

EFFECT OF THE ADDITION OF ETHYLENE GLYCOL  
ON THE POTENTIALS OF CELLS  
OF THE WESTON TYPE

By

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## INTRODUCTION

The effect of the addition of organic compounds to water on the potentials of galvanic cells has been studied in some detail by Harned and co-workers, as well as a few others. Methyl alcohol (1, 7), ethyl alcohol (3), glycerol (12), dioxane (4), sucrose (13), and ethylene glycol (9) have been studied as additives using the hydrogen electrode in combination with a silver-silver chloride electrode in a cell without liquid junction. In all these cells, hydrochloric acid was used as the electrolyte. Work was also done at this institution by Trimble and Ebert (14) on the activity of sulfuric acid, using ethylene glycol as the additive and employing the hydrogen and mercury-mercurous sulfate electrodes.

The effect generally found was a lowering of the potential amounting to about one hundredth of a volt for the addition of ten percent of the organic compound.

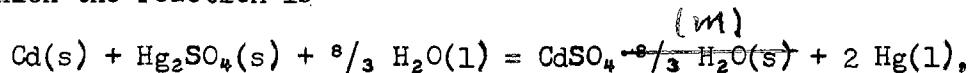
The Weston cell is, with its modification the Eppley cell, the unit of standard of the world. Its reliability, ease of assemblage, and constancy, are without equal. Mainly for these reasons, it was felt that information of interest could be obtained by a study of the effect of the addition of ethylene glycol upon the potentials of cells of the Weston type.

## THEORETICAL

In our cell:

Cd.Hg (12.5% Cd) / CdSO<sub>4</sub>·<sup>8</sup>/<sub>3</sub> H<sub>2</sub>O(m), (X H<sub>2</sub>O, Y Glycol), Hg<sub>2</sub>SO<sub>4</sub>(s) / Hg,

in which the reaction is



the free energy is given by

$$\Delta F = \Delta F^\circ - RT \ln a_{\text{CdSO}_4}. \quad (1)$$

$\Delta F^\circ$  is a constant called the standard free energy change for the reaction, R is the gas constant, T is the absolute temperature, and  $a_{\text{CdSO}_4}$  is the activity of the electrolyte, cadmium sulfate.

If the reaction shown takes place reversibly, then

$$\Delta F = -n\mathcal{F}E, \quad (2)$$

where E is the electromotive force, or EMF, for any given value of the activity of the cadmium sulfate; n is the number of equivalents reacting; and  $\mathcal{F}$  is Faraday's constant. If all the substances contained in the cell are in their standard states, that is at unit activity, the EMF is then  $E^\circ$ , or the standard EMF for the cell as written above. In this special case

$$\Delta F^\circ = -n\mathcal{F}E^\circ. \quad (3)$$

Substituting into equation 1,

$$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln a_{\text{CdSO}_4}, \quad (4)$$

which gives us a method of calculating thermodynamic values using our EMF values. The variable  $a_{\text{CdSO}_4}$  cannot be directly evaluated, but is given by

$$a_{\text{CdSO}_4} = m^2 \gamma^2, \quad (5)$$

where m is the molality of the electrolyte, and  $\gamma$  is a proportionality

constant called the activity coefficient.

Thus, equation 4 becomes

$$E = E^{\circ} - \frac{RT}{nF} \ln m^2 \gamma^2, \quad (6)$$

or in our case, as n is equal to 2,

$$E = E^{\circ} - \frac{RT}{F} \ln m \gamma. \quad (7)$$

Expanding and rearranging:

$$E + \frac{RT}{F} \ln m = E^{\circ} - \frac{RT}{F} \ln \gamma. \quad (8)$$

Equation 8 is the basis of the classical method used by Lewis and Randall (11) for finding  $E^{\circ}$ . In this method the left side of equation 8 is plotted against the square root of the molality. The curve is very nearly a straight line at the lower concentrations and may be extrapolated to zero to give a value of  $E^{\circ}$ . It is found however, that the data obtained here show a considerable curvature in the lower molalities, thus making the extrapolation difficult, if not impossible. The simpler method of Debye and Hückel offers another method of determining  $E^{\circ}$ , through an evaluation of the  $\ln \gamma$  term. This also proves unsatisfactory, because although it takes into account the dielectric constant of the solvent, it does not take into account the average ionic diameter.

