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The Rate of Corrosion of Silver in Ferric Perchlorate Solutions. A manuscript submitted for publication to the Journal of the Electrochemical Society,

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THE RATE OF CORROSION OF SILVER IN FERRIC PERCHLORATE SOLUTIONS[1]

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ABSTRACT

Silver dissolves much more slowly in ferric perchlorate and nitrate than in ferric sulfate solutions. A detailed study of the rate in perchlorate solutions has been made, with the effect of concentration of ferric, ferrous and silver ions, of other salts including sulfates, of stirring speed, temperature and electrical polarization. Two factors are responsible for the difference in rates: (a) silver perchlorate is more strongly adsorbed on silver than silver sulfate is, and (b) a sulfato-ferric complex ion reacts more rapidly than the normal hydrated ferric ion. Spectrophotometric evidence is given for the existence of the sulfato-ferric ion. (auth)

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[1] From a thesis submitted by Frances S. Lang to the Graduate School of New York University in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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INTRODUCTION

Much work in this Laboratory on metal dissolution rates has been devoted to the study of conditions under which the metal reacts rapidly without formation of adsorbed or insoluble films and consequently diffusion of reagent to the metal surface is rate controlling. A study of the dissolution of silver in ferric salt solutions was undertaken for several reasons. No insoluble films are formed ordinarily, but the rate is too low to be diffusion controlled (1). The reaction

$$Ag + Fe^{+++} \rightleftharpoons Ag^{+} + Fe^{++} \tag{I}$$

reaches a measurable equilibrium, and the influence of the back reaction might be studied. The reversible potentials of $Ag-Ag^{+}$ and Fe^{++} -- Fe^{+++} electrodes are of similar magnitudes and rates might be correlated with potential differences.

It was actually found in ferric - ferrous - silver sulfate solutions, that adsorption of the various ions is the principal rate controlling factor (2). The rate was found to be much higher in ferric sulfate than in ferric nitrate or perchlorate solutions; the present study in perchlorate solutions was made to find the reasons for this difference.

EXPERIMENTAL

Pure silver (99.97%) cylinders were rotated in 500 ml of solution, at controlled temperatures and speeds as described before (2). Stock solutions of the best commercial reagents were standardized and diluted to prepare mixtures. Perchloric acid was added to the ferric and ferrous solutions and its molar concentration in the final dilute solutions was always one half that of the ferric perchlorate.

Five silver cylinders were used. Their dimensions were 2.0 cm diameter x 1.5 cm and changed very little during the entire work. The cylinders were polished with very fine emery paper before each run after it was shown that etching or electropolishing gave identical rates. The rates were followed by weight loss, which was reproducible to 0.1 or 0.2 mg. Solutions containing several hundredths molar ferric perchlorate or an appreciable concentration of silver ions gave rates which decreased rapidly with time, and for this reason most runs were of two minute duration. Weight loss varied from 70 mg down to 0.1 mg or less in two minutes, and for the lowest rates longer time intervals were necessary. Rates are reported in grams x 10^{-4} per cm^2 per min.

Adsorption measurements were made by rotating bottles containing 10 g. of precipitated silver and 25 ml of solution in a thermostat. The solutions were filtered through sintered glass, and aliquots titrated with standard KBr solutions with Rhodamine 6 G indicator. Detailed adsorption experiments will be reported later.

Potentials given are for the silver cylinder vs a platinum electrode immersed in the solution. Small springs ensured contact between the silver and the motor shaft extension, and a mercury cup was mounted on the top of the motor shaft. Potentials were measured with a student type potentiometer.

In the polarization experiments a dry cell was used to pass current between the silver and a large platinum electrode. The current was measured with a calibrated milliammeter, the imposed potentials, which were all less than one volt, with a vacuum tube voltmeter. Reversible potentials were not measured.

DATA AND COMMENTS

Rotational speed. -- Fig. 1 shows the dissolution rate in ferric perchlorate solutions compared to the rate in ferric sulfate. At a peripheral speed of 300 cm sec^{-1} the rate in the ferric sulfate solution used is about half that to be expected for diffusion control (2). The curves for ferric perchlorate probably indicate the presence of concentration gradients at the metal surface, with diffusion playing a small role.

Temperature coefficients. -- Rates were measured at various temperatures in two solutions: a) 0.05 M ferric perchlorate alone, and b) in a solution containing enough ferrous and silver ions to make the rate very low at 20°. Fig. 2 shows the rate logarithms plotted vs 1/T. The activation energies are a) 11,500 cal. and b) 19,500 cal. respectively. These values are much larger than for diffusion controlled rates.

Acid and salt additions. -- There was no change in weight when a silver cylinder was rotated in 0.1 M perchloric acid for two hours, and concentration of the acid up to 0.3 M did not affect the rate in 0.05 M $Fe(ClO_4)_3$. Sodium and zinc perchlorates up to 0.1 N had little effect. Sulfates have an enormous effect, as shown in Table I. While $ZnSO_4$ increases the dissolution rate it decreases the potential.

TABLE I

The Effect of Sulfates on the Rate. 30°, 4000 rpm.

