CHANGES IN THE RESISTANCE OF MOLYBDENUM FILMS DUE TO THE CHEMISORPTION OF CARBON MONOXIDE

by

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SECTION I

INTRODUCTION

Adsorption is the process in which a gas molecule becomes bound to the surface of a solid. The solid is called the adsorbent and the adsorbed species is called the adsorbate.

Adsorption is divided into two broad classifications, physical adsorption and chemical adsorption or chemisorption. In physical adsorption, the binding of the gas takes place through van der Waals forces and the energies involved are generally of the order of 10 Kcal/mole (0.5 eV) or less. These are of the same order of magnitude as heats of condensation. In chemisorption the binding of the gas is thought to entail the formation of a chemical bond, that is, one involving an electronic interaction between the adsorbent and adsorbate. The energies involved here are generally on the order of 50 Kcal/mole (2.5 eV) or more.[1] The work described in this paper is concerned with chemisorption.

Historically, the modern study of adsorption began around 1911 with the work of I. Langmuir and his associates. The period 1911 to 1950, when ultrahigh vacuums became a practical research tool, may be considered the first phase of modern adsorption study. A critique of the experiments and an evaluation of the conclusions of principal investigators of this period has been given by J. A. Becker.[2] During this period the principal methods of studying adsorption were measuring the amounts of gas adsorbed, measuring the heats of adsorption, and determining the effects of adsorbed gases on the work function. Many of the basic concepts behind present theories of adsorption were developed from this work.

With the development since 1950 of ultrahigh vacuum systems and their use in conjunction with other techniques such as field emission microscopy, flash filament techniques, and low-energy electron diffraction, much more exact and detailed studies of adsorption have been made possible. Not only can the cleanliness of surfaces be controlled to a higher degree, but also a better picture of the actual adsorbing surfaces involved can be obtained. Along with these newer studies, investigation of heats of adsorption and amounts of gas adsorbed have continued, and there has been additional emphasis on studying adsorption through the effects of the electronic interaction which takes place between the adsorbate and metal or semiconducting adsorbents. Types of experiments dealing with these effects are measurements of changes in the work function, changes in the magnetic susceptibility, and changes in the electrical resistance of the adsorbent.

Molecules adsorbed on a surface will become polarized, that is, their electron clouds will be shifted with respect to their positive charges, due to the electric field which exists at the surface. The polarization of the molecule can be great enough to switch the electrons irreversibly into new states, thus forming a chemical bond. The direction and strength of the dipole moment of the bond modifies the electric field at the surface and can therefore be determined by work function measurements. A change in work function is to be expected if an electron shift to or from the metal surface occurs even if no actual electron transfer takes place. On the other hand, if electrons of the adsorbed molecule become part of the metal electron gas, or if metal electrons become part of the electron shells of the molecule, not only a change in work function but also a change in resistance of the metal will occur. These changes are detectable if the adsorbent is not more

than the order of a thousand times the thickness of the layer affected by adsorption. Because of this, resistance measurements on thin films can yield information as to the nature of the chemical bond formed in chemisorption.[3] However, only as recently as 1959 have quantitative results regarding the chemical bond been obtained as a result of this type of experiment.[4] These results have concerned the effective valency of the metal surface atom and the number of bonds formed by each adsorbed molecule for certain metal-gas systems. The validity of these conclusions is in some doubt, however, because of a lack of knowledge of the structure of the films involved.

The purpose of the present project is to further investigate the phenomenon of adsorption through the study of resistance changes in thin metal films. It is anticipated that this work will continue to become a doctoral thesis. The phase of the project reported in this paper was limited to include only the design and construction of apparatus suitable for making resistance measurements on metal films, and the preliminary investigation of carbon monoxide adsorbed on molybdenum.

SECTION II

BACKGROUND

I. CHEMISORPTION ON METAL SURFACES

Description of Metal Surfaces

Physical Description. Since adsorption is primarily a surface interaction, a study of adsorption must begin with a consideration of the nature of the surface involved. The ideal metal surface would be a known face of a single perfect crystal. However, perfect crystals do not occur in nature and so the ideal metal surface also does not occur.

