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A microcoulometric study of adsorption on the hydrogen electrode

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A MICROCOULOMETRIC STUDY OF
ADSORPTION ON THE HYDROGEN
ELECTRODE

BY

RAY DOUGLAS SOTHERN

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
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MASTER OF SCIENCE

Approved by
Thomas C. Frankelton

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INTRODUCTION

Adsorption is the accumulation of a chemical substance at the interface separating two phases¹. These phases may consist of two liquids, a liquid and a gas, a liquid and a solid, two solids, or a solid and a gas. The substance adsorbed at the interface is known as the adsorbate, while the phase upon whose surface the adsorbate concentrates is called the adsorbant. Special techniques have been developed for each of these systems. The system involved in the present research was of the type liquid- solid.

This work was begun with the intention of studying the adsorption of organic compounds upon the hydrogen electrode. The fact that certain substances, even when present in extremely low concentration, will poison the electrode with which they are in contact shows clearly that these substances must be strongly adsorbed on the electrode surface. The problem of determining the amount adsorbed at various concentrations, temperatures, and pressures, however, required a method capable of detecting quantities of adsorbate in the order of 10^{-11} moles.

Since the usual titrimetric and gravimetric methods could not be expected to be applicable in this situation, the problem was resolved by developing a microcoulometric procedure. This method, described in more detail in the chapter dealing with experimental techniques², depends upon the competitive adsorption of hydrogen and the organic adsorbate upon the electrode.

This method was then applied to the study of the adsorption of various nitriles upon the hydrogen electrode. Included in the objectives of this work were:

- (1). The determination of adsorption isotherms for the nitriles studied.
- (2). The correlation of the potential of the reversible hydrogen electrode with the amount of hydrogen adsorbed on it.
- (3). The determination of the heat of adsorption from the effect of varying the temperature.
- (4). A study of the effect of pressure upon the amount of adsorbed hydrogen.
- (5)..A correlation of the adsorption of the various nitriles with steric and structural factors.

1. R. J. Hartman, Colloid Chemistry, 2d ed., pp.17, 18. Houghton Mifflin Co., Inc., New York (1940).
2. p.9

HISTORY

The study of adsorption can be traced back at least to 1773³, when C. W. Scheele observed that wood charcoal possessed the ability to adsorb gases. In 1785 T. Lowitz noticed that coloring matter could be removed from solution by adsorption on charcoal. Since the methods used in the measurement of adsorption of gases are well known, and since they have no direct bearing on the work discussed in this paper, there would be nothing gained in a discussion of them.

The overwhelming majority of work done on the adsorption of substances from solution has depended upon the measurement of concentration changes of the adsorbate in solution caused by the addition of an adsorbant to the solution. In order that the concentration change be measurable, adsorbates with large active surfaces have been used. Surface area is maximized in porous or finely divided solids such as activated charcoal⁴ and silica gel⁵.

3. S. Glasstone, Textbook of Physical Chemistry, p.1172.
D. Van Nostrand Co., Inc., New York (1940).

Consequently, these and similar materials have received most of the attention of those investigating adsorption from solution.

However, there has been some work done more recently, more as a sideline to the problem of the kinetics of electrode reactions than for its own intrinsic value, relating to the adsorption of substances from solution on electrodes. Bowden⁶, in measuring the amount of electricity passed in changing the electrode potential from that of hydrogen to that of oxygen on a platinum electrode, found that 9×10^{-4} coulombs passed. From his calculations 8.1×10^{-4} coulombs should have been required to replace a monolayer of hydrogen with one of oxygen. He concluded that the layer of hydrogen was discontinuous and consisted of distorted oriented dipoles on the surface of the platinum electrode. Butler and Armstrong⁷ later achieved essentially the same results.

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4. F. C. Bartell and E. J. Miller, J. Am. Chem. Soc. 44, 1866.
 5. N. H. Holmes and J. A. Anderson, Ind. Eng. Chem. 17, 28, (1925).
 6. F. P. Bowden, Proc. Roy. Soc. (London), A125, 446, (1929).
 7. J. A. V. Butler, and G. Armstrong, *ibid.*, A127, 604, (1932).

Some of the most pertinent research bearing on this present project was that carried on by Frumkin and his associates^{8,9,10,11}. in their rather thorough investigations of the kinetics of electrode reactions. Using slow-charging curves for the most part, this group investigated the changes occurring at smooth or platinized platinum electrodes while changing between the reversible hydrogen and the reversible oxygen potentials. In running the charging curves from the reversible hydrogen potential to the reversible oxygen potential in acid media, three distinct regions were observed corresponding to the following three processes: (1) oxidation of approximately a monolayer of hydrogen, (2) the building up of a double layer, and (3) formation of a layer of oxygen. In the first region the potential was observed to vary linearly with the number of coulombs passed, indicating that the differential heat of adsorption decreases as the fraction of surface occupied by adsorbed hydrogen increases.

-
7. Butler and Armstrong, *Loc. Cit.*, p. 604.
 8. A. Glyzin, and A. Frumkin, *Acta. Physicochim. U.R.S.S.*, A, 911-923, (1936).
 9. A. Frumkin, and A. Glyzin, *ibid.*, 5, 819.
 10. P. Dolan, B. Erahler, and A. Frumkin, *ibid.*, 13, 779, (1940).
 11. B. Erahler, *Trans. Far. Soc.* 43, A. (1947).

Bruns and Maidanowskaja¹² in their measurement of the differential heat of adsorption of hydrogen gas on platinum black have shown this to be the case. Further confirmatory work¹³ has shown the heat of adsorption of hydrogen on platinum in 0.01 normal sulfuric acid to vary approximately linearly with the degree of saturation, ranging from 23,600 to 10,100 Kcal./mole. This could be interpreted as indicating that the surface is heterogeneous.

Glygin and Ershler¹⁴ investigated the effects upon the amount of hydrogen adsorbed on smooth and platinized platinum electrodes when mercury and arsenic were used as poisons. The number of atoms of hydrogen displaced by one molecule of arsenic, potassium cyanide, and mercury, each in dilute solution, was 4, 10, and 40 respectively. The effects were found to be due to a type of interaction rather than to a mere blocking of the electrode surface.

Aten¹⁵ has noticed the effect of poisoning by ammonia, hydrogen sulfide, cyanides, and compounds of arsenic and mercury upon the potential of the reversible hydrogen electrode. It was noticed that when arsenious oxide was the poison, poisoning became complete only after two or three weeks. Aten also noticed that the electrode could be depolarized by anodic polarization.

Since this research was begun, several papers dealing with the adsorption on metal electrodes have appeared, two of which are especially noteworthy. The first is that of Hillson¹⁶, in which the strength of adsorption of hexyl alcohol and several other compounds on various metal electrodes was determined by studying their effects upon the overvoltages and capacities of the electrodes. The raising of the overvoltage was considered to have been due to the formation of a continuous adsorbed film, which inhibited the discharge of hydrogen ions on the electrode.

The second is that of Oikawa and Mukaibo¹⁷, in which the amount of acetic acid adsorbed on a platinum electrode was measured as a function of the decrease of adsorbed hydrogen. The amount of hydrogen adsorbed was determined from an oscillographic potential - time curve. The results obtained were in agreement with the Freundlich adsorption isotherm.

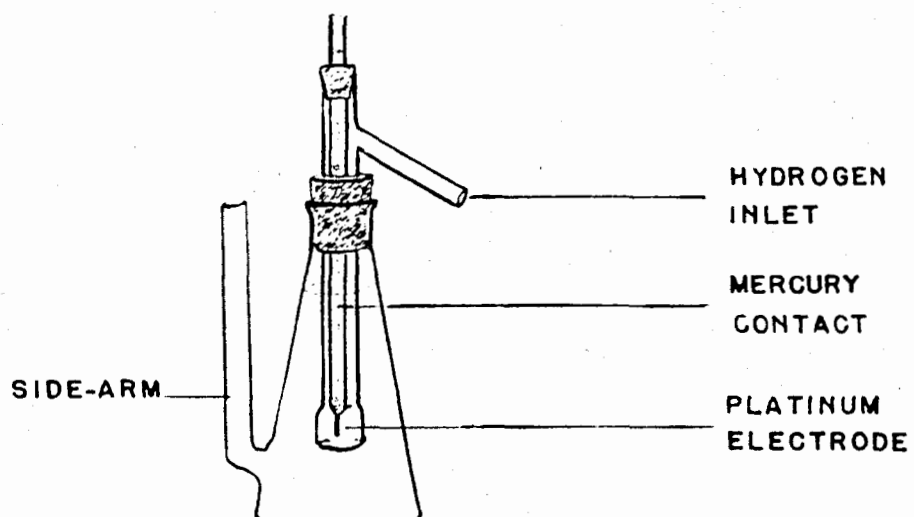
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12. Acta Physicochim. U.R.S.S., 9, 927, (1938).
 13. A. Frumkin and A. Slygin, 2, 173- 179, (1934) Compt. rend.
 14. A. Slygin, and B. Ershler, Acta Physicochim. U.R.S.S. 11, 45- 58, (1939).
 15. A.H.W. Aten, and Miss W. Zieren, Trans. Am. Electrochem. Soc. 59, C. A. 24, 1256.
Aten, P. Bruin, and W. DeLange, Rec. Trav. Chim. 46, 417- 429, (1927). C.A. 21, 3537.
 16. P.J. Hillson, J. Chim. Phys. 49, 688-96, (1952).
 17. M. Oikawa, and T. Mukaibo, J. Electrochem. Soc. Japan 20, 568-71 (1952)

APPARATUS AND EXPERIMENTAL TECHNIQUES

The adsorbants in this series of experiments consisted of platinized platinum wire microelectrodes. The number 20 wire was cut into lengths averaging 2 cm., and sealed into 15 cm. lengths of pyrex tubing. These electrodes were then platinized for about three minutes in a solution of chloroplatinic acid, using an applied potential of 3 volts. The electrodes were then washed briefly in distilled water, concentrated sulfuric acid, and finally allowed to age for several hours in 2 N sulfuric acid. Just prior to use these electrodes were anodically polarized at oxygen evolution for twenty to thirty minutes.

The electrode compartments first used were constructed from 125 ml. erlenmeyer flasks to each of which had been sealed a side-arm. The electrode itself was inserted in a sleeve of pyrex, through which hydrogen could be passed down onto the electrode. This assembly was immersed in the electrode solution through a stopper in the neck of the flask. Figure 12 is a schematic diagram of the apparatus. The side-arm accommodated a salt bridge, through which was established contact to the calomel cell.

