# Mass Transfer of Bromine to a Rotating Zinc Hemisphere in NaBr Solution

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## Abstract

Bromine diffusion coefficients are determined by measuring the weight change of a small rotating zinc hemisphere in aqueous bromine, salt solutions. The diffusion coefficients are $2.70 \times 10^{-6}$ $cm^2/s$ and $1.99 \times 10^{-6}$ $cm^2/s$ for $Br_2$ in 1 M and 3 M NaBr, respectively.


## Introduction

The flow through zinc bromine battery is currently being developed for load-leveling and electric car applications. Here, 1 and 3M NaBr solutions are used as supporting salt solutions in determining the diffusion coefficient, D, for the bromine attack of the zinc electrode. The discharge reactions are:

$$Zn^{\circ}_{(s)} + Br_{2(aq)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

$$Br_{2(aq)} + 2e^{-} \rightarrow 2Br^{-}_{(aq)}$$

It is believed that this reaction goes to completion very quickly. Thus, the battery discharge will be limited by mass transfer of $Br_2$ to the surface, and D will be a significant parameter in modeling the discharge.

This mass transfer and reaction can be accurately studied using a rotating Zn hemisphere in a NaBr/$Br_2$ solution. The rotating hemisphere produces a known attack velocity. The rate of reaction (or weight loss of the Zn hemisphere) for a given area and $Br_2$ concentration will be proportional to the square root of the rotational speed if the process is mass transfer limited. Using Levich's equation for diffusion layer thickness for laminar flow and the limiting current as a function of D with Newman's correction:

$$I_1 = .451\, nFC_L\, D^{2/3}\, v^{-1/6}\, w^{1/2}\, A.$$

.451 = correction for hemisphere. The hemisphere is chosen since its geometry is unchanged by the reaction. The limiting current can also be defined as a function of weight loss:

$$I_1 = \frac{\Delta WnF}{Mt}$$

Equating the two, the masstransfer coefficient, $k_c$ is:

$$k_c = \frac{\Delta W}{MAC_b t} = .451\ v^{-1/6}\ D^{2/3}\ w^{1/2}$$

A straight line plot of $k_c$ vs. $w^{1/2}$ will have a slope proportional to $D^{2/3}$. This equation will be valid as long as A, $C_b$ remain constant through a given run and flow across hemisphere surface is laminar. At high rotational speeds or with large surface roughness, localized turbulence can be initiated and the equation will no longer be valid.

The specification that $Br_2$ concentration be constant demands special attention due to the volatility of $Br_2$ in aqueous solution. The vapor pressure of $Br_2$ at room temperature (20°C) is near 160 torr. The effect of varying molarities of NaBr on $Br_2$ vaporization will be studied. It is hoped that the NaBr will stabilize the $Br_2$ concentration through the run.

## Experimental

The zinc which actually undergoes the corrosion is a 6-32 Zn screw with a hemispherical head. The screw was machined from 1/2 inch diameter rod (99.999% New Jersey Zinc). The diameter of the hemispheres ranged from .987 to .995 cm. These measurements were made with a hand micrometer to an accuracy of .001 cm or 0.1% error. The reaction surface was polished with jewelers' rouge to a mirror finish. Twelve screws were produced. Each hemisphere was rinsed in deionized water, then isopropyl alcohol and weighed on a Mettler balance both before and after each run. The error in the weight loss measurement was 0.01%.

The hemisphere screw was inserted through a Teflon coat into a threaded hole in the end of a stainless steel spindle (Figure 1). The spindle was machined to fit a Pine Instrument ASR rotator with a range of 0-10,000 rpm. The experiment was performed in a ventilated hood to sweep away any escaping $Br_2$.

This escaping $Br_2$ caused $Br_2$ concentration to change during the run. NaBr was utilized to reduce the activity and the vapor pressure of the $Br_2$ species due to complexation according to the reactions:

$$Br_2 + Br^- \rightarrow Br_3^- \qquad K = 16$$

$$2Br_2 + Br^- \rightarrow Br_5^- \qquad K = 40$$

The effect of NaBr concentration on $Br_2$ loss was measured (Figure 2).

