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CHANGES IN PHOTOELECTRIC WORK FUNCTION OF MOLYBDENUM DUE TO ADSORPTION OF CARBON MONOXIDE

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ABSTRACT

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The photoelectric work function of a polycrystalline molybdenum sample in both the clean state and during chemisorption of carbon monoxide is found experimentally. The experimental procedure is outlined and results are compared to previous work and predicted values. A decrease in the rate of change of work function of molybdenum upon exposure to carbon monoxide after ion bombardment is attributed to mechanical roughening of the surface during bombardment.

Background discussion is presented in the fields of adsorption, surface physics and photoelectric measurements. The change in surface potential due to the addition of a dipole layer is calculated.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION AND PROBLEM STATEMENT

When a solid and a gas are brought into contact, it is always noted that there is an increase in the concentration of the gas phase near the solid surface. This behavior is given the name adsorption and it is common practice to refer to the solid as the adsorbent and the gas which is bound to the surface as the adsorbate.

Experience has shown that there are two distinct bonding mechanisms responsible for adsorbing gas on a solid surface and adsorption is classified according to the type of bonding which occurs. Physical adsorption, which resembles condensation, involves the attraction of inert particles to one another by means of van der Waals forces which are electrical in nature but do not include charge transfer. On the other hand, chemical adsorption or chemisorption describes a bond in which there is either a permanent exchange or sharing of electrons between adsorbent and adsorbate. Chemisorption denotes a chemical reaction between the gas and solid phases. It is well established(1) that the type of adsorption discussed in this report, i.e. between carbon monoxide and molybdenum, is chemisorption.

More explicitly, the change in photoelectric work function of molybdenum as carbon monoxide is adsorbed is of interest. The work function is expected to change because it is a sensitive indicator of the surface condition of a metal and adsorption will have an effect on the surface condition. By applying solid state theory to work function behavior it is possible to learn something of the bonding mechanism which exists between metal and adsorbed gas.

The surface states of a clean metal and the effects of adsorbates have long been of interest to both physicists and chemists. Phase interactions and the kinetics of most chemical reactions are controlled by surface conditions of the constituents. Since the electrons which determine the surface states cannot be observed directly, researchers have had to examine related phenomena which can be measured and then interpret their results in terms of electronic states and perturbations of these states by adsorbed gases. These theories are supplemented by others which are derived from mathematical models of simple systems. As more combinations of solid and gas are treated, the basic mechanism of adsorption will become better understood. It is to this end that the investigation reported in this thesis has been undertaken.

Considerable knowledge in the fields of photoelectric work function measurement, preparation of clean surfaces and control of adsorption rates was gained during this research. Several improvements on the apparatus were made and more are suggested; in addition, new areas of interest associated with the work already done have arisen. It is hoped that this work can be continued with refinements, perhaps to include work with single crystals, to become the basis for a doctoral thesis.

CHAPTER II

BACKGROUND

I. CLEAN SURFACE STRUCTURE

In order for a metallic surface to take up gas by chemisorption it must possess some unoccupied adsorption sites. In practice this state may be achieved in a number of ways. A small metal sample may be heated in a vacuum to the point where it evaporates and is allowed to condense on a cool substrate. The resulting film will be free of adsorbed gas and have a high surface to volume ratio which may be helpful in adsorption studies. Another common method is to place the metal in a vacuum and heat it strongly until all surface contamination has been volatilized and removed. This method is suitable only for metals with very high melting point for otherwise some of the surface contaminants may have a ~~higher~~ lower vapor pressure than the metal itself. A third method is to bombard the surface with inert gas ions which mechanically remove surface layers of the metal and with them any adsorbed gas.[2]

The atomically clean metal surface has some significant properties which are vital in the study of adsorption and its effect on work function. Ideally the metal surface would be a single plane of a perfect crystal exposing a regular array of metal atoms. In practice the surface consists of many crystals each with its own surface plane and the overall arrangement of exposed atoms is far from regular. Each surface plane has a different interatomic spacing and there are often imperfections in the individual crystal faces. These imperfections may be classed as physical, which include vacancies, interstitial sites, and various types of dislocations; or chemical, which denote the presence of foreign atoms in the crystal. These foreign atoms may be present as impurities or intentionally added as alloying agents.[3]

Since the surface represents a break in the symmetry of a crystal, a change from the bulk properties is expected in this region. For adsorption studies the most notable change occurs in the electron distribution with respect to the metallic nuclei. In the crystal interior, electrons associated with each nucleus are confined quite closely by the presence of neighboring nuclei with their electron clouds. Electrons associated with the surface atoms are not bounded by other electron clouds on one side and as a result they tend to spread toward the vacuum region. This behavior is shown schematically in Figure 1.

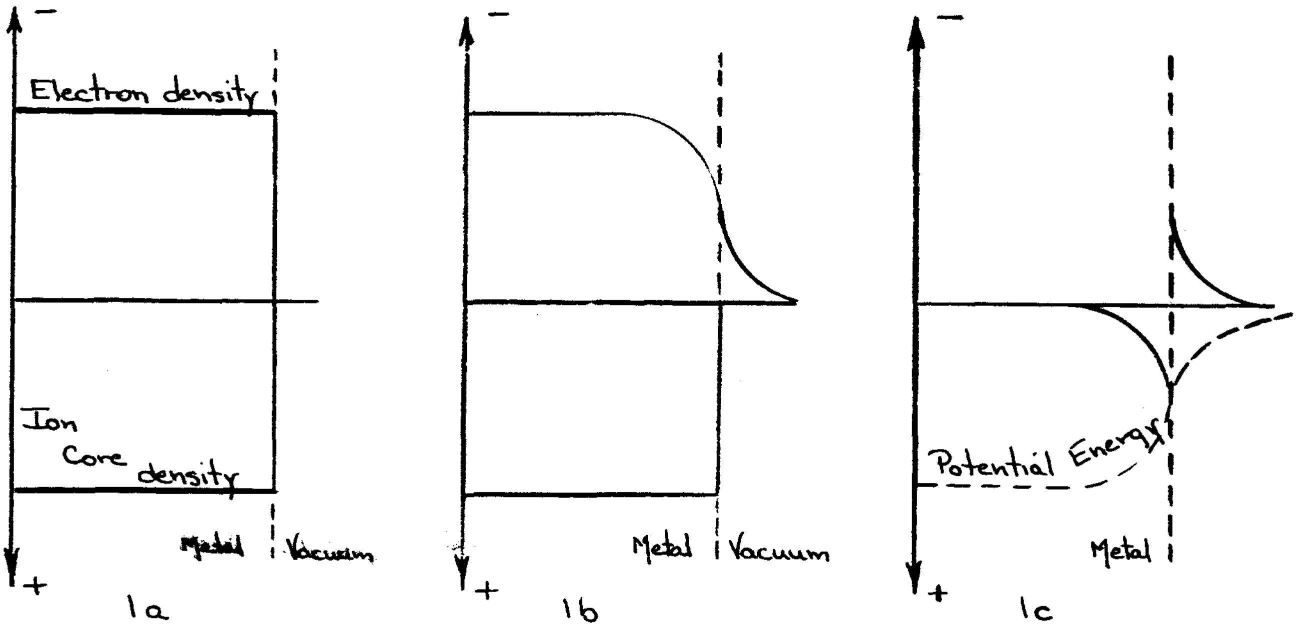


Figure 1. Electron distribution and potential energy at a metal surface.

Figure 1a shows the electron and ion core distribution at the surface if there were no shifting; the metal-vacuum boundary line is understood to be the electron cloud limit for the surface atoms if they behaved as interior atoms. Figure 1b schematically illustrates the spreading of the electron cloud into the vacuum region while the ion core density remains unchanged. To see the net effect of this shift it is necessary to subtract state 1a from state 1b obtaining Figure 1c which is equivalent to a charge double layer with negative side away from the metal. This surface double layer is of importance in connection with the metal's work function properties, for the electron potential energy must increase in moving from the metal interior to the vacuum region; this is shown by the curved broken line in Figure 1c.