FIGURE 12.



The temperature of the cell was regulated by placing it in a thermostated constant temperature bath. The cell was connected to a Fisher Type S potentiometer, and to a Sargent Model XXI polarograph.

The platinum electrode compartment contained 2 normal sulfuric acid as the electrolyte. The salt bridge contained saturated ammonium sulfate in agar.

The procedure was to pass hydrogen over the electrode until a steady potential was attained, then to allow sufficient time for equilibrium to be approached between hydrogen dissolved in solution and that adsorbed on the electrode. A polarogram was then run in order to determine the potential range in which complete oxidation of the hydrogen could be achieved without introducing undesirable electrode reactions. Further runs were made at the potential so determined, plotting current against time by means of the Brown X-Y pen recorder of the polarograph. The number of coulombs passed was determined from the area under the curves.

After making several determinations of the amount of hydrogen adsorbed when no poison was present, a measured quantity of poison was then added and the amount of hydrogen adsorbed again determined. The decrease in area under the curves was taken as a measure of the amount of poison adsorbed. This procedure was repeated for each poison studied at several different concentrations of poison.

Preliminary work was carried out to determine a procedure which would yield reproducible results. Freshly platinumized electrodes were found to decrease appreciably in activity in consecutive runs, but somewhat irregularly. Using electrodes seasoned by soaking in 2 normal sulfuric acid, three methods of adsorbing hydrogen were investigated. First was the bubbling of hydrogen into the solution and onto the electrode for various lengths of time. Second was the prepolarization at hydrogen evolution, and third was prepolarization at a less negative potential than hydrogen evolution. Very good reproducibility was attained by the third method when no poison was present, but in the presence of a poison both methods two and three caused the poisons to be displaced from the electrode and only slowly reabsorbed. However, reproducibility of results by method one was reasonably satisfactory on still electrodes and quite satisfactory on rotating electrodes. Most of the work has been with still electrodes for the sake of convenience.

The current-time curves were run first at a constant applied potential, but irregularities in the tails of the curves limited the precision in measuring the areas under these curves. This shortcoming was avoided by a second method using an increasing electromotive force over a short

span, 0.6 v. to 0.7 v. Since the latter method resulted in greater duplicability, the former method was abandoned in favor of it.

The areas under the curves were measured by a planimeter. The quantities of electricity measured have been between 6 and 2000 microcoulombs. This represents from 3×10^{-11} to 1×10^{-8} moles of hydrogen adsorbed. Smaller quantities than this could be measured without modification of the apparatus.

The apparatus described above was used without modification to determine the effect of temperature on the amount of material adsorbed.

However, to determine the effect of pressure a more elaborate cell was required. The electrode compartments consisted of two 200 ml. round bottom flasks into which side-arms and stopcocks were sealed as shown. The two electrode compartments were connected by means of a salt bridge compartment. The apparatus is shown schematically in Figure 13. The diagram also shows the connections to the manometer, ballast tank, aspirator, and hydrogen.

Plate I is a photograph of the apparatus used. The curves visible on the polarograph are hydrogen oxidation curves of the type frequently encountered. The relative prominence of the two peaks varies considerably, the second peak often disappearing as the electrode becomes more poisoned.

The nitriles used

ELECTRODES

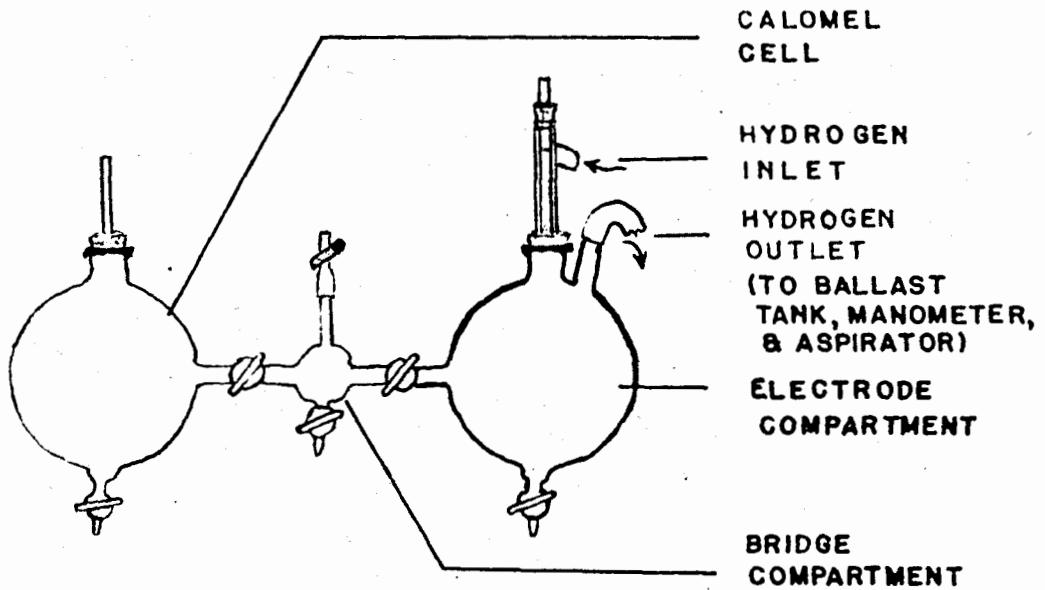


FIGURE 13

soned.

The nitriles used in this research were manufactured by the Eastman Kodak Company, and were the best grade commercially available.



PLATE I. APPARATUS USED

PRINCIPLES AND PROCESSES

Before presenting and discussing the data, a short discussion of the processes occurring on the surface of the electrode and the region immediately around it would, perhaps, be in order. The hydrogen electrode is the very heart of this investigation. Upon its surface are the organic adsorbate, hydrogen, and solvent molecules, all held by the forces of adsorption. An explanation promulgated by Haber¹⁸ attributed these forces to "residual valencies" possessed by atoms on the surface of a mass. These residual valencies were thought to exist since an atom at the surface interacts cohesively only with atoms in the bulk of the medium, thus leaving unsatisfied half of its cohesive capacity. It follows from this that the amount of residual valence at any point is a function of the curvature of the surface at that point. Such a situation obviously would not give rise to a regular stoichiometric ratio of adsorbate to adsorbant.

18. Haber, Z. Electrochem., 20, 521 (1914).

A second factor influencing adsorption is the electrostatic attraction of adsorbate and adsorbant molecules.¹⁹ The polarizabilities both of adsorbate and adsorbant are involved together with the permanent dipole moments. In addition to these fields, fields produced by rotation of electrons within the molecules contribute significantly to the forces of adsorption.

However, it is not necessary to consider the actual nature of the forces acting to develop a theory which can be quantitatively tested. The thermodynamic theory merely postulates an "adsorption potential" holding the adsorbate in such a way that the equation of state and the laws of thermodynamics are applicable.

Similarly the molecular kinetic theory of adsorption as proposed by Langmuir²⁰ merely postulates that after an adsorbate molecule strikes the surface of the adsorbant, it will adhere for an appreciable length of time before leaving the surface. A simple kinetics treatment, when applied to this problem gives rise to Langmuir's adsorption isotherm:

$$\frac{x}{M} = \frac{k_1 k_2 p}{1 + k_1 p}$$

Since the derivation of this isotherm provides a very lucid

19. Hartman, R., loc. cit., p 83.

20. Glasstone, S., loc. cit., p 1176.

picture of the kinetics of adsorption, its consideration at this time is in order.

Consider first the electrode surface, at which adsorption is occurring. Let Q represent the fraction of available surface covered by adsorbate at any time. Then $1 - Q$ will be the fraction of available surface remaining bare. The rate of adsorption will be proportional to the amount of bare surface ($1-Q$) and to the concentration of adsorbate in solution, c . Furthermore, the rate of desorption will be proportional to the amount of surface covered. The process of adsorption will proceed until, at equilibrium, the rates of adsorption and desorption will become equal. Thus

$$k_1(1-Q)c = Q, \text{ or } Q = \frac{k_1 c}{1 + k_1 c} .$$

But since the fraction of surface covered, Q , is proportional to x/a (the amount of adsorbate per unit area),

$$k_2 Q = \frac{x}{a} .$$

Therefore

$$\frac{x}{a} = \frac{k_1 k_2 c}{1 + k_1 c}$$

This derivation is strictly valid only for adsorption of a single adsorbate on a homogeneous surface. The system studied in this work involved the competitive adsorption of hydrogen, solvent, and organic solute. In addition to this fact, it must be remembered that the platinized platinum surface is not entirely homogeneous. Some departure of the

data from prediction based upon this simple theory might therefore be expected.

An additional consideration which should be discussed briefly at this time is the relationship of electrode potential to the processes occurring at the electrode-solution interface.

Whenever a substance capable of existing in solution in an ionized form shares an interface with a polar liquid, there is a tendency for that substance to form solvated ions, which then pass out into the bulk of the solution. When this substance is an isolated metal or hydrogen electrode, neutral atoms on the electrode surface give rise to positive solvated ions in solution.²¹ This means that one or more electrons were left behind at the electrode. If there is no easily reducible substance in solution, the electrons will accumulate on the electrode, where their charge will induce a double layer in the solution adjacent to the electrode. The charge density of this double layer contributes largely to the electrode potential. However, the presence of adsorbed hydrogen atoms on the surface of the platinum

21. Glasstone, S., loc. cit., p 919.

electrode in a deformed state also contributes to the electrode potential, since the distortion introduces a separation of charge, or dipole character, to the adsorbed hydrogen.²² Frumkin²³ has shown that in the case of platinum, both of the above factors are important in establishing the electrode potential.

The actual potentials measured on the potentiometer are the sum of three separate potentials. Two of these are the electrode potentials, while the third is the liquid junction potential. Upon addition of organic poisons to the hydrogen electrode compartment, there will be an equilibrium established between poison adsorbed on the platinum surface and dissolved in the solution. This adsorption of the poison on the electrode surface will cause a diminution in the amount of adsorbed hydrogen, thus altering the potential.

22. Bowden and Rideal, Proc. Roy. Soc. 120A, 59 (1928).
23. Sow. Phys. 4, 260, (1930).

DISCUSSION OF DATA

The tables and graphs included in this section summarize data taken over a two year period. Most of the tables and figures have been placed in with the discussion of the data which they represent.

