A STATISTICAL ANALYSIS OF DATA ON THE CORROSION

OF ALUMINUM IN HYDROCHLORIC ACID VAPORS

by

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CHAPTER I. Introduction

In the winter and spring of 1961 an experiment, concerning corrosion of aluminum by hydrochloric acid in the vapor phase, was executed in the Department of Chemical Engineering. H. H. Forsten conducted the experiments and published the results in his master's thesis. [2] In summary, he stated

Aluminum has high resistance to attack in many environments but corrodes rapidly in most inorganic acids. The purpose of this investigation was to attempt to determine the rates and mechanism of the surface reactions for the corrosion of aluminum in hydrochloric acid vapors as a function of the vapor concentration, vapor composition, and temperature.

Corrosion tests were made by suspending aluminum foil samples, five centimeters by two centimeters, by a glass thread. The samples were located in the vapor over hydrochloric acid solutions. The glass thread with the sample was attached to the center of a glass rod. One end of the rod was fixed; the other was suspended from one end of the arm of an analytical balance, permitting periodic weighing of the corroding samples without removal from the flask.

The tests were conducted above hydrochloric acid solutions whose concentration varied from 2 to 32 weight per cent. Ten temperature levels, from zero to 48°C., were employed so that the vapor pressures of the various acid concentrations overlapped. Weighings were made at 10 minute intervals for 200 minutes. The corrosion products were analyzed by standard x-ray diffraction techniques.

Forsten's analysis of data was a preliminary one only, being based upon sketches and graphs. In the present thesis an attempt has been made to obtain a more detailed statistical analysis of results.

The experiment was designed so as to cover as large a range of temperature and concentration as was experimentally feasible. Combinations were taken in such a way that each test fitted approximately into one of eight levels of hydrochloric acid partial pressure. The resulting design appears in Table I. Forty tests were performed.

The statistical analysis was divided into two main sections: the estimation of specific reaction rates at various temperatures and of the energy of activation; the study of the relative effects of pressure and temperature on the amount corroded and the estimation of these effects.

The first step in the estimation of the specific reaction rates and the energy of activation was to estimate the reaction rate of each test. The data from the straight line portion of each test run were subjected to a linear regression analysis of weight gain on time. The estimated regression coefficients divided by the area of the original aluminum samples were the estimates of rate, since the corrosion reaction rate may be defined as the amount of corrosion product formed per unit time, per unit area of reacting material, [5]. With each of these estimates of rate was

TABLE I
Experimental Design

log p \ °C.	48	44	41	35	28	17	9	7	2	0
1.501	28% (8)			30% (35)	32% (12)					
.925	24% (18)			26% (27)	28% (7)	30% (36)				
.250	20% (5)			22% (25)	24% (15)	26% (32)		28% (11)		
- .502		16% (29)		18% (26)	20% (4)	22% (21)		24% (14)		
-1.125		12% (28)		14% (40)	16% (34)	18% (13)	20% (10)		22% (20)	
-1.825			8% (17)	10% (30)	12% (23)	14% (37)	16% (33)		18% (22)	
-2.520		4% (2)		6% (6)	8% (16)	10% (31)	12% (24)	14% (38)		
-3.250		2%	2% (3)		4% (1)	6% (9)	8% (19)	10% (39)		

The entries are weight per cent HCl used in order to produce, approximately, the desired vapor pressure, and are of no consequence to the further analysis. (test run number in parentheses).

associated an estimate of variance. The specific rates of reaction for various temperatures were then estimated by weighted linear regression analysis of log rate on log pressure. Actual values of pressure, rather than the approximate levels, were used. Finally, the estimate of the energy of activation was obtained from inspection of a graph of the natural logarithm of specific rate versus the inverse of absolute temperature, based on the Arrhenius equation, [5].

The study of the relative effects of pressure and temperature on corrosion was based on an analysis of variance. The designed experiment was reduced to a general two-way classification. In addition to the pressure and temperature variables, a third variable, time, was introduced as a covariate. Main effects, correction or interaction terms, and the coefficient of the time variable were estimated in accordance with the model

$$\ln y_{ijk} = \mu + \pi_i + \tau_j + \delta_{ij} + \beta(t_k - \bar{t}) + e_{ijk}$$

where $\ln y_{ijk}$ = natural logarithm of the observed weight gain
    under pressure i and temperature j at time k

μ = general effect

π_i = relative effect of pressure i

τ_j = relative effect of temperature j

δ_{ij} = correction term for cell (i,j)

β = coefficient of regression on the covariate, time

t_k = time k

$\bar{t} = 1/6 \sum_k t_k$, since there were six observations

$(t_k = 80, 90, \ldots, 130$ minutes) in each cell.

The relation of these parameters to chemically interpretable quantities is stated in Chapter III.

The major part of the statistical analysis dealt with the data from the lower pressure levels, i.e., the portion of the experiment in which the corrosion product was aluminum oxide, as observed in an independent x-ray analysis. [2, p. 61] At the higher pressure levels, aluminum chloride was formed, and a completely different reaction mechanism observed. Since, however, only very few experiments had been conducted at these high levels of pressure, no more than tentative suggestions could be made regarding the nature of this mechanism. On the other hand, sufficient data were available to justify useful predictions in the lower pressure range.

CHAPTER II. Specific Rate of Reaction
and Energy of Activation

2.1 Estimation of Reaction Rates

It was necessary to establish the rate of reaction for each test run, as a first step toward the estimation of the energy of activation involved in the corrosion of aluminum in hydrochloric acid vapor. Since the rate of reaction is proportional to the slope of the line in the linear portion of a graph of weight gain against time (the proportionality factor being the inverse of the area of reactant), the graphs of each of the test runs were inspected. It was found that some reactions were approximately linear beginning with the first observation at ten minutes; in other runs a linear pattern could be found only after as much as seventy minutes. This behavior should not be surprising, since in most reactions an initial or introductory period precedes the period during which the reaction demonstrates a linear trend.

A simple linear regression analysis of weight gain on time was obtained for the straight line portion of each of the forty test runs by use of the linear regression program (Number 6.2.004.3 V. P. I.) for the I. B. M. 650. The model for a regression is simply

$$y_i = \alpha + \beta t_i + e_i$$

where y_i is weight gain in mg. at time t_i .

The output of this program furnished estimates of the regression coefficient β and the variance σ_e^2, $\hat{\beta}$ and MSE respectively, for each test run. $S_{tt} = \Sigma(t_i - \bar{t})^2$, was also obtained for each run.

The desired estimates of reaction rate were found by dividing each $\hat{\beta}$ by twenty, the proportionality constant, since the original aluminum samples had an area of 20 cm². The variance of β is equal to $\frac{\sigma_e^2}{S_{tt}}$; the estimate of this variance is given by $\frac{MSE}{S_{tt}}$. Thus it can be shown that since

$$\hat{r} = \frac{1}{20}\hat{\beta},$$

then

$$\text{var}(\hat{r}) = \frac{1}{400}\text{var}(\hat{\beta})$$

$$= \frac{1}{400}\frac{MSE}{S_{tt}}.$$

Table II gives the observations used, the estimates of rate and the associated estimates of variance. The table also includes other data which are necessary later in the study. The values of the partial pressures were taken from Perry, Chemical Engineer's Handbook, pp. 166-167. [3] Where necessary, interpolations were made.

2.2 Suggested Mechanism

Graphs of log (rate) versus log (partial pressure of HCl) were drawn. Figure 1 is a graph over all experimental

TABLE II
Corrosion Data

Test Number	HCl Concentration weight percent	Temperature °C	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	Rate, mg./cm.² x min.	$\frac{1}{var(r)} \times 10^{-2}$	Log r	Log p (HCl)	Log p (H₂O)
																								Weight gain during linear period, mg. Time, min. →				
1	4	28		0.4	1.0	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.4	1.6	1.8	1.8	1.8	2.0	2.0	2.2	0.00035438596	7,252,232.256	-3.451	-3.214	1.428
2	4	44							3.8	5.2	6.4	7.2	8.0	8.8	9.8	10.6	11.2	12.0	12.6	13.0			0.0037032967	243,034.628	-2.431	-2.464	
3	2	41			2.8	3.0	3.0	3.2	3.2	3.4	3.4	3.6	3.6	3.8	4.0	4.4	4.4	4.6	5.0	6.2			0.0008676470	1,105,842.099	-3.062	-3.279	
4	20	28	4.4	8.4	15.2	20.0	25.2	31.0	35.4	41.2	46.2	51.4	56.8	62.4	68.4	73.8	79.2	84.6	91.2				0.026970588	439,949.840	-1.569	-0.397	1.225
5	20	48	13.8	36.4	59.2	81.8	106.8	128.4															0.11525714	12,136.724	-0.938	0.274	
6	6	35	1.6	2.0	2.6	2.8	3.2	3.6	4.6	4.8	5.0	5.0	5.2	5.4	5.4	5.6	5.8	6.0	6.2	6.2	6.4	6.8	0.0012548872	1,395,973.500	-2.901	-2.421	1.596
7	28	28	3.6	8.4	13.2	18.0	23.8	28.4	31.6	37.0	41.6	46.4	52.2	55.8	60.8	66.2	71.2	76.2	81.4	85.4	89.6	94.4	0.024000000	891,923.168	-1.620	0.935	1.019
8	28	48	5.8	9.2	14.6	20.6	25.6	30.0	34.6	39.6	46.0	-	55.0	59.2	63.4	71.2	75.0	79.6	84.6	89.0	94.4	99.2	0.024772268	533,250.620	-1.606	1.501	
9	6	17	0	0.2	0.2	0.4	0.6	0.8	1.2	1.2	1.4	1.8	2.0	2.0	2.2	2.4	2.6	2.8	2.8	2.8	3.2	3.4	0.0009082706	18,689,951.068	-3.042	-3.275	1.123
10	20	9		0.8	1.6	2.6	3.6	4.6	5.4	6.6	7.6	8.6	9.4	10.6	11.4	-	-	-	15.2	16.2	17.2	18.0	0.0048351272	201,693.435	-2.316	-1.124	0.702
11	28	7		4.0	6.8	10.2	12.2	15.6	18.4	21.6	25.6	28.0	31.4	34.8	38.6	42.0	45.0	48.6	52.4	55.6	59.2	62.8	0.016428070	441,991.296	-1.784	0.254	
12	32	28								24.0	29.4	30.8	33.8	37.6	44.8	45.8	50.4	55.0	59.8	65.4	70.6	75.2	0.021236264	23,816.042	-1.673	1.590	0.884
13	18	17	0.4	1.4	2.4	4.0	5.6	6.8	8.2	10.2	11.2	12.6	13.4	15.4	17.4	19.0	20.4	22.0	23.2	24.2	25.2	26.4	0.007154135	1,482,332.244	-2.145	-1.146	0.970
14	24	7						6.0	8.2	10.4	12.0	13.8	15.8	18.0	19.8	22.2	25.0	27.0	29.2	31.6	34.4	36.4	0.010839286	405,791.691	-1.965	-0.478	
15	24	28		12.8	24.4	36.2	48.2	60.2	72.0	84.6	96.6	108.8	120.6	133.8	144.6	156.6	168.8	180.4	192.2	204.0	215.4	225.4	0.05969474	359,393.304	-1.224	0.268	1.133
16	8	28		0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.6	0.6	0.6	0.6	0.8	0.8	0.8	0.8	1.0	1.0	1.0	0.00027719298	51,331,785.160	-3.557	-2.388	
17	8	41		4.4	5.0	5.6	7.0	8.0	9.0	10.2	10.8	11.6	12.6	14.0	15.4	16.6	17.2	17.6	18.4	19.0	20.4	22.4	0.0049035088	1,319,627.421	-2.309	-1.832	1.393
18	24	48	8.0	26.4	44.2	62.2	79.0	91.4	106.8	119.0	136.2	151.8	166.0	181.0	194.2	208.0	221.0	235.2	249.8	262.4	278.0	294.2	0.07347518	26,072.520	-1.134	0.888	
19	8	9	0.2	0.2	0.2	0.2	-	-	-	-	0.4	0.4	-	0.4	-	0.4	0.4	0.6	-	-	-	0.6	0.00011027458	573,803,587.740	-3.957	-3.293	0.880
20	22	0							3.6	4.8	5.6	7.2	7.6	8.4	9.2	10.2	10.8	11.8	12.6	13.4	13.8	15.2	0.0042527472	1,218,989.216	-2.371	-1.134	
21	22	17		3.2	6.6	9.8	12.6	16.0	19.2	22.4	26.0	29.4	32.8	36.2	39.2	42.4	45.8	49.2	52.6	56.2	60.6	64.2	0.016766667	922,225.376	-1.775	-0.459	0.879
22	18	0					1.4	1.6	1.8	2.0	2.4	3.0	3.4	3.6	3.8	4.0	4.2	4.4	4.6	5.0	5.2	5.4	0.0013779412	4,589,252.457	-2.861	-1.870	
23	12	28		1.0	1.6	2.4	2.6	3.2	3.8	4.0	4.6	5.2	5.6	5.8	6.4	6.6	7.0	7.4	7.8	8.2	8.8	9.2	0.0021842105	6,426,178.040	-2.661	-1.718	1.352
24	12	9	0	0.2	0.6	0.6	0.8	0.8	1.0	1.0	1.2	1.2	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.6	1.6	0.00035413534	7,697,191.335	-3.451	-2.561	0.839
25	22	35		17.4	33.0	47.0	62.0	79.0	94.2	109.0	123.2	137.4	154.2	169.2	184.8								0.07590909	95,661.868	-1.120	0.176	1.358
26	18	35	3.4	7.8	13.8	21.8	26.8	32.6	38.2	44.0	50.0	57.0	63.6	69.8	76.0	82.4	88.2	93.8	99.6	104.0	108.8	114.4	0.029936842	194,524.288	-1.524	-0.463	1.439
27	26	35	5.4	13.0	22.0	31.2	39.2	48.0	57.2	65.2	73.0	80.8	87.2	95.6	103.6	111.8	119.4	127.4	135.0	143.2	150.8	158.6	0.040157894	199,759.344	-1.396	0.813	1.255
28	12	44			12.8	15.2	17.0	18.2	20.4	22.8	25.4	28.2	31.4	33.4	35.8	38.2	40.2	42.0	44.2	46.4	48.6	50.4	0.011421052	461,139.644	-1.942	-1.087	
29	16	44		13.6	20.2	26.6	33.2	40.0	46.6	53.0	58.8	64.2	70.6	77.0	83.8	89.8	96.0	102.6	108.6	114.0	118.2	125.0	0.031005263	283,520.952	-1.508	-0.465	
30	10	35	0	0.6	1.4	1.4	1.8	4.6	6.4	7.4	8.4	9.0	10.2	10.8	11.2								0.005280220	115,454.864	-2.277	-1.751	1.550
31	10	17	0	0	0.2	0.4	0.4	0.6	0.6	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1.0	1.0	1.0	1.0	1.0	1.0	0.00026240602	16,717,527.334	-3.581	-2.545	1.085
32	26	17	3.4	7.8	11.8	17.8	23.8	29.8	35.4	40.0	46.2	52.2	57.6	63.2	69.4	75.4	81.2	87.0	92.8	98.4	103.6	109.4	0.028412782	512,323.696	-1.547	0.234	0.774
33	16	9		0.2	0.4	0.6	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.2	0.0010624060	61,066,745.126	-2.974	-1.842	0.792
34	16	28	2.4	4.6	6.2	7.0	8.4	10.4	12.0	14.0	15.4	16.6	18.2	19.4	21.0	22.4	23.4	25.4	27.6	29.0	30.8		0.007671930	1,594,900.794	-2.115	-1.055	1.294
35	30	35	2.8	6.0	8.8	12.4	15.2	18.0	20.4	22.4	25.0	28.2	30.8	33.8	38.0	41.8	45.0	48.4	51.8	55.8	60.4		0.015433333	1,243,787.608	-1.812	1.456	1.137
36	30	17	1.0	3.2	5.2	7.8	10.6	13.4	16.6	19.2	21.6	22.6	25.8	28.0	29.4	31.6	33.8	36.2	38.0	39.6	41.8		0.011468421	273,822.458	-1.940	0.935	0.649
37	14	17	0.2	0.2	0.2	0.4	0.4	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.4	2.6	2.8	3.0	0.0008060150	12,244,346.334	-3.094	-1.842	1.040
38	14	2				0	0.2	0.2	0.2	0.4	0.4	0.6	0.6	0.8	1.0	1.0	1.2	1.2	1.4	1.6	1.8	2.0	0.0005931372	15,337,596.283	-3.227	-2.526	
39	10	2			0	0.2	0.2	0.4	-	1.0	-	-	1.2	-	-	1.4	-	1.6	-	1.8	2.0	2.0	0.0005848848	8,734,944.436	-3.233	-3.280	
40	14	35	0.6	3.0	5.0	6.8	8.6	10.0	11.4	12.8	14.2	15.8	17.4	18.8	20.4	22.0	24.0	25.8	27.6	29.6	31.4	33.0	0.008197744	1,209,743.291	-2.086	-1.108	1.504