II. WORK FUNCTION

The definition of work function developed here follows that of Culver and Tompkins[4] and Herring and Nichols.[5] The most convenient starting point is to define the so-called electrochemical potential of the n electrons in a single isolated system of temperature T and volume V with total internal energy U and entropy S. In this case the electrochemical potential $\bar{\mu}$ is given by

$$\bar{\mu} = (\partial F/\partial n)_{T,V}$$

where F is the Helmholtz free energy of the system. As defined here $\bar{\mu}$ has the units of energy per electron. In the case of a conductor $\bar{\mu}$ may be altered by external conditions such as shifting charges outside the conductor or adding a dipole layer to its surface. It is convenient, therefore, to define the chemical potential μ as

$$\mu = \bar{\mu} + e\Phi_{\text{internal}}$$

where Φ may be regarded as the electrostatic potential within the volume. Now μ is a function only of the internal state of the system and cannot vary with surface or external changes.

The work function $e\varphi$ may now be defined as the difference between the electrochemical potential $\bar{\mu}$ of the electrons within the conductor and the potential energy $(-e\Phi_{\text{external}})$ of the electrons in a vacuum just outside the conductor's range of influence. It is assumed[6] that there are no significant interactions with the surface beyond a distance of 10^{-4} cm. In symbols the definition is

$$e\varphi = -e\Phi_{\text{external}} - \bar{\mu} = e\Phi_{\text{internal}} - e\Phi_{\text{external}} - \mu$$

It is customary to call $e\Phi_{\text{int}} - e\Phi_{\text{ext}}$ the outer work function and the chemical potential μ the inner work function. Dividing the last equation by e gives

$$\varphi = \Phi_{\text{int}} - \Phi_{\text{ext}} - \frac{\mu}{e}$$

Here the expression $\Phi_{\text{int}} - \Phi_{\text{ext}}$ is referred to as the surface potential since it represents the potential change across the surface and will be affected by changes in the surface condition such as the addition of a dipole sheet in the form of adsorbed gas.

Potential Due to Dipole Sheet

The potential due to a double layer or dipole sheet made up of ∂ charge per unit area can be computed using elementary electrostatic theory. Imagine a parallel plate capacitor with charge density ∂ and plate separation d; Gauss' law gives the field between the plates as

$$\int \vec{E}\cdot\vec{n}\, da = 4\pi \int \partial\, da \quad \text{(Gaussian units)} \tag{1}$$

When the electric field between the plates is constant and perpendicular to the plates (1) reduces to

$$E = 4\pi\partial \qquad (2)$$

Multiplying (2) by d yields

$$Ed = V = 4\pi\partial d = 4\pi \frac{qd}{A} \qquad (3)$$

but qd is the dipole moment associated with each charge pair and A is the area per dipole. In order to obtain V in volts with qd = β in Debye units (1 Debye unit = 10^{-18} esu - cm) the right side of (3) must be multiplied by 3×10^{-16}, so finally

$$V = 4\pi \frac{\beta}{A} \times 3 \times 10^{-16} \qquad (4)$$

As an example, the surface potential due to carbon monoxide may be computed using (4) and assuming the dipole moment of CO to be 0.10 Debye unit.[7] This is the dipole moment of free CO and does not take into account electron transfer due to bonding with the metal surface. The area per dipole will be taken to be 1.14×10^{-15} cm^2 which is the site area for polycrystalline molybdenum surfaces.[8]

$$V = 4\pi \times \frac{0.10}{1.14 \times 10^{-15}} \times 3 \times 10^{-16} = 0.33 \text{ volts}$$

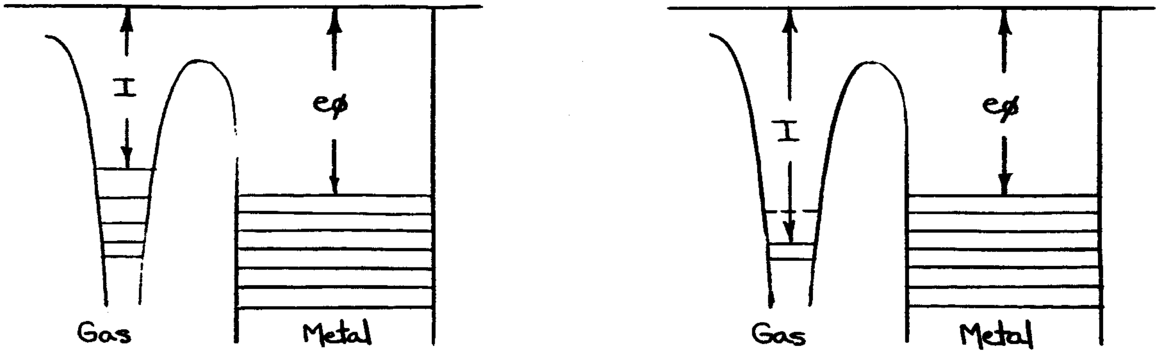
Since the oxygen end of CO is negative, V will add to the work function if the carbon atom is near the surface and decrease it for the reverse orientation.

III. CHEMISORPTION

As stated in the introduction, chemisorption involves the formation of a chemical bond between adsorbent and adsorbate which is not present in the case of physical adsorption. It is usually possible to say on an experimental basis whether a certain system represents physical or chemical adsorption. There are several methods available, the most popular being a measurement of the heat of adsorption. For a particular gas there will be a distinct gap between the lowest heat for chemisorption and the highest heat for physical adsorption. With carbon monoxide on metals, for example, heats of chemisorption exceed 20 Kcal/mole while heats of physical adsorption are less than 6 Kcal/mole.[9]

If any activation energy is required for the adsorption process it must be chemisorption because physical adsorption requires no activation energy. Often the type of adsorption may be determined from the conditions under which it occurs, for chemisorption will take place only on a clean surface and is usually limited to monolayer thicknesses.

There are two types of bonds associated with chemisorption. One is heteropolar or ionic and denotes the ionization of metal and gas atoms as a result of a permanent displacement of an electron from one to the other; the second is homopolar or covalent and denotes an electron sharing arrangement. In ionic bonding there are two possibilities, either the metal or the gas may act as electron donor. Figure 2 will help in deciding which type of bond is likely to occur for different metal-gas combinations.



2a

2b

Figure 2. Energy level diagrams for two metal-gas combinations

If the ionization energy I of the adsorbed atom or adatom is less than the metal work function $e\varphi$ as shown in Figure 2a an electron may exothermally transfer from adatom to metal. Similarly if $e\varphi$ is less than I as in Figure 2b an electron may be transferred from metal to adatom. In both cases an ionic bond will be formed; however, a covalent bond could result from the condition shown in 2b. This would happen if there exists an unoccupied level (dotted line) in the adatom with nearly the same energy as an occupied level in the metal; then an electron from the occupied level may be shared between the two phases in a covalent bond. Another possibility is that both metal and adatom may contribute an electron with unpaired spin to form a so-called binding orbital.[10] As might be expected the condition of sharing an electron or forming a binding orbital will produce a smaller dipole or double layer effect than would result from ionic bonding. The adsorbate may have its own dipole moment and this must be added to the bond's dipole moment (with proper regard for sign) to obtain the total effect of chemisorption on the surface potential. Unfortunately the chemisorption bond seriously disrupts the electronic configuration of the adsorbed molecule so its dipole moment in the adsorbed state may be quite different from that in the free state.

Although the discussion so far has suggested a one to one ratio of metal atoms to adatoms with a bonding mechanism as shown in Figure 3, this is not always the case. For example, there is strong evidence[11] due to infrared studies that a carbon monoxide molecule can bond to two metal atoms by one of the three double site mechanisms shown in Figure 3.

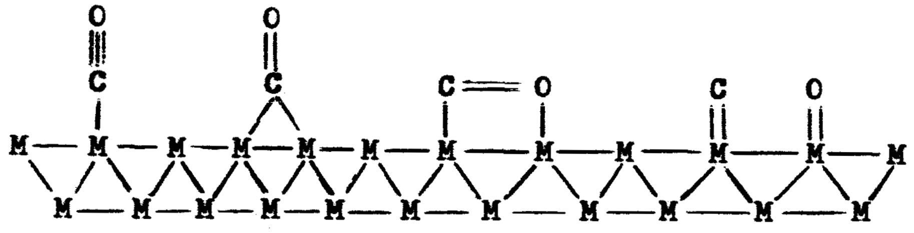
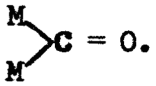


Figure 3. One and two site bonding mechanisms for carbon monoxide.

