INTEGRATED SWEEP VOLTAMMETRY AND STUDIES OF INTEGRATED CURRENT DECAY APPLIED TO IODIDE-IODINE AND FERRIC-FERROUS REDOX COUPLES

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The research conducted during the second term unfortunately failed to show any conclusive results. The initial goal of the project was to use use integrated sweep voltammetry as a means of measuring adsorption on electrodes in various electrochemical reactions. Integrated sweep voltammetry, however, was discarded in favor of a study of integrated current decay, which seemed to be a more promising means of interpreting the electrode kinetics of various irreversible reactions. The evaluation of the data has been delayed by difficulties with the electronics. Therefore, I feel it is best to report the data found and evaluate it with respect to the expected results.

INTEGRATED SWEEP VOLTAMMETRY

In sweep voltammetry a ramp voltage (one varying linearly with time, $E = E_i + vt$) is applied across the cell, and the resulting current is; $i = Kv^{\frac{1}{2}}P(vt)$[1], where K is a gross constant and P is a function of v, the sweep rate, and t, the time. By substiuting $vt = E - E_i$ in this equation, the resultant expression for i is; $i = K't^{-\frac{1}{2}}P(E-E_i)$, and the function P is now independent of time. Integrating this with respect to t and substituting back in for v the resulting expression for coulombs is $Q = K''v^{-\frac{1}{2}}$. The validity of this expression is subject

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[1] Delahay, P. "New Instrumental Methods in Electrochemistry", Interscience Publishers, New York, 1954, p. 118.

to two stringent conditions. First, the end-points, E_i and E_f, of the potential range over which the sweep is made must be held constant. Second, the current peak of the potential-current curve cannot shift with the application of various sweep rates. If these two conditions are met, then the product, $Qv^{-\frac{1}{2}}$, must be constant, and plots of Q vs. $v^{-\frac{1}{2}}$ must yield straight lines. If no adsorption occurs on the electrode these lines will pass through the origin. If adsorption occurs, then the total coulombs will be increased by Q_{ads} , and the plots of Q vs. $v^{-\frac{1}{2}}$ will give a straight line with intercept Q_{ads}.

Iodide-Iodine System:

The iodide-iodine system, which is known to be reversible, was used first because it had been studied previously and was found to give good results. If iodine is reduced, the resulting Q vs. $v^{-\frac{1}{2}}$ curve should be a straight line with a positive intercept corresponding to Q_{ads}. Several different sets of data were compiled for the I^--I_2 system, The most representative of these is given below and in Graph A. A solution was prepared that was 0.1 M in I^-, 10^{-3}M in I_2 and 1 M in H_2SO_4, by adding enough IO_3^- to the acidified iodide solution to give the desired quantity of I_2. The interval over which the current was integrated was 300 mV cathodic from the equlibrium potential of the solution. Q is obtained from the scope reading by applying the formula, Q = 0.056 DS/R., where D is the number of divisions on the scope, S is the sensivity, R is the current measuring resistance, and Q is in coulombs.

V(volts/cm)	Dial Setting	$(D.S.)^{-\frac{1}{2}}$	SET I Q(micro-coul.)	SET II
0.0675	0.50	1.41	140	154
0.135	1.00	1.00	98	113
0.270	2.00	0.71	71.4	82.6
0.540	4.00	0.50	50.8	63.0
1.08	8.00	0.35	36.4	40.6
2.16	16.00	0.25	23.0	
4.32	32.00	0.18	14.0	

Both sets of data give good representations of a straight line when Q is plotted against $v^{-\frac{1}{2}}$, or, as in Graph A, against the reciprocal square root of the dial setting. Both straight lines give positive intercepts, indicating that iodine is adsorbed on the electrode. The last two points of the first set of data do not correspond to the straight line for the other five points. This is most probably due to the fact that a smaller capacitor was needed to get a faster sweep rate from the sweep generator. Since the two capacitors are not perfectly accurate with respect to another a deviation from linearity would occur. It is also noticed that the straight line for Set II has a slightly greater slope and a noticeably larger intercept than Set I. This is due to the fact that the second set of data was taken two days later, and in the two days air oxidation of I^- increased the iodine concentration. An increase in I_2 concentration would not only increase the slope but the intercept as well. The slope is a linear function of concentration and would increase correspondingly. The intercept, Q_{ads}, would also increase with concentration, but would reach a limit when the electrode became "saturated" with iodine. As a result it is rather supriding that a large increaae in Q_{ads} is observed for such a small increase in concentration.

Other data were also taken for I^--I_2 systems, but they led to non-linear graphs or negative intercepts. This cannot be considered as valid data since the behavior noted above has been confirmed for an I^--I_2 system.

Ferric-Ferrous Systems:

A solution was prepared consisting of 4mM Fe^{+++}(from $FeCl_3$), 4mM Fe^{++}(from $FeSO_4$) and 1M HCl. The equilibrium potential of this Fe^{+++}-Fe^{++} couple was approximately 400mV. Since it was desired to study both ferric reduction and ferrous oxidation, the current was integrated over 300mV intervals to either side of this equilibrium. Plots of Q vs. $v^{-\frac{1}{2}}$ (Graph 8) were compiled from the following data on 4mM Fe^{+++}, 4mM Fe^{++} and 1M HCl.

		Fe^{+++} RED.	Fe^{++} OXID.
V(volts/cm)	(Dial Setting)$^{-\frac{1}{2}}$	Q(micro-coulombs)	
0.0675	1.41	84.0	77.0
0.135	1.00	59.4	53.3
0.270	0.71	39.2	34.8
0.54	0.50	27.4	23.0
1.08	0.35	19.6	15.4
1.35	0.31	16.5	11.8

It is true that both oxidation and reduction processes give ggod straight lines, but the negative intercepts(and therefore "negative" coulombs) is a result that can have no chemical explanation. It is expected that plots of Q vs. $v^{-\frac{1}{2}}$ go through the origin for systems involving no adsorbtion. Apparently these curves bend when $V^{-\frac{1}{2}}$ is sufficiently small and pass through the origin. Since the equipment being used would not generate a fast enough sweep rate to allow the detection of this curvature it was decided to try a method of analysis other than sweep voltammetry.

STUDIES OF INTEGRATED CURRENT DECAY

Ferric-Ferrous Systems:

This segment of the experiment was devoted entirely to the study of a redox couple that is known to be irreversible, the ferric-ferrous couple. This couple was studied in both 1M HCl and 1M H_2SO_4. No study was made of a reversible system, such as iodide-iodine, using the method of integrated current decay.

