PURPOSE

The purpose of this experiment is to determine the changes in free energy F, enthalpy H, and entropy S of a chemical reaction in a cell. In addition the E^0 of the cell is to be determined.

THEORY

An irreversible reaction may be brought about reversibly in an electrochemical cell. Since this process is now reversible the change in free energy may be calculated from the following equation

F' = faraday
E = cell pot.

$$\Delta F = -nF'E$$

Then, according to the Gibbs-Helmholtz equation, one may proceed to calculate the change in enthalpy and entropy of the reaction. Accordingly

$$\Delta F - \Delta H = T\left(\frac{\partial \Delta F}{\partial T}\right)_p = -T\Delta S$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$

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PROCEDURE

The procedure and equipment is essentially the same as that described in the laboratory text. The formulae used to calculate ΔF, ΔH, and ΔS are presented on page 1. The E^{o} of the cell was determined by plotting $E + 2A \log m$ vs $m^{\frac{1}{2}}$ and extrapolating back to zero molality.

Errors, literature values, and confidence limits are shown on table 2.

$= \pm\sqrt{9311}$ [illegible] $= \pm 1.305$ [illegible]

$= \pm\sqrt{92949}$ [illegible]

$$\sigma_{AS} = \pm\sqrt{(n\mathcal{E}')^2\sigma_F^2 + (nF)^2\sigma_{\mathcal{E}'}^2}$$

$$= \pm\sqrt{(2\times .00048)^2(7)^2 + (2\times 96{,}493)^2(.00005)^2}$$

$$= \pm\sqrt{45.1607} = \underline{\pm 6.72} \text{ joule mole}^{-1} \quad \text{or} \quad \underline{\pm 1.6\times 10^{-3}} \text{ k.c}$$

$$\sigma_{E+2A\log m} = \sqrt{\sigma_E^2 + \left(\frac{A}{m}\right)^2 \sigma_m^2 + (\log m)^2 \sigma_A^2}$$

$$= \sqrt{(.005)^2 + \left(\frac{.059}{.0055}\right)^2 (.0025)^2 + (-2.2596)^2 (.002)^2}$$

$$= \pm\sqrt{.000762} = \pm .0241$$

$6,493)^2(.00005)^2$

really 95% limits should be [illegible] to include random errors and [illegible] to [illegible] exp and [illegible] variability

95% Intervals ($n = 5$)

$\Delta H_{exp} = -32.55 \pm .73$ kcal/mole

$2.7 \times \pm .73 = \pm 1.97$

ΔH Range: $-30.58 - -34.52$

'$\Delta H_{Lit} = -33.62$ kcal/mole'

$E^\circ_{exp} = .3600 \pm .0241$ V

$2.7 \times \pm .0241 = \pm .0651$

E°_{ε} Range: $.2949 - .4251$

'$E^\circ_{Lit} = .41079$ V'

TABLE I

RAW DATA

	.0110m			25°C			
	0°C	25°C	40°C	.0056m	.00275m	.001375m	.0006875m
	.5682	.5603	.5555	.5541	.5620	.5725	.5806
	.5728	.5610	.5560	.5541	.5625	.5727	.5806
	.5667	.5617	.5569		.5630	.5727	
	.5679	.5618	.5482		.5630		
	.5677	.5619	.5490				
ε in volts	.5680	.5627	.5490	1.0 HR	1.0 HR	1.0 HR	0.5 HR
	.5690	.5627	.5567				
	.5695		.5575				
	.5695		.5569				
	.5709		.5575				
	.5713		.5550				
	.5713		.5546				
			.5543				
			.5543				
TIME FOR EQUILIB.* →	3.25 HR	1.6 HR	2 HR				

* final readings remained constant for 20 min.

EXP. VALUES FOR CALC.

$F = 96{,}493 \pm 7$

$n = 2$

$\varepsilon = 0.5627 \pm .005$ v.