For the actual corrosion of the hemisphere 3 M ± .5% NaBr was used initially. Viscosity data was taken from CRC. The $Br_2$ source was liquid $Br_2$(99.9% $Br_2$); it was transferred by pipet to produce $Br_2$ concentration ranging from .02 - .07 M $Br_2$. The measurement of this $Br_2$ concentration involved using KI to quantitatively produce $I_2$ from the $Br_2$ and then titrating against 0.01 M $Na_2S_2O_3$ solution to a clear end point. These measurements were reproducible within 2%.

Several reaction tanks were utilized. A 1 ℓ teflon tank was weakened by the $Br_2$ and was replaced by a 1 ℓ glass beaker. Both of these tanks were fitted with teflon covers. At high rotational speeds (~4000 rpm) bubbles swirled down onto the reaction surface, causing spiral marks (Figure 3) and very high weight losses. To allow study at higher w, a 2 ℓ flat tank was used, allowing for good results up to 9,000 rpm.

The reaction surface of 7 or 8 of the screws was not altered by the first corrosion run. The finish was removed but there was not pitting or spiral marking and the hemisphere retained uniform color. These screws were used, without refinishing, in later runs.

## Results & Discussion

The effectiveness of NaBr solutions for reducing $Br_2$ vaporization out of aqueous solution is shown in Figure 2. The relative loss of the $Br_2$ species is reduced by a factor of $27/7 \simeq 4$, between the 1 M and 3 M NaBr solutions.

3 M NaBr was chosen for the initial study for this reason and also because batteries are more likely to operate at a 3 M $Br^-$ condition. The results from the individual runs are shown in Table 1 and plotted in Figure 3. The points representing screws with spiral marks were not included in the straight line fitted to the data. An $r^2$ value of 0.98 was obtained for this straight line. The slope of this line leads to a value for D of $1.99 \times 10^{-6}$ $cm^2/sec$. This D is an average value for all reacting species of bromine (i.e., $Br_2$, $Br_3^-$, $Br_5^-$) as they diffuse to the reaction surface. A 1 M NaBr solution was also investigated. A straight line with an $r^2$ value of 0.96 lead to a value for D of $2.70 \times 10^{-6}$ $cm^2/sec$.

A non-zero intercept was obtained for both cases, an indication that bromine can diffuse and react at the surface even when there is no attack velocity. An actual run was performed with no rotation of the spindle to support this finding.

The assumption of an average concentration of bromine is valid since the zinc weight loss is proportional to bromine concentration. Therefore, the total weight loss of zinc divided by a time average bromine concentration should be equal to any instantaneous weight loss divided by the corresponding concentration.

The $Br_2$ loss during the low rpm runs was 8% for an hour run. The higher speeds produced bubbles which increased the surface area of air-liquid contact and increased $Br_2$ loss to an average of 15% in a 1/2 hour run.