The variation of the amount of hydrogen adsorbed with the quantity of acetonitrile added is shown in Figure 1. A_0 represents the amount of hydrogen adsorbed on the surface of the electrode in the absence of a poison. A is the amount of hydrogen adsorbed after the electrode has become poisoned. The decrease in the amount of hydrogen adsorbed, $A_0 - A$, results from the adsorption of acetonitrile on sites previously occupied by the hydrogen. If equal increments of nitrile are successively added to the solution, each increment has a slighter poisoning effect than the one before it. This is shown by the curvature of the graph in Figure 1, which resembles the simple Freundlich isotherm.

A further test of the data to show that it actually adhered to the Freundlich equation was to determine the variation of the log of $A_0 - A$ with concentration.

Because the active area of the electrode may change from one run to another, the factor A_0 is introduced into the denominator to reduce the separate runs to a comparable base. $(A_0 - A)/A_0$ is then analogous to Freundlich's x/m .

The logarithmic form of the Freundlich equation may be written $\log x/m = \log k + (1/n) \log c$. From this it is obvious that a plot of $\log x/m$ against $\log c$ should be a straight line. The graphs of Figure 2 show this to be the case. Since the Freundlich equation is an empirical one, no simple physical meaning can be attached to the slopes of these graphs, represented by the empirical factor $1/n$. It will be noticed that although each of the sets of data follow the Freundlich equation, runs taken in different solutions do not duplicate each other. Curves HF, JD, and JS are not duplicates, as one might expect them to be, but show a decrease in slope with successive runs. This may be attributed to a slow aging process occurring on the electrode.

The data upon which the graphs were based is tabulated in Tables I and II. The same data is presented in an altered form in Table III for the purpose of determining whether it also adheres to the Langmuir adsorption isotherm. This equation may be written in the form:

$$\frac{q}{\pi/m} = \frac{1}{k_1 k_2} \frac{q}{k_2}.$$

The linearity of Figure 3 shows that this equation is satisfied. The displacement of curve JG from JA shows that the active area was greater in run JG. The similarity of slope shows that the nature of the surface has not changed. Curve HF has a different slope, indicating that the aging process changed the nature of the surface between the time HF and JA were run.

Adsorption isotherms were also determined for propionitrile, butyronitrile, n-capronitrile, iso-capronitrile, and phenylacetoneitrile.

Throughout the work it was found that the treatment of the electrode was a vital factor in the reproducibility of the results. Much of the scatter in the data can probably be traced back to slight variations in electrode treatment. As an illustration of this Figure 4 and Table IV show two adsorption isotherms for propionitrile. Experimental conditions were the same for curves A and B except that the electrode was anodically polarized for short periods of time before each run on curve B. This polarization markedly reduced the poisoning effect on the electrode. It is very likely that this sensitivity of the electrode to oxidizing currents is responsible for such

TABLE I
 ADSORPTION ISOTHERMS OF ACETONITRILE
 ON PLATINIZED PLATINUM

RUN #	CONC Mg/ 900 ml	AREA	AREA 100	A/A ₀	log ¹⁰ $\frac{A}{A_0}$	log CONC
JB	0	151	-	-	-	-
JC	0	172	-	-	-	-
JD	9.8	111	.58	.34	.53	1.53
JE	"	111	.58	.34	.53	"
JF	"	86	.83	.49	.69	"
JG	"	99	.70	.41	.61	"
JH	20.8	75	194	.56	.75	1.84
JI	"	66	103	.61	.79	"
JI'	"	62	107	.67	.83	"
JJ	34.8	39	130	.78	.89	2.06
JK	"	37	132	.96	.89	"
JL	60.8	6	163	.87	.98	2.30
JM	"	22	147	.89	.94	"
JN	"	18	151	.99	.95	"
JQ	"	1	168	.99	1.00	"
JS	0	218 av.		-		
JT	0	"				
JU	0	"				
JV	0	"				
JW	0	"				
JX	0	"				
JY	0	"				
KA	0	"				
KB	0	"				
KC	39.0	50	1168	.77		
KD	"	57	1.61	.74		
KE	"	45	1.73	.79		
KF	"	32	1.86	.84		
KK	"	57	1.61	.74		
KL	"	63	1.55	.71		
KM	"	53	1.65	.76		
KN	"	129	.89	.41		
KO	"	106	1.12	.51		
KP	"	24	1.84	.84		
KQ	69.4	75	1.43	.66		
KR	"	65	1.53	.70		
KS	"	30	1.88	.86		
KT	"	41	.77	.81		
KU	"	53	1.65	.76		
KX	95.2	44	1.74	.80		
KZ	"	12	1.06	.95		

TABLE II

ADSORPTION ISOTHERMS OF ACETONITRILE
ON PLATINIZED PLATINUM *

RUN #	CONCENTRATION SE/900 ml.	AREA	$\frac{A}{A_0}$
HP	-	2.35av	-
HQ	0	-	-
HR	0	-	-
HS	0	-	-
HT	0	-	-
HU	22.8	1.21	-
HV	"	1.61	.265
HW	"	1.65	.246
HX	"	1.35	-
HY	61.8	0.09	.822
HZ	"	0.03	.941
IA	"	0.03	.972
IB	"	0.14	.990
IC	"	0.55	.749
ID	"	0.44	.799
IE	"	0.15	.932
IF	"	0.11	.949
IG	"	0.07	.968
IH	"	0.03	.964
II	"	0.26	.881
IJ	"	0.27	.876
KA	0	3.19av	-
KB	0	-	-
KC	97.4	1.32	.59
KD	97.4	1.23	.60
KE	150.5	1.13	.65
KF	150.5	0.46	.86
KG	150.5	0.72	.77

* HF - HZ RUN @ 27°C.
LA - LG RUN @ 14.6°C.

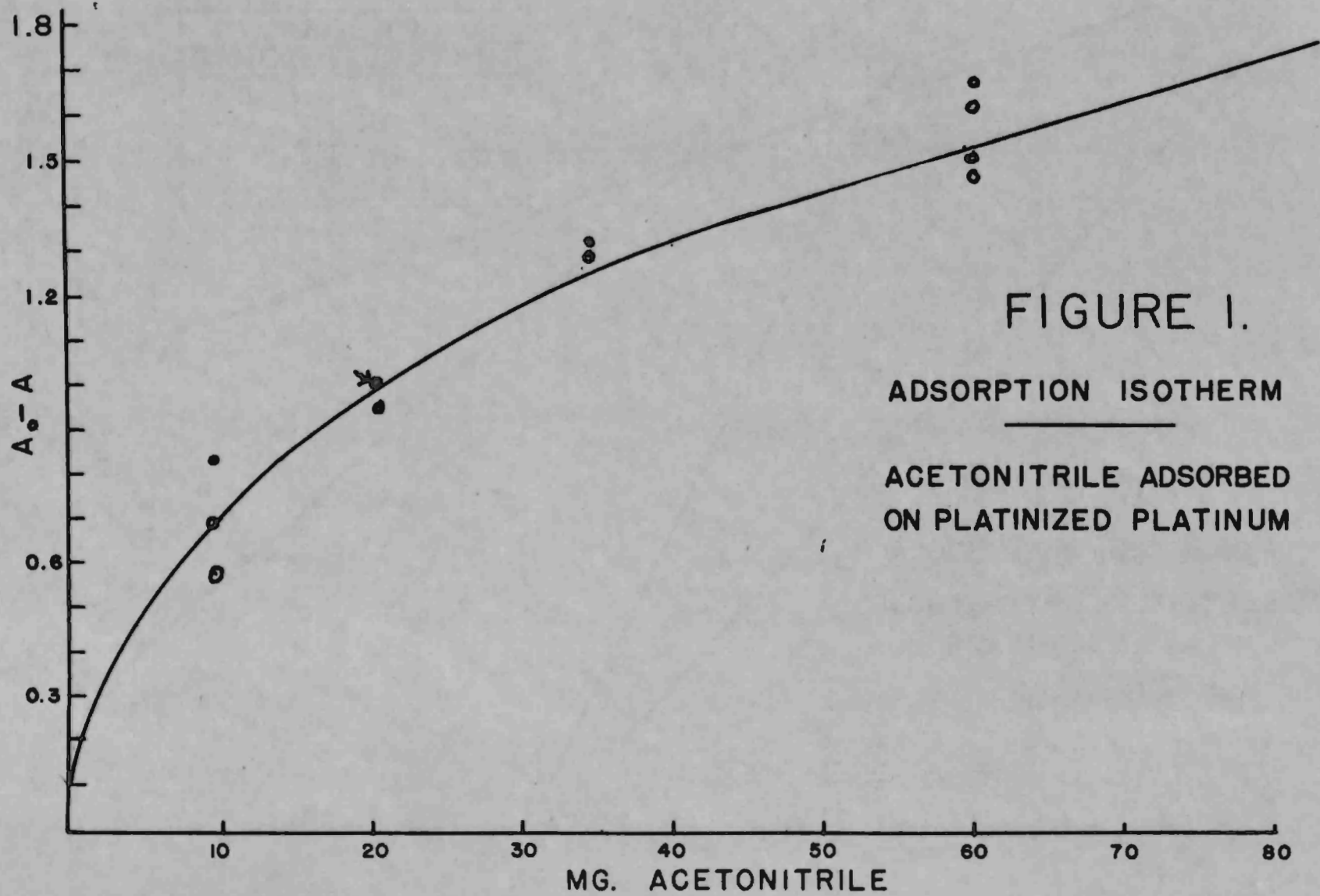


FIGURE 1.

