The Effect of Various Organic Vapors

on the

Contact Potential of Metals

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CHAPTER I

INTRODUCTION

<u>Historical Development</u>   Volta recognized the existence of a contact potential between two different metals over a century ago, and ascribed the origin of the electromotive force of galvanic cells to it. The existence of this contact potential is rather difficult to demonstrate, and further, its actual value depends to a great extent on the cleanliness of the surface. In fact, to get a true value for a clean metal it is necessary to use metal evaporation methods combined with a high standard of vacuum technique. (1)

Three general methods have been used to date to measure the contact difference of potential (or Contact Potential). Volta, and later Lord Kelvin, used an electric condenser, the two plates of which were different metals, connected across an electrometer. Thus, a separation of the leaves of the electrometer indicates the existence of the contact potential. If a potentiometer is now interposed in the condenser circuit, it is possible to adjust the potentiometer so that no current flows when the separation of the condenser plates is varied, as indicated by the electrometer. The potentiometer setting then represents a potential equal and opposite to the contact potential.

A second method for measuring the Volta potential involves ionizing the air between the condenser plates and adjusting the potential applied to them until no current passes across the air gap. This method was first used by Righi (2) and later by Andersen and Morrison (3), and others.

The third method, and the method used in this work, is a very ingenious and sensitive modification of the first method as developed by Zisman at Harvard University (4). Here, one of the plates is made to vibrate rapidly parallel to itself, thus altering the distance between the condenser plates in a periodic manner. The AC current thus produced is amplified and used to operate a loudspeaker, a sensitive vacuum tube voltmeter and/or a cathode ray oscilloscope. A potentiometer is used to vary the potential applied across the plates and equality to the contact potential is indicated when any of the indicating methods shows a null.

Within the last fifteen years many workers have become interested in the effect on contact potential of various adsorbed films, particularly with the view towards using contact potential techniques as a powerful tool in the general study of surface chemistry. Metal evaporation techniques have been developed which have aided materially in the production of clean, non-contaminated surfaces. Thus, Antes (5) using the Zisman method, plus

vacuum sputtering, has studies the effect of air, water, and nitrogen vapor on evaporated aluminum, copper, and iron films.

J.C.P. Mignelet (6) has studied the effect of hydrogen and nitrogen on nickel and concludes "We have here a striking example of the ability of contact potential to distinguish between the Van der Waals adsorption and chemisorption by virtue of its having a sign . ... The positive sign may well be a feature common to all Van der Waals films of non-polar gases on bare metals. If this turns out to be true, a negative contact potential on a bare metal will point to chemisorption ...."

Contact potential measurements have not been limited to metal-metal systems. Thus, adsorption has been studied by means of contact potentials in liquid-metal systems (7), paraffin vs. gold and collodion vs. gold (8), and even systems of metal vs. semiconductors such as silica and metal oxides. (9)

The value of contact potential measurements in the surface chemistry field has been cited by several men; thus J. H. v Duhn (10) states "Contact potential in some cases was found to be a function of pressure of the vapor, this effect is ascribed to the thickness of the adsorbed layer." and Frost and Hurka (8) go even further in concluding that plots of contact potential versus relative pressure are equivalent to adsorption isotherms.

Outline of Work

In reviewing various metals and vapors to be investigated in this work it was decided to employ organic vapors of varying dipole moment to compare with water vapor which was known to have a large effect upon contact potential. It was hoped that the alteration in contact potential would prove to be a direct measure of the strength and type of interaction between the film and the surface. It is believed that this hope has been borne out in the experimental results. In addition, the work was designed to "shake down" the apparatus, and to lay the groundwork for further work leading to data that would perhaps be useful in the fields of lubrication, corrosion inhibition and catalysis.

Thus the following systems were investigated:

Platinum vs. Aluminum

Platinum vs. Copper

Platinum vs. Gold

Vapors introduced to each of the above systems were:

Water

Ethyl alcohol

1-Nitropropane

n-Butylamine

n-Butyric Acid

Platinum was used as a reference because of its chemical inertness. However, it was realized that work function changes would take place on the Pt because of physical adsorption. To separate the adsorption effect on Pt from that on the test metals a further series of measurements were made employing an aluminum plate coated with Teflon. It was felt that since Teflon was not wet by organics, a Pt vs. Teflon system would show only the effect of the vapor on the work function of the platinum. Curves of contact potential change vs. time for each of the vapors on Pt could then be added to the corresponding "composite" system curves to show the effect of the vapor on the work function of the test metal.

CHAPTER II

EXPERIMENTAL PROCEDURE

What is Contact Potential?

Any metal possesses a potential energy barrier just outside
its surface in the form of an electric field. The work function of a
metal is a measure of the strength of this electric field in that it
measures (in volts) the electrostatic potential needed to bring an
electron from just inside that surface to just outside it. Therefore,
if two metals with dissimilar work functions are brought into close
proximity electrons will tend to flow from the surface of lower
work function to that of the higher work function. That is, they will
flow towards the surface with the stronger electric field. Since
the electrons carry a negative charge, the surface with the higher
work function becomes negatively charged with respect to the surface
of lower work function. The electron flow continues until an equilib-
rium is reached where the escaping tendency of an electron is the
same on both surfaces. At this point the metal with a lower work
function carries a positive charge with respect to the surface of
higher work function. The amount of this charge is called the
"Contact Difference of Potential" and is equal to the difference in
work functions of the two metals.

Description of the Apparatus

Essentially, the method used for measurement of the contact potential is that of Zisman.(4) A schematic of the apparatus is shown in figure A, and the loudspeaker and pre-amplifier circuit in figure B.

The vibrating plate of the condenser is a 25 x 0.1 mm Pt disc soldered to a quarter-inch square brass plate, which in turn is soldered to the end of a small brass screw about 1-1/2" long. The lower end of this screw is affixed to a brass sleeve which is wound with a coil of fine wire. This sleeve fits over the permanent magnet of a loudspeaker which acts as the driver. Just below the Pt disc the brass screw goes through a small hole drilled in a section of hack-saw blade, a solid juncture is made by the use of two small set screws either side of the blade. The hack-saw blade is cantilever anchored at its outer end by means of a clamp attached to the peri- phery of the loudspeaker frame. The vibrating plate projects through a hole in a copper shielding plate which covers the loud- speaker. The speaker and vibrating plate assembly is electrically insulated from its supporting structure.