The heterogeneity of a real single crystal surface may be classed as either physical heterogeneity or chemical heterogeneity. Physical heterogeneity of the surface arises primarily from lattice defects. These include vacancies, interstitials, and dislocations. However, it has also been shown that the surface of a crystal may become roughened and develop steps because of thermal motion of the atoms. Chemical heterogeneity means the imperfections in the crystal due to foreign atoms. These may be present unintentionally as impurities, or intentionally as alloying agents.[5]

Actual metal surfaces are of course very often polycrystalline, and the varying properties of the different crystal faces exposed then give rise to heterogeneity over the surface. The most obvious difference between crystal faces is the different density of packing of the surface atoms. This means that in adsorption the number of metal atoms surrounding each adatom may vary. It has also been found that the work function, a very important property in determining the interaction of atoms at the surface, varies with the crystal face of the metal.

The surfaces presented by evaporated thin films are more complicated still, and a discussion of them is given in a later section.

Theoretical Description. Brattain[6] has defined a surface as a boundary across which there is a difference in concentration of some essential chemical constituent and across which there is an electrostatic potential difference. This potential difference is generally associated with some kind of a charge double layer. One theory for the origin of this charge double layer for metals is in the unsymmetric distribution of electronic charge. At the surface, the electronic charge distribution spreads outward. The result is just as if a charge double layer, with negative sign outward, had been imposed on the surface of the metal with otherwise bulk electronic distribution. This creates a difference in electrostatic potential between the inside and the outside of the metal which is called the surface potential. Related to the surface potential is a property called the work function.[7]

The work function is the change in potential energy of an electron in moving from inside the metal to a point just outside the surface, divided by the electronic change. There is, of course, some ambiguity in the term "just outside the surface". If there were no surface potential, the work function would be just equal to $-\mu/e$, where μ = chemical potential and e = electronic charge. The chemical potential may be thought of as the work done in adding an electron isothermally to the metal, and will depend only on the temperature and "internal conditions" of the metal. If a surface potential is present, then the work function will be given by

$$\Phi = (\Phi_{inner} - \mu/e) - \Phi_{outer} = -(X + \mu/e)$$

where Φ_{inner} = electrostatic potential inside the metal

Φ_{outer} = electrostatic potential just outside the metal

$X = \Phi_{outer} - \Phi_{inner}$ = surface potential

Adsorbed molecules will alter the surface potential of a metal and this change can be experimentally observed as a change in the work function.

Due to the nature of the surface potential, it is a structure sensitive property. The chemical potential, on the other hand, is essentially a bulk property. Therefore the work function would be expected to change from face to face of a crystal, and this is indeed found experimentally.[7]

Types of Bonding in Chemisorption

The exact nature of the binding forces involved in chemisorption is not completely understood in most cases. However, a distinction is generally made between weak and strong chemisorption, and these are associated respectively with predominantly covalent and ionic type bonding.

Covalent Bonding. Covalent forces are also called exchange forces or homopolar forces, and adsorption due to this type of force is called weak chemisorption. Covalent bonding is characterized by the fact that the electron shell of the adsorbed atom may penetrate that of the metal atom. Both the metal and adsorbed atom give up an electron with unpaired spin to a so-called binding orbital.[5]

The fact that the transition metals are markedly more active than other metals in chemisorption has led to the hypothesis that this bonding is related to the d-band structure of the metal.[8] However, Ehrlich[1] has pointed out that the evidence for d-band interaction is not conclusive, and if dissociated atoms rather than diatomic molecules, such as N_2 and H_2, were used as the adsorbate, there would be no great difference between the transition metals and other metals.

Another model for weak chemisorption suggests that the bond is formed between a single surface atom which has "unused" metal-metal

bonds and the adsorbed molecule. However, this model fails in that it requires a positive heat of adsorption for any dissociative adsorption on any metal surface, and this is not found experimentally.[1]

Ionic Bonding. Ionic bonding forces, also called hetropolar forces, give rise to strong chemisorption. In contrast to the covalent forces, which involve an interpenetration of the electron shells of the adatom and the metal, the hetropolar forces are associated with the transfer of an electron from the adatom to the metal or vice versa. Thus a layer of ions is formed which is bound to the surface by the Coulomb image force. The condition for electron transfer to the metal is that the ionization potential of the adsorbed atom be less than the work function of the metal, $V_i < \Phi$. However, even if this condition does not hold, adsorption of positive ions will still take place provided that

$$Q_a + eV_i < Q_i + e\Phi ,$$

where Q_a is the adsorption energy of the adsorbed atom in atomic form and Q_i is its adsorption energy in ionic form. These quantities are illustrated in Figure 1 for the case of sodium adsorption on tungsten.[9] Ionic bonding is commonly found in the case of alkali and alkaline metals adsorbed on such metals as tungsten, molybdenum, and platinum.