On some metals, namely molybdenum and rhodium, the two site bonding seems to account for nearly all of the adsorbed gas; while on iron and tungsten there is a mixture of one and two site mechanisms. Eischens and his coworkers[12] have obtained infrared spectra of CO adsorbed on various metals and have reached the following conclusions:

1. Both one and two site mechanisms occur to some extent on nickel, platinum and palladium.
2. Single site mechanism should be represented by $M - C \equiv O$.
3. Two site mechanisms should be represented by  $\begin{matrix} M \\ M \end{matrix} \!> C = O$.
4. The relative amounts of one and two site adsorption depend on the metal and the coverage.

CHAPTER III

MEASURABLE EFFECTS OF CHEMISORPTION

I. HEAT OF ADSORPTION

The amount of heat released when a quantity of gas is adsorbed is called the heat of adsorption. This is indicative of the strength of the chemical bond formed during the adsorption process. Heats of adsorption are normally measured calorimetrically by admitting a small amount of gas to the clean adsorbent surface and measuring the heat liberated. This method yields an integral heat or average heat over the coverage produced. By reducing the amount of gas introduced in each step the measured heats approach a differential heat which is the precise value for a particular coverage.

II. WORK FUNCTION

Since surface potential and work function are so closely related it is not surprising that work function measurements are a common means of studying adsorption.[13] By noting changes in work function with adsorption it is possible to infer the electronic bonding configuration present. If the adsorbed gas has a permanent dipole moment it may be possible to tell how the gas molecules are oriented on the surface and if their dipole moment is altered during adsorption.

There are three principal methods of measuring work functions and any comprehensive review of surface potentials[14] will have data from each of these sources. One of these methods, the photoelectric measurements, was used in this investigation and will be discussed in a later section. A more recent development is field emission microscopy[15] in which the metal sample is made the cathode in a strong electric field. This modifies the surface barrier so there exists a finite probability for an electron to tunnel through the barrier and become free of the metal. The theoretical expression for this is the Fowler-Nordheim equation:

$$\frac{i}{V^2} = Abe^{-\frac{c\varphi^{3/2}}{KV}}$$

where i is the current, V the applied voltage, A the emitting area, $b = 6.2 \times 10^6\ K^2(E_F/\varphi)^{\frac{1}{2}}/E_F + \varphi$; $K = F/V$ where F is the field due to the applied potential and E_F is the Fermi energy and finally $c = 6.84 \times 10^7$. By plotting $\log \frac{i}{V^2}$ against $1/V$, a straight line whose slope is $-\frac{c\varphi^{3/2}}{K}$ should result and from this the value of φ may be deduced. By arranging a fluorescent screen behind the anode in the manner of a cathode ray tube it is possible to obtain a crude surface pattern with a linear magnification of 10^5 to 10^6.

The third method is that of contact potential difference which has a number of variations all of which are based on the properties of conductors in electrical contact.[17] If two metals with work functions φ_1 and φ_2 respectively are brought in contact by an external circuit, then at equilibrium there will be a potential V between the two surfaces given by $V = \varphi_2 - \varphi_1$. Suppose that the two metal samples form a parallel plate capacitor. Then if the plate spacing is suddenly changed a current surge will be detected in the external circuit. If, however, a source of emf V', provided in the external circuit, is adjusted to exactly offset V, a sudden change in plate spacing will produce no current surge and one may conclude that $V' = V = \varphi_2 - \varphi_1$. If one metal is used as a standard then φ for the other may be determined. The variation described above is known as the capacitor method; others are the magnetron method[18] and the space charge-limited diode method.[19]

Recently Holscher[16] has introduced a method for measuring work function combining field emission and contact potential techniques in which electrons are produced by field emission from a suitable source. After becoming free of the emitter the electrons are slowed and collimated by electric fields before impinging on the collector whose work function is to be found. If the emitter and collector are connected electrically, their Fermi levels are equal and the electrons must overcome the work function barrier $e\varphi$ of the collector before being collected. By putting a source of emf in the external circuit connecting emitter and collector and slowly raising the collector potential until current flows in the circuit, it is possible to determine the collector work function because this is just equal to the energy supplied to the electrons by the external emf whose voltage is known. The accuracy of this method is estimated to be ± 0.01 eV.

III. ELECTRICAL CONDUCTION

Electrical conductivity, while normally considered a bulk property, can yield valuable information on surface conditions when applied to the study of thin metallic films.[20] Because of their high surface to volume ratio thin films will show a measurable change in conductivity if there is an increase or decrease in the number of conduction electrons in the metal due to adsorption. Conductivity measurements have been used to differentiate between bonds which (1) remove electrons from the metal, (2) add electrons to the metal or (3) do not change the number of electrons in the metal. Often this information cannot be obtained from other types of measurement. The experimental procedures involved in getting conductivity data are straightforward provided a suitable film is used. Suhrmann[21] states that the film thickness should not exceed several thousand atomic layers and to achieve this requires careful control of the deposition process.

IV. LOW ENERGY ELECTRON DIFFRACTION

The classic experiment of Davisson and Germer[22] in which the wave character of electrons was confirmed revealed that the method of electron diffraction could be applied to adsorption studies. By using slow electrons with energies of 100 eV or less it is possible to limit the beam penetration and diffraction depth to several atomic layers so surface effects are readily detectable. Patterns of both adsorbate and adsorbent can be observed for low coverages.

There are two experimental methods currently in use for low energy electron diffraction measurements. Farnsworth and Parks[23] use an automated movable Faraday collector for measuring the diffracted beam strength point by point. This method gives precise intensity measurements and a complete set of data may be obtained in about one minute which allows study of slowly changing surface conditions. Scheibner, Germer and Hartman[24] have developed a system in which the diffracted electrons are accelerated by a grid system and strike a fluorescent screen where they produce a pattern of the surface configuration. In this manner it is possible to observe the dynamics of adsorption by rapid sequence photography.

V. FLASH FILAMENT MEASUREMENTS

None of the techniques discussed so far yield information on the amount of gas adsorbed on a surface. One means of obtaining this information would be to admit a known volume of gas to a system and then note departure of measured gas pressure from the theoretical value; this would be due to adsorption. The main difficulty with this method is the inability to differentiate between gas adsorbed on the surface under study and that adsorbed on the rest of the system. This source of error is overcome in the flash filament technique where the sample is rapidly heated to liberate the adsorbed gas while the resulting pressure peak is noted on a gauge of the Bayard-Alpert type. By taking into account the system volume and pumping speed it is possible to calculate the amount of gas which was released. Rapid heating of the sample prevents appreciable release of gas from the surrounding system.

If a sample is initially cleaned and then exposed to a gas at known pressure for a given time before flashing, the sticking probability may be found. Sticking probability is the ratio of gas adsorbed (found from flash filament measurements) to gas colliding with surface (found from kinetic theory). Becker and Hartman[25] found the sticking probability varied from 0.6 to 5×10^{-5} during the formation of a monolayer of nitrogen on tungsten.

A modification of the flash filament technique is used by Redhead[26] and Ehrlich.[27] They heat the sample at a slower rate and are able to note several pressure peaks as the sample temperature rises. By noting the temperature at which a peak occurs they are able to calculate the strength of the bond or heat of adsorption for that particular species. Relative amounts adsorbed are easily noted from the size of the pressure peaks.

VI. RADIOTRACER METHOD

Another experimental method capable of determining the amount of gas present on a surface is radiotracer technique.[28] If the gas being investigated is tagged with a radioactive tracer, for example C^{14} in carbon monoxide, its presence may be detected by a Geiger-Mueller counter. This method has the advantage over the flash filament technique of measuring the gas while it is still on the surface rather than desorbing it first.