The upper (test) plate is mounted upon a brass universal joint structure with "Sauereisen" brand porcelain cement supplemented with silver powder for electrical contact. The universal joint allows

FIGURE A

THE ELECTRICAL SYSTEM

FIGURE B
PRE-AMPLIFIER CIRCUIT

the upper plate to be aligned exactly parallel to the lower Pt plate. The upper end of the universal joint structure is a brass screw that projects through, but is insulated from, the lower closure of the amplifier case. This pre-amp case is a short section of iron pipe, electrically grounded, which is brazed to a supporting section containing a threaded hole. A long threaded rod, which rests in and is supported by a socket, goes through this threaded hole. Thus the entire upper assembly, including the upper plate, can be moved vertically in relation to the lower plate. This arrangement allows for precise adjustment of the separation between plates.

The loudspeaker coil is driven by a standard audio oscillator through an external step-down transformer. The natural vibration frequency of the system is about 73 cycles per second.

The vacuum system consists of an all glass, two stage, umbrella type mercury diffusion pump backed by a Welch "Duo-Seal" forepump rated at 10^{-4} mm. of Hg. A cold trap is mounted between the diffusion pump and the mechanical pump.

The "bucking" potential for measuring the contact potential is supplied by two 1-1/2 volt ignition type dry cells in series across a Leeds & Northrup potentiometer. The potentiometer can be calibrated, through a switching arrangement, using a Standard Cell and galvanometer. The potentiometer is connected to the lower

plate through a reversing switch in order to supply a positive or negative bucking potential, as necessary.

The null detecting instruments consist of a vacuum tube voltmeter ("Signal Tracer" type) and a cathode ray oscillograph connected in parallel. The AC signal generated at the vibrating condenser feeds to these instruments through the pre-amplifier and then through an audio amplifier. The shape of the voltage wave obtained is non-sinusiodal for sinusoidal plate vibration and the distortion increases as the plates are brought closer together. For higher precision work harmonic frequencies might be eliminated by the use of a suitable filter.

The vacuum system contains a McLeod gage for reading ultimate pressure, and a Dubrovin Vacuum gage, capable of being read from 0.05 to 20 mm. of Hg, and used to measure vapor pressure of the organic vapor introduced into the system. The vapor under study was introduced into the system from a glass vial sealed to a stopcock fitted with a standard taper joint. (ST 10-30) All stopcocks were lubricated with Apiezon M. Mercury vapor was prevented from entering the bell jar by using a gold wool plug in the main vacuum take-off.

The best, consistently obtainable, vacuum achieved with the apparatus was 1.95 microns as measured on the McLeod gage,

therefore all runs were started at this pressure. It was realized that a higher vacuum would be desireable, but the size of the vacuum chamber and the in-leakance conditions prevailing, precluded obtaining much better. The effect of air in-leakance on the contact potential was investigated and found to be negligible. For this reason, and because it was felt that there was little point in attempting an extreme standard of vacuum technique since evaporated metal films were not to be used, no attempt was made to redesign the apparatus for better vacuum.

Experimental Procedure

The general scheme of procedure for each run was as follows:

1. The test plate was mounted and installed on the universal joint. The plates were brought into close proximity and adjusted for parallelism.

2. The electrical circuits were allowed to warm up and the plate separation adjusted for best signal in air, with the amplitude control of the audio oscillator at maximum. When the system was evacuated it was always found that the amplitude had to be reduced since with the air "damping" effect removed, the lower plate tended to strike against the upper plate. Changing the vibration amplitude showed no effect on the value of the contact potential.

3. The system was pumped down and allowed to remain at ultimate vacuum with the pumps running for 24-48 hours.

4. The vapor sample was prepared, the vial sealed onto the stopcock and then pumped out on an auxiliary vacuum pump to remove air and to insure that the vial was saturated with the test vapor.

5. The sample vial was attached to the vacuum line, and the glass entrance tubing (which was separated from the main vacuum line by an auxiliary stopcock) was pumped down to ultimate vacuum.

6. At the start of a run the main vacuum stopcock was shut, and the zero time contact potential was read. Immediately thereafter the timing watch was started and simultaneously the system was "dosed" with the test vapor for 30-45 seconds. Pressure of the system was read, and the variation of the contact potential with time was recorded.

7. When the contact potential had reached an equilibrium value, usually after 20-30 minutes, the system was "dosed" again, without pumping out, and the pressure read. Again the contact potential vs. time variation was recorded.

8. The system was then pumped down to an equilibrium contact potential (30-50 minutes) and the "dosage" procedure repeated a third time.

9.   The system was then pumped out for 24-36 hours and a "final" contact potential recorded.

10.   Prior to the initial mounting of each test plate, the plate was polished to a mirror finish. However, between each run of a series involving a single test plate no attempt was made to clean the plate other than pumping out for 24-48 hours, depending on when a stable contact potential was reached. It was felt that this investigation was primarily concerned with the direction of the contact potential change, rather than the absolute magnitude - i.e. the effect looked for was relative change. Therefore, some contamination, such as might be found as a result of residual adsorption from a prior run at the start of a subsequent run, was deemed permissable. To minimize contamination, each series was run with the following order of introduction of vapors:

1st - Water

2nd - Ethanol

3rd - 1-nitropropane

4th - Butylamine

5th - Butyric Acid

This order was chosen after preliminary results showed that Butylamine and Butyric Acid would have the greatest contamination effect.

11. All runs were made at room temperature, about 25°C. The usual precision of measurement of the contact potential was $\pm$ 1 millivolt.

12. The results were plotted as "Change in Contact Potential" (Δ CP) versus Time. The initial contact potential was taken as the "zero". This form of plotting eliminated variations in the absolute magnitude of the contact potential that might arise from different positioning of the two surfaces relative to one another after a test plate had been changed.