temperatures; Figures 2, 3, 4, and 5 are similar graphs at
constant temperatures. When the graph of all rates (Figure 1)
was examined, it became apparent that not one but two reactions
were taking place. X-ray analysis of the corrosion products
showed that at lower HCl pressure levels the product of the
reaction was aluminum oxide, while at higher levels $AlCl_3x6H_2O$
was formed. After consideration of chemical theory, the
following explanation has been suggested by N. F. Murphy and
H. H. Forsten: At the lower levels of hydrochloric acid
partial pressure, the water vapor is the reactant with alumi-
num and the acid serves only as a catalyst; at the higher
levels hydrochloric acid is the reactant and water is the
catalyst. Further, it is proposed*that the rate of reaction
is directly proportional to the concentration of catalyst
present. This situation, which is somewhat at variance with
the theory of catalysis, has also been observed by Berkman,
Norrell, and Egloff. They discuss this phenomenon in their
book Catalysis. [1] "...in many instances, the velocity
coefficient varies in direct proportion to the concentration
of the catalyst."

2.3 Order of Reaction under HCl Catalysis

The study was, therefore, broken into two parts with
log (partial pressure of HCl) = .250 as the cut-off value.
In the following paragraphs the formulae involving the hydro-
chloric acid vapor pressure will be derived. These are
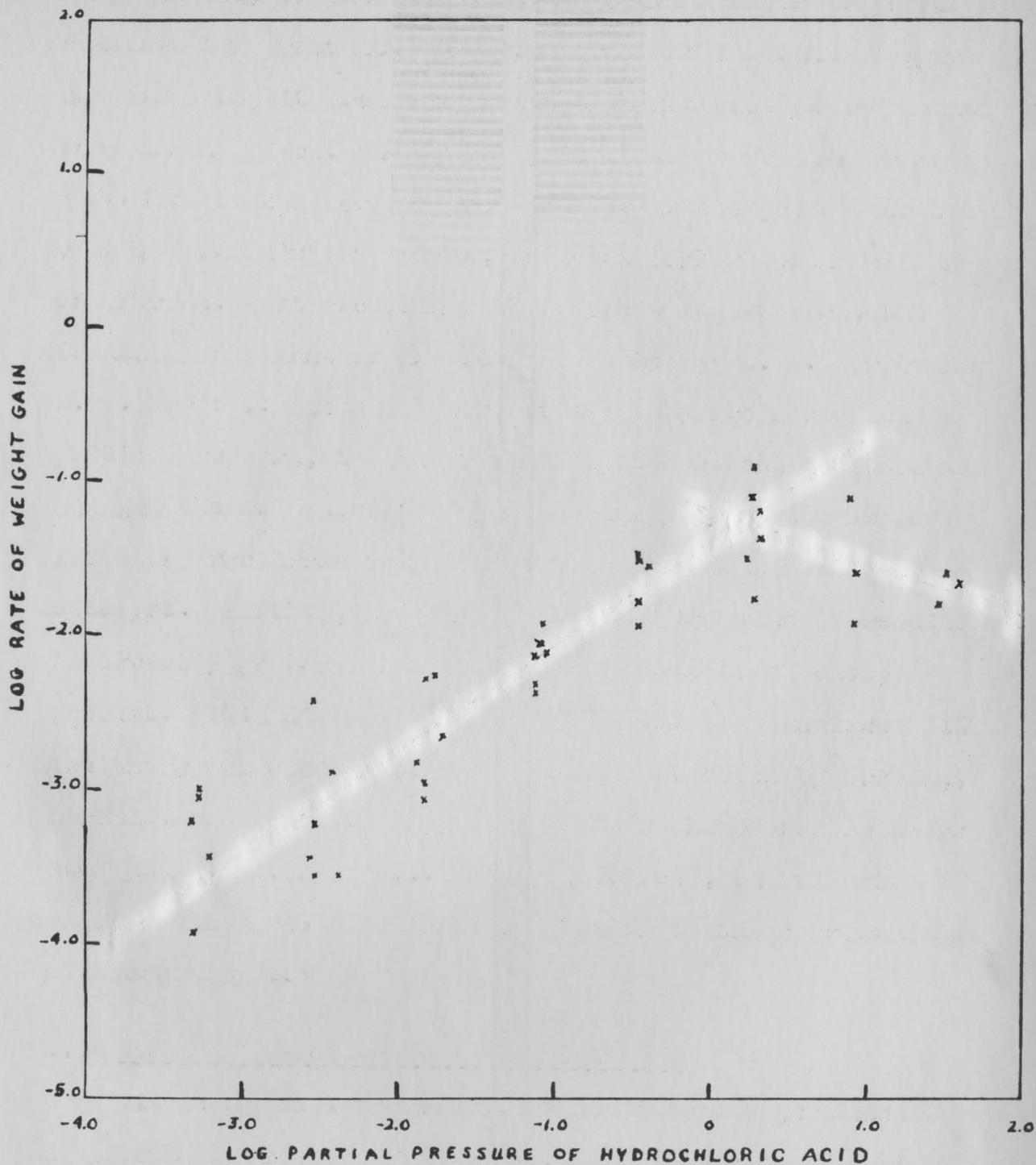
* In a private conversation with N. F. Murphy.

FIGURE I. LOG PARTIAL PRESSURE OF
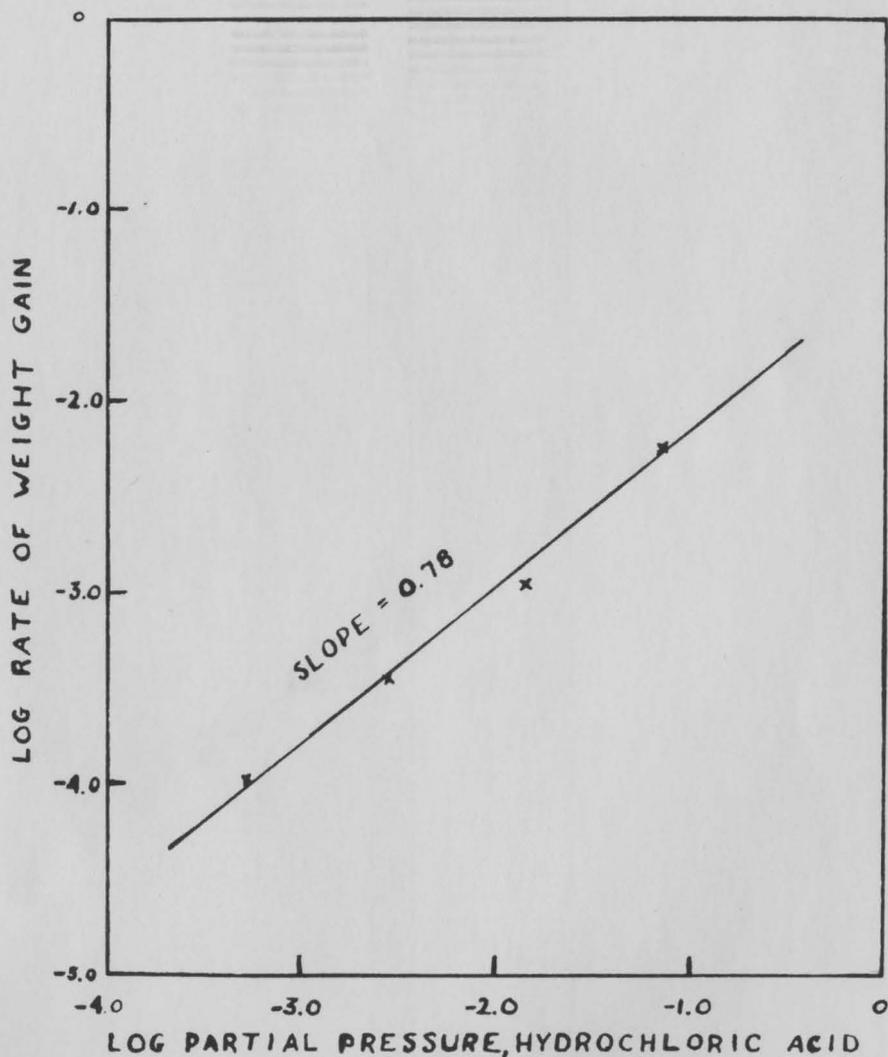HYDROCHLORIC ACID vs. LOG RATE
OF WEIGHT GAIN

FIGURE 2. LOG PARTIAL PRESSURE
OF HYDROCHLORIC ACID vs. LOG
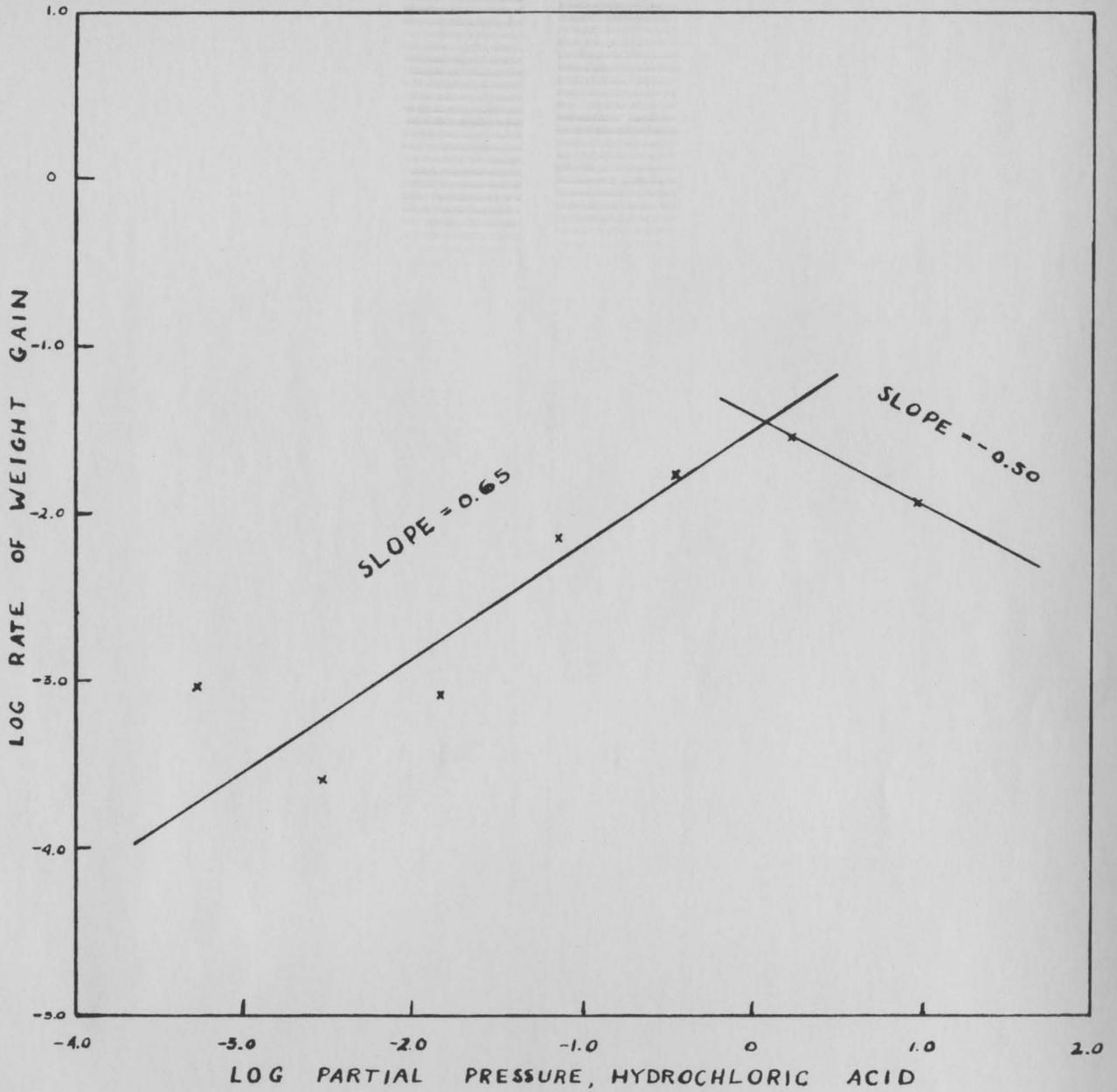RATE OF WEIGHT GAIN, 9°C.