$0.03\ M\ Fe(ClO_4)_3$

sulfate		R, g x 10^{-4} cm^{-2} min^{-1}
----		2.4
Na_2SO_4,	0.01 M	6.9
	.02	9.8
	.04	13.0
H_2SO_4,	0.01 M	10.8
	.036	13.9

$0.03\ M\ Fe(ClO_4)_3$,
$0.005\ M\ AgClO_4$

----	0.23
H_2SO_4, 0.01 M	14.1

$0.03\ M\ Fe(ClO_4)_3$,
$0.0025\ M\ AgClO_4$

----	0.47
$NaSO_4$, 0.01 M	14.3

$0.005\ M\ Fe(ClO_4)_3$, $0.005\ M\ Fe(ClO_4)_2$,
$0.003\ M\ AgClO_4$

C_{ZnSO_4}, M	emf, volts	R
0	0.060	< 0.01
0.01	.053	0.37
.05	.023	.53
.08	.019	.64

Electromotive force measurements. -- With a rotating silver cylinder and a platinum wire electrode immersed in ferric perchlorate solution, the silver is normally anodic. Variation of rotational speed has little or no effect on the measured emf; the latter decreases with time, especially in solutions containing silver ions originally.

As shown in Fig. 3, addition of ferrous perchlorate to 0.05 M ferric perchlorate reduces the emf normally, but addition of silver perchlorate has a much greater effect. In these solutions the emf becomes zero with 0.03 M Ag^+ present, whether ferrous ion has been added or not, and larger additions reverse the polarity of the cell; no silver is precipitated in the solution. With 0.01 M ferric perchlorate, the emf approaches zero at ca. 0.02 M Ag^+, again with or without the addition of ferrous ion.

Adsorption of silver perchlorate on silver. -- Measurements are given in Table II. When reciprocals of equivalents and concentrations are plotted, a line with small curvature is obtained (approximation to a Langmuir isotherm). The saturation value is obtained by extrapolation. The precipitated silver used had an apparent area of 500 ± 5 cm^2 per gram, as measured with a microscope; the saturation adsorption is then 105×10^{-10} equivalents[1] per cm^2.

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[1] It has been proposed by R. B. Dean, J. Phys. and Colloid Chem. 55, 611 (1951), that the adsorption unit 1×10^{-10} moles per cm^2 be called the Gibbs.

Similar analysis of the adsorption of silver nitrate on silver sheets, measured by Rudberg and von Euler (3) gives 90 x 10^{-10} equivalents per cm^2.

Approximately one third as much silver sulfate is adsorbed, but the available measurements are not very concordant. There was no detectable adsorption of ferrous perchlorate when experiments were carried out in the same way.

TABLE II

Adsorption of Silver Perchlorate on Silver at 25°.

C_{AgClO_4},M	Equiv. per gram x 10^6
0.0087	1.27
.0186	2.30
.0260	2.85
.0681	4.00
.0877	4.28
(∞)	(5.26)

Polarization of the silver. -- A silver cylinder rotating in 0.01 M $Fe(ClO_4)_3$ was subjected to anodic and cathodic polarization as shown in Fig. 4. Corrosion by the solution, aside from faraday dissolution, disappears at an anodic current density of 15 ma/cm^2. The "difference effect" (decrease in free corrosion due to the current) is linear with current density. Except for details, this is similar to the result found by Streicher (4) with aluminum in 0.3 N NaOH.

The gradual disappearance of free corrosion may be due to stepwise polarization of local elements on the silver surface, but the total effect is to raise the reversible potential to a point where the silver can no longer reduce ferric ions; or the positive surface charge becomes sufficient to repel ferric ions completely.

The difference effect under cathodic polarization may be called cathodic protection (4). Sufficient cathodic potential brings the metal into a "domain of passivity" as defined by Pourbaix (5); that is, the bare surface is stable thermodynamically without the presence of silver ions or silver compounds. Adsorbed silver ions are discharged, any silver ions formed are redeposited, and ferric ion is reduced by the current. At small cathodic current densities there is an increase in corrosion from 1.20 to a maximum of 1.36 g $\times 10^{-4}$ cm^{-2} min^{-1}, no doubt due to partial neutralization of the normal positive charge on the silver, leaving more bare surface for reaction.

Evidence for a sulfato-ferric complex. -- There is indirect evidence that a ferric ion forms a stable complex with sulfate ion, such as the fact that excess sulfate ion destroys the color of the complex with thiocyanate (6), and there is direct evidence in the absorption measurements of von Kiss, Ábrahám and Hegedüs (7). To obtain more information the absorption curves shown in Fig. 5 were obtained. Each solution contained 1×10^{-4} M ferric ion and 5×10^{-5} M added hydrogen ion; the anion was changed from ClO_4^- in curve A through mixtures in curves B - C - D to $SO_4^=$ in curve E. Measurements were made with a Beckman DU spectrophotometer. The extinction coefficients plotted are apparent molar values based on the total ferric concentration.