For experiments of this nature the potential of the cell was adjusted to the equilibrium potential of the redox couple. Then, instead of scanning a certain potential range at various rates, the potential was "stepped" instantaneously to a chosen potential. In this case the current decays as a function of time, and, for an irreversible process, Delahay[1] has given the current-time relationship as,

$$i = nFAC^o k_{f,h} \left[\exp(K^2 t) \operatorname{erfc}(K t^{\frac{1}{2}}) \right],$$

where, $K = \dfrac{k_{f,h}}{(D_{ox})^{\frac{1}{2}}} + \dfrac{k_{b,h}}{(D_{red})^{\frac{1}{2}}}$.

If this expression is integrated with respect to time the resulting expression for coulombs is,

$$Q(t) = \frac{nFAC^o k_{f,h}}{K^2} \left[\exp(K^2 t) \operatorname{erfc}(K t^{\frac{1}{2}}) + \frac{2Kt^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} - 1 \right].$$

Since the function $\exp(K^2t)\operatorname{erfc}(Kt^{\frac{1}{2}})$ goes to zero as t goes to infinity it can readily be seen that at large t, $Q(t) = A't^{\frac{1}{2}} - B'$, where A' and B' are gross constants. Thus, if Q is plotted against $t^{\frac{1}{2}}$ for very large t, the resulting graph while be a straight line with a positive slope and negative intercept. At t=0, Q=0 since exp(0)erfc(0) equals unity, and the actual curve of Q vs. $t^{\frac{1}{2}}$ must pass through the origin. For times that are too small to neglect $\exp(K^2t)\operatorname{erfc}(Kt^{\frac{1}{2}})$ the plot of Q vs. $t^{\frac{1}{2}}$ must round itself off in some manner so as to pass through the origin. At these small times it has been suggested that

Q is a linear function of t, $Q(t) = A't$. In this experiment, Q was plotted against t at small times to see if this assumption held true.

In this experiment the effect of stepping over different potential ranges was studied. As the size of the potential step is increased so are the number of coulombs, and therefore the slope of the curve. The increase in the slopes of the curves diminishes as the potential steps are increased beyond a certain value because there is a limitation to the amount of material that can be instantaneously reduced or oxidized. This can be seen by looking at the current-potential curves from sweep voltammetry. After a certain potential the current from the particular reaction being studied dies out, approaching zero. As a result the Q vs. $t^{\frac{1}{2}}$ plots for increasing potential steps should start to fall on top of one another. This can never be realized unless a blank is taken for each solution studied. Other electroactive species, most notably H^+, are present and will cause interference. In this example, hydrogen ion will be reduced before the current from ferric ion reduction has completely died out. Since it is impossible to distinguish where the coulombs come from it is necessary to take blanks of the particular solutions being used. Attempts were made to take blanks during the end of the experimentation, but the electronics had detriorated to such an extent that the blanks were unquestionably invalid.

With one exception all ferric-ferrous solutions contained 4mM Fe^{+++} and 4mM Fe^{++}. The HCl solution contained ferric ion as a chloride and ferrous ion as a sulfate. The H_2SO_4 solutions contained both ferric and ferrous ions as sulfates, the only chloride present being that due to impurities.

The first set of graphs (C and D) presented are those of ferric-ferrous systems in HCl. The potential step taken was 285 mV from equilibrium in both anodic and cathodic directions. In all cases, however, the current was measured for a period of only 200 milliseconds. Since the curves do not straighten out it is apparent that times of more the 200 msecs. must be used of the graph of Q vs. $t^{\frac{1}{2}}$ is to approach a straight line. Increasing the concentration or the size of the potential step would also have the same effect as lengthening the time of observation.

In Graph D, the points connected by the heavy line represent the data taken using a similar solution but with a potential step of 400 mV rather than 285 mV. The resulting straight line leads to the conclusion that the additional 125 mV was sufficient to give a linear relation between Q and $t^{\frac{1}{2}}$.

Graphs E and F are tabulations of data taken under the same conditions. The solution used consisted of 4mM Fe^{+++}; 4mM Fe^{++} and 1 M HCl, and the potential step was taken from equilibrium (approx. 460 mV) to zero volts. As before (in Graph D) a potential step from equilibrium to zero volts gave a nearly perfect straight line with a negative intercept. Here the potential interval and the time increments may be too large to see that portion that is curved. It is also very difficult to know where the curve is approximated by a straight line and where it is curved without a knowledge of the diffusion constants and the hetrogeneous rate constants, As a result, it is difficult to comment on the validity of each piece of data.

In graphs G and H, Q was plotted against $t^{\frac{1}{2}}$ at longer times and against t at shorter times for various potential steps. The solution contained 0.1M Fe^{+++}, 0.1M Fe^{++} and 1M H_2SO_4. The increase in concentration was done to make it easier to measure the coulombs at the shorter times.

In the plots of Q vs. $t^{\frac{1}{2}}$ (Graph G), the curve for the 350 mV step should be disregarded because the amplifier was overdriven. At the other potential steps (200, 250, 300 mV) the curves followed quite closely the theoretical expectations. There is a pronounced curvature up until a time of several hundred milliseconds, and then the curve begins to straighten put. The plots also curve around as if to pass through the origin. It should also be noticed that the number of coulombs generated does not really become measurable until a potential step of 150-200 mV is used.

In graph H, Q was plotted against t for times up to 20 milliseconds, and a linear relationship was found to be the case at each of the various potential steps. Once again it seems as if the peak of the potential-current curve does not begin to form until 150-200mV, and that its maximum value falls somewhere between 250 mV and 300 mV. The final point of interest in this data concerns the positive intercepts in Graph H. These could result from three possible sources. The first is the presence of adsorbed reactant on the electrode, which seems highly unlikely for ferric ion in a strong sulfuric acid medium. The second possible source is the possibility of charging of the double layer, but anything upwards of 5 microcoulombs is a little too much to assign entirely to the double layer effect. The third and most probable source is the electronic system. It was noticed that the amplifier emitted an almost instantaneous pulse of current (at approx. 100 microseconds) which would be integrated by the remainder of the circuit to give coulombs. In support of the observations made from the data, the size of the current pulse would increase with increasing potential steps.