FIGURE 3. LOG PARTIAL PRESSURE OF
HYDROCHLORIC ACID vs. LOG RATE
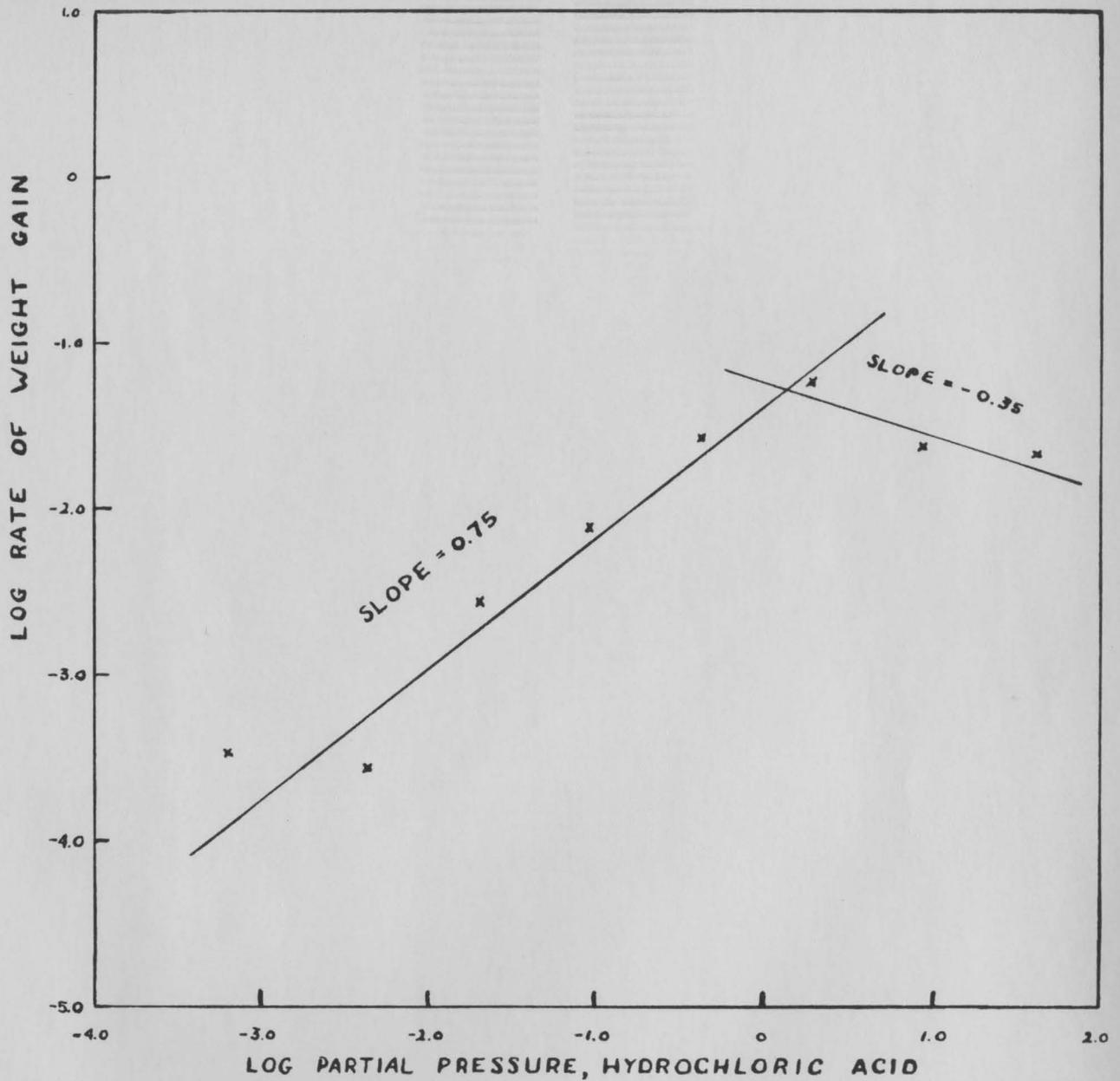OF WEIGHT GAIN, 17°C.

FIGURE 4. LOG PARTIAL PRESSURE
OF HYDROCHLORIC ACID vs. LOG
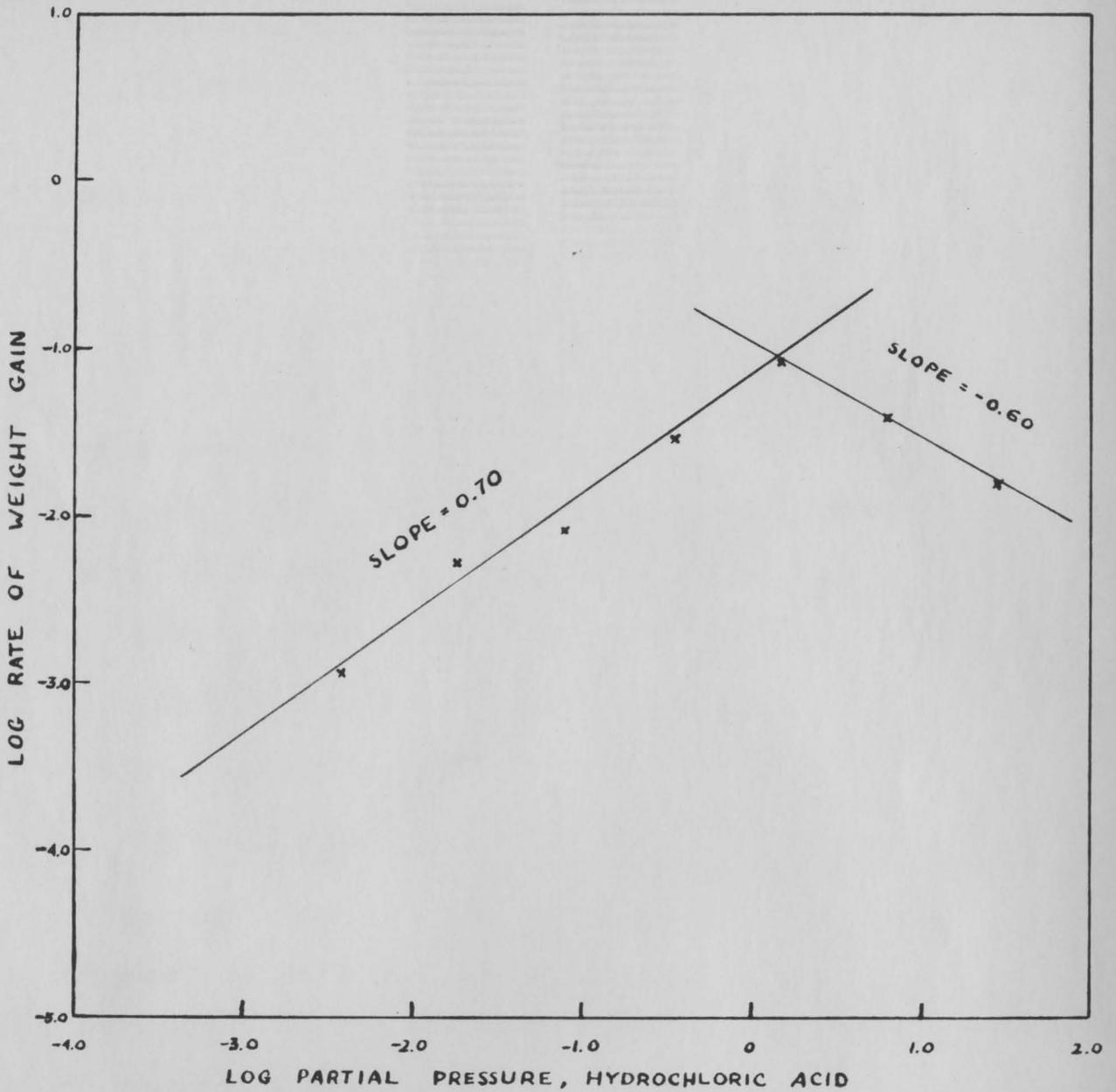RATE OF WEIGHT GAIN, 28°C.

FIGURE 5. LOG PARTIAL PRESSURE OF
HYDROCHLORIC ACID vs. LOG RATE
OF WEIGHT GAIN, 35°C.

completely analogous to those for the part of the study where water vapor is the catalyst.

The rate r of a reaction is defined as

$$r = k \, (p*)^{\alpha}$$

where k is the specific rate of reaction, (min.$^{-1}$)

p* is partial pressure of HCl (a measure of concentration),

$$\left(\frac{\text{mg.}}{\text{cm.}^2}\right)$$

α is the order of the reaction.

Taking logarithms

$$\log r_i = \log k + \alpha \log p_i^* \quad.$$

The r_i's were estimated in the previous analysis as $\hat{r}_i = 1/20 \, \hat{\beta}_i$. To estimate k and α we may use

$$\mathcal{E}(\hat{r}_i) = k \, p_i^{*\alpha} \quad \text{and, thus, approximately (first term}$$

of the Taylor expansion)

$$(1) \qquad \mathcal{E}(\log \hat{r}_i) = \log k + \alpha \log p_i^* \quad.$$

This approximation is quite good as long as the errors around the regression lines are small.

The pressure variable was given in units of mm of mercury, and the weighted regression analysis was performed using these values. A simple transformation

$$[p_i^* , \frac{mg}{cm^2}] = 1359.6 \ [p_i, \ mm \ Hg]$$

was used to bring the results into corresponding units.

Again using the Taylor expansion formula the variance of $\log r_i$ can be approximated. If the expected value of an arbitrary variable x is ξ, then

$$f(x) \doteq f(\xi) + (x - \xi)f'(\xi) \ .$$

By transposing, squaring and taking expected values of both sides, this becomes

$$\mathcal{E}[f(x) - f(\xi)]^2 \doteq \mathcal{E}\{(x - \xi)^2[f'(\xi)]^2\}$$

or

$$\text{var} \ [f(x)] \doteq \text{var} \ (x) \ [f'(\xi)]^2 \ .$$

Let the variance of r_i be called v_i. The expected value of r_i is obviously $kp_i^{*\alpha}$. Therefore,

$$\text{var} \ [\log r_i] \doteq v_i \ \times \ [\frac{1}{k(p_i^*)^\alpha}]^2$$

$$= \text{constant} \ \times \ [\frac{v_i}{p_i^{2\alpha}}] \ .$$

There were four temperatures at which there was a sufficient number of test runs for statistical analysis. The data at these levels (35°, 28°, 17°, 9°) were used to find estimates of the specific reaction rate k at various temperatures. Equation (1) became the regression model. An approximation to the weighted regression in this case (as described in Rao, Advanced Statistical Methods in Biometric Research [4]) makes use of the fact that

$$\text{var} \ [\log r_i] \sim \frac{v_i}{p_i^{2\alpha}}$$

and hence a weighted regression with weights

$$w_i = \frac{p_i^{2\alpha}}{v_i}$$

was indicated.

However, since the weights depended in part on the regression coefficient α, an iterative procedure was used so as to approximate more closely the slope and intercept of this line. The slopes of the sight lines in Figures 2, 3, 4, and 5 gave first estimates of α and hence at each temperature

$$w_{1i} = \frac{p_i^{2\hat{\alpha}_1}}{v_i} \ .$$

With this set of weights the regression analysis was performed and a new estimate $\hat{\alpha}_2$ found. A new set of weights w_{2i} could then be calculated. This procedure was repeated until the absolute difference between successive values of $\hat{\alpha}$ was less than .005. An example of these iterations is given in Table III. The results at the four levels were as follows:

$$
\begin{aligned}
\text{At } 9° \quad & \hat{\alpha} = 0.889, \quad C = -1.334 \\
17° \quad & \hat{\alpha} = 0.623, \quad C = -1.660 \\
28° \quad & \hat{\alpha} = 0.739, \quad C = -1.408 \\
35° \quad & \hat{\alpha} = 0.848, \quad C = -1.135
\end{aligned}
$$

where $\hat{\alpha}$ is the regression coefficient

C is the estimate of intercept.

TABLE III

Iterations of Weighted Linear Regression (28°C.)

x = log pressure (HCl)	y = log rate
-3.214	-3.451
-0.397	-1.569
.268	-1.224
-2.388	-3.557
-1.718	-2.661
-1.055	-2.115

$\hat{a}_{(j)}$ weights$_{(j)}$ resulting equation

(1) .75   .110
            110.
            907.
            13.4   log r = -1.408 + .736 log p
            17.0
            41.7

(2) .736   .135
            113.
            891.
            15.7   log r = -1.408 + .743 log p
            19.0
            44.6

(3) .743   .122
            112.
            899.
            14.5   log r = -1.408 + .739 log p
            18.0
            43.2

Hence   C = -1.408

         $\hat{a}$ = .739

2.4 Specific Rate

To obtain the estimates of log k, the estimate of inter-
cept C (see above) must be altered slightly because of a
difference in units. The pressure variable used in the
weighted regressions was entered in units of mm. of mercury.
Since the rates were measured in $\frac{mg}{cm^2 \times min}$ and the specific
rate constant in min^{-1}, pressure was converted to units of
mg/cm^2 , i.e.,

$$[p_i^* \, , \, \frac{mg}{cm^2}] = 1359.6 \ [p_i \, , \, mm \ Hg] \ .$$

The regression equation in corresponding units would be

$$\log \hat{r}_i = \log \hat{k} + \hat{a} \log (1359.6 \ p_i)$$
$$= \log \hat{k} + \hat{a} \log 1359.6 + \hat{a} \log p_i \ .$$

Hence the estimate of intercept obtained in the weighted
regressions is

$$C = \log \hat{k} + \hat{a} \log 1359.6$$

or

$$\log \hat{k} = C - \hat{a} \log 1359.6 \ .$$

2.5 Energy of Activation

The energy of activation can be estimated as soon as
estimates of the specific rate of reaction are available.
The estimation procedure makes use of the Arrhenius equation

$$k_i = A_i \ e^{-\frac{E}{RT_i}}$$

or

$$\ln k_i = \ln A_i - \frac{E}{R}\left(\frac{1}{T_i}\right)$$

where A_i is the frequency factor at temperature i

E is energy of activation

R is the gas constant (= 1.986)

T_i is absolute temperature

and where k is defined by the equation

$$r = k\,(p^*)^\alpha .$$

Hence, from the slope of the sight line obtained by plotting ln k against $\frac{1}{T}$ (the so-called Arrhenius plot), very simple calculations give the estimate of activation energy.

2.5.1 Order Assumed to Be One

Theoretically, on the basis of a stoichiometric argument, the order of a reaction is a whole number. The estimates of order in Section 2.3 indicate that the formation of aluminum oxide is close to first order. If the order of the reaction were assumed to be one, then

$$r_i = k\,p_i^*$$

$$w_i = \frac{p_i^2}{v_i}$$

and

$$\log r_i = \log k + \log 1359.6 + \log p_i + e_i .$$

In a simple linear regression

$$\hat{y}_i = C + Dx_i$$
$$= \overline{y} + D(x_i - \overline{x}) \ .$$

Then the estimate of intercept C is

$$\hat{C} = \overline{y} - D\overline{x} \ .$$

In a weighted regression analysis

$$\overline{x} = \frac{\sum\limits_{i} w_i x_i}{\sum\limits_{i} w_i}$$

$$\overline{y} = \frac{\sum\limits_{i} w_i y_i}{\sum\limits_{i} w_i} \ .$$

Hence, in this case where

$$y_i = \log r_i$$
$$x_i = \log p_i$$

and

$$D = 1 \ ,$$

the estimate of intercept C is

$$\hat{C} = \frac{\sum\limits_{i} w_i \ (\log r_i)}{\sum\limits_{i} w_i} - \frac{\sum\limits_{i} w_i \ (\log p_i)}{\sum\limits_{i} w_i}$$

$$= \frac{\sum\limits_{i} w_i \ (\log r_i - \log p_i)}{\sum\limits_{i} w_i}$$

and

$$\log \hat{k} = \hat{C} - \log 1359.6 \ .$$

The calculations were performed for each of the four temperature levels with the following results:

temperature, °C.	temperature, °K.	$\hat{k}$	$\ln \hat{k}$	$1/T$
35	308.16	0.00006709	-9.60933	.0032451
28	301.16	0.00002494	-10.60065	.0033205
17	290.16	0.00001324	-11.23530	.0034464
9	282.16	0.00005379	-9.83024	.0035441

The natural logarithm of k (ln k) is plotted against $1/T$ in Figure 6.

It was apparent both from the numbers in the preceding table and from the graph that the data for 9° must be disregarded. The reaction is so slow at this temperature that results may be of doubtful value. In any event the estimate of specific rate at 9° is higher than those estimates for 17° and 28° whereas both theory and practice confirm that rate decreases in direct proportion to decreasing temperature.