The absorption from 220 - 260 mμ in curve A, Fig. 5, is due to hydrated Fe^{+++} and hydrated $FeOH^{+2}$, and the band at 270 - 320 mμ is due to the ion $FeOH^{++}$. Most investigators have been unduly concerned about further hydrolysis and formation of colloidal ferric hydroxide; for example, Rabinowitch and Stockmayer (8) calculated the extinction of $FeOH^{++}$ from measurements in strongly acid ferric perchlorate solutions. However, Olson and Simonson (9) found no further hydrolysis in dilute $Fe(ClO_4)_3$ with ~ 0.002 M $HClO_4$ present and their calculated values for $FeOH^{++}$ agree well with the experimental curve in Fig. 5. Brønsted and Volquartz (10) considered the hydrated Fe^{+++} in ferric nitrate to behave as a monobasic acid up to a considerable degree of ionization:

$$Fe(H_2O)_6^{+++} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{++} + H_3O^+$$

Replacing perchlorate by sulfate increases the absorption over the whole range shown and eliminates the transmission maximum at 260 mμ. A new ionic species is evidently present, having larger extinction coefficients than $FeOH^{++}$. The low concentrations used suggest that this is the ion $FeSO_4^+$, probably in hydrated form.

The rate as a function of concentrations. -- The rate equation derived previously (2) can be applied to solutions of ferric perchlorate alone and with additions of silver and ferrous perchlorates:

$$R = \frac{k_1c_3 - k_2c_1c_2}{1 + k_3c_3 + k_4c_1 + k_5c_1^2 + k_6c_2 + k_7c_2^2 - k_8c_1c_2} \qquad \text{(II)}$$

In this equation R is the dissolution rate, c_1,c_2 and c_3 are molar concentrations of silver, ferrous and ferric ions respectively, and the k's are constants which are determined experimentally. The constants vary with temperature and with rotational speed, and were determined only for 30° and 4000 rpm (peripheral speed 419 cm sec^{-1}).

The method of determining rate constants from the data was discussed in the previous paper (2). Values of k_1 and k_3 are found from rates in ferric perchlorate alone and are given in Table IV, with a comparison of observed and calculated rates. Values of k_4 and k_5 are found from experiments in which silver perchlorate is added to the ferric perchlorate. Table V gives these constants with observed and calculated rates. The rate becomes too low to measure accurately with more than 0.01 M silver ion present. A very large part of this inhibition is due to the c_1^2 term in equation (II).

The effect of ferrous perchlorate was somewhat erratic and difficult to measure accurately. It is pronounced at low temperatures and disappears at high temperatures, as shown in Table VI.

TABLE IV

The Rate in Ferric Perchlorate Solutions at 30°, 4000 rpm.

R in g x 10^{-4} cm^{-2} min^{-1}.

k_1 = 161 g x 10^{-4} liters $moles^{-1}$ cm^{-2} min^{-1},

k_3 = 30.6 liters $moles^{-1}$.

$C_{Fe^{+++}}$, M	R, obs.	R, calc.
0.005	0.70	0.70
.01	1.24	1.23
.02	1.96	2.00
.03	2.44	2.52
.05	3.18	3.18
.06	3.50	3.40
.08	3.78	3.73
.10	3.98	3.97
.20	4.52	4.52
.30	4.77	4.73

TABLE V

The Effect of Silver Perchlorate on the Rate at 30°, 4000 rpm.

k_4 = 800 liters $moles^{-1}$, k_5 = 9.4 x 10^5 $liters^2$ $moles^{-2}$.

0.05 M Fe^{+++}			0.08 M Fe^{+++}		
C_{Ag^+}, M	R, obs.	R, calc.	C_{Ag^+}, M	R, obs.	R, calc.
0	3.18	3.18	0	3.78	3.73
0.0005	2.70	2.70	0.001	2.39	2.48
.001	1.80	1.88	.0025	1.32	1.14
.0015	1.17	1.38	.005	0.47	0.42
.0025	0.80	0.76	.006	.32	.31
.0035	.44	.48	.0075	.21	.21
.004	.37	.39	.009	.16	.15
.005	.28	.27			
.006	.16	.19			
.007	.11	.15			
.008	.05	.12			

TABLE VI

The Effect of Ferrous Perchlorate on the Rate.

0.03 M $Fe(ClO_4)_3$, 4000 rpm.

$C_{Fe^{++}}$, M	R, grams cm^{-2} min^{-1} x 10^4		
	16.5°	40°	50°
0	1.12	5.1	7.3
0.005	0.95	4.8	7.4
.01	.76	4.9	7.4
.02	.76	5.0	7.1
.03	.68	5.0	7.4

Observed and calculated rates with ferrous perchlorate at 30° are given in Table VII. The term in C_2^2 in equation (II) is negligible and an average value of k_6 from scattered points must be chosen.

TABLE VII

The Effect of Ferrous Perchlorate at 30°, 4000 rpm.

k_6 = 10 liters $moles^{-1}$, k_7 = 0.

$C_{Fe^{++}}$, M	0.06 M Fe^{+++}		0.08 M Fe^{+++}	
	R, obs.	R, calc.	R, obs.	R, calc.
0	3.50	3.41	3.78	3.74
0.01	3.50	3.29	3.78	3.63
.03	3.20	3.05	3.78	3.44
.06	2.80	2.81	3.30	3.18
.08	--	--	3.00	3.03

When much silver ion is present the effect of small amounts of ferrous ion becomes almost negligible. The rates are very low and precise only to one or two figures. Some rate values in mixed solutions are given in Table VIII. In attempting to determine the constants k_2 and k_8 (see ref. (2), equation XI and Fig. 10) it is found that the function F is very erratic; it can be concluded that k_2 and k_8 are both negligible.

TABLE VIII

The Rate in Solutions Containing Ferrous, Ferric and Silver Ions. 30°, 4000 rpm. $k_2 = 0$, $k_8 = 0$.