The method finally used, a slight modification of the combined efforts of Lewis and Randall and Debye and Hückel, was used by Harned and co-workers in working with mixed solvents in the hydrogen and silver-silver chloride electrodes. The equation elucidated by Harned (6) was developed from interionic attraction theory, and is

$$\begin{aligned} E^{\circ'} &= E + 2k \log m - \frac{2kS(\epsilon)\sqrt{c}}{1 + A\sqrt{c}} - 2k \log (1 + 0.002 M_{xy} m) \\ &= E^{\circ} + f(m). \end{aligned} \quad (9)$$

$f(m)$  here indicates a function of  $m$ , the molality;  $E$  is the EMF of the cell;  $k$  is a constant used by Harned:



$$k = \frac{2.3026 RT}{nF} \quad (10)$$

$S(f)$  is a symbol used by Harned to represent the limiting slope of the equation:

$$\ln \gamma = -\frac{1}{\nu} \sum \nu_j z_j^2 \left( \frac{\pi N e^6}{1000 (kDT)^3} \right)^{1/2}, \quad (11)$$

and is equal to

$$S(f) = -\frac{1}{\nu} \sum \nu_j z_j^2 (DT)^{-3/2} \times 1.28 \times 10^6, \quad (12)$$

where  $\nu$  is the total number of ions of which  $\nu_j$  are of the  $j$  kind, and  $z_j$  is the valence of the  $j$  ion.  $D$  is the dielectric constant of the solvent, and  $T$  is the absolute temperature. The sum is taken over all of the ions present.  $1.28 \times 10^6$  is a constant taking into account all of the constant terms in equation 11, and  $c$  is the molar concentration of the electrolyte.  $A'$  is a parameter involving the average ionic diameter:

$$A' = 35.57 \bar{a} \times (DT)^{-1/2}. \quad (13)$$

$\bar{a}$  is the average or mean ionic diameter, or the mean distance of approach of the ions.  $M_{xy}$  is the mean molecular weight of the composite solvent:

$$M_{xy} = \frac{100}{x/M_x + y/M_y}, \quad (14)$$

where  $x$  is the percentage by weight of the solvent component of molecular weight  $M_x$ , and  $y$  is the percentage by weight of the solvent component  $M_y$ .

Equation 9 was modified for our use to

$$E^{\circ'} = E^{\circ} + .05915 \log m - \frac{.05915 S(f) \sqrt{F}}{1 + A' \sqrt{F}} - .05915 \log (1 + .002 M_{xy} m) \\ = E^{\circ} + f(m), \quad (15)$$

where  $\nu$  is the ionic concentration.

In this special case

$$S(f) = |z_1 z_2| (DT)^{-3/2} \times 1.28 \times 10^6, \text{ and} \\ \sqrt{F} = 2\sqrt{2d_o m},$$

where  $d_o$  is the density of the solvent and  $m$  is the molality of the electrolyte in the solution.

In our work we have determined the EMF values at various molalities at 25° C. The other values are known with the exception of the average ionic diameter, density of the solvent, and dielectric constant of the solvent. These values were found in the literature and will be discussed more fully later. It is seen, then, that by plotting  $E^{\circ}$  against the molality, an extrapolation to the zero of molality should give a value of  $E^{\circ}$ . This expectation was realized as will be seen from Figure 2.

## REAGENTS AND APPARATUS

Ethylene Glycol The glycol was technical grade or better, and was purified by vacuum distillation, discarding the first and last quarters. Previous experiments have proved that this method of purification gives pure glycol within experimental error.

Water All water used was purified by distilling previously distilled water from alkaline permanganate in pyrex apparatus.

Cadmium Amalgam The 12.5 percent amalgam (12.5 percent because this is the percentage used in the standard Weston cell) was prepared by electrolyzing a cadmium sulfate solution, with a stick of cadmium as the anode and a mercury pool as the cathode. It has been reported that all cadmium amalgams between 9 and 15 percent cadmium will give constant potentials, but it was felt more desirable to stay with the accepted 12.5 percent.

Cadmium Sulfate The CP salt was recrystallized once by slow dehydration of a saturated solution over sulfuric acid.

Mercury Distillation by the method of Hulett (8) was used in the purification of the mercury. Prolonged standing showed no oxide film.

Mercurous Sulfate CP mercurous nitrate dissolved in dilute nitric acid (1-1) and titrated with dilute sulfuric acid (1-6) produced mercurous sulfate of acceptable quality. The salt was washed several times with 1-6 sulfuric acid and stored under this acid. The salt remained very well characterized throughout the experiments. No hydrolysis was noticed, as would be shown by a change of color from the white of the mercurous to the lemon yellow of the basic mercuric sulfate.

Apparatus All the measurements were made using a Leeds and Northrup K-2 potentiometer coupled with a Leeds and Northrup type E table top galvanometer with a sensitivity of 0.5 microvolt per scale division.

A saturated Weston cell, checked frequently with an Eppley cell standardized by the National Bureau of Standards, was used as the standard cell.

The cells were of the usual H type, being constructed of pyrex glass.

The measurements were carried out with the use of two constant temperature baths, one stationary at 25° C for the standard cell, and the other for the experimental cells used at the various temperatures. All temperatures were maintained at  $\pm 0.05$  degrees as was indicated by calibrated thermometers.