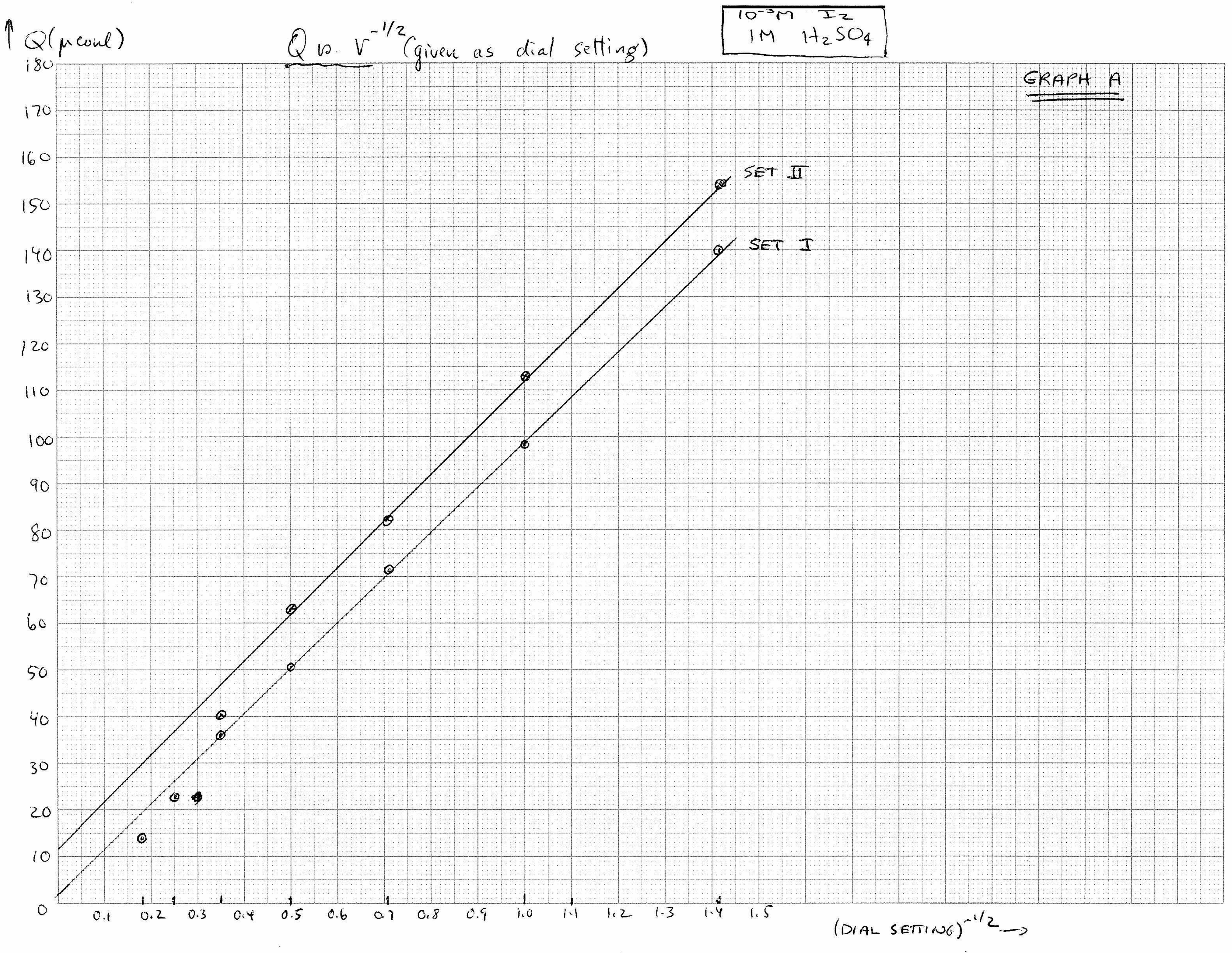
The final piece of data taken was a plot of Q vs. $t^{\frac{1}{2}}$ for 4 mM Fe^{+++} 4mM Fe^{++} and 1M HCl (Graph I). In asolution containing the same concentrations of ferric and ferrous ions in 1M HCl (Graphs E and F) it was noted that for times of 16-200 milliseconds a plot of Q vs. t gave a straight line. In Graph I the plot clearly is curved in this time interval, and only at t = 200-400 milliseconds does it begin to approximate a straight line. This latter set of data (Graph I) is then a direct contradiction to an earlier set of data (Graphs E and F).

If the approximations of the straight lines are plotted back to time t = 0, it is observed that the intercepts are both negative, but the intercept for the 400 mV step is a good 20-30 microcoulombs more negative than the intercept for the 200 mV step. The size of the intercept is thus also dependent upon the size of the potential step.

Because of the numerous errors that could have been introduced by the electronic system it is rather difficult to make any concrete deductions about the chemistry going on in the cell. By integrating Delahay's expression for the current of an irreversible reaction it was found that Q should vary as $t^{\frac{1}{2}}$ for very large times. Experimental observations do seem to indicate this fact as well as the fact that Q varies linearly with t at very small times. It is unfortunate that no comparison was made between an iodide-iodine system and a ferric-ferrous system in the current decay studies because this would give a better picture of the validity of the data. Nevertheless, the behavior of Q with time seems to be reasonable in view of the mathematical derivations, so that perhaps some progress has been made.

TABLE OF GRAPHS

Number	Co-ordinates	Composition of Solution
A	Q vs. $V^{-\frac{1}{2}}$	0.1M I^-, 0.001M I_2, 1M H_2SO_4
B	Q vs. $V^{-\frac{1}{2}}$	4mM Fe^{+++}, 4mM Fe^{++}, 1M HCl
C	Q vs. $t^{\frac{1}{2}}$	"
D	"	"
E	"	"
F	"	"
G	"	0.1M Fe^{+++}, 0.1M Fe^{++}, 1M H_2SO_4
H	Q vs. t	"
I	Q vs. $t^{\frac{1}{2}}$	4mM Fe^{+++}, 4mM Fe^{++}, 1M HCl

