1948

A Study of the Electromotive Force Developed in Grignard Solutions

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A Study of the Electromotive Force Developed In Grignard Solutions

By

Frank P. Cassaretto

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy
in Loyola University.

June, 1948

Vita

Frank P. Cassaretto was born in Chicago, Illinois. He attended Lake View High School and Crane Junior College in that city. In June, 1930 he received the Bachelor of Science degree in Chemistry from Loyola University. The Master of Science degree in Chemistry was conferred by the University of Chicago in August, 1939.

From 1930 to 1942 the writer has been engaged in teaching in the Department of Chemistry of Loyola University. He served in the Army of the United States from August, 1942 until January, 1946. During the last two years the writer has been engaged in graduate research and part time instruction in Loyola University.

The writer has contributed several articles to journals of chemical education and apparatus design:

I "A Method for Salvaging Mercury."
Chemist Analyst. February, 1941.

II "An Inexpensive Dissicator."
Journal of Chemical Education. February, 1941.

III "A Combined Condenser Receiver."
Journal of Chemical Education. May, 1946.

IV "A Modification of the Victor Meyer Molecular Weight Apparatus.
Journal of Chemical Education, April, 1948.

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Acknowledgments

The author would like to take this opportunity to thank Professor W.V. Evans for his guidance, inspiration and encouragement in this work.

Gratitude is also expressed to the Reverend Alphonse R. Schmitt, S.J., Chairman of the Department of Physics in Loyola University, for the use of special equipment used in this study.

CHAPTER I

INTRODUCTION

In 1917, Evans[1.] found solutions of the Grignard reagent in ethyl ether were comparatively good conductors of electricity and that an electromotive force was produced when poles of different metals were inserted in these solutions. The magnitude of the potential varied, in some cases developing as much as 1.5 volts and in others only 0.5 volts. N.W. Kondyrew[2.] measured the temperature resistance coefficient of cells containing ether solutions of ethyl magnesium bromide and found that such cells produced an electromotive force. Work has been done on the potential developed by Grignard solutions by Dufford[3,4.] who studied over one hundred cells containing organo-magnesium halides with various metallic electrodes and found the cells polarized readily, showed a voltage drift, reversal and oscillation. The electrode system Pt-Zn, Pt-Mg, and Pt-Fe were found erratic. All

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1. J. Am. Chem. Soc., 39, 82 (1917)
2. Ber. D. Deutsch. Chem. Gesell. 58, 464 (1925)
3. J. Phys. Chem. 34, 1544 (1930)
4. Phys. Rev. 33, 191 (1923)

the above cells showed a photo-voltaic effect.

Hammond[5.] found that the electromotive force of Grignard cells varied with age, mechanical agitation and illumination and believed the seat of the phenomena was at or near the surface of the electrodes. Dufford and Gaddum[6.] in a preliminary study of the electrode potentials in cells containing ether solutions of Grignard compounds reported that the voltage of such cells is very sensitive to light and that following a change of illumination, the voltage may be a periodic function of time. Evans and Fosdick[7.] found that by using a hydrogen electrode as an anode in cells containing iso amyl ether solutions of Grignard reagents potentials could be obtained which checked with subsequent determinations. A conclusion was drawn that the fluctuation of potentials of cells composed of Grignard solution as observed by other authors may be due to the adsorption of gases on the anode.

The equipment used in this investigation was the standard apparatus used for the determination of the electromotive force of a cell in the physical chemistry laboratory by the potentiometric method. The diagram

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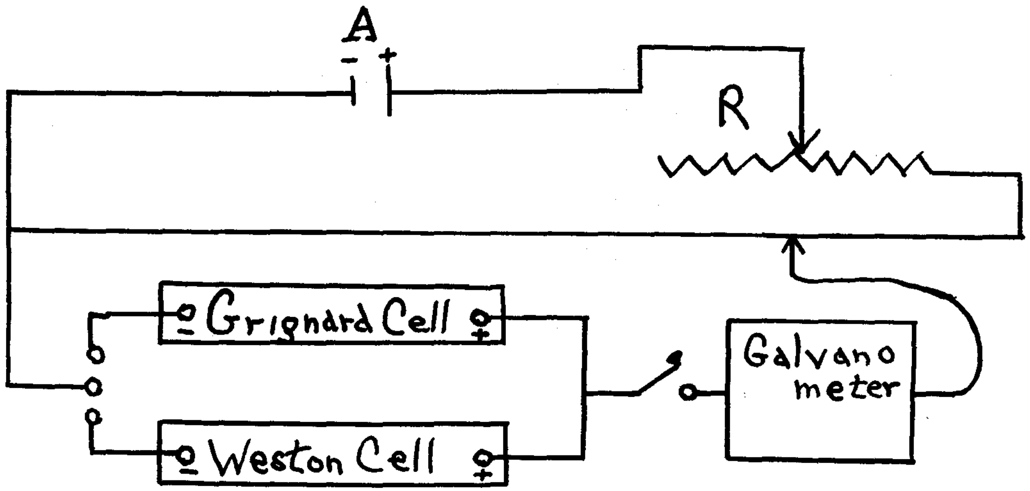
5. Phys. Rev. 33, 998 (1930)
6. J. Am. Chem. Soc. 49, 1858 (1927)
7. Doctor's Thesis, Northwestern University (1932)

is given below. The sensitive potentiometer used was a Leeds and Northrup Type K-2, #7552. The galvanometer used in the circuit was a Leeds and Northrup wall type #67,362 with a sensitivity of 0.0116 microamperes per millimeter. A saturated type Weston Cell was used to check and standardize the potentiometer.



CHAPTER II

PRELIMINARY EXPERIMENTS

A few preliminary experiments were performed to observe the potential drift of cells containing Grignard solutions as observed by Dufford,[1,2.] Hammond,[3.] Gaddum,[4.] and Evans and Fosdick.[5.]

Squibbs ether was washed with a saturated solution of calcium chloride and dried over calcium chloride, redistilled at 35°C. and stored over metallic sodium shavings. Ethyl Bromide (Eastman) and magnesium turnings (Eastmann) were used.

An approximately molar solution of ethyl magnesium bromide was prepared in ethyl ether. The ethyl bromide was added slowly (two hour period) to the magnesium turnings after being diluted with 25 ml of ether to retard the reaction. The solution was allowed to stand overnight and the following morning was found to be still very dark grey due to colloidal magnesium. One milliliter of C_2H_5Br was added (in excess of theoretical amount)

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1. J. Phys. Chem. 34, 1544 (1930)
2. Phys. Rev. 33, 191 (1929)
3. Phys. Rev. 33, 998 (1930)
4. J. Am. Chem. Soc. 49, 1858 (1927)
5. Doctors Thesis, Northwestern University (1932)

and solution allowed to stand another two days. The Grignard reagent was quickly transferred to the "H" type cell as shown in Fig. 1. This cell carried a magnesium metal rod electrode and platinum wire electrode similar to those used as an anode in electrodeposition determinations. The magnesium electrode was cleaned to a shiny bright surface by immersion in dilute HC_1, rinsing with distilled water, drying rapidly and inserting in a dessicator over $CaCl_2$. The data collected in tables 1 and 2 indicated a voltage drift over a period of several days. Graphs 1 and 2 illustrate this fall in potential with time. Evans and Fosdick[6]. found that the potential of cells containing ethyl magnesium bromide in ethyl ether using magnesium rods as cathodes and platinum as an anode showed a marked voltage increase when the platinum electrode was removed, cleaned and reinserted in a cell that had been showing a voltage drift. Similar effects were found in these experiments but it was observed that the platinum electrode did not have to be cleaned but merely exposed to the air for

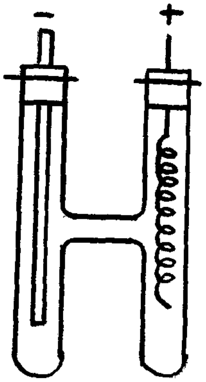

Fig. 1

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6. Doctors Thesis, Northwestern University, (1932)

TABLE 1

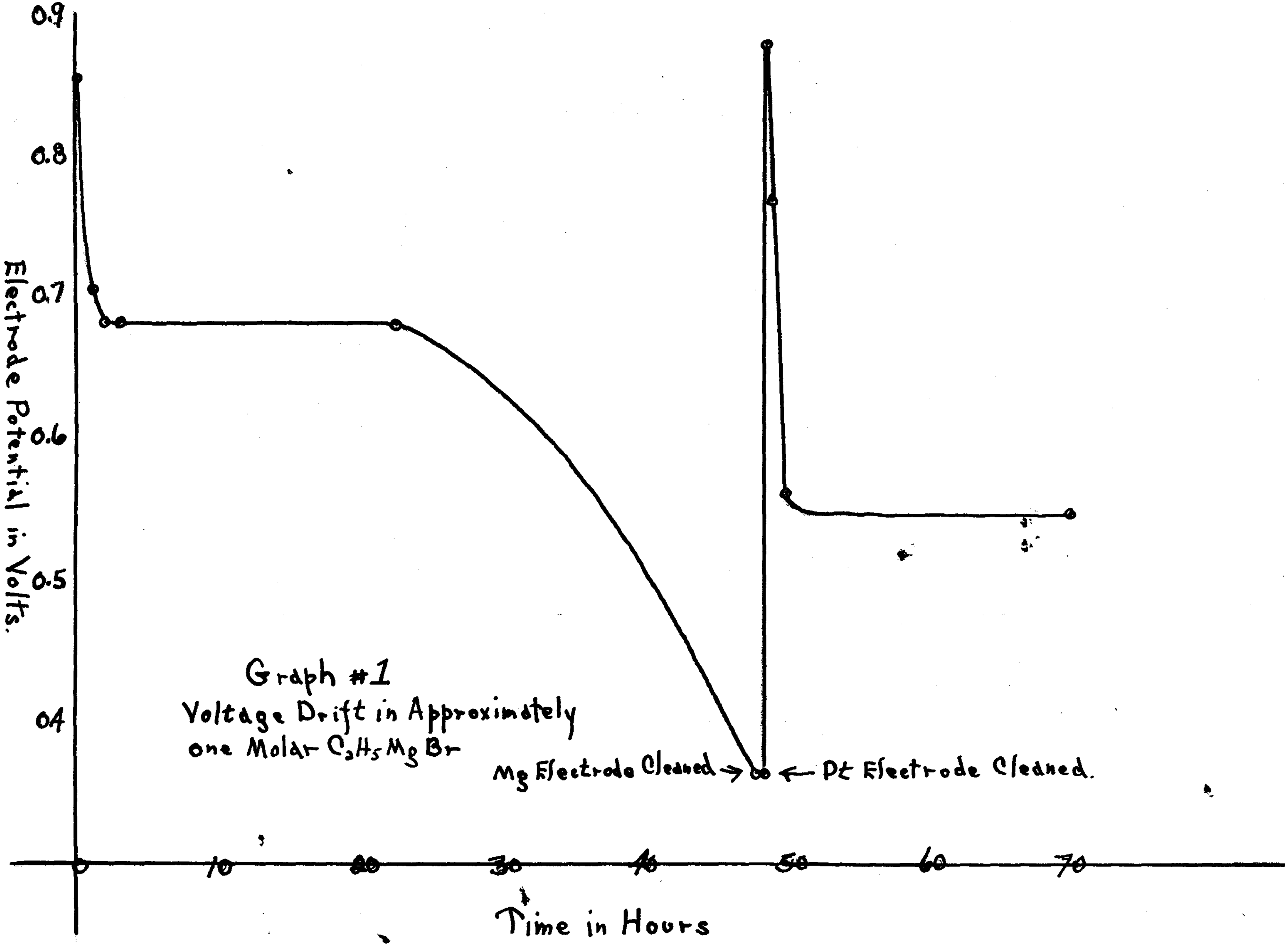
Voltage drift in cell of approximately one molar ethyl magnesium bromide using electrodes of magnesium and platinum.

Time in Hours	Temperature °C	Electromotive Force
0.0	23	0.855
0.25	22	0.760
0.50	22	0.745
1.00	22.5	0.705
2.00	23	0.682
2.25	23	0.682
2.50	23.5	0.682
3.00 *	23.5	0.682
22.5 *	25.5	0.681
48.0 @	26	0.363
48.25 @@	26	0.363
48.50	26	0.878
49.00	26	0.768
50.00	26	0.560
70.00	24	0.546

* Cell was allowed to stand overnight.

@ Magnesium electrode was removed, washed, dried and scraped with emery paper and reinserted in solution.

@@ Platinum electrode cleaned, heated to redness in a bunsen burner flame, cooled in a dessicator and reinserted in solution.



Graph #1

Voltage Drift in Approximately one Molar C_2H_5MgBr

TABLE 2

Voltage drift in cell of approximately one molar ethyl magnesium bromide using electrode of magnesium and platinum.

Time in Hours	Temperature °C	Electromotive Force
0:00	23	0.847
0:11	23	0.720
1:00	23	0.673
2:00 *	23	0.664
48:00 **	23	0.458
264:00 ***	24	0.405
288:00 ***	24	0.344
309:00 @	24	0.312
310:00 @@	24	0.311
311:00	24	0.844
311:15	24	0.670
311:30	24	0.655

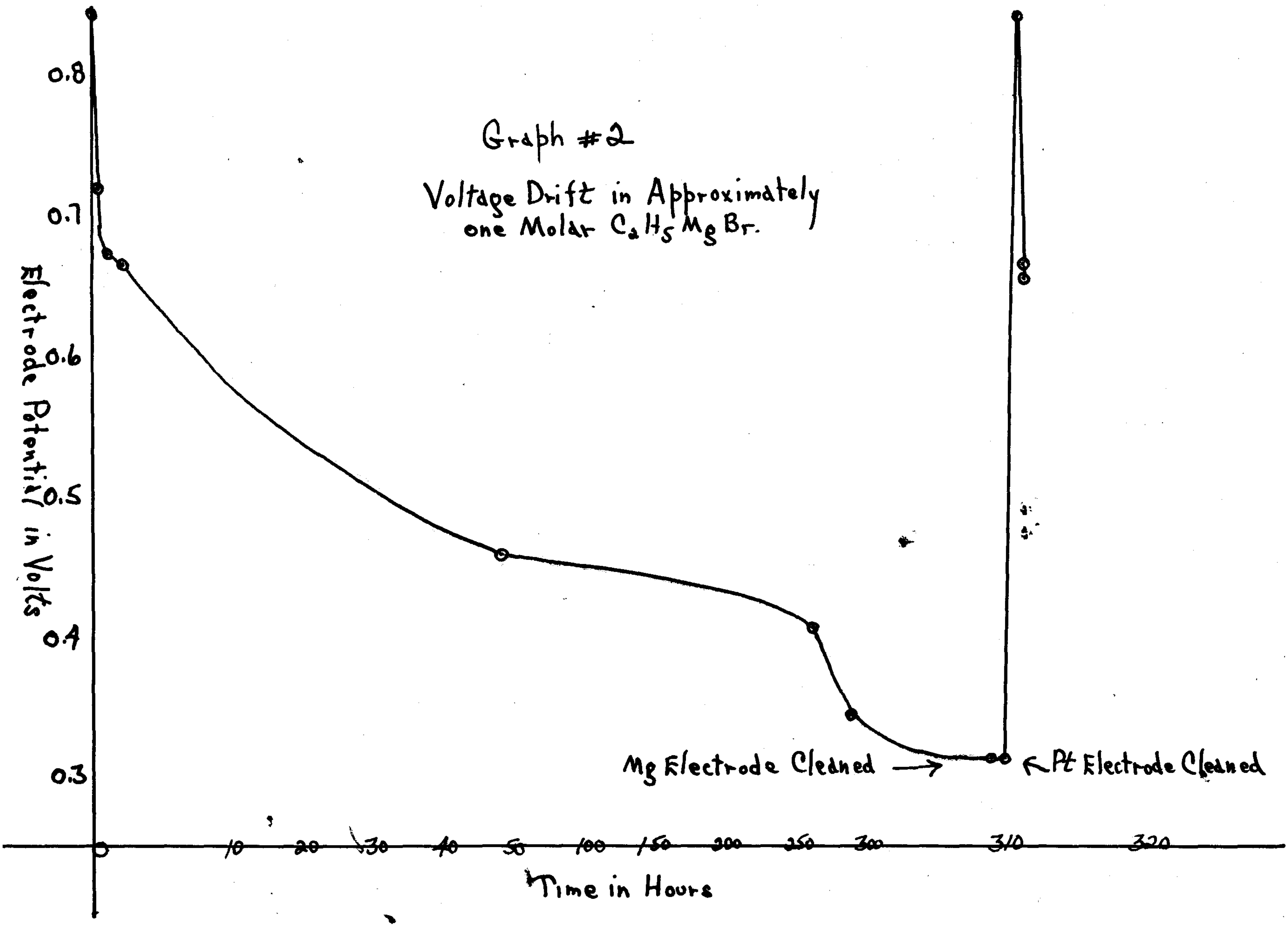
* Cell allowed to stand two days.

** Cell allowed to stand nine days.

*** Cell allowed to stand overnight.

@ Magnesium electrode removed and cleaned and reinserted in solution.

@@ Platinum electrode cleaned, dried, heated to redness, cooled, and reinserted in solution.



Graph #2

Voltage Drift in Approximately one Molar C_2H_5MgBr.

a few seconds and reinserted. Removing and cleaning the magnesium rod electrode had little or no effect on the observed electromotive force of the cell when it was reinserted. The surge in potential induced by reinserting the platinum electrode was short lived, and the electromotive force dropped very rapidly. The platinum electrode in the cell seemed to be the critical member of the electrode system Mg-Pt.

Since evident evaporation was taking place in these cells it was thought that perhaps the voltage drift might be due to a concentration change of the Grignard solution. Accordingly, a cell was devised that could be sealed after the introduction of the Grignard solution. It was interesting to note that the Grignard solution prepared above after standing for four days separated into two layers. One a dense oily layer with a brownish color, the other clear water white. Evans and Rawley[7.] report that magnesium bromide forms etherates with the solvent ethyl ether. A trietherate exists below 13°C ± 0.5°, above 13°C a liquid appears. This temperature is the transition

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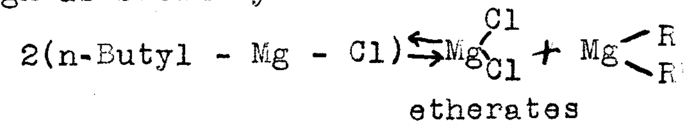
[7.] J. Am. Chem. Soc. 52, 3523 (1930)

point to the dietherate. At a temperature above 28°C ± 1° the dietherate undergoes transition to the mono etherate with the formation of a large amount of liquid and a fine white crystalline precipitate which is the mono etherate. The oily liquid observed could be the dietherate described above because MgX_2 is known to precipitate from Grignard solutions on standing, and MgX_2 is in equilibrium with MgR_2 and RMgX as shown by Noller and Castro[8].



$$2(\text{n-Butyl} - \text{Mg} - \text{Cl}) \rightleftarrows \underset{\text{etherates}}{\text{Mg}\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}} + \text{Mg}\begin{matrix}\text{R}\\ \text{R}\end{matrix}$$

To study the effect of evaporation of the Grignard solution on the voltage drift experienced in these cells, the following cell was constructed from a 50 ml distilling flask. Fig. 2. The magnesium, carbon, and platinum electrodes were sealed into the cell by means of fine platinum wire which was wound tightly around the electrodes. The electrodes were cleaned by immersing the Mg electrode in HCl, washing quickly, drying with a towel and then inserting in a dessicator

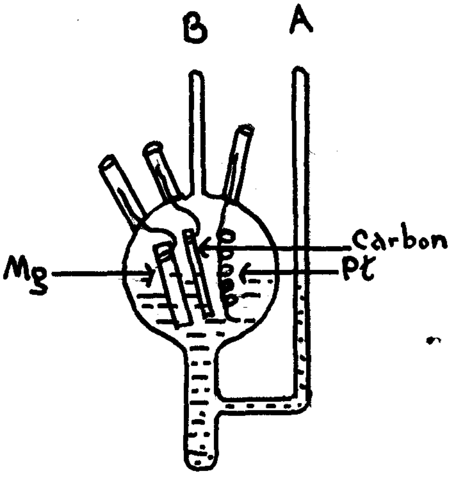


Fig.2

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[8] J. Am. Chem. Soc. 64, 2503 (1942)

until sealed in cell. The platinum electrode and the carbon electrode were heated to redness in a bunsen burner flame and cooled in a dessicator until sealed in cell. After the cell was blown it was evacuated by a vacuum pump and filled with nitrogen gas.

A new supply of C_2H_5MgBr was prepared of approximately one molar concentration. The reaction did not take place until the contents were warmed. The ethyl bromide diluted in ether was added slowly over a four hour period. Colloidal magnesium was again in evidence with excess magnesium in the reaction flask. After standing overnight 5 ml of C_2H_5Br were added and allowed to stand in the reaction flask for another 24 hours. The following day the solution was gently refluxed for two hours and allowed to stand overnight. The next day the Grignard solution was pumped by N_2 gas into the storage cylinder and allowed to stand, some of the oily layer was transferred to the storage cell but settled in the trap. Fig. 3.

The clear solution above the oily layer was transferred to a cell filled with N_2 gas and the inlet and outlet tubes A and B (Fig. 2) were sealed.

The electromotive force of this cell was studied for twenty-four days, the drift is shown in graph 3 drawn from data in table 3. The potentials were read using a cell Mg-Pt and Mg-C in the same solution. The electromotive force of these systems eventually levelled off at approximately the same potential. This seemed to indicate that the electromotive force may be independent of the cathode material. The one molar (approximately) cell was treated with dry oxygen by allowing the gas to bubble through the inlet tube A and out of tube B in Fig. 2. The solution warmed and became murky and within one hours time the E.M.F. of the cell had jumped to 1.60+ volts. The limit of the Type K-2 potentiometer was just slightly exceeded by this procedure. The oxygen was bubbled through the

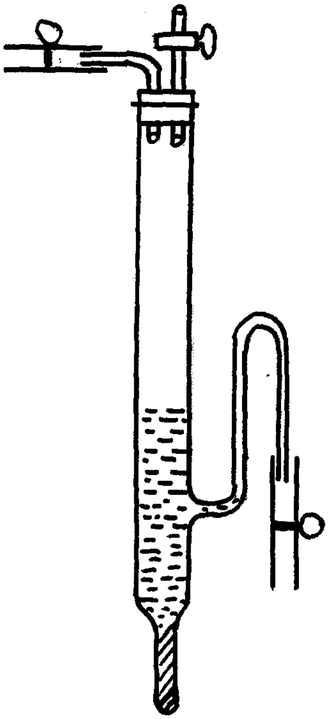


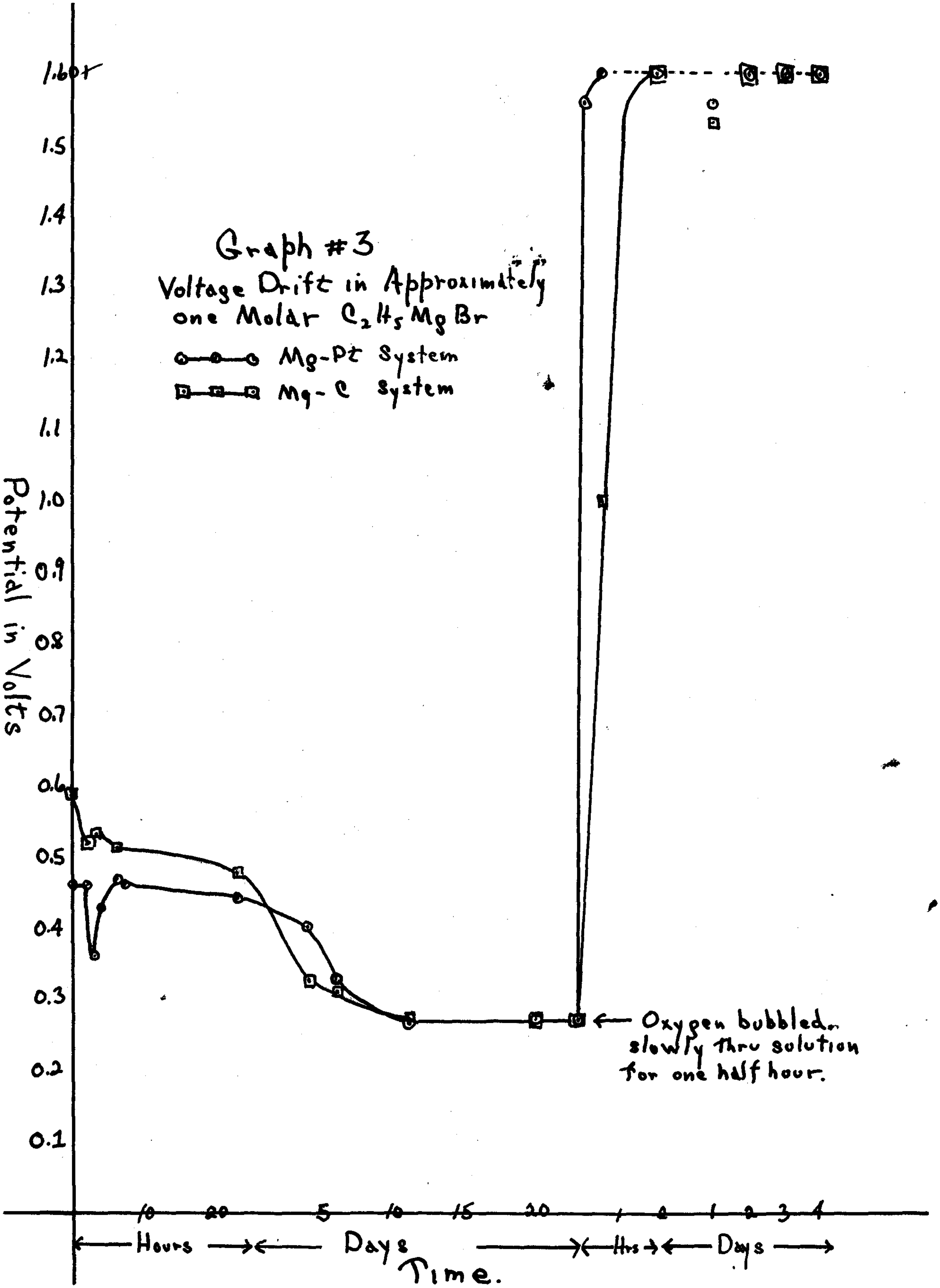
Fig. 3

TABLE 3

Voltage drift in approximately one molar Grignard solution using Mg-Pt and Mg-C electrode systems.