## EXPERIMENTAL PROCEDURES

The solutions used were made up in glass stoppered bottles into which weighed amounts of water and glycol were introduced, the water percentage being a little lower than finally desired. The cadmium sulfate $\cdot\frac{8}{3}\text{H}_2\text{O}$  was then weighed separately and introduced into the bottle, water being added finally to bring the ratio of water to glycol to the desired figure. Dr. Trimble previously determined, by a series of analyses of the cadmium content of such solutions, that this method introduces no error greater than the experimental error. It was found through the method of trial and error that the practical range of molalities was 0.01 to 0.60 molal. Solutions very much under the lower limit were of doubtful molality and solutions above the upper limit gave sluggish galvanometer response, due probably to lower ionization due to an increase in viscosity rather than any action between the components of the cell. Data on the three ratios of water to glycol (10 moles, 6.5 moles, and 3 moles of water respectively to 1 mole of glycol) were obtained at the four temperatures (20°, 25°, 30°, and 35° C) within the limits of molality of cadmium sulfate stated above.

Cadmium sulfate $\cdot\frac{8}{3}\text{H}_2\text{O}$  is stable up to about fifty percent by weight of glycol. In more concentrated solutions the salt becomes anhydrous, and this salt is practically insoluble in the solvent. Thus no values of EMF of higher concentration of glycol could be obtained.

Data on the dilute cadmium sulfate in pure water solutions were taken from Getman (2).

Some time was required to form the more concentrated cadmium sulfate solutions, but it was felt that no essential error due to evaporation was introduced.

The H cells were soaked with concentrated nitric acid, and rinsed copiously with conductivity water. They were set in a hot air bath until dry, and allowed to cool with air being drawn through. The cadmium amalgam was heated until homogeneous and introduced through a thistle tube of wide diameter into one side of the H cell. On the other side of the H cell mercury was placed. The level on both sides was just high enough to cover the platinum electrode wires.

Because the mercurous sulfate was stored in a sulfuric acid solution it had to be repeatedly washed with the solution to be used. It was washed 6 or 7 times, or until no sulfuric acid was present, thus also insuring the absence of mercuric sulfate. The mercurous sulfate thus treated was introduced through another thistle tube of wide diameter on top of the mercury. The solution was then carefully poured onto the amalgam, care being taken not to disturb the mercurous sulfate layer on the other side of the H cell. The H cell was stoppered with rubber stoppers slightly greased with stopcock grease to prevent evaporation of the water.

The cells, usually run in duplicate, were placed in the water bath at 35° C. Constant readings were attained rapidly, usually within thirty minutes, and remained constant for varying periods of time. Some were found to be constant over weeks, while others were found to drop off over night.

After at least two readings 5 or 6 hours apart were found to be the same, the temperature was lowered and the procedure repeated. Spot checks were made from time to time by returning to a temperature again, but no

appreciable difference was ever found at a given temperature.

All the measurements were made to five decimal places. Readings that did not check to  $\pm 0.00005$  volt were discarded. Readings to five decimal places were readily attained on the instruments used, but other procedures of the experiment and especially the nature of the calculations warranted retaining the first four decimals only.

## EXPERIMENTAL DATA

The results obtained are listed in Table I and represented in Figure 1. The EMF values given by Getman in his article were determined using an alpha cadmium electrode, made by depositing fine crystals of alpha cadmium on a platinum electrode by slow electrolysis. Getman compared his values with a ten percent cadmium amalgam and found a difference of 0.0474 volt. We have subtracted this value from his to secure potentials corresponding to our values.

Table I EMF Values for the Three Ratios of Solvent and also for Getman's data.

No Glycol (Getman's data, adjusted)

<u>m</u>	<u>EMF (volts) 25° C</u>
0.0055	1.1010
0.0139	1.0925
0.0554	1.0811
0.1328	1.0704
0.2217	1.0656



Solvent 10 moles water to 1 mole glycol

<u>m</u>	<u>EMF (volts)</u>			
	<u>35° C</u>	<u>30°</u>	<u>25°</u>	<u>20°</u>
0.00853			1.0887	
0.02403	1.0746	1.0749	1.0753	1.0756
0.03878			1.0693	
0.04510			1.0674	
0.08074			1.0604	
0.09985	1.0568	1.0573	1.0578	1.0582
0.1611	1.0516	1.0521	1.0526	1.0531
0.3283	1.0441	1.0446	1.0451	1.0456
0.6543	1.0365	1.0370	1.0375	1.0380