$C_{Fe^{+++}}$,M	$C_{Fe^{++}}$,M	C_{Ag^+},M	R,obs.	R,calc.
0.05	0.02	0.007	0.15	0.15
.05	.03	.009	.09	.09
.05	.04	.009	.09	.09
.03	.01	.007	.09	.09
.05	.01	.010	.08	.08
.05	.01	.005	.26	.27

DISCUSSION

The rate equation. -- Equation (II) may be derived by making the following assumptions. a) Ferric ion is not adsorbed, but reacts when it encounters a bare silver atom. b) The back reaction may occur when a silver ion strikes an adsorbed ferrous ion, or vice versa. c) Silver and ferrous ions formed by reactionare not desorbed instantly. Then

$$R = kc_3 (1-\theta) - k'c_1\theta_2 - k''c_2\theta_1 \qquad \text{(IIIa)}$$

$$\theta_1 = a_1c_1 (1-\theta) + a'R \qquad \text{(IIIb)}$$

$$\theta_2 = a_2c_2 (1-\theta) + a''R \qquad \text{(IIIc)}$$

where θ_1 and θ_2 are fractions of the surface covered by adsorbed silver and ferrous ions respectively, $\theta = \theta_1 + \theta_2$, the k's are rate constants and the a's are adsorption constants. When these equations are solved equation (II) is obtained.

The constants are made up as follows:

$k_1 = k$

$k_2 = k'a_2 + k''a_1$

$k_3 = k\ (a' + a'')$

$k_4 = a_1 + k'a''$

$k_5 = k'a_1\ a''$

$k_6 = a_2 + k''a'$

$k_7 = k''a_2a'$

$k_8 = k'a_2a' + k''a_1a''$

The rate and other data indicate that a_2 and k'' are very small under the conditions used. The terms in k_2, k_7 and k_8 vanish because they contain a_2 and k'' and because the square or product of low concentrations is small.

The importance of the terms k_4c_1 and $k_5c_1^2$ indicates that most of the back reaction occurs between silver ions and newly formed ferrous ions. With numerical values for k_4 and k_5 it should be possible to solve for a_1 and $k'a''$, and the fact that imaginary values are obtained shows that the assumptions made are approximations. The same anomaly appears in the previous work with sulfate solutions (2).

The values of k_4 and k_5 can be adjusted until a solution is possible without causing much discrepancy between observed and calculated values in Table V, but any possible value of a_1 would give an unreasonable ratio between θ_1 and $1-\theta$ in equation (IIIb). The adsorption experiments show that at 0.01 M $AgClO_4$ the surface is only one-third covered with silver ions, and the rate must be low because of back reaction. The difficulty probably arises from lack of a term in equation (II) for reaction between adsorbed silver and adsorbed ferrous ions.

In solutions containing only ferric perchlorate initially, all terms in c_1 and c_2 are dropped from the rate equation. Nevertheless, inhibition arises from the formation of silver and ferrous ions, which results in the presence of $a' + a''$ in k_3.

The fact that the term $k_2c_1c_2$ vanishes does not mean that the rate of the back reaction is negligibly small. All terms in c_1 and c_2 contain k' or k'', the rate constants of the back reaction. Forward and backward rates cannot be separated as suggested previously (2).

It is useful to compare the constants found for the perchlorate solutions with those for sulfate solutions (2). Expressed in the same units, k_1 is about one-third as large; this represents reaction per unit area of bare silver and a real decrease in the specific rate constant k of equation (IIIa). Whether or not local areas of different potential are present, the greater surface charge and the higher charge of hydrated Fe^{+++} compared with $FeSO_4^+$ result in only one-third as many collisions, or effective collisions, with the surface. The remarkable effect of added sulfates (Table I) is to increase k_1 because of decreased electrostatic repulsion.

The value of k_3 is about twice as great in perchlorate solutions. This must be due to a larger value of a' in equation (IIIb); in addition to greater adsorption of silver perchlorate the silver ion formed in the reaction is desorbed more slowly.

The constants k_4 and k_5 are about 22 and 1000 times as large as in the sulfate system, which again reflects the greater adsorption of silver perchlorate. On the other hand k_6, dependent on the adsorption of ferrous ion, is about the same, and k_7 is unimportant in either case.

The equilibrium constant. -- The equilibrium constant for reaction (I), in terms of activities, can be calculated from the standard electrode potentials:

$$\log K_o = - \frac{0.028}{0.059}, \quad K_o = 0.336$$

The equilibrium constant in terms of concentrations, K_c, should approach K_o as the ionic strength of the solution approaches zero. K_c has been determined by Noyes and Brann (11) and by Shaw and Hyde (12) for nitrate solutions, by equilibrating solutions of ferric nitrate with silver. Their values of K_c ranged from 0.06 to 0.120 depending on the total concentration.

When the emf of the cell considered in Fig. 3 reaches zero, the ion ratio $C_{Ag^+}C_{Fe^{++}}/C_{Fe^{+++}}$ should be equal to the equilibrium constant if both electrodes measure the reversible emf corresponding to the solution composition. The platinum electrode probably behaves normally, but the slowly dissolving silver electrode, partly covered with adsorbed silver and ferrous ions, apparently reaches the potential of the platinum electrode before equilibrium is attained. The values of the ion ratio in solutions made up to give zero emf, or obtained by extrapolation to zero emf, are 0.006 to 0.02, and are too small to be considered equilibrium K/λ values for the solutions used. The probable variation in K/λ with ionic strength has been described previously (13).