Time in Hrs.	Temp. °C.	Electromotive Force	
		Mg-Pt Couple	Mg-C Couple
0	27	0.460	0.590
2	29	0.460	0.520
3	29	0.560	0.532
4	29	0.430	0.513
6	26	0.470	0.507
7	25	0.460	0.510
23	28	0.443	0.476
Time in Days			
4	28	0.400	0.322
6	22.5	0.328	0.309
7	25	0.319	0.300
8	27	0.275	0.283
11	27	0.265	0.276
12	27	0.270	0.272
13	23	0.270	0.272
19	23	0.270	0.270
20	24	0.272	0.271
21	26	0.267	0.267
22	22	0.267	0.267
23	19	0.271	0.271
Time in Minutes			
0	19	0.267	0.271
7	19	0.590	
10	19	1.56	
35	19	1.60 +	1.00
120	19	1.60 +	1.60 +
Time in Days			
1	23	1.57	1.53
2	24	1.60 +	1.60 +
3	22	1.60 +	1.60 +
4	23	1.60 +	1.60 +

The inlet and outlet tubes of the cell were broken and dry oxygen from a tank was slowly bubbled up through the Grignard solution for one-half hour. The solution clouded but cleared up after one hour.



Graph #3
Voltage Drift in Approximately one Molar C_2H_5MgBr

← Oxygen bubbled slowly thru solution for one half hour.

solution slowly for about five minutes and then the cell was sealed by means of pinch clamps and rubber tubing. The E.M.F. of the molar Grignard remained at 1.60+for three days with no apparent drifting. The voltages were identical for the electrode Mg-Pt system and Mg-C system.

The "molar" Grignard solution cell contained a yellowish oily layer in bottom of cell along with a white solid precipitate.[9.] The solid reacted with water and the liquid reacted vigorously when the cell was washed at the end of the experiment.

A study of ethyl magnesium bromide in normal butyl ether was attempted in the hope that more sensitive solutions might result with greater stability due to the higher boiling point of n butyl ether. (140.9° C). The n butyl ether (Eastmann Chemical) was dried over metallic sodium shavings. The ethyl bromide was redistilled collecting the fraction which distilled between 38.4° and 38.8° C. (Boiling point ethyl bromide 38.4° C.) Approximately one molar ethyl magnesium bromide was prepared using a mercury sealed stirrer in this preparation. The reaction took place smoothly on

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9. Precipitate may be R-O-Mg-Br. 2 $MgBr_2$ as is similarly reported by Noller and Castro for R-O-Mg-Cl. 2$MgCl_2$. J. Am. Chem. Soc. 64, 2503 (1942)

warming the mixture slightly and no catalyst was necessary to activate the reaction. The ethyl bromide was added slowly over a period of two hours and the Grignard solution was very dark due to colloidal magnesium. The reagent was transferred to a storage chamber (Fig. 3) by being pumped over by N_2 gas dried over $CaCl_2$.

The ethyl magnesium bromide in n-butyl ether was transferred to a "U" cell carrying a platinum electrode and a magnesium rod electrode as shown. The system was swept out with dry N_2 gas, filled with the Grignard reagent and sealed by means of pinch clamps as shown in Fig. 4 The potential was followed for five days. The cell was not as sensitive as when ethyl ether was used as the solvent and the cell was sluggish and difficult to balance. Graph 4. shows the result of this study taken from the data in table 4. The graph shows definitely the great sensitivity of the platinum electrode in the Mg-Pt couple in the solvent n-butyl ether as well as diethyl ether.

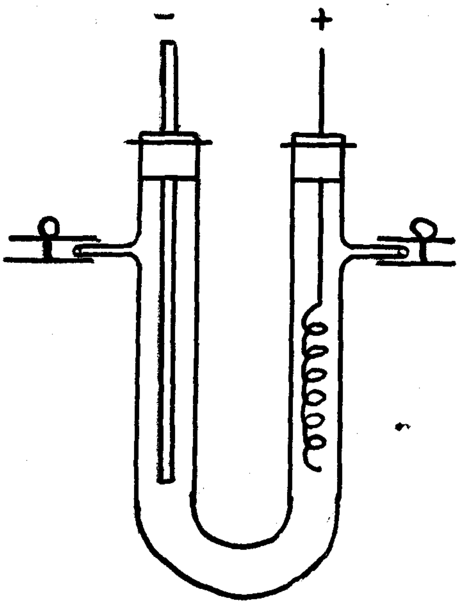


Fig. 4

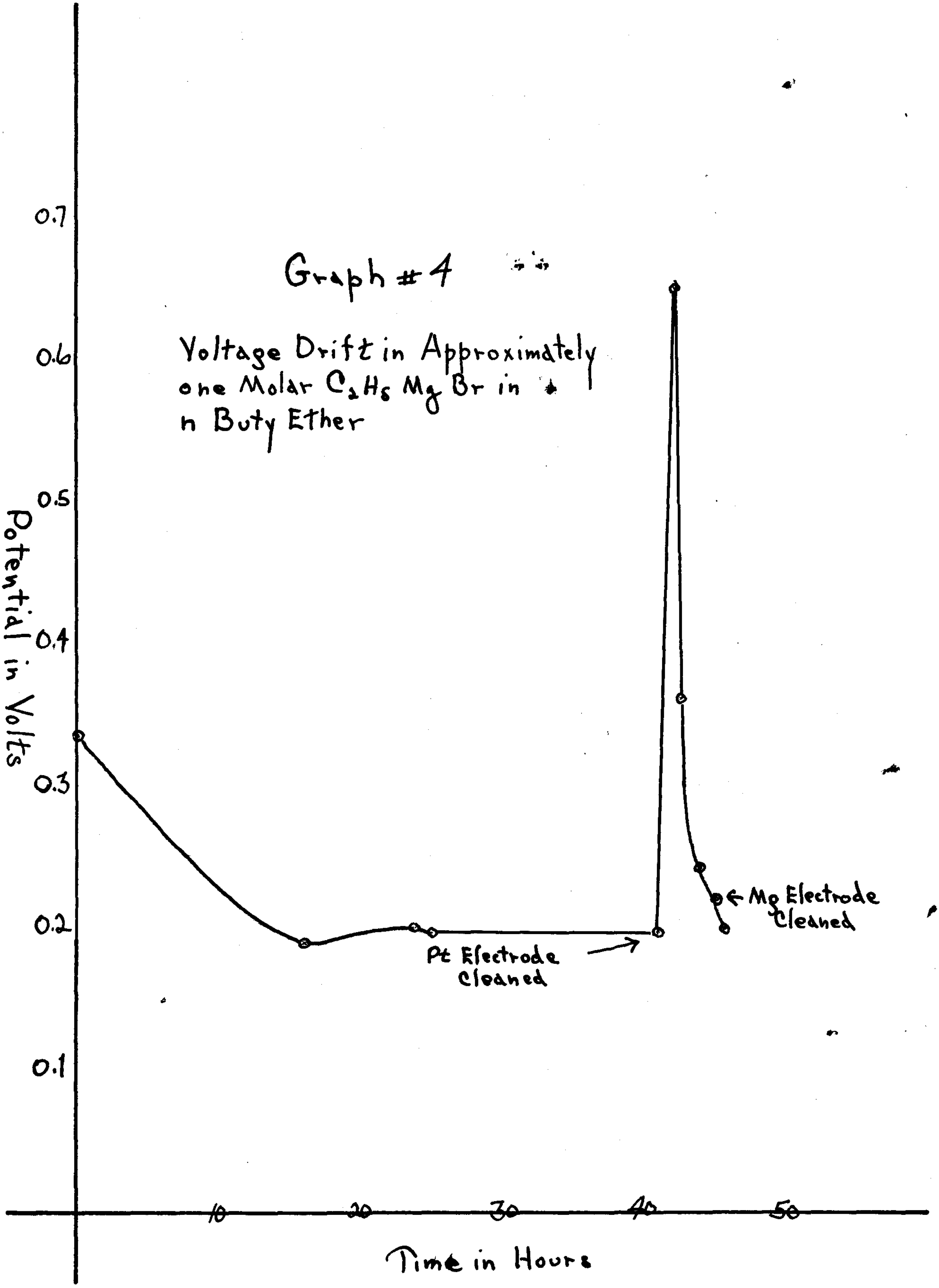
TABLE 4

Voltage drift in cell of approximately one molar ethyl magnesium bromide in n butyl ether using electrodes of magnesium and platinum.

Time in Hours	Temperature °C	Electromotive Force
0:0	27	0.330
16:0	24	0.186
24:0	24	0.200
25:0	25	0.195
41:0 *	24	0.197
42:0	24	0.650
42:30	24	0.365
44:00**	25	0.244
45:00	25	0.220
45:05	25	0.200

* Platinum electrode was washed with water, heated to redness in a bunsen burner, cooled in a dessicator and reinserted in cell.

** Magnesium electrode replaced with a clean magnesium rod.



Graph #4

Voltage Drift in Approximately one Molar C_2H_5MgBr in n Buty Ether

Evans and Fosdick[10] found that the molar concentration of the Grignard solution had little effect, if any, on the electromotive force of Grignard cells. A concentration cell of one molar ethyl magnesium bromide against one-half molar ethyl magnesium bromide was arranged so that each half cell could be read individually and as a concentration cell as shown in Fig. 5, by connecting the two platinum electrodes together. The result of this study are shown in graphs 5 and 6 taken from data in tables 5 and 6. Each half cell showed a drift and the concentration cell also showed a drift of electromotive force. The dilute cell was electro negative and the molar half cell was electro positive as a concentration cell. This cell was studied for seven days when continued evaporation caused the discontinuance of the concentration cell. The concentration cell when discontinued still showed an electromotive force but drift of potential seemed to indicate

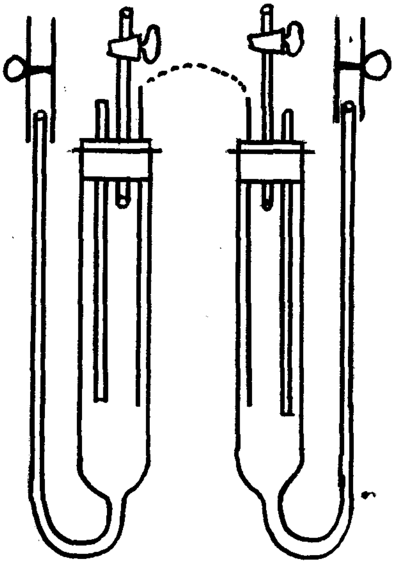


Fig.5

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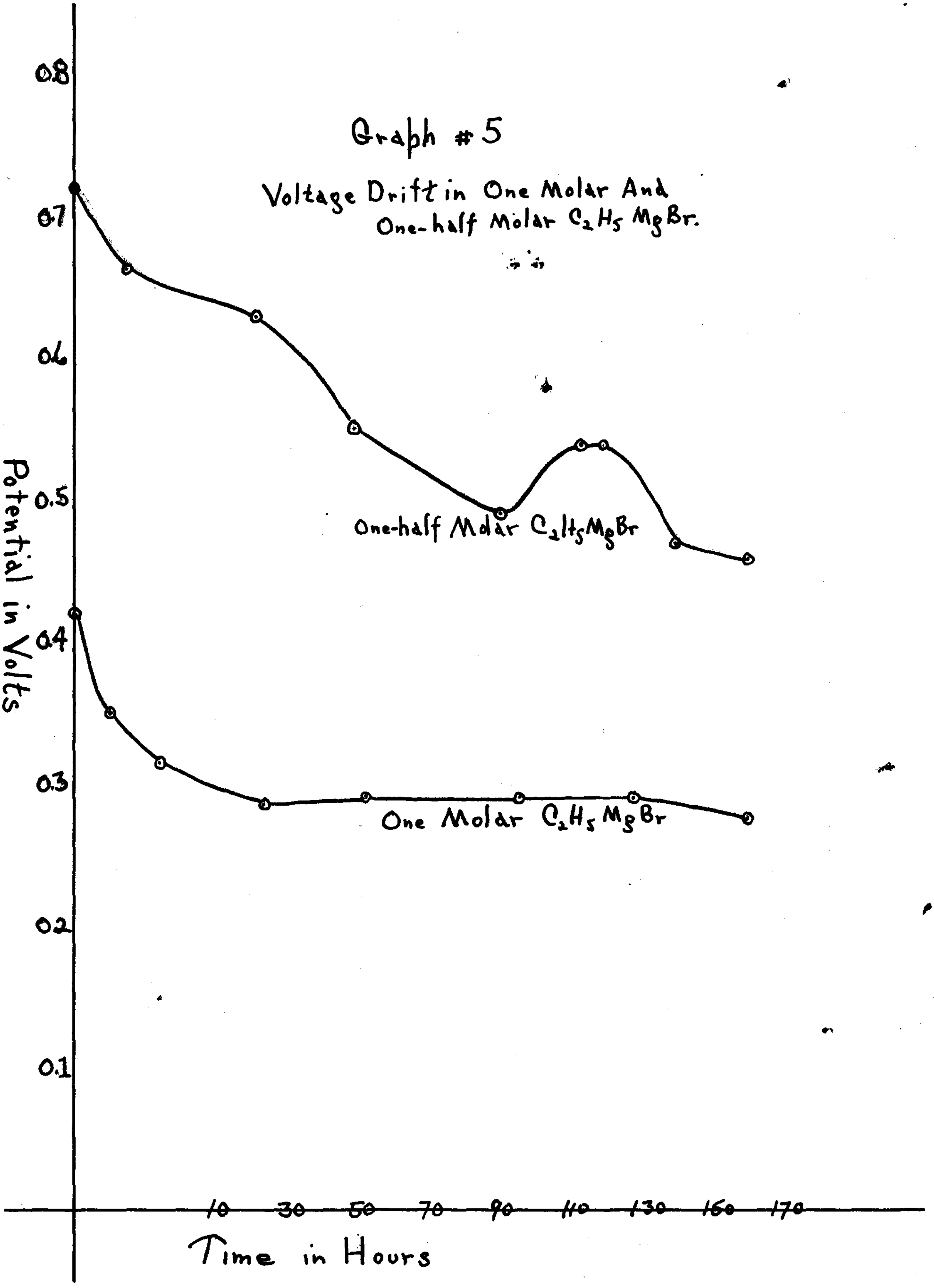
[10] Doctors Thesis, Northwestern University, (1932)

TABLE 5

Voltage drift in cell of approximately one molar ethyl magnesium bromide using electrode of magnesium and platinum, and also for an approximately one-half molar solution using similar electrodes.

Time in Hrs.	Temp. °C.	E.M.F.	Time in Hrs.	Temp. °C.	E.M.F.
0:00	25	0.420	0:00	27	0.720
0:35	26	0.390	1:00	27	0.695
1:15	26.5	0.380	2:20	28	0.675
2:35	27	0.350	3:40	28	0.664
3:40	27	0.349	21:15	24	0.630
5:00	28	0.330	25:00	25.5	0.610
6:12	28	0.315	44:37	24	0.580
23:30	24	0.285	49:45	20	0.550
25:15	25	0.275	90:00	21	0.490
28:00	26.5	0.274	95:00	24	0.450
47:00	24	0.280	113:35	26.5	0.540
52:43	20	0.290	119:00	26.5	0.540
96:00	21	0.290	141:45	28	0.470
106:22	24	0.290	160:32	25	0.46
124:30	23	0.292			
128:00	26	0.290			
141:00	28	0.283			
160:35	25	0.275			



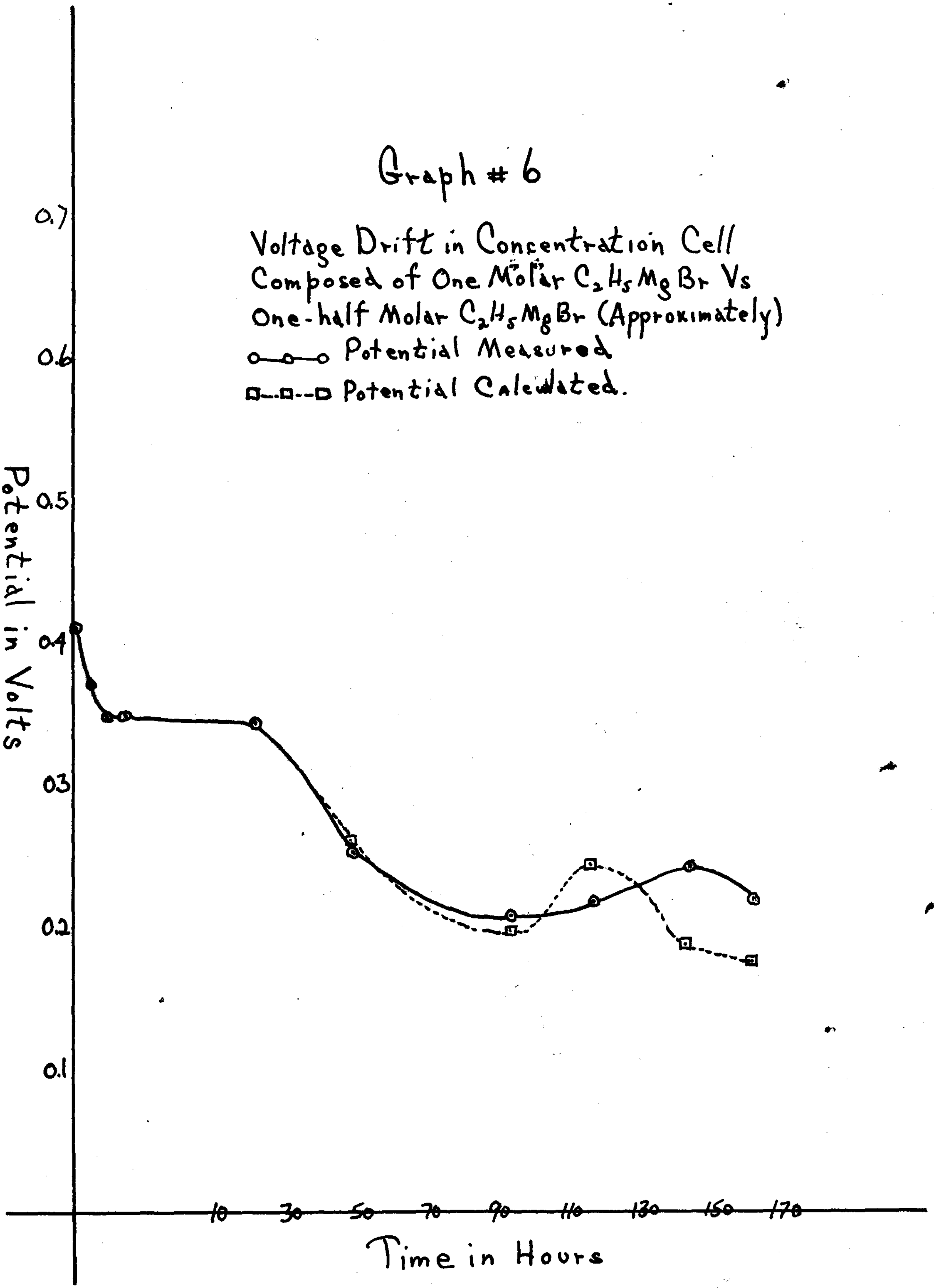
Graph #5

Voltage Drift in One Molar And One-half Molar C_2H_5MgBr.

TABLE 6

Voltage drift when approximately one molar ethyl magnesium bromide cell was treated as a half cell and coupled with the approximately half molar ethyl magnesium bromide cell. The dilute half cellwas found to be electronegative with respect to the approximately one molar ethyl magnesium bromide. The platinum electrode of each cell was connected in series.

Time in Hrs.	Temp. °C.	E.M.F. of	Conc. Cell
		Measured	Calculated
0:00	27	0.409	0.410
1:00	27	0.370	0.370
2:17	28	0.350	0.345
3:36	28	0.350	0.350
20:39	24	0.345	0.345
22:53	25	0.340	0.340
24:21	25	0.340	0.336
46:58	24	0.255	0.255
48:16	20	0.254	0.260
93:25	21	0.210	0.200
98:46	24	0.1700	0.160
116:51	23	0.2200	0.248
122:31	26	0.250	0.248
143:00	28	0.245	0.187
161:50	25	0.220	0.185



Graph # 6

Voltage Drift in Concentration Cell Composed of One Molar C_2H_5MgBr Vs One-half Molar C_2H_5MgBr (Approximately) eventual zero reading. A cell (Fig. 6.) was devised which could be sealed to prevent evaporation and which made use of a sintered glass micro filter to prevent diffusion of the Grignard solution of different concentrations. The micro filter did not permit the filtration of ether unless suction was applied. Ethyl magnesium bromide of approximately one molar concentration was introduced into one-half cell of the N_2 gas filled system. Approximately one-half molar ethyl magnesium bromide was introduced into the other half cell and the system sealed. The magnesium rod electrodes were polished with a file and were fairly bright after being sealed into the system.

An attempt was made to study the E.M.F. of this concentration cell but it was very difficult to balance the cell and the sensitivity was not very high. Unequal gas volumes in the sealed half cell soon caused enough pressureto force Grignard solutions through the micro filter barrier and the cell was abandoned.

A supply of anhydrous ether was prepared and stored over

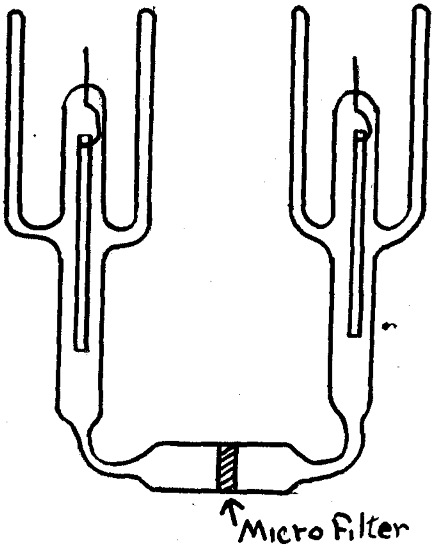


Fig. 6

phosphorous pentoxide. Some one molar ethyl magnesium bromide was prepared. The preparation of this Grignard went smoothly without the necessity of a crystal of I_2 as a catalyst.

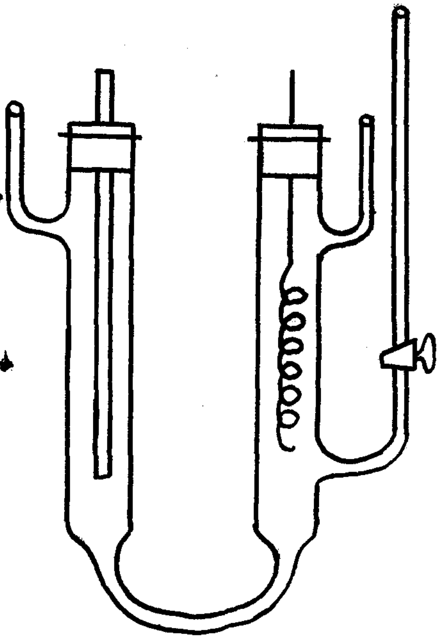


Fig. 7

A check was desired on the data which showed the electromotive force of the Grignard cell was increased by the bubbling of oxygen slowly through the cell. To more effectually study this voltage change, a cell, (Fig. 7.) was blown to introduce the dry oxygen gas more readily and to control the addition more satisfactorily.