CHAPTER IV

PHOTOELECTRIC MEASUREMENT OF WORK FUNCTION

According to the photoelectric theory proposed by Einstein in 1905 an electron in a metal may absorb a photon of energy hf and escape from the metal if the total energy it then possesses is greater than the work required to overcome the potential barrier existing at the metal surface. As shown in Figure 4 the total height of the surface energy barrier is W while at zero degrees Kelvin the most energetic electrons have energy E_F, the Fermi energy. This energy corresponds to the electrochemical potential $\bar{\mu}$ introduced in Chapter III, Section II; where zero energy is taken at infinity.

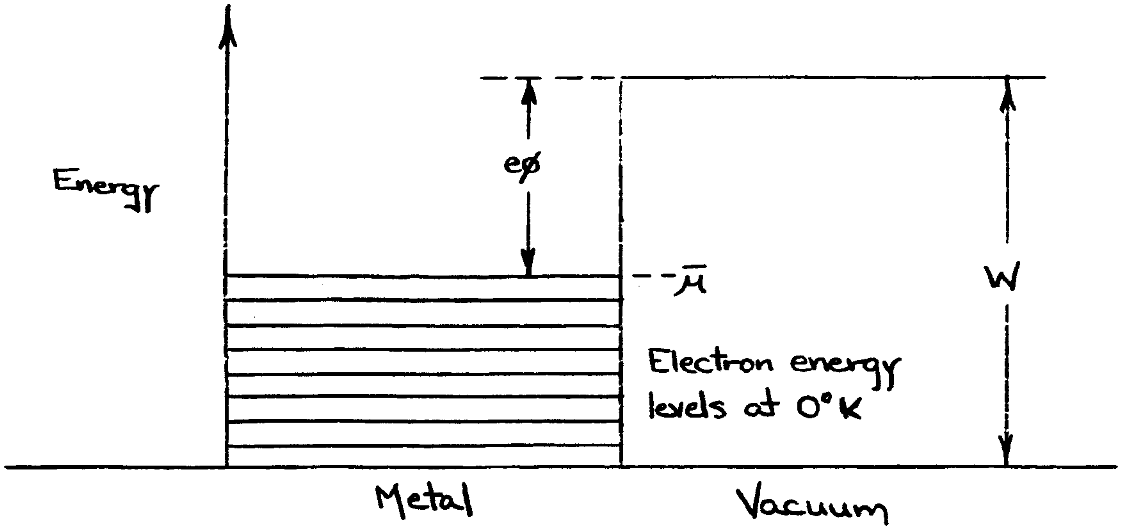


Figure 4. Energy level diagram for photoelectric theory

The minimum photon energy required to free an electron is denoted by hf_o where $hf_o = W - \bar{\mu}$ and f_o is called the threshold frequency. If the electron absorbs a more energetic photon of frequency f it will possess kinetic energy upon leaving the metal given by $\frac{1}{2} mv^2 = hf - (W-\bar{\mu}) = hf - hf_o$.

It would seem that one could measure the barrier height or work function by simply noting the lowest frequency light which would produce photo current. This method would work if the metal were at absolute zero, but for positive temperatures there are some electrons in the metal with energies greater than the Fermi energy. Thus there will be some photocurrent for light of frequency less than f_o, making an accurate determination of f_o impossible by this method. In 1931 Fowler[29] devised a theory which allowed an accurate determination of f_o to be made at room temperature. Assuming the photoelectric effect to be a surface phenomenon, Fowler began with an expression, which had been developed by Nordheim[30], for the number of electrons striking a unit area of surface per second and having energy normal to the surface in the range E_n to $E_n + dE_n$.

$$n(E_n)dE_n = (4\pi mkT/h^3) \log (1 + e^{(\bar{\mu}-E_n)/kT}) \, dE_n \qquad (1)$$

where m = mass of electron

k = Boltzmann constant

T = absolute temperature

h - Planck's constant

At this point Fowler made several simplifying assumptions that overcame most of the mathematical difficulties encountered by the exact theories and allowed the development of a spectral distribution for emitted electrons which was very close to experimental data. He assumed a constant probability α for the absorption of an incident photon by an electron, an emission probability of zero for those electrons whose total energy (initial plus hf) is less than W and one for those electrons whose energy exceeds W.

As a result the number of electrons escaping per second per incident photon from a unit area is given by N where

$$N = \alpha \int_{W-hf}^{\infty} n(E_n)dE_n \qquad (2)$$

and the integrand is given by equation (1).

Carrying out the integration and multiplying by the electronic charge e to change from electrons emitted per second per photon per area to current per photon flux per area one gets

$$I' = 4\pi e\alpha mk^2T^2/h^3 \; p(x) \qquad (3)$$

where $p(x) = \frac{x^2}{2} + \frac{\pi^2}{6} - (e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} - \ldots)$ and $x = (hf - hf_o)kT$.

Taking the logarithm of (3) results in

$$\log I' = B + q(x) \qquad (4)$$

where $B = \log 4\pi e\alpha mk^2T^2/h^3$

$q(x) = \log p(x)$

Now B is a constant for fixed T, as was the case in this research, and q(x) may be plotted against x with T fixed at room temperature. The resulting curve is called a Fowler plot and is shown by the solid line in Figure 5. In an experiment the logarithm of I' is plotted against hf for several values of frequency. The resulting curve must have the same shape and orientation as the Fowler curve when plotted on the same set of axes but it will be displaced by an amount B vertically and by an amount hf horizontally. The work function $e\varphi$ is determined by measuring the horizontal separation between the Fowler curve and the experimental curve in electron volts. Figure 5 shows a typical experimental curve as a dashed line with the vertical and horizontal shifts necessary to make it coincide with the Fowler curve indicated as arrows.

As the work function changes, the photoelectric yield for each frequency will change with the result that a different horizontal shift will be required to make the experimental curve coincide with the Fowler curve. By this means changes in work function may be followed provided they are not so rapid that an appreciable change occurs during an individual run.