$\left(\partial \varepsilon / \partial T\right)_p = -.00048 \pm .00005$ (see fig. #1)

$T = 298 \pm 1$ °K

$R = 8.3144 \pm .00034$ joule mole^{-1}

CALC. of ΔF, ΔH, + ΔS

$\Delta F = -nF\varepsilon = -(2)(96{,}493)(0.5627) = -108{,}573 \pm 965$ joules mole^{-1}

or $25.95 \pm .23$ k cal

$\Delta H = -nF\varepsilon + nFT\left(\partial \varepsilon / \partial T\right)_p = -108{,}573 + (2)(96{,}493)(298)(-4.8 \times 10^{-4})$

$= -136{,}177.72 \pm 3050$ joules mole^{-1} or $-32.55 \pm .73$ k cal

$\Delta S = nF\left(\frac{\partial \varepsilon}{\partial T}\right)_p = (2)(96{,}493)(-4.8 \times 10^{-4}) = -92.63 \pm 6.72$ joules mole^{-1}

or $(2.21 \pm .16) \times 10^{-2}$ K cal.

CALCULATION OF $\mathcal{E}^\circ$ & $\gamma_\pm$ (SEE MOORE, p. 495)

$\mathcal{E} + \left(2A/2 \times \log m\right)$ vs. $\sqrt{m}$

$A = \frac{RT}{nF}$

$\mathcal{E}$	+ $\left[\,2A/2 \times \log m\,\right]$	=		$\sqrt{m}$
.5627	.0591 × -1.9586		.4473	.1049
.5541	.0591 × -2.2596		.4208	.0742
.5630	.0591 × -2.5607		.4119	.0524
.5727	.0591 × -2.8617		.4039	.0371
.5806	.0591 × -3.1625		.3940	.0262

(SEE fig 2 for plot & extrapolation to $\mathcal{E}^\circ$)

$\mathcal{E}^\circ_{EXP} = .3600 \pm .0241\,v$ $\mathcal{E}^{\circ\,*}_{THEOR} = .41079\,v$

* COWPERTHWAIT & LA MER, J. Am. Chem. Soc. 53:4333 (1932)

too low

What are the [illegible] values for m

$$\log \gamma_\pm = \frac{\mathcal{E}^\circ - (\mathcal{E} + .059 \log m)}{(.059)}$$

		ANTILOG $= \gamma_\pm$ ↓	m
$= \frac{.3600 - .4473}{.0591}$	$= -1.4790$	.0332	.0110
$= \frac{.3600 - .4208}{.0591}$	$= -1.0290$	.0935	.0055
$= \frac{.3600 - .4119}{.0591}$	$= -0.8780$	.1324	.00275
$= \frac{.3600 - .4039}{.0591}$	$= -0.6530$	.2223	.001375
$= \frac{.3600 - .3940}{.0591}$	$= -0.5760$	.2655	.0006875

THEOR. ΔH (calorimetric for irreversible react.)