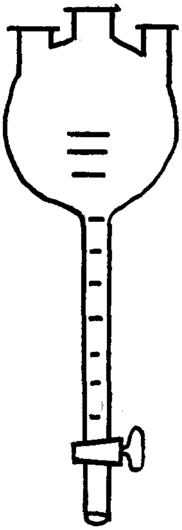


Fig. 8

Some of the Ethyl Mg-Br prepared approximately one molar was diluted with an equal quantity of anhydrous ether and shaken well in a calibrated mixing chamber. (Fig. 8.) On dilution of the molar

Grignard solution a white murky precipitate formed which on shaking appears to go back into solution. This diluted M/2 Grignard was introduced into a cell which had been swept out with dry N_2 gas and sealed by means of rubber tubing and pinch clamps at the outlets. Graph 7 shows the result of this study using the data in table 7. The cell warmed appreciably as the O_2 was bubbled through it, turned murky and an oily dense liquid formed in the "U" tube of the cell. The electromotive force developed soon reached 1.60+ volts slightly beyond the range of the potentiometer. Since one of the products of the oxidation of a Grignard solution is MgX_2 it was thought wise to investigate the potential, if any, developed by $MgBr_2$ in anhydrous ether. Some $MgBr_2$ was prepared (0.1 mole) in anhydrous ether by permitting Br_2 to react with an excess of magnesium turnings and then reflexing for two hours. A yellowish oil appeared as the reaction progresses with the oil layer deepening to a browning red. Some of the $MgBr_2$ thus prepared in ethyl ether was introduced into a "U" type cell carrying a magnesium electrode freshly sanded to brightness and a platinum electrode. The cell developed a potential of 1.60 volts and did not drift while being studied for a period of four days. Graph 8 indicates the

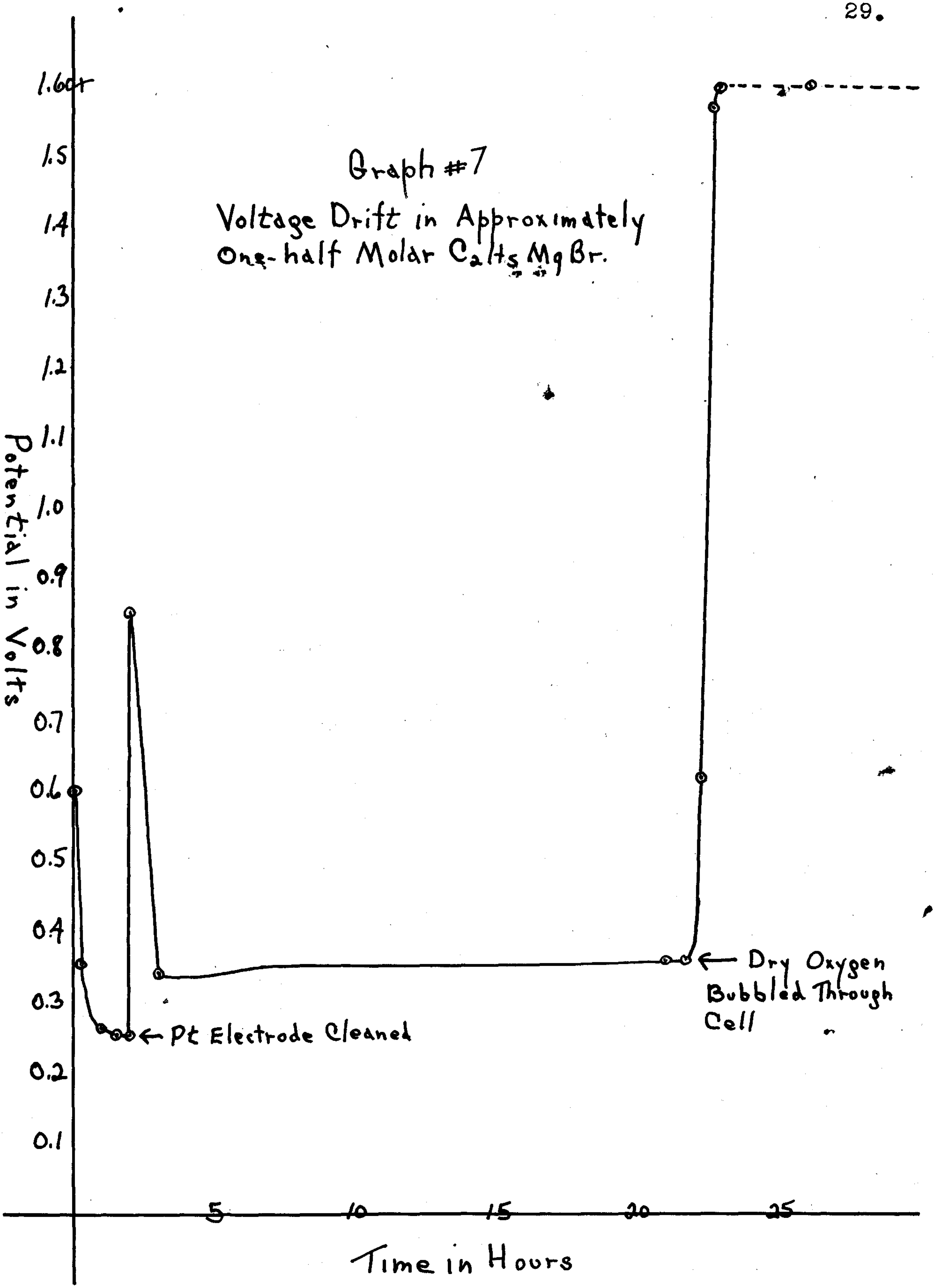
TABLE 7

Voltage drift in cell of approximately one-half molar ethyl magnesium bromide using magnesium and platinum electrodes with subsequent treatment with dry oxygen gas.

Time in Hours	Temperature °C	Electromotive Force
0:00	23	0.598
0:15	23	0.350
1:00	23	0.260
1:30	23	0.250
2:00 *	23	0.85
3:00	22	0.338
21:00	20	0.360
21:48 **	20	0.360
22:15	20	0.619
22:30	20	1.57
22:40	20	1.60 +
26:00	22	1.60 +
69:00	20.5	1.60 +

* Platinum electrode removed, cleaned, heated in a bunsen burner to redness, cooled and reinserted in solution.

** Oxygen gas from a cylinder was passed through a $CaCl_2$ tube and into cell for twenty-five minutes very slowly. An oily liquid formed in "U" portion of cell and increased as oxygen was added.



Graph #7

Voltage Drift in Approximately One-half Molar C_2H_5MgBr.

TABLE 8

Electromotive force developed in an ether solution saturated with magnesium bromide using magnesium and platinum electrodes.

Time in Hours	Temperature °C	Electromotive Force
0:00	25	1.60 +
3:00	25	1.60 +
6:00	25	1.60 +
24:00	20	1.60 +
31:00	21	1.60 +
48:00	20	1.60 +
74:00	21	1.60 +

Graph #8

Electromotive Force Developed in an Ether Solution Saturated with $MgBr_2$

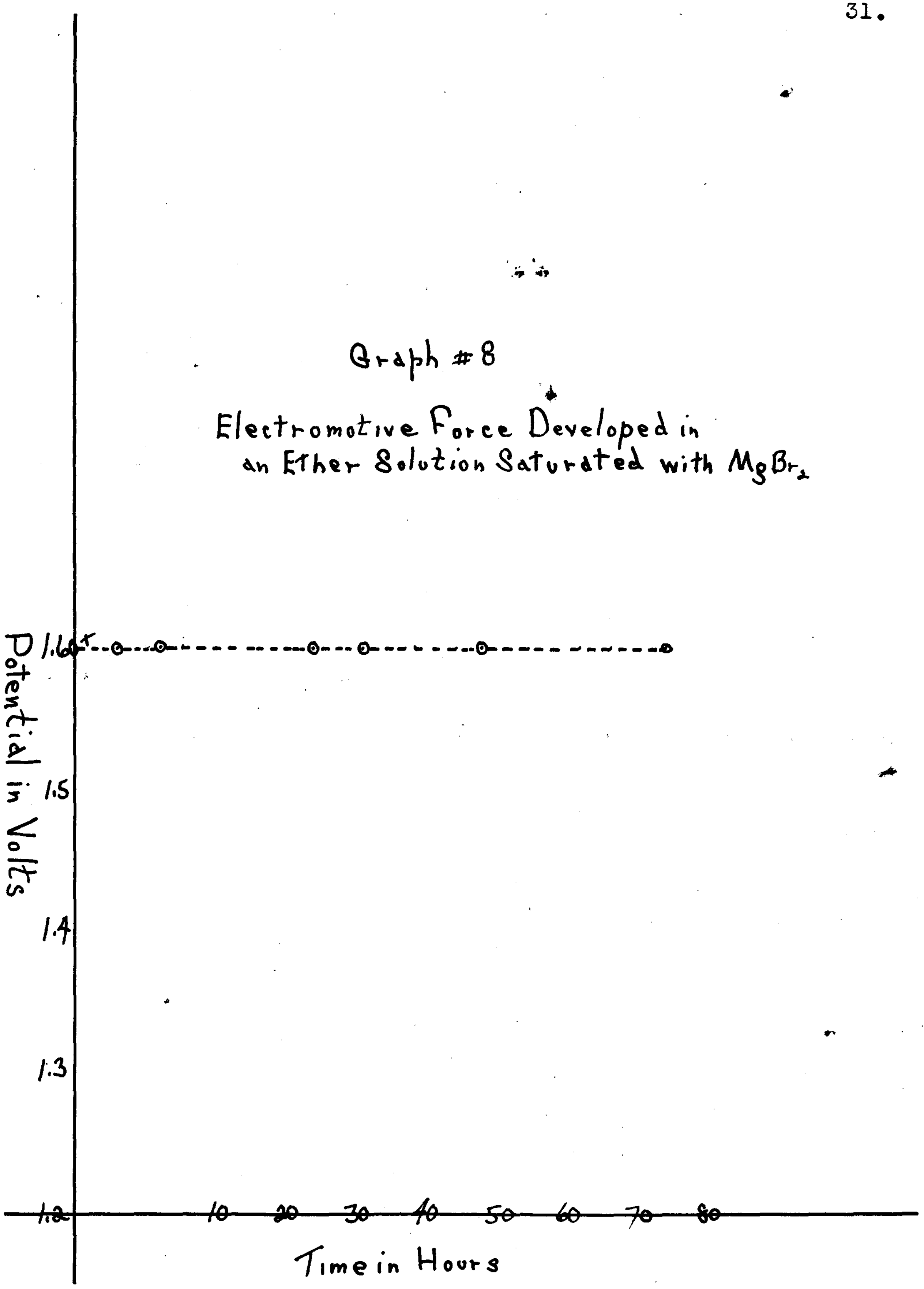


TABLE 9

Voltage drift in cell of approximately one molar ethyl magnesium bromide using magnesium and platinum electrodes with the subsequent addition of a slight excess of ethyl bromide.

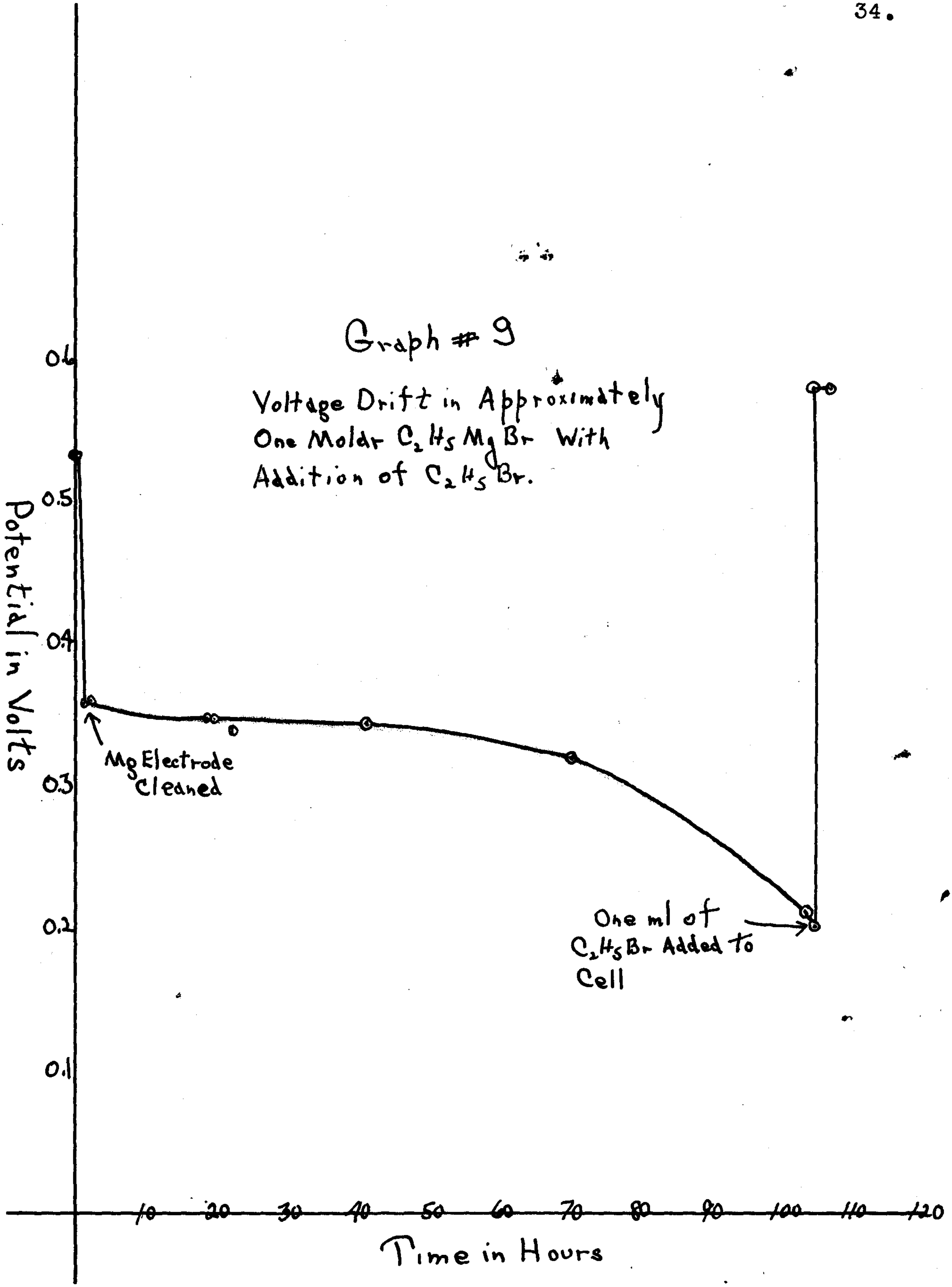
Time in Hours	Temperature °C.	Electromotive Force
0:00	20	0.532
1:10	20	0.358
2:00	20	0.360
18:30 *	19	0.347
19:00 **	19	0.343
19:11	19	0.345
20:00	19.5	0.342
22:00	22	0.335
40:30	20.5	0.344
64:30	21	0.337
70:00	22	0.320
113:00 @	25	0.210
114:00 @@	25	0.200
114:08	25	0.580
115:08	25	0.580
116:00	25	0.580

* Magnesium electrode cleaned, dried and replaced.

** Ethane from a cylinder was bubbled at the rate of one bubble per second through the cell for five minutes.

@ Magnesium electrode cleaned by sanding with emery paper cooled and reinserted in solution.

@@ 1 ml of redistilled ethyl bromide added to cell.



Graph # 9

Voltage Drift in Approximately One Molar C_2H_5MgBr With Addition of C_2H_5Br.

summarizes this experiment.

Another approximately one molar solution of C_2H_5Mg-BR in ethyl ether was introduced into a cell (Fig. 7.) for subsequent study. It was desired to study the effect of the addition of ethylene gas and $MgBr_2$ to the system. The ethylene gas was bubbled through the cell for five minutes very slowly. The $MgBr_2$ prepared in anhydrous ether (4 or 5 ml were taken) was added to the dell. Considerable bubbling took place but the expected two layer system did not materialize. Noller[11.] indicated that $MgCl_2$ is more soluble in the Grignard solution than in ether. The potential fell approximately 0.1 volts as shown in Graph 10.

A cell containing a magnesium electrode and a tantalum electrode as shown in Fig. 9 was constructed. The magnesium was sealed in the cell through a tungsten copper wire connection. The tantalum electrode was obtained from a radio tube and was sealed into the cell through a tungsten connection. The approximately one molar Grignard s olution was diluted with an equal quantity of ether and placed in cell and the potential studied. After being closed

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TABLE 10

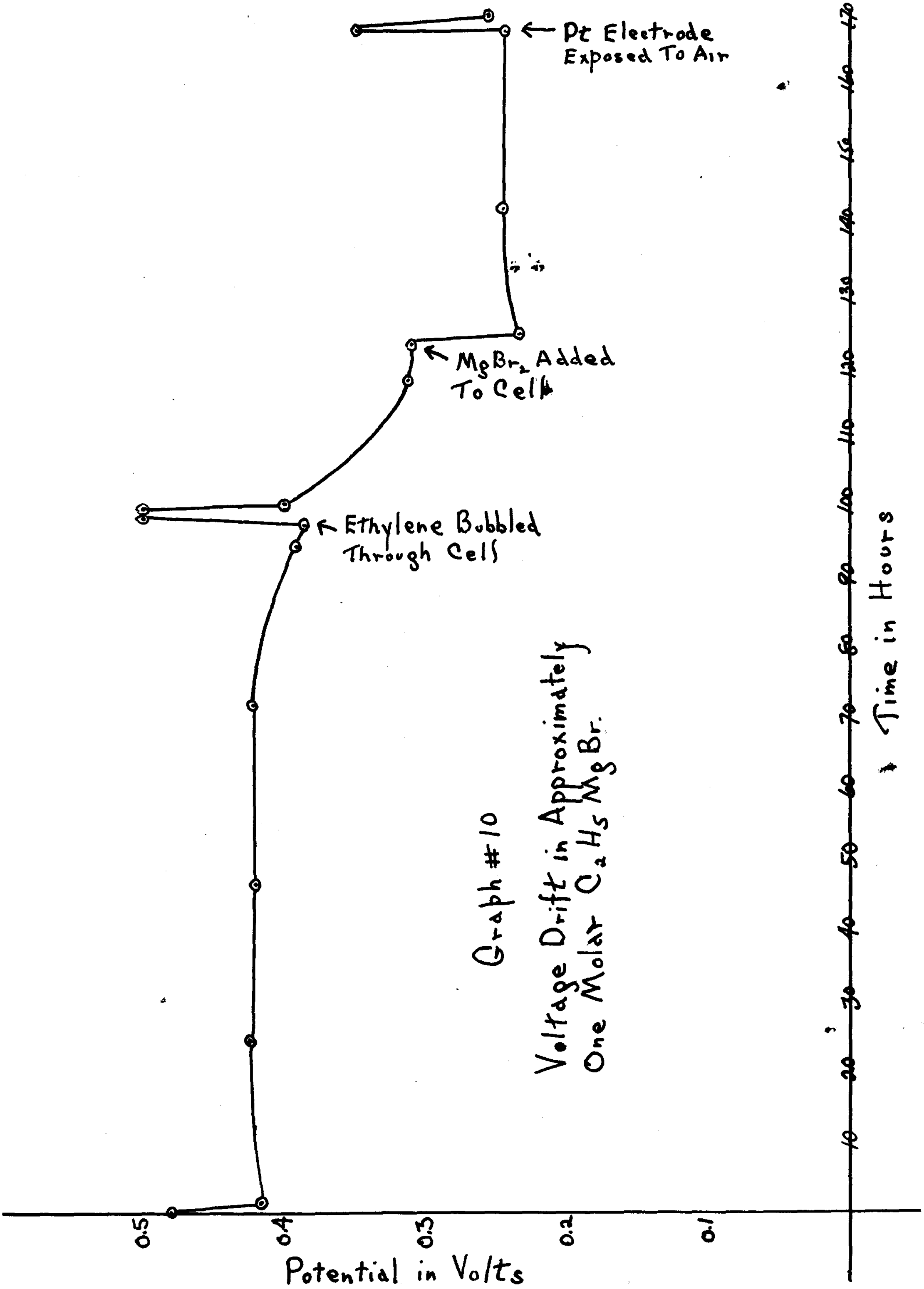
Voltage drift of approximately one molar ethyl magnesium bromide using magnesium and platinum electrodes.

Time in Hours		Temperature °C.	Electromotive Force
0:00		25	0.480
1:00		25	0.418
24:00		25	0.425
46:00		26	0.420
70:30		27	0.423
94:00		24	0.392
97:00	*	25	0.387
97:30		25	0.415
97:45		25	0.500
98:00		23	0.500
98:30		24	0.450
99:00		24	0.417
99:15		24	0.398
117:30		20	0.318
122:30	**	21	0.314
122:40		21	0.226
123:40		21	0.235
126:30		21	0.237
141:30		20	0.245
147:30		22	0.240
167:00	@	21	0.245
167:10		21	0.350
167:13		21	0.300
167:30		21	0.270
169:00		21	0.256

* Ethylene from a cylinder bubbled slowly through solution for five minutes.

** Some magnesium bromide prepared from magnesium turnings in excess with bromine in ether was added to cell. The $MgBr_2$ reacted violently with the ethyl magnesium bromide with considerable bubbling of solution.

@ Platinum electrode exposed to air and reinserted



Graph #10

Voltage Drift in Approximately One Molar C_2H_5MgBr.

overnight with rubber tubing, pinch clamp seals, the outlet tubes were sealed and the cell studied since May, 1947. After being sealed, the drift in the electromotive force of the cell continued to occur. Results are graphed in Graph 11, illustrating the data taken from Table 11.

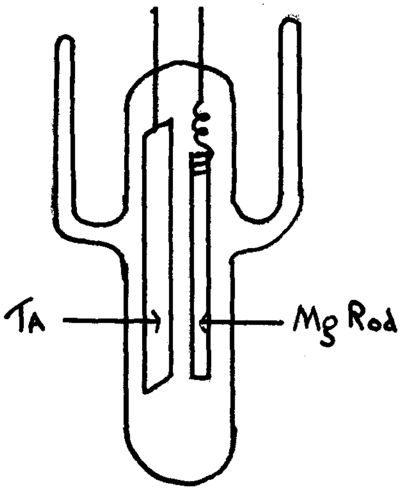


Fig. 9

A two molar solution of ethyl magnesium bromide in ethyl ether was prepared to study the potential developed in a more concentrated Grignard solution using Mg-Pt electrodes. The Grignard solution was very colloidal and was pumped into a storage cell. Ten days later the solution was still very dark gray. Some of this 2M (approximately) Grignard solution was transferred to cell and the potential studied. The cell was found to lack sensitivity in adjusting the electromotive force balance and readings more accurate than ten - twenty millivolts could not be relied upon. The cell was studied for two days. The platinum electrode was removed and a tungsten wire electrode was inserted. Repeated removal and

TABLE 11

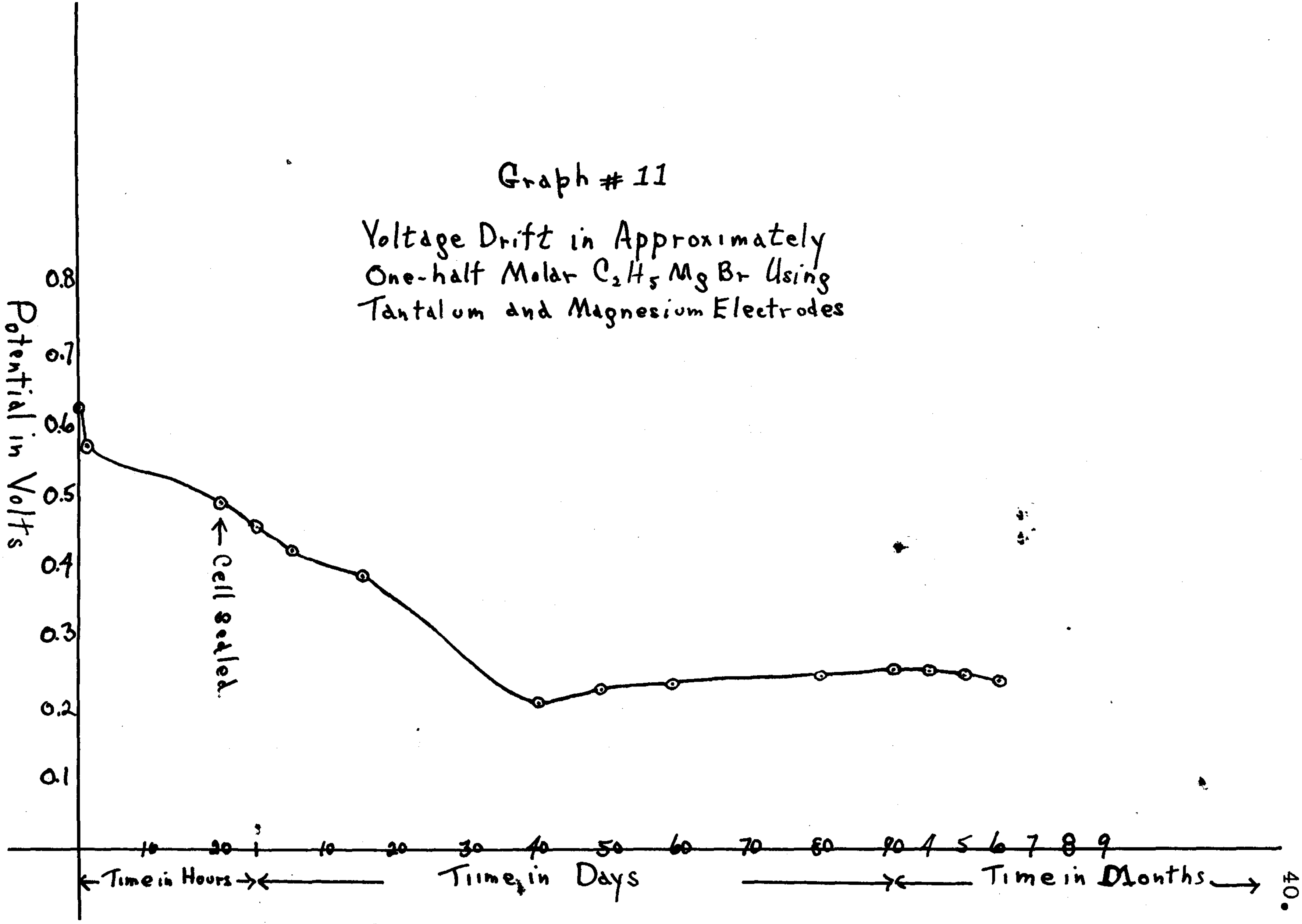
Voltage drift in approximately one-half molar ethyl magnesium bromide using electrodes of magnesium and tantalum.