CHAPTER III

DISCUSSION AND RESULTS

Contact Potential Change

Let two different metals, α and β, be initially separate and at zero electrostatic potential. Let χ^α represent the thermionic work function of metal α, and χ^β represent the thermionic work function of metal β, with metal β having a higher work function than metal α. If the metals are now brought into close proximity, as in a condenser, and connected momentarily, electrons will flow from the metal of lower work function (α) to the metal of higher work function (β). Since the electrons carry a negative charge an electrostatic potential is set up at metal α (V^α) which is positive relative to that of metal β (V^β). The Contact Potential is equal to the difference in electrostatic potential caused in turn by the difference in thermionic work functions of the metals. (1) Thus, mathematically;

$$CP = V^\alpha - V^\beta = \chi^\beta - \chi^\alpha \qquad (1)$$

Note that the sign of CP has no meaning. It is a quantity having magnitude, but no sign. (See Ref. 1, p. 307)

The major concern of this investigation was not to study CP magnitude however, but rather to study CP <u>change</u> in both direction and magnitude, resulting from the simultaneous change in work

functions of metals α and β upon adsorption of various vapors.
And further, to determine from this CP change the effect of adsorption
upon the individual work functions of the test metals.

Therefore, from equation (1):

$$\triangle CP = \triangle \chi^{\beta} - \triangle \chi^{\alpha} \tag{2}$$

If it could be assumed that adsorption on β (The metal with higher
work function) did not occur, then $\triangle \chi^{\beta}$ would be equal to zero,
and:

$$\triangle CP = -\triangle \chi^{\alpha} = -[\chi_2^{\alpha} - \chi_1^{\alpha}] \tag{3}$$

Thus an increase in the work function of metal α would cause a
decrease in CP (i.e. a negative $\triangle$ CP) and conversely, a decrease
in the work function of α would cause an increase in CP (i.e. a
positive $\triangle$ CP)

To particularize the notation to the systems used in this
investigation, let:

χ^{Tf} = work function of Teflon coated plate

χ^{Pt} = work function of Pt

χ^{α} = work function of the test metal(i.e. Al, Cu, Au)

Also: $\chi^{Tf} > \chi^{Pt} > \chi^{\alpha}$

Then, for the so-called "composite" system: (i.e. Pt vs. α)

$$\triangle CP_c = \triangle \chi^{Pt} - \triangle \chi^{\alpha} \tag{4}$$

and for the Teflon system: (i. e. Tf vs. Pt)

$$\Delta CP_{TF} = \Delta \chi^{Tf} - \Delta \chi^{Pt} \tag{5}$$

Plots of equation (4), ΔCP_c vs. time, are shown in figures 12-25 of the Appendix for the test metals and vapors used. Plots of equation (5), ΔCP_{Tf} vs. time, are shown in figures 26-30.

If it is assumed that $\Delta \chi^{Pt}$ is the same in both systems, under comparable pressure conditions, equations (4) and (5) may be added:

$$\Delta CP_c = \Delta \chi^{Pt} - \Delta \chi^{\alpha} \tag{4}$$

$$\Delta CP_{Tf} = \Delta \chi^{Tf} - \Delta \chi^{Pt} \tag{5}$$

$$[\Delta CP]_{Added} = [\Delta CP_c + \Delta CP_{Tf}] = \Delta \chi^{Tf} - \Delta \chi^{\alpha} \tag{6}$$

Now if it is assumed that no adsorption takes place on the Teflon coating, the change in the Teflon work function will be zero. That is: $\Delta \chi^{Tf} = 0$

and

$$[\Delta CP]_{Added} = -\Delta \chi^{\alpha} = -[\chi_2^{\alpha} - \chi_1^{\alpha}] \tag{7}$$

Thus equation (7) is equivalent to equation (3) and the sign of $[\Delta CP]_A$ determines whether the work function of the test metal has increased or decreased.

The assumption above can be justified when it is considered

that Teflon is a low energy surface and is not readily wet, even by organic liquids. (15) Non-wetting systems, (i. e. those with a finite contact angle) are associated with Type III vapor adsorption isotherms. Thus, it is reasonable to expect that, at low pressures, only a very small amount of organic vapor is adsorbed on Teflon. The approximation in this investigation is that this amount has a negligible effect on the contact potential.

Figures I - 11 represent the plots of equation (7) versus time for the metals and vapors under study. As indicated by equations (4), (5) and (6), these curves are the result of adding the contact potential changes of the "composite" systems to those of the Teflon system at equal or nearly equal vapor pressures. For example; - the $\triangle$ CP values of the Pt vs. Al with Nitropropane curve (Fig. 14) from time 10 to 40, and at a pressure of 1.0 mm, were added to the $\triangle$ CP values of the Pt vs. Tf with nitropropane curve (Fig. 28) from time 20 to 45, and at 1.1 mm. The result is the curve shown in Figure 3, showing the effect of nitropropane vapor on Al. $[\triangle CP]_{Added}$ on this curve is negative, indicating that the work function of Al has increased. i. e. $\chi_2^{Al} > \chi_1^{Al}$ in equation (7).

Dipole Orientation

The question now arises whether, from the direction of the contact potential change, and hence from the direction of the work function change, the orientation of the adsorbed polar molecule to the metal surface may be determined. That is, is the negative end of the dipole towards the surface or away from it? Mignolet, (6) using the Zisman method, investigated the adsorption of nitrogen, hydrogen, ethylene, argon and xenon on nickel and concluded that in all cases physical adsorption produced potential changes due to the formation of a dipole layer oriented positive away from the metal. Anderson and Alexander, (13) also using the Zisman method found that adsorption of water or isopropanol on a gold surface causes an increase in the work function, but concluded, probably following Adam (1941, p. 311) that this was due to the formation of a dipole layer oriented negative away from the metal. They further make the general statement - "A decrease in work function results from the formation of a dipole layer oriented positive away from the metal".

Thus it is seen that there is doubt as to the exact relationship between the dipole orientation of the adsorbed layer and its effect on the direction of change of the metal work function.

A tentative conclusion regarding dipole orientation is reached below. Later this conclusion will be examined in the light of the experimental results. Assume for example, an increasing work function. What orientation of adsorbed dipoles would tend to increase the work function? Intuitively it can be said that the more negative end of the dipole must be towards the metal surface. The negative ends of the dipoles repel the surface electrons of the metal making it more difficult for them to leave, thus increasing the work function. Conversely, if the work function decreases, the dipoles must be oriented with their positive ends toward the metal surface, thus attracting the surface electrons.

Discussion Summary

The preceding discussion may be summarized by postulating the following "rules". (Note 1)

1. A positive $[\Delta CP]_{Added}$ is equivalent to a decrease in work function, and indicative of dipole orientation plus end toward the metal surface. ($+-+$ rule)

2. A negative $[\Delta CP]_{Added}$ is equivalent to an increase in work function, and indicative of dipole orientation minus end toward the metal surface. ($-+-$ rule).