A sight line was drawn through the remaining three points and the slope estimated to be -8890 (Figure 6). Then, since the slope of an Arrhenius plot is equal to $-E/R$, the activation energy could be estimated. Under the assumption that α is one, $\hat{E} = 17,656$ cal. This value, based on the more rigorous numerical analysis, is about twice as large as the
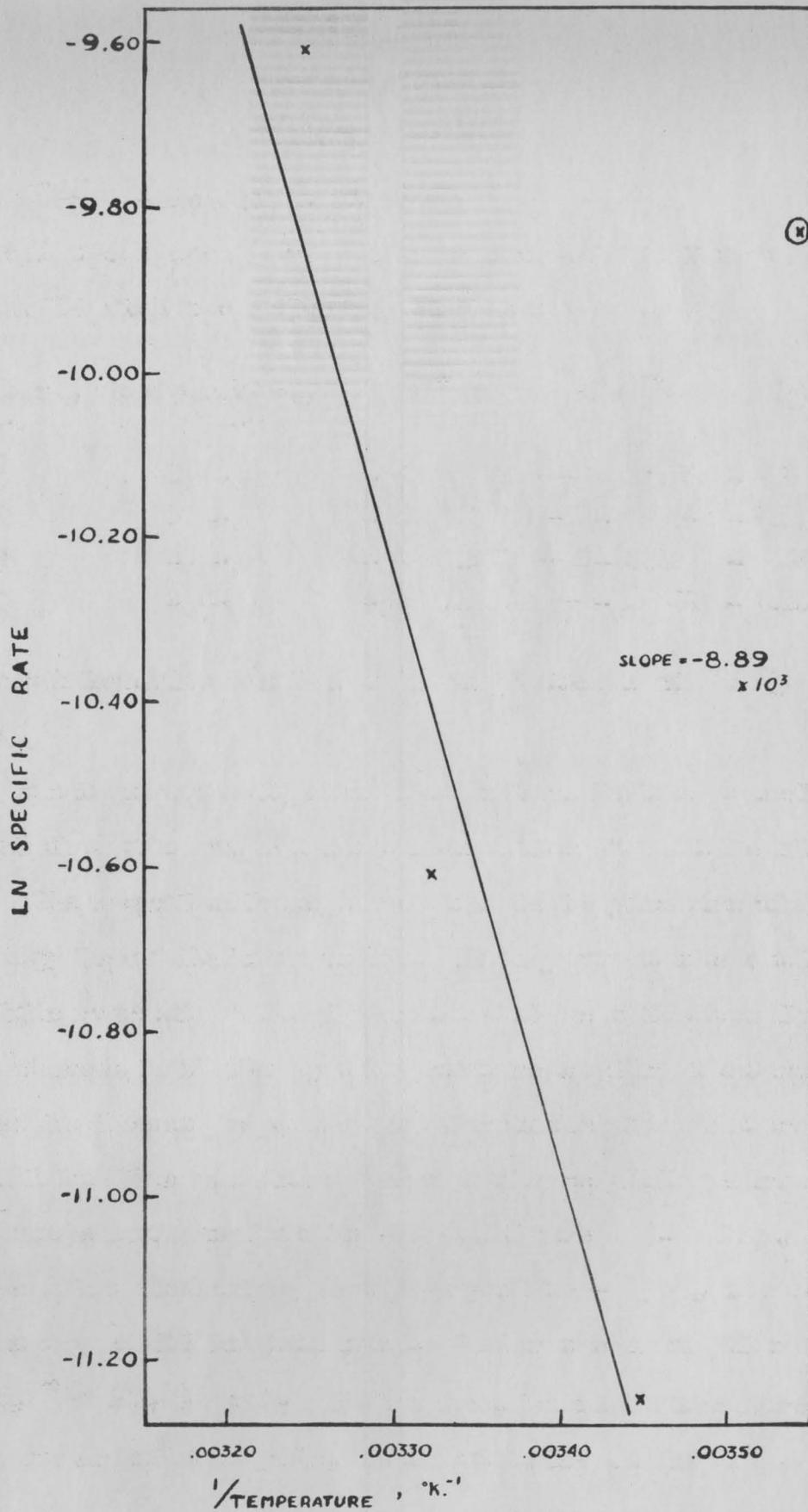
SLOPE = -8.89 x 10³

FIGURE 6. ARRHENIUS PLOT, ORDER = 1

one quoted by Forsten [2, p.58] under the same assumption of
a first order reaction.

2.5.2 "Average" Order Assumed

From the experimental data, however, a more realistic
assumption of the order would be some weighted average of the
three $\hat{a}_i$'s obtained previously. In order to obtain an esti-
mate of k in this way, the notation was changed as follows:

Let r_{ij} be the estimated rate of the j'th experimental
unit under temperature level i. The model then becomes

$$(2) \quad r_{ij} = c_i(p_{ij})^\alpha(1 + e_{ij})$$

where c_i is a constant depending on temperature i

$\quad$ p_{ij} is pressure in mm. mercury

$\quad$ α is the order of the reaction.

The rate equation is

$$r_{ij} = k_i(p_{ij}^*)^\alpha(1 + e_{ij}^*)$$

where k_i is the specific rate at temperature i and can be
$\qquad$ obtained from c_i and α

$\quad$ p_{ij}^* is pressure in $^{mg}/_{cm^2}$.

Then from equation (2),

$$\log r_{ij} = \log c_i + \alpha \log p_{ij} + e_{ij} \text{ , approximately,}$$

or

$$y_{ij} = \theta_i + \alpha x_{ij} + e_{ij}$$

where $y_{ij} = \log r_{ij}$

$\theta_i = \log c_i$

$x_{ij} = \log p_{ij}$.

Again the approximation

$$\text{var } [\log r_{ij}] \doteqdot \text{var } r_{ij} \; [-\frac{1}{\mathcal{E}(r_{ij})}]^2$$

was used. Since $\mathcal{E}(r_{ij}) = c_i(p_{ij})^\alpha$ and $\text{var } r_{ij} = v_{ij}$, then

$$\text{var } [\log r_{ij}] \sim \frac{v_{ij}}{c_i^2(p_{ij})^{2\alpha}} \; .$$

The estimation procedure used was a weighted analysis of covariance with the weights

$$w_{ij} = \frac{c_i^2(p_{ij})^{2\alpha}}{v_{ij}} \; .$$

Obtained in the analysis were t_i's which estimate the θ_i's and a which estimates α. Taking the $t_i^{(0)}$ from the separate analyses (the intercept at $p_{ij} = 0$ for each i) and $a^{(0)}$ as the simple average of the slopes of the three lines, the initial set of weights were

$$w_{ij}^{(0)} = \frac{\text{antilog } [2t_i^{(0)} + 2a^{(0)} \log p_{ij}]}{v_{ij}}$$

The iterative procedure was again used.

The computational steps of a weighted analysis of covariance are

Obtain $T_{iy}^W = \sum_j w_{ij} y_{ij}$, $i=1,2,3$

$$T_{ix}^W = \sum_j w_{ij} x_{ij} , \qquad i=1,2,3$$

$$S_{xy}^W = \sum_{all} w_{ij} x_{ij} y_{ij} - \frac{T_{1x}^W T_{1y}^W}{\sum_j w_{1j}} - \frac{T_{2x}^W T_{2y}^W}{\sum_j w_{2j}} - \frac{T_{3x}^W T_{3y}^W}{\sum_j w_{3j}}$$

$$S_{xx}^W = \sum_{all} w_{ij} x_{ij}^2 - \frac{(T_{1x}^W)^2}{\sum_j w_{1j}} - \frac{(T_{2x}^W)^2}{\sum_j w_{2j}} - \frac{(T_{3x}^W)^2}{\sum_j w_{3j}}$$

Then $a = S_{xy}^W / S_{xx}^W$.

Obtain $m_i = \dfrac{T_{iy}}{\sum_j w_{ij}}$, $i = 1, 2, 3$

$$\bar{x}_i = \frac{T_{ix}^W}{\sum_j w_{ij}} , \quad i = 1, 2, 3 .$$

A conversion of units was again necessary to find estimates of k_i. In the equation

$$\hat{r}_{ij} = \hat{k}_i (p_{ij}^*)^{\hat{\gamma}} ,$$

where $\hat{\gamma}$ is the estimated order of reaction, the units of $(p_{ij}^*)^{\hat{\gamma}}$ must be mg/cm^2 . Hence

$$p_{ij}^* = (1359.6 \ p_{ij})^{\hat{\gamma}}$$

and

$$\hat{r}_{ij} = \hat{k}_i \ (1359.6 \ p_{ij})^{\hat{\gamma}^2} \ .$$

Therefore

$$\log \hat{r}_{ij} = \log \hat{k}_i + \hat{\gamma}^2 \log 1359.6 + \hat{\gamma}^2 \log p_{ij} \ ,$$

which implies that the ANOCVA estimates are the following
quantities

$$t_i = \log \hat{k}_i + \gamma^2 \log 1359.6$$

$$a = \hat{\gamma}^2 \ (\text{or} \ \hat{\gamma} = +\sqrt{a}) \ .$$

Therefore, the desired estimates of k_i are

$$\hat{k}_i = \text{antilog} \ [t_i - a \log 1359.6] \ , \ \min^{-1}$$

These $\hat{k}_i$'s were converted to their natural logarithms.
The weights and results of the final iteration are given in
Table IV. The Arrhenius plot (Figure 7) has a slope of
-4945; thus the estimate of activation energy when order is
assumed to be 0.715 is $\hat{E} = 9821$ cal. (This is the empirical
order of the reaction as indicated by the observations.)

2.6 Reaction under H_2O Catalysis

When a similar attempt was made to estimate the order
and the specific reaction rate when water serves as the

TABLE IV

Final Iteration of Weighted Covariance Analysis

Temperature, °C.	Weights	t	$\log \hat{k}$	$\hat{k}$, min^{-1}	$\ln \hat{k}$
17	.164	-1.6672	-3.90759	0.0001237	-8.995
	15.3				
	93.5				
	1.66				
	519.				
	12.6				
28	.243	-1.4068	-3.64719	0.0002253	-8.399
	169.				
	1270.				
	26.8				
	31.0				
	69.6				
35	1.56	-1.2344	-3.47479	0.0003351	-8.001
	145.				
	1.19				
	106.				

$$a = 0.715$$

The estimate of order is a

The estimate of specific rate is obtained:
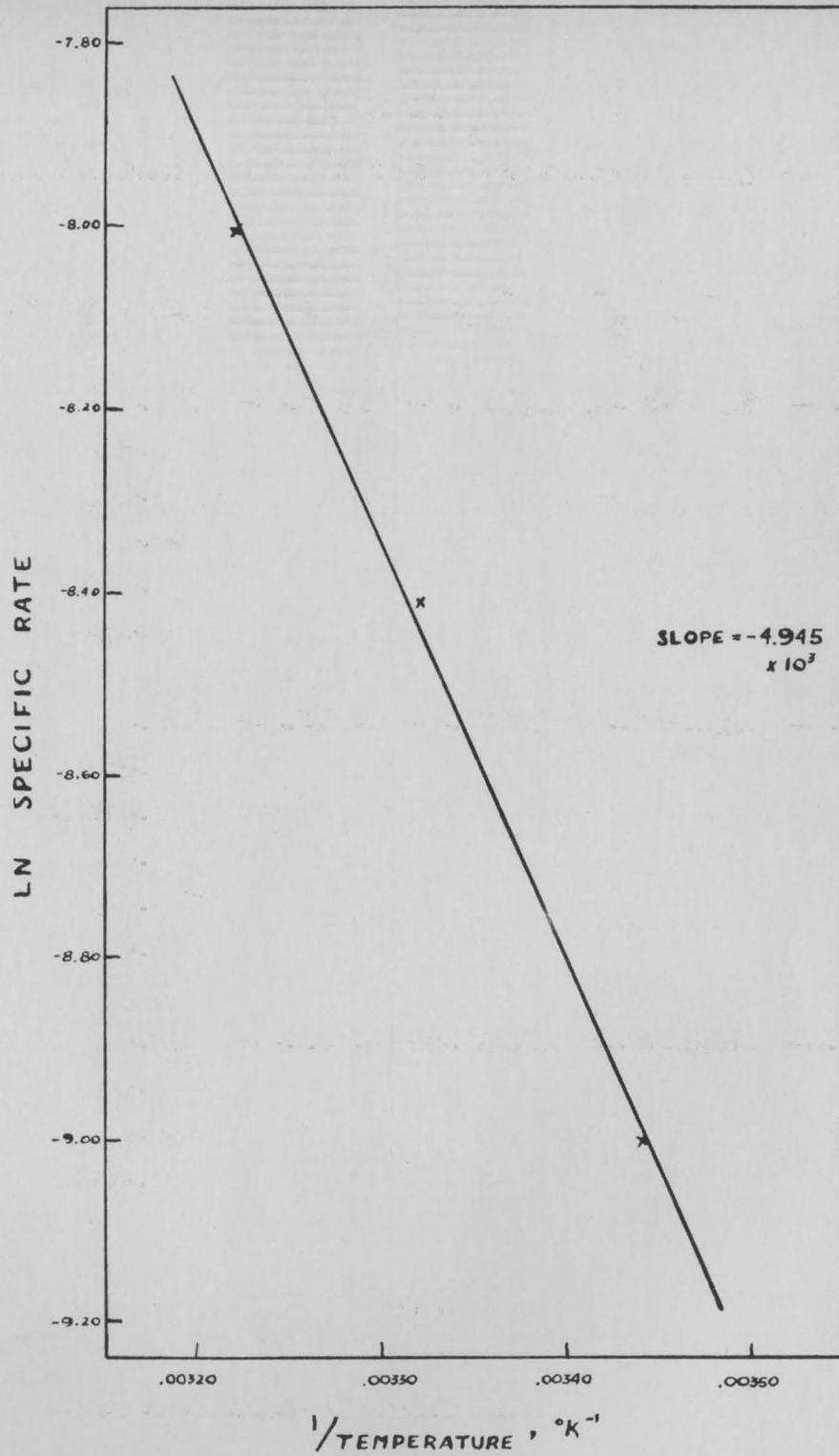
$$\log \hat{k}_i = t_i - a \log 1359.6$$