Time in Hours	Temperature °C.	Electromotive Force
0:00	22	0.620
0:10	22	0.600
1:10	22	0.571
3:30	22	0.545
20:00 *	21	0.486
22:30	21.5	0.455
25:30	22.5	0.455
Time in Days		
2.0	22.5	0.458
5.0	23	0.420
7.0	25	0.410
15.0	21	0.380
26.0	25	0.378
29.0	23	0.342
38.0	18	0.300
40.0		0.200
49.0	22	0.220
52.0	22	0.220
59.0	21	0.230
62.0	21	0.227
80.0	22	0.240
93.0	23	0.250
Time in Months		
	25	0.250
4	20	0.240
5	21	0.238
6		
9		
10		
11		
12		

* Cell was sealed.

Graph # 11

Voltage Drift in Approximately One-half Molar C_2H_5MgBr Using Tantalum and Magnesium Electrodes

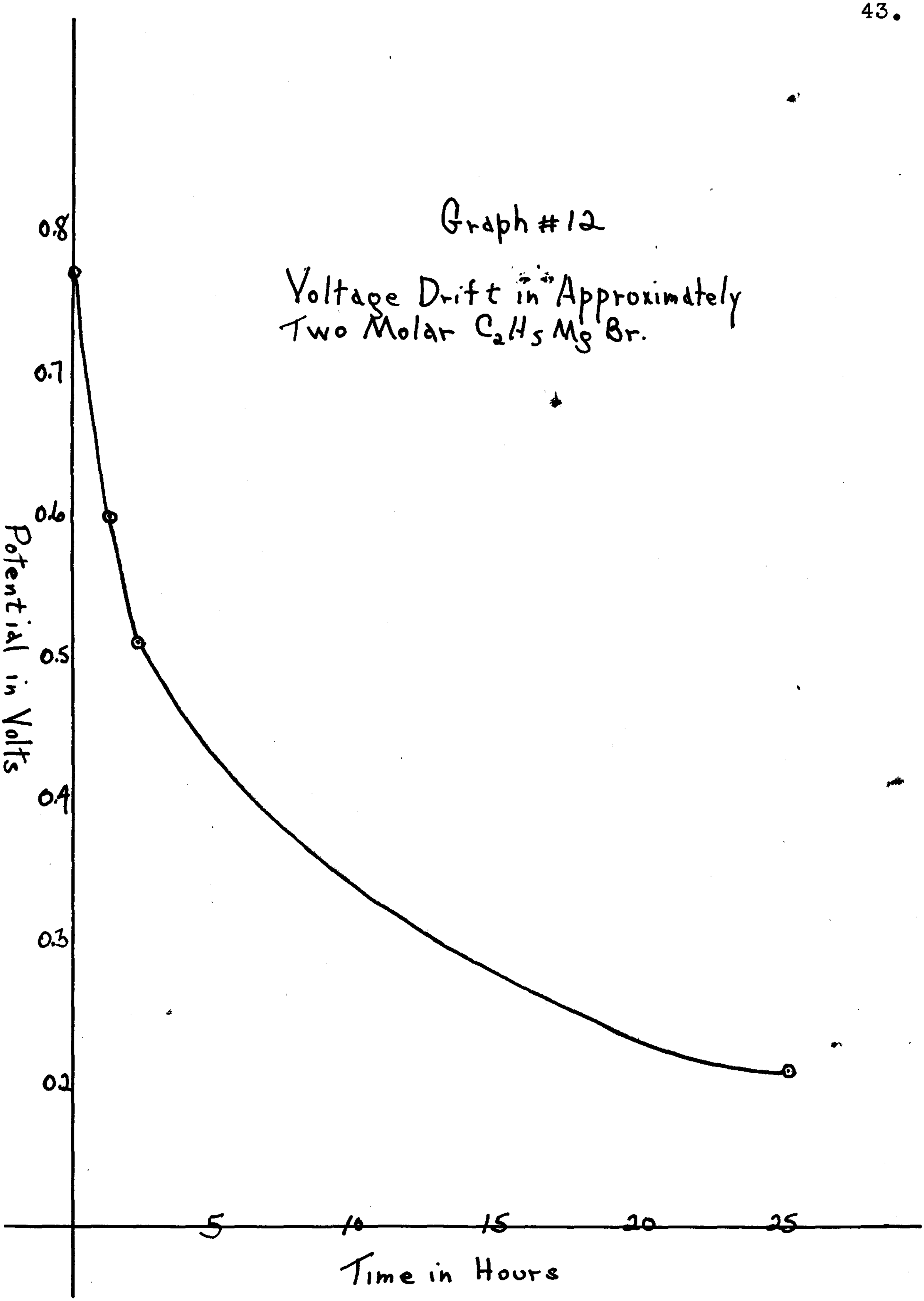


reinsertion in the Grignard solution increased the voltage up to 1.60+volts. This was also done with a Pt electrode which formed a heavy white crust on the electrode which still delivered 1.60+volts. A similar build up in potential was obtained by using a carbon electrode. The peculiar electromotive force increased with the platinum electrode is, therefore, not unique to the platinum electrode. The white crust formed on the anode material seems to be the requisite for the electromotive force increase observed in cells studied so far. The electromotive force drift of the approximately 2M C_2H_5Mg-Br in shown in graph 12. The data for this graph are found in table 12.

TABLE 12

Voltage drift in approximately two molar ethyl magnesium bromide using electrode of magnesium and platinum.

Time in Hours	Temperature °C.	Electromotive Force
0:00	25	0.770
1:20	25	0.600
2:20	25	0.510
25:20	25	0.210



Graph #12

Voltage Drift in Approximately Two Molar C_2H_5MgBr.

CHAPTER III

EXPERIMENTAL STUDIES IN ETHYL MAGNESIUM BROMIDE SOLUTIONS

We thought it might be interesting to know when the potential of the Grignard cells actually developed. Accordingly, a cell was devised so that the potential could be studied as the Grignard reaction took place in the reaction flask. An additional outlet was blown on a three necked Grignard flask as shown in Fig. 10.

The ether stored over P_2O_5 was found to give a slightly acid reaction to litmus so it was decanted from the P_2O_5 and syrupy H_3PO_4 and redistilled. This ether was used for the preparation of approximately one molar ethyl magnesium bromide. 150 ml of anhydrous ether was placed in the flask with 5 gm. (slightly excess) of magnesium turnings. 15 ml. of C_2H_5Br (redistilled) in 50 ml. of anhydrous ether was added slowly (during the three

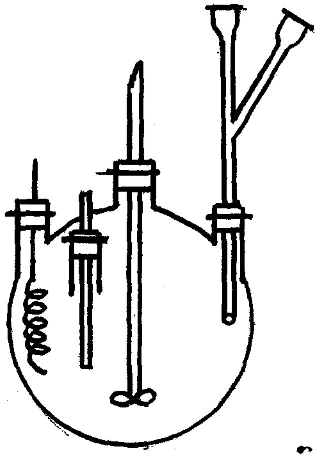


Fig.10

hour period) through the dropping funnel.

No definite electromotive force could be detected until the Grignard reaction actually started. Approximately 10 ml of C_2H_5Br in anhydrous ether was added and the flask warmed with an electric hot plate but the Grignard did not start. After cooling the reaction flask, a crystal of I_2 was added and the solution warmed again. A slight opalescence appeared in cell as the Grignard solution started. The electromotive force developed was now 1.60+ volts and the cell was very sensitive to small changes in the bucking resistance of the potentiometer system. A fine white precipitate seemed to form near and around the magnesium turnings as the reaction progressed. The solution took on a slightly clouded gray appearance and the potential fell rapidly for the first three hours. The addition of C_2H_5Br seemed to retard the fall of the E.M.F. somewhat, but the speed of formation of the Grignard reagent appeared to be rapid during the first three hours of preparation. The fall in potential seemed to level off in the neighborhood of 0.5 volts as the reaction appeared to stop. The stirrer was in continuous operation during the preparation of the Grignard compound. The cell was made airtight and allowed to stand overnight.

The following morning, the potential had fallen to 0.195 volts and remained approximately at 0.195 volts throughout the day with the stirrer in operation. The cell was again allowed to stand overnight and when read again the voltage was found to be 0.190 volts. The stirrer was started and the potential remained at 0.190 volts. Some Ethyl Bromide, 0.3 ml, was added to the reaction flask with an immediate electromotive force increase of 0.28 volts. The voltage drifted off again until five hours later an electromotive force of 0.199 was again reached. The cell was allowed to stand overnight and the next morning an E.M.F. of 0.193 volts was obtained. Some $MgBr_2$ in ether (2 ml) was added with a slight increase of potential of 20 millivolts. Some oxygen was slowly bubbled through the cell for ten minutes. The solution warmed and a voltage increase of o.1 volts was observed. When the cell again reached a voltage of 0.190 some CO_2 gas was bubbled through the solution for five minutes, and a voltage increase of 0.07 volts was obtained. A grayish-white precipitate was obtained in the flask which settled slowly. The cell was allowed to stand overnight with little or no drift from the potential observed when the CO_2 was bubbled through the solution the day before. 0.3 ml. of C_2H_5Br was added to the cell with an immediate electromotive force response of 0.25 volts an additional 2.7 ml. portion of C_2H_5Br increased the potential to 0.600 volts. Graph 13 drawn from table 13 summarizes this experiment.

Another supply of anhydrous ether was prepared and stored over sodium shavings. It was decided to repeat the above experiment with a new supply of anhydrous ether.

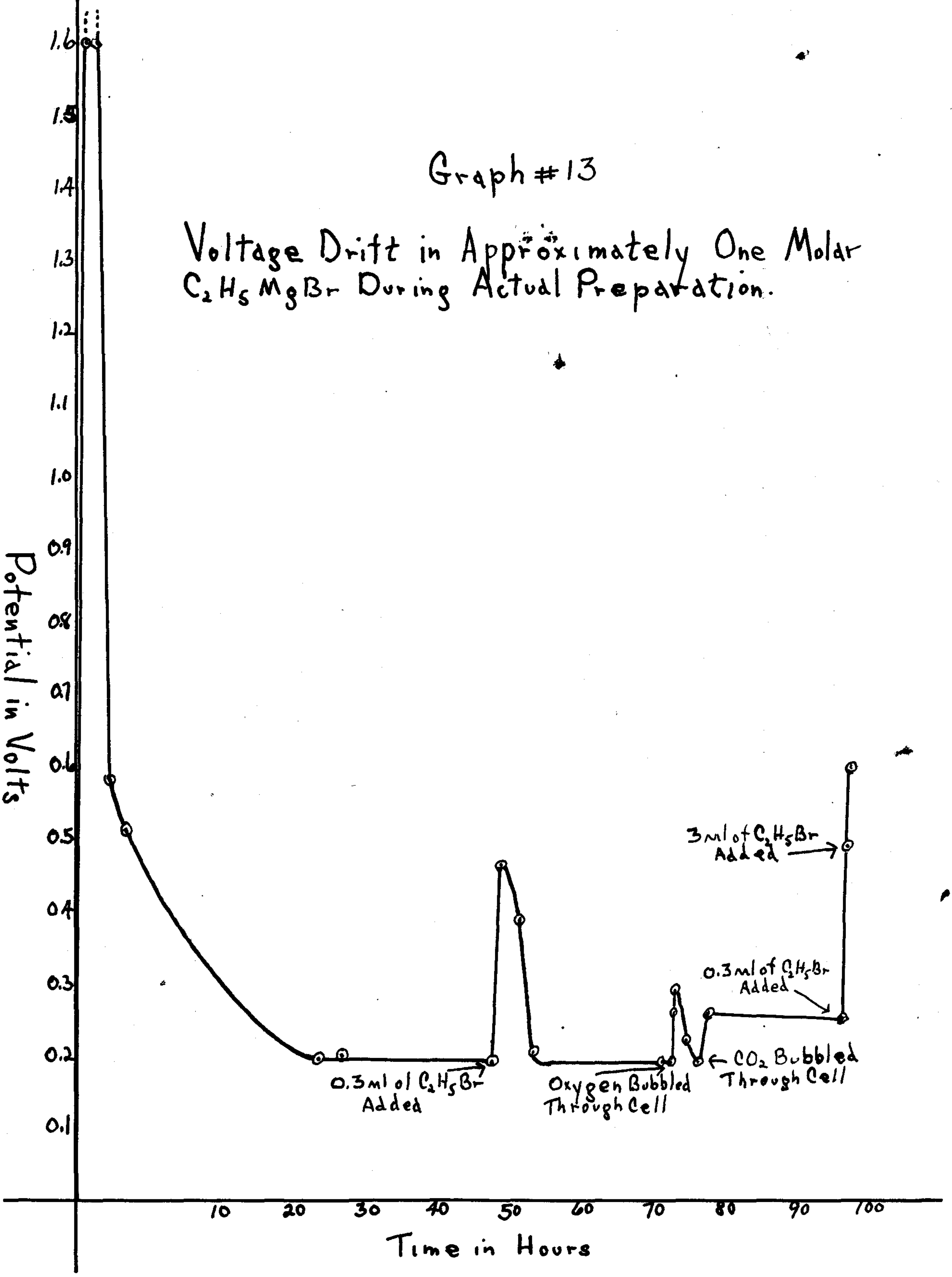
175 ml. of anhydrous ether was added to 2.15 gms. of magnesium turnings in the reaction flask. The electromotive force of the cell was 0.000 using the magnesium rod electrode and the platinum spiral electrode. 25 ml. of anhydrous ether was added to the dropping funnel in the addition tube. 15 ml. of redistilled ethyl bromide was added and approximately 15 ml. of this solution was added to the reaction flask. The Grignard reaction did not appear to start and no voltage was developed. The reaction flask was warmed and the expected reaction did not take place. An additional 10 ml. of the ethyl bromide dissolved in anhydrous ether was added through the addition tube from the dropping funnel and the solution warmed again with no evidence of a reaction taking place. When the solution had cooled to room temperature, a crystal

TABLE 13

Voltage drift in approximately one molar ethyl magnesium bromide during preparation of Grignard solution using platinum and magnesium electrodes.

Time in Hours	Temperature °C.	Electromotive Force
0:00	24	0.000
0:40 *		1.60+
1:10		1.60+
1:15		1.50
1:30		1.30
2:40		0.580
3:30		0.513
24:00	22	0.195
27:00	22	0.199
31:00	22	0.193
48:00	20	0.190
49:30 **	20	0.465
50:00	20	0.469
51:00	20	0.435
52:00	20	0.390
53:00	20	0.320
54:00	20	0.204
72:00	19	0.193
72:30 ***	19	0.215
73:00	19	0.194
73:20 @	19	0.260
73:30	19	0.290
74:00	19	0.280
75:15	19.5	0.225
77:00 @@	19	0.190
78:00	20	0.260
79:00	20	0.260
97:00	20	0.250
97:24 @@@	20	0.250
97:25	20	0.490
97:28 @@@	20	0.600

* Grignard solution definitely reacting.
** 0.3 ml of C_2H_5Br added.
*** 2 ml. of $MgBr_2$ in ether added.
@ Oxygen bubbled into solution slowly for ten minutes.
@@ CO_2 bubbled through solution for five minutes.
@@@ 0.3 ml. of C_2H_5Br added.
@@@ 3 ml. of C_2H_5Br added.



Graph #13

Voltage Drift in Approximately One Molar C_2H_5MgBr During Actual Preparation.

of I_2 was added to catalyze the reaction but this too failed. The voltage of the cell remained at 0.000. When the crystal of iodine was added there was a very slight indication of an electromotive force being developed but not definite. The cell was just about to be abandoned when the reaction started after two hours. The reaction flask had to be hurriedly cooled because of the rapidity of the Grignard reaction caused by the relatively large amount of ethyl bromide which had been added. The potential jumped definitely to 1.60+ volts and remained at this value for approximately ten minutes and then fell rapidly. Within two hours the Grignard reaction apparently had been completed as the ether solution no longer gave any evidence of bubbling and the solution had reached room temperature. The voltage of the cell at this time read 0.58 volts and it was allowed to stand overnight. The following morning the voltage had dropped to 0.46 volts. The stirrer was started and the drift of the electromotive force was followed until the voltage levelled off at approximately 0.240 volts. The data are recorded in table 14 and the experiment is summarized in graph 14.

The cell of approximately one molar ethyl magnesium

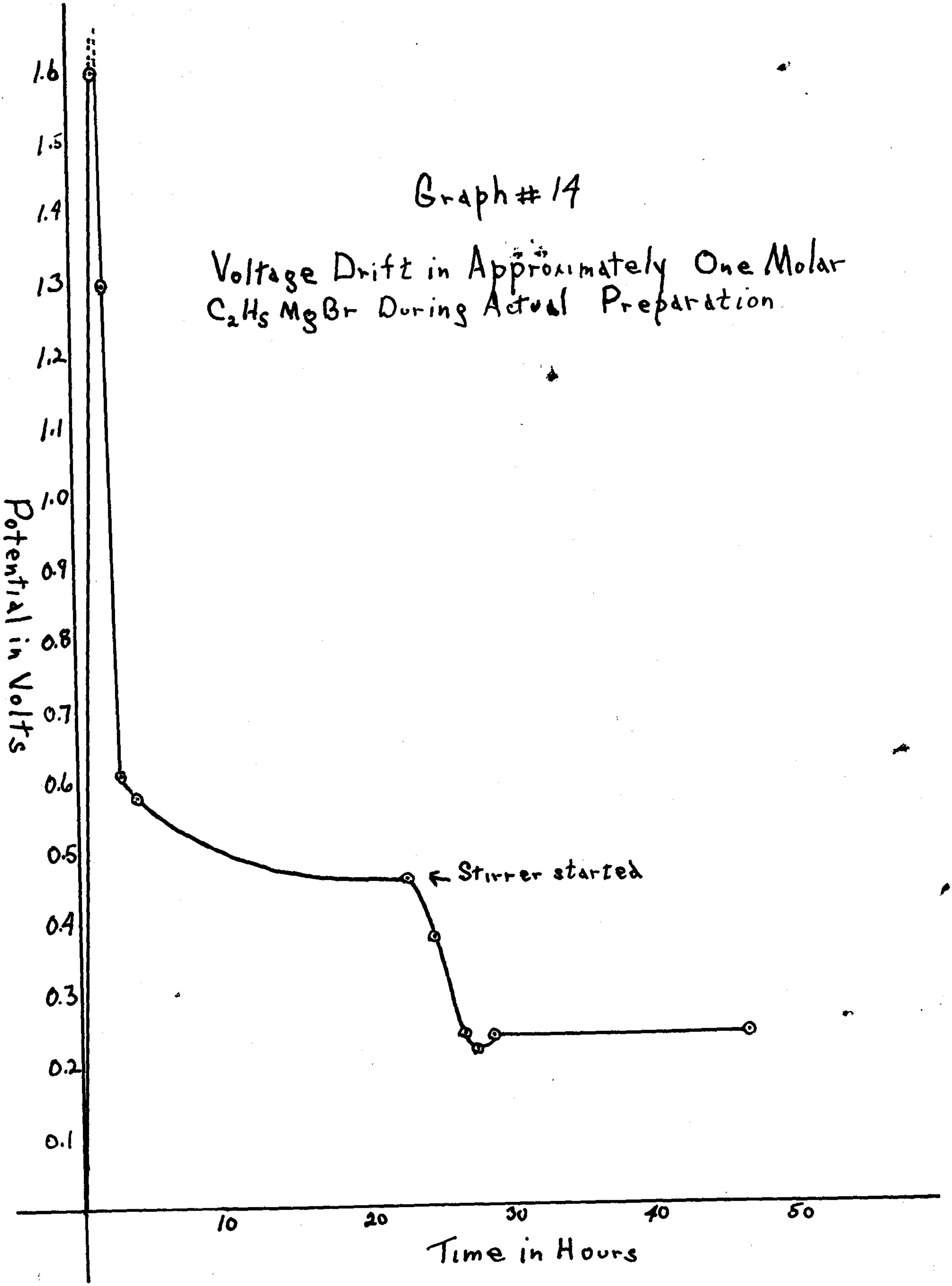
TABLE 14

Voltage drift in approximately one molar ethyl magnesium bromide during preparation using platinum and magnesium electrodes.

Time in Hours	Temperature °C.	Electromotive Force
0:00	-	0.000
1:00	-	0.000
1:55 *	-	1.60+
2:00	-	1.60+
2:06	-	1.30
2:32	-	0.68
3:00	-	0.61
4:00	-	0.58
23:00 **	-	0.46
25:00	Room Temperature	0.38
26:00	"	0.28
27:00	"	0.24
28:00	"	0.220
29:00	"	0.240
30:00	"	0.235
47:00	"	0.246

* Reaction definitely started.

** Stirrer started.



Graph #14

Voltage Drift in Approximately One Molar C_2H_5MgBr During Actual Preparation bromide in anhydrous ether was further studied. This cell had been treated with oxygen so the electromotive force had reached a potential of 0.41 volts. The effect of the addition of one-half a milliliter of water on the potential was investigated. After the addition of the water the potential jumped to 0.092 volts and then fell rapidly as shown in graph 15 drawn from data in table 15.

It was decided to check on the possibility that a potential might be developed in a cell containing a platinum electrode and a magnesium electrode in a solution of redistilled ethyl bromide although this seemed improbable. Accordingly, a "U" type cell was set up according to the above specifications and although checked for two days no indication of the development of an electromotive force occurred. Previously, in the preparation of the ethyl magnesium bromide, no electromotive force was developed in the system platinum versus magnesium in anhydrous ether and furthermore, since no electromotive force was developed even after the addition of ethyl bromide, it would seem to be fairly conclusive proof that the potential developed in these cells was definitely dependent on the Grignard reagent.

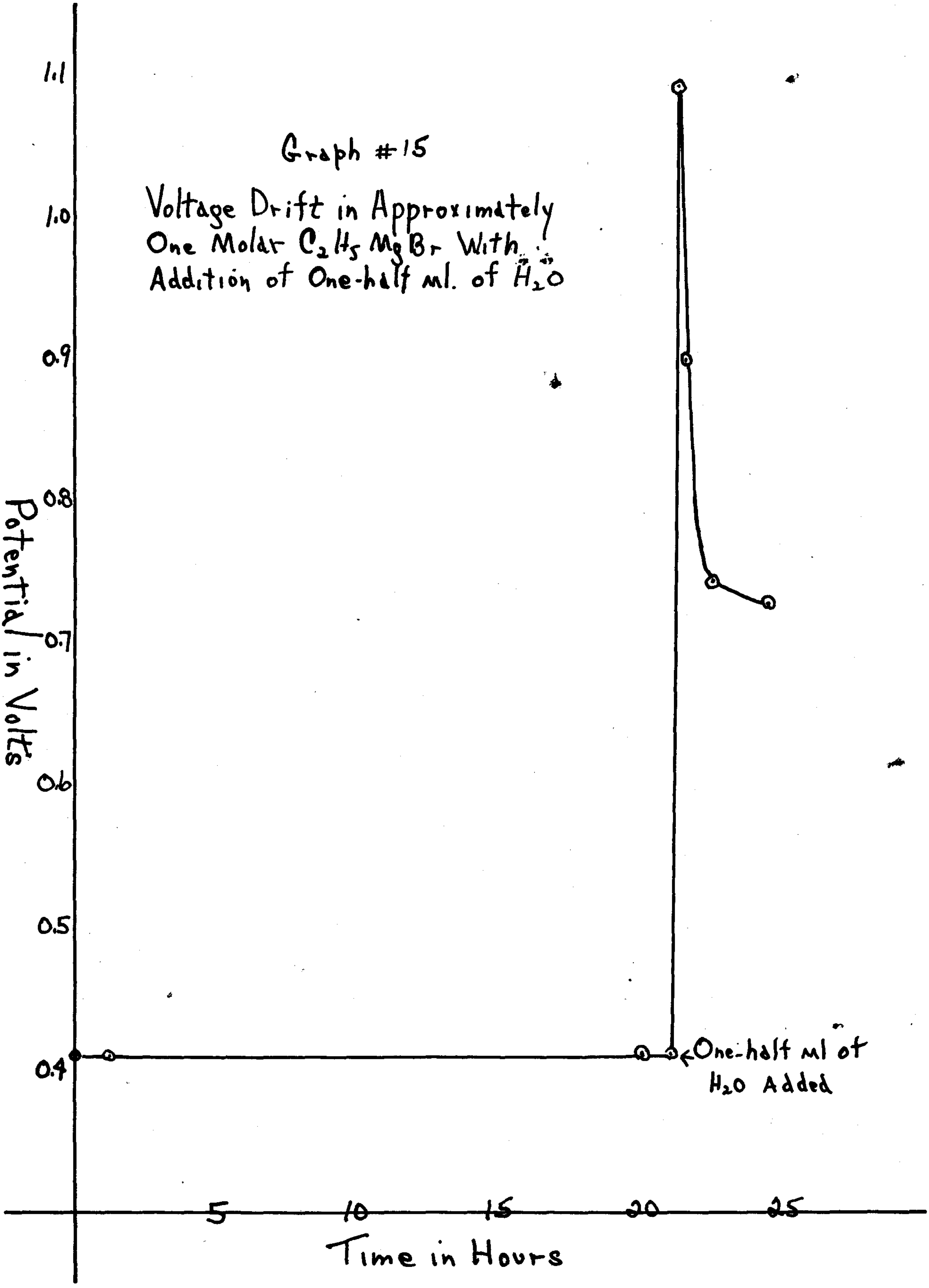
TABLE 15

Voltage drift in approximately one molar ethyl magnesium bromide in anhydrous ether using magnesium and platinum electrodes with the subsequent addition of one-half milliliter of water.