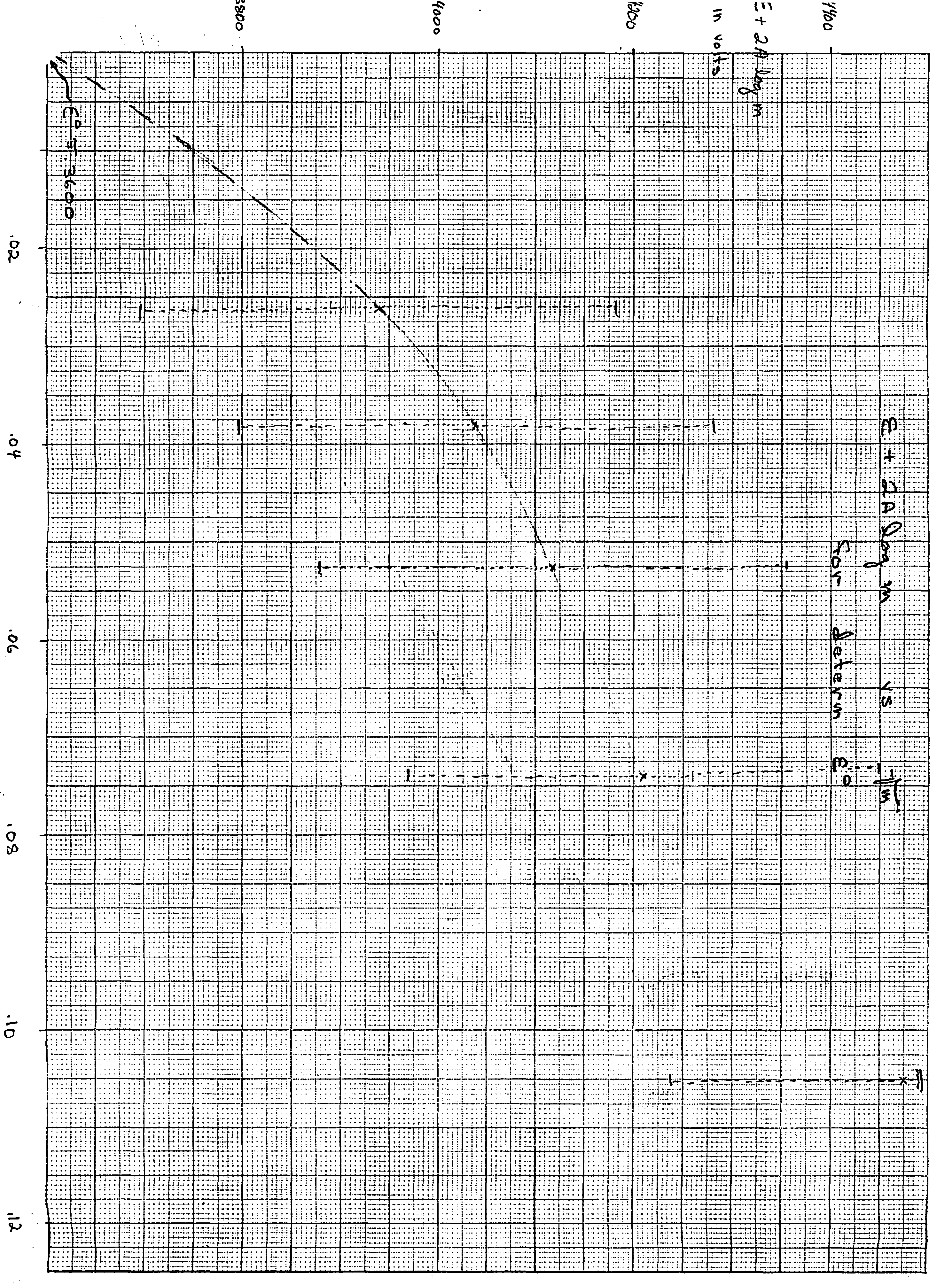
ref.

$\Delta H f^\circ$ $ZnSO_4 = -253.12$ k. cal.

$PbSO_4 = \underline{-219.50}$

HANDBOOK OF CHEM. & PHYS.

$\Delta H = -33.62$ k. cal.



