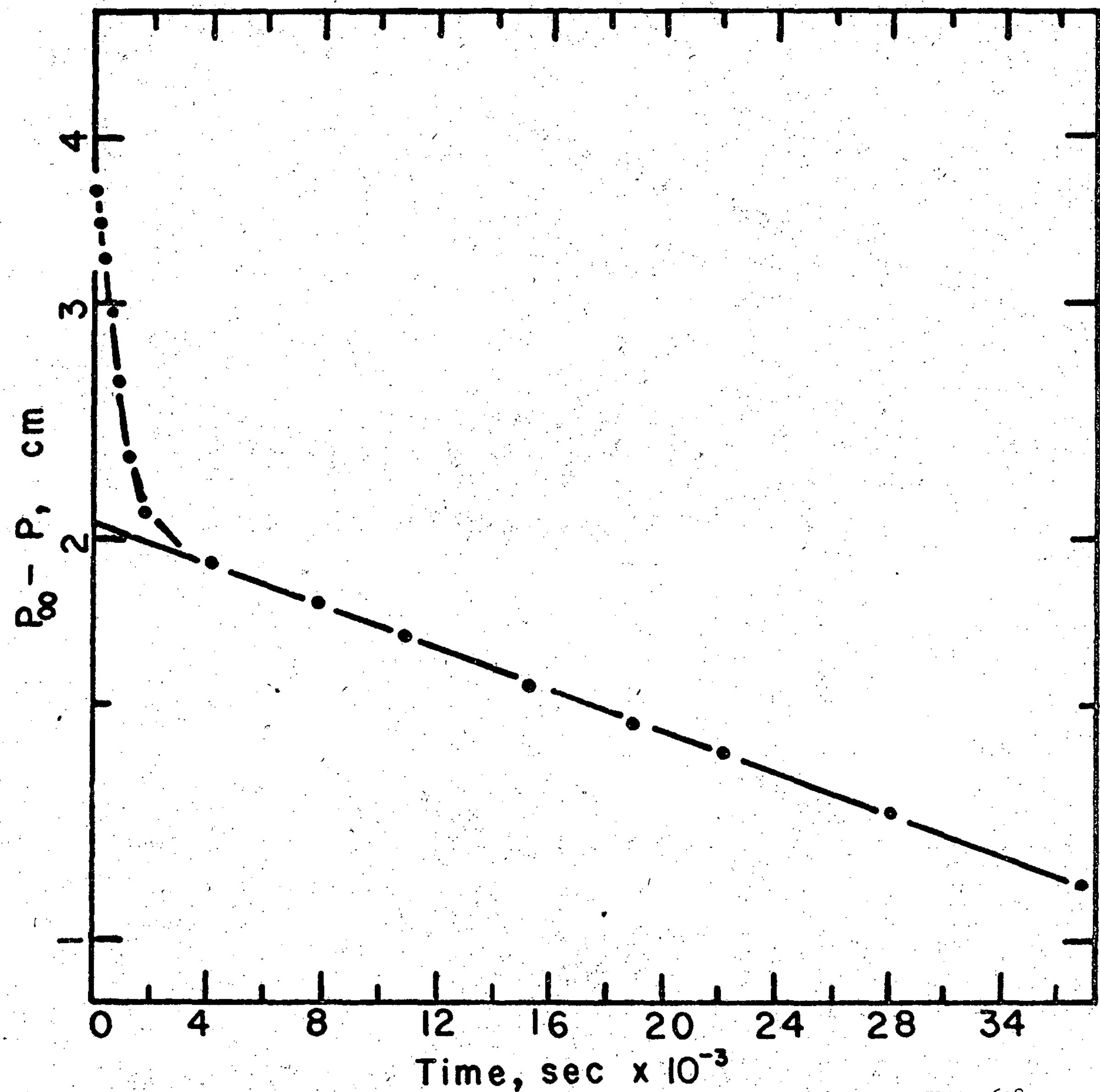
XBL 7111-7635

Fig. 8.