Note 1. The reader may consider the rules a "memory aid" to help in interpreting subsequent curves.

Results

The curves shown in the main body of the text are the results of the addition of the Teflon series of curves to the composite curves. The original curves for the series Al, Cu, and Au vs. Pt for the vapors noted, and the Pt vs. Teflon curves for the same vapors are shown in the Appendix. Note that the ordinates of the text curves are labelled $[\Delta CP]_A \equiv [\Delta CP]_{Added} \equiv -\Delta \chi^{\alpha}$

Aluminum

Figures 1 through 4 show the effect of the vapors noted on the work function of aluminum. The amine curve is characteristic of the form found also with copper and gold, and results in a decrease of the work function of all three metals. It is reasonable to expect that the butylamine molecule would adsorb on the metal surface amine-end down, with the hydrogen adjacent to the surface. This, coupled with the fact that the work function decreases, tends to support the conclusions regarding dipole orientation reached above. Alternatively it is possible to view the effect as produced by chemisorption. The amine would act as an electron donor, thus decreasing the work function.

As shown on the Pt vs. Al, and Pt vs. Teflon curves in the Appendix, the rate of adsorption of amine on Pt is evidently more

FIGURE 1
AL WITH BUTYRIC ACID
AND WITH ETOH

FIGURE 2
AL WITH H_2O

FIGURE 3

AL WITH 1-NITROPROPANE

FIGURE 4

AL WITH BUTYLAMINE

rapid than on the Al - as evidenced by the sharp dip followed by a slower rise shown on the composite curve. The process of adding the curves, ordinate by ordinate, in effect accentuates any slightly doubtful portion of the separate curves. (i. e. those with a large slope). It is felt that this inherent plotting uncertainty explains the cusp in the curve of figure 4. This same plotting uncertainly also is probably responsible for the cusp shown on the Al with H_2O curve of figure 2. In addition, the initial rise of figure 2 can be explained by noting that the Pt vs. Teflon with H_2O curve (figure 26 in Appendix, time 0-1 min.) indicates slight water adsorption initially on the Teflon coating. After five minutes the curve begins to show a negative CP change, indicating an increase in the work function. This again is expected, if it is reasonable to suppose that the H_2O molecule adsorbs with oxygen adjacent to the surface.

The butyric acid, ethanol, and nitropropane curves (figures 1 and 3) all show a decrease in contact potential, indicative of the expected increase of work function. The nitropropane curve, figure 3 is particularly interesting in that it is representative of the NP effect on all the test metals. Note that figures 3, 6 and 10 are practically identical in form, direction and magnitude. The conclusions reached previously regarding dipole orientation

FIGURE 6
CU WITH
NITROPANE

NP

FIGURE 5
CU WITH BUTYRIC ACID

BuCO₂H

TIME (MIN)

FIGURE 7

CU WITH BUTYLAMINE

thus gain credence when it is considered that by far the most reasonable picture of the manner in which the NP molecule is adsorbed on the metal is with the $-NO_2$ group down with the electronegative oxygens adjacent to the surface.

Copper

Figures 5, 6, and 7 show the effect of the indicated vapors on copper. The effect of H_2O on the Pt vs. Cu system was studied during the early course of the investigation and unfortunately comparable pressures at which to add the curves were not available. Qualitative evaluation of the applicable curves (Figures 17 and 26 in the Appendix) indicate however, that the contact potential of Cu with H_2O will show a slight downward drift indicating an increase in the work function.

Figure 19 in the Appendix shows the effect of butylamine on Pt vs. Cu. Here the relative adsorption rates are indeterminate; however, addition of the Teflon curve results in the characteristic rapid rise followed by slight fall off of contact potential. (Figure 7) Again, this is indicative of a decrease in the work function of the copper.

Butyric acid, (Figure 5) departs from anticipated behavior in that it shows a contact potential rise, indicative of a work function decrease. The explanation may lie in a chemisorption

effect. Since Cu is coated with an oxide film it is not unexpected that butyric acid would tend to chemisorb. This is borne out by the curve shown in figure 20, where the rise in $\triangle$ CP noted initially is approximately equal to the irreversible change recorded after pumping on the system for 46 hours.

Gold

Figures 8 through 11 show the effect of the indicated vapors on gold. The ethanol, nitropropane, and butylamine curves (figures 9, 10, and 11) are similar in form to their counterparts with Al and Cu. The composite Pt vs. Au with butylamine curve (Figure 19, Appendix) is interesting in that it shows an apparent reversal of relative adsorption rates in comparison to the composite Pt vs. Al with butylamine curve. (Fig. 15, Appendix)

Anderson and Alexander, (13) who have investigated the adsorption of ethanol on Au using the Zisman method, found an increase of 50-100 mv. in the work function of gold. This compares favorably with the value of 50-55 mv. found here. However, they claim the effect is due to formation of a dipole layer oriented negative away from the metal surface. This is opposite to the orientation postulated in the rules given previously.

The effect of H_2O and butyric acid on gold appear to be somewhat erratic, at least on the final "added" curves. This may be

due to equal adsorption effects on the composite and Teflon systems. After 23 hours of pumping the $\triangle$ CP of the Pt vs. Au with H_2O system had a value of only -6 mv., while after 21.5 hours of pumping the $\triangle$ CP of the system with butyric acid had a value of zero. (See Fig. 21 and 25, Appendix)