The potentials reported were measured within a few minutes after immersing the electrodes. While they do not drift rapidly with time, they no doubt represent a state of very slow change with respect to the bulk of the solution.

Temperature coefficients. -- The measured rates can be divided into four factors which can be affected by temperature changes. a) Chemical reaction takes place on the bare surface and b) contains a considerable electrostatic component. The area available for reaction is limited by c) the equilibrium adsorption of silver ion and d) slow desorption of ions formed. The activation energy of a) must be very low since the measured rate can approach diffusion controlled values; the effect of electrical repulsion would decrease at higher temperatures because of the higher kinetic energy of the ions, but this effect would not be large. Rudberg and von Euler (3) found no significant difference in the adsorption of silver nitrate on gold between 0° and 50° and we may assume little temperature effect on c). The rate of desorption of the ions formed d) will, however, be increased at higher temperature.

It may be concluded that the activation energies found are mainly those of the desorption process.

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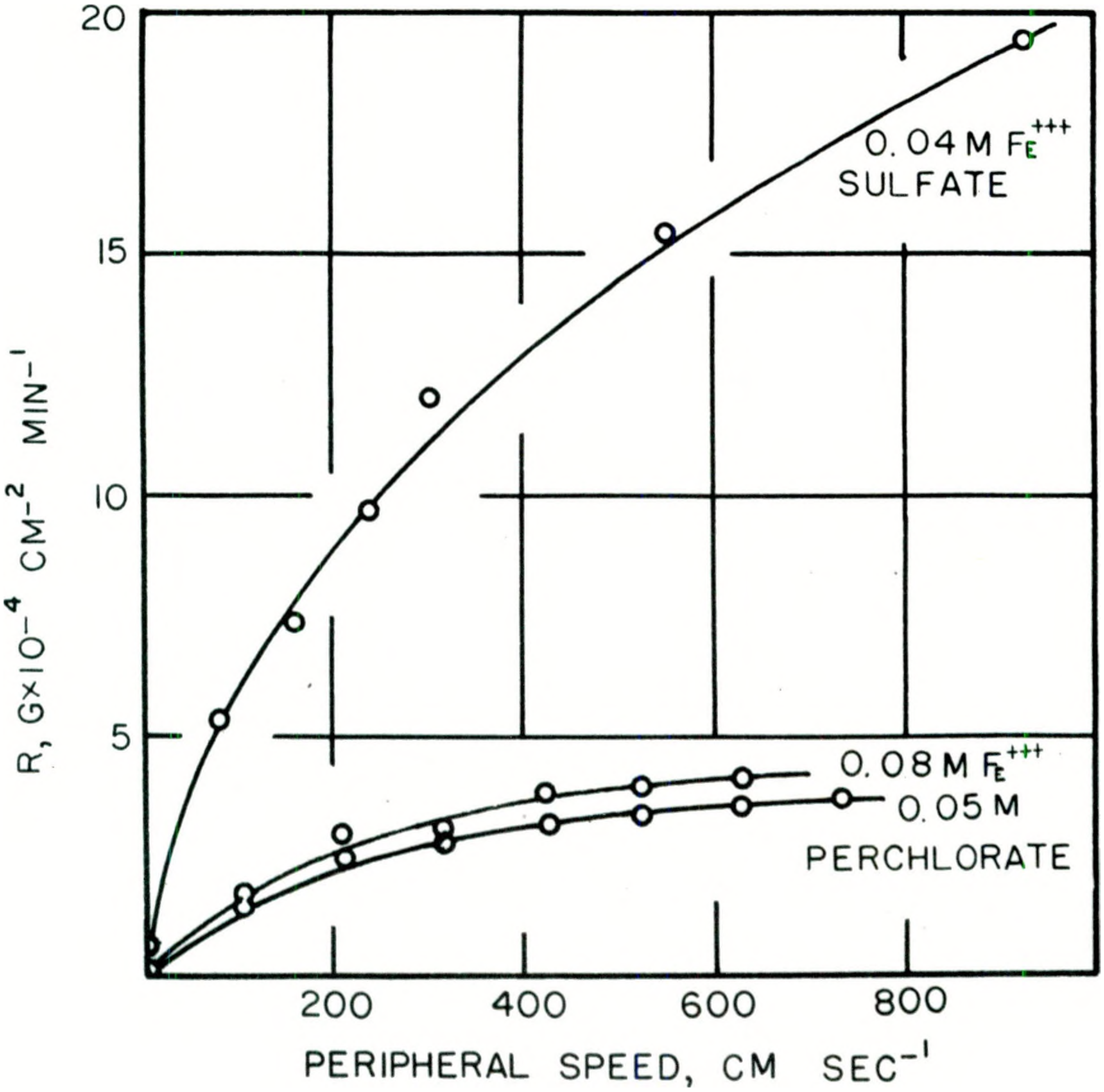

Fig. 1 The Effect of Rotational Speed of Silver Cylinders at 30°.