Time in Hours	Temperature °C	Electromotive Force
0:00 *	22	0.41
0:40	22	0.41
1:00	22	0.41
20:00	21	0.41
21:00 **	21	0.41
21:15	21	1.092
21:20	21	1.000
21:30	21	0.900
22:30	21	0.740
24:00	21.5	0.725

* Cell had been previously treated with oxygen gas and flowers of sulfur so the "plateau" voltage of approximately 0.20 to 0.24 volts was not recorded here.

** One half ml. of distilled water added from a pipette to the cell.



Graph #15

Voltage Drift in Approximately One Molar C_2H_5MgBr With Addition of One-half ml. of H_2O

In order to study the effect of the concentration of the Grignard solution on the potential developed at equilibrium a solution of approximately half molar ethyl magnesium bromide in anhydrous ether was prepared. It was desired to prepare 200 ml. of this half molar Grignard solution. 2.5 gms. of magnesium turnings (Eastmann) were added to 170 ml. of anhydrous ether in the reaction flask. The reaction flask carried a freshly sanded magnesium rod electrode as well as the platinum spiral electrode. The system was swept out with dry nitrogen gas. 7.5 ml. of redistilled ethyl bromide in 30 ml. of anhydrous ether (dried over sodium shavings) was added through the dropping funnel. The reaction flask was similar to the flask used in previous preparations. (Fig. 10.)

There was no evidence of an electromotive force being developed before the addition of the ethyl bromide from the dropping funnel. Approximately 10 ml. of the ethyl bromide in anhydrous ether from the dropping funnel was added through the addition tube and although the solution was warmed on an electric hot plate and stirred rapidly there was no evidence of an electromotive force being developed. The Grignard reaction had not started. After one hour of further attempts to activate the reaction between the magnesium and the ethyl bromide a small crystal of iodine was added to serve as a catalyst. On subsequent warming, there was evidence of the Grignard readtion starting and the voltage jumped rapidly to 1.60+ volts. The voltage remained at 1.60+ volts for about ten minutes, then fell rapidly to 1.20 volts. The ethyl bromide was slowly added during a period of approximately one hour and the electromotive force of this cell continued to fall. The voltage fell to a value of 0.46 volts when the stirrer was stopped and the cell was allowed to stand overnight. The next morning the voltage had fallen to 0.216 volts. The stirrer was started and the voltage drifted to an apparent plateau at approximately 0.200 volts. The data are recorded in table 16 and summarized in graph 16.

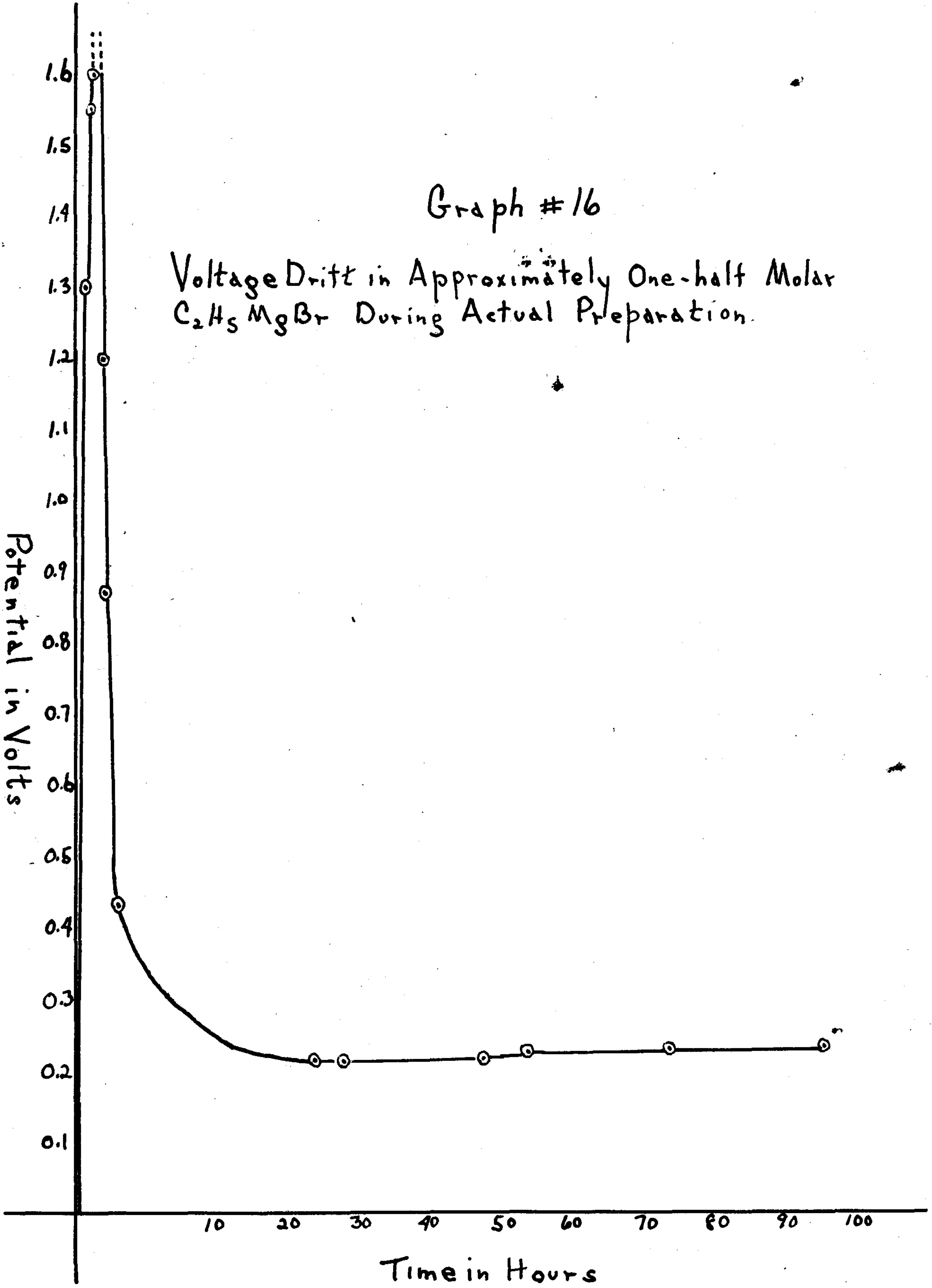
To investigate the effect of various cathode electrodes coupled with the magnesium rod electrode in this approximately half molar ethyl magnesium bromide solution electrodes of tungsten, copper, carbon, and zinc were used. The electromotive force of the cells were studied with a simultaneous check in the same solution of a magnesium platinum system. The "plateau" voltage of the control electrode system varied somewhat during the course of these experiments, but not appreciably, the variance being from 0.215 volts to 0.247 volts.

TABLE 16

Voltage drift during the preparation of approximately half molar ethyl magnesium bromide using platinum and magnesium electrodes.

Time in Hours	Temperature °C.	Electromotive Force
0:00	-	0.000
0:55 *	-	0.000
0:57	-	1.30
1:00	-	1.55
1:15	-	1.60+
1:30	-	1.60+
1:45	-	1.20
1:50	-	1.04
2:00	-	0.87
2:30	-	0.60
3:00	-	0.58
4:00	-	0.57
5:00	-	0.48
6:00	-	0.43
24:15	21	0.216
28:37	21.5	0.215
48:00	20.5	0.220
54:00	21	0.230
72:30	21	0.233
74:00	21	0.236
96:00	22	0.240
144:00	23	0.260

* Some evidence of reaction taking place as indicated by very mild bubbling of a solution.



Graph #16

Voltage Drift in Approximately One-half Molar C_2H_5MgBr During Actual Preparation.

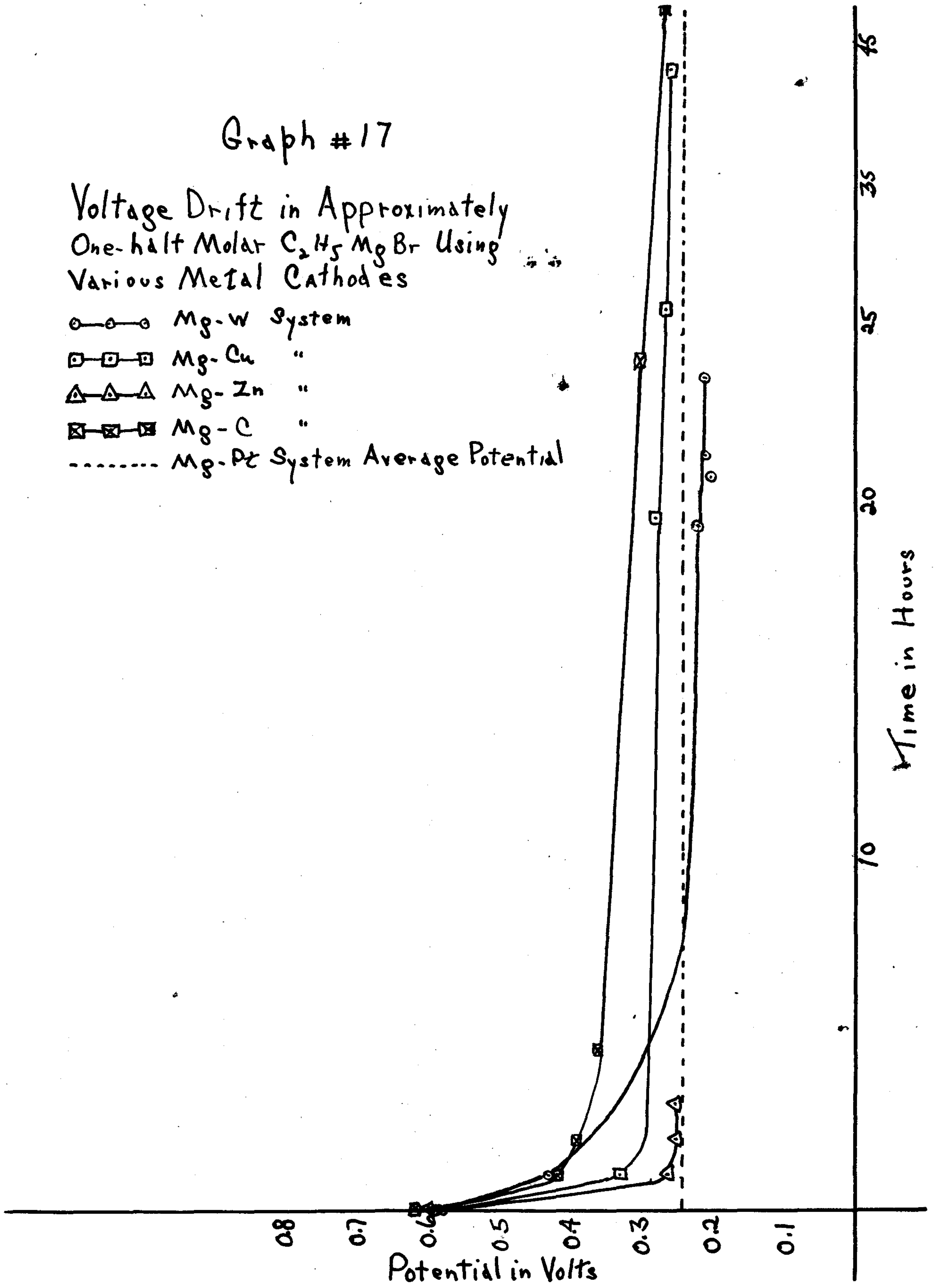
The average voltage of the control electrode system magnesium platinum was approximately 0.24 volts as is shown in graph 17. As a result of this study it seemed to indicate that the potential developed in a Grignard solution may be independent of the cathode material used. In the cells studied all seemed to drift in the direction of the magnesium platinum control system.

Before this solution of approximately one-half molar ethyl magnesium bromide was discarded, it was decided to study the effect of the further addition of redistilled ethyl bromide on the electromotive force developed by the cell. Since the ethyl bromide in former experiments had been introduced through a dropping funnel, it was thought that perhaps some entrapped air may have caused the voltage surge. To avoid the possibility of introduction of air in the system with the introduction of the ethyl bromide an addition tube was used. An 8 mm. glass tube was drawn to a small capillary at one end. Some ethyl bromide was introduced in the tube and then the tube was warmed and some of the ethyl bromide was vaporized. The heavy ethyl bromide vapors displaced the air and while the tube was warm the top of the tube was sealed. This sealed tube was placed in the reaction.

TABLE 17

Voltage drift in approximately one-half molar ethyl magnesium bromide solution using various metals as cathode material. The magnesium platinum electrode system was maintained simultaneously as a control. (Temperature varied between 21°C. and 23°C.)

	Mg-Tungsten System	Mg-Pt System
Time in Hours	Electromotive Force	Electromotive Force
0:00	0.58	
1:00	0.43	
19:15	0.220	0.216
20:45	0.200	0.198
21:15	0.206	0.202
23:30	0.207	0.203
	Mg-Cu System	Mg-Pt System
0:00	0.587	0.220
0:10	0.500	
1:00	0.330	0.206
1:30	0.327	0.205
19:30	0.280	0.215
25:30	0.265	0.230
44:00	0.260	0.235
	Mg-C System	Mg-Pt System
0:00	0.620	0.235
0:30	0.460	0.237
1:00	0.425	0.236
2:00	0.390	0.237
4:30	0.360	
24:00	0.300	0.240
48:00	0.256	0.250
	Mg-Zn System	Mg-Pt System
0:00	0.60	
0:02	0.48	
0:04	0.40	0.246
0:12	0.33	
0:23	0.30	0.247
0:38	0.285	
1:08	0.263	
2:08	0.250	0.247
3:08	0.250	0.247



Graph #17

Voltage Drift in Approximately One-half Molar C_2H_5MgBr Using Various Metal Cathodes flask as shown in Fig. 11. The voltage of the cell was checked and then the addition tube was broken in the cell with the help of the leverage of the stirrer. The weight of the ethyl bromide in the tube was 0.5149 gms. When this sample was broken in the cell, the voltage jumped approximately 0.20 volts, and then fell again to the original voltage after twenty-four hours. Graph 18 drawn from table 18 illustrates these results.

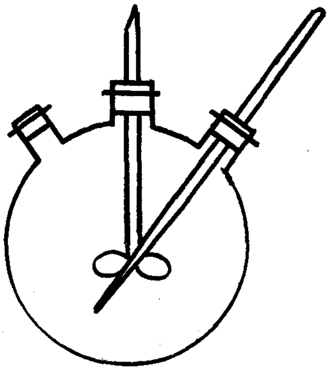


Fig. 11

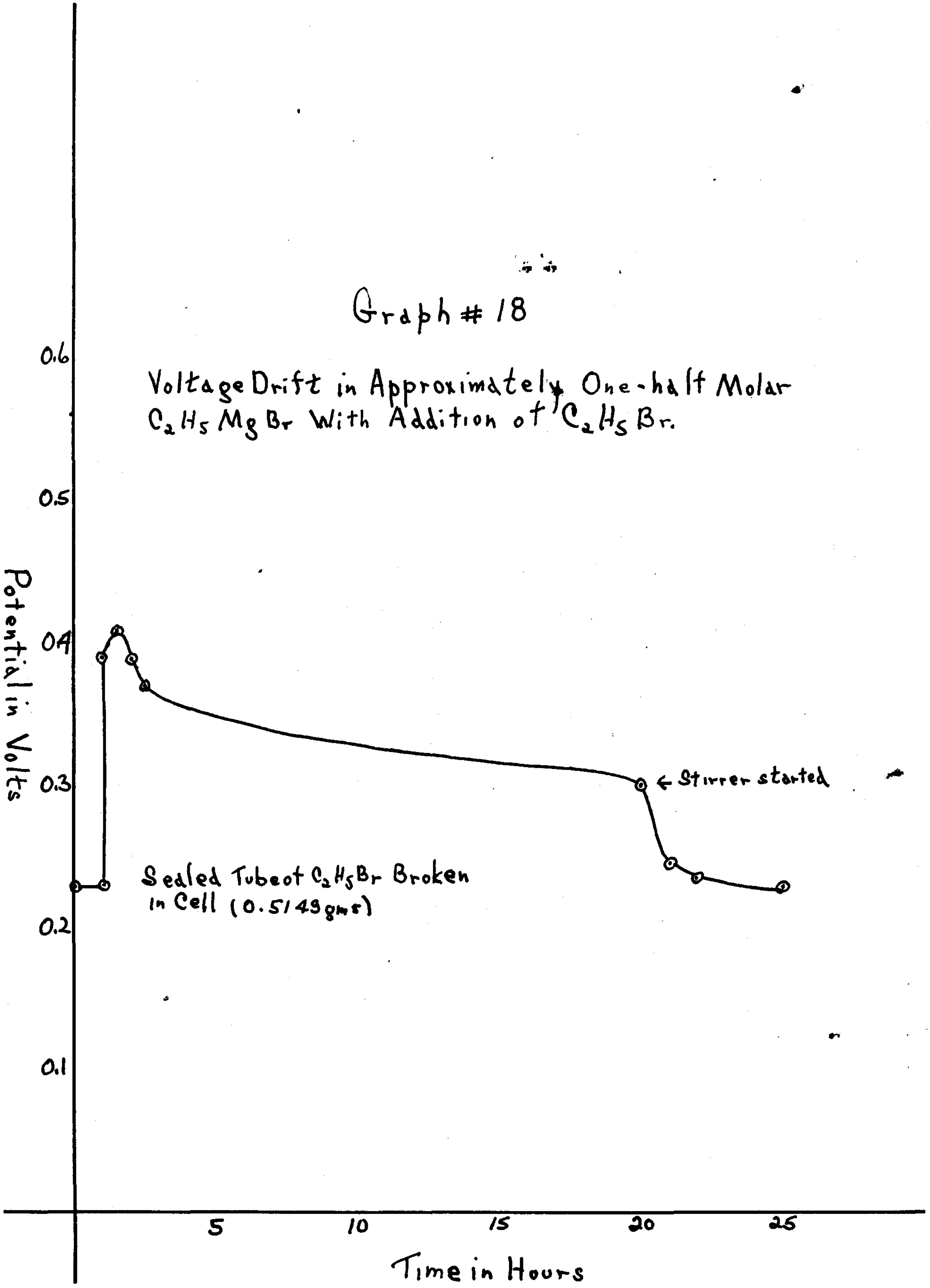
An approximately two molar solution of magnesium ethyl bromide in anhydrous ethyl ether was prepared for further study. Ten grams of magnesium turnings, 200 ml. of anhydrous ether and 30.5 ml. of redistilled ethyl bromide were used. The procedure followed in previous preparations was followed. In this experiment all stoppers used were well rolled corks. In this more concentrated Grignard solution, the reaction took place smoothly without the necessity of a catalytic agent, mere warming being sufficient to to activate the reaction. The electro-

TABLE 18

Voltage drift in approximately one-half molar ethyl magnesium bromide using magnesium and platinum electrodes with subsequent addition of excess ethyl bromide.

Time in Hours	Temperature °C.	Electromotive Force
0:00	22	0.228
0:55 *	21.5	0.230
0:57	21.5	0.390
1:00	21.5	0.400
1:30	21.5	0.410
2:00	21.5	0.390
2:30	21.5	0.370
20:00	20	0.300
21:00	20	0.240
22:00	20	0.235
25:00	20	0.230

* Sealed tube of C_2H_5Br (0.5149 gms.) Broken in reaction flask.



Graph # 18

Voltage Drift in Approximately One-half Molar C_2H_5MgBr With Addition of C_2H_5Br.

motive force of 1.60+ volts did not develop until the Grignard reaction was definitely taking place. The voltage of 1.60+ volts was maintained for approximately twenty minutes and then fell rapidly. The ethyl bromide in anhydrous ethyl ether was added during the course of two hours. The solution of the Grignard reagent was very dark due to colloidal magnesium and the voltage had dropped to 0.51 volts. The solution was allowed to stand overnight and the drift in potential was studied the following day with the stirrer in continuous operation. The potential fell to 0.230 volts. The cell was studied for three more days, and the electromotive force reached a value of 0.2000 volts during the last two days. The "plateau" voltage was the same as that obtained for the one molar and the half molar ethyl magnesium bromide solutions. The data for this experiment are recorded in table 19 and graphed in graph 19.

The magnesium rod and platinum spiral electrodes were left in the solution as control electrodes and various other metal cathodes were introduced to substitute for the platinum electrode. The following electrodes were used as cathodes: aluminum, zinc, carbon, tungsten, and copper. The potential of the cell magnesium versus

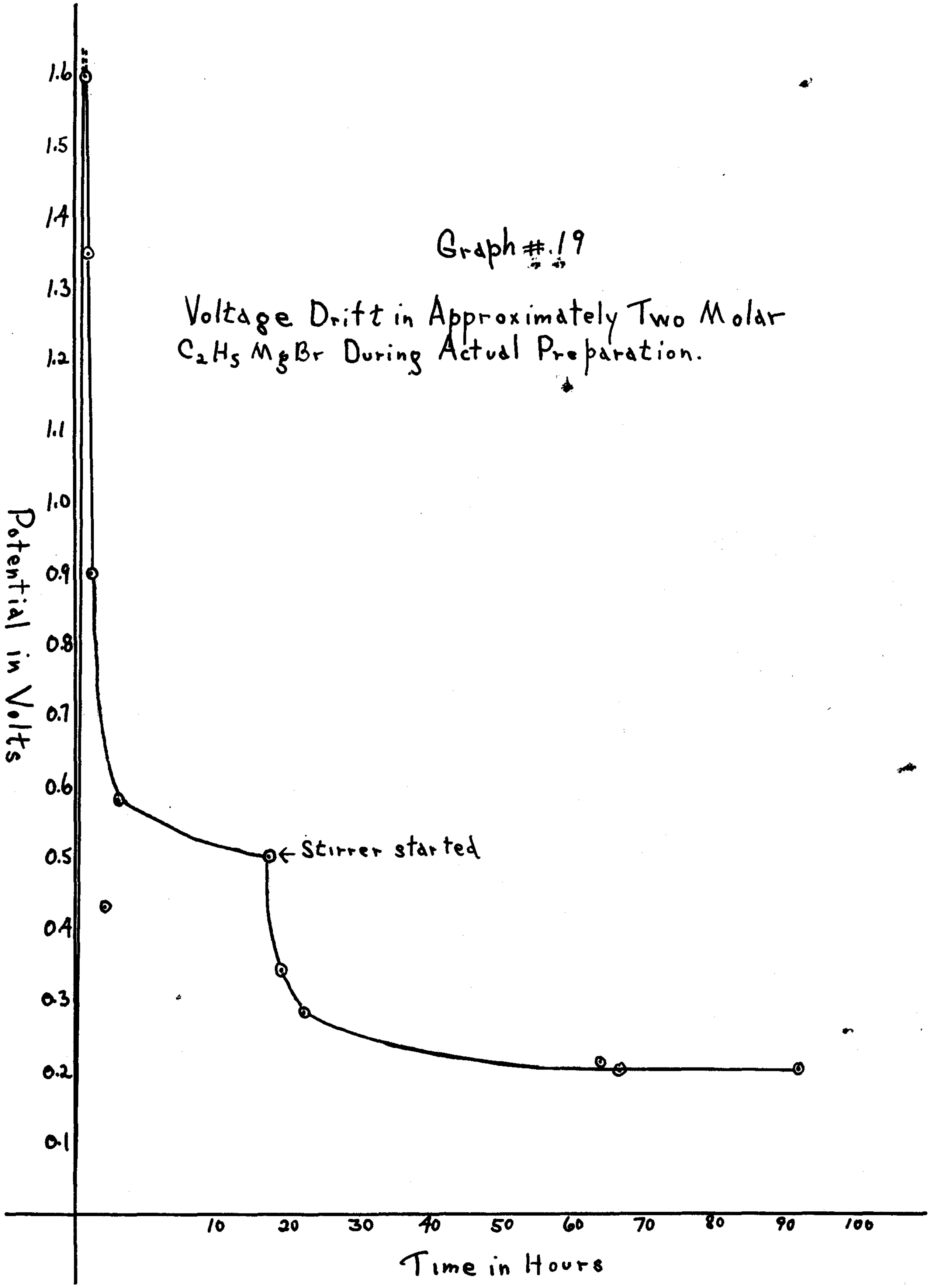
TABLE 19

Voltage drift in approximately two molar ethyl magnesium bromide in anhydrous ethyl ether using magnesium and platinum electrodes. Voltage traced during the Grignard preparation.

Time in Hours	Temperature °C.	Electromotive Force
0:00	-	0.000
0:20	-	0.000
0:26	-	1.60 +
0:31	-	1.60 +
0:50	-	1.60 +
0:53	-	1.35
0:55	-	1.20
1:00	-	0.90
1:30	-	0.58
2:00	-	0.43
2:30	-	0.50
3:00 *	-	0.58
17:05	23	0.50
19:00	23	0.34
21:45 **	23	0.280
64:30	23	0.213
66:45	23	0.200
68:30	25	0.218
91:45	25	0.204

* Cell allowed to stand overnight.