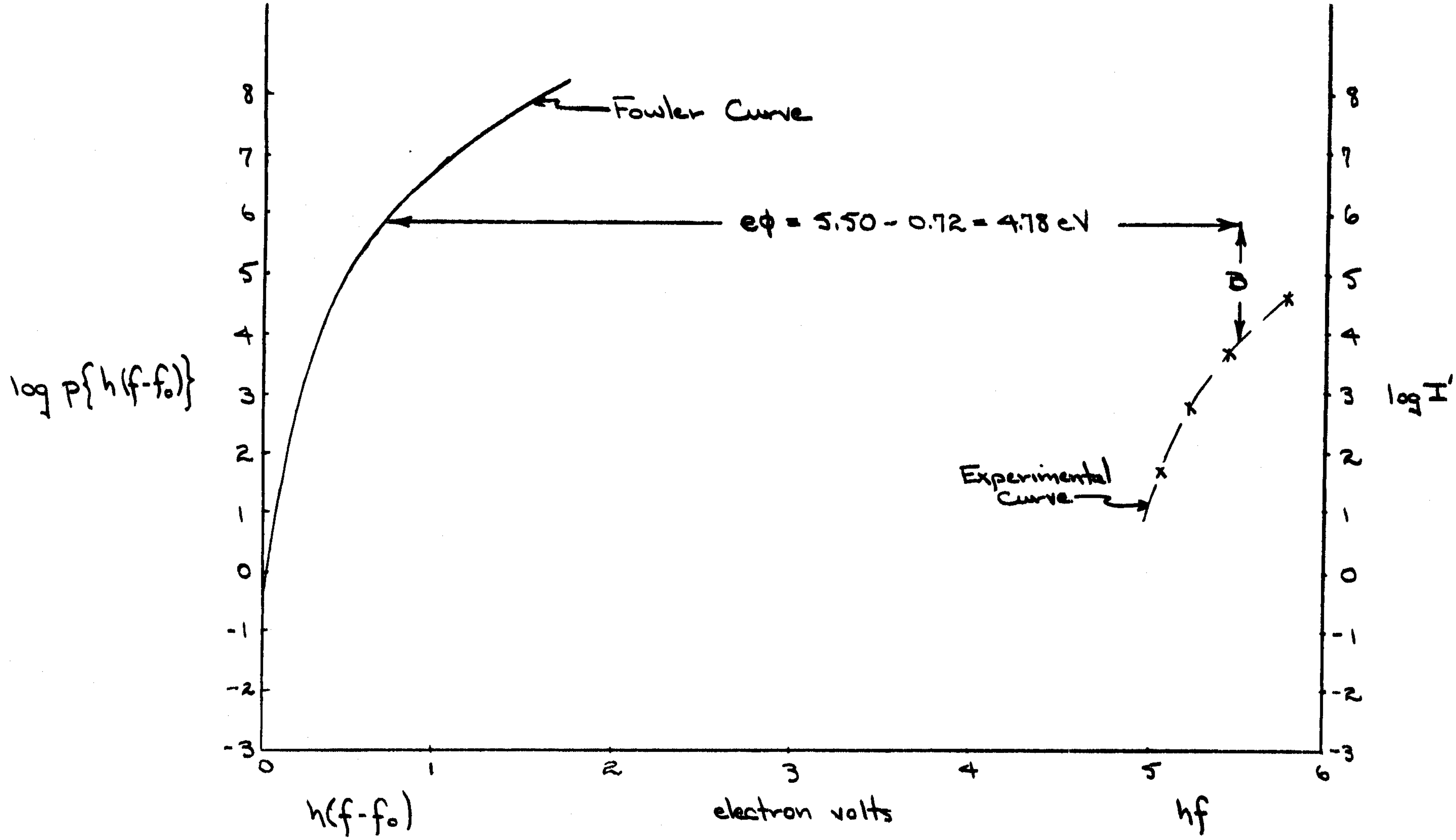


Figure 5 Fowler curve (solid line) plotted as $\log p(x)$ vs. x where $x = h(f \cdot f_0)$ for $x = 0$ to 1.8 and experimental curve (dashed line) plotted as $\log I'$ vs. hf in electron volts from experimental data. Work function is horizontal component of shift required to make experimental curve coincide with Fowler curve.

CHAPTER V

RELATED WORK

Before discussing the experimental investigation a short review of related work is appropriate. Although no reports of work function changes for carbon monoxide on molybdenum have been found in the literature, such work has been reported for tungsten which is also a member of group VI B in the periodic table. Both molybdenum and tungsten are body centered cubic; molybdenum having a lattice constant of 3.140 A compared to 3.1585 A for tungsten. Eisinger,[31] working with the 113 crystal face of tungsten, found a maximum change in the work function occurs when the number of carbon monoxide molecules chemisorbed equals the number of sites; at this point $\Delta(e\varphi) = + 0.86$ eV, the plus sign indicating an increase over the clean surface value. For coverages greater than a monolayer there is a decrease of about 0.1 eV. Because of the similarity of molybdenum and tungsten it is expected that a maximum work function change of roughly 0.8 eV might be noted for molybdenum.

Dubridge and Roehr[32] obtained a value of 4.15 eV for the photoelectric work function of a very thin molybdenum ribbon that had been outgassed for several hundred hours at 1900° K. Subsequent heating for up to six months failed to produce any change in the work function which suggests a clean surface. Thus a lower limit for $e\varphi$ of about 4.15 eV is expected although exact agreement may not be obtained because of the polycrystalline nature of the surfaces being compared.

The rate at which adsorption takes place can be controlled by maintaining a very low carbon monoxide pressure over the clean molybdenum surface. Hopefully the process would be slow enough so at least ten readings over a period of fifty minutes could be taken during the formation of a monolayer. Wagener[33] has found the initial sticking probability of carbon monoxide on molybdenum to be 0.3 which means that a monolayer would be formed in not less than one hour at a pressure of 10^{-9} torr.

CHAPTER VI

EXPERIMENTAL PROCEDURE AND RESULTS

I. DESCRIPTION OF APPARATUS

A diagram of the vacuum system used in this investigation is shown in Figure 6. The system was of conventional glass construction and all parts shown above the dotted line could be baked at 250° C. During bakeout the ion pump was not operated, but normally it was operating with the ball and socket joint closed. This pump was a Varian Vac Ion pump rated at 5 ℓ/sec, the diffusion pump was a CVC model GF21, air cooled, with a capacity of 20 ℓ/sec and the mechanical pump was a Welch Duo-Seal model 1400.

Pressure in the experimental chamber was measured by a Veeco RG-75 ion gauge of the Bayard-Alpert type which, with the control circuit used, was capable of reading pressures as low as 10^{-9} torr. Flasks of carbon monoxide and argon were connected to the system through Granville-Phillips type C ultrahigh vacuum valves. The argon line was provided with a molybdenum getter in a 0.5 liter flask which could be flashed to help pump the whole system or merely to clean the argon gas as it was admitted. A low torque driver was installed on the carbon monoxide valve to permit accurate pressure control when CO was admitted.

A detailed view of the experimental chamber is shown in Figure 7. To permit transmission of ultraviolet radiation to the sample a quartz window was provided at A. At B is shown a magnetically controlled shutter which was closed during ion bombardment of the sample to prevent coating the quartz window with molybdenum. The sample C was surrounded by a nichrome barrel D which had a slit S directly in front of the ion bombardment filament E. To allow for electron heating of the sample another filament was mounted at F, just behind the sample. Both filaments were made of 1% thoriated tungsten wire with a diameter of 0.005". The sample itself was made from 0.010" molybdenum sheet in the shape of a disk 0.22" in diameter and was thoroughly cleaned before being installed in the system.

A mercury light source was used in conjunction with an L234-150 Gaertner quartz prism monochromator with a dispersion of 23A at 2500 A. Monochromator output was calibrated with a thermopile for the six frequencies used in the Fowler plots. The photoelectrons were collected on the barrel, maintained at a potential of 22 volts above the sample, and measured by a Carey 32 vibrating reed electrometer. Photo currents were of the order of 10^{-12} amperes and it was necessary to shield the electrometer circuit for stable readings.

II. PROCEDURE AND RESULTS

The first task in obtaining work function data by the Fowler photoelectric method was to calibrate the monochromator output intensity for the six ultraviolet lines which were to be used to obtain photocurrent from the molybdenum sample. From the thermopile circuit readings used for calibration, it was possible to calculate the number of photons per second which would be incident upon the target for each line. When the various lines were then focused on the sample and the