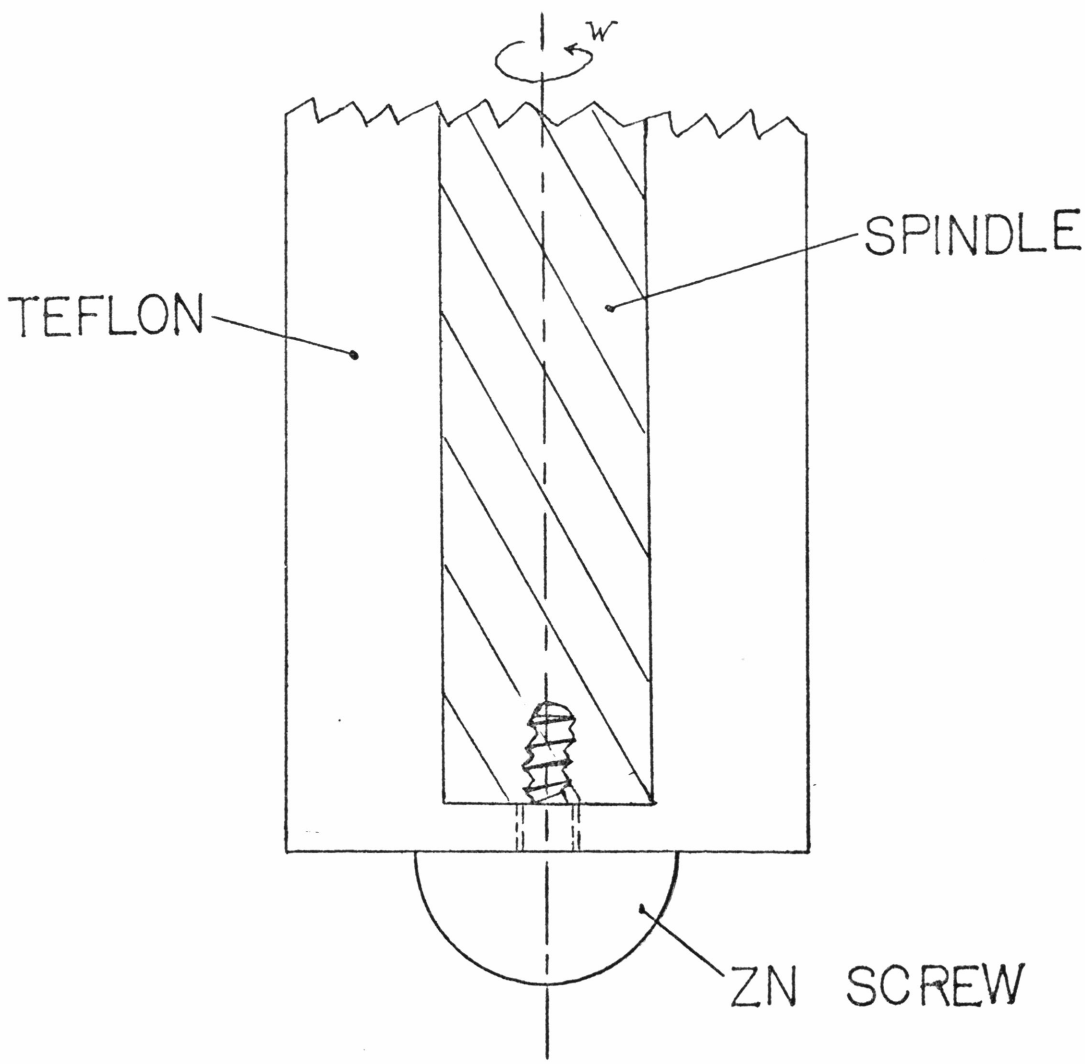
The bubbles produced at higher rpm did not appear to affect the reaction at the zinc surface unless they were drawn to the surface itself. In the cases where the bubbles did reach the zinc, spiral markings were noticed, as were large weight losses. These points are noted in Figure 3. The spiral marks apparently result from localized turbulent flow caused by the bubbles' rolling across the reaction surface. At very high speeds (7000 to 9000 rpm) coupled with higher bromine concentration, bubbles caused pitting of the surface to occur. These bubbles, however, were eventually controlled by using a sufficiently wide reaction tank, in which the bubbles did not penetrate down to the zinc surface. Reliable data was obtained for speeds up to 9000 rpm.

Several of the zinc screws were acceptable after their first run to be used again. The criteria used to determine the quality of a surface after a run included no pitting or spiral markings and uniform color and surface. The reproducibility of polished versus reused buttons was checked and was found to be good.

A possible side reaction which could affect weight loss was the hydrogen attack of the zinc surface. Runs at 0 and 3,000 rpm were performed with 3 M NaBr and no bromine. The weight loss under these conditions was less than 1% that for the cases with bromine. Hydrogen evolution was negligible.