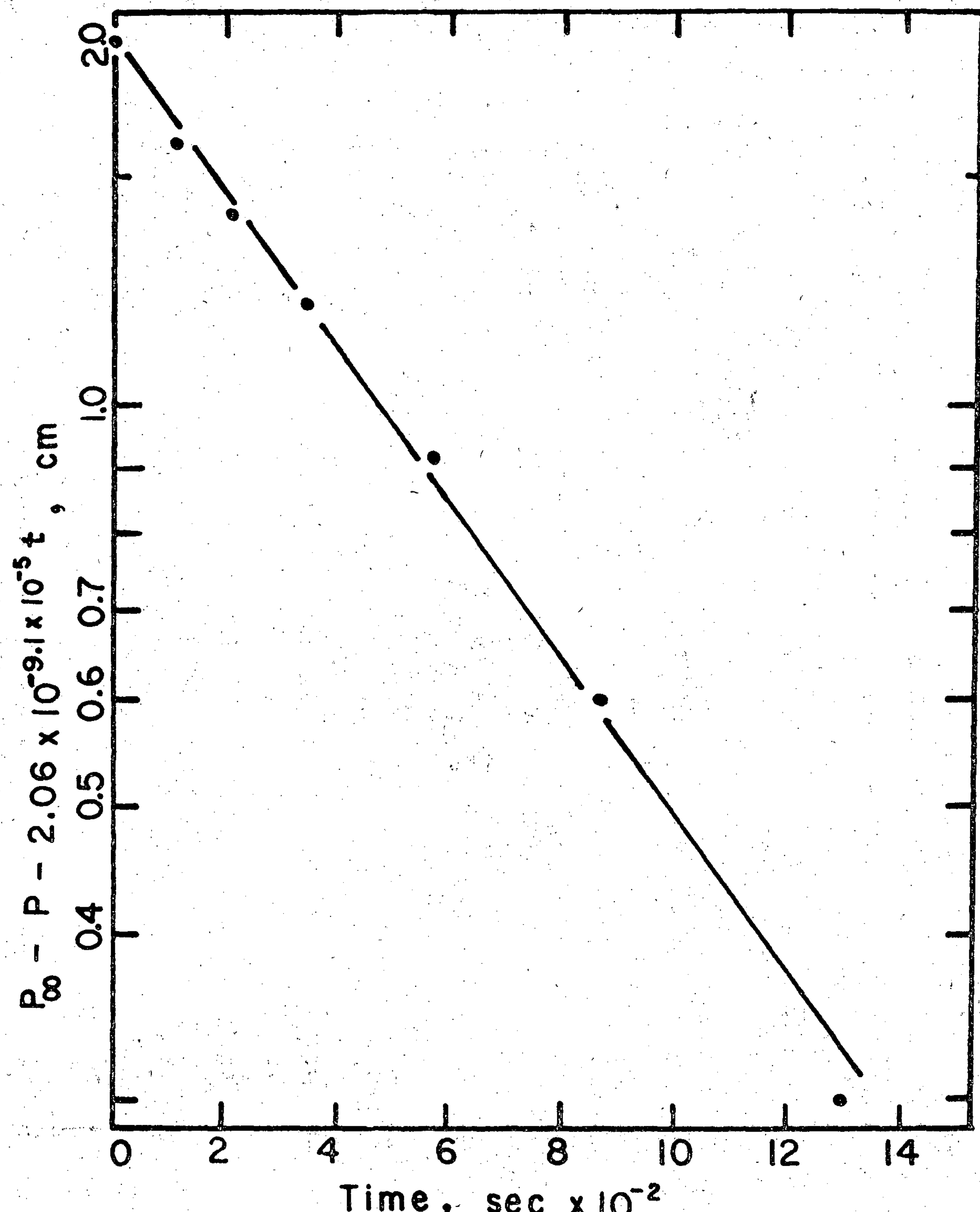
XBL 7111-7636

Fig. 9.



XBL 7111-7638

Fig. 10.