Platinum

The Teflon series of curves (Figs. 26-30, Appendix) in addition to their use to separate adsorption effects in the Pt vs. Test metal series, of course show directly the effect of the various vapors upon the work function of platinum.
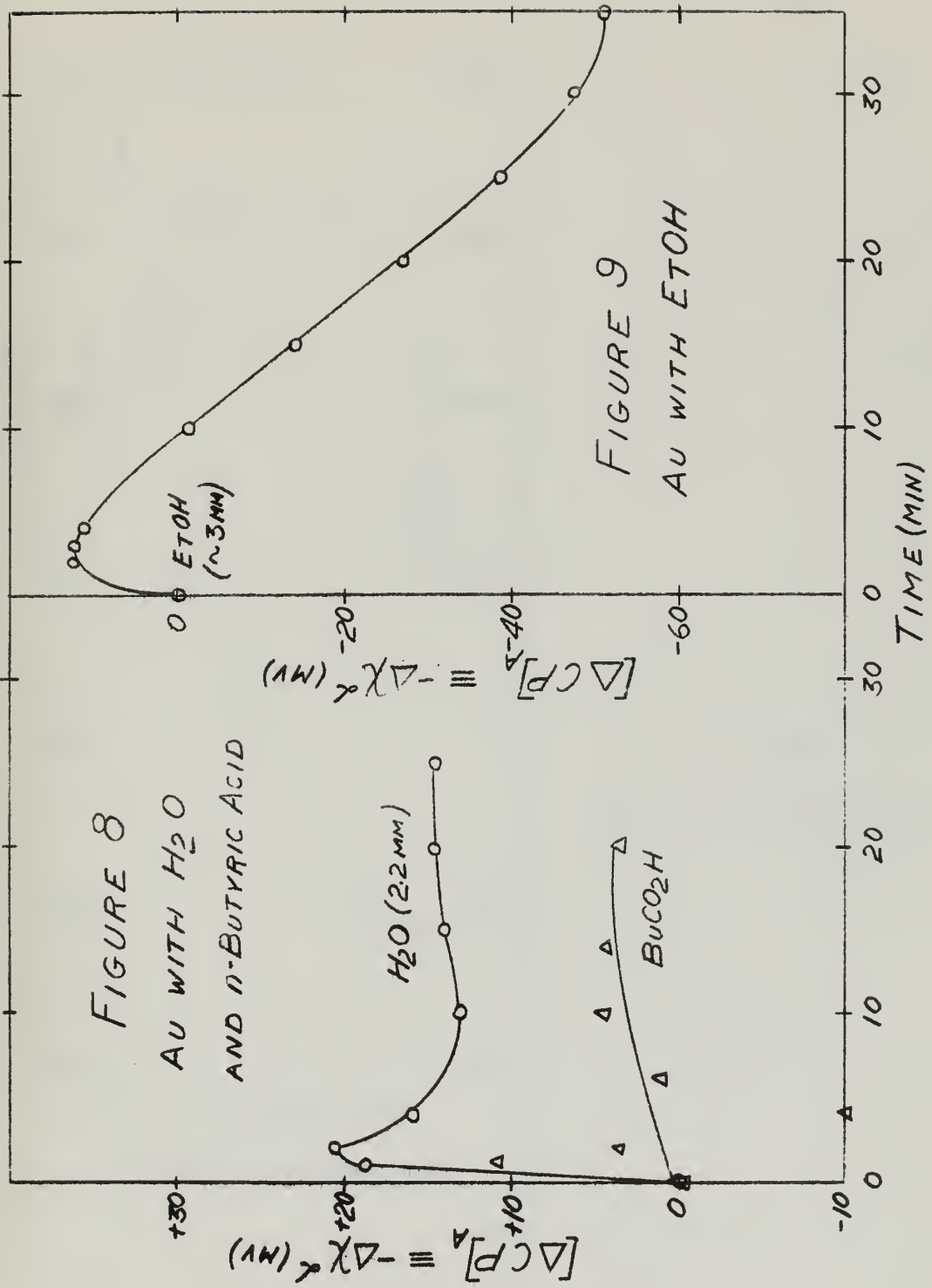
Nitropropane and butylamine, (Figs. 28 and 29) again show the characteristic curve form that was noted with these vapors on Al, Cu, and Au.

Figure 30, butyric acid on Pt, would indicate that there is a small amount of adsorption taking place on the Teflon immediately after dosage. This is indicated by the dips in the curve at time 0-5 minutes, and again at 95-100 minutes. After time 22, at the second dosage, the curve rises showing a decrease in work function. This is not the expected effect and cannot be explained.

Adsorption of the H_2O and EtOH (Figs. 26 and 27) show the expected effect of work function decrease.

FIGURE 9
AU WITH ETOH

FIGURE 8
AU WITH H₂O
AND n-BUTYRIC ACID

FIGURE 11

AU WITH BUTYLAMINE

FIGURE 10

WITH NITROPROPANE

NP (0.3 MM)

$BuNH_2$ (0.6MM)

$[\Delta CP]_A \equiv \Delta \chi^\alpha$

$[\Delta CP]_A \equiv -\Delta \chi^\alpha$

TIME (MIN)

Physical Adosrption vs. Chemisorption

The question arose in this investigation as to whether a determination could be made in regard to the amount of vapor physically adsorbed versus that chemisorbed. Frost and Hurka (8) conclude that plots of contact potential versus relative pressure are equivalent to adsorption isotherms, therefore it can be said that contact potential is proportional to the volume of vapor adsorbed. Anderson and Alexander (13), using the Zisman method, plotted values of contact potential versus relative pressure for the systems Au-Au, Au-Cu, and Au-Ni, using the vapors of H_2O, isopropyl alcohol and ethyl acetate. They obtained so-called "hysteresis loops" which after an initial, irreversible change, retraced the same curve. This initial, irreversible change, which varied somewhat for different methods of surface preparation, was felt to be due to chemisorption.

In order to make an evaluation of possible chemisorption effects during these runs, the system was pumped down for approximately 22 hours (and in a few cases, as long as 72 hours) following a run. The irreversible contact potential changes were thus determined and are shown in Table I. The results of the addition of the composite system irreversible values to the Teflon system values are also given. Note that the values given in the Teflon column represent, in fact, the work function change due to chemisorption of the various vapors on Pt.