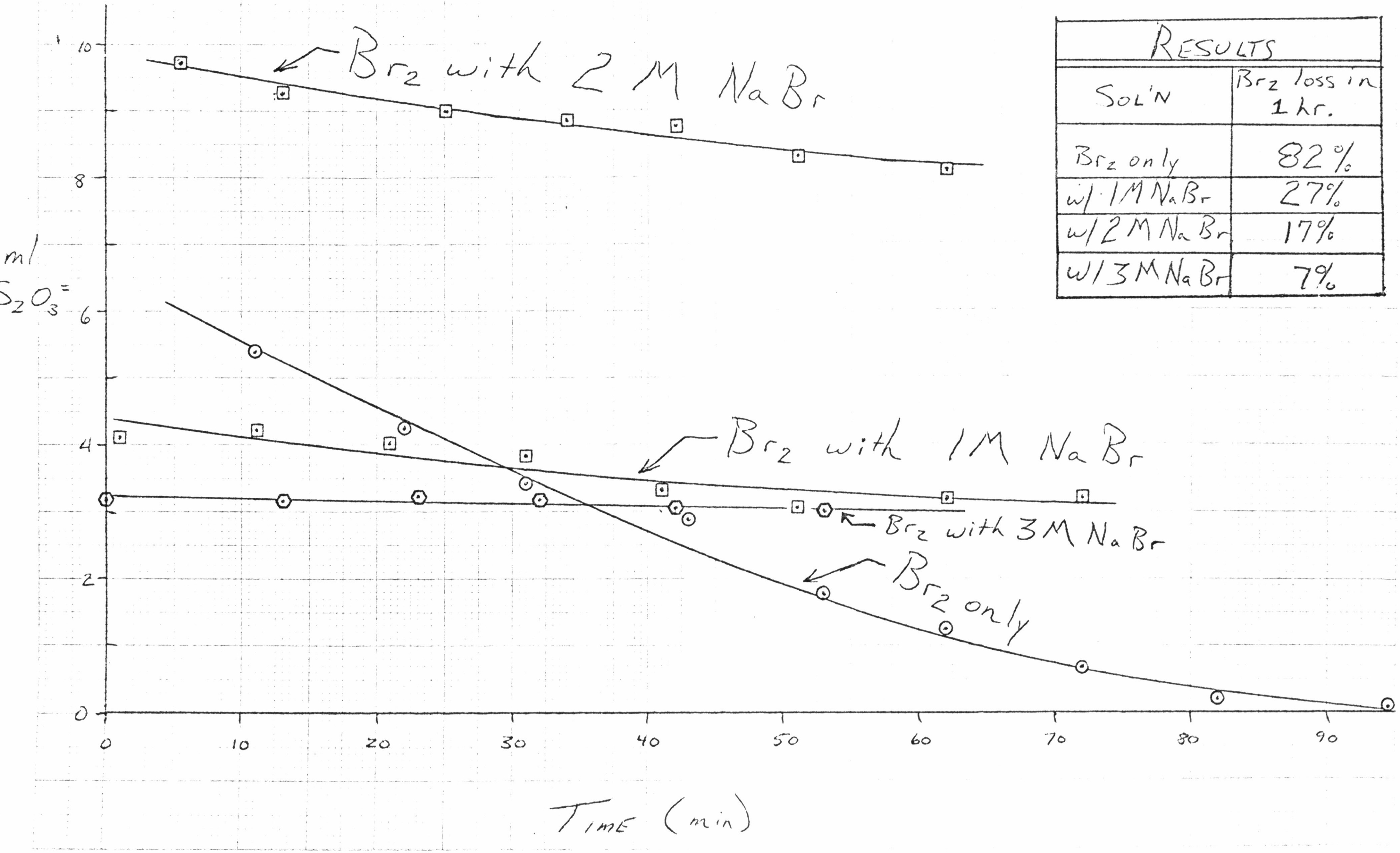
The geometry for which the Levich equation was determined is shown in Figure 4. A study of this geometry versus that used here was done by Kim and Jorne. Their findings indicate that edge effects due to the present geometry were unnoticeable.