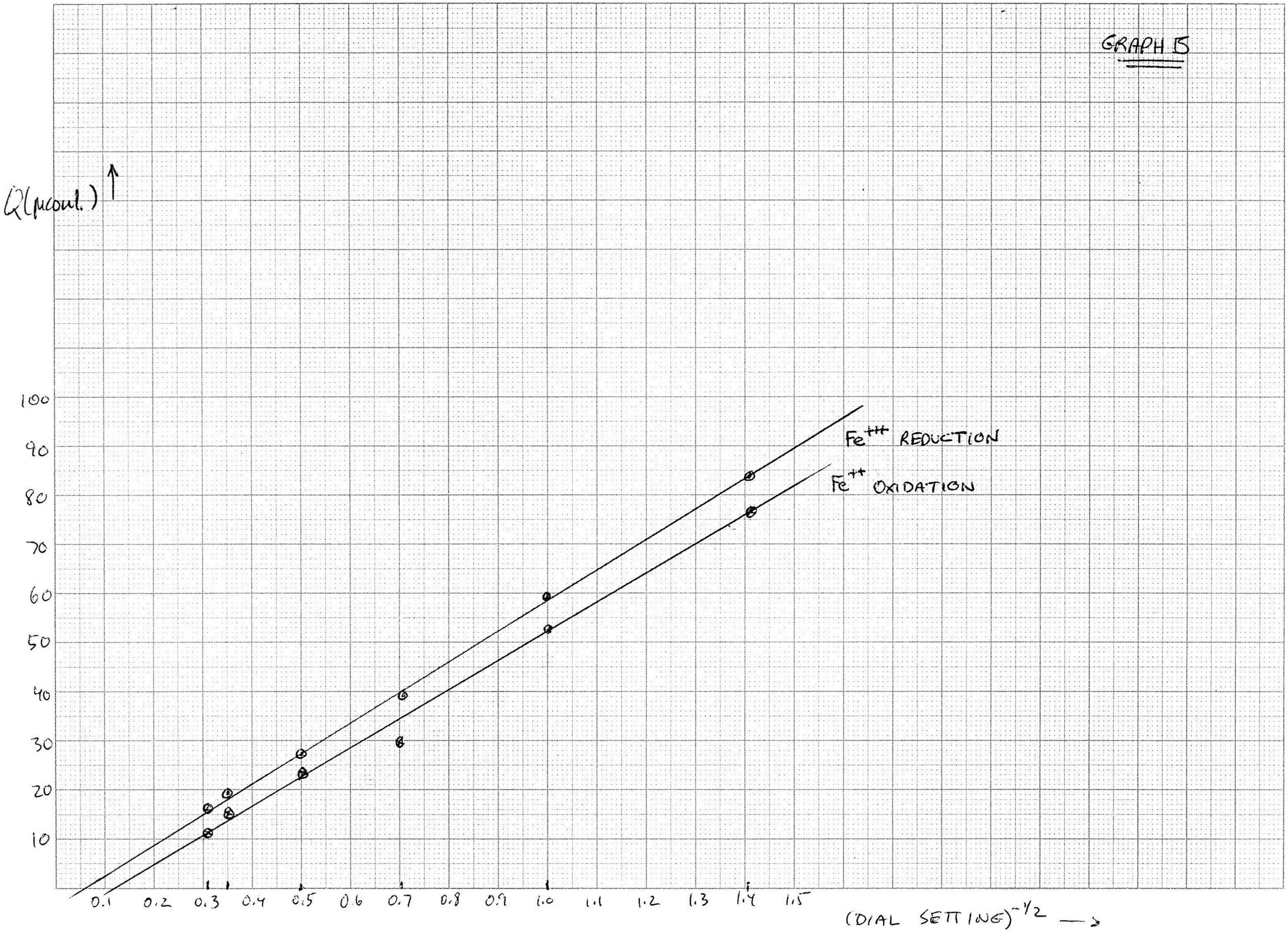


Q vs. $V^{-1/2}$ (given as dial setting)