Table I

"Ultimate" Contact Pot. Change (mv)

Vapor	System	Time	Composite	Teflon	"True"
H_2O	Pt-Al	24 hrs.	+61	-67 (72 hrs)	-6
	Pt-Cu	22.5	+17	-67	-50
	Pt-Au	23	-6	-67	-73
EtOH	Pt-Al	17.5	-9	-140 (21 hrs)	-149
	Pt-Cu	---	--		---
	Pt-Au	22	+13	-140	-127
NP	Pt-Al	23	- -44	-140 (24 hrs)	-184
	Pt-Cu	22	+3	-140	-137
	Pt-Au	24	-29	-140	-169
$BuNH_2$	Pt-Al	21	+47	-160 (24 hrs)	-113
	Pt-Cu	22	+18	-160	-142
	Pt-Au	20	+14	-160	-146
$BuCO_2H$	Pt-Al	22.5	-65	-150 (70 hrs)	-215
	Pt-Cu	46	+45	-150	-105
	Pt-Au	21.5	0	-150	-150

This table indicates that chemisorption occurred with all vapors
on all the test metals; water showing the least amount by a considerable
margin. Nitropropane shows the greatest average amount (-163 mv)
closely followed by butyric acid (-157 mv.). The butylamine results
are interesting in that they show a final negative contact potential
charge, indicating an increase in work function due to chemisorption.
Apparently then the initial work function decrease (figures 4, 7, and
11) is a transient effect due to physical adsorption alone. This final

35.

result tends to lead to the conclusion that the initial work function <u>decrease</u> is due only to dipole orientation plus end toward the metal, and not to the alternative chemisorption effect advanced as an explanation.

Evidentally, there is very little chemisorption of water on any of the test metals; this can be explained by the fact that the metal surfaces had already been well exposed to water vapor in the air.

Kinetics

In this investigation an empirical mathematical analysis was undertaken midway in the study. The dosage portions of the composite curves of Pt vs. Al, with nitropropane, butylamine, and butyric acid were evaluated, and shown to follow, to a good approximation, 1st order kinetics. An attempt was made to evaluate the kinetic order of the final Al curves with the above vapors, however this was unsuccessful. It is felt that with more exact control of pressure and temperature variables, and the use of a proven, non-adsorptive plate coating, a detailed analysis of the kinetics of adsorption effects on the contact potential could be undertaken with a fair assurance of success.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The value of the contact potential method in studying
adsorption phenomena, as cited by Frost and Hurka, Mignolet, and
others, is too well known to need reiteration here. It has become
a standard technique in the field.

A summary of the adsorption effects on the work function
found in this investigation is given in Table II below. In addition
the deduced dipole orientation is given.

Table II

Vapor	Work function change on:			Dipole Orientation Toward Metal		
	Al	Cu	Au	Al	Cu	Au
H_2O	Increase	Increase	Decrease[2]	-	-	+
EtOH	Increase	---	Increase	-		-
NP	Increase	Increase	Increase	-	-	-
$BuNH_2$	Decrease	Decrease	Decrease	+	+	+
BuCOOH	Increase	Decrease[3]	Decrease[2,3]	-	+[4]	+[4]

[2] Slight
[3] Possible chemisorption effect
[4] Resulting from chemisorption effect

Recommendations

The following recommendations for improving the accuracy of the equipment, and thereby the results, are given:

1. Evaluate Teflon Performance more precisely, to determine the effect of any adsorption on this coating.

2. Reduce size of the vacuum chamber with a view towards obtaining a better vacuum.

3. Design a more precise means of pressure measurement, and vapor introduction.

4. On the electrical side, an automatic contact potential balancing device, coupled with an automatic recorder, possibly using the principles of servo-mechanisms, would yield a more precise delineation of CP changes and in addition leave the operator free to concentrate on pressure and temperature effects.

BIBLIOGRAPHY

1. Adam, N.K., "The Physics and Chemistry of Surface" Oxford University Press (1938), p. 308

2. Righi, J. Phys, Rad., $\underline{7}$, 153 (1888)

3. Anderson and Morrison, Phil. Mag., $\underline{24}$, 302 (1912)

4. Zisman, Rev. Sci, Inst., $\underline{3}$, 367 (1932)

5. Antes, N.L., Doctoral Dissertation, "Behavior of Evaporated Metal Films at Low Pressure", Univ. of Texas, Austin, Tex. (1951)

6. Mignolet, J.C.P., Disc. Faraday Soc., $\underline{8}$, 105 (1950)

7. Porter, E.F., J. Am. Chem. Soc., $\underline{59}$, 1883-8, (1937)

8. Frost and Hurka, J. Am. Chem. Soc., $\underline{62}$, 3335, (1940)

9. Yoneda, Y., Oyo Butsuri $\underline{22}$, 307 (1953); C.A. $\underline{48}$, 3752 (1954)

10. Duhn, J.H., Ann. Physik $\underline{43}$, 37-52, (1943)

11. Adam, N.K. loc. cit. p. 303

12. Porter, E.F. and Wyman, J., J. Am. Chem. Soc., $\underline{59}$, 2746 (1937)

13. Anderson J.R. and Alexander A.E., Austr. Journal of Chem., $\underline{6}$, 109-122 (1953)

14. Hackerman, N. and Lee, E.H., Tech. Report to ONR, "The Effect of Gases on the Contact Potentials of Evaporated Metal Films", p. 16. Nonr-375 (02), 1 Jan. 1955, Univ. of Texas.

15. Zisman, W.A. and Ellison, A.H., J. Phys. Chem. $\underline{58}$, 260 (1954)

VITA

Deming Waite Smith was born July 1, 1923, at Worcester, Massachusetts, the son of Clarendon Waite and Margaret Deming Smith. He attended the public schools of Worcester, and Boston, Mass., and graduated from the Boston English High School in June 1941. He attended the Massachusetts Institute of Technology, under a Hayden Scholarship, from September 1941 to March 1943 when he entered the Navy as an aviation cadet. He received a Fleet Appointment to the United States Naval Academy and entered in June 1944 with the class of 1948-A. In June 1947 he graduated with the degree of Bachelor of Science and was commissioned an Ensign in the Regular Navy.

During his service with the Fleet Mr. Smith has served on the USS ROGERS (DDR876), the USS R. K. HUNTINGTON (DD781), and the USS TIDEWATER (AD31). From August 1952 to June 1954 he attended the United States Naval Postgraduate School, Monterey, California, graduating with the degree of Bachelor of Science in Electrical Engineering. His present rank in the Navy is Lieutenant.

Mr. Smith was married in July 1950 to the former Carol Elizabeth Peeling of Waltham, Mass. They have two children, Brooke Kincaid, age 2, and Bradford Deming, age 5 months.