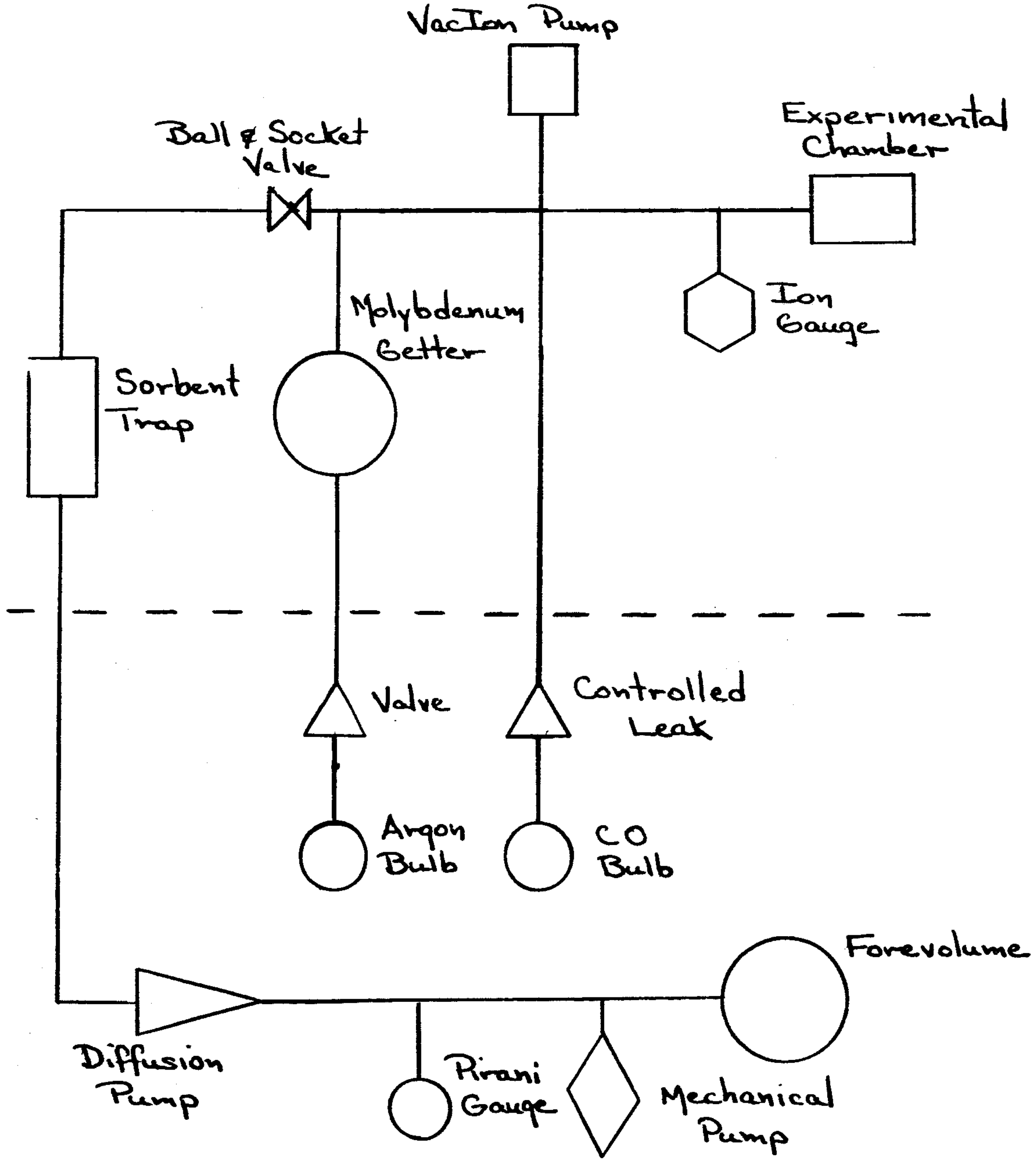


Figure 6. Vacuum system used in this investigation

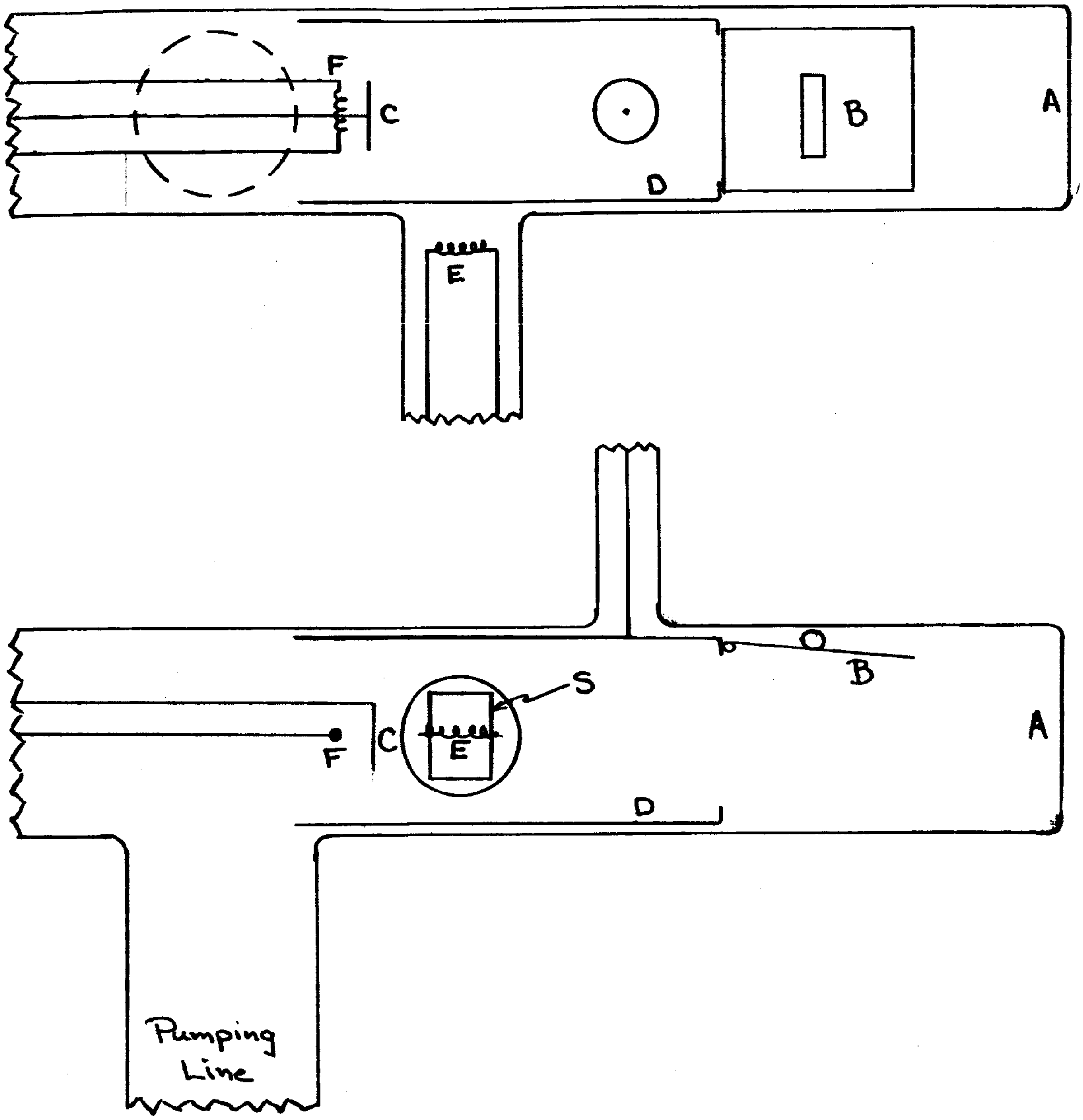


Figure 7. Detail views of experimental chamber

resulting current noted, another simple calculation provided I', the number of electrons emitted per incident photon for each line. When log I' was plotted against hf for each line the work function could be obtained by the method outlined in Chapter IV.

When the molybdenum was first placed in the vacuum system no photocurrent could be detected. Initial attempts to clean the sample sufficiently for observation of photocurrent were made by electron heating. When this proved unsuccessful the sample was cleaned by ion bombardment followed by a short pulse of electron heating. After several sessions of ion bombardment photocurrents were detected and measured.

In attempting to get a work function near 4.15 eV it was found that ion bombardment with no subsequent electron heating would produce a work function as low as 4.19 eV. No lower work function could be obtained by further ion bombardment or electron heating so this was taken to be the clean surface condition.

For the investigation of change in work function due to adsorption of CO it was necessary to begin with a clean molybdenum surface, admit CO, and record work function values until no further change was noted. Details for several runs are described below:

Run #1

The sample was cleaned by ion bombardment which ended in a glow discharge condition for at least 30 minutes. There was evidence of heavy sputtering from the molybdenum surface which indicated the removal of many surface layers. The initial work function was 4.23 eV with a background pressure of 1.6×10^{-9} torr. Figure 8 shows CO pressure and work function versus time. The unexpectedly slow rise in work function required increasing the CO pressure several times to obtain a reasonable rate of change. When the work function reached 4.89 eV, the CO valve was closed and the pressure returned to 3.6×10^{-9} torr overnight. After 960 minutes the work function was steady at 5.02 eV, an increase of 0.79 eV over the clean condition.

Run #2

The system was baked for 10 hours at 225° C after Run #1; the sample was electron heated and then ion bombarded for about 2½ hours with an ion current of 70 microamperes. The initial work function was 4.19 eV and the background pressure was 3×10^{-7} torr. Figure 9 shows $e\varphi$ versus time for Run #2 with the CO pressure constant at 1×10^{-7} torr for time 0 to 145 minutes. After 115 minutes $e\varphi$ appeared to stabilize at 4.96 eV; the CO valve was closed at 145 minutes and the pressure dropped to 4×10^{-9} torr overnight. At 900 minutes $e\varphi$ was steady at 5.02 eV giving a maximum $\Delta(e\varphi)$ of 0.83 eV.

Run #3

The system was baked after Run #2; the sample was electron heated and then ion bombarded for about 1¼ hours with an ion current of 60 microamperes. Again the initial work function was 4.19 eV and the background pressure was 1×10^{-7} torr. Figure 10 shows $e\varphi$ versus time with the CO pressure constant at 1×10^{-7} torr. After 95 minutes $e\varphi$ was 5.02 eV and had not changed further after 315 minutes. The total $\Delta(e\varphi)$ was again 0.83 eV.