** Cell allowed to stand two days without reading.



Graph #19

Voltage Drift in Approximately Two Molar C_2H_5MgBr During Actual Preparation.

the various metal cathodes followed the same general pattern drifting rapidly to the potential of the control magnesium - platinum system. The results of these experiments are depicted in graph 20, drawn from the data in table 20.

One more check was desired on the voltage drift occurring when approximately one molar ethyl magnesium bromide was prepared in anhydrous ethyl ether. A fresh supply of anhydrous ether was prepared and the reaction flask swept out with dry nitrogen gas. The magnesium and platinum electrodes were sanded to brightness with fine emery paper, wiped clean with a towel and placed in a dessicator over $CaCl_2$ for two hours before insertion in the reaction flask. The stoppers used in this experiment were all cork, well rolled to give air tight closures. The reaction flask carried a magnesium electrode and two platinum electrodes. It was thought wise to use one of the platinum electrodes to study the voltage drift in the cell, and after the cell had reached an equilibrium potential the other electrodes might be used to see if the same potential was obtained. The second platinum electrode merely was allowed to stand in the Grignard solution. The question arose that perhaps

TABLE 20

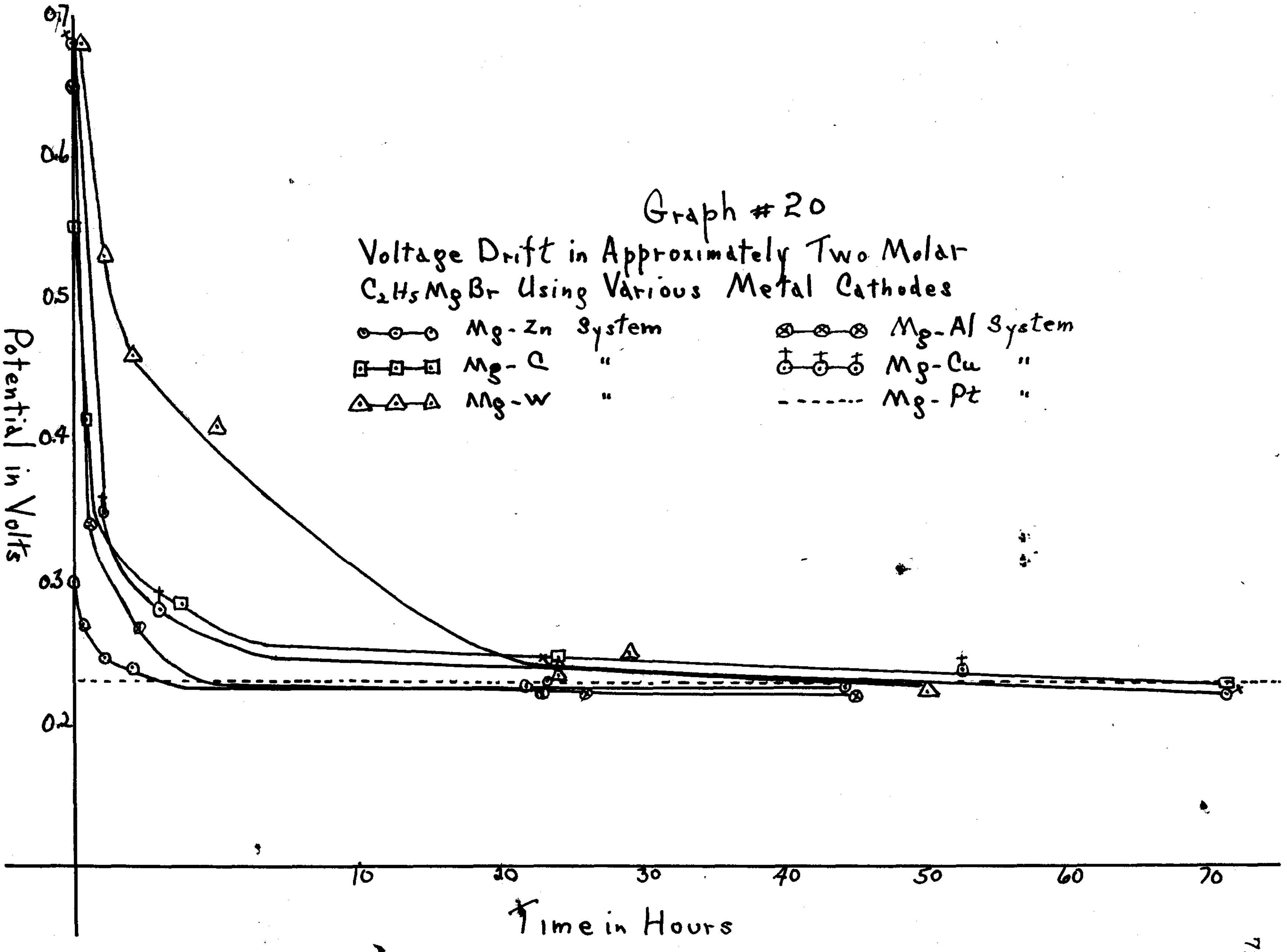
Voltage drift in approximately two molar ethyl magnesium bromide solution in anhydrous ethyl ether using electrodes of magnesium and various metals. The magnesium platinum electrode system was maintained as a control and readings were taken simultaneously using the system magnesium platinum and magnesium metal.

System Mg-Zn			System Mg-Pt		
Time in Hrs.	Temp. °C.	E.M.F.	Time in Hrs.	Temp. °C.	E.M.F.
0:00	25	0.300			
0:05	25	0.280			
0:10	25	0.270	0.10	25	0.225
0:25	25	0.260	0:25	25	0.210
1:05	25	0.247	1:05	25	0.208
1:50	25	0.240	1:50	25	0.205
21:50	26	0.227	21:50	26	0.197
23:50	26	0.230	23:50	26	0.210
44:20	25	0.225	44:20	25	0.225
System Mg-C			System Mg-Pt		
0:00	25	0.55			
0:10	25	0.47	0:10	25	0.238
0:20	25	0.415	0:20	25	0.240
0:45	25	0.285	3:45	25	0.237
24:15	25	0.246	24:15	25	0.220
71:30	25	0.230	71:30	25	0.232
System Mg-W			System Mg-Pt		
0:00	25	0.760			
0:15	25	0.680	0:15	25	0.250
1:00	25	0.530	1:00	25	0.230
2:00	25	0.460	2:00	25	0.226
5:00	25	0.410	5:00	25	0.225
24:10	25	0.233	24:10	25	0.230
29:00	26	0.250	29:00	26	0.226
50:00	26	0.220	50:00	26	0.229

TABLE 20 (cont.)

System Mg-Al			System Mg-Pt		
Time in Hrs.	Temp. °C.	E.M.F.	Time in Hrs.	Temp. °C.	E.M.F.
0:00	26	0.650			
0:05	26	0.510			
0:30	26	0.340			
0:45	26	0.310	0:45	26	0.230
2:15	26	0.267	2:15	26	0.225
22:45	26	0.225	22:45	26	0.230
25:35	26	0.220	25:35	26	0.230
45:45	25	0.218	45:45	25	0.235

System Mg-Cu			System Mg-Pt		
0:00	25	0.680			
0:03	25	0.530			
0:05	25	0.430			
1:00	25	0.350			
1:30	25	0.323	1:30	25	0.248
3:00	25	0.230	3:00	25	0.240
24:00	26	0.243	24:00	25	0.240
26:00	26	0.223	26:00	26	0.220
52:30	27	0.236	52:30	27	0.229
71:50	27	0.224	71:50	27	0.220



Graph #20

Voltage Drift in Approximately Two Molar C_2H_5MgBr Using Various Metal Cathodes the drift in potential might be due to some product of possible slight electrolysis while the cell was being balanced during the many readings. The preparation was similar to those formerly studied. There was no evidence of the development of an electromotive force until there was an indication of the Grignard reaction taking place. The potential jumped to 1.60 + volts and after three minutes fell rapidly. The ethyl bromide was added during the course of one hour and forty minutes to the reaction flask. Within three and one half hours the voltage had fallen to 0.198.

The platinum electrode which had been standing in the solution during the Grignard preparation was now used as a cathode and the electromotive force of the cell measured. The electromotive force of the cell remained practically constant (0.193 volts). This result indicated to us that the drift in potential of the cell was not due to possible electrolysis products being built up on the electrodes during the balancing of the cell with the potentiometer.

The voltage of the cell remained in the neighborhood of 0.2000 volts for over fifty five hours. The data recorded in table 21 are graphed in graph 21.

TABLE 21

Voltage drift in cell of ethyl magnesium bromide (0.71 M) in anhydrous ethyl ether using electrodes of magnesium and platinum.

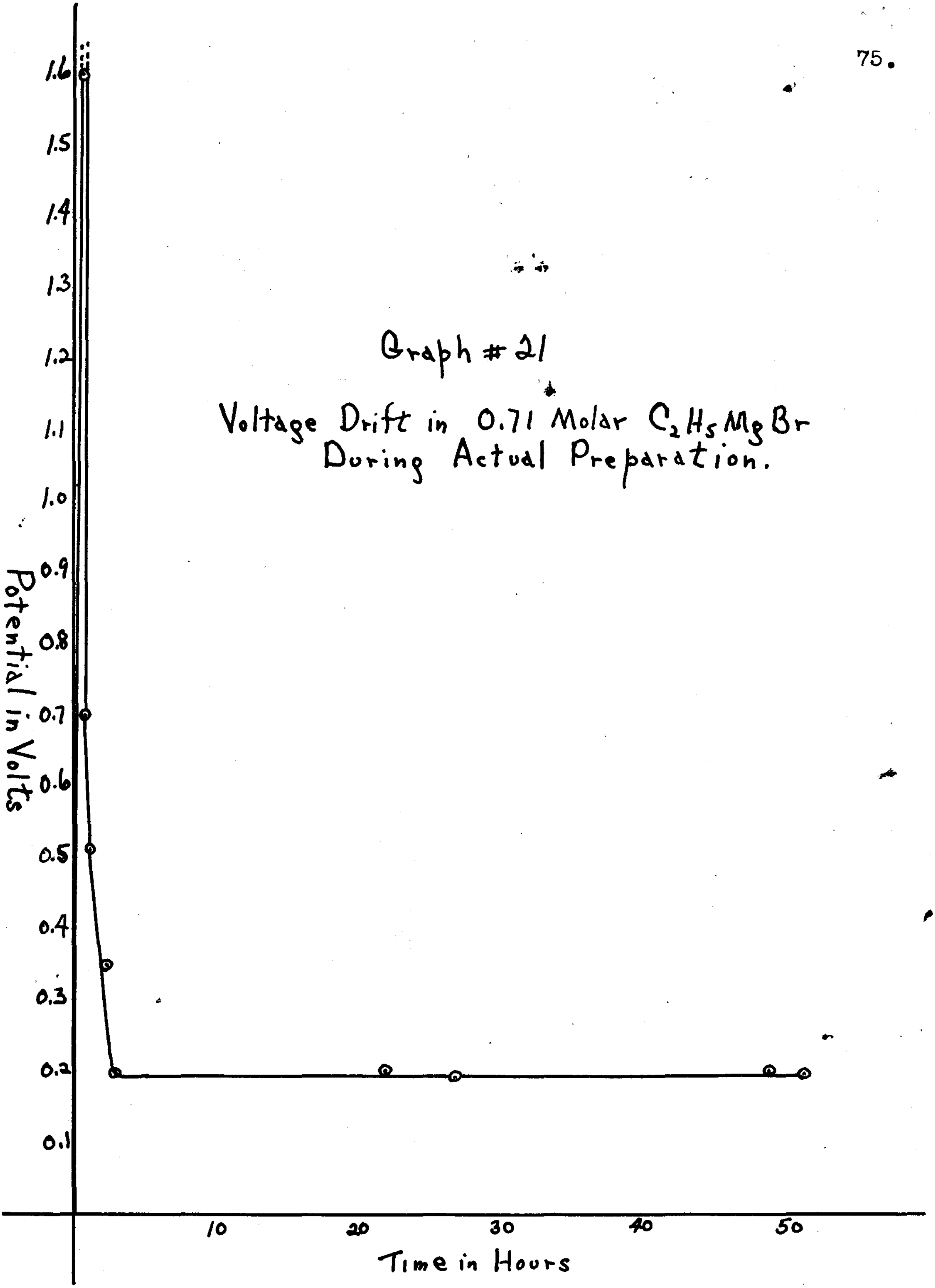
Time in Hours	Temperature °C.	Electromotive Force
0:00	25	0.000
0:07 *	25	0.000
0:18 **	25	0.000
0:21 @	-	1.60
0:24	-	0.70
1:05 @@	-	0.51
1:45	(all C_2H_5Br added)	0.51
2:15	-	0.350
3:00	-	0.196
3:30	-	0.198
22:00	26	0.200
23:00	26	0.200
27:00	26	0.190
49:00	27	0.205
51:30	27	0.196

* 5 to 10 ml. of diluted C_2H_5Br added through dropping funnel.

** Ether solution warmed.

@ Grignard solution reacting definitely.

@@ Grignard solution very dark and colloidal negnesium.



Graph # 21

Voltage Drift in 0.71 Molar C_2H_5MgBr During Actual Preparation.

Various metal electrodes were inserted in the cell as a third electrode probe. The metals used were aluminum wire, and copper wire, size #18, and a zinc strip eledtrode 1.5 cm. x 8 cm. The electrodes were filed and sanded to brightness with emery paper wiped with a towel and stored in a dessicator over $CaCl_2$ until removed for use. The electrodes were inserted as quickly as possible and the voltage drift on the systems Mg-Cu, Mg-Zn, and Mg-Al studied. The cell Mg-Pt was read generally either just before or after the voltage of the others were recorded. The voltage of the Mg-Pt system remained practically constant through these determinations and the electromotive force of the other cells drifted to the equilibrium or plateau voltage of the Mg-Pt system. Data from table 22 illustrated in graph 22 depict these findings.

A sample of the approximately one molar ethyl magnesium bromide was removed and analyzed by the titration method of Gilman.[1.] The ethyl magnesium bromide had been standing in contact with excess magnesium for six days with intermittent stirring. The analysis indicated a molarity of 0.71. The reaction was only 70% complete on the basis of the expected one molar preparation.

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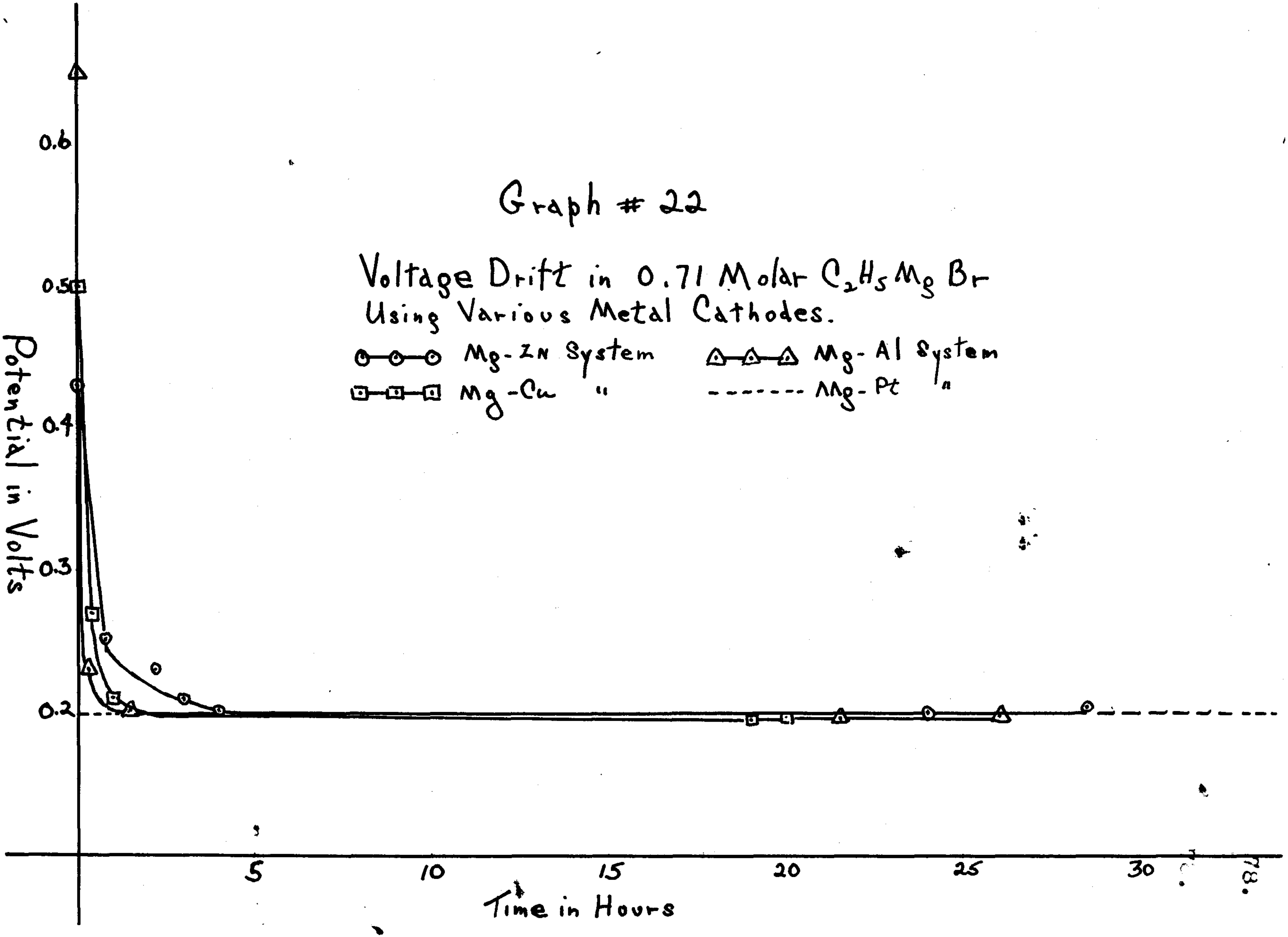
TABLE 22

Voltage drift in cell of (0.71 M) molar ethyl magnesium bromide in anhydrous ethyl ether using magnesium and various metal electrodes. The magnesium platinum electrode system was kept as a control electrode pair.

	Mg-Cu System			Mg-Pt System	
Time in Hours	Temp. °C.	E.M.F.	Time in Hours	Temp. °C.	E.M.F.
0:00	26	0.500	0:00	26	0.198
0:02	26	0.430			
0:12	26	0.270			
1:00	26	0.210	1:00	26	0.198
19:00	26	0.194	19:00	26	0.200
20:00	26	0.198	20:00	26	0.200
	Mg-Zn System			Mg-Pt System	
0:00	25	0.430	0:00	25	0.200
0:47	25	0.250			
2:10	26	0.230	2:10	26	0.200
3:00	26	0.210			
4:00	26	0.200			
24:00	27	0.200			
28:30	27	0.206	28:30	27	0.196
	Mg-Al System			Mg-Pt System	
0:00	26	0.650	0:00	26	0.200
0:10	26	0.300			
0:15	26	0.230			
1:30	26	0.200	1:30	26	0.190
21:30	27	0.194			
26:00	27	0.198	26:00	26	0.200

Graph # 22

Voltage Drift in 0.71 Molar C_2H_5MgBr Using Various Metal Cathodes.



CHAPTER IV

EXPERIMENTAL STUDIES WITH N-PROPYL MAGNESIUM BROMIDE SOLUTIONS

A further study of the voltage drift in a one-half normal propyl magnesium bromide solution in anhydrous ethyl ether was attempted. It was thought that the effect of the n-propyl group might influence the equilibrium voltage of the cell and throw some insight into the relative electronegativity of the ethyl and n-propyl radicals.

An approximately one-half molar solution of n-propyl magnesium bromide was prepared in anhydrous ethyl ether using the previously described techniques. N-propyl bromide (Eastman) was redistilled collecting the fraction boiling between 71° and 72° C. for use.

The voltage of the cell was found to be 0.0000 before the addition of the n-propyl bromide. Approximately 5 - 10 ml. of the n-propyl bromide (9.1 ml. of C_3H_7 Br in 25 ml of ether) was added and the voltage remained 0.0000. After standing for one hour a slight white precipitate was in evidence around the magnesium turnings in the reaction flask. The solution took on a gray opaqueness and the voltage jumped to 1.604 volts, and there was definite indication of the Grignard reaction taking place. The voltage remained in the range of 1.60+volts for approximately twelve minutes and then fell rapidly within the next two hours to 0.76 volts. The voltage continued to drift slowly for eleven days when a plateau or equilibrium potential of approximately 0.22 volts was attained. The results are illustrated in graph 23 drawn from table 23.

Various metal poles were inserted in the cell to be used as cathodes to study the effect, if any, of interchanging a copper, zinc, or aluminum electrode for the platinum electrode used. The platinum electrode remained in the solution so that a control Mg-Pt voltage could be checked against the various other Mg-metal pairs. In this experiment difficulty was encountered in the drift of the Mg-Cu system. After 91:30 hours the Mg-Cu cell was shorted for one hour and permitted to stand over the week-end. The voltage after shorting for the one hour period was found to be 0.050 volts. The voltage rose to 0.230 and remained at 0.230 volts for twenty-four hours.

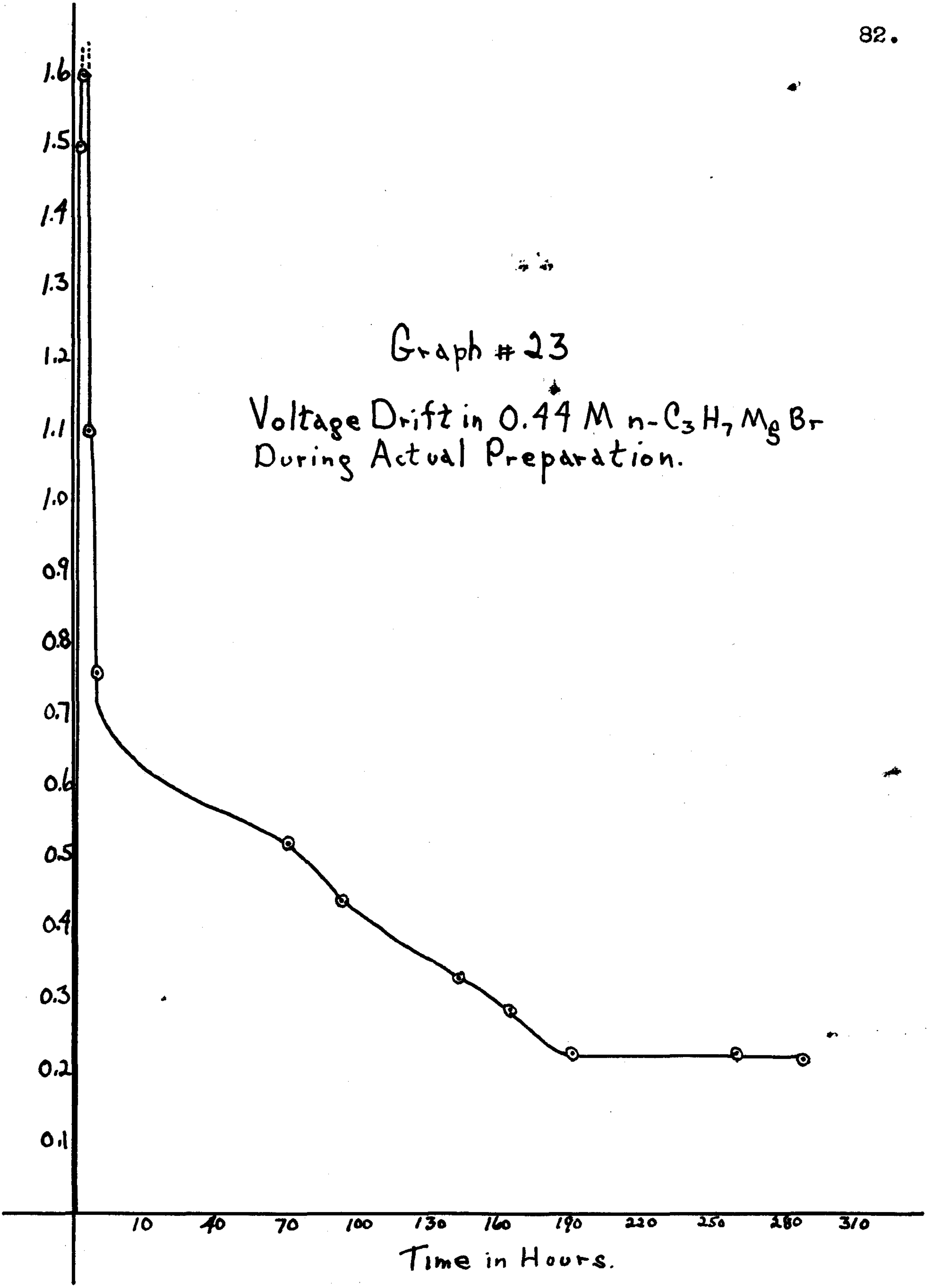
The data which again seemed to indicate that the voltage developed in this Grignard solution is independent of the cathodes used so far, namely platinum, copper, aluminum, and zinc, are listed in table 24 and graphed in graph 24.

TABLE 23

Voltage drift in 0.44 M solution of n-propyl magnesium bromide in anhydrous ethyl ether using magnesium and platinum electrodes.