APPENDIX

FIGURE 12
Pₜ⁻ vs Aₗ⁺ with EtOH

FIGURE 13
P_T^- vs AL^+
with H_2O

Figure 14
Pt⁻ vs Al⁺ with
1-Nitropropane

FIGURE 15

PT^- vs AL^+ with
1-BUTYLAMINE

FIGURE 16

PT⁻ vs AL⁺ with n-BUTYRIC ACID

FIGURE 17
P_T^- vs Cu^+
WITH H_2O

FIGURE 18
Pt⁻ vs Cu⁺
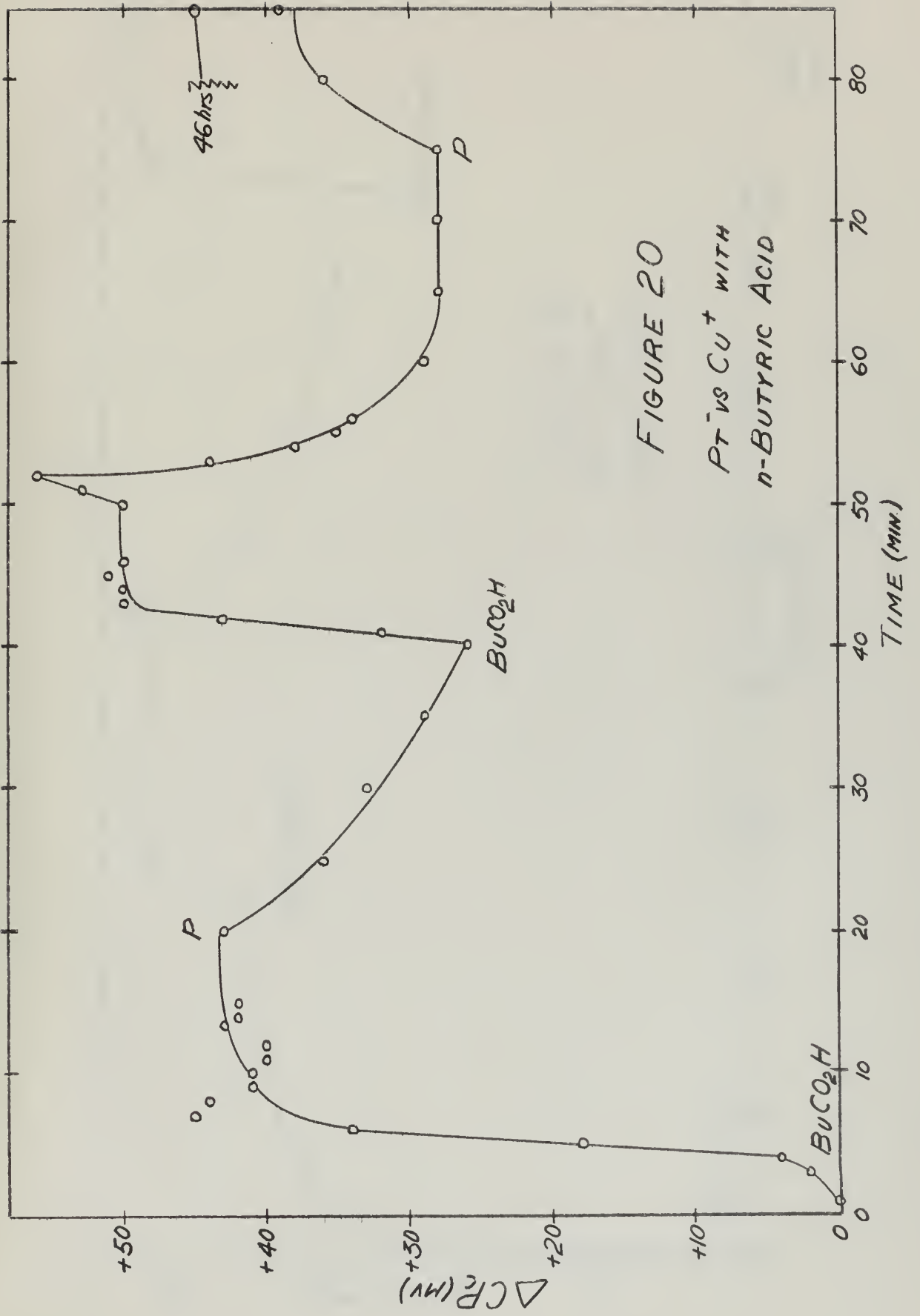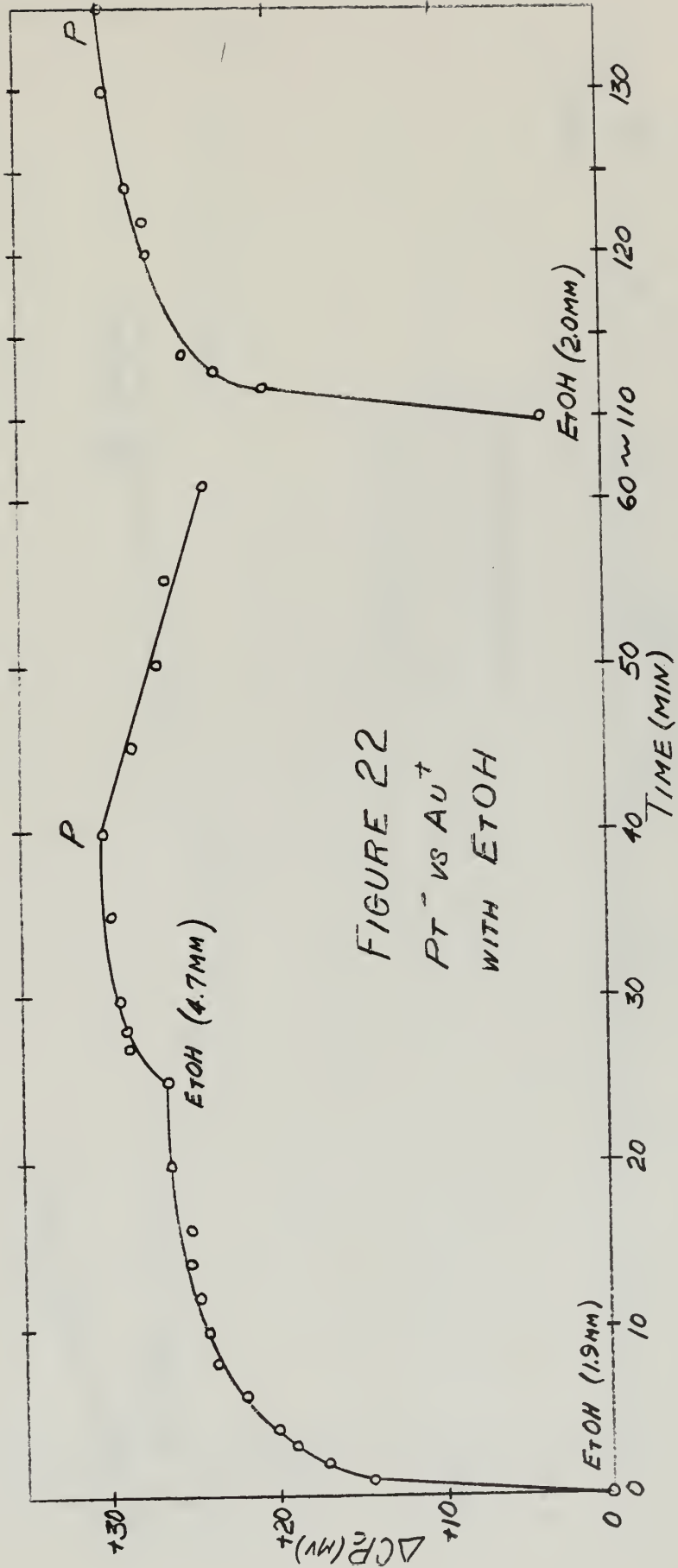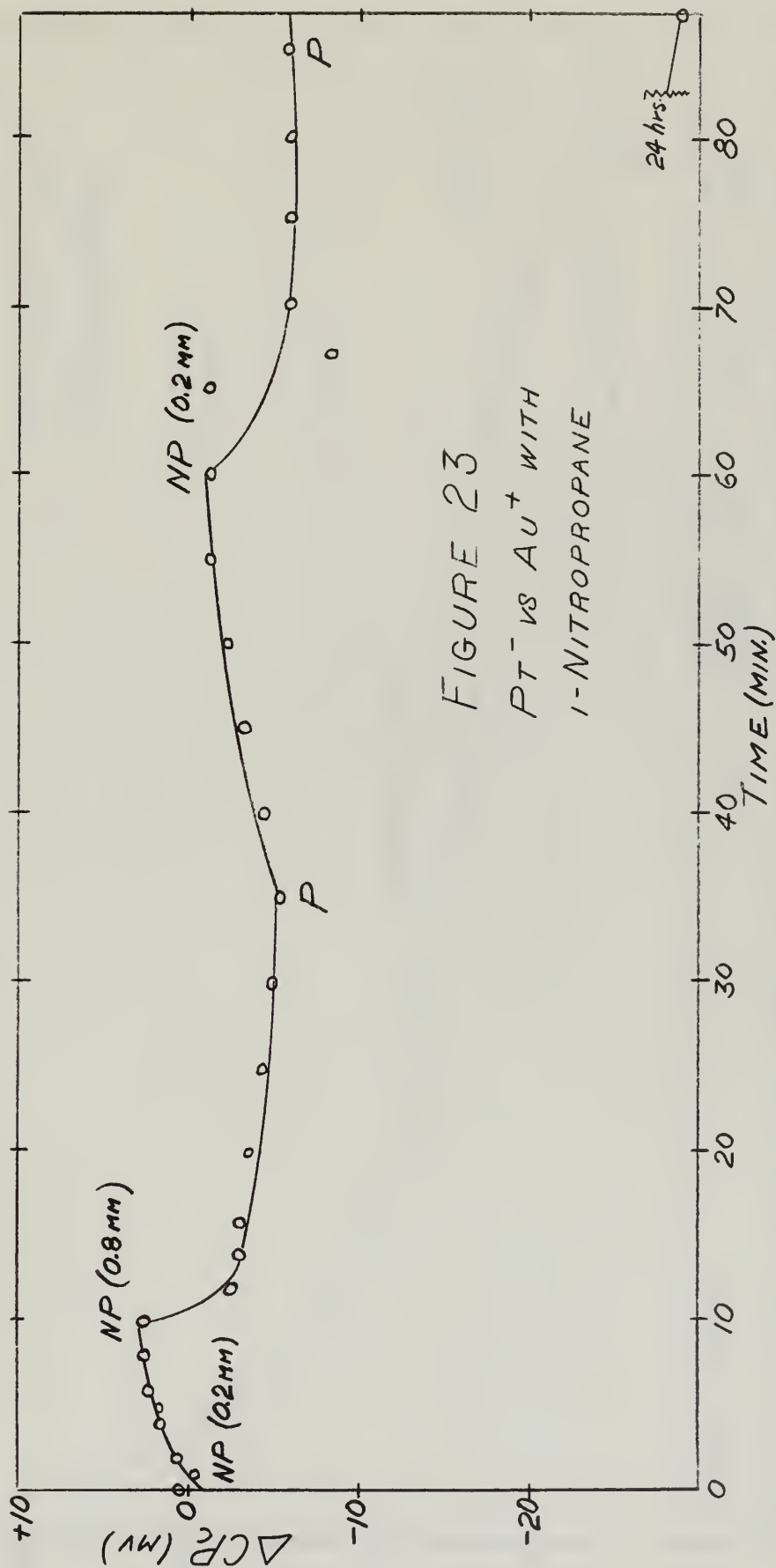
WITH 1-NITROPRANE

FIGURE 19

Pt⁻ vs Cu⁺
WITH n-BUTYLAMINE

FIGURE 20

Pt⁻ vs Cu⁺ WITH
n-BUTYRIC ACID

FIGURE 21
PT⁻ VS AU⁺
WITH H₂O

FIGURE 22
PT⁻ vs Au⁺
WITH EtOH

FIGURE 23

PT⁻ vs Au⁺ WITH

1-NITROPROPANE

FIGURE 24

PT⁻ vs AU⁺ WITH
n-BUTYLAMINE

FIGURE 25
PT⁻ vs AU⁺ WITH
n-BUTYRIC ACID

FIGURE 26
PT$^+$ VS TEFLON$^-$
WITH H$_2$O

FIGURE 27
Pt⁺ vs TEFLON
WITH ETOH

FIGURE 28
Pt^+ vs TEFLON$^-$
WITH 1-NITROPROPANE

FIGURE 29
PT⁻ VS TEFLON⁺
WITH n-BUTYLAMINE

FIGURE 30

P_T^+ vs Teflon with
n-Butyric Acid