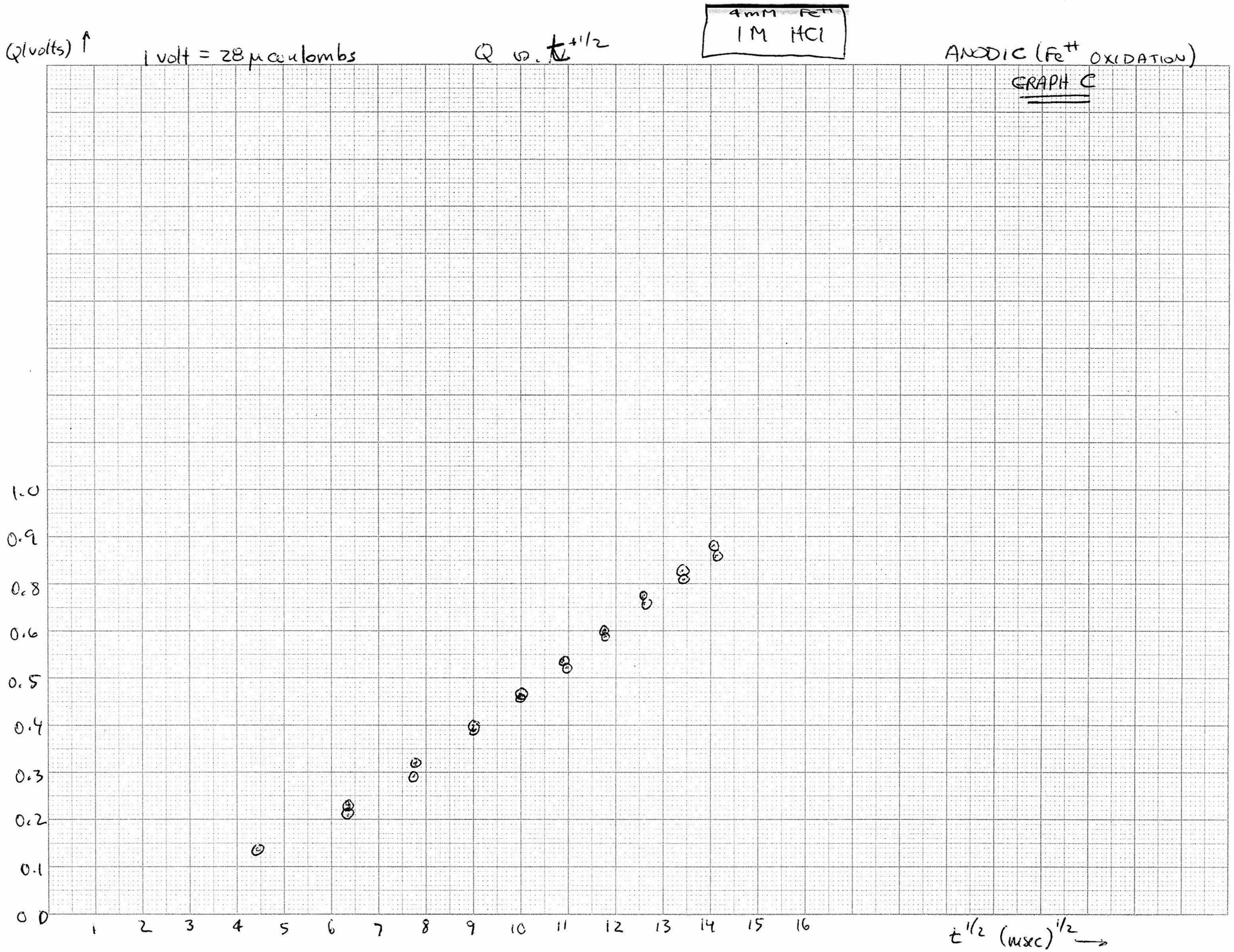
10^{-3}M I_2
1M H_2SO_4

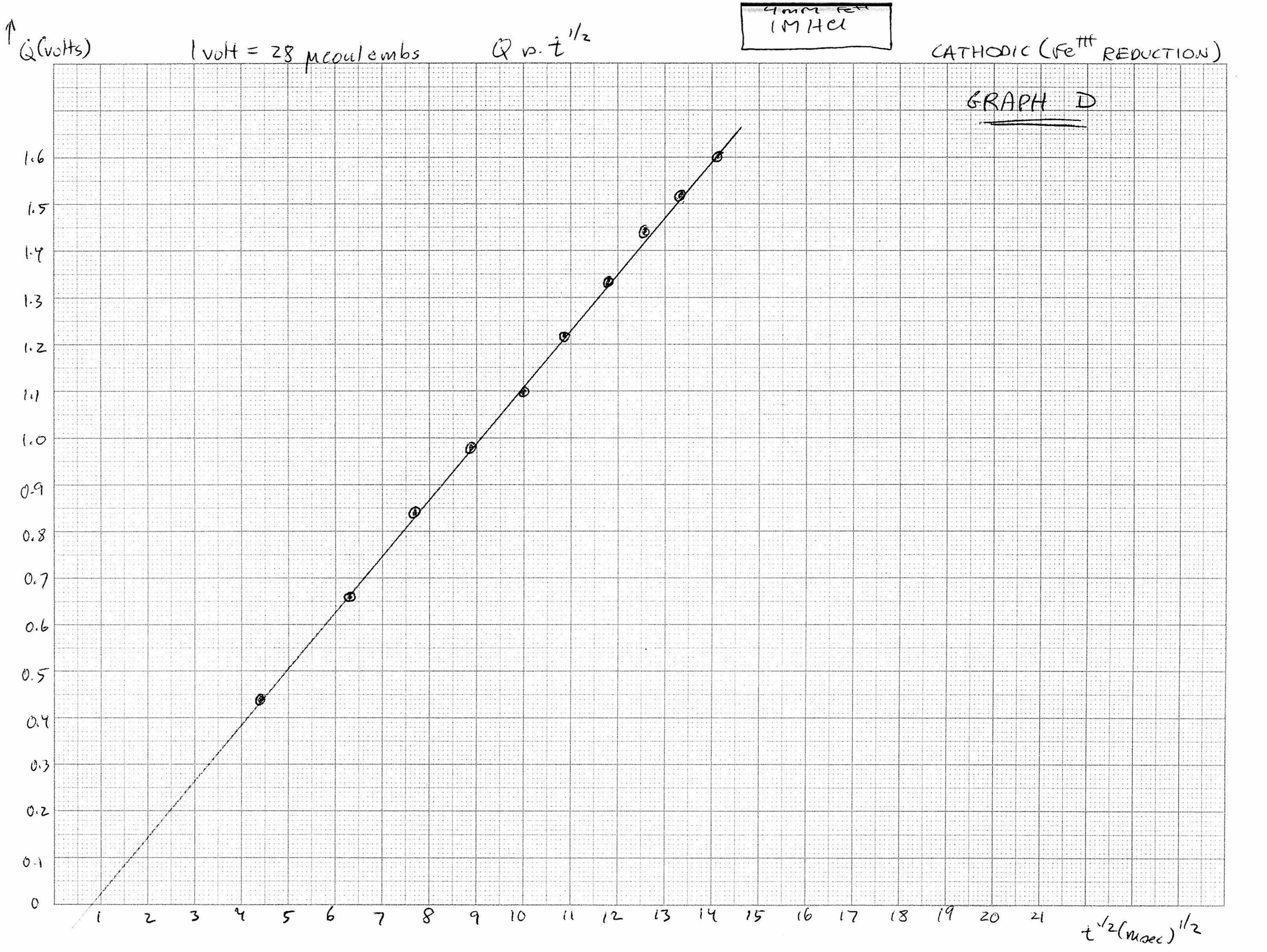
Q vs. $V^{-1/2}$

4mM Fe^{++}
1M HCl

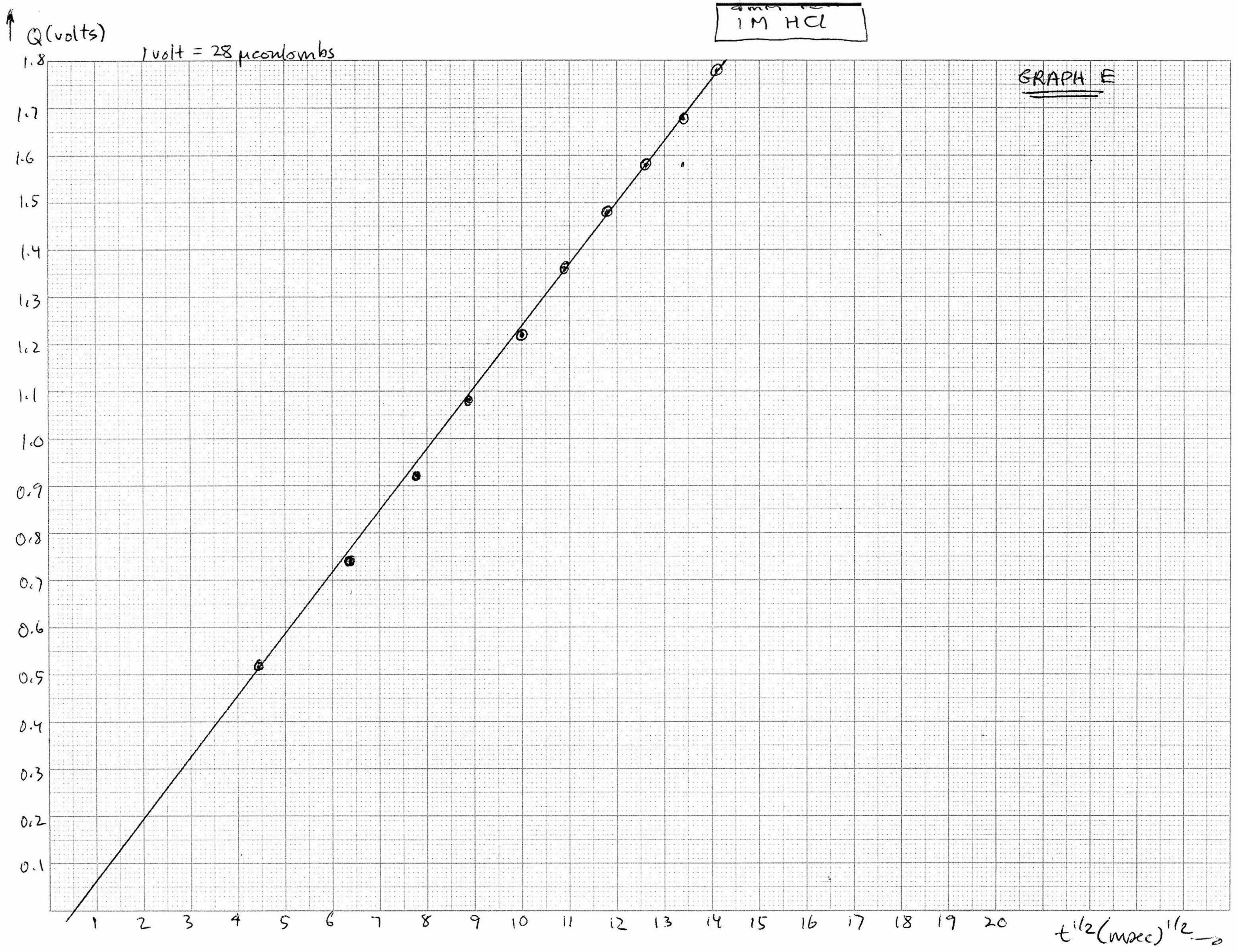


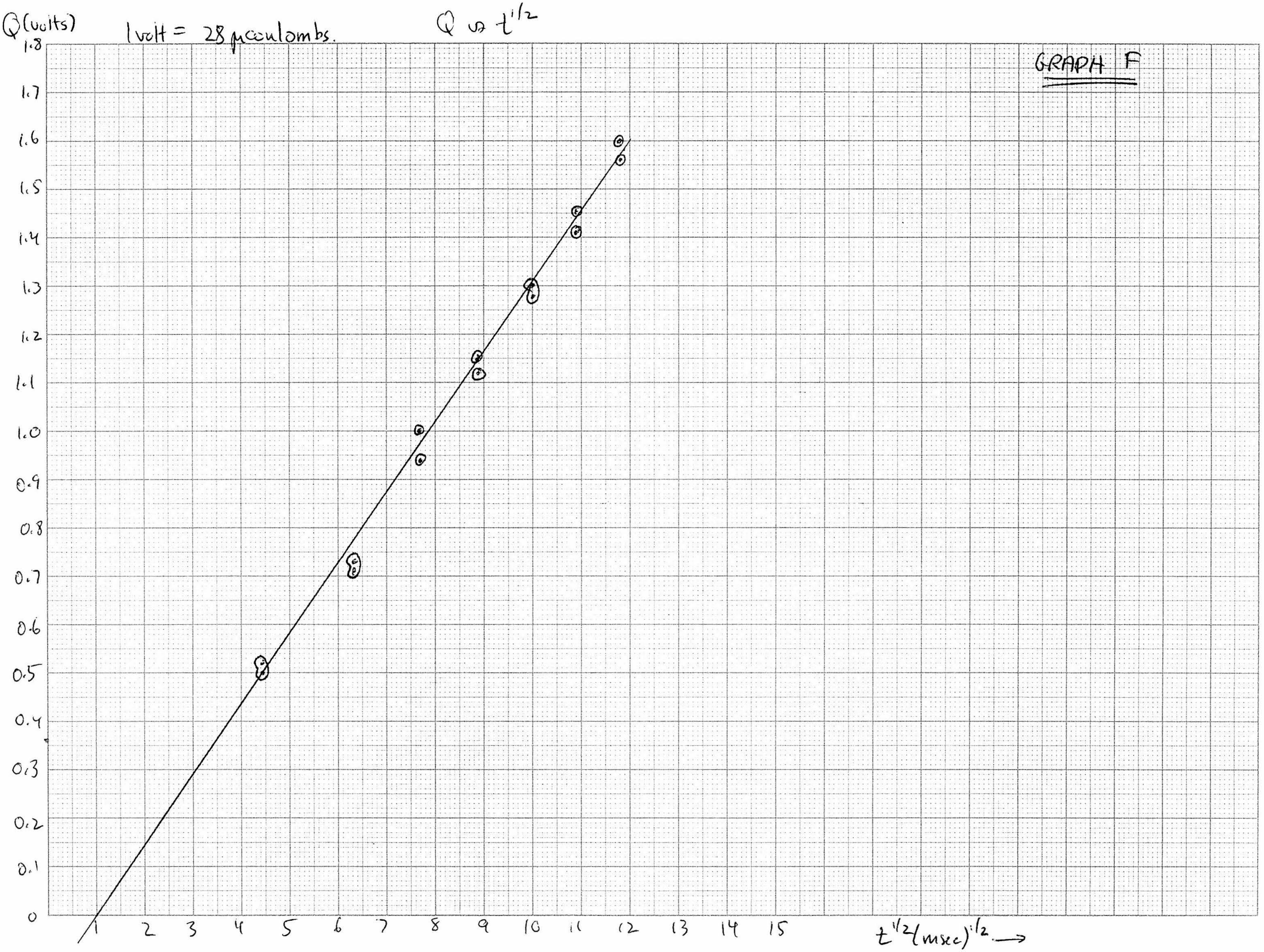
GRAPH 5


4mM Fe⁺⁺
1 M HCl
(Q(volts)) ↑
1 volt = 28 μcoulombs
Q vs. t+1/2
ANODIC (Fe⁺⁺ OXIDATION)
GRAPH C
1.0
0.9
0.8
0.6
0.5
0.4
0.3
0.2
0.1
0 0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
t1/2 (msec)1/2 →