FIGURE 7. ARHENIUS PLOT,
ORDER = 0.715

catalyst, the experiment appeared to be inadequate. (See

Figures 8, 9, 10, 11) At only two temperature levels were

there more than two observations in the range where H_2O

vapor pressure was to be considered. Also, the observation

on the 28° graph at which log p = 0.884, log r = -1.673 is

from test run number 12 for which there were only thirteen

observations in the linear period. The 28° graph is,

therefore, of rather dubious value. As a result, the only

iterations performed were on the three 35° points. This

led to estimates of $\hat{a}$ = 3.106, log $\hat{k}$ = -5.329. Further

experiments should be made, if possible, in this pressure

range. However, at this time it can be said that there is

an indication that the formation of $AlCl_3x6H_2O$ is approxi-

mately of order three. Any further work with the data at
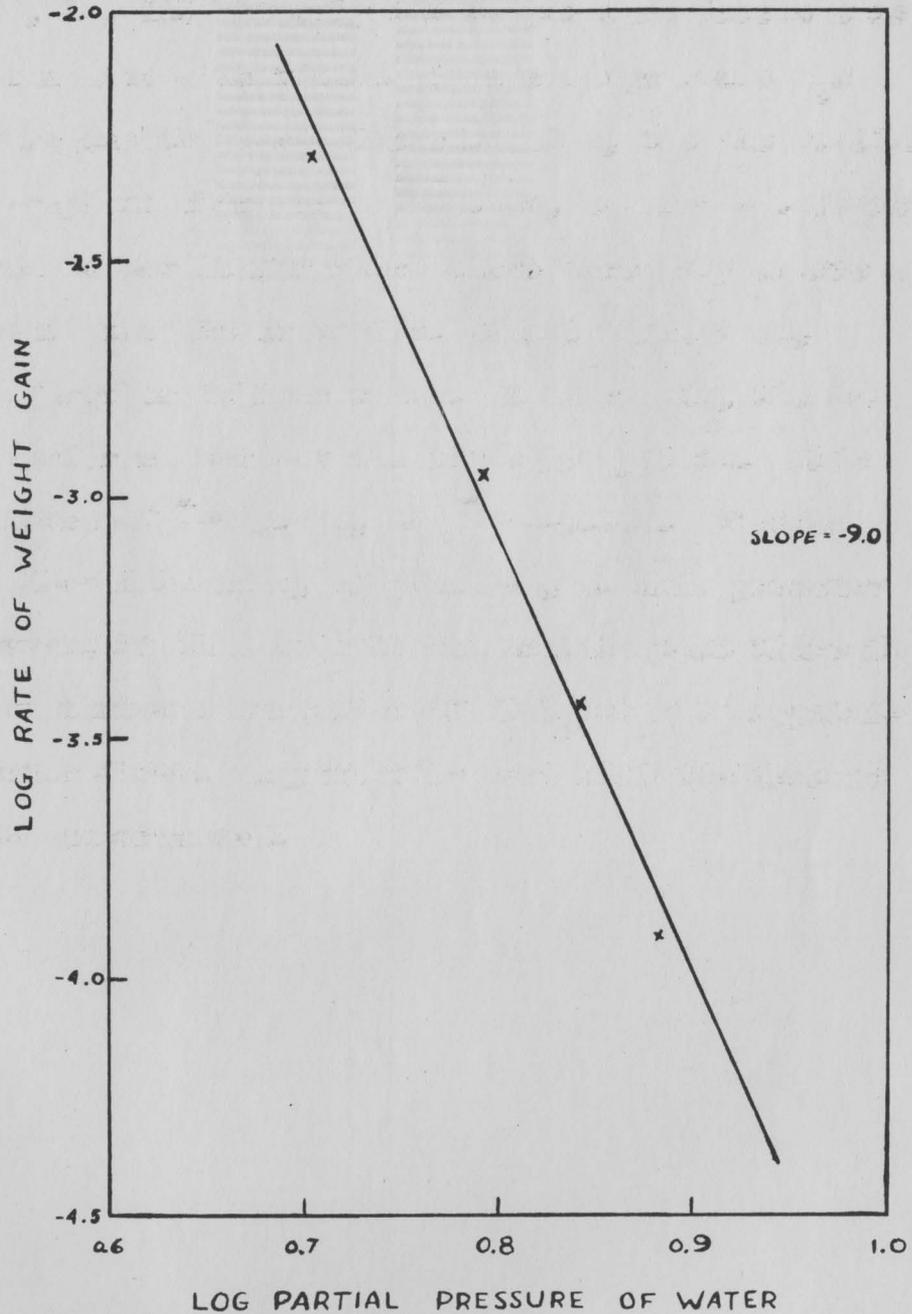
hand would be unwarranted.

FIGURE 8. LOG PARTIAL PRESSURE
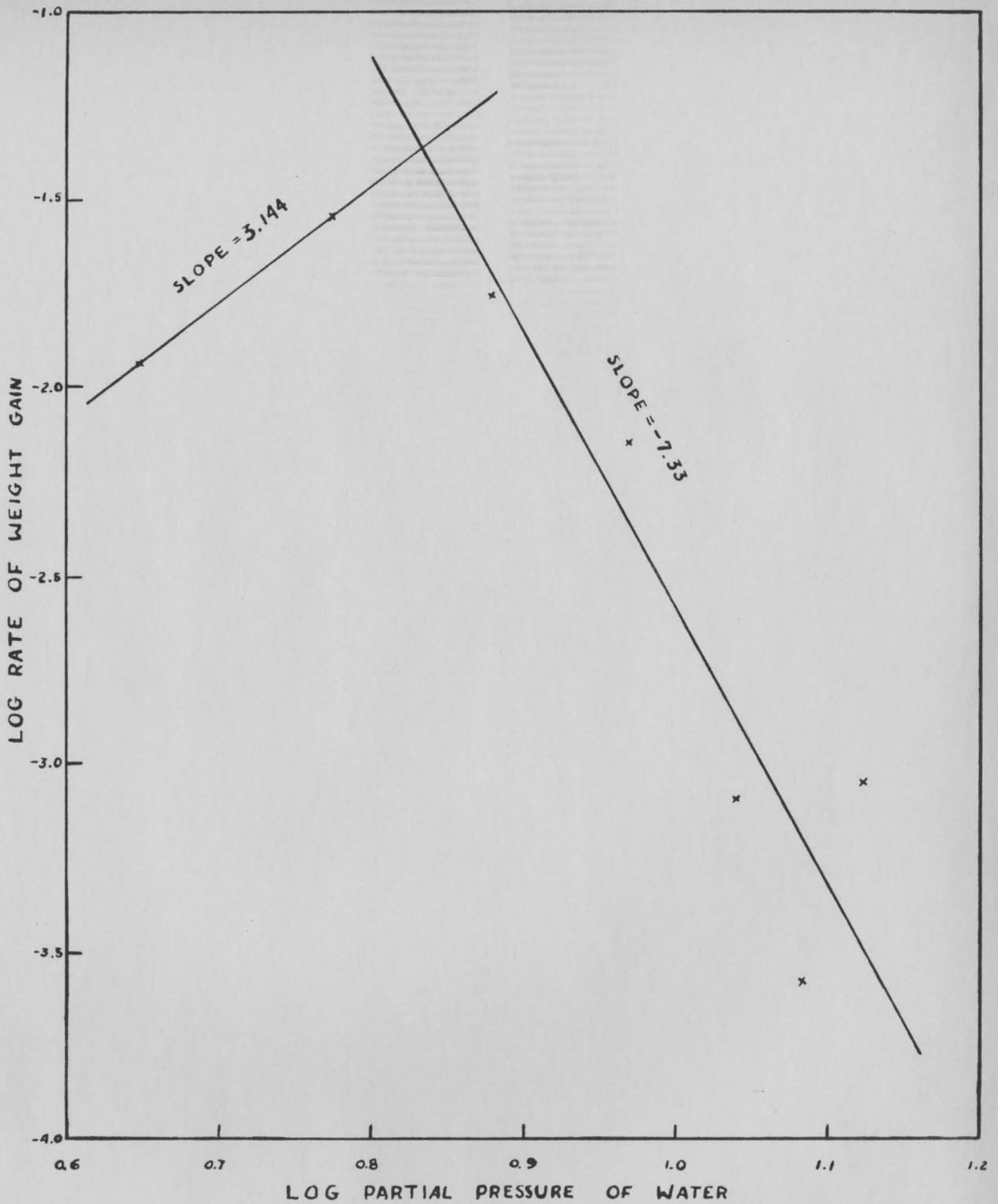OF WATER vs. LOG RATE
OF WEIGHT GAIN, 9°C.

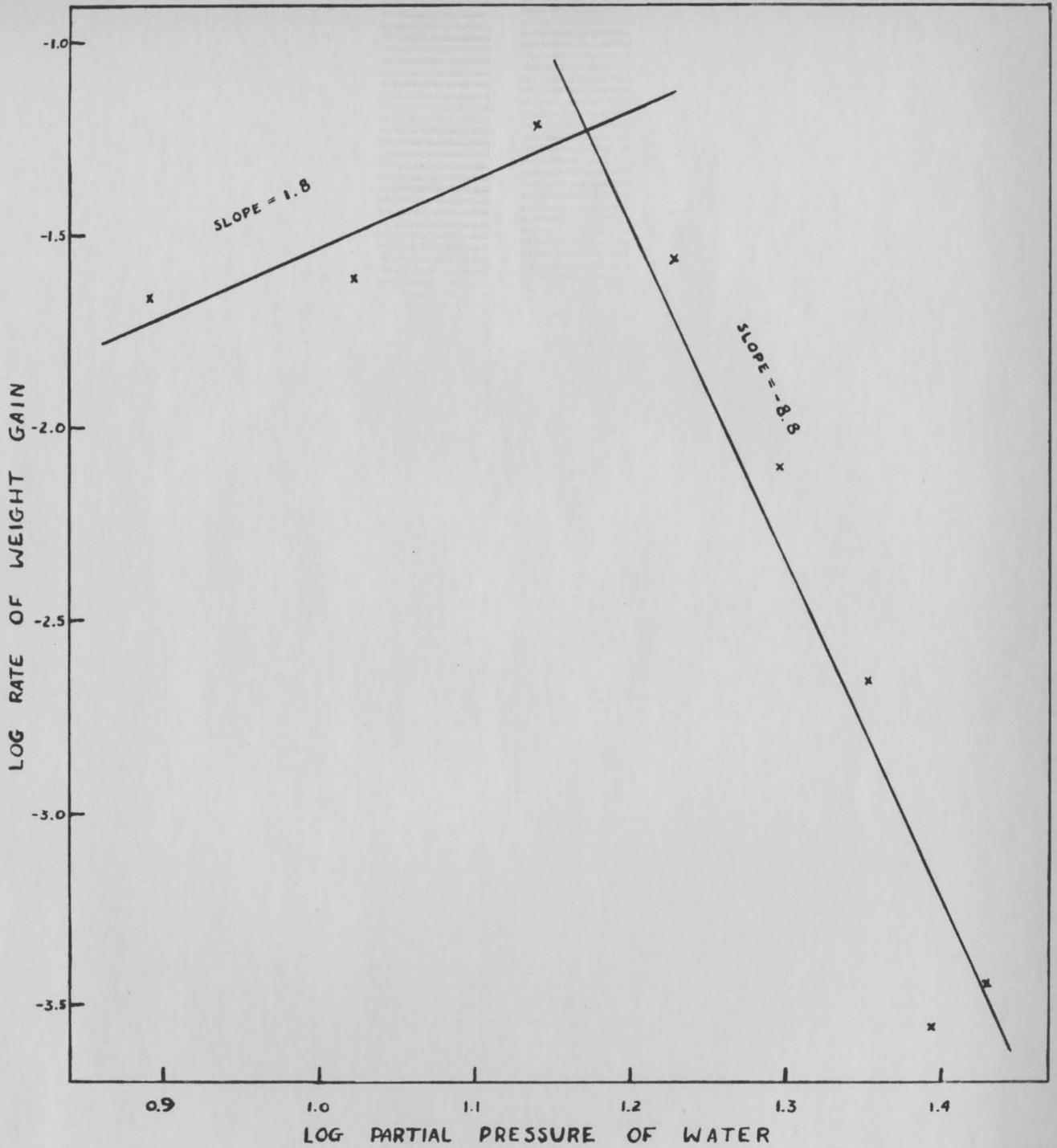FIGURE 9. LOG PARTIAL PRESSURE OF WATER vs. LOG RATE OF WEIGHT GAIN, 17°C.

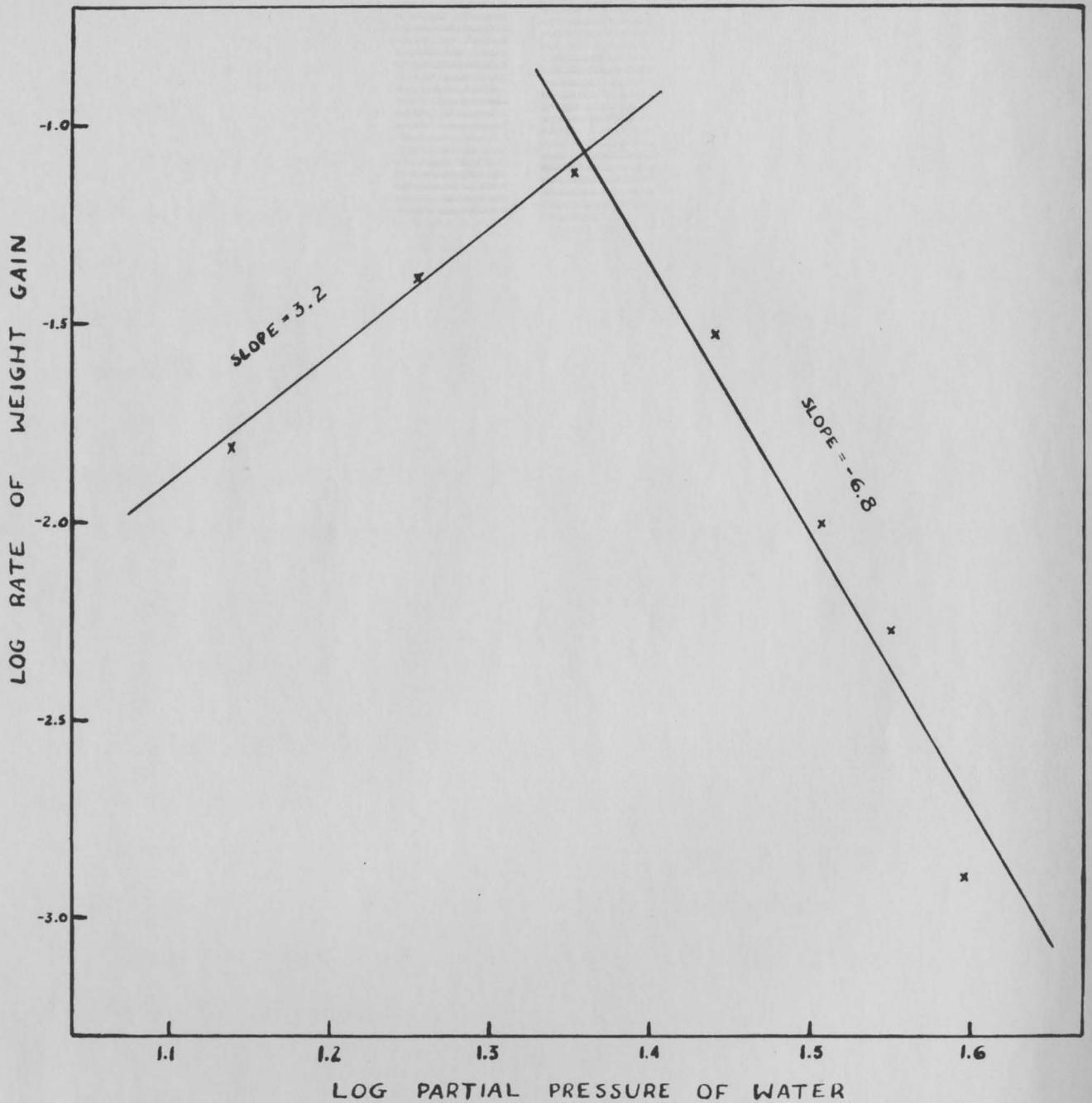FIGURE 10. LOG PARTIAL PRESSURE OF WATER vs. LOG RATE OF WEIGHT GAIN, 28°C.

FIGURE II. LOG PARTIAL PRESSURE OF WATER vs. LOG RATE OF WEIGHT GAIN, 35°C.

CHAPTER III. Empirical Response Equation
for Prediction of Corrosion

3.1 Model

The second section of the study of the corrosion of
aluminum in hydrochloric acid vapor was an analysis of the
relative effects of temperature and pressure in such a cor-
rosion. The original experiment was not subjected to a
complete statistical analysis. Only the data obtained from
the portion in which aluminum oxide is the product under
hydrochloric acid catalysis was analyzed.