Electron transfer from the metal to the adatom can also take place. The condition for this is that the work function of the metal be less than the ionization potential of the adatom, $\Phi < V_i$, while the condition for negative ion adsorption is now

$$Q_a - eV_i < Q_i - e\Phi .$$

An example of this is the adsorption of hydrogen on potassium, in which each hydrogen atom takes one electron from the potassium surface.

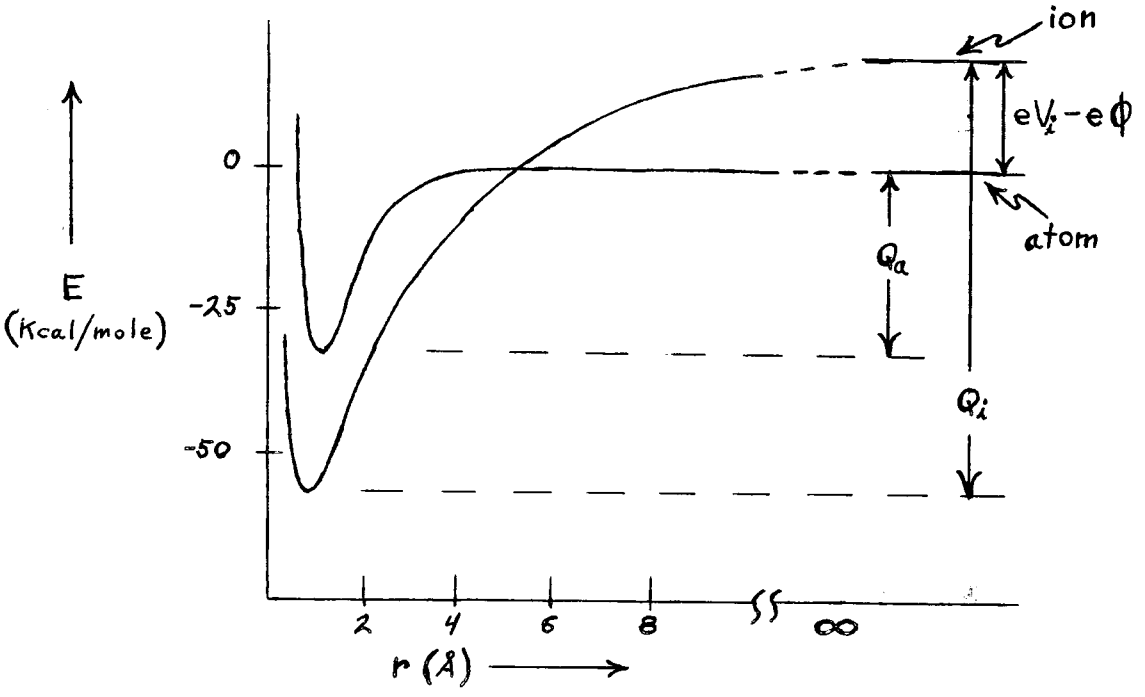

Figure 1: Potential energy curves relating to the adsorption of sodium on a tungsten surface.

Effects of Chemisorption on Metal Properties

Work Function. In either ionic or covalent chemisorption, the effect on the surface can be approximated by a charge double layer of density σe and separation distance d, where σ = number of dipoles per unit area and e = electronic charge. If this charge double layer is idealized to the point where it may be regarded as uniform, then the change in potential across this layer is $\pm 4\pi\sigma ed = \pm 4\pi\sigma M$ (Gaussian units) where M is the dipole moment. This potential then adds to the already present surface potential, and thus changes the work function of the metal. The work function will be increased when the negative side of the double layer is outward, and decreased when the positive side is outward. Therefore measurements of the change in work function due to adsorbed molecules can be interpreted to give information regarding the adsorption process.(7)

Conductivity. In a metal the free electrons are responsible for conductivity. Therefore if electrons of the adsorbed molecule become part of the metal electron gas, or if metal electrons become part of the electron shell of the adsorbed molecules, a change in electrical conductivity will occur.(10) This point will be covered in more detail in later sections.