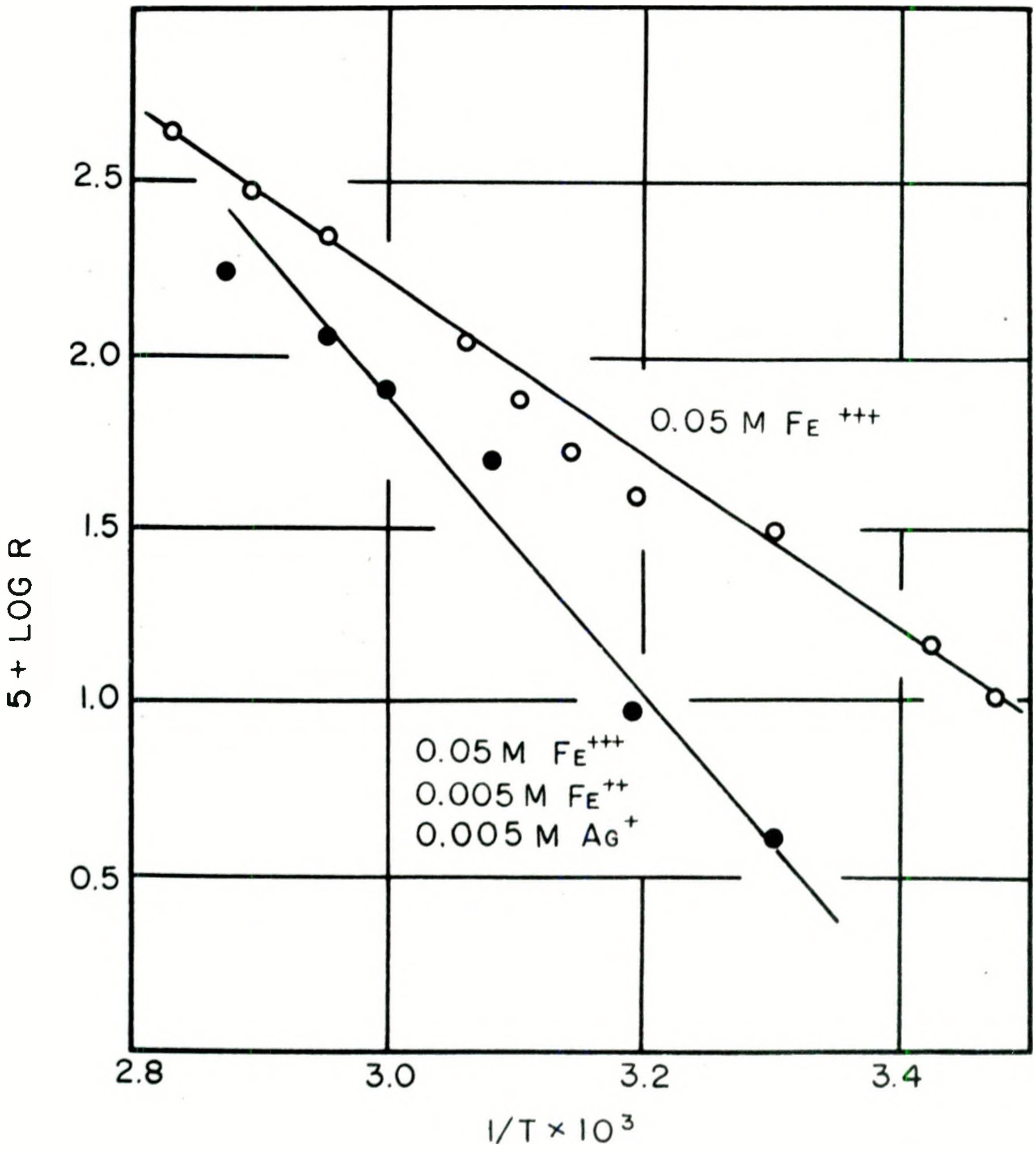

Fig. 2. Determination of Activation Energies in Perchlorate Solutions. Rotational Speed 4000 rpm.