XBL 7111-7639

Fig. 11.

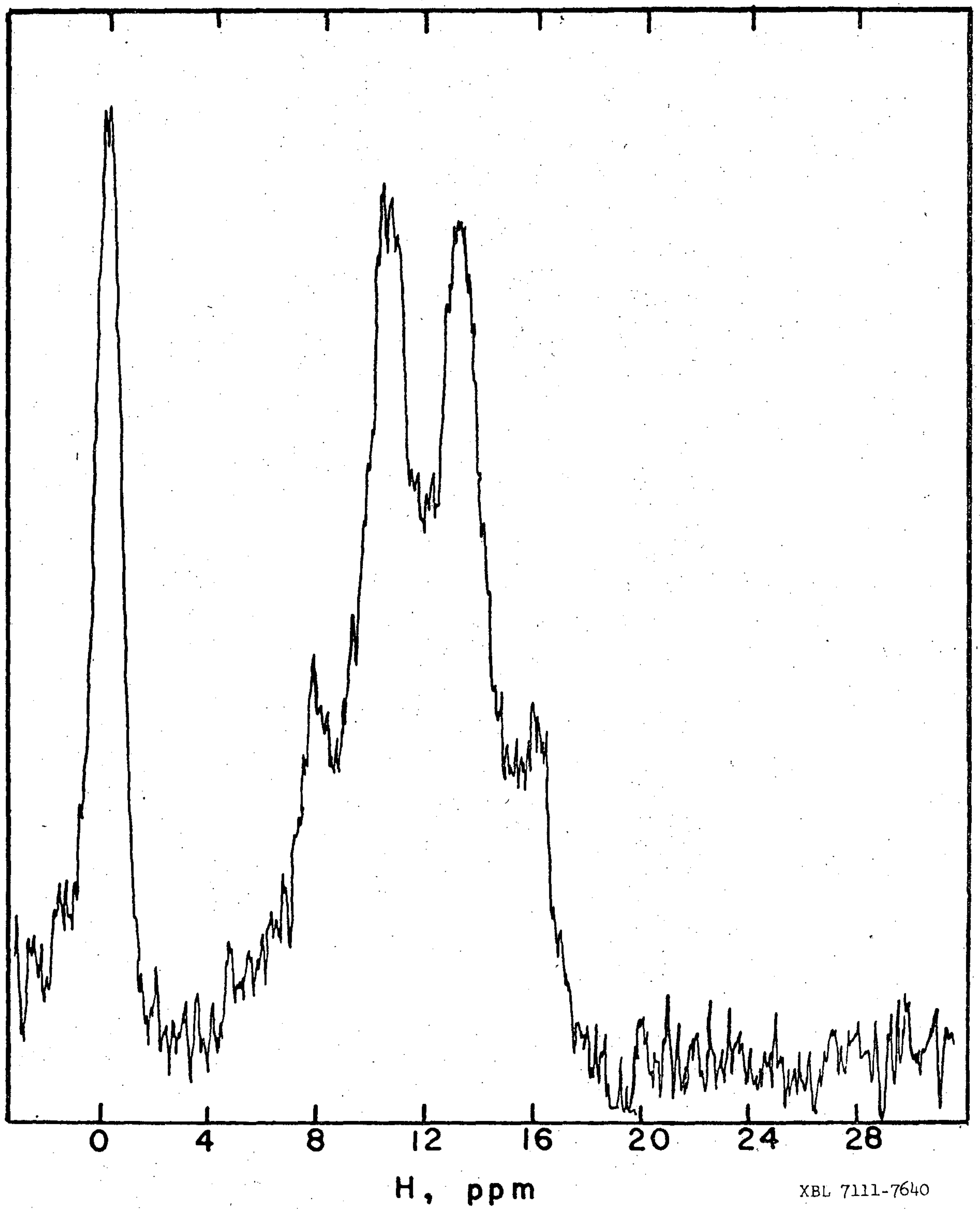


Fig. 12.