ADSORPTION ISOTHERM

ACETONITRILE ADSORBED
ON PLATINIZED PLATINUM

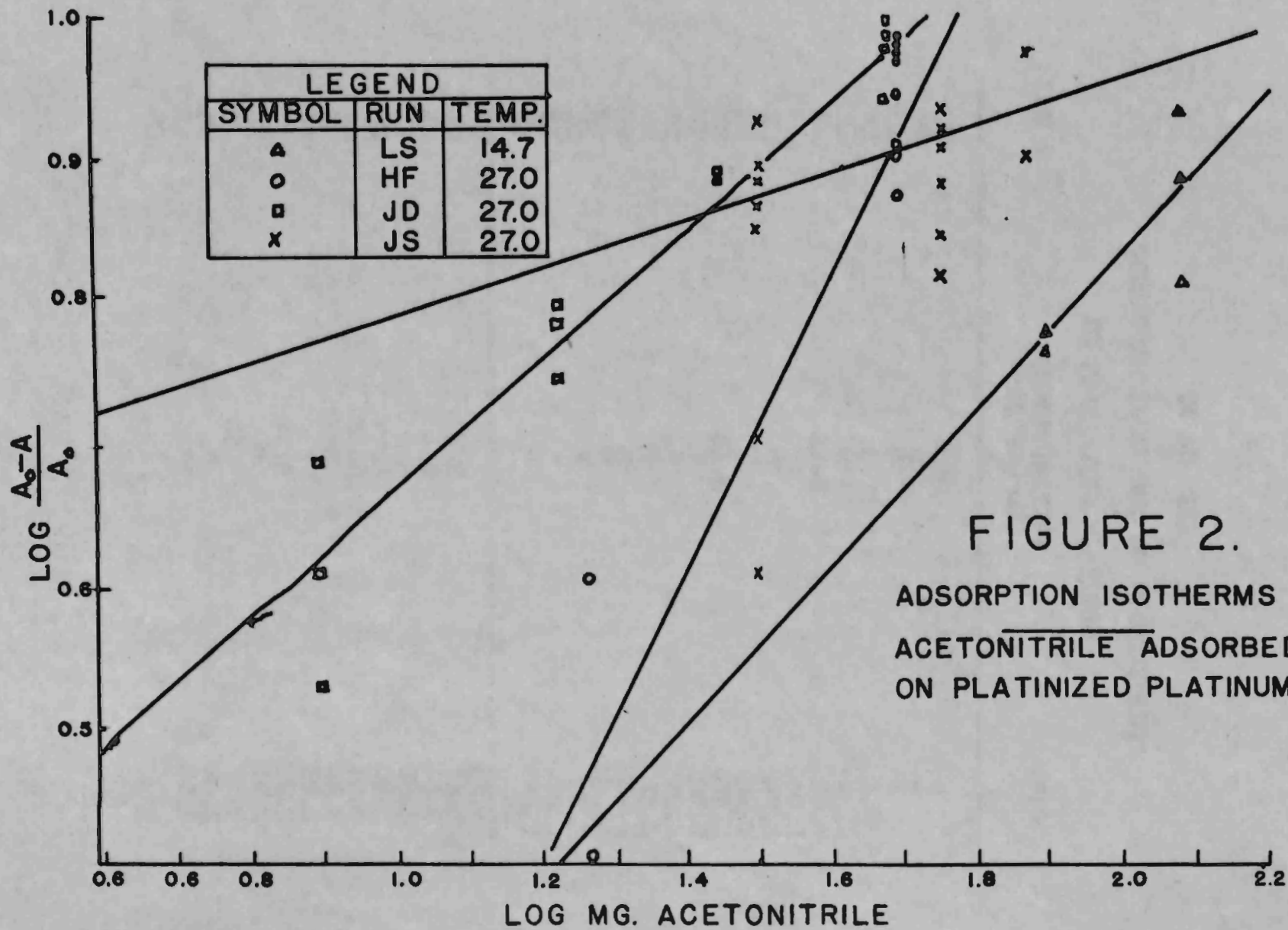


FIGURE 2.
 ADSORPTION ISOTHERMS
 ACETONITRILE ADSORBED
 ON PLATINIZED PLATINUM

TABLE III
ADSORPTION ISOTHERMS OF ACETONITRILE
ON PLATINIZED PLATINUM

RUN #	CONCENTRATION Mg/900 ml.	C/A
HF	0	-
HG	0	-
HH	0	-
HI	0	-
HJ	0	-
HK	22.8	20
HL	"	30.8
HM	"	32.6
HN	"	21.7
HO	61.8	31.6
HP	"	27.9
HQ	"	28.1
HR	"	29.3
HS	"	34.4
HT	"	32.4
HU	"	28.1
HX	"	29.6
HY	"	29.7
<hr/>		
JD	9.8	16.9
JE	9.8	11.8
JF	9.8	14.0
JG	9.8	22.1
JH	20.8	20.2
JI	2	19.5
JJ	"	26.7
JK	34.8	26.5
JL	"	36.9
JM	60	40.8
JN	"	39.8
JQ	"	35.8
		35.8

TABLE III

CONTINUED

ADSORPTION ISOTHERMS OF ACETONITRILE
ON PLATINIZED PLATINUM

RUN #	CONCENTRATION	C/L A
JS- KB	0	-
KC	39.0	23.2
KE	"	24.2
KF	"	22.6
KK	"	21.0
KL	"	24.2
KM	"	25.3
KN	"	23.6
KQ	69.4	37.7
KT	"	37.0
KU	"	39.3
KV	"	42.1
KX	95.2	53.7
KZ	"	46.2

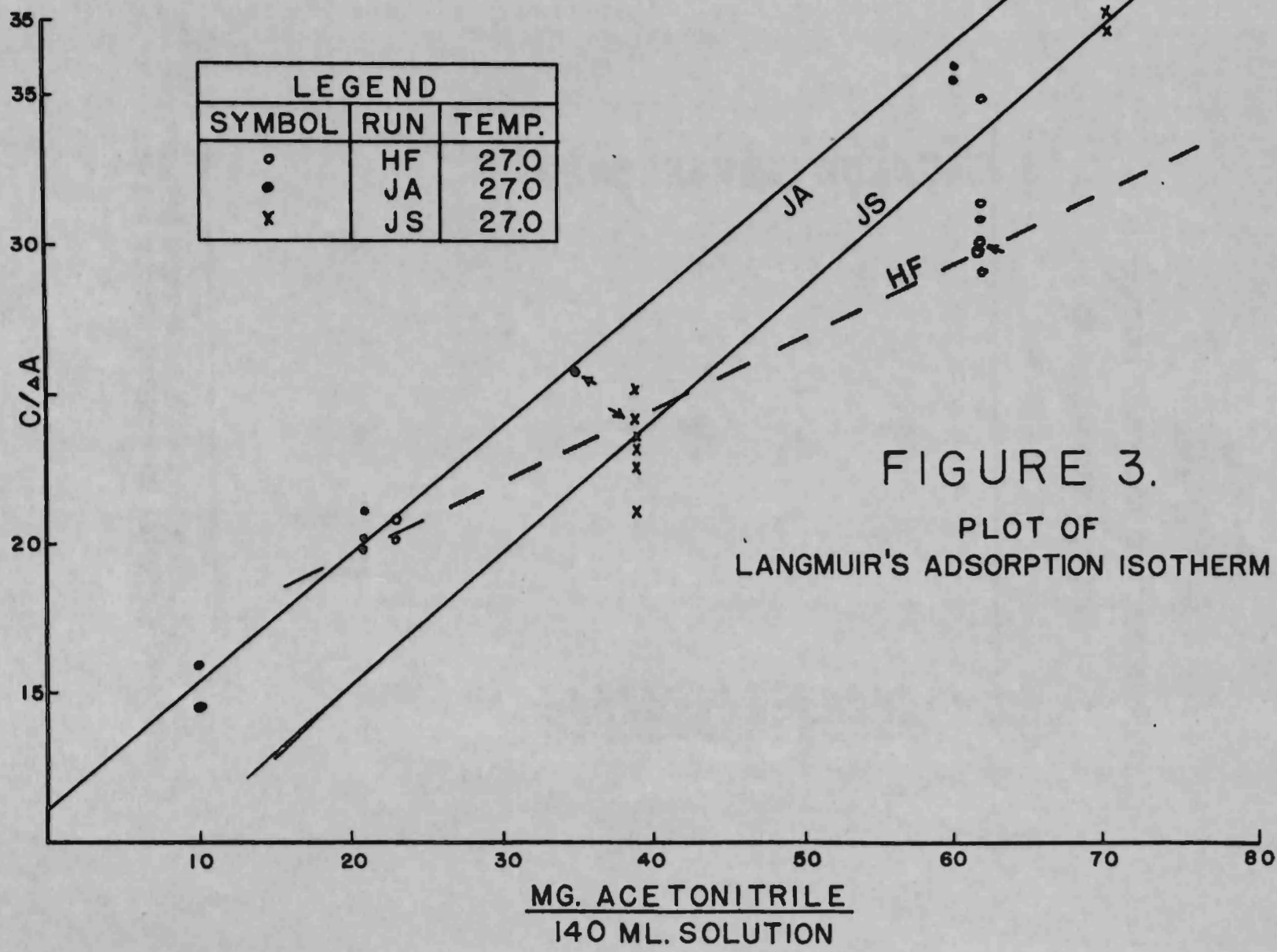


FIGURE 3.
 PLOT OF
 LANGMUIR'S ADSORPTION ISOTHERM

TABLE IV

ADSORPTION ISOTHERMS OF PROPIONITRILE
ON PLATINIZED PLATINUM

RUN #	CONCENTRATION	$\frac{\Delta A}{A}$
RR	0	-
RS	0	-
RT	.631	.666
RU*	"	.174
RV*	"	.057
RW	"	.597
RX*	1.437	.539
RY	"	.714
RZ	"	.806
SA	"	.866
SB	3.011	.946
SC	"	.902
SD*	"	.624
SE*	"	.655
SF	"	.811
SG	"	.811
SH	4.793	.757
	"	