Magnetization. The paramagnetism of the transition metals is due to electrons with unpaired spin in the partly filled d-band. Therefore if adsorption changes the number of electrons in the d-band, the magnetic susceptability of the metal will also change. For example, Selwood(11) has utilized this phenomenon in his investigations of adsorption on nickel. Nickel contains 9.4 electrons, 0.6 holes, and 0.6 unpaired electron spin per atom in the d-band. In the formation of an ionic bond, the number of unpaired d-electrons will either increase or

decrease by one for each atom adsorbed. This means that for nickel the adsorption of a positive ion will decrease the magnetization, while the adsorption of a negative ion will increase it. When a covalent bond is formed, however, an electron from the adsorbate and an electron from the d-band of the metal, both with unpaired spins, occupy a bonding orbital in which their electron spins are paired. It follows that in covalent bonding the magnetization will decrease no matter in which direction the polarization of the resulting bond is. To distinguish between positive ion formation and covalent bonding an additional measurement, such as change in work function or resistance, which tells the direction of electron transfer is needed.[7]

II. METHODS OF STUDYING ADSORPTION

Observation of changes in the work function, conductivity, and magnetization give a method of studying the electronic interaction between adsorbed molecules and metal surfaces. Qualitative results have been obtained for many systems by these methods. A large amount of work has also been done to determine heats of adsorption and adsorption isotherms and isobars. The former work is generally done by calorimetric methods and the latter by volumetric or gravimetric techniques. There has also been interest in the kinetics or rate processes of adsorption, in the details of the surfaces involved, and in the structures which the adsorbed molecules form. These latter studies have had to wait, however, for the more recent development of ultra-high vacuum technique, flash desorption methods, field emission microscopy, and low-energy electron diffraction.

Flash Desorption

The kinetics of adsorption are most simply expressed by the sticking coefficient, that is, by the probability that a molecule striking the surface will actually be adsorbed on it. Flash desorption is one method for determining this coefficient. In this method a clean sample of known area is exposed to a gas at known pressure for a certain length of time. At the end of that time the sample is heated (flashed) at a temperature high enough so that the gas is desorbed. From the subsequent pressure rise in the system, the number of molecules evolved can be calculated. The "pumping" rate as the filament cools can also be observed. From this information the sticking coefficient is then calculated. However, flash desorption is capable of yielding still more information. If the temperature of the sample is changed continuously, a qualitative picture of the nature of the binding energies of the adsorbed species can be obtained by observing the amount of gas desorbed as a function of time and temperature. It is in this way that a detailed view of intermediate binding states in adsorption on metals has been obtained.[1] It is also possible to distinguish between first and second order reactions at the surface.[13]

While some early studies by this method were done by Langmuir in the 1930's, most flash desorption work has been possible only since the development of the Bayard-Alpert ionization gauge for the rapid measurement of low pressures.

Field Emission Microscopy

While flash desorption is a powerful technique because it gives a direct and rapid count of the number of an adsorbed species on a surface, it is a macroscopic technique and yields information on properties of the adsorbed layer only indirectly. Field emission microscopy

provides a technique for direct microscopic examination of the adsorbed layer which supplements the macroscopic information found by other means.

Field emission microscopy includes the two techniques of field electron and field ion microscopy developed by E. W. Müller in 1937 and 1951 respectively. In field electron microscopy a small tip ($\sim$1000 Å diam.) of the material to be studied is placed at high negative potential ($\sim 10^4$ volts) with respect to a fluorescent screen which partially surrounds the tip. This creates a field at the tip of the order of 10^8 volts/cm. Electrons can then tunnel out of the surface of the metal and are accelerated to the screen. The rate of tunneling depends upon the work function of the metal which in turn depends upon the crystal face and impurities on the surface. Thus, the resulting pattern on the fluorescent screen can be interpreted to give information on an atomic scale about the surface of the material and adsorption on the surface.