The most general chemical model for corrosion is of the
form

$$Y = y_0 \, f_1(p) \, f_2(T) \, e^{f_3(t)} \, ,$$

i.e., weight gain is a function of pressure, absolute temper-
ature, and time. This model is stated merely to show that
the usual theory does not allow for interaction among the
three factors, time, concentration, and temperature.

Error is usually proportional to response; therefore,
the statistical model is

$$y_{ijk} = Y_0 \, f_1(p_i) \, f_2(T_j) \, e^{f_3(t_k)} \, (1 + \varepsilon_{ijk})$$

or, except for terms of order ε^2_{ijk} , ε^3_{ijk} , etc.,

$$\ln y_{ijk} = \ln Y_0 + \ln f_1(p_i) + \ln f_2(T_j) + f_3(t_k) + \varepsilon_{ijk} \, .$$

The functions of pressure and temperature have some form not yet established. Usually, $f_1(p_i)$ would be expected to be of the form p_i^ρ ; $f_2(T_j)$ would be expected to be of the form $e^{\frac{\gamma}{T_j}}$. For the time being these unknown functions will be introduced as levels of pressure, i.e., π_1, π_2, ..., and as levels of temperature, i.e., τ_1, τ_2, ... Time enters as a concomitant variable. It has been established that the reaction is of approximately first order; hence $f_3(t_k)$ can be replaced by $\beta(t_k - \bar{t})$, where k = 1, 2, ..., 6

$$\bar{t} = 1/6 \sum_k t_k \ .$$

Interaction, if any, is usually dealt with in quantitative analysis as an "empirical correction". An interaction term may, therefore, be included in the model. Thus the following model is assumed:

(3) $\ln y_{ijk} = \mu + \pi_i + \tau_j + \delta_{ij} + \beta(t_k - \bar{t}) + e_{ijk}$.

Since the δ_{ij}'s would, if present, play the role of correction terms, the condition may be stated that they are to be as small as possible. (Note that this is not a constraint, but rather a condition or restriction on the model.) This is equivalent to setting

$$\sum_i n_{ij} \delta_{ij} = 0 , \quad \text{for all } j$$

and

$$\sum_j n_{ij} \delta_{ij} = 0 , \quad \text{for all } i$$

where n_{ij} is the number of observations in cell (i, j).
Thus, the analysis indicated is a standard two-way classifi-
cation with a covariate.

3.2 Analysis of Covariance

The experiment was originally designed to include ten
temperature levels and eight pressure levels, i.e., those
runs performed at approximately the same pressure were
assigned to an "average level" of pressure. When the two
highest pressure levels were deleted from the study, the $48°$
column was also discarded since only one observation remained.
Test runs 19 and 39 were also discarded, because of the
small number of observations available. This brought about
the elimination of the $2°$ column. Thus the analysis dealt
with eight temperature levels and six pressure levels. Six
observations ($t = 80, 90, ..., 130$ minutes) from each test
run were used. This data may be seen in Table V. The
analysis is based on the logarithm of weight gain, however.
Table VI is the record of $\log y_{ijk}$ and includes cell,
column and row totals. (In order to work with positive
quantities, all observations were multiplied by 10 before
the logarithms were recorded; i.e.,

$$1 + \log z = \log y$$

where z = original observation.)

TABLE V

Corrosion Data in Two-Way Classification Form

Temperature, °C. — t= 80 / = 90 / =100 (left sub-column) and t=110 / =120 / =130 (right sub-column)

log pressure, HCl	44 (80/90/100)	44 (110/120/130)	41 (80/90/100)	41 (110/120/130)	35 (80/90/100)	35 (110/120/130)	28 (80/90/100)	28 (110/120/130)	17 (80/90/100)	17 (110/120/130)	(80/90/100)	(110/120/130)	(80/90/100)	(110/120/130)	(80/90/100)	(110/120/130)
.250					109.0	154.2	84.6	120.6	40.0	57.6			21.6	31.4		
					123.2	169.2	96.6	133.8	46.2	63.2			25.6	34.8		
					137.4	184.8	108.8	144.6	52.2	69.4			28.0	38.6		
- .502	53.0	70.6			44.0	63.6	41.2	56.8	22.4	32.8			10.4	15.8		
	58.8	77.0			50.0	69.8	46.2	62.4	26.0	36.2			12.0	18.0		
	64.2	83.8			57.0	76.0	51.4	68.4	29.4	39.2			13.8	19.8		
-1.125	22.8	31.4			12.8	17.4	14.0	18.2	10.2	13.4	6.6	9.4			4.8	7.6
	25.4	33.4			14.2	18.8	15.4	19.4	11.2	15.4	7.6	10.6			5.6	8.4
	28.2	35.8			15.8	20.4	16.6	21.0	12.6	17.4	8.6	11.4			7.2	9.2
-1.825			10.2	12.6	7.4	10.2	4.0	5.6	0.8	1.4	1.6	2.2			2.0	3.4
			10.8	14.0	8.4	10.8	4.6	5.8	1.0	1.6	1.8	2.4			2.4	3.6
			11.6	15.4	9.0	11.2	5.2	6.4	1.2	1.8	2.0	2.6			3.0	3.8
-2.520	5.2	8.0			4.8	5.2	0.4	0.6	0.6	0.8	1.0	1.4				
	6.4	8.8			5.0	5.4	0.4	0.6	0.6	0.8	1.2	1.4				
	7.2	9.8			5.0	5.4	0.6	0.6	0.8	0.8	1.2	1.4				
-3.250			3.4	3.6			1.2	1.2	1.2	2.0						
			3.4	3.8			1.2	1.2	1.4	2.0						
			3.6	4.0			1.2	1.4	1.8	2.2						

TABLE VI
Logarithms of Corrosion Data

Temperature, °C — Log Pressure, HCl	48	41	35	28	17	9	7	0	Totals $\{^{y}_{(t)}$
	t= 80 t=110 = 90 =120 =100 =130								Σt = 630, any cell
.250			3.0374 3.1881 3.0906 3.2284 3.1380 3.2667 18.9492	2.9274 3.0814 2.9850 3.1265 3.0366 3.1602 18.3171	2.6021 2.7604 2.6646 2.8007 2.7177 2.8414 16.3869		2.3344 2.4969 2.4082 2.5416 2.4472 2.5866 14.8149		68.4681 (2520)
- .502	2.7243 2.8488 2.7694 2.8865 2.8075 2.9232 16.9597		2.6434 2.8035 2.6990 2.8439 2.7559 2.8808 16.6265	2.6149 2.7544 2.6646 2.7952 2.7110 2.8351 16.3952	2.3502 2.5159 2.4150 2.5587 2.4684 2.5933 14.9015		2.0170 2.1987 2.0792 2.2553 2.1399 2.2788 12.9689		77.8318 (3150)
-1.125	2.3579 2.4969 2.4048 2.5238 2.4502 2.5539 14.7875		2.1072 2.2406 2.1523 2.2742 2.1987 2.3096 13.2826	2.1461 2.2601 2.1875 2.2878 2.2201 2.3222 13.4238	2.0086 2.1271 2.0492 2.1875 2.1004 2.2406 12.7134	1.8195 1.9731 1.8808 2.0253 1.9345 2.0569 11.6901		1.6812 1.8808 1.7482 1.9243 1.8573 1.9638 11.0556	76.9530 (3780)
-1.825		2.0086 2.1004 2.0334 2.1461 2.0645 2.1875 12.5405	1.8692 2.0086 1.9243 2.0334 1.9542 2.0492 11.8389	1.6021 1.7482 1.6628 1.7634 1.7160 1.8062 10.2987	0.9031 1.1461 1.0000 1.2041 1.0792 1.2553 6.5878	1.2041 1.3424 1.2553 1.3802 1.3010 1.4150 7.8980		1.3010 1.5315 1.3802 1.5563 1.4771 1.5798 8.8259	57.9898 (3780)
-2.520	1.7160 1.9031 1.8062 1.9445 1.8573 1.9912 11.2183		1.6812 1.7160 1.6990 1.7324 1.6990 1.7324 10.2600	0.6021 0.7782 0.6021 0.7782 0.7782 0.7782 4.3170	0.7782 0.9031 0.7782 0.9031 0.9031 0.9031 5.1688	1.0000 1.1461 1.0792 1.1461 1.0792 1.1461 6.5967			37.5608 (3150)
-3.250		1.5315 1.5563 1.5315 1.5798 1.5563 1.6021 9.3575		1.0792 1.0792 1.0792 1.0792 1.0792 1.1461 6.5421	1.0792 1.3010 1.1461 1.3010 1.2553 1.3424 7.4250				23.3246 (1890)
Totals $\{^{y}_{(t)}$	42.9655 (1890)	21.8980 (1260)	70.9572 (3150)	69.2739 (3780)	63.1834 (3780)	26.1848 (1890)	27.7838 (1260)	19.8815 (1260)	342.1281 (18,270)

Thus the incidence matrix N is

$$
N = \begin{bmatrix} 0 & 0 & 6 & 6 & 6 & 0 & 6 & 0 \\ 6 & 0 & 6 & 6 & 6 & 0 & 6 & 0 \\ 6 & 0 & 6 & 6 & 6 & 6 & 0 & 6 \\ 0 & 6 & 6 & 6 & 6 & 6 & 0 & 6 \\ 6 & 0 & 6 & 6 & 6 & 6 & 0 & 0 \\ 0 & 6 & 0 & 6 & 6 & 0 & 0 & 0 \end{bmatrix} \quad \begin{matrix} n_{i\cdot} \\ 24 \\ 30 \\ 36 \\ 36 \\ 30 \\ 18 \end{matrix}
$$

$n_{\cdot j}$ 18   12   30   36   36   18   12   12 $n = 174$

If $\hat{\underline{\pi}}$ is the vector of relative effects due to pressure, and $\hat{\underline{\tau}}$ the corresponding vector of temperature effects, the normal equation may be written

$$
(4) \quad \begin{bmatrix} D_{n_{i\cdot}} & N \\ N' & D_{n_{\cdot j}} \end{bmatrix} \begin{bmatrix} \hat{\underline{\pi}} \\ \hat{\underline{\tau}} \end{bmatrix} = \begin{bmatrix} \underline{P} - \underline{n}_{i\cdot}\, \hat{\mu} \\ \underline{T} - n_{\cdot j}\, \hat{\mu} \end{bmatrix}
$$

where $D_{n_{i\cdot}}$ is the diagonal matrix the elements of whose main

diagonal are the $n_{i\cdot}$'s. Its dimensions: 6 x 6

$D_{n_{\cdot j}}$ is the diagonal matrix the elements of whose main

diagonal are the $n_{\cdot j}$'s. Its dimensions: 8 x 8

$\underline{P}$ is the vector of row totals; i.e.,

$$
P_i = \sum_j \sum_k \log y_{ijk} , \quad i = 1, 2, \ldots, 6
$$

$\underline{T}$ is the vector of column totals; i.e.,

$$T_j = \sum_i \sum_k \log y_{ijk} , \quad j = 1, 2, \ldots, 8$$

$$\hat{\mu} = \frac{\sum_i \sum_j \sum_k \log y_{ijk}}{n} = \frac{G}{n} .$$

Rewriting (4) the equations become

(5) $\quad D_{n_{i\cdot}} \hat{\underline{\pi}} + N \hat{\underline{\tau}} = \underline{P} - \underline{n}_{i\cdot} \hat{\mu}$

(6) $\quad N'\hat{\underline{\pi}} + D_{n_{\cdot j}} \hat{\underline{\tau}} = \underline{T} - \underline{n}_{\cdot j} \hat{\mu}$

or, multiplying equation (6) by $N D_{1/n_{\cdot j}}$ and subtracting from equation (5), the adjusted normal equations for $\hat{\pi}_i$ are

$$(D_{n_{i\cdot}} - N D_{1/n_{\cdot j}} N') \hat{\underline{\pi}} = \underline{P} - N D_{1/n_{\cdot j}} \underline{T}$$

which may be written

(7) $\quad C \hat{\underline{\pi}} = \underline{Q}$

where the elements of the matrix C are of the form

$$c_{ii} = n_{i\cdot} - \left(\frac{n_{i1}^2}{n_{\cdot 1}} + \frac{n_{i2}^2}{n_{\cdot 2}} + \ldots + \frac{n_{i8}^2}{n_{\cdot 8}} \right)$$

$$c_{ij} = - \left(\frac{n_{i1} n_{j1}}{n_{\cdot 1}} + \frac{n_{i2} n_{j2}}{n_{\cdot 2}} + \ldots + \frac{n_{i8} n_{j8}}{n_{\cdot 8}} \right)$$

and the elements of the vector $\underline{Q}$ are

$$q_i = P_i - \left(\frac{n_{i1}T_1}{n_{\cdot 1}} + \frac{n_{i2}T_2}{n_{\cdot 2}} + \ldots + \frac{n_{i8}T_8}{n_{\cdot 8}} \right)$$

The symmetric matrix C is, therefore,

$$C = \begin{bmatrix} 17.8 & -6.2 & -3.2 & -3.2 & -3.2 & -2.0 \\ & 21.8 & -5.2 & -3.2 & -5.2 & -2.0 \\ & & 25.8 & -8.2 & -7.2 & -2.0 \\ & & & 24.8 & -5.2 & -5.0 \\ & & & & 22.8 & -2.0 \\ & & & & & 13.0 \end{bmatrix} .$$

This matrix is singular. (Note that the sum of elements in each row and in each column is zero.) In order to have a non-singular matrix, the constraint

$$\sum_i \hat{\pi}_i = 0$$

is imposed. The resulting matrix C_1 is

$$C_1 = \begin{bmatrix} 21.0 & -3.0 & 0 & 0 & 0 & 1.2 \\ & 25.0 & -2.0 & 0 & -2.0 & 1.2 \\ & & 29.0 & -5.0 & -4.0 & 1.2 \\ & & & 28.0 & -2.0 & -1.8 \\ & & & & 26.0 & 1.2 \\ & & & & & 16.2 \end{bmatrix} .$$

The vector Q is

$$Q = \begin{bmatrix} 18.3086 \\ 13.3505 \\ 7.6945 \\ -7.8959 \\ -21.7569 \\ -9.7007 \end{bmatrix} .$$

The sum of these elements should equal zero. In this case

$$\sum_i q_i = 0.0002$$

which is correct except for rounding errors.

The vector $\hat{\underline{\pi}}$ is obtained from equation (7), i.e.,

$$\hat{\underline{\pi}} = C_1^{-1} Q .$$

The matrix inversion and the multiplication of vector by matrix were accomplished by use of Program Number 5.2.001.2 (G864) on the I.B.M. 650 electronic computer with the following results (rounded to five decimal places):

$$C_1^{-1} = \begin{bmatrix} .04874 & .00617 & .00069 & -.00009 & .00077 & -.00418 \\ & .04155 & .00370 & .00069 & .00400 & -.00403 \\ & & .03696 & .00069 & .00663 & -.00279 \\ & & & .03743 & .00384 & .00332 \\ & & & & .04024 & -.00340 \\ & & & & & .06316 \end{bmatrix}$$

$$\hat{\underline{\pi}} = \begin{bmatrix} 1.00460 \\ .64261 \\ .17478 \\ -.35075 \\ -.75438 \\ .71686 \end{bmatrix} \quad , \quad \sum_i \hat{\pi}_i = 0 \ .$$

The analysis, as was mentioned earlier, follows the general scheme of the analysis of a two-way classification with missing cells. Although the presence of a covariate complicates the procedure, the analysis is quite straight-forward if the computations performed upon, in this case, $\log y_{ijk}$ are applied also to t_k and similar computations are applied to $(\log y_{ijk})t_k$. Then the adjusted sums of squares for $[\log y_{ijk}$ given $t_k]$ are easily calculated.