* THESE RUNS WERE ANODICALLY POLARIZED JUST PRIOR TO THE PASSAGE OF HYDROGEN OVER THEM

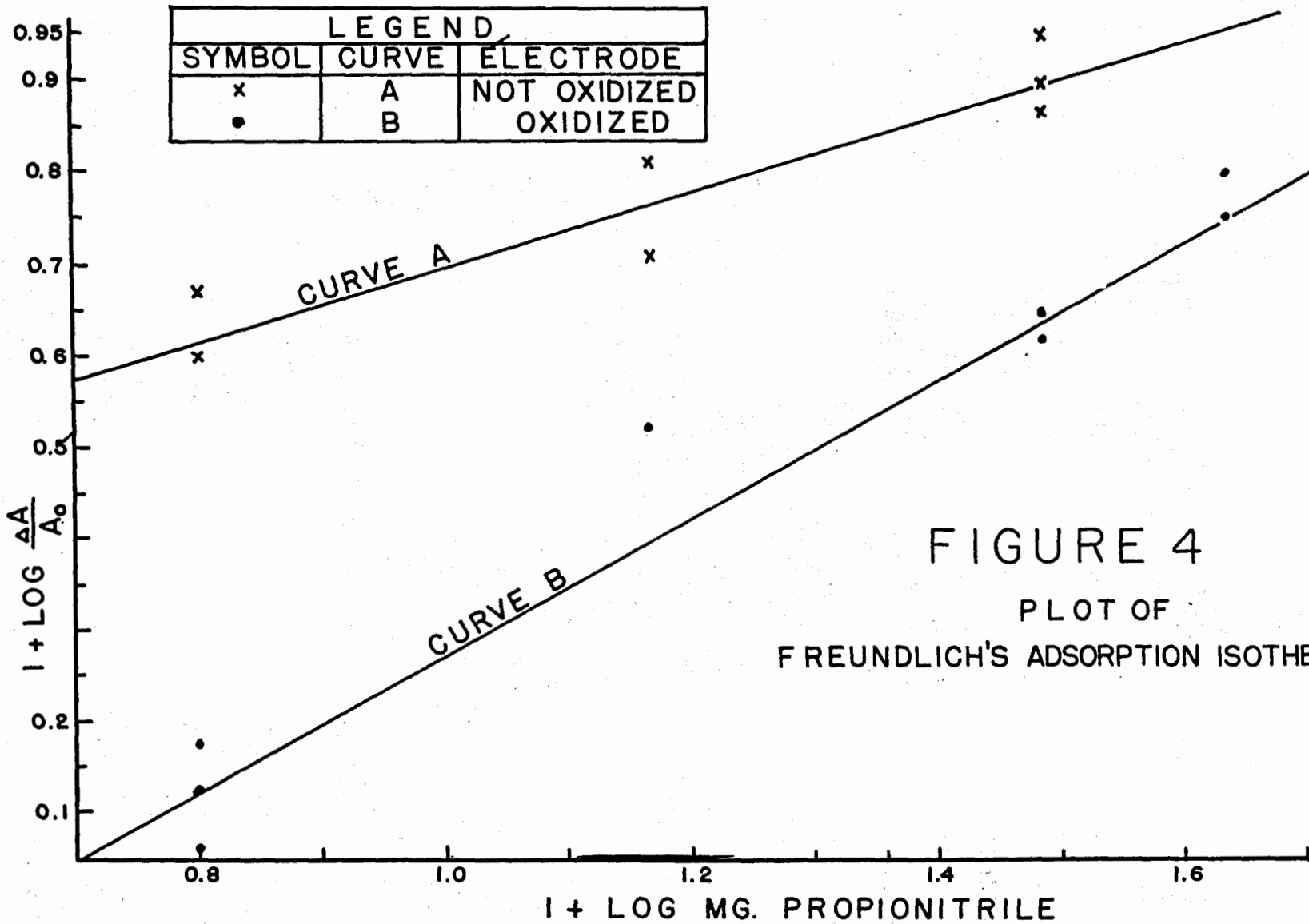


FIGURE 4
 PLOT OF
 FREUNDLICH'S ADSORPTION ISOTHERM

TABLE V

ADSORPTION ISOTHERMS OF NITRILES
ON PLATINIZED PLATINUM

RUN #	CONCENTRATION	$10x \frac{4A}{A_0}$
SL	-	-
SM	-	-
SN	-	-
SO	-	-
SP	-	-
SQ	0.130 ^a	-
SR	"	1.04
SS	0.302	0
ST	"	1.02
SU	0.686	.39
SV	"	2.67
SW	1.454	1.17
SX	"	2.18
SY	"	3.79
SZ	"	3.74
TA	"	3.77
TB	2.85	3.22
TC	"	4.22
TD	"	4.84
TE	"	"
TF	4.68	6.07
TG	"	5.27
TY	"	5.47
TI	7.33	6.56
TJ	"	6.62
TK	10.39	8.10
TL	"	6.34
TM	"	6.50
TN	"	"
TO	"	8.77
VT	-	-
VU	-	-
VV	-	-
VW	3.0 ^b	3.51
VX	"	3.16
VY	18.9	8.21
VZ	"	8.72
WA	"	8.65

a Mg. of butyronitrile in 175 ml. of solution.
b " " phenylacetonitrile in 175 ml. of " .

TABLE V_a
 ADSORPTION ISOTHERMS OF NITRILES
 ON PLATINIZED PLATINUM

RUN #	CONCENTRATION	$10 \times \frac{4A}{A_0}$
UA	-	-
UB	-	-
UC	-	-
UD	-	-
UE	-	-
UF	-	-
UG	-	-
UH	2.35 ^a	.338
UI	"	
UJ	"	
UK	4.65	3.23
UL	"	2.11
UM	5.93	2.36
UN	"	4.40
UO	"	1.97
UP	7.65	3.61
UQ	"	3.82
UR	12.45	4.58
US	"	5.09
UT	"	5.29
UU	"	5.73
UV	"	7.81
UW	"	9.19
UX	"	8.77
UY	"	8.77
VH	-	-
VI	4.2 ^b	1.70
VJ	"	1.66
VK	"	1.45
VL	10.8	2.84
VM	"	4.53
VN	"	4.35
VO	62.2	6.63
VP	"	7.18

a n-capronitrile, mg. per 175 ml.
 b iso-capronitrile, " " " .

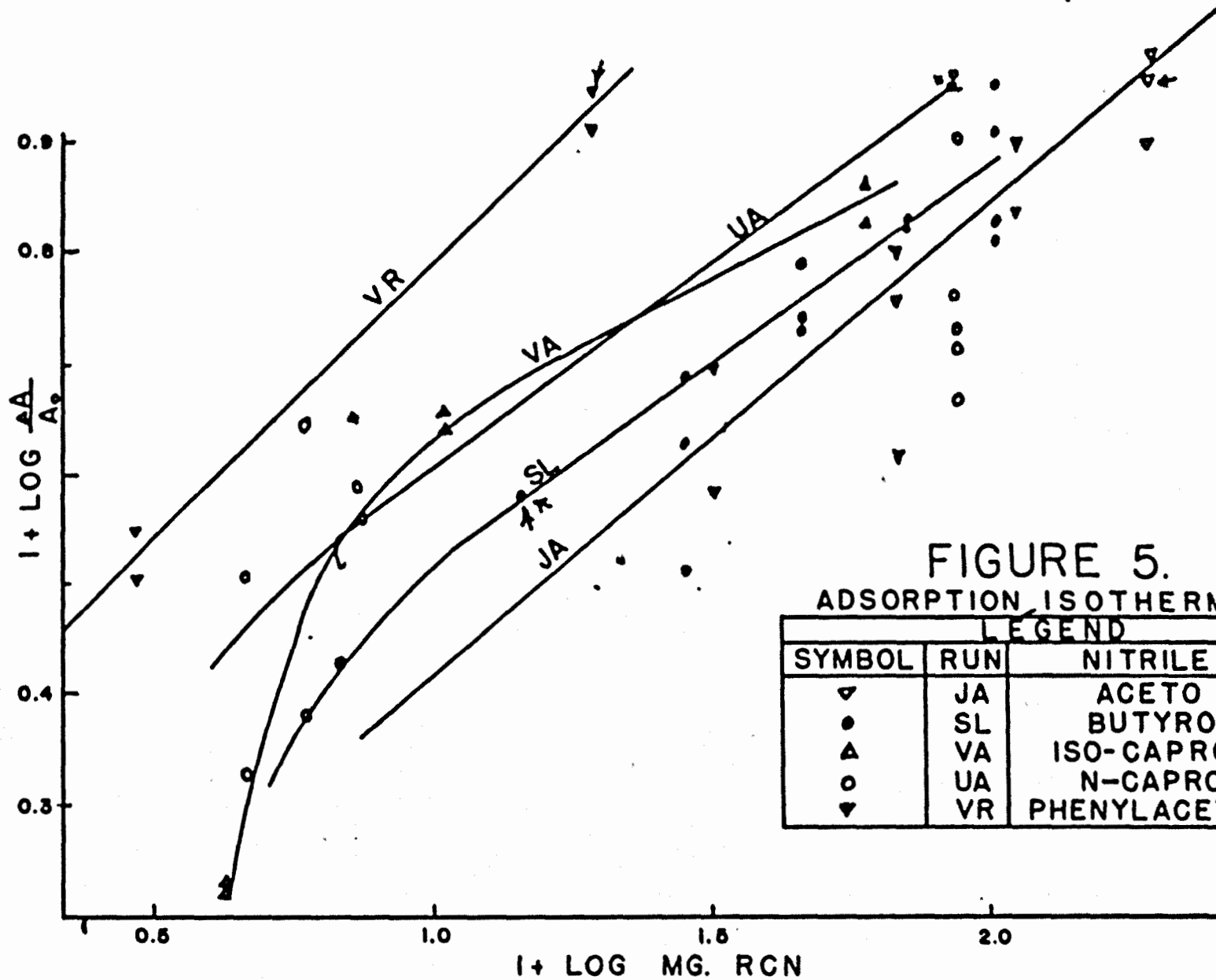


FIGURE 5.
ADSORPTION ISOTHERMS

LEGEND		
SYMBOL	RUN	NITRILE
▽	JA	ACETO
●	SL	BUTYRO
▲	VA	ISO-CAPRO
○	UA	N-CAPRO
▽	VR	PHENYLACETO

TABLE VI
 VARIATION OF POTENTIAL
 WITH AMOUNT OF
 ADSORBED HYDROGEN

RUN #	TEMPERATURE	POTENTIAL	AREA
JJ	27 ⁰ C	.2842	0.39
JM	"	.2873	0.22
JN	"	.2871	0.18
KG	"	.2858	0.50
KE	"	.2888	0.57
KF	"	.2860	0.45
KK	"	.2852	0.32
KL	"	.2853	0.57
KM	"	.2872	0.63
KN	"	.2840	0.53
LQ *	20 ⁰	.2946	2.55
LR *	"	.2946	2.48
LW *	40 ⁰	.2853	2.22
MB	"	.2788	0.22
MC	"	.2798	0.52
MD	20 ⁰	.2899	0.39
ME	"	.2912	0.46
MN	40 ⁰	.2807	0.85
MO	"	.2792	0.52
MP	"	.2807	0.86

* These runs were made on freshly prepared, unpoisoned electrodes.