The field ion microscope is an improvement over the field electron microscope in that it has greatly increased resolution ($\sim$3 Å). The operation is similar to the field electron microscope except that the experimental tube is filled with hydrogen at about 10^{-3} torr, and the metal tip is at positive potential with respect to the screen. Adsorbed hydrogen on the tip is then pulled off in the form of ions which are accelerated to the screen. The ionization of the hydrogen again depends upon the work function of the metal and so the pattern on the screen gives a picture of the surface on an atomic scale. With the field ion microscope, the positions of individual adatoms can be determined.

Field emission and flash desorption studies supplement each other quite well. Field emission microscopy yields information on the distribution of adsorbed material over the surface and on the rates of atomic processes occuring in the adsorbed layer itself. Flash desorption, on the other hand, provides data on the kinetics of adsorption and also information on the energetics of binding at the surface. The field emission data allow this information to be related to the structure and properties of the surface layer. Conversely, information from the flash desorption studies allow an interpretation of the processes responsible for the changes observed in the field emission microscope.[14]

Low-Energy Electron Diffraction

Another method which gives information on an atomic scale is low-energy electron diffraction. This method dates back to the Davisson-Germer experiment of 1927, but has seen little use as a research tool in adsorption until recently. New developments in the technique have made the process considerably less laborious.

The method consists of focusing a beam of low-energy electrons (50 - 150 eV) at normal incidence on the crystal to be studied. The electrons are diffracted in a backward direction and are accelerated to a fluorescent screen. The resulting pattern on the screen can then be photographed. Because of the low energy of the electrons, their penetrating power is small and diffraction is due mainly to the two dimensional array of atoms at the surface. Thus the diffraction pattern can be interpreted to give the position or spacings of atoms on the surface.

In its most simple application, low-energy electron diffraction is used for two dimensional crystallography of clean surfaces. However, by observing changes in the diffraction pattern as the energy of the electrons is varied, the three dimensional aspects of surface structure can be determined as well.

The application of low-energy electron diffraction to adsorption studies is the determination of the locations and surface structure of adsorbed atoms relative to the substrate structure. One interesting observation from this technique is that in some systems the substrate atoms become rearranged due to adsorption.[15]

Germer[16] has suggested a classification of adsorption into four groups according to monolayer structure as observed by low-energy electron diffraction. They are (a) when the adsorbed layer has no detectable structural arrangement, (b) when the layer has a perfectly regular arrangement, (c) when there is some randomness in the arrangement of the layer which cannot be removed by annealing, and (d) when the adsorbed atoms have caused rearrangement of the surface atoms of the substrate.

III. CONDUCTIVITY OF METALS

A fairly simple, yet useful, determination of the conductivity of metals can be obtained from the free electron model.[12] In this model the valence electrons of the metal atoms are able to move freely throughout the volume of the sample and are responsible for the conduction of electricity. The electrostatic interaction of these conduction electrons with the ion cores of the metal lattice and with each other is neglected. Calculations then proceed as if the conduction electrons, which obey Fermi-Dirac statistics, were free in the space bounded by the sample.

The important result of the free electron model for the conductivity is

$$\sigma = \frac{Ne^2\tau}{m} \tag{1}$$

where N = number of electrons per unit volume, e = electronic charge, m = mass of electron, and τ = relaxation time. The relaxation time may be thought of, in this model, as the mean time of flight between collisions of the electron. A related quantity, the electron mobility, is defined by

$$\mu = \frac{\vec{V}_b}{\vec{E}} = \frac{e\tau}{m} \tag{2}$$

where $\vec{V}_b$ = electron drift velocity and $\vec{E}$ = applied electric field, In terms of electron mobility the expression for conductivity is then

$$\sigma = Ne\mu \tag{3}$$

More advanced theories of metals take into account the interaction of the electrons with the ion cores. The only modification necessary to equation (1) on the basis of these theories is to replace m, the mass of the electron, by m*, called the effective mass of the electron. The physical interpretation of this is that due to interactions with the lattice, the electron in the metal does not respond to an applied electric field like a free electron of mass m, but rather as if it were an electron of mass m*.