Since there are missing cells in the 6 x 8 design, the sum of squares due to pressure must be adjusted for temperature effects. Likewise, the sum of squares due to temperature must be adjusted for pressure effects. SS Pressure, adjusted, is:

SS Pressure, adj. $= \hat{\underline{\pi}}' \ \underline{Q}$.

The sum of squares due to temperature, unadjusted; the subtotal sum of squares; and the total sum of squares are computed in the usual manner, i.e.,

SS Temperature, unadj. $= \dfrac{T_1^2}{n_{\cdot 1}} + \dfrac{T_2^2}{n_{\cdot 2}} + \ldots + \dfrac{T_8^2}{n_{\cdot 8}} - \dfrac{G_y^2}{n}$

where $G_y = \sum_i \sum_j \sum_k \log y_{ijk}$

$$\text{SS Subtotal} = \frac{1}{6}(C_{11}{}^2 + C_{12}{}^2 + \ldots + C_{68}{}^2) - \frac{G_y^2}{n}$$

where $C_{ij} = \sum_k \log y_{ijk}$; i.e., the total of observations in

cell (i,j)

$$\text{SS Total}_y = \sum_i \sum_j \sum_k (\log y_{ijk})^2 - \frac{G_y^2}{n} \ .$$

Since the t_k's are the same in each cell, it is obvious that all sums of squares for time are equal to zero except for the total and error sums of squares. For the same reason, corresponding entries in the $(\log y_{ijk})t_k$ column are equal to zero. Thus in this covariance analysis only the error line in the $[(\log y_{ijk})$ given $t_k]$-column will need to be corrected. The total sum of squares for t_k and the total sum of products for $(\log y_{ijk})t_k$ are

$$\text{SS Total}_t = \sum_i \sum_j \sum_k t_k^2 - \frac{G_t^2}{n}$$

$$= 29 \sum_k t_k^2 - \frac{G_t^2}{n}$$

where $G_t = \sum_i \sum_j \sum_k t_k = 29 \sum_k t_k$

$$\text{SP Total}_{yt} = \sum_i \sum_j \sum_k (\log y_{ijk})t_k - \frac{G_y G_t}{n} \ .$$

The ANOCVA Table is presented in Table VII.

In order to find the sum of squares due to temperature, adjusted for pressure effects, the following procedure is used:

Obtain SS Pressure, unadj. $= \dfrac{P_1^2}{n_{1.}} + \dfrac{P_2^2}{n_{2.}} + \ldots + \dfrac{P_6^2}{n_{6.}} - \dfrac{G_y^2}{n}$

Then SS Temperature, adj. = SS Subtotal - SS Pressure, unadj.
- SS Interaction,

where SS Subtotal and SS Interaction are transferred directly from Table VII.

The numerical results of the analysis, a general two-way classification with covariate, were

$n = 174$

$G^2/n = 672.71056$

SS Temperature, unadj. $= 17.19189$

SS Pressure, adj. $= 54.45335$

SS Subtotal $= 76.20915$

SS Total$_y$ $= 77.21657$

SS Total$_t$ $= 50,750.00$

SP Total$_{yt}$ $= 210.5085$

SS Pressure, unadj. $= 59.70054$

SS Temperature, adj. $= 11.94470$.

By subtraction,

SS Error$_y$ $= 1.00742$

TABLE VII

Table of ANOCVA Equations

Source	Sums of Squares and Products				Degrees of Freedom
	log y	t	(log y)t	log y|t	log y|t
Temperature, unadjusted	$\dfrac{T_1^2}{n_{\cdot 1}}+\dfrac{T_2^2}{n_{\cdot 2}}+\ldots+\dfrac{T_8^2}{n_{\cdot 8}}-\dfrac{G_y^2}{n}$	0	0	$\dfrac{T_1^2}{n_{\cdot 1}}+\dfrac{T_2^2}{n_{\cdot 2}}+\ldots+\dfrac{T_8^2}{n_{\cdot 8}}-\dfrac{G_y^2}{n}$	7
Pressure, adjusted	$\underline{\hat{\pi}}'\underline{Q} = \sum_i \hat{\pi}_i\, q_i$	0	0	$\underline{\hat{\pi}}'\underline{Q} = \sum_i \hat{\pi}_i\, q_i$	5
Interaction T x P	difference	0	0	difference	16
Subtotal	$\frac{1}{6}(C_{11}^2+C_{12}^2+\ldots+C_{68}^2)$ $-\dfrac{G_y^2}{n}$	0	0	$\frac{1}{6}(C_{11}^2+C_{12}^2+\ldots+C_{68}^2)$ $-\dfrac{G_y^2}{n}$	28
Error	difference	difference	difference	$SSE_y - \dfrac{(SPE_{yt})^2}{SSE_t}$	144
Total	$\underset{ijk}{\Sigma\Sigma\Sigma}(\log y_{ijk})^2-\dfrac{G_y^2}{n}$	$\underset{ijk}{\Sigma\Sigma\Sigma}t_k^2-\dfrac{G_t^2}{n}$	$\underset{ijk}{\Sigma\Sigma\Sigma}(\log y_{ijk})t_k$ $-\dfrac{G_y G_t}{n}$		

$$SS\ Error_t = 50{,}750.00$$

$$SP\ Error_{yt} = 210.5085$$

The table of sums of squares, mean squares, and F ratios appears as Table VIII.

3.3 Estimation of Effects

The error term in the analysis is extremely small in comparison with the other mean square values in the table. Thus every F ratio with MSE in the denominator is significant at the one per cent level. The significance of the interaction effect indicates that the correction term in the model is needed. F ratios have been computed also for pressure and temperature, using MS Interaction as the denominator. Both ratios are significant at the one per cent level; therefore, both temperature and pressure contribute appreciably to the rate of corrosion above and beyond the effect of an interaction of temperature and pressure. Since we assumed that an interaction effect was only a correction term and for this reason placed the condition on the model that interaction effects be as small as possible, and since both temperature and pressure are very significant when compared with interaction, the estimates of main effects justify interpretation. A detailed discussion of the significantly large interaction term will be given later. (3.4)

TABLE VIII

Numerical ANOCVA Table

Source	S.S.	d.f.	M.S.	F
Temperature	11.94470	7	1.70639	$\dfrac{\text{MS Temperature}}{\text{MS Interaction}} = 5.9823$**
Pressure	54.45335	5	10.89067	$\dfrac{\text{MS Pressure}}{\text{MS Interaction}} = 38.1807$**
Interaction T x P	4.56391	16	.28524	$\dfrac{\text{MS Interaction}}{\text{MS Error}} = 306.7097$**
Subtotal	76.20915	28	2.72176	
Error	.13424	144	.00093	

The vector of estimates of relative effects due to pressure has already been estimated as $\underline{\hat{\pi}}$. In order to obtain $\underline{\hat{\tau}}$, we make use of equation (6), i.e.,

$$\underline{\hat{\tau}} = D_{1/n._{j}} \; (\underline{T} - N'\underline{\hat{\pi}} - \underline{n}._{j}\hat{\mu}) \; .$$

The operational procedure for the estimation of the $\hat{\tau}_{j}$'s is as follows:

Obtain $N'\underline{\hat{\pi}}$, the vector whose typical element is equal
   to six times the sum of those $\hat{\pi}_{i}$'s which correspond
   to non-zeroes in the particular column of N.

Add to these eight elements the corresponding term
   of $\underline{n}._{j}\hat{\mu}$; i.e., to the first element add 18 G/n ;
   to the second, 12 G/n ; etc.

Subtract these quantities from the corresponding T_{i}'s,
   the column totals.

Multiply each element by the proper term of $D_{1/n._{j}}$;
   i.e., divide the first element by 18, the
   second by 12, etc.

Here $\hat{\mu}$ = 1.96625. Hence the $\underline{\hat{\tau}}$ vector is

$$\underline{\hat{\tau}} = \begin{bmatrix} .39971 \\ .39239 \\ -.04198 \\ -.21116 \\ -.20143 \\ -.47454 \\ -.22148 \end{bmatrix} \quad , \; \underset{j}{\Sigma} \; \hat{\tau}_{j} = -.10288 \; .$$

The constraint

$$\sum_i n_{i.} \hat{\pi}_i + \sum_j n_{.j} \hat{\tau}_j = 0$$

has been used in this estimation operation. As a check of calculations, these sums are

$$\sum_i n_{i.} \hat{\pi}_i = 1.51916$$

$$\sum_j n_{.j} \hat{\tau}_j = -1.51901 .$$

Hence

$$\sum n_{i.} \hat{\pi}_i + \sum n_{.j} \hat{\tau}_j = .00015 ,$$

a difference from zero which can be explained as a rounding error.

For a neater presentation of data the estimated temperature effects $\hat{\underline{\tau}}$ have been adjusted so that the sum of these estimates is zero. This is accomplished in the following manner:

Let $\hat{\tau}_j^* = \hat{\tau}_j + c$

where $\sum_j \hat{\tau}_j^* = 0$.

Then $\sum_j \hat{\tau}_j + 8c = 0$

which implies that

$$c = -1/8 \sum_j \hat{\tau}_j .$$

Thus

$$\hat{\tau}_j{}^* = \hat{\tau}_j - \frac{1}{8} \sum_j \hat{\tau}_j$$

$$= \hat{\tau}_j + .01286 \ .$$

The $\hat{\underline{\tau}}^*$ vector is

$$\hat{\underline{\tau}}^* = \begin{matrix} .41257 \\ .40525 \\ .26847 \\ -.02912 \\ -.19830 \\ -.18857 \\ -.46168 \\ -.20862 \end{matrix} \quad , \quad \sum_j \hat{\tau}_j{}^* = 0 \ .$$

However, since we decreased the value of the $\hat{\tau}_j$'s by a constant amount, we must increase $\hat{\mu}$ by the same amount. Then

$$\mathcal{E}(\log y_{ijk}) = \hat{\mu}^* + \hat{\pi}_i + \hat{\tau}_j{}^* + \hat{\delta}_{ij} + \hat{\beta}(t_k - \overline{t})$$

where $\hat{\mu}^* = \hat{\mu} + \frac{1}{8} \sum \hat{\tau}_j$

$$= \hat{\mu} - .01286$$

or, in other words,

$$\hat{\mu} + \hat{\tau}_j = \hat{\mu}^* + \hat{\tau}_j{}^* \ .$$

The estimate of $\hat{\mu}^*$ is 1.95339.

The $\hat{\delta}_{ij}$'s, the correction terms, are computed thus:

$$\hat{\delta}_{ij} = \overline{C}_{ij} - (\hat{\pi}_i + \hat{\tau}_j + \hat{\mu})$$

or

$$\hat{\delta}_{ij} = \overline{C}_{ij} - (\hat{\pi}_i + \hat{\tau}_j^* + \hat{\mu}^*)$$

where $\overline{C}_{ij}$ is the mean of the observations in cell (i,j).
For example, $\overline{C}_{2,1} = 2.82662$. $\hat{\delta}_{ij}$ is calculated only for
those cells for which observations are available (i.e., 29
cells). The $\underline{\hat{\delta}}$ vector is as follows:

$$
\hat{\underline{\delta}} =
\begin{bmatrix}
-.18195 \\
-.07616 \\
.25814 \\
.08219 \\
-.08220 \\
-.06826 \\
-.09339 \\
-.18287 \\
.10204 \\
.24252 \\
.12398 \\
.16232 \\
.13825 \\
.14293 \\
-.45039 \\
-.11706 \\
-.02854 \\
.08588 \\
.18903 \\
-.30637 \\
-.13924 \\
.19927 \\
.00875 \\
-.09774 \\
.08901 \\
-.02716 \\
.02716 \\
-.07695 \\
.07696
\end{bmatrix}
\begin{matrix}
\text{(Cell)} \\
(2,1) \\
(3,1) \\
(5,1) \\
(4,2) \\
(6,2) \\
(1,3) \\
(2,3) \\
(3,3) \\
(4,3) \\
(5,3) \\
(1,4) \\
(2,4) \\
(3,4) \\
(4,4) \\
(5,4) \\
(6,4) \\
(1,5) \\
(2,5) \\
(3,5) \\
(4,5) \\
(5,5) \\
(6,5) \\
(3,6) \\
(4,6) \\
(5,6) \\
(1,7) \\
(2,7) \\
(3,8) \\
(4,8)
\end{matrix}
$$

Recalling the conditions imposed on the original model,

$$\sum_i n_{ij} \, \delta_{ij} = 0$$

and

$$\sum_j n_{ij} \delta_{ij} = 0$$

which are equivalent to

$$\sum_i \delta_{ij} = 0$$

and

$$\sum_j \delta_{ij} = 0$$

since $n_{ij} \equiv 6$, we have another check on calculations:

$$\sum_i \hat{\delta}_{i1} = .00003 \qquad \sum_j \hat{\delta}_{1j} = .00002$$

$$\sum_i \hat{\delta}_{i2} = -.00001 \qquad \sum_j \hat{\delta}_{2j} = .00002$$

$$\sum_i \hat{\delta}_{i3} = .00004 \qquad \sum_j \hat{\delta}_{3j} = .00005$$

$$\sum_i \hat{\delta}_{i4} = .00003 \qquad \sum_j \hat{\delta}_{4j} = .00001$$

$$\sum_i \hat{\delta}_{i5} = .00003 \qquad \sum_j \hat{\delta}_{5j} = .00004$$

$$\sum_i \hat{\delta}_{i6} = .00002 \qquad \sum_j \hat{\delta}_{6j} = .00001$$

$$\sum_i \hat{\delta}_{i7} = 0$$

$$\sum_i \hat{\delta}_{i8} = .00001$$

All of these sums are, within rounding, equal to zero.