Q(volts)
1 volt = 28 μcoulombs
Q vs. t^1/2
4mM Fe+++
1M HCl
CATHODIC (Fe+++ REDUCTION)
GRAPH D
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
t^1/2 (msec)^1/2


1M HCl
GRAPH E
Q (volts)
1 volt = 28 μcoulombs
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
t^1/2 (msec)^1/2



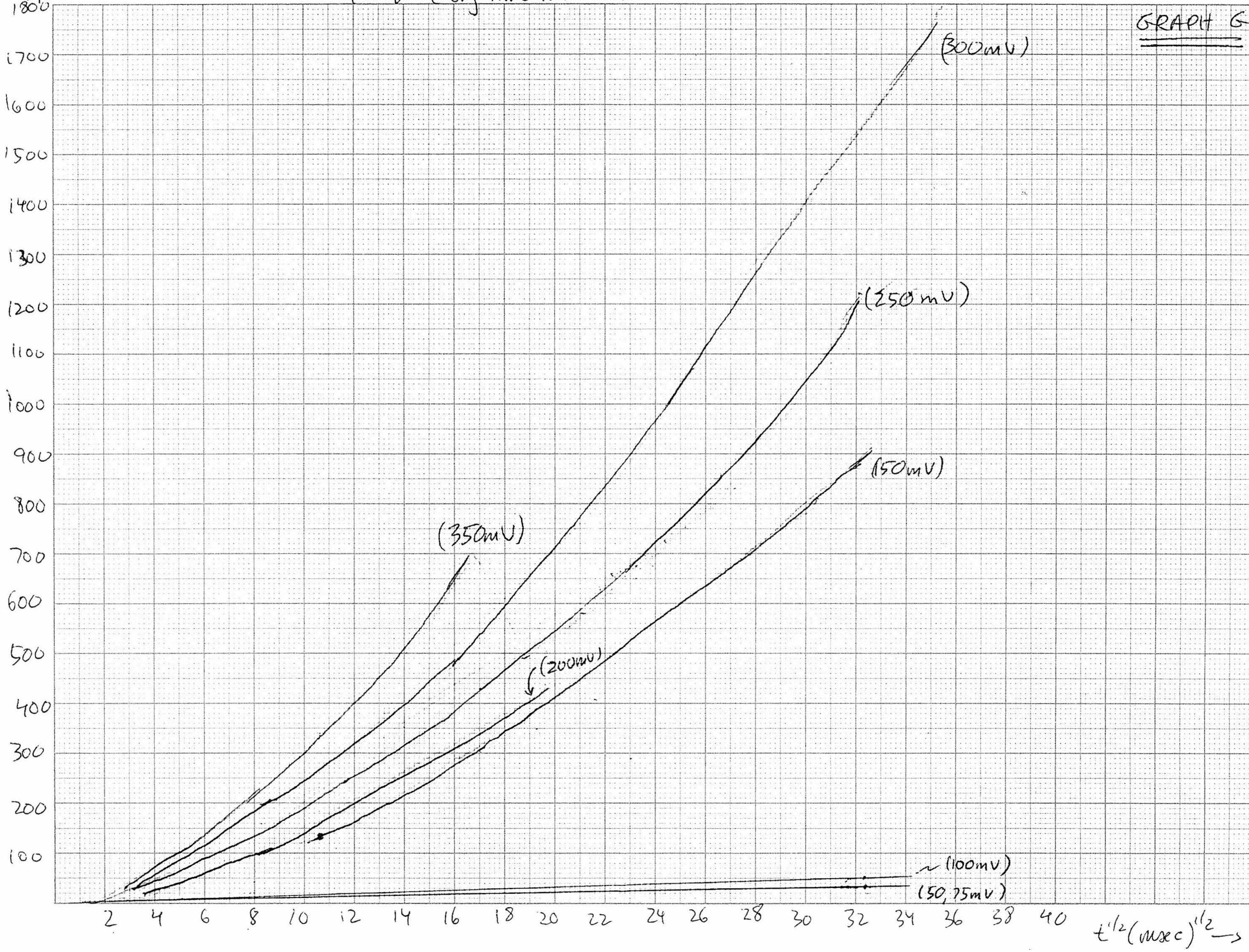
GRAPH F

Q vs $t^{1/2}$

1 volt = 28 μcoulombs.