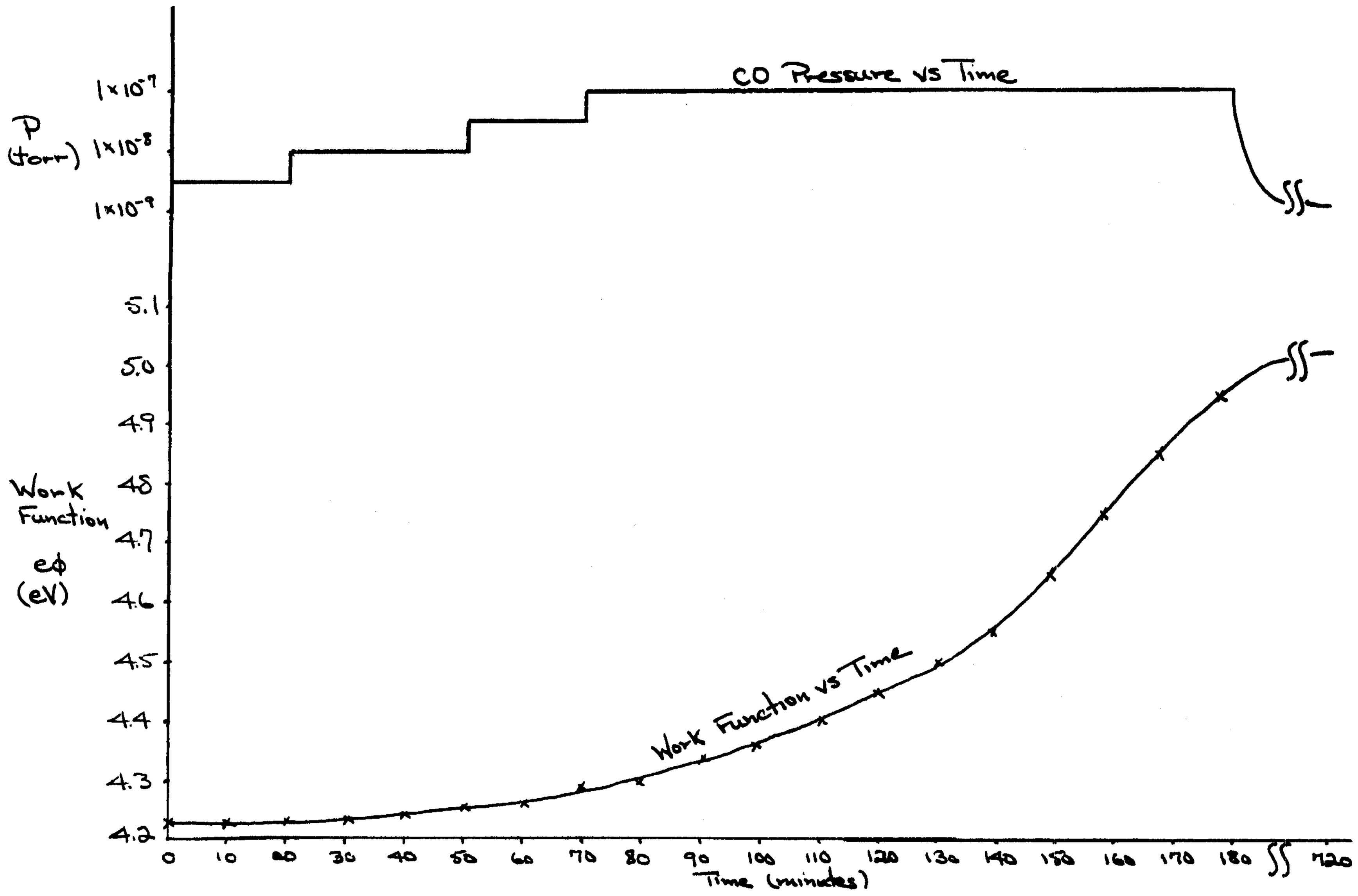


Figure 8, Work Function and Pressure vs Time Run #1 After cleaning by continuous discharge ion bombardment, no annealing

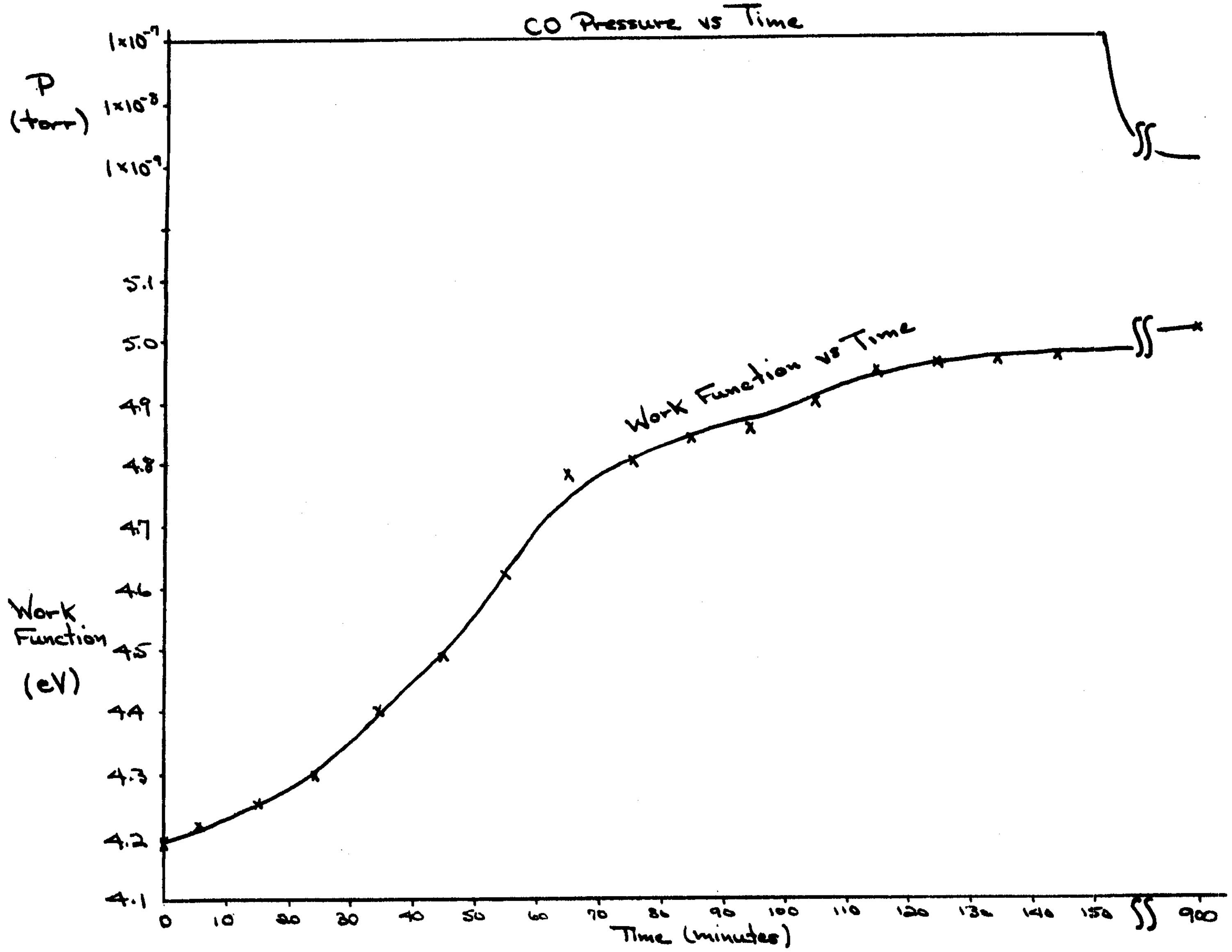


Figure 9. Work Function and Pressure vs Time Run #2
After cleaning by ion bombardment for 2½ hours, no annealing