FIGURE 1
ROTATING ZN HEMISPHERE



# EFFECT OF COMPLEXING AQUEOUS BROMINE

FIGURE 2




| RESULTS | |
|---|---|
| SOL'N | $Br_2$ loss in 1 hr. |
| $Br_2$ only | 82% |
| w/ 1M NaBr | 27% |
| w/2M NaBr | 17% |
| w/3M NaBr | 7% |

TABLE 1

DATA - 3 M NaBr Solutions

| Rotational speed (rpm) | Reaction time (min) | Bromine concentration (gmol/cc) | Weight loss (mg) | $\frac{W}{MAC_b t}$ (cm/sec) |
|---|---|---|---|---|
| 000 | 46 | $7.751x10^{-5}$ | 10.73 | 0.000495 |
| 40 | 60 | 5.79 | 22.60 | 0.00107 |
| 148 | 60 | 6.72 | 28.24 | 0.00117 |
| 305 | 61 | 7.17 | 49.38 | 0.00185 |
| 500 | 60 | 6.99 | 53.14 | 0.00207 |
| 750 | 60 | 6.73 | 51.88 | 0.00211 |
| 1000 | 60 | 5.85 | 42.93 | 0.00204 |
| 1500 | 60 | 5.44 | 45.06 | 0.00228 |
| 2000 | 60 | 4.18 | 43.50 | 0.00284 |
| 7000 | 30 | 2.66 | 24.40 | 0.00503 |
| 9000 | 30 | 1.99 | 19.11 | 0.00524 |

1 M NaBr Solutions

| Rotational speed (rpm) | Reaction time (min) | Bromine concentration (gmol/cc) | Weight loss (mg) | $\frac{W}{MAC_b t}$ (cm/sec) |
|---|---|---|---|---|
| 124 | 32 | 5.80 | 16.69 | 0.00150 |
| 500 | 30 | 4.14 | 19.66 | 0.00258 |
| 1200 | 45 | 2.65 | 20.77 | 0.00285 |
| 2900 | 30 | 2.60 | 16.95 | 0.00355 |
| 7000 | 30 | 2.91 | 32.97 | 0.00626 |