Solvent 6.5 moles water to 1 mole glycol

<u>m</u>	<u>EMF (volts)</u>			
	<u>35° C</u>	<u>30°</u>	<u>25°</u>	<u>20°</u>
0.00955			1.0782	
0.02297	1.0667	1.0672	1.0675	1.0677
0.05147			1.0588	
0.07134			1.0550	
0.08059	1.0526	1.0531	1.0536	1.0539
0.1703	1.0441	1.0446	1.0451	1.0456
0.3626	1.0361	1.0367	1.0372	1.0378
0.6661	1.0285	1.0293	1.0304	1.0308

Solvent 3 moles water to 1 mole glycol

<u>m</u>	<u>EMF (volts)</u>			
	<u>35° C</u>	<u>30°</u>	<u>25°</u>	<u>20°</u>
0.00966			1.0622	
0.02314	1.0507	1.0511	1.0515	1.0520
0.04655			1.0432	
0.08203			1.0365	
0.09201	1.0346	1.0352	1.0359	1.0363
0.1837	1.0245	1.0281	1.0287	1.0292
0.3697	1.0206	1.0212	1.0218	1.0223
0.4966	1.0173	1.0182	1.0192	1.0198

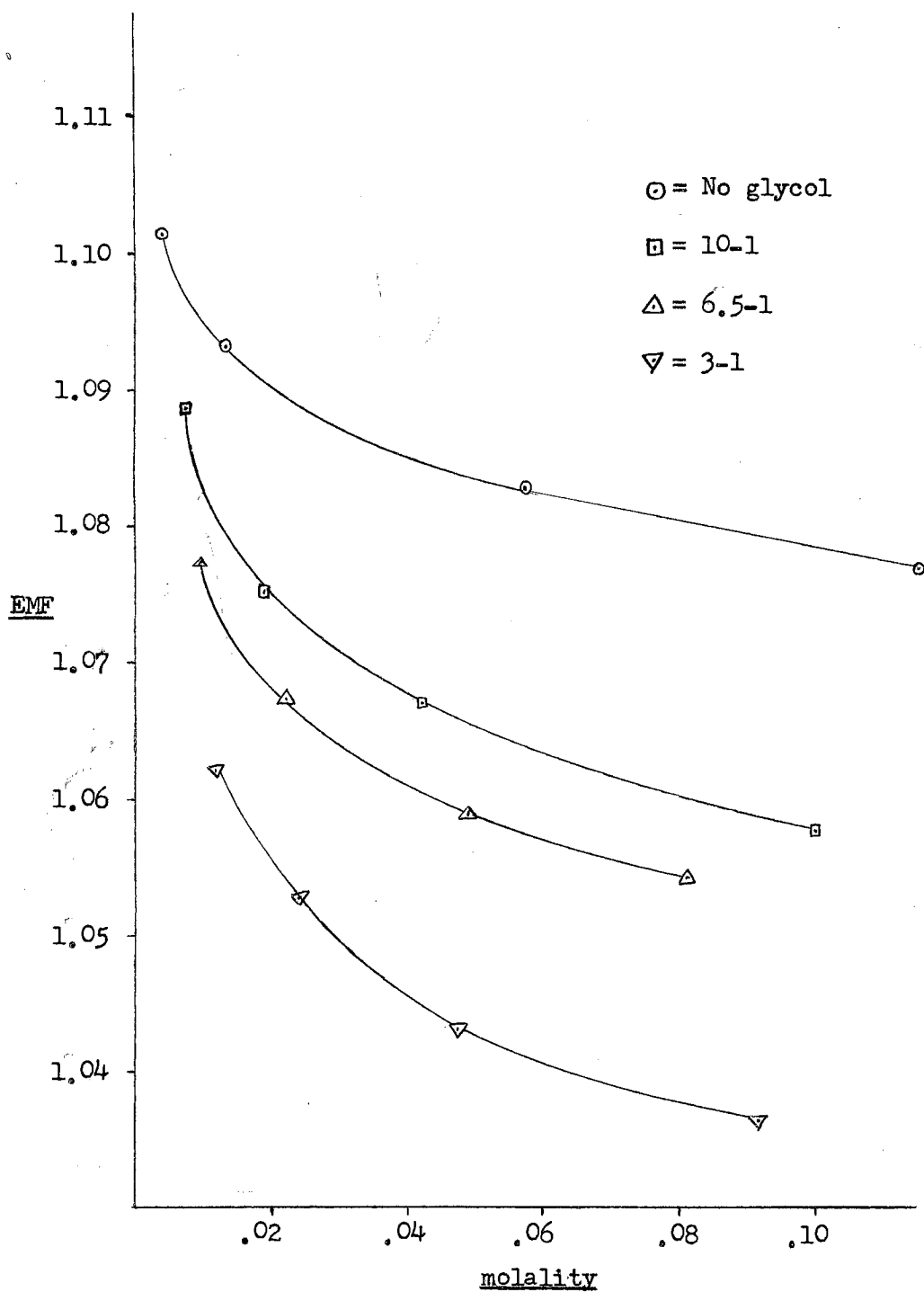


Figure 1 EMF plotted against molality for the three concentrations of solvent studied and also for Getman's data, all at 25° C.