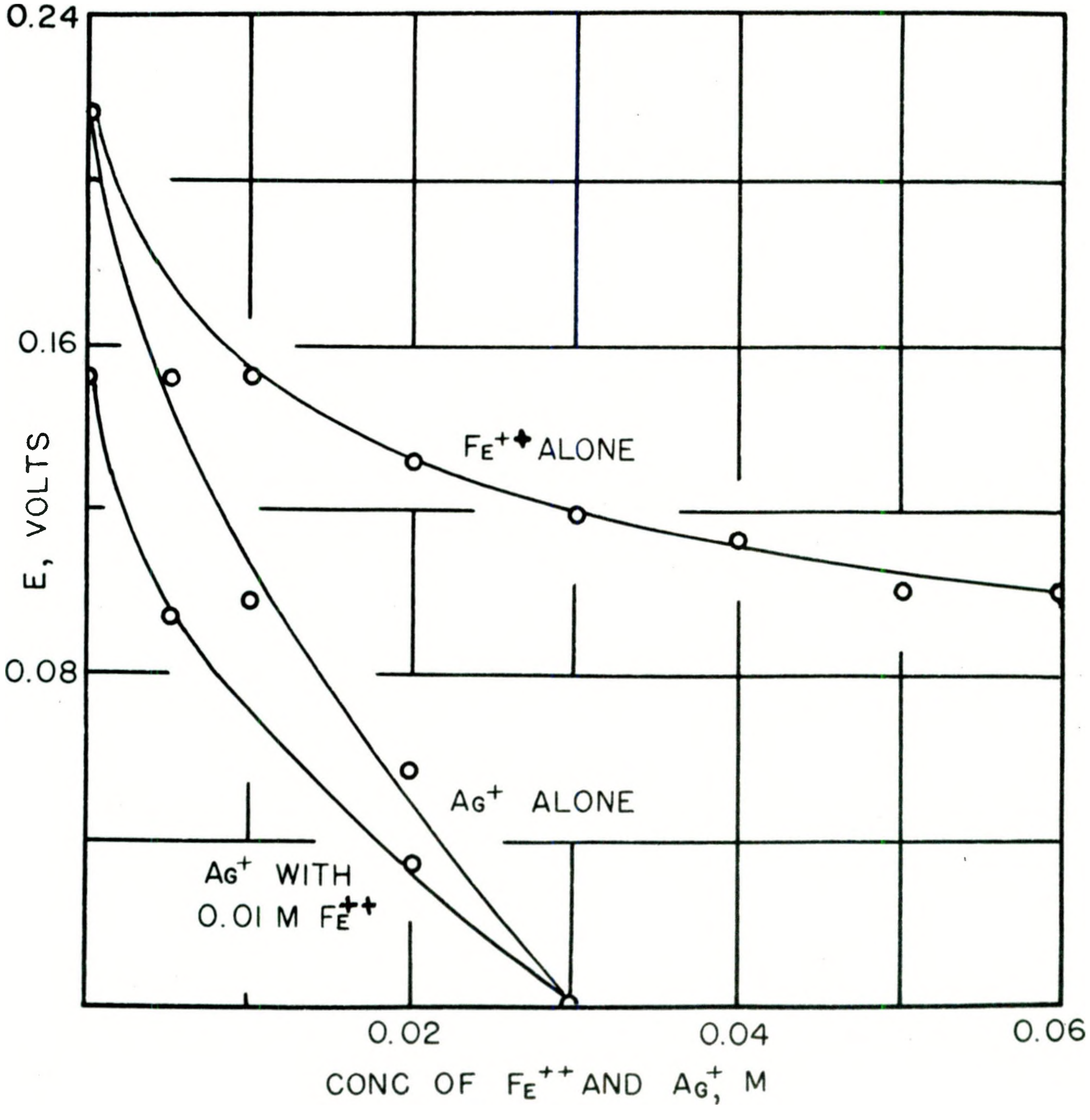

Fig. 3. The Potential of Silver versus Platinum in 0.05 M Ferric Perchlorate with Addition of Ferrous and Silver Perchlorates. 30°, 4000 rpm.