E + 2A log m vs 1/√m for determ E0

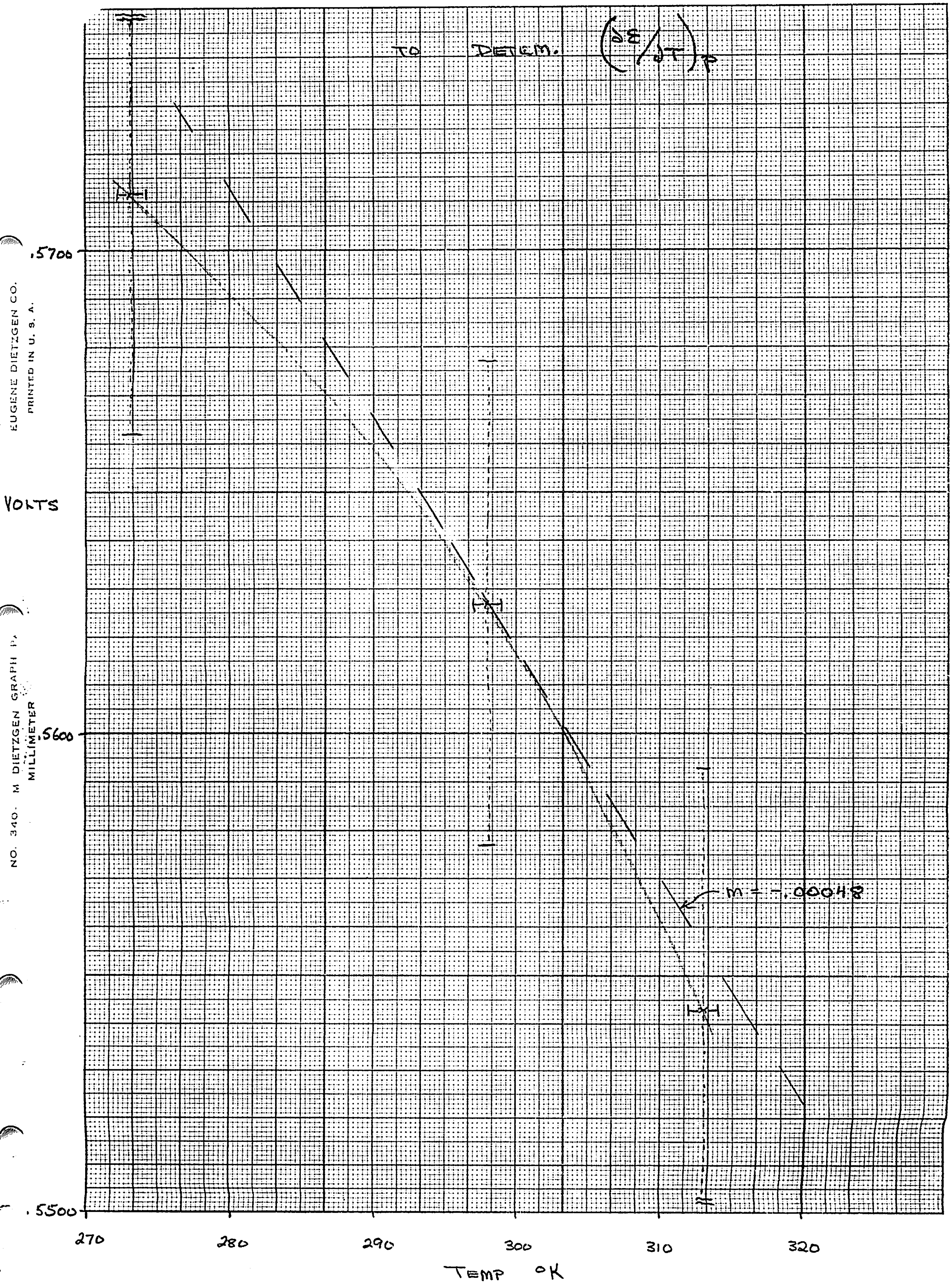
FIG. #2

DISCUSSION AND CONCLUSION

The literature (theoretical) value obtained for ΔH is -33.62 kcal/mole; the value arrived at experimentally is -32.55 ± 0.73 kcal/mole. The literature value falls well within the statistical population calculated (see table 2). Considering the number of erros which can enter into the results, the experimental figure is relatively accurate and precise. The greatest relative error seems to result from the concentration mixtures. This is evident because the respective concentrations were arrived at by a series of dilutions; therefore, errors would tend to be compounded for at least additive.

That experimental figure of E^o of the cell is not as accurate as was the determination of ΔH. However, as may be seen in table 2 and figure 2, the inaccuracy resulted from the same parameter, molalities of the solutions. As may be seen in the error computations, errors in molality will more influence the E^o of the cell than the ΔH of the reaction. From table 2, the experimental value for E^o is .3600 v; the literature value .41079 v. The determined range is .2949 - .4251. Although the literature value falls within the experimental population, there is some indication of a somewhat [illegible] large systematic error, yet insignificant at the 95% level.

FIG. # 1


TO DETEM. $\left(\frac{\partial E}{\partial T}\right)_P$
.5700
.5600
.5500
VOLTS
m = -.00048
270
280
290
300
310
320
TEMP °K

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An estimate could be made by using $E = E^0 - \frac{RT}{nF} \ln m\gamma$ — actually the [illegible] would be [illegible], but one could [illegible] [illegible] magnitude [illegible]

In an attempt to calculate the change of E^0 with what is suspected to be the major factor in the inaccuracy, i.e. the molality, it was realized that the mathematical formulation for the curve plotted in figure 2 was necessary. Since this is not immediately available and would involve a relatively rigorous mathematical application, - and also since the values were not significantly different at the 95% interval- it sufficed to show the relative magnitude of the molality with respect to the other parameters (table 2). One may also observe the relative magnitude of the errors in figure 2.

In conclusion one may say that there is evidence of both sytematic and random error in the results of this experiment, although not to the extent where they deviate sinificantly from the literature values.

BIBLIOGRAPHY

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