## CALCULATIONS

Taking equation 15,

$$E^{\circ'} = E + .05915 \log m - \frac{.05915 S(f)\sqrt{F}}{1 + A'\sqrt{F}} - .05915 \log (1 + .002 M_{xy} m) \\ = E^{\circ} + f(m), \quad (15)$$

We can make the following simplifications:

$$A = .05915 \log m, \quad (16)$$

$$B = \frac{.05915 S(f)\sqrt{F}}{1 + A'\sqrt{F}}, \text{ and} \quad (17)$$

$$C = .05915 \log (1 + .002 M_{xy} m), \quad (18)$$

The equation will then read

$$E^{\circ'} = E + A - B - C = E^{\circ} + f(m), \quad (19)$$

In evaluating these terms we must make use of the following data. The values of  $d_o$ , the density of the solvent, are taken from a communication with the Carbide and Carbon Chemical Corporation (15); and the values of  $D$ , the dielectric constant of the solvent, from Harned (5).

Table II Values of the Density and Dielectric Constant of the Solvent,

<u>Ratio</u>	<u>% glycol</u>	<u><math>d_o</math></u>	<u><math>D</math></u>
no glycol	00.00	0.9960	78.6
10-1	25.60	1.0300	71.0
6.5-1	34.70	1.0430	68.3
3-1	53.50	1.0655	62.3

Since the average ionic diameter  $\bar{a}$  cannot be measured, it must be estimated. La Mer and Parks (10) have stated that the value for cadmium sulfate is  $3.6 \text{ \AA}$ , a value they arrived at by trial and error, and we deduced a value of  $3.4 \text{ \AA}$  by comparison with data for other salts of

a similar nature. A value of  $3.5 \text{ \AA}$  was used in the following calculations.

Since only the lower concentrations of cadmium sulfate will obey equation 15, we have used only those values of the molality below 0.10 molal.

We find then:

Table III Calculations of  $E^\circ'$  at  $25^\circ \text{ C}$

No Glycol (Getman's data)

<u>m</u>	<u>E</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u><math>E^\circ'</math></u>
0.0055	1.1010	-0.1337	0.0158	-----	0.9515
0.0139	1.0925	-0.0998	0.0235	-----	0.9692
0.0554	1.0811	-0.0745	0.0404	0.0001	0.9662
0.1328	1.0704	-0.0518	0.0545	0.0001	0.9640

10-1 Water to Glycol

<u>m</u>	<u>E</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u><math>E^\circ'</math></u>
0.00853	1.0887	-0.1224	0.0228	-----	0.9435
0.02403	1.0753	-0.0963	0.0347	-----	0.9443
0.03878	1.0693	-0.0835	0.0419	-----	0.9439
0.04510	1.0674	-0.0796	0.0443	0.0001	0.9435
0.08074	1.0604	-0.0704	0.0543	0.0001	0.9357
0.09985	1.0578	-0.0592	0.0583	0.0002	0.9403

6.5 - 1 Water to Glycol

<u>m</u>	<u>E</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>E°'</u>
0.00955	1.0782	-0.1195	0.0250	-----	0.9337
0.02297	1.0675	-0.0970	0.0359	-----	0.9346
0.05147	1.0588	-0.0762	0.0484	0.0001	0.9321
0.07134	1.0550	-0.0678	0.0543	0.0001	0.9328
0.08059	1.0536	-0.0647	0.0567	0.0001	0.9321

3-1 Water to Glycol

<u>m</u>	<u>E</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>E°'</u>
0.00966	1.0622	-0.1192	0.0289	-----	0.9141
0.02314	1.0515	-0.0968	0.0412	-----	0.9145
0.04655	1.0432	-0.0788	0.0533	0.0001	0.9110
0.08203	1.0365	-0.0642	0.0647	0.0001	0.9175
0.09201	1.0359	-0.0613	0.0671	0.0001	0.9074

The data of Table III are represented as curves in Figure 2.