VARIATION OF POTENTIAL
WITH AMOUNT OF
ADSORBED HYDROGEN

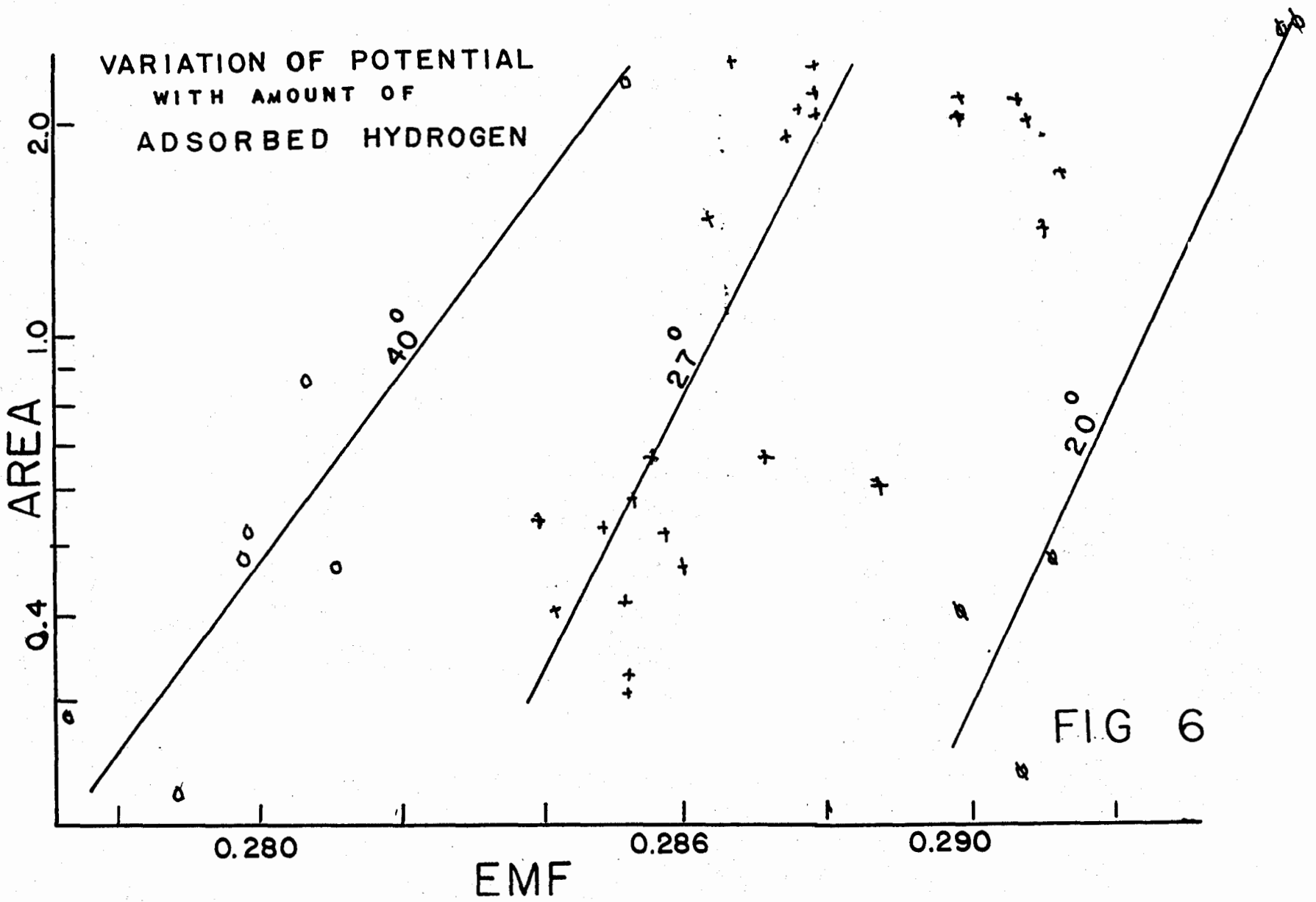


FIG 6

of the observed scatter.

The remaining nitriles have been plotted with acetonitrile in the logarithmic plot of the Freundlich equation in Figure 5 in order to point up the similarities in these curves and their relative positions on the graph. It will be noted that their slopes are nearly the same, indicating that the same type of equilibrium regulates their adsorption resulting in similar values for $1/n$ in the Freundlich equation. The departure of the curves from linearity in the regions of low concentration shows that the amount of hydrogen displaced by the first small addition of nitrile is less than that predicted by the Freundlich equation. Several factors could be contributing to this. There may be appreciable amounts of hydrogen adsorbed and absorbed in regions not accessible to the nitrile. Another possible explanation for this is that the nitrile is adsorbed to some extent on the liquid-glass and liquid-air interfaces. This then reduces the amount available for adsorption on the electrode.

It was pointed out previously (p. 17) that the amount of hydrogen adsorbed on the electrode has an effect upon the electrode potential. The greater the concentration of adsorbed hydrogen on the electrode surface, the greater will be the tendency for them to leave the electrode as solvated ions. This is in agreement with Le Chatelier's

principle. From thermodynamic considerations the relationship should be of the form

$$E = \frac{RT}{F} \times \ln a$$

where E is the electrode potential
 R is the gas law constant
 T is the absolute temperature
 F is the Faraday
 a is the activity of the hydrogen on the electrode surface.

Figure 6, in spite of considerable scatter, indicates that this relation is valid. First of all there is a linear relationship between the voltage and the logarithm of the area, which is proportional to the activity of the hydrogen. In addition, as the temperature increases the slope increases.

The same kind of data can be plotted for the poisoning due to the other nitriles. This is done in Figure 7. In this case the runs were made using a different nitrile for each run. Again there is a great deal of scatter. Probably this scatter is the cause of the apparent curvature observed in some of the lines.

The slopes of these isotherms are seen to vary with temperature. To determine the effect of temperature on the amount of adsorbed hydrogen, let us consider the Van't Hoff isochore:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

TABLE VII
 VARIATION OF POTENTIAL
 WITH AMOUNT OF
 ADSORBED HYDROGEN

RUH #	NITRILE	POTENTIAL	AREA
SS	BUTYRO	.2500	1025
ST	"	.2500	919
SU	"	.2492	984
TC	"	.2483	590
TD	"	.2482	528
TF	"	.2456	400
TG	"	.2462	482
TH	"	.2468	460
TK	"	.2388	192
TL	"	.2430	373
TM	"	.2406	357
TO	"	.2437	123
TT	n-CAPRO	.2503	714
TV	"	.2491	738
TZ	"	.2491	687
UQ	"	.2466	530
UR	"	.2429	465
UT	"	.2459	404
UU	"	.2478	733
UV	"	.2475	377
UW	"	.2428	140
UX	"	.2448	224
VG	iso-CAPRO	.2486	820
VH	"	.2489	878
VI	"	.2457	704
VN	"	.2434	448
VO	"	.2398	427
VP	"	.2395	273
VU	PHENYLACETO	.22463	603
VV	"	.2463	660
VS	"	.2445	437
VX	"	.2446	461
VY	"	.2405	120
VZ	"	.2470	85
WA	"	.2461	90

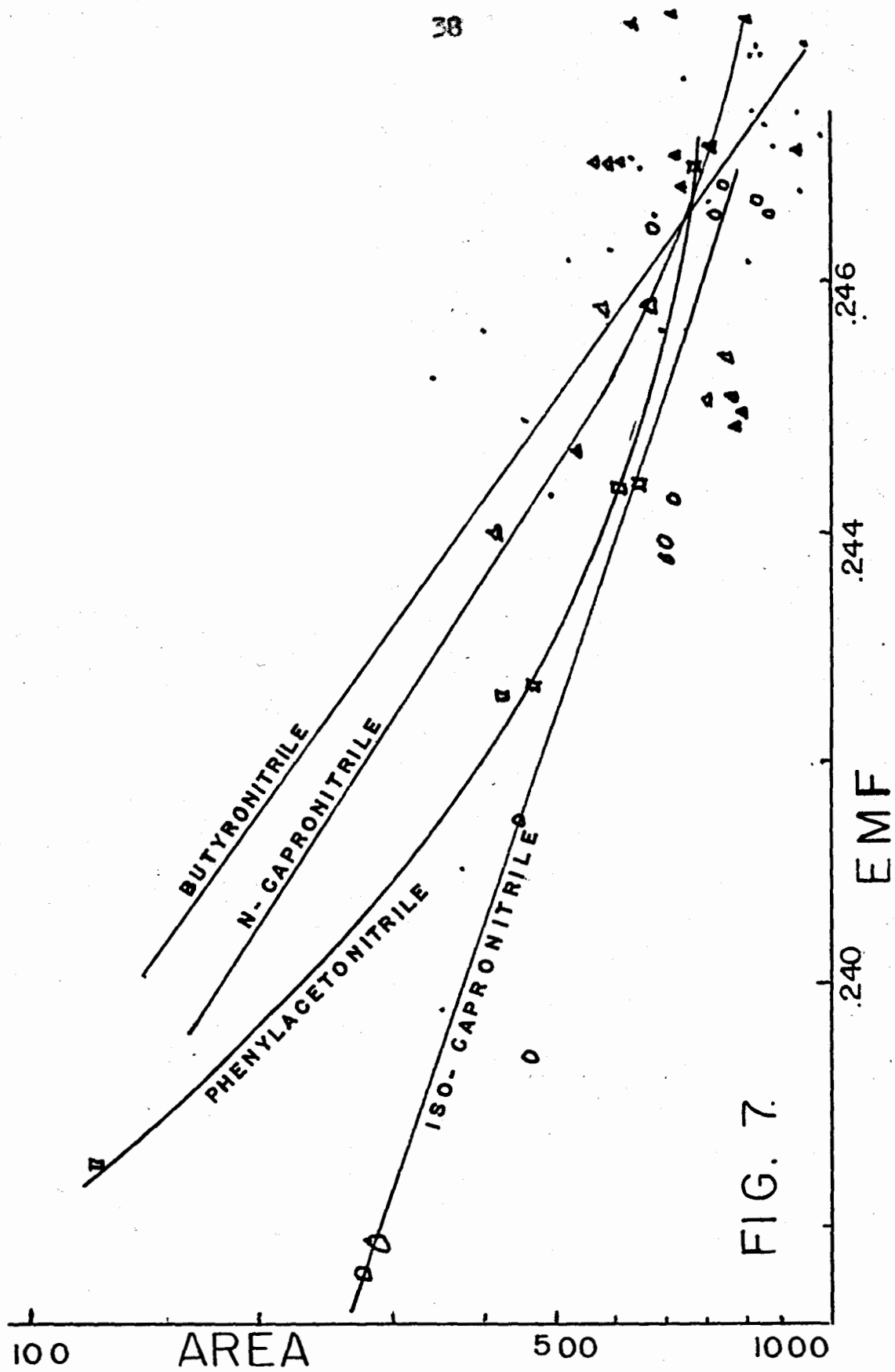


FIG. 7.