On the basis of more advanced theory it is shown that electrical resistance is due only to imperfections in the crystal lattice. These imperfections may be separated into those associated with the thermal motion of the atoms and those associated with impurity atoms and lattice defects. The former are reversibly temperature dependent and are responsible for the so-called ideal resistance, while the latter are essentially temperature independent and are responsible for the so-called residual resistance. This is expressed by Mathiessen's

rule

$$\rho_{total}(T) = \rho_{ideal}(T) + \rho_{residual} \tag{4}$$

where ρ = resistance = $1/\sigma$.

In talking about the conductivity of thin metal films, a contribution to the resistance due to the boundaries of the metal must be taken into account.[17] The mean free path of a conduction electron may be defined as

$$\ell = u\tau \tag{5}$$

where u = mean velocity of the electron and τ = relaxation time. In terms of the mean free path, equation (1) for the conductivity may be written

$$\sigma = 1/\rho = \frac{Ne^2}{m}\frac{\ell}{u},$$

This implies that if the thickness of a film is reduced so that it is comparable to the mean free path, then the resistance of the metal will be increased due to this artificial limitation of the mean free path by the boundaries. Much useful work has been done using this so-called mean free path effect in determining basic metal conductivity parameters. It has been suggested that Matthiessen's rule for thin films be written

$$\rho_{total}(T) = \rho_{ideal}(T) + \rho_{residual} + \rho_{thickness}$$

Mean free path effects begin to show up in films in the thickness range of 100 - 500 Å and less.

Another factor which must be taken into account with thin films is that the residual resistance, which is due to impurities and defects, may be temperature dependent. Due to the nature of film deposition, the concentration of lattice defects is generally higher than in the bulk metal. These defects may be partially annealed out at higher temperatures,

thereby decreasing the resistance. This temperature dependence is therefore not reversible and is quite different from the normal temperature dependence of the ideal resistance.

IV. THIN FILMS

Thin films of various materials have been used in adsorption studies primarily for two reasons. First, they offer a convenient way of obtaining a clean surface. Second, it has been shown that under certain conditions films may have a surface area available for adsorption which is many times greater than their geometrical surface area. This last feature is not particularly well understood and for that reason is a mixed blessing.

Thin films may be formed in several ways, but the most common method used today is vacuum evaporation. In this method the film material is vaporized by heating it in a vacuum, and the vapor then condenses upon a suitable substrate to form the film. There is considerable literature upon this subject since it is of commercial as well as scientific interest.[18] It has been found that the structure and properties of the film are dependent upon the parameters of deposition.

To understand how the deposition parameters affect the resulting film, it is first necessary to understand something of the initial nucleation and growth of the film on the substrate. Indeed, this might even be considered an adsorption problem since it deals with the interactions of foreign atoms on a surface. This subject has been reviewed by Bassett et al.[19]

When an evaporated atom strikes the substrate surface it may either remain on the surface or re-evaporate. Those atoms remaining on the

surface may move over the surface and strike a particularly low-energy site, or may perhaps combine with another adatom to form a more stable "doublet." In either case, if the adatom loses enough energy to become non-mobile on the surface, it then acts as a nucleus and subsequent adatoms may collect on it.

Once a sufficiently high density of nuclei has formed on the surface, growth may take place in the following ways: (a) direct deposition onto existing nuclei; (b) interchange of atoms between near-neighboring nuclei, causing large nuclei to grow at the expense of smaller nuclei; and (c) physical growing together of neighboring nuclei. Depending upon the type of growth which predominates, the film may become continuous even at low thicknesses or may form large isolated crystallites which remain separate until greater thicknesses are reached. Thus the structure of the film is determined by the number of nuclei initially formed and the way in which the resulting aggregates grow.

There are three factors which affect the number of initial nuclei formed. One is the number of favorable, or low-energy, sites found on the substrate. These include such things as vacancies, steps and kink sites, dislocations, and foreign atoms. A second factor is the rate of deposition, that is, the number of impinging atoms per unit area per unit time. The higher the rate, the more initial nuclei are likely to form.

The third factor is the mobility of the atom on the substrate surface. High mobility will favor fewer initial nuclei. An atom is mobile on the surface as long as it has enough energy to pass over the potential barriers on the surface. Therefore, mobility will depend upon such things as the substrate material, temperature, and cleanliness and the energy of the impinging atom.