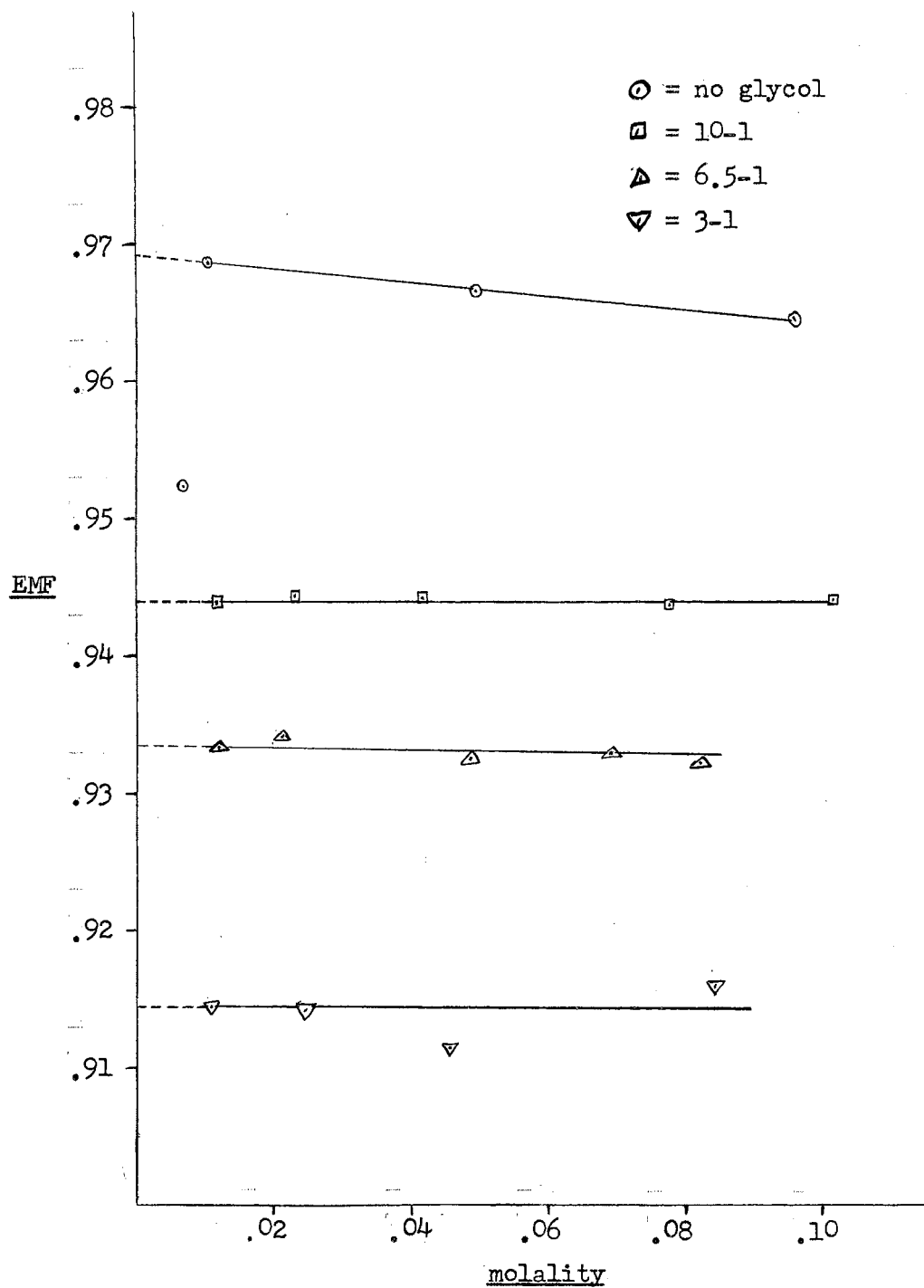


Figure 2  $E^{\circ}$  plotted against the molality and extrapolated to  $E^{\circ}$  for the three ratios of solvent and Getman's data, all at 25° C.

The  $E^\circ$  values, as given by the extrapolation in Figure 2, are listed in Table IV.

Table IV  $E^\circ$  Values for Three Ratios of Solvent and Getman's data, all at 25° C.

<u>Ratio</u> <u>Water to Glycol</u>	<u>Percentage</u> <u>glycol</u>	<u><math>E^\circ</math></u>
no glycol	00.00	0.9690
10-1	23.60	0.9440
6.5-1	34.70	0.9344
3-1	53.50	0.9150

In conjunction with the calculation of the  $E^\circ$  values, the calculation of the activity coefficient follows.

Rearranging equation 8:

$$-.05915 \log \gamma = E - E^\circ + .05915 \log m \quad (8)$$

The results in Table V follow. The values for cadmium sulfate in aqueous solutions as given by La Mer and Parks (10) are included for comparison.



Table V Activity Coefficients.

<u>No Glycol</u>		<u><math>\gamma</math></u>	
<u>m</u>		<u>Getman</u>	<u>La Mer and Parks</u>
0.01		0.390	0.383
0.02		0.320	0.285
0.05		0.240	0.215
0.10		0.180	0.160
0.20		0.110	0.105
0.50		0.068	0.060

<u>10-1</u>		<u>6.5-1</u>		<u>3-1</u>	
<u>m</u>	<u><math>\gamma</math></u>	<u>m</u>	<u><math>\gamma</math></u>	<u>m</u>	<u><math>\gamma</math></u>
0.00853	0.420	0.00955	0.388	0.00966	0.336
0.02403	0.264	0.02297	0.245	0.02314	0.213
0.03878	0.209	0.05147	0.153	0.04655	0.146
0.04510	0.182	0.07134	0.128	0.08203	0.109
0.08074	0.167	0.08059	0.120	0.09201	0.098
0.09985	0.119	0.10	0.104	0.10	0.088
0.20	0.092	0.20	0.084	0.20	0.074
0.50	0.058	0.50	0.052	0.50	0.045

The values listed in Table V are represented as curves in Figure 3.