It is apparent that the ΔH of the adsorption will determine the variation of the equilibrium constant with temperature. If ΔH is assumed to be constant over the small temperature range considered, the equation integrates to

$$\ln K_p = c - \frac{\Delta H}{RT} .$$

Thus the plot of $\ln K_p$ against $1/T$ should be a straight line of slope $-\Delta H/R$. In the case of hydrogen alone, the equilibrium involved is simply of the form:



Since the concentration of adsorption sites may be considered large with respect to the number occupied by the adsorbed hydrogen, the approximation may be made of A for K_p . The equation then becomes

$$\ln A = c - \frac{\Delta H}{RT} .$$

This is plotted in Figure 8 for hydrogen in the absence of added poison.

The heat of adsorption was calculated from the graph to be 4,000 calories/mole. This value is lower than those reported in the literature. This may be accounted for by a probable partial poisoning of the electrode.

The linear variation of the potential of the hydrogen electrode with pressure has been well established.²⁵ The

TABLE VIII

HEAT OF ADSORPTION FOR HYDROGEN

RUN #	AREA	ln 10A	(1/T)x 10 ⁴
LS			
LT	3.19	5.765	34.8
LQ			
LR	2.56	5.545	34.2
LU			
LV	2.52	5.529	33.1
LW	2.22	5.403	32.0

The values recorded above are averages of all the data at each temperature.

ΔH OF ADSORPTION FOR HYDROGEN

ΔH OF ADSORPTION FOR HYDROGEN

FIG. 8

5.8

5.6

5.4

41

LN (10 A)

30

30.5

31

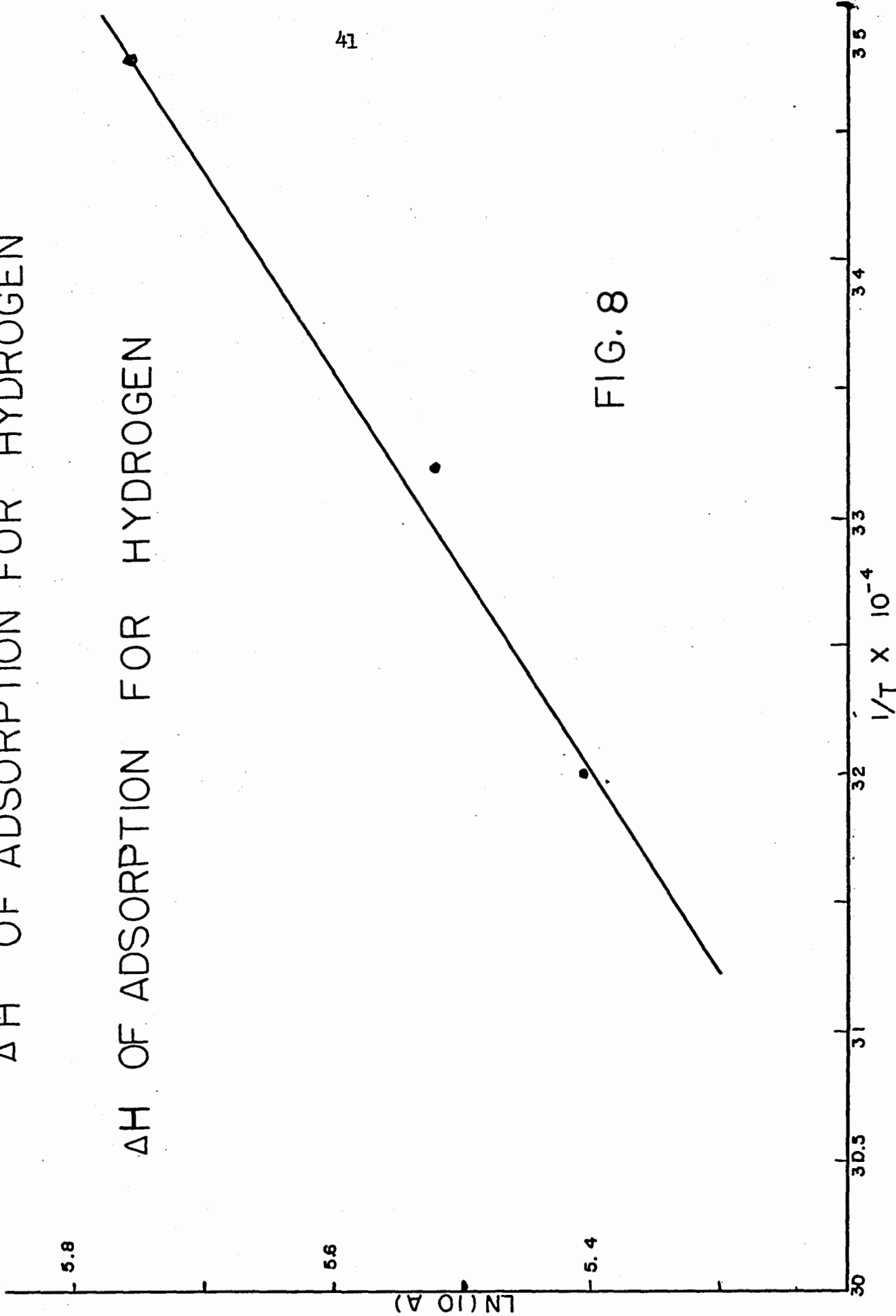
32

33

34

35

$1/T \times 10^{-4}$



graph in Figure 10 shows this to be the case.

The amount of hydrogen adsorbed appears from Figure 9 to be a linear function of the hydrogen pressure over the range of pressures studied. This shows that the electrode is not nearing saturation. This data also serves as a check on the data in Figures 6, 7, and 10, since if potential is proportional to the log of area and area is directly proportional to pressure, then potential must also be directly proportional to the log of pressure.

Finally, the poisoning effect was studied as a function of the molecular weight. It is to be expected that the larger molecules should occupy a larger area on the electrode surface than the smaller molecules. This effect has been shown to a certain extent in Figure 5. However a more direct comparison of this is shown in Figure 11, in which the quantity of nitrile necessary to produce the same degree of poisoning of the electrode is plotted as a function of molecular weight. The data was taken from the level portion of the adsorption isotherms and is listed separately in Table XI. The regular increase in the poisoning effect as molecular weight increases shows that the larger molecules are much more effective in blocking the electrode

or that the equilibrium favors adsorption in the higher nitriles.

TABLE IX
VARIATION OF PRESSURE
WITH AREA

<u>RUN #</u>	<u>AREA</u>	<u>PRESSURE</u>
OS	2900	76.5 cm Hg
OZ	2900	"
PA	3130	"
PB	1610	66.5
PC	1370	"
PD	570	56.5
PE	550	"
PF	2680	76.5
PG	2900	"
PH	2900	"
PI	2880	86.5
PK	3520	"
PL	3860	"
PM	3580	"

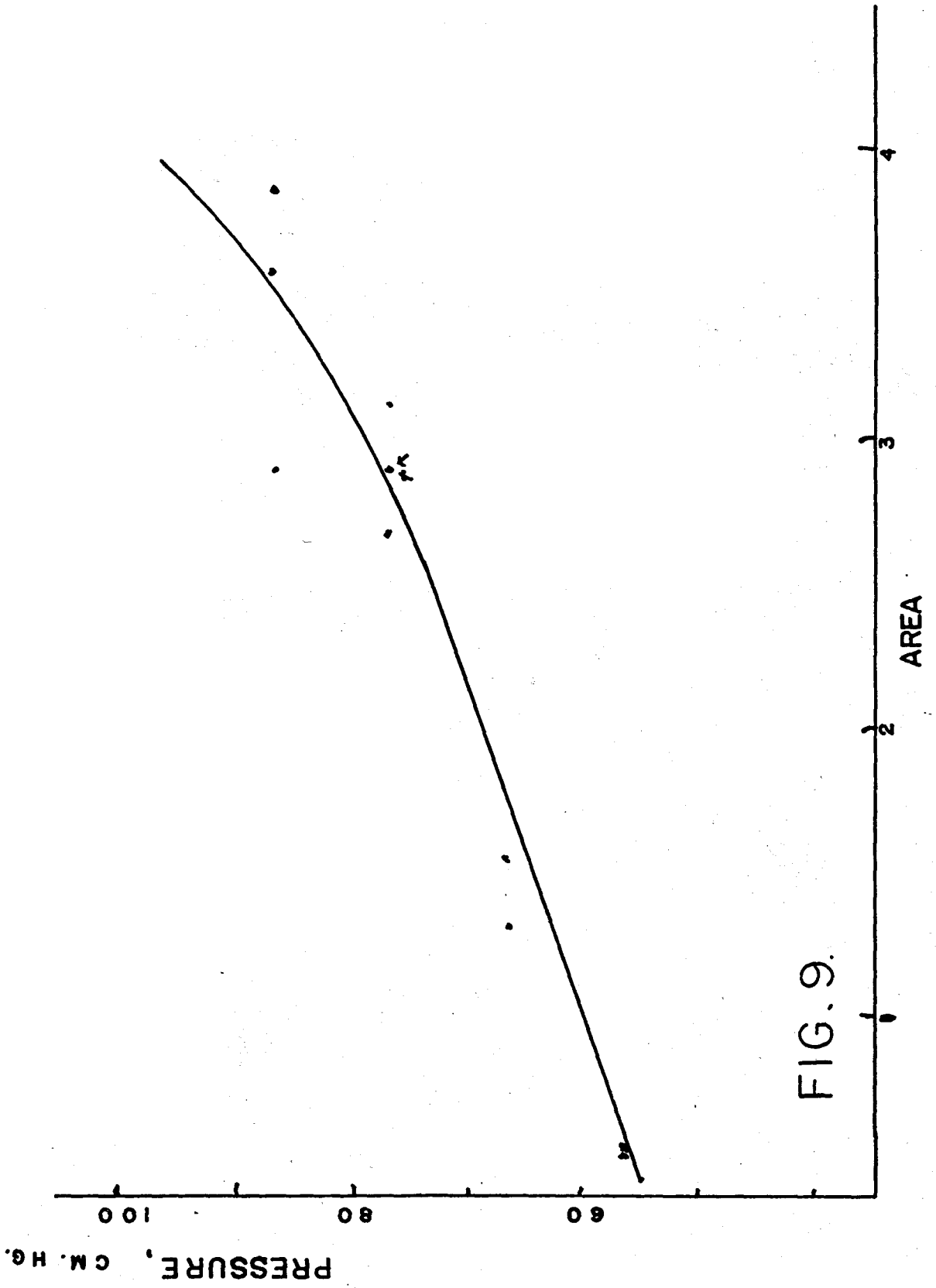


FIG. 9.