The subsequent growth of the nuclei also depends upon the mobility of the deposited atoms. Low mobility will favor lateral growth of the nuclei, whereas high mobility will favor growth normal to the surface. This is because in general the most favorable sites will be on the already formed nuclei.

The combination of a large number of initial nuclei and a low mobility of the atoms gives rise to continuous films at low thicknesses. These same films also show a higher density of lattice defects and less crystallographic orientation with respect to the substrate than films deposited under different conditions.

In addition to lattice defects, it is known that films as deposited may contain high stresses.[20] These stresses, unless relieved by annealing, may have an effect on the properties of the film, particularly the electrical properties.

The factors just described which determine film structure are dependent upon parameters which can be controlled during deposition. These parameters fall into three areas. The first is the substrate. This may be controlled with respect to material, temperature, and preparation. The second is the evaporation source. This may be controlled as to type of source, temperature, and distance from the substrate. The third is the vacuum environment. This may be controlled as to degree of vacuum and type of residual gas present. All of these parameters can be interpreted in terms of their effect on the initial nucleation rate and mobility of the deposited atoms.

It is now established that by careful control of these deposition parameters films can be made with reproducible properties. At least in the case of conductivity studies, what were once called anomalous effects have now been traced to poor experimental techniques.[17]

One structural property of films which has not yet been fully explained is the apparent porosity of films prepared under certain conditions. Several investigators have found by adsorption studies that the surface area of films is proportional to the mass of material deposited.[21] This can only be interpreted as meaning that the films are porous. It has been shown that this porosity depends upon the conditions of deposition and the subsequent treatment of the films. For example, films of copper deposited at liquid oxygen temperature (-183° C) show a linear relationship between surface area and mass. Similar films deposited at -183° C but annealed at 18° C for two hours still show a linear relationship, but the slope is smaller. Films deposited at room temperature and higher no longer show a linear relationship but still have an effective surface greater than their geometrical surface.[21]

Evans and Mitchell[22] have proposed two models for porous films. One pictures the initially deposited film as being composed of spheres in a close packed arrangement, the large surface area being accounted for by the surfaces of the spheres. The decreasing surface area upon annealing is due to surface migration of atoms. The other model pictures the film as composed of rod shaped elements which form an open polyhedral structure. The latter model has been more successful in interpreting certain conductivity data. Both models, however, are highly idealized and seem to be of limited applicability.

On the other hand, there is some evidence that flat, or nonporous, films of certain materials can be produced. Swaine and Plumb[27] evaluated the effect of substrate temperature, film thickness, and angle of vapor incidence on the structure of aluminum films. They concluded that with normal vapor incidence flat films are always produced except at very low substrate temperatures.

V. CONDUCTIVITY CHANGES IN METALS DUE TO CHEMISORPTION

As was pointed out in the preceding sections, one of the effects of chemisorption on a metal is to change the conductivity of the metal. From measurements of these changes in conductivity it is possible to get information about the adsorption process. Physical adsorption may also affect conductivity, but this is generally due to conductivity in the adsorbed layer itself rather than electronic interaction with the adsorbent. In the instances when physical adsorption affects the bulk conductivity of the adsorbent, it is difficult to interpret the findings in relation to the adsorption process.[23]

The conductivity of a metal is given by $\sigma = Ne\mu$ where N = number of conduction electrons per unit volume, e = electronic charge, and μ = electron mobility. Changes in conductivity are generally interpreted as reflecting a change in N, the concentration of electrons, while the mobility is assumed to be essentially unchanged. Experiments to detect changes in mobility with adsorption have not yet been performed.

Suhrmann and his co-workers have done considerable work with conductivity changes in thin films due to chemisorption. By combining his conductivity data with results of work function measurements he has developed a qualitative picture of the adsorption process. He summarized his results in 1955.[3] His work involved the adsorption of oxygen, hydrogen, nitrogen, and carbon monoxide on films of nickel. Suhrmann concluded that the type of adsorption interaction taking place could be explained on the basis of the following five factors: (a) work function of the metal surface, (b) electron affinity of the adsorbate, (c) dissociation energy for diatomic molecules, (d) assymmetry