The only parameter not yet estimated is β. The estimation of the coefficient of the covariate t_k makes use of two quantities found in setting up the ANOCVA table, since

$$\hat{\beta} = \frac{SPE_{yt}}{SSE_t} \ .$$

In this analysis

$$\hat{\beta} = .00415 \ .$$

3.4 Response Equation

As has been stated, the chemical model would usually be expected to be of the form

$$\hat{y}_{ijk} = Y_0 \, (p_i)^\rho \, e^{\frac{\check{Y}}{T}_j} \, c_{ij} \, e^{\beta t_k}$$

or

$$\ln \hat{y}_{ijk} = \ln Y_0 + \rho \ln p_i + \frac{\check{Y}}{T}_j + \ln c_{ij} + \beta t_k \ .$$

The statistical model will be recalled as

$$\ln \hat{y}_{ijk} = \hat{\mu} + \hat{\pi}_i + \hat{\tau}_j + \hat{\delta}_{ij} + \hat{\beta}(t_k - \overline{t}) \ .$$

Thus an indication of the correspondence of the results obtained with the theoretical model can be obtained by plotting $\hat{\pi}_i$ against $\ln p_i$ and $\hat{\tau}_j$ against $1/T_j$. These graphs appear in Figures 12 and 13. (For ease of graphing $\hat{\tau}_j$ was plotted against $1000/T_j$.) The pressure graph is
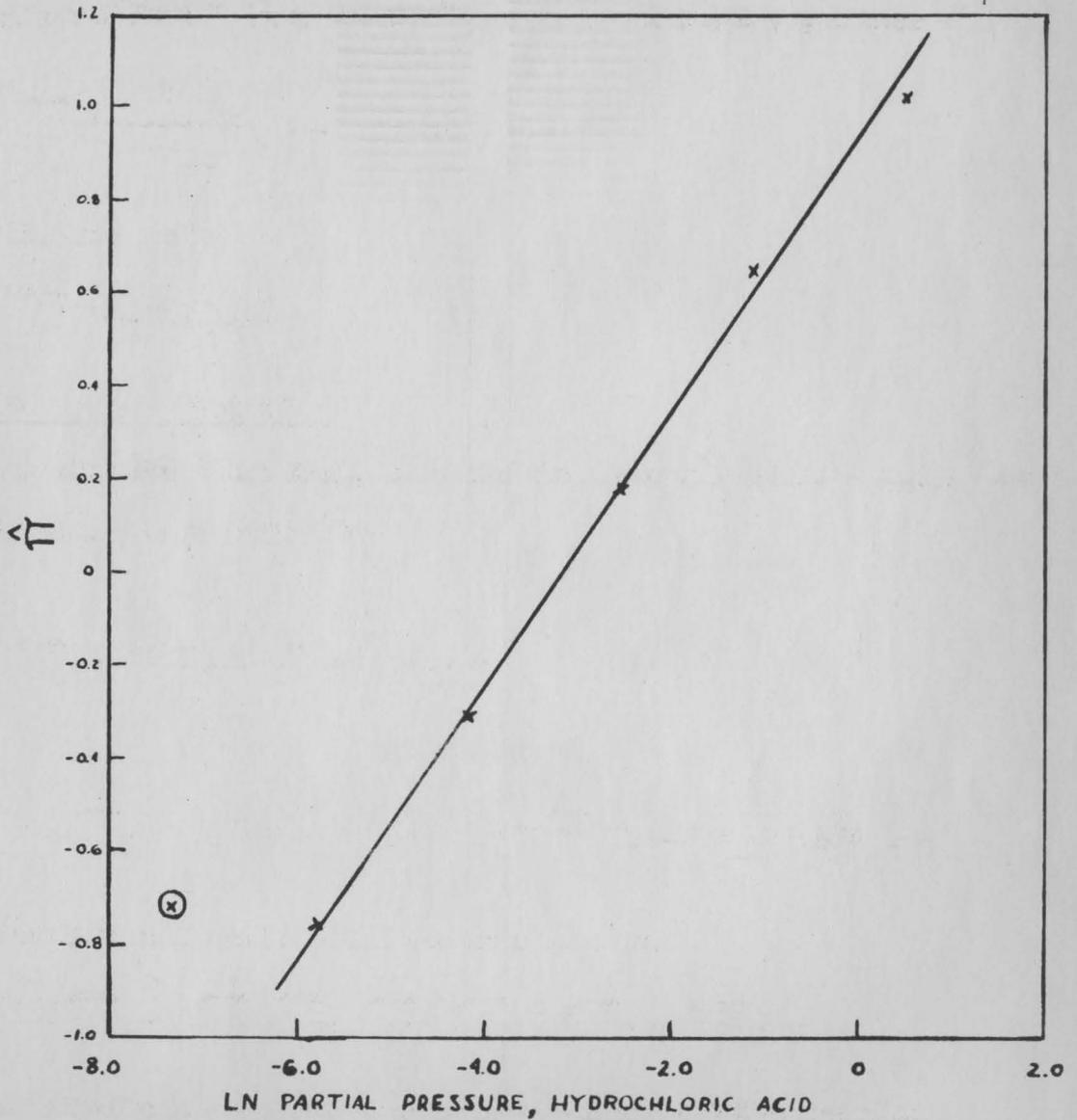
FIGURE 12. LN PRESSURE vs.
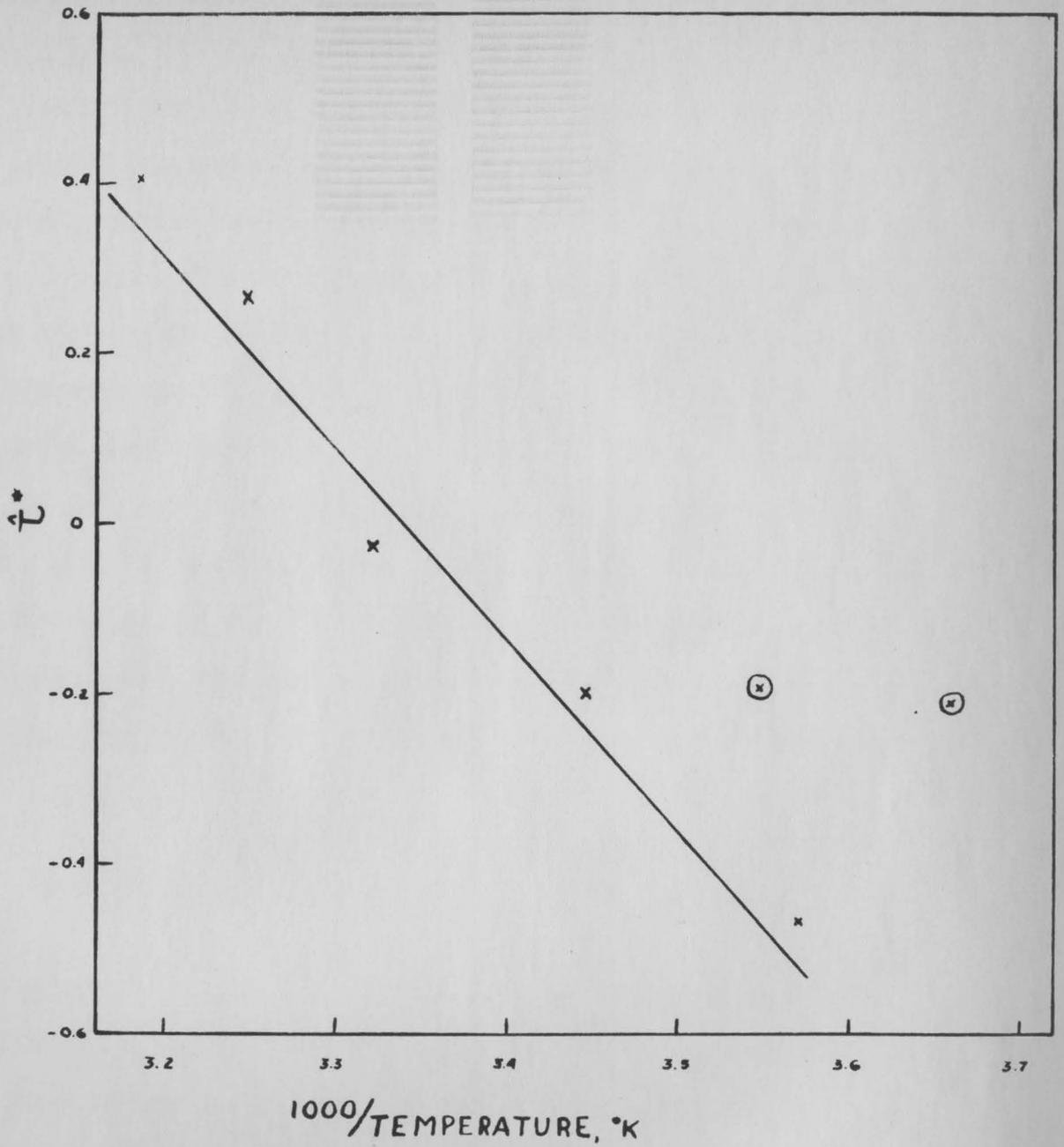ESTIMATES OF PRESSURE
EFFECTS $\hat{\pi}$

FIGURE 13. 1000/TEMPERATURE vs. ESTIMATES OF TEMPERATURE EFFECTS $\hat{\tau}^*$

approximately linear except for the lowest pressure level point ($\hat{\pi}_6$).

The linearity of the temperature graph is questionable. The points representing 17°, 28°, and 35° are the most precisely determined since more tests were performed at these levels. Therefore, a sight line was fitted through these three points. The line obtained is satisfactory also for temperatures 44°, 41°, and 7°. The 9° and 0° points on the graph and the corresponding test runs do not fit this pattern at all; they were dropped from the study at this point, and it was concluded that whatever response function may be suggested will be restricted to the temperature range 17° to 44° and pressure range 0.003 to 1.9 mm. mercury. From the graphs the following equations can be found:

$$\hat{\pi}_i = .944 + .299 \ln p_i$$

$$\hat{\tau}_j^* = 7.902 - 2.362 \frac{1000}{T_j}$$

When the interaction terms, the correction terms, are recorded in tabular form (see Table IX), it is noticeable at once that there is no regular trend with pressure or temperature. Rather than being broken down systematically, the significant interaction effect is concentrated in one test run, that in which $\log p = -2.52$, $T = 301.16°K$ or 28 °C (number 16). The weight gain in this run is far below

TABLE IX

Correction Terms

	Temperature				
	1	2	3	4	5
1			-.06826	.12398	-.02854
2	-.18195		-.09339	.16232	.08588
Pressure 3	-.07616		-.18287	.13825	.18903
4		.08219	.10204	.14293	-.30637
5	.25814		.24252	-.45039	-.13924

Temperature levels 6-8 and Pressure level 6 omitted.

expectation indicated by both the temperature and the pressure trends; there is considerable doubt about the accuracy of the experimental conditions of this set. The second largest interaction estimate occurs in the set under log p = -1.825, T = 290.16 °K or 17 °C (number 37). The departure in this run from expectation is not quite as conspicuous, although it is a marked interruption of the temperature trend. In conclusion, it must be stated that the interaction terms show no systematic trends with increasing temperature or increasing pressure and thus are not amenable to chemical interpretation. The sporadic behavior of these terms indicates some experimental inadequacy. Consequently, in spite of the overall significance of "interaction", there is no justifiable reason for suggesting correction terms in the prediction of corrosion weight gain in terms of pressure and temperature, on the basis of the present data.

Hence, for the prediction of weight gain, the equation

$$\log \hat{y}_{ijk} = \hat{\mu}* + \hat{\pi}_i + \hat{\tau}_j* + \hat{\beta}(t_k - \bar{t})$$

is used. Upon substitution and recalling that

$$1 + \log z_{ijk} = \log y_{ijk}$$

(see Tables IV and V), the equation becomes

$$1 + \log \hat{z}_{ijk} = 1.95339 + .944 + .299 \ln p_i + 7.902$$

$$- 2.362 \frac{1000}{T_j} + .00415 (t_k - 105) .$$

After simplification, the prediction equation is

$$(8) \quad \log \hat{z}_{ijk} = 9.364 + .688 \log p_i - 2.362 \frac{1000}{T_j} + .00415 \, t_k$$

where $\hat{z}_{ijk}$ = predicted weight gain, mg/cm^2

p_i = partial pressure HCl, mm Hg

T_j = absolute temperature, °K

t_k = time, min.

This equation is valid for hydrochloric acid partial pressures between 0.003 and 1.900 mm Hg, temperatures from 17 °C to 44 °C, and for a time of exposure between 80 and 130 minutes. At t_k = 100, predictions, observed values, and the corresponding errors for the test runs within this range are given in Table X. The maximum discrepancies between predicted and observed values, i.e., $|e| > 0.220$, occur at the lowest pressure and temperature levels.

TABLE X

Prediction of Corrosion Using Response Equation ($t_k = 100$)

Test number	log z (observed)	log $\hat{z}$	error
2	0.857	0.636	.221
4	1.711	1.663	.048
6	0.699	0.448	.251
13	1.100	0.850	.250
15	2.037	2.120	-.083
16	-0.222	0.293	-.515
17	1.064	1.000	.064
21	1.468	1.323	.145
23	0.716	0.754	-.038
25	2.138	2.235	-.097
26	1.756	1.796	-.040
28	1.450	1.584	-.134
29	1.808	2.012	-.204
30	0.954	0.909	.045
31	-0.097	-0.112	.015
32	1.718	1.800	-.082
34	1.220	1.210	.010
37	0.079	0.371	-.292
40	1.199	1.352	-.153

Equation: $\log \hat{z}_{ijk} = 9.364 + .688 \log p_i - 2.362 \frac{1000}{T_j}$

$$+ .00415 \, t_k$$

$t_k = 100$ minutes

log z read from TABLE VI

log p_i read from TABLE II

CHAPTER IV. Summary

In this thesis, corrosion data have been subjected to a
statistical analysis for the purpose of obtaining meaningful
estimates of the specific rate of reaction and the energy of
activation and obtaining a response equation for prediction
of weight gain.

A two-stage analysis was used in the estimation of
specific rate and activation energy. First, an estimate of
the reaction rate for each of the forty test runs was
obtained from linear regression analysis of weight gain on
time (Section 2.1). Using equation (1) a weighted linear
regression was then performed with reciprocals of estimated
variances of rates as weights. Hence a weighted regression
analysis was performed on rate estimates so that estimates
of the order of reaction could be obtained.

It was shown that the mechanisms of the two possible
reactions, i.e., formation of aluminum oxide or $AlCl_3 x 6H_2O$,
are different (Section 2.2). At the lower HCl partial
pressures, in which aluminum oxide is the product, the energy
of activation was estimated in two ways: Section 2.5.1
gives the estimated specific rates of reaction and energy of
activation when the stoichiometric first order is assumed
and uses the method of weighted linear regression; Section
2.5.2 gives as the method of estimation a weighted covariance

analysis when the order of reaction is assumed to be the empirically determined quantity 0.715. The data in the $AlCl_3 \cdot 6H_2O$ portion of the study were inconclusive (Section 2.6).

In order to investigate the relative effects of temperature and pressure on corrosion, an analysis of covariance was performed. The model [equation (3)] was that of a general two-way classification with time as a covariate. As was expected, both temperature and pressure contributed significantly to the amount of corrosion product formed; their relative effects were estimated (Section 3.3). Finally a response equation [equation (8)] was found for purposes of predicting the weight of the corrosion product, i.e., aluminum oxide. This equation is valid for HCl partial pressure of 0.003 to 1.900 mm Hg, temperatures 17 °C to 44 °C, and for a time of exposure between 80 and 130 minutes during which the rate was observed to be constant.

CHAPTER V. Bibliography

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ABSTRACT

In this thesis, corrosion data were subjected to statis-
tical analysis for the purpose of obtaining meaningful
estimates of the specific rate of reaction and the energy of
activation and obtaining a response equation for prediction
of weight gain.

A two-stage analysis was used in the estimation of
specific rate and activation energy. First, an estimate of
the reaction rate for each test run was obtained from linear
regression analyses of weight gain on time. A weighted
linear regression was then performed with reciprocals of
estimated variances of rates as weights; the estimated order
of reaction was obtained.

It was shown that the mechanisms of the two possible
reactions, i.e., formation of aluminum oxide or $AlCl_3 x 6H_2O$,
are different. At the lower HCl partial pressures (Al_2O_3
the product), the specific rates and the activation energy
were estimated in two ways: (1) the method of weighted linear
regression when stoichiometric first order is assumed;
(2) the method of weighted covariance analysis when empirical
order is assumed. The data in the $AlCl_3 x 6H_2O$ portion were
inconclusive.

The prediction equation was obtained by an analysis of
covariance; the model was that of a two-way classification

with time as a covariate. Main effects (temperature and pressure) were estimated. Finally, a response equation, for prediction of the weight of corrosion product (Al_2O_3), was found. This equation is valid for HCl partial pressures 0.003 to 1.90 mm Hg, temperatures 17 °C to 44 °C, time of exposure 80 to 130 minutes.