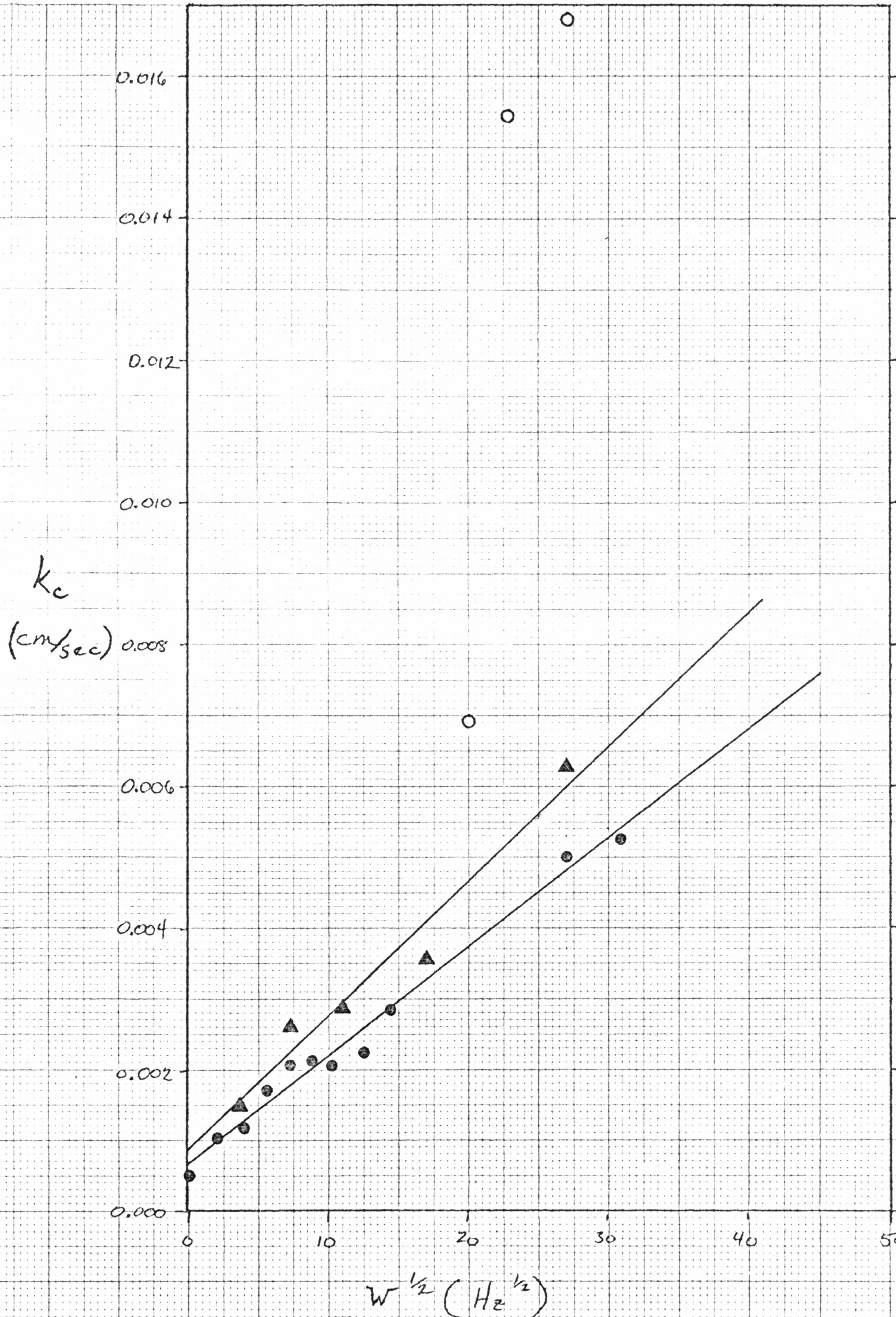
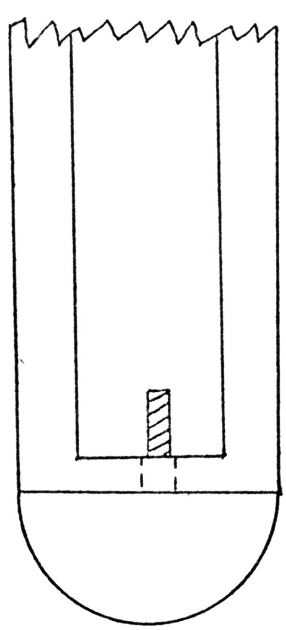



FIGURE 3. REACTION RATE VS. SQ. ROOT OF ANGULAR VELOCITY
▲ 1M; ● 3M NaBr. Empty points, spiral marks.

FIGURE 4

STRICT HEMISPHERICAL GEOMETRY



## Nomenclature

A hemisphere's surface area, $cm^2$

$c_b$ bulk concentration, g $mol/cm^3$

D diffusion coefficient, $cm^2/sec$

F Faraday's constant, 96,487 c/g-equiv.

$I_\ell$ limiting current, Amp

$k_c$ mass transfer coefficient, cm/sec

M molecular weight of Zn

n number of electrons transferred in electrode reaction

t time, sec

$\Delta W$ Zn weight loss, g

v kinematic viscosity, $cm^2/sec$

w angular velocity, rad/sec

REFERENCES

*Handbook of Chemistry and Physics, 56th ed.*, CRC Press, Cleveland, 1975, p. D-251.

Kim, Jung Taek and Jacob Jorne, "Mass Transfer of Dissolved Chlorine to a Rotating-Zinc Hemisphere in $ZnCl_2$ Solution", *Journal of the Electrochemical Society, vol. 125, no. 1*, January 1978, pp. 89-94.