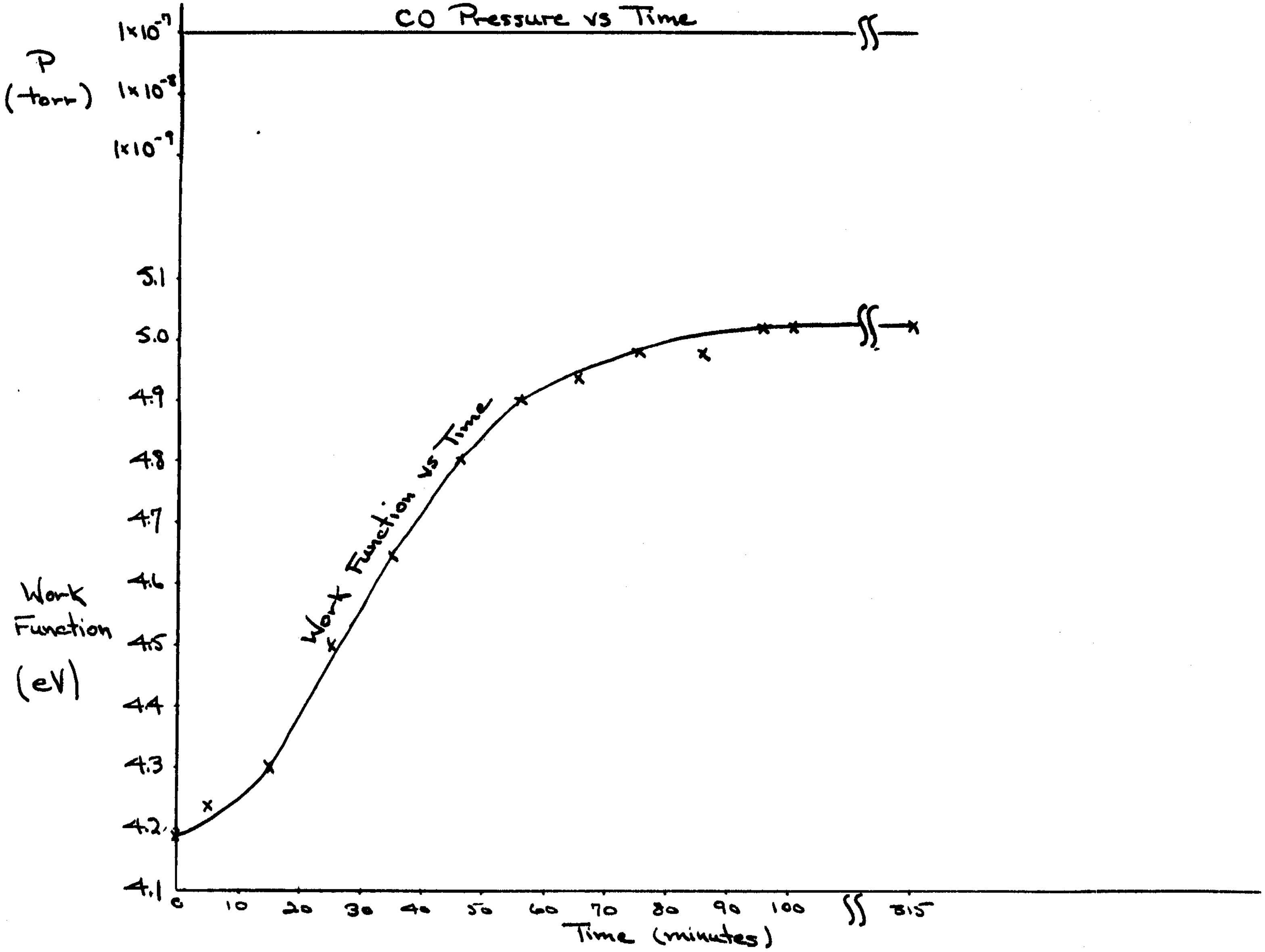


Figure 10. Work Function and Pressure vs Time Run #3
After cleaning by ion bombardment for 1¼ hours, no annealing

CHAPTER VII

DISCUSSION

Agreement among the three runs was quite good, with the final work function equal for all three cases. It is possible that the surface was not as clean in run #1 as in the subsequent runs. A difference of 0.04 eV is certainly detectable with good Fowler plots, but it represents an extremely small contamination of the truly clean state. The average $\Delta e\varphi$ is then 0.82 eV with the clean conditions taken as 4.19 eV; both of these figures agree with the predictions made in Chapter V.

No maximum peak and subsequent drop in work function with further coverage was noted, but in some earlier runs in which the molybdenum was contaminated with background gas such a behavior was noted. The decrease in $e\varphi$ for tungsten for coverages greater than a monolayer was attributed by Eisinger[31] to the fact that subsequent CO molecules were oriented in such a manner that their effective dipole sheet had positive side outward, which has the effect of subtracting from the work function. This behavior has been analyzed in a theoretical manner by Crowell and Norberg.[34] Probably the reason it was not noted in this investigation is due to the fact that the complex nature of the polycrystalline surface allowed variations between different crystal planes to overshadow small changes in the behavior of an individual face. Eisinger had a single crystal face with only a small number of different types of adsorption sites.

Certainly the most unexpected result was the slow increase of work function noted when no electron heating was done after ion bombardment. Some earlier runs were made in which the sample had been cleaned with electron heating ($e\varphi = 4.25$ eV) and CO was admitted at a pressure of 1 x 10^{-9} torr. The work function increase was nearly as rapid as run #2 even though the CO pressure was two orders of magnitude lower.

If the target area is taken to be its normal geometric area and the number of collisions per second per square centimeter is found from kinetic theory, then for low coverages the rate of increase of work function is 5.3 x 10^{-16} eV per collision after electron heating and 7.1 x 10^{-18} eV per collision after ion bombardment. Two possible explanations are offered for this behavior in order of preference by the author.

First, ion bombardment may create a rough condition on the surface so that it resembles an unannealed thin film with numerous lattice defects. It has been noted with thin films[35] that gas is adsorbed more slowly than is predicted by kinetic theory. It is assumed that while only the geometric area of the film is exposed to the gas there are many more adsorption sites in the fine metal pores which can take up gas that has migrated from the exposed sites where it was initially adsorbed. By comparing figures 8, 9 and 10 it appears that increased ion bombardment leads to slower changes in work function. With thin films annealing tends to close the pores and reduces this effect, and electron heating after ion bombardment should do the same. Dillon[36] feels that ion bombardment leads to great distortion of the crystal lattice and occlusion of inert atoms below the surface. However, he finds that for germanium, at least, this produces no great change in the photoelectric work function.

Second, there may be argon atoms adsorbed on the surface after ion bombardment which might greatly reduce the sticking coefficient for CO. When the sample was heated after ion bombardment, a slight pressure rise could be noted, suggesting that some gas had been present on the surface. However, it seems quite unlikely that the work function would be the same with argon adsorbed on the surface as it was for a supposedly clean surface. Work function values of 4.19 eV were obtained by electron heating after ion bombarding as well as by ion bombarding only. Surface potentials for inert gases are normally positive (decrease work function) with xenon on tungsten reported to be + 1.1 eV.[37] When the sample was flashed by electron heating and exposed to argon at 1×10^{-9} torr for twenty hours, the work function changed from 4.23 to 4.26 eV. It appears that argon does not adsorb on molybdenum at such low pressures but during ion bombardment, when the argon is ionized and at a pressure of 1×10^{-4} torr or greater, adsorption may take place as suggested by Leck.[38]

In conclusion the following points can be made:

1. Work function values were found for clean molybdenum which are in agreement with published data.[29]
2. Beginning with the clean condition, work function changes due to adsorption of carbon monoxide were observed. The average dipole moment per molecule is 0.25 Debye compared to a value of 0.10 Debye for a free CO molecule. This suggests a transfer of electrons from the metal toward the

CO molecule which is in agreement with conclusions drawn from electrical conduction studies.[20]

3. The rate of change of work function depends on previous treatment of the surface. The relatively low rate of change following ion bombardment is thought to be due to the presence of a number of hidden sites which can be filled only by CO molecules migrating from exposed sites. This theory is in keeping with a similar one proposed for thin films which also exhibit a slow reaction rate.[35]

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