1 M H_2SO_4

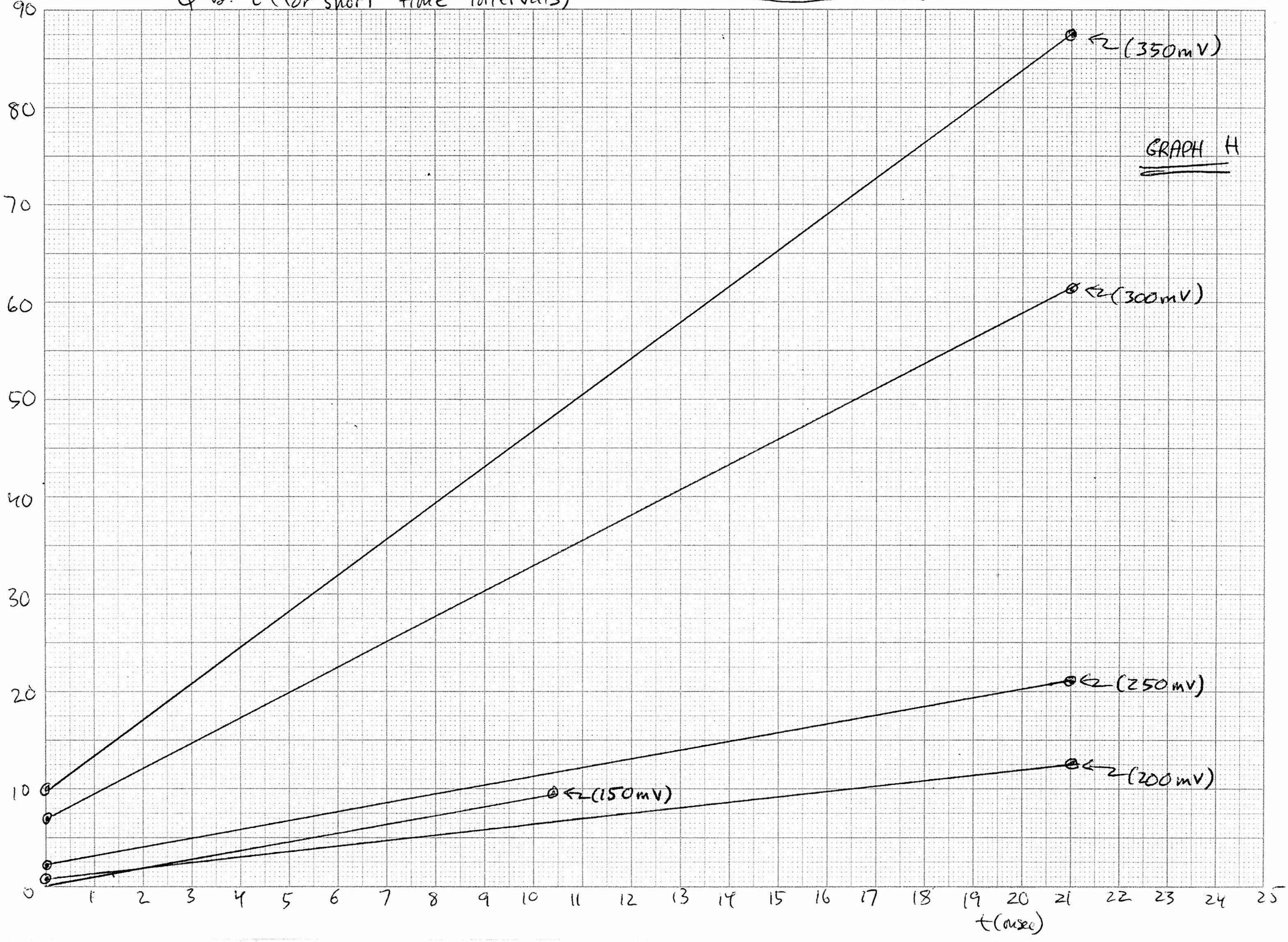
Q vs $t^{1/2}$ (long time intervals)



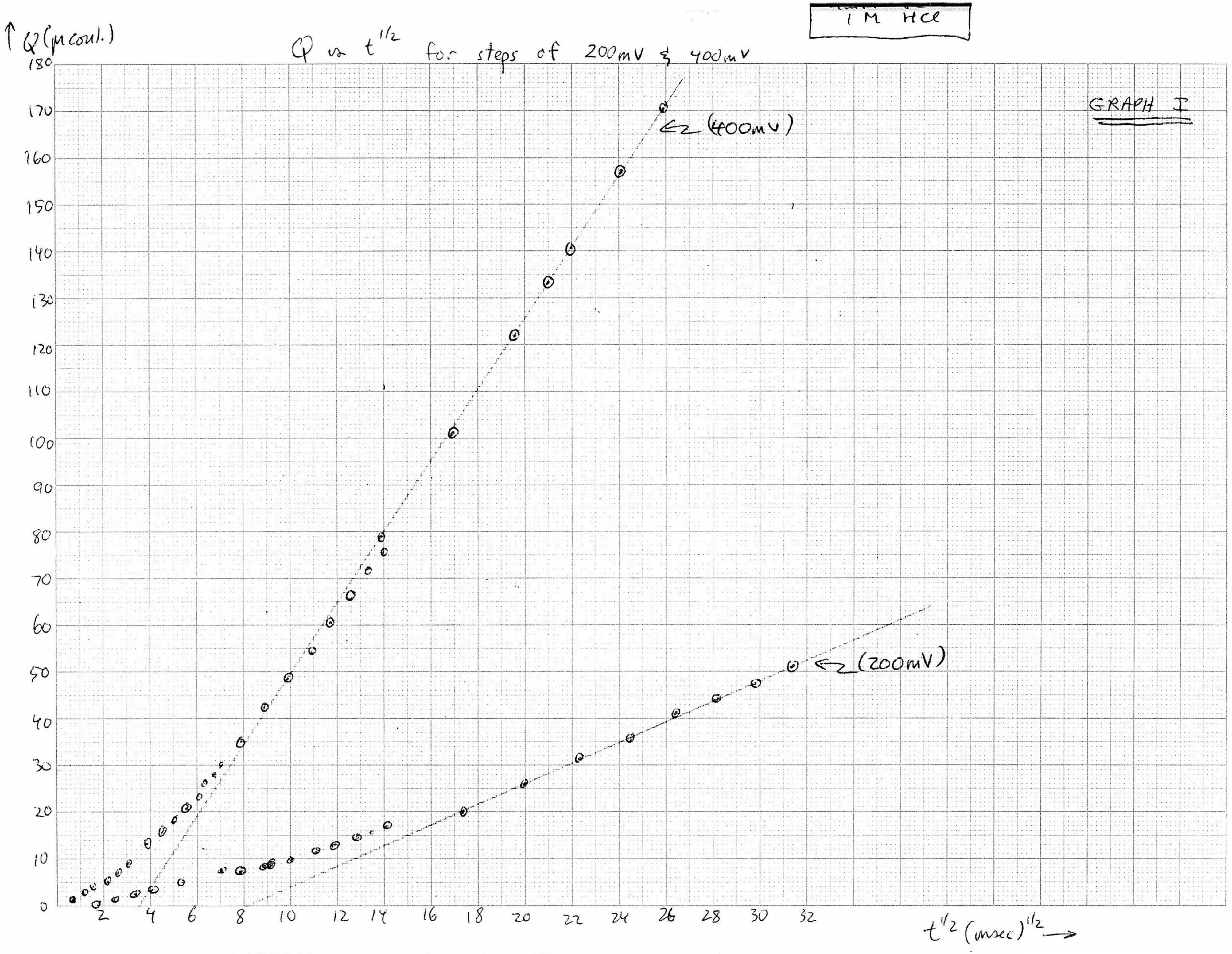
1M H_2SO_4

Q vs. t (for short time intervals)

GRAPH H



1 M HCl



Q vs $t^{1/2}$ for steps of 200mV & 400mV