The latter values of the activity coefficient are calculated for the higher rounded concentrations; and the glycol-free solvent is also calculated for rounded values, in order to show the comparison with the literature values.

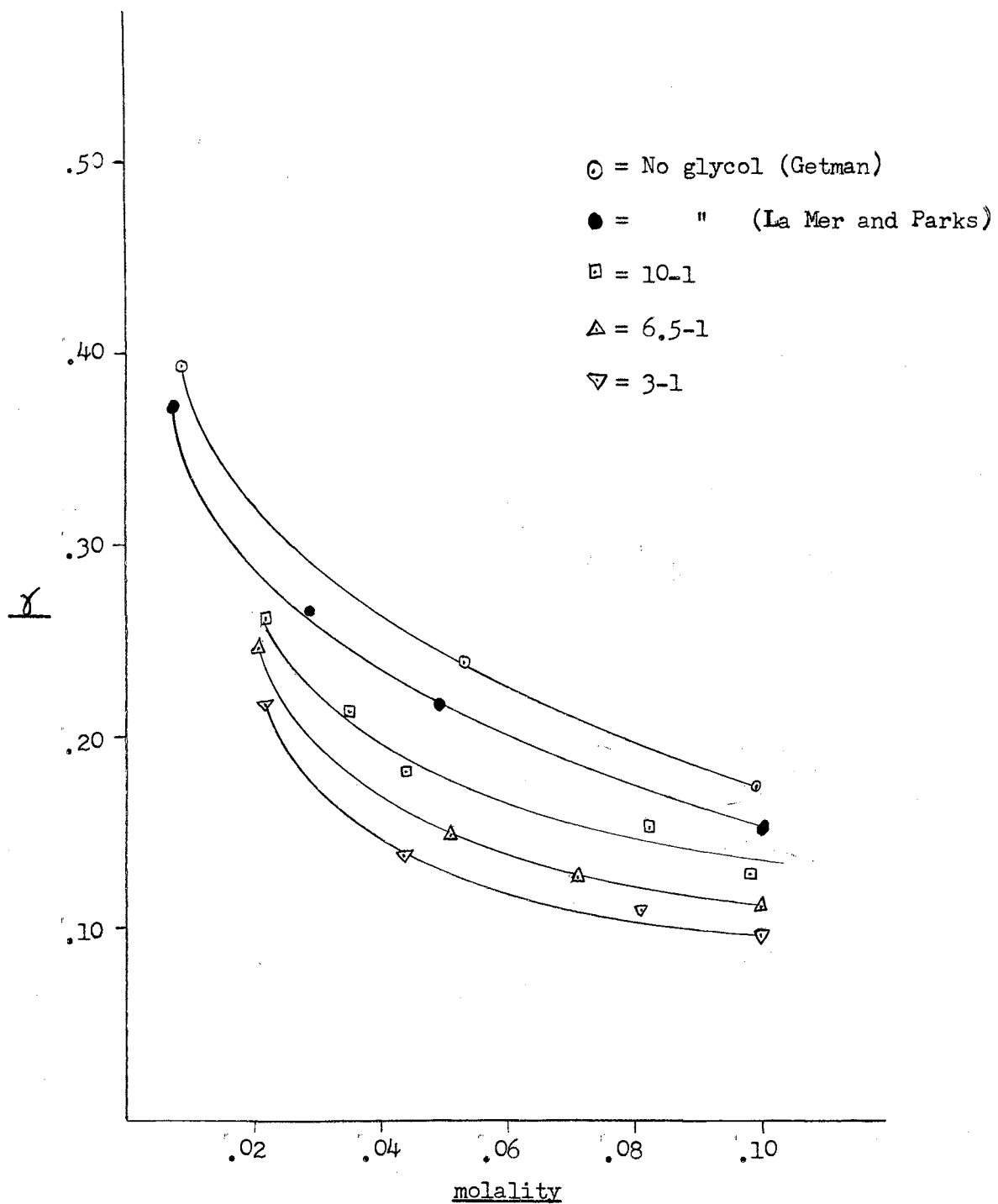


Figure 3 Activity coefficients plotted against the molality for the three ratios of solvent and also for Getman's data and the data calculated by La Mer and Parks, all at 25° C.