Time in Hours	Temperature °C.	Electromotive Force
0:00	15	0.000
0:05 *	15	0.000
0:30	16	0.000
1:02 **	-	1.500
1:08	-	1.58
1:15	-	1.60+
1:20	-	1.60+
1:23 ***	-	1.20
1:30	-	1.10
1:55	-	0.92
2:35	-	0.85
3:00	-	0.80
3:30	-	0.76
71:00	20	0.52
71:10 @	20	0.52
94:00	24	0.44
143:00	26	0.33
166:00	25	0.29
192:00	23	0.228
263:00	24	0.230
290:00	25	0.220

* 5 ml. of C_3H_7Br in anhydrous ether added.
** Evidence of Grignard reaction starting.
*** All C_3H_7Br in anhydrous ether now added.
@ Mg electrode cleaned and reinserted.



Graph #23

Voltage Drift in 0.44 M $n-C_3H_7MgBr$ During Actual Preparation.

TABLE 24

Voltage drift in 0.44 M n-propyl magnesium bromide solution using various metal probes as cathodes. The magnesium platinum couple was maintained as a control electrode pair with an average voltage of 0.240.

Mg-Cu System

Time in Hrs.	Temp. °C.	E.M.F.
0:00	25	1.10
0:15	25	0.80
0:30	25	0.70
1:00	25	0.60
3:00	25	0.52
7:00	25	0.45
19:45	25	0.43
43:30	26	0.40
67:30	26	0.40
91:30	24	0.39
139:00	20	0.230
163:00	22	0.230

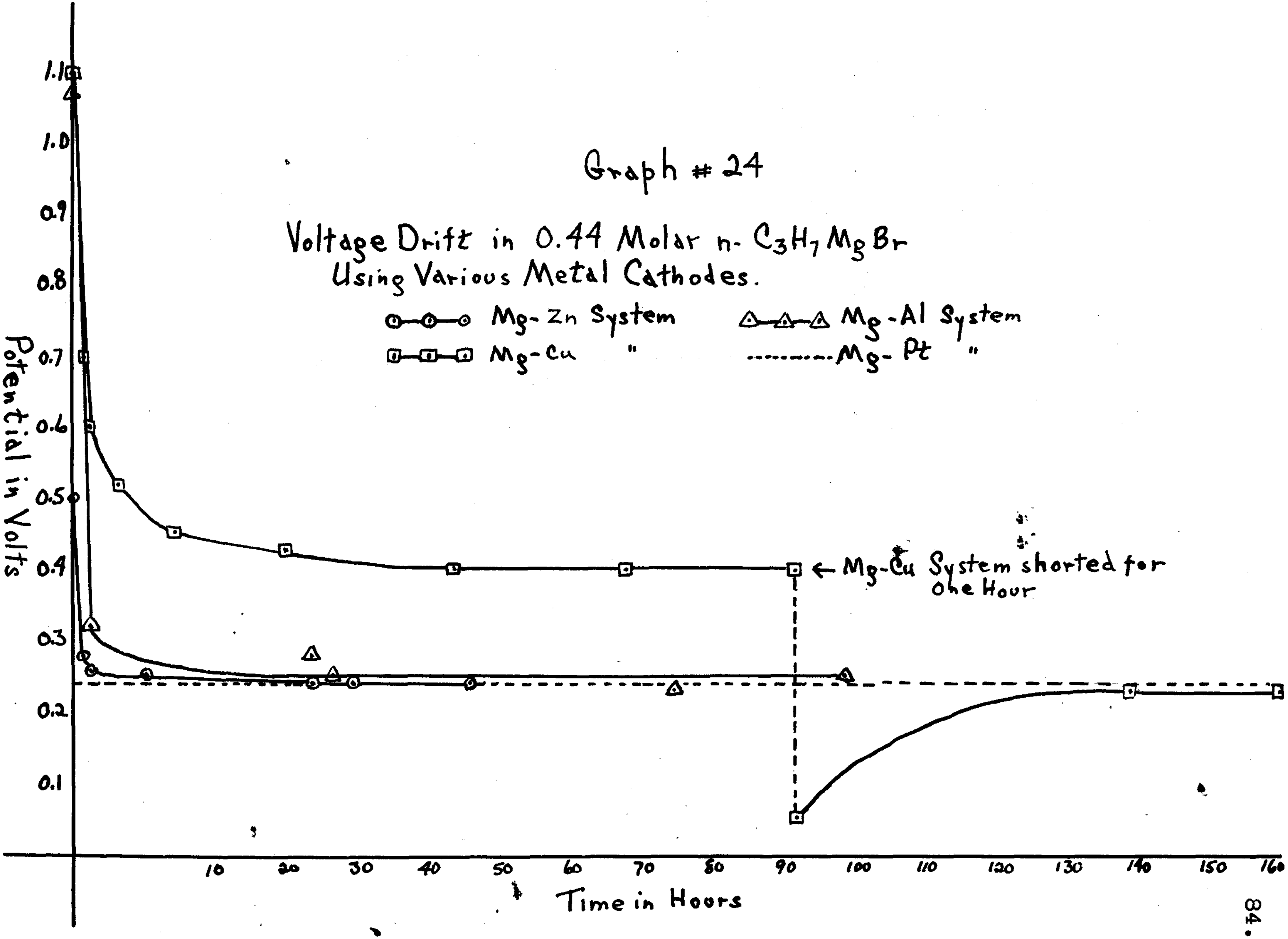
Mg-Zn System

Time in Hrs.	Temp. °C.	E.M.F.
0:00	24	0.500
0:05	24	0.42
0:40	24	0.280
2:00	24	0.260
5:00	24	0.254
23:33	26	0.240
29:00	26	0.240
45:30	25	0.240

Mg-Al System

Time in Hrs.	Temp. °C.	E.M.F.
0:00	25	0.07
0:05	25	0.92
0:10	25	0.72
1:00	25	0.32
1:30	25	0.30
23:30	26	0.280
26:30	23	0.250
74:30	21	0.230
98:30	25	0.250

* Mg-Cu electrode system shorted for one hour and the E.M.F dropped to 0.050 volts. Cell was allowed to stand over week-end.



Graph # 24

Voltage Drift in 0.44 Molar n- C_3H_7MgBr Using Various Metal Cathodes.

To study the effect of an addition of a small quantity of n-propyl bromide to a cell near the equilibrium or plateau voltage the pole electrodes were removed from the above cell. 0.3912 gms of redistilled n-propyl bromide wereintroduced into the cell by the technique previously described in Fig. 11. The voltage of the cell was approximately 0.275 volts before the sample of n-propyl bromide was broken in it and then jumped rapidly to 0.46 volts in a period of three minutes and continued to rise until a value of 0.700 volts had been attained and then the E.M.F. fell. This result is similar to those previously studied in the ethyl magnesium bromide cells. The data in table 25 depicts these results in graph 25.

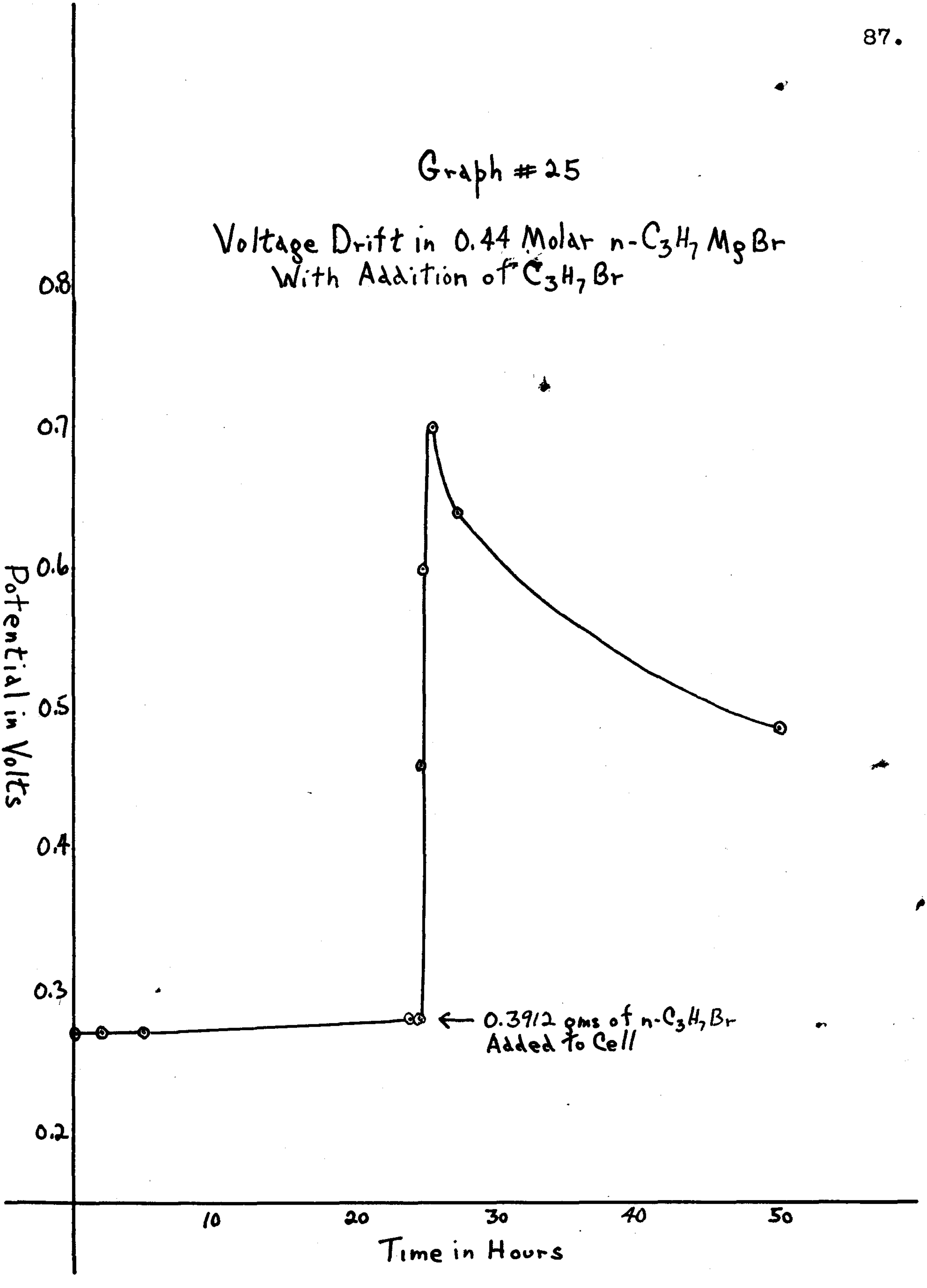
The reaction cell was set up following previously discussed techniques and an approximately one molar solution of n-propyl magnesium bromide in anhydrous ethyl ether was prepared. No voltage was in evidence until the Grignard solution had started working. The voltage jumped to 1.60+ and then fell rapidly to 0.620 volts. The required amount of n-C_3H_7Br was added through the dropping funnel during the course of three hours. The stirrer was stopped and the solution allowed to stand overnight. The following day the voltage of the cell continued to fall until a plateau

TABLE 25

Voltage drift in cell of n-propyl magnesium bromide in anhydrous ether using magnesium and platinum electrodes with subsequent addition of a small excess of n-propyl bromide.

Time in Hours	Temperature °C	Electromotive Force
0:00	20	0.270
2:00	23	0.272
5:00	24	0.270
24:00	22	0.280
24:30 *	22	0.280
24:33	22	0.460
24:35	22	0.590
24:40	22	0.600
24:50	22	0.600
25:15	24	0.700
27:00	24	0.640
50:00	24	0.490

* Small quantity of n-C_3H_7Br added (0.3912 gms.)



Graph #25

Voltage Drift in 0.44 Molar n-C_3H_7MgBr With Addition of C_3H_7Br

← 0.3912 gms of n-C_3H_7Br Added to Cell had been reached in the neighborhood of 0.240 volts. A sample of the solution was withdrawn for analysis according to the method of Gilman[1] and found to be 0.87 M instead of approximately one molar as anticipated. The fall in potential with time for this cell is shown in graph 26 drawn from data in table 26.

Zinc, copper and aluminum electrodes were substituted for the platinum electrode as the cathode in the Mg-Pt couple. The Mg-Pt couple was kept in the same solution as a control electrode pair. The results of this study seemed to verify previous findings that the potential of these Grignard cells studied is independent of the metal coupled with magnesium in the electrode system. The data are listed in table 27 and graphed in graph 27.

A similar experiment was performed with a solution of n-propyl magnesium bromide prepared so that the concentration of the Grignard solution would approximate two molar. The voltage of the cell remained at 0.000 until definite evidence of the Grignard reaction was apparent. The voltage then jumped to 1.60+ and remained in this vicinity for approximately ten minutes and then fell

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[1] J. Am. Chem. Soc., 45, 150 (1923)

TABLE 26

Voltage drift in 0.87 M n-propyl magnesium bromide in anhydrous ethyl ether using electrodes of magnesium and platinum.

Time in Hours	Temperature °C.	Electromotive Force
0:00	-	0.000
0:20 *	-	0.000
0:30 **	-	0.000
1:00	-	0.000
2:00 ***	-	1.60 +
3:00	-	1.60 +
3:15	-	0.24
3:30	-	0.90
4:00	-	0.81
5:00 @	-	0.78
6:00	-	0.62
24:00 @@	17	0.61
26:00	17	0.38
29:00	19	0.27
53:00	19	0.258
76:00	19	0.240
99:00	20	0.237
124:00	19	0.240

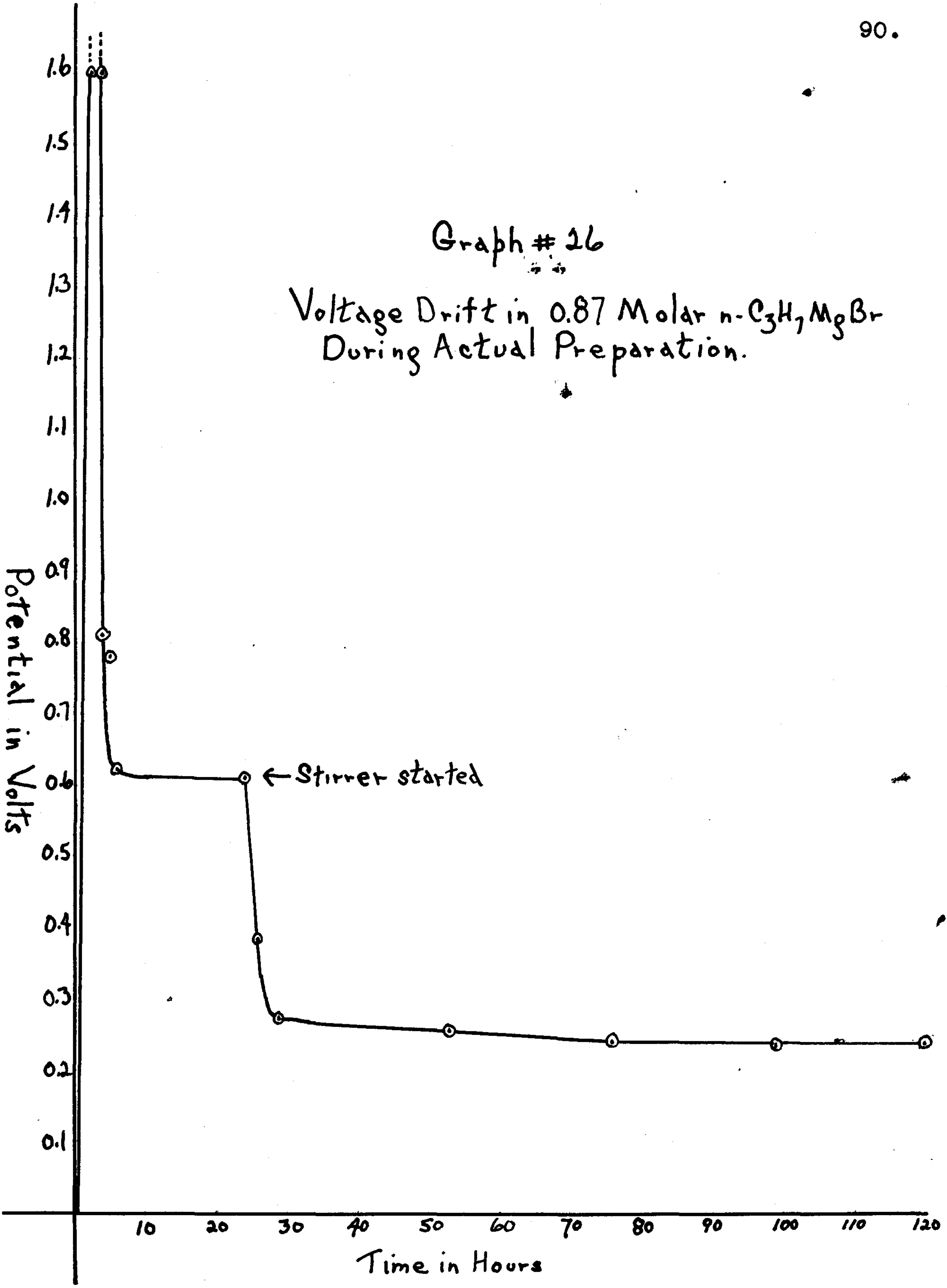
* 3 ml of n C_3H_7Br in ether solution added.

** Solution warmed until gentle reflexing took place.

***Evidence of Grignard reaction starting.

@ All the required C_3H_7Br added.

@@ Stirrer started.



Graph #26

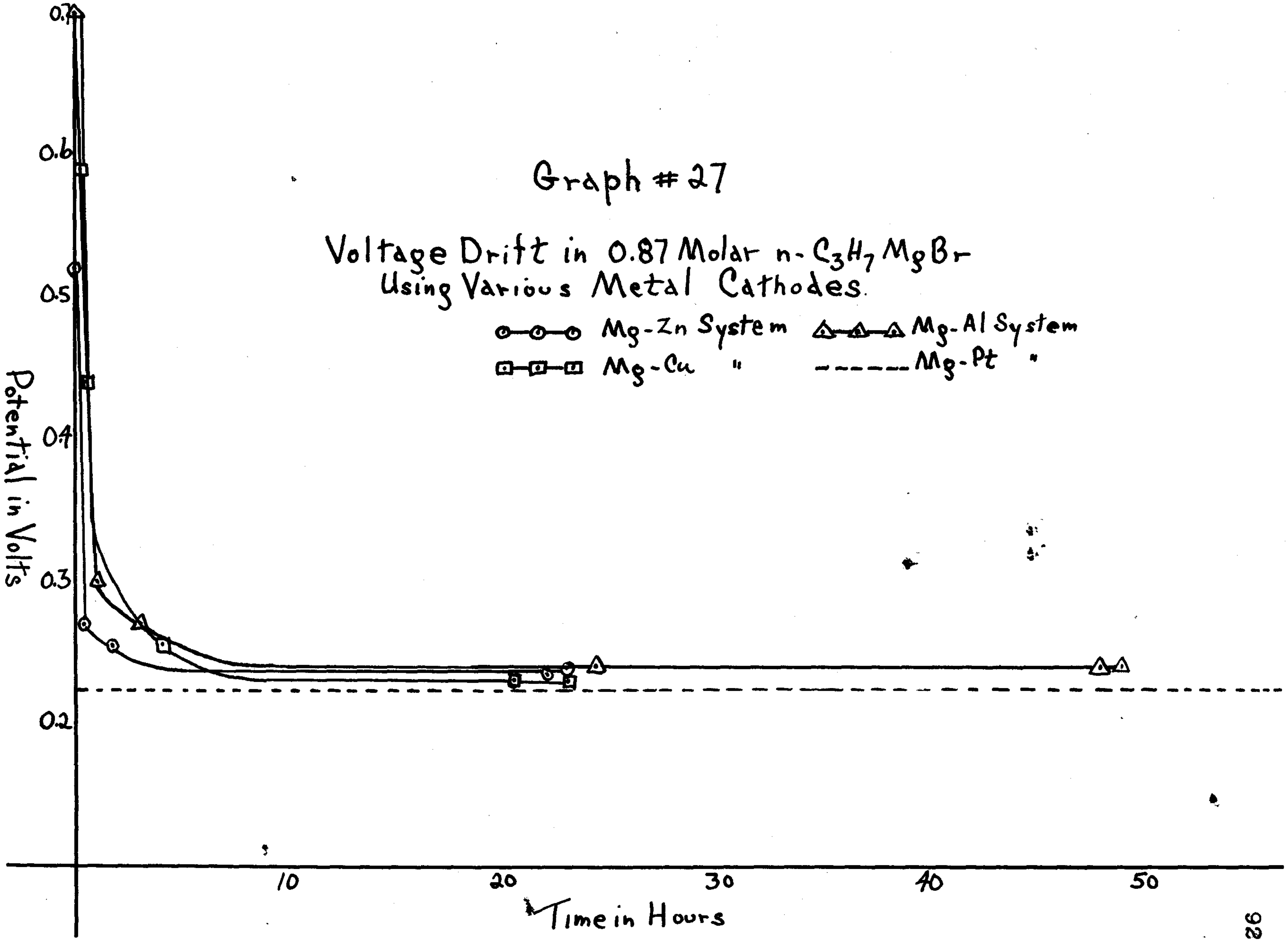
Voltage Drift in 0.87 Molar n-C_3H_7MgBr During Actual Preparation.

TABLE 27

Voltage drift in 0.37 M n-propyl magnesium bromide in anhydrous ether using various metal electrode systems with a magnesium platinum electrode pair as a control electrode system.

Mg-Cu System			Mg-Zn System		
Time in Hrs.	Temp. °C.	E.M.F.	Time in Hrs.	Temp. °C.	E.M.F.
0:00	20.3	1.02	0:00	19	0.520
0:05	20.3	0.59	0:05	19	0.330
0:10	20.3	0.54	0:18	19	0.270
0:30	20.3	0.44	1:45	19	0.253
1:00	20.3	0.41	20:30	19	0.230
4:00	20.3	0.255	21:30	19	0.230
21:30	20	0.230	22:00	19	0.235
23:30	20	0.230	23:00	19	0.240

Mg-Al	System	
0:00	19	0.70
0:03	19	0.51
0:07	19	0.38
0:45	19	0.30
1:06	18.5	0.29
3:00	19	0.27
24:15	20	0.240
25:00	20	0.232
48:00	20	0.240
49:00	20.3	0.238



Graph # 27

Voltage Drift in 0.87 Molar n-C_3H_7MgBr Using Various Metal Cathodes rapidly until an equilibrium or plateau voltage of approximately 0.200 volts was obtained. A sample of the solution was removed and analyzed in accordance with the titration method recommended by Gilman[2] and found to be 1.69 molar instead of the anticipated molarity of two. Apparently the reaction had not gone to completion. The data in this experiment are recorded in table 28 and graphed in graph 28.

Probes of zinc, copper and aluminum were again used as cathode material with the usual Mg-Pt system as a control electrode pair. The average Mg-Pt voltage during these experiments was approximately 0.21 volts. The various cathodes listed above when coupled with the magnesium electrode as an anode showed a characteristic voltage drift which eventually approximated the voltage of the Mg-Pt electrode system. The Mg-Cu couple which was approaching the Mg-Pt control voltage slowly was shorted for approximately fifteen minutes. The voltage fell to 0.090 volts and then rose to the control voltage of the Mg-Pt system and remained there for two days. The data for these experiments are recorded in table 29 and the results illustrated in graph 29.

To study the effect of the addition of a small quantity

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[2] J. Am. Chem. Soc., 45, 150 (1923)

TABLE 28

Voltage drift in 1.69 M n-propyl magnesium bromide in anhydrous ethyl ether using magnesium and platinum electrodes.

Time in Hours	Temperature °C.	Electromotive Force
0:00	23	0.000
0:20 *	23	0.000
1:15	23	0.000
1:22 **	-	1.60 +
1:30	-	1.60 +
1:32	-	1.15
1:35	-	1.00
2:00 ***	-	0.66
3:00	-	0.75
4:00	-	0.75
4:30 @	-	0.75
5:00	-	0.675
5:15	23	0.665
23:35 @@	25	0.660
23:30	25	0.590
30:00	25	0.220
47:10	25.5	0.200
51:30	25	0.190
72:00	25	0.193
73:30 @@@	25	0.205

* A few ml of C_3H_7Br in ether added (36 ml of C_3H_7Br +20 ml of ether.)