Table X

<u>RUN #</u>	<u>POTENTIAL</u>	<u>PRESSURE</u>
OS	.2423	76.5 cm Hg
OX	.2450	"
OZ	.2458	"
PA	.2447	"
PB	.2437	66.5
PC	.2445	"
PD	.2466	56.5
PE	.2456	"
PF	.2472	76.5
PG	.2486	"
PH	.2486	"
PI	.2487	86.5
PK	.2488	"
PL	.2488	"
PN		"

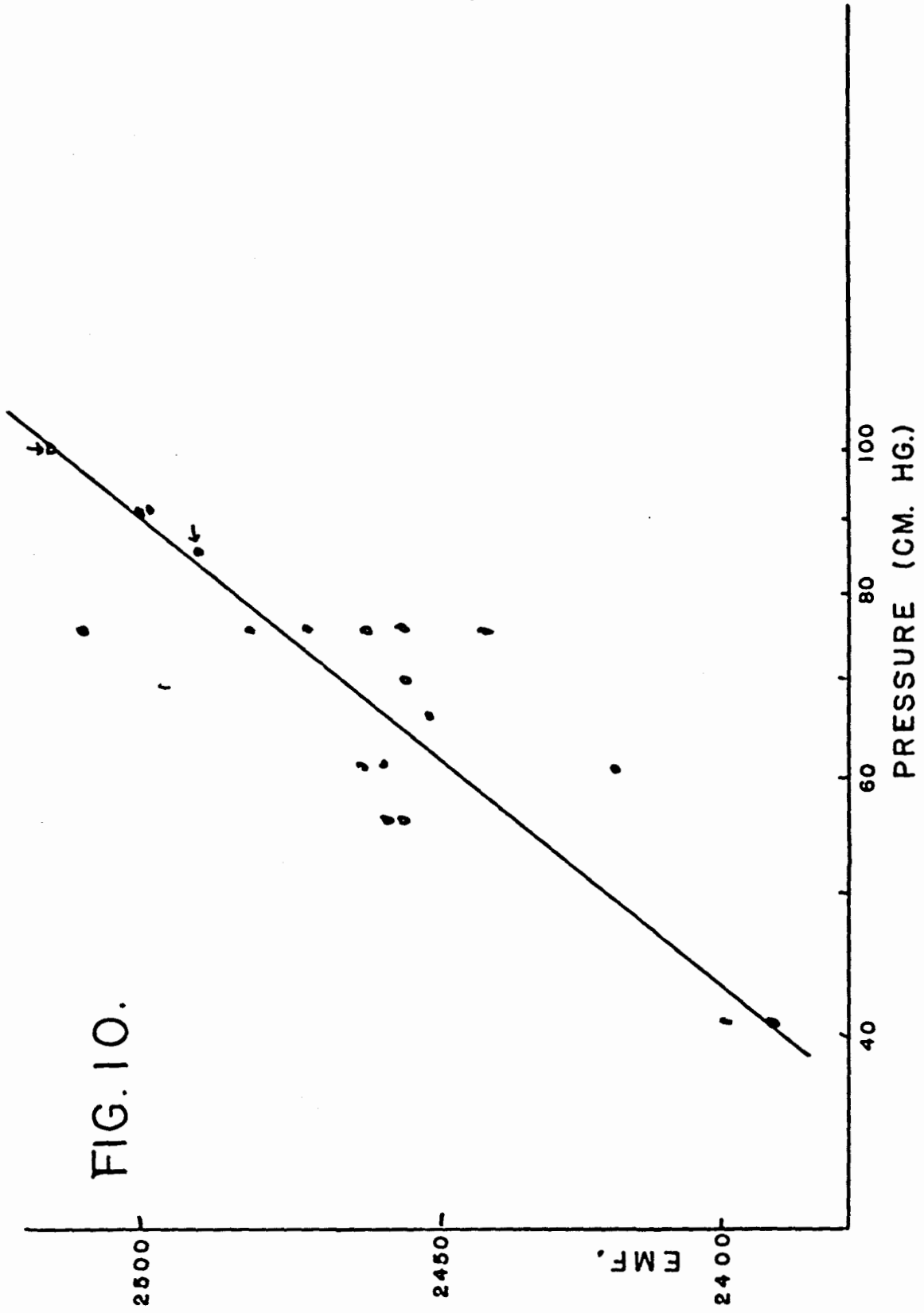
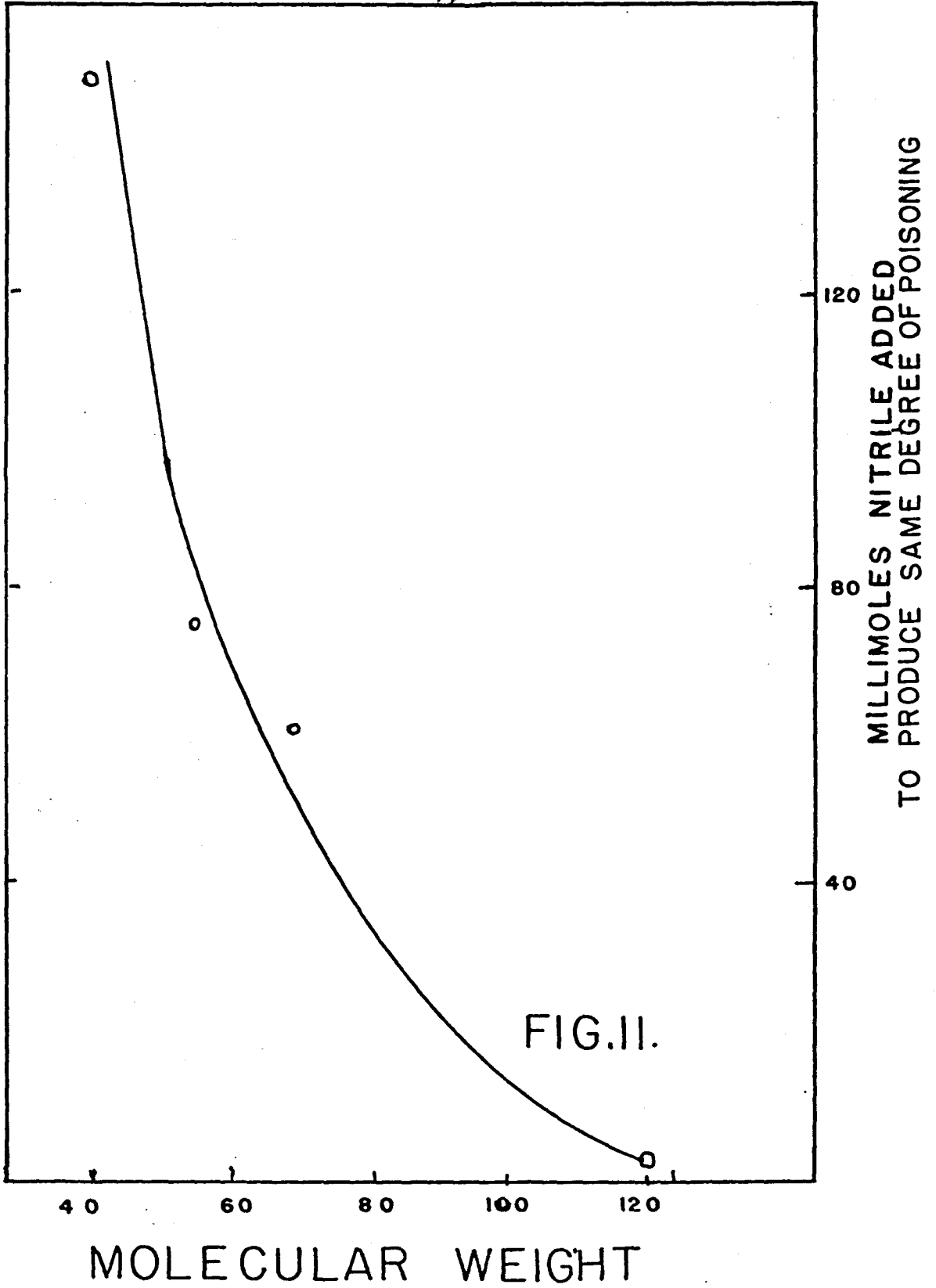


FIG. 10.

Table XI

STRUCTURAL EFFECTS
UPON DEGREE OF POISONING

NITRILE	MOLECULAR WEIGHT	WEIGHT TO PRODUCE SAME DEGREE OF POISONING
ACETONITRILE	41	150
PROPIONITRILE	55.1	76
BUTYRONITRILE	69.1	62
n-CAPRONITRILE	97.2	14
iso-CAPRONITRILE	97.2	14
PHENYLACETONITRILE	116.1	3



SUMMARY

A microcoulometric method has been developed for the measurement of the comparative adsorption of Organic adsorbates and hydrogen on the hydrogen electrode. This method has been applied to the study of the adsorption of nitriles. The work has shown the the adsorption adheres both to the Freundlich and Langmuir Adsorption equations.

The potential of the electrode was found to vary linearly with the amount of adsorbed hydrogen as well as to the logarithm of the hydrogen pressure. The integral heat of adsorption was measured to be 4,000 calories/mole. The poisoning capacity of the various nitriles was found to increase regularly with the molecular weight.

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AUTOBIOGRAPHY

I, Ray Douglas Sathern, was born in Valley Stream, New York on August 14, 1928. I attended the public schools of Valley Stream, graduating from high school in 1946. I served a term of enlistment in the United States Army from 1946 until 1948. I then completed my undergraduate work at Ursinus College, receiving a B. S. degree in 1951.

Upon completion of my undergraduate work, I accepted a Puryear Fellowship at the University of Richmond. In July, 1952 Research Corporation of America granted me a research fellowship to carry out the work discussed in this thesis. This thesis is submitted in a partial fulfillment of the requirements of the Master of Science degree.