Having calculated  $E^\circ$ , which is the standard electromotive force, we can calculate  $\Delta F^\circ$  by the use of equation 3.  $\Delta F^\circ$  will then be the standard free energy, or the free energy of the reaction if all the components were at unit activity. These values are listed in Table VI. They perhaps represent the driving forces of the reaction in the various solvents more satisfactorily than would those for non-standard conditions.

Table VI Standard Free Energies at 25° C.

<u>Ratio</u> <u>Water to Glycol</u>	<u><math>\Delta F^\circ</math></u> <u>cal./mole at 25° C</u>
no glycol	-44,690
10-1	-43,540
6.5-1	-43,090
3-1	-42,200

We are given from thermodynamics:

$$\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_P \quad (20)$$

$\left( \frac{\partial E}{\partial T} \right)_P$  can be approximated very satisfactorily by setting  $\left( \frac{\partial E}{\partial T} \right)_P$  equal to  $\left( \frac{\Delta E}{\Delta T} \right)_P$ . Since the values of  $E$  found during this research were found at 20°, 25°, 30°, and 35° C,  $\left( \frac{\Delta E}{\Delta T} \right)_P$  can be calculated and was found to be  $-0.0000984 \pm 0.0000014$  volt per degree, which is the temperature coefficient of the cell. Values were calculated for each mixed solvent ratio, but the margin of error in each case encompassed the other two values, so an overall average was taken. Since the value is comparable for all of the cells studied, it seems justifiable to say that this is a standard temperature coefficient, and using equation 20, we can calculate a standard entropy change,  $\Delta S^\circ$ . This value is  $-4.54$  cal./degree.

$\Delta H^\circ$  can now be calculated using the equation

$$\Delta F = \Delta H - T \Delta S, \quad (21)$$

which in this special case becomes

$$\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ. \quad (22)$$

The results in Table VII follow.

Table VII Standard Heat of Reaction.

Ratio <u>Water to Glycol</u>	$\Delta H^\circ$ <u>cal./mole at 25° C</u>
10-1	-42,190
6.5-1	-41,740
3-1	-40,850

No values of  $\Delta S^\circ$  or  $\Delta H^\circ$  can be calculated for Getman's data, because of the absence of a temperature coefficient. If we assume the same temperature coefficient for his work, then  $\Delta S^\circ$  would be -4.54 cal./degree, and  $\Delta H^\circ$  would equal -43,340 cal./mole.

## DISCUSSION AND CONCLUSIONS

In this research as in other similar researches, the range of concentration is the limiting factor. These limits have been discussed earlier.

Results attained within the limits set forth seem satisfactory. Work within these limits has been treated, and is to our knowledge the best and perhaps the only work of this nature done with this system.

Getman's data were found lacking in many respects. The uncertainty in EMF values as reported in his article, insufficient data in the lower concentration range worked with here (0.01 to 0.10 molal), and a somewhat shaky extrapolation to  $E^\circ$ , cast an amount of uncertainty on the calculations based on his values.

Glycol has no effect upon the reproducibility of EMF values in these cells nor upon their reversibility.

The addition of glycol caused a drop in the activity coefficient, the drop being about 0.01 for the addition of ten percent glycol.

The addition of ten percent glycol had the same effect on  $\Delta F^\circ$  and  $\Delta H^\circ$ , the effect being a drop of about 500 cal./mole.

The addition of 23.60 percent glycol caused a drop of 0.016 volt, the addition of 34.7 percent caused a drop of 0.023 volt, and the addition of 53.5 percent caused a drop of 0.039 volt. It appears in general, then, that the addition of ten percent glycol caused a drop of about 0.008 volt, while previous investigators found with other systems a drop of about 0.01 volt for the addition of ten percent additive.

## SUMMARY

1. A study was made of the effect of the addition of ethylene glycol on the potential of cells of the Weston type.
2. The results were obtained for the ratios of 10 moles, 6.5 moles, and 3 moles of water, respectively, to 1 mole of glycol. Measurements were made in the range of 0.01 to 0.60 molal in cadmium sulfate at 20°, 25°, 30°, and 35° C.
3. A decrease of about 0.008 volt was found for the addition of ten percent glycol.
4.  $E^\circ$  values were calculated by extrapolation to zero molality, using the method of Harned and co-workers, and  $\Delta F^\circ$  values found directly from these values.
5. The temperature coefficient of the cell studied was found to be  $-0.0000984 \pm 0.0000014$  volt per degree. With the use of this value and the appropriate formulae,  $\Delta S^\circ$  and  $\Delta H^\circ$  values were calculated.
6. The activity coefficients were calculated and found to decrease with the addition of glycol, the decrease being about 0.01 for the addition of ten percent glycol.
7.  $\Delta H^\circ$  and  $\Delta F^\circ$  were found to decrease by about 500 cal./mole for the addition of ten percent glycol.

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