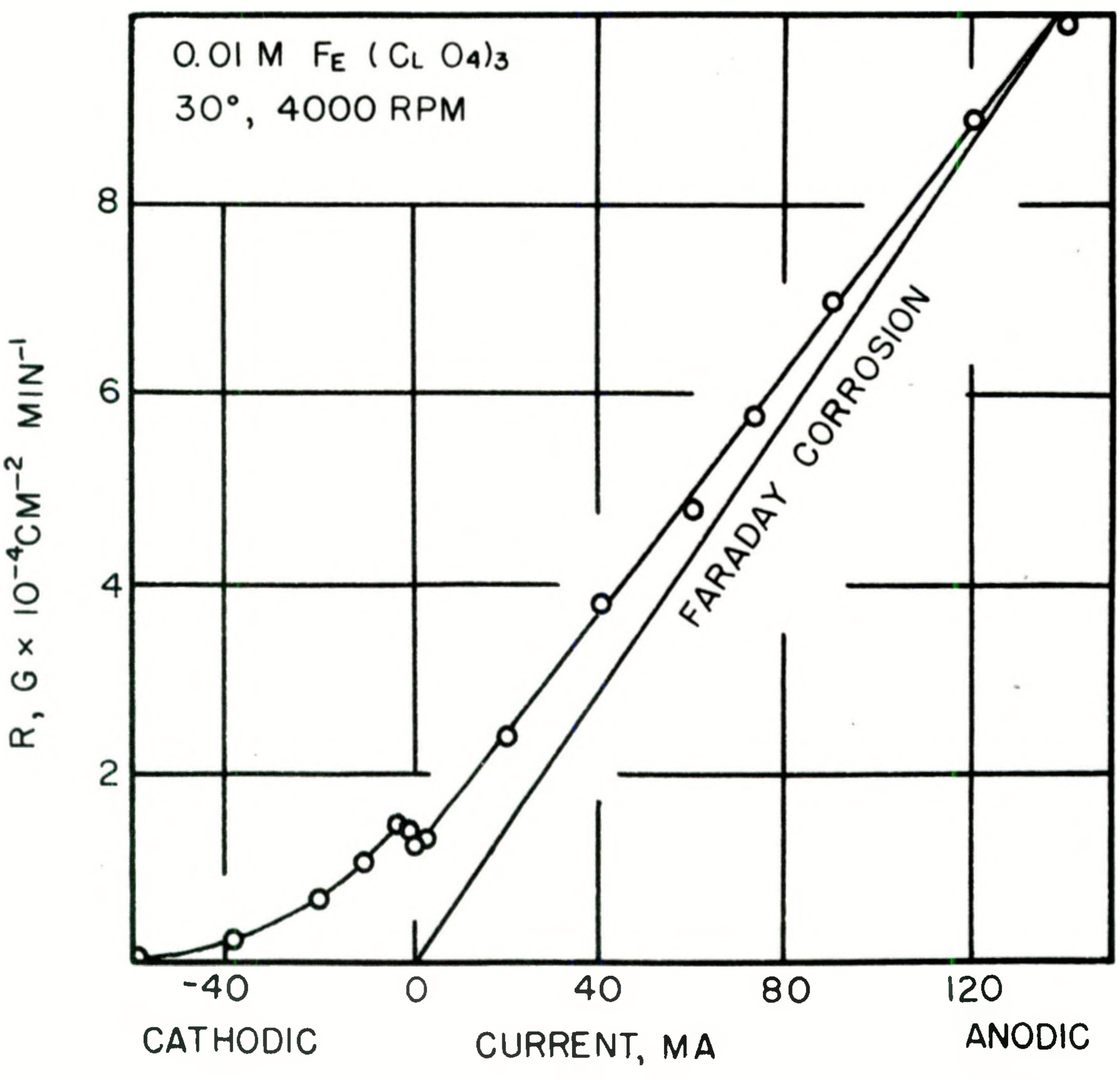

Fig. 4. The Corrosion of Silver when Externally Polarized.

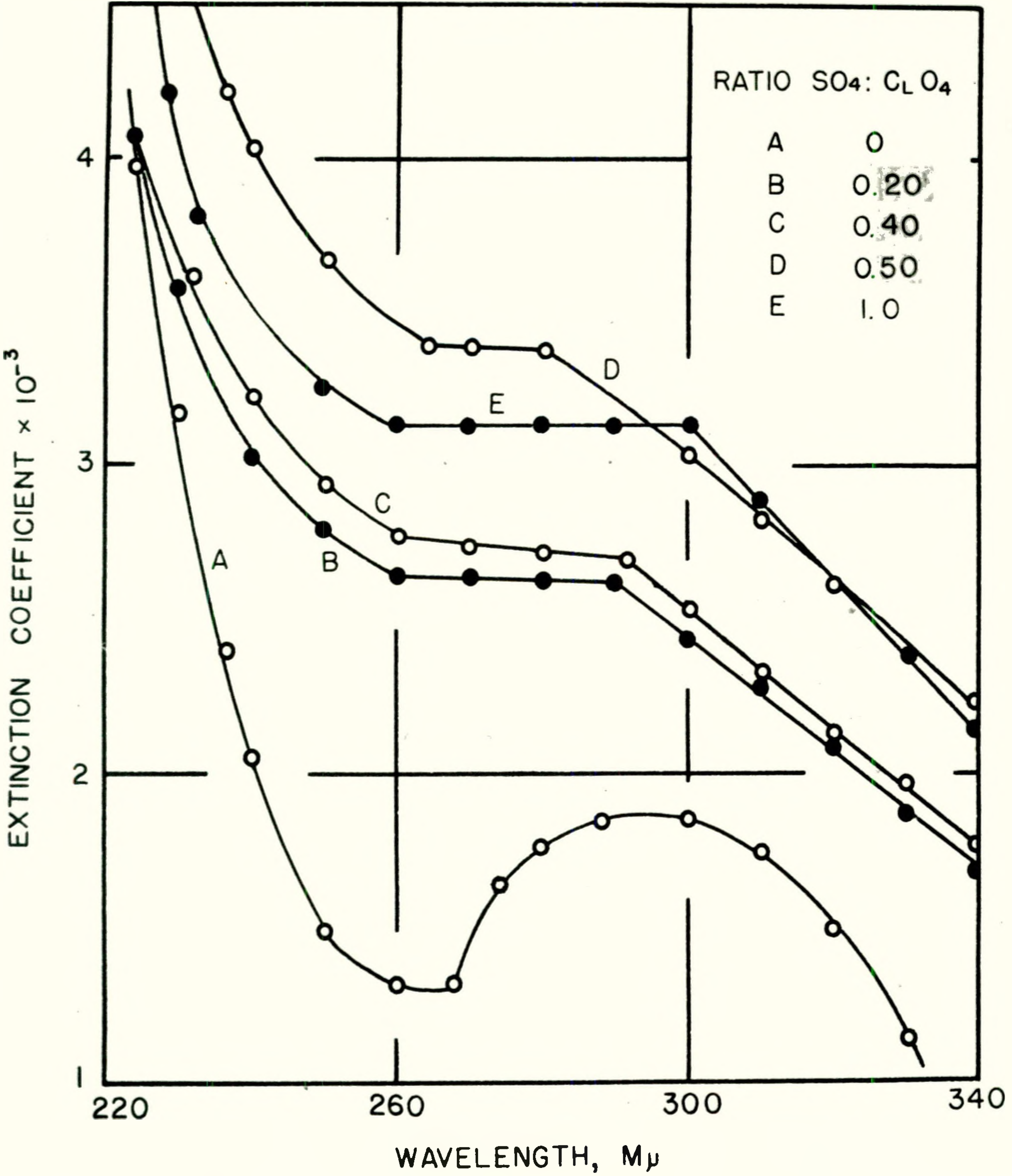

Fig. 5. Molar Extinction Coefficient of 10^{-4} M Fe^{+++} Solutions as Perchlorate, Sulfate and Mixtures of the two, with 5×10^{-5} M H^{+}. A curve for a ratio of 0.80 falls between D and E.