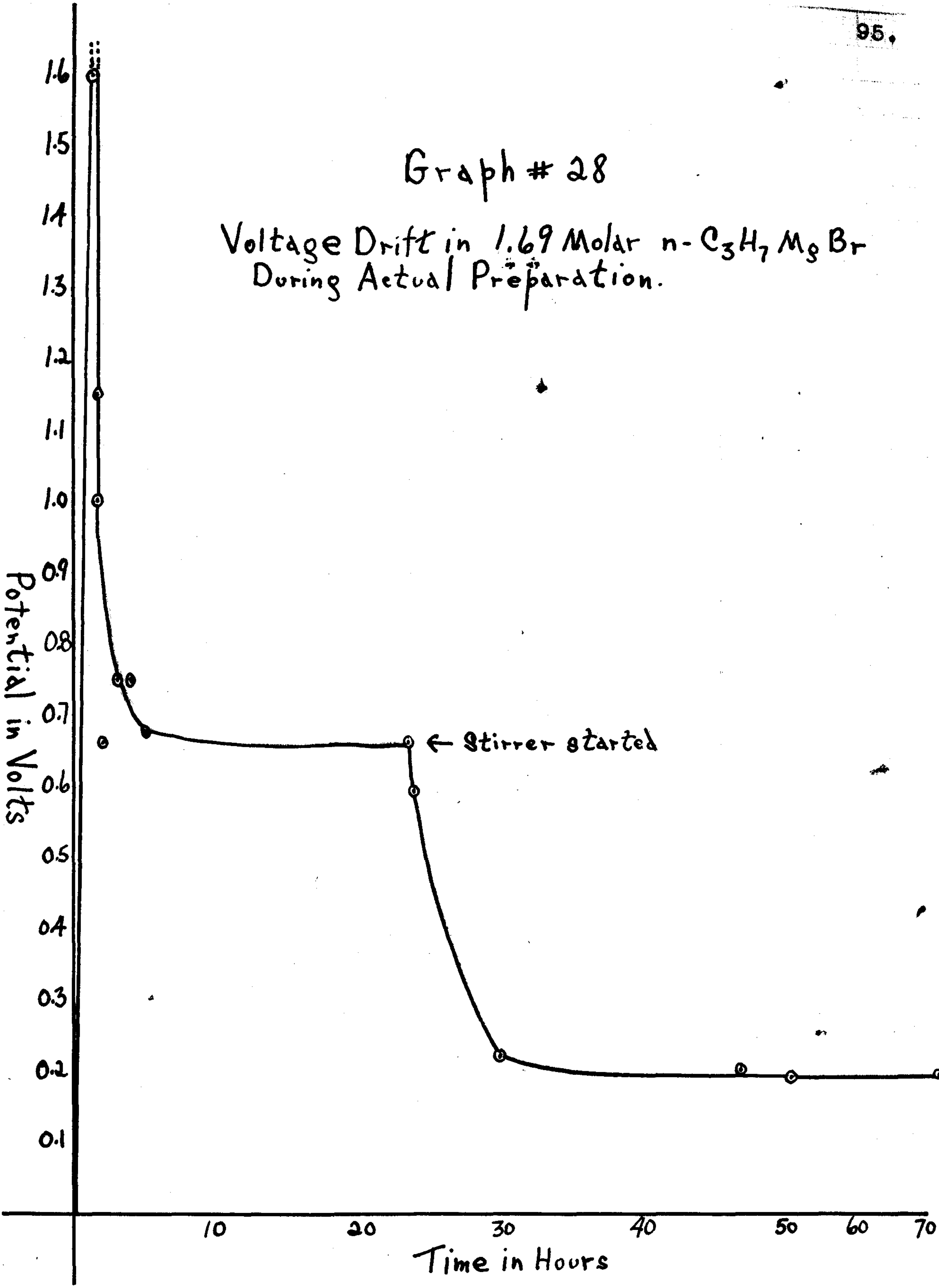
** Solution warmed, Grignard solution started.

*** Solution darkening, evidence of colloidal magnesium.

@ All necessary C_3H_7Br added.

@@ Stirrer started.

@@@ Sample taken for analysis



Graph # 28

Voltage Drift in 1.69 Molar n-C_3H_7MgBr During Actual Preparation.

TABLE 29

Voltage drift in 1.69 M n-propyl magnesium bromide solution using various metals as cathodes (zinc, copper and aluminum) and maintaining the magnesium platinum electrode system as a control electrode pair.

Zn-Mg-System

Time in Hrs.	Temp. °C.	E.M.F.
0:00	25.5	0.300
0:13	25.5	0.270
0:15	25.5	0.250
2:25	25.5	0.235
3:25	25.5	0.240
21:55	25.	0.230
23:55	25.	0.222
26:25	25.	0.217

Al-Mg System

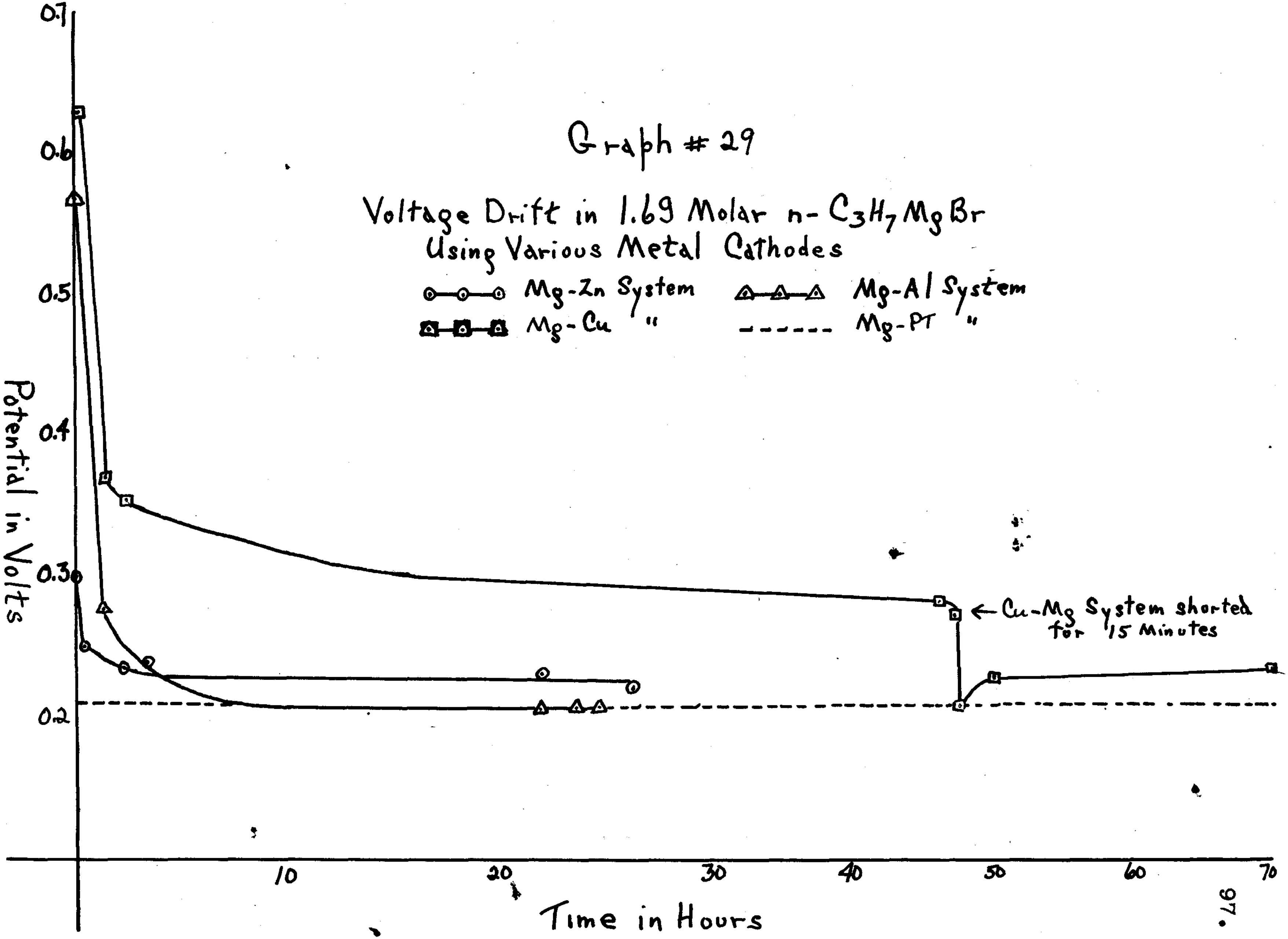
Time in Hrs.	Temp. °C.	E.M.F.
0:00	25	0.800
0:04	25	0.570
0:06	25	0.470
0:10	25	0.370
0:20	25	0.330
0:40	25	0.300
1:20	25	0.277
21:55	24	0.204
22:40	24	0.200
23:40	24	0.205
24:40	24	0.206

Cu-Mg System

0:00	19	0.800
0:02	19	0.630
0:20	19	0.480
1:20	19	0.370
2:20	19	0.355
46:20	20	0.280
47:20 *	20	0.270
48:20	20	0.206
49:50	20	0.230
71:20	20	0.236

Average electromotive force of Mg-Pt control electrode system during these readings was 0.2100 volts.

* Copper magnesium electrodes shorted for 15 minutes.



Graph # 29

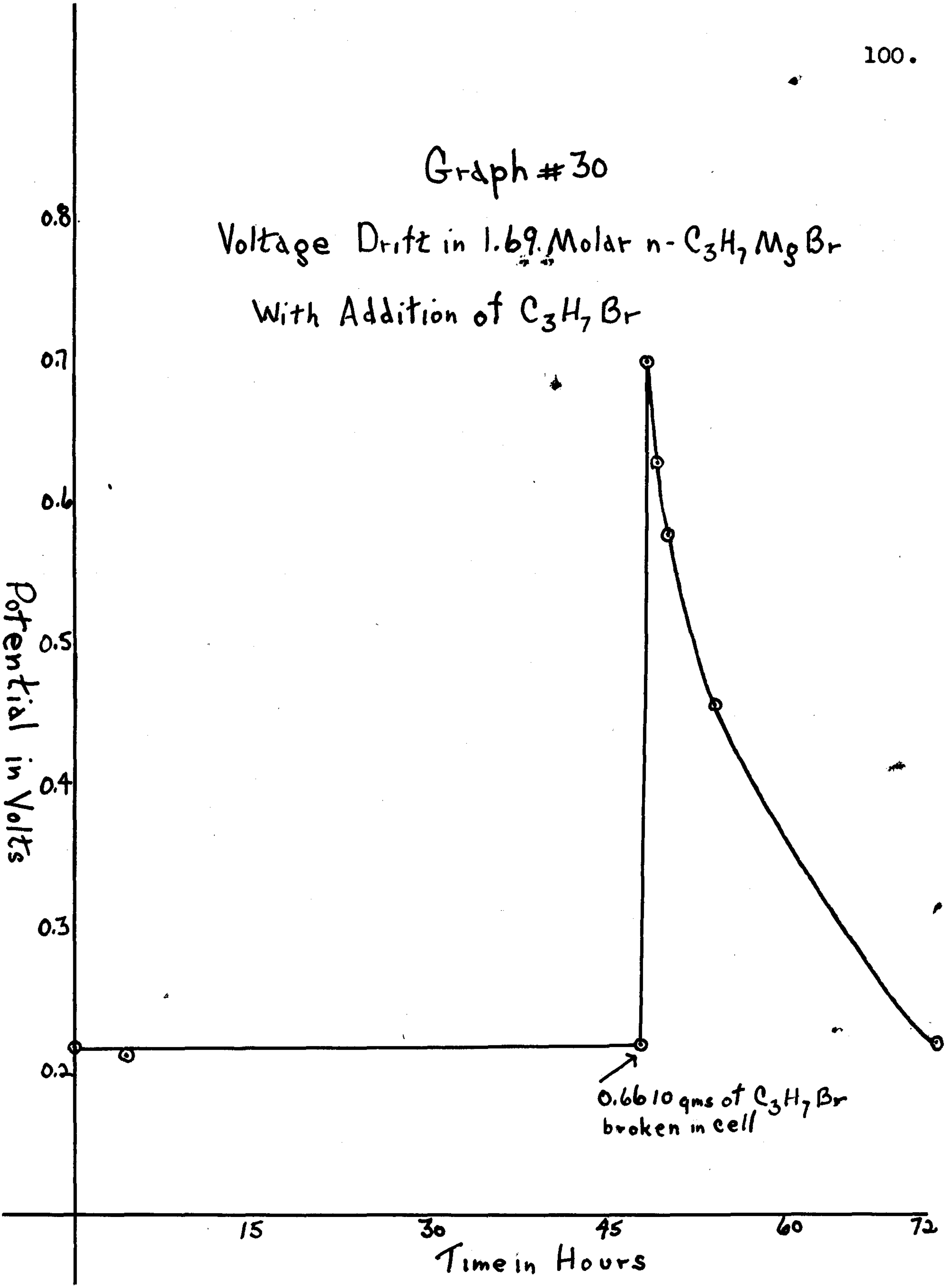
Voltage Drift in 1.69 Molar n-C_3H_7MgBr Using Various Metal Cathodes of n-propyl bromide on the 1.69 molar cell at equilibrium voltage, a small quantity of n-C_3H_7Br was weighed out. 0.6610 grams were weighed out and sealed in a tube free from air, and introduced into the cell by means of the technique previously described. (Fig. 11.) The Mg-Pt electrode system had been at a voltage of approximately 0.220 for two or three days when the sample of n-C_3H_7Br was introduced. The voltage jumped to 0.7000 volts within five minutes and then drifted to the equilibrium voltage of 0.223 again in about twenty four hours. It is interesting to note that the Mg-Pt electrode system was shorted for a period of forty minutes. The voltage dropped to 0.05 volts but climbed back to 0.230 volts again in a period of about six hours. The results of the effect of the addition of n-C_3H_7Br to this cell are tabulated in table 30 and depicted in graph 30.

TABLE 30

Voltage drift on the addition of 0.6610 grams of n-propyl bromide to cell of 1.69 M n-propyl magnesium bromide using electrodes of magnesium and platinum.

Time in Hours	Temperature °C.	Electromotive Force
0:00	20	0.217
1:10	20	0.210
5:00	20	0.215
48:00	19	0.220
48:15 *	20	0.220
48:20	20	0.700
48:30	20	0.700
49:00	21	0.630
50:00	21	0.580
53:00	21	0.490
54:00	21	0.460
73:00	22	0.223

* 0.6610 grams of C_3H_7Br broken in cell.



Graph #30

Voltage Drift in 1.69 Molar n-C_3H_7MgBr With Addition of C_3H_7Br

0.6610 gms of C_3H_7Br broken in cell

CHAPTER V

DISCUSSION OF RESULTS

The chemistry of the Grignard solution is not simple. To adequately describe and interpret experimental facts gathered since Grignard[1] reported his work with these solutions, a highly complex system of equilibria must be postulated. Many of the facts concerning the nature of the Grignard reagent have been made possible by the study of the electrolysis products of these solutions and the fact that dioxane is capable of precipitating R-Mg-X and $Mg\,X_2$ but does not precipitate R_2Mg.

Jolibois[2] suggested that Grignard reagents should be designated as $R_2Mg \cdot Mg\ X_2$ and not R-Mg-X. Evidence was presented by Schlenk and Schlenk[3] and Gilman and Fothergill[4] for the following equilibrium:

$$2\ R\ MgX \rightleftarrows R_2Mg + Mg\ X_2$$

Gilman and Brown[5] have distilled R_2Mg from methyl magnesium chloride underreduced pressure whereas Noller [6,7]

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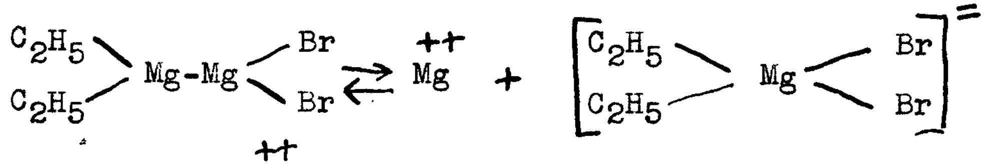
[1] Compt. rend., 130, 1322 (1900)
[2] ibid 155, 353 (1912)
[3] Ber., 62, 920 (1929)
[4] J. Am. Chem. Soc., 51, 3149 (1929)
[5] Rec. trav. Chem., 48, 1133, (1929)
[6] J. Am. Chem., Soc., 53, 635 (1931)
[7] J. Am. Chem. Soc., 59, 1354 (1937)

has shown that dioxane precipitates $Mg\,X_2$ and $R\,Mg\,X$ from ether solutions, and proposes for the Grignard reagent the formula:

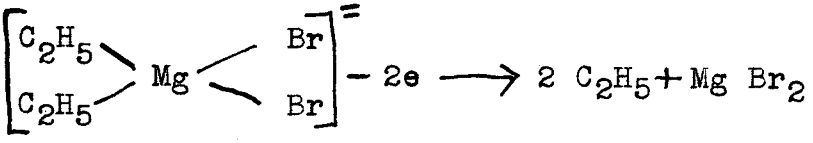
$$R_2\,Mg\,Mg\,X_2 \rightleftarrows R_2Mg + \overset{++}{Mg}\,X_2$$

Evans and Lee[8] electrolyzed ether solutions of Grignard compounds. On electrolysis of C_2H_5MgBr an equivalent weight of spongy active magnesium was deposited on the cathode per Faraday. The concentration of $MgBr_2$ increased in the anode compartment and anodic products of the electrolysis were ethane, ethylene and traces of hydrogen. To explain their findings the following mechanism was suggested. It was assumed that the $(C_2\,H_5)_2Mg\,Mg\,Br_2$ was slightly ionized yielding a $(\overset{++}{Mg})$ and a $\left[(C_2\,H_5)_2Mg\,Br_2\right]^{=}$. The $\left[(C_2H_5)_2\,MgBr_2\right]^{=}$ lost two electrons at the anode and liberated two free ethyl radicals and $Mg\,Br_2$. The two free ethyl radicals disproportionated, forming C_2H_6 and C_2H_4.



$$(C_2H_5)_2Mg\text{-}MgBr_2 \rightleftarrows \overset{++}{Mg} + \left[(C_2H_5)_2MgBr_2\right]^{=}$$

$$\overset{++}{Mg} + 2e \longrightarrow Mg \text{ (Active spongy on cathode).}$$



$$\left[(C_2H_5)_2MgBr_2\right]^{=} - 2e \longrightarrow 2\,C_2H_5 + Mg\,Br_2$$

$$2\,C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

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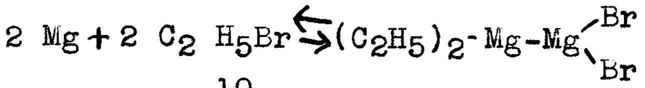
[8] J. Am. Chem. Soc., 56, 654, (1934)

In our investigation the following experimental facts had to be interpreted: The cathode in the electromotive force cells studied was extremely sensitive to exposure to the atmosphere. The voltage drift could not be attributed to change in concentrations of the cells due to evaporation. The minimum voltages attained in these cells, which leveled off at approximately 0.2000 volts, was independent of the anode metals used and the concentration of the Grignard solutions studied.

We believe the sensitivity of the cathode electrode to the atmosphere may be explained by the rapid oxidation of the Grignard reagent due to absorbed oxygen on the cathode electrode on reinsertion in the cell. Goebel and Marvel[9] have shown that Grignard reagents react relatively slowly with O_2 at room temperature and that the reaction rate increases as the temperature is lowered. Such an oxidation taking place in a cell in which equilibrium had been approached would disturb that equilibrium and increase the electromotive force of the cell until equilibrium had been again established.



$$2\,Mg + 2\,C_2H_5Br \rightleftarrows (C_2H_5)_2\text{-}Mg\text{-}Mg\begin{matrix}\diagup Br\\ \diagdown Br\end{matrix}$$

Noller and Castro[10] have shown that oxygen may cause

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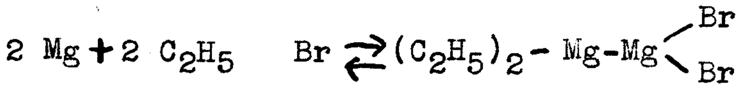
[9] J. Am. Chem. Soc., 55, 1693 (1933)

[10] J. Am. Chem. Soc., 64, 2509 (1942)

precipitation of relatively insoluble R-O-Mg-Cl which may bring down with it $MgCl_2$ to form an ultimate precipitate of the complex form.

$$R\text{-}O\text{-}Mg\text{-}Cl.\quad 2Mg\,Cl_2$$

This reaction would further disturb the equilibrium, driving it to the right, and thus increase the potential of the cell if the potential is due to the oxidation and reduction reaction.



$$2\,Mg + 2\,C_2H_5\quad Br \rightleftarrows (C_2H_5)_2-Mg\text{-}Mg\begin{matrix}Br\\ Br\end{matrix}$$

The drift in potential in a sealed cell, we believe, is due to the establishment of an equilibrium in the Grignard solution. The fact that an equilibrium or plateau voltage is encountered in our studies after long periods of observation seems to check with the results of Noller[10] in his work of studying the composition of alkyl magnesium chloride in ethyl ether. Noller found that equilibrium in these solutions is not approached rapidly, but may take as longas 50 to 150 hours.

If the reaction at the cathode in these cells is merely that of reducing the $[C_2H_5]^+$ radical to $[C_2H_5]^-$ as found in the Grignard reagent then the electromotive forces of these cells

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10. J. Am. Chem. Soc., 64, 2509 (1942)

should not be affected by the nature of the cathode metals studied. The cathode metals studied: platinum, copper, zinc and aluminum apparently served as inert electrodes, facilitating the reduction of the positive $(C_2H_5)^+$ radical to $(C_2H_5)^-$. Such an explanation seems plausible because the nature of the cathode metals studied so far seems to have no unique effect on the equilibrium voltage attained in these cells.

The experimental fact that an equilibrium voltage of approximately 0.2000 volts was reached for cells of various concentrations of ethyl magnesium bromide is most interesting. The cells studied were approximately 0.5 molar, one molar and two molar in concentration and all reached the same potential. One would expect a difference in the equilibrium potentials built up in such cells. Similar results were obtained in n-propyl magnesium bromide solutions studied over the concentration range 0.44 molar, 0.87 molar and 1.69 molar. In these cells, if the concentration of the magnesium bromide was constant at equilibrium and controlled the potential, then the electromotive force should have bee n constant.

Noller and Castro[11. 12.] have proposed an equilibrium for Grignard solutions

$$2RMg\,X \rightleftarrows Mg\,X_2 + Mg\,R_2$$

Evans and Lee[13.] in their electrolysis of Grignard solutions proposed the 2R Mg X structure for the Grignard reagent. Schlenk and Schlenk[14.] and Cope[15.] found that Grignard solutions will deposit $Mg\,Cl_2$ on standing. We also found a transparent crystalline solid forming in the cells studied after several days standing.

The Grignard solution apparently becomes saturated with $Mg\,X_2$ on standing and precipitates this component, hence a saturated solution of $Mg\,X_2$ is maintained at equilibrium. A saturated solution of $Mg\,X_2$ in the Grignard reagent would ultimately result in solutions of varying Grignard concentrations. The electromotive force developed in such solutions if controlled by the ionization of the $Mg\,X_2$ would be constant as soon as the solution became saturated with $Mg\,X_2$.

The anomaly of the constancy of the electromotive force developed in solution of varying Grignard concentration may also be explained if the findings of Evans and Lee[16.] are

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11. J. Am. Chem. Soc., 64, 2509 (1942)
12. J. Am. Chem. Soc., 62, 2238 (1935)
13. J. Am. Chem. Soc., 56, 654 (1934)
14. Ber., 62, 290 (1929)
15. J. Am. Chem. Soc., 57, 2238 (1935)
16. J. Am. Chem. Soc., 56, 654 (1934)

used. These experimenters indicated the structure of the Grignard reagent to be on ionization:

$$2\ R\ Mg\ X \rightleftarrows \overset{++}{Mg} + \left[R_2\text{-}Mg\text{-}X_2\right]^{=}$$

The constant of equilibrium for this ionization may be represented by the expression:

$$K = \frac{\left[\overset{++}{Mg}\right]\left[R_2MgX_2\right]^{=}}{\left[R\ MgX\right]^{2}}$$

In this expression K would be independent of the concentration because on dilution the concentration factor of both numerator and denominator would be equally affected.

If we consider the electromotive force of the cell to be determined by the expression

$$E = E_0 + 2.303\ \frac{RT}{NF}\ \log K$$

then potential of such a system should remain constant as long as the factor K, the equilibrium constant, remained the same. The interpretation given above would also explain the experimental facts noted in this investigation.

CHAPTER VI

CONCLUSION

In this study, we have made the following contributions to the electrochemistry of the Grignard reagent.

1. We have found that the voltage drift in cells containing solutions of ethyl magnesium bromide in anhydrous ethyl ether using magnesium and platinum electrodes is not due to a concentration change due to evaporation. Cells sealed to the atmosphere showed this voltage drift.
2. The cathode electrode is the sensitive member of the electrode system in the cells studied. The magnesium anode had little, if any, effect upon influencing the electromotive force of the cell once equilibrium had been approached.
3. There is no~~t~~ indication of a development of an electromotive force until there is evidence of the Grignard reaction taking place in these cells.
4. The equilibrium potential, using a magnesium anode, is independent of the cathode metals used in these studies. Cathode metals used were: platinum, copper, zinc, and aluminum.
5. The equilibrium potential of these cells studied is independent of the concentration of the Grignard solutions

studied. Concentrations varied approximately from 0.5 molar to 2 molar.

6. A cell at or near the equilibrium potential is very sensitive to small additions of the alkyl halide, oxygen or water. The electromotive force rises suddenly, indicating a probable dependence upon equilibrium conditions.

7. The equilibrium voltage reached by the cells studied, ethyl magnesium bromide and n-propyl magnesium bromide, is independent of the two alkyl groups present in the Grignard reagents.

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APPROVAL SHEET

The dissertation submitted by Frank P. Cassaretto has been read and approved by five members of the Department of Chemistry.

The final copies have been examined by the director of the dissertation and the signature which appears below verifies the fact that any necessary changes have been incorporated, and that the dissertation is now given final approval with reference to content, form, and mechanical accuracy.

The dissertation is therefore accepted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

June 1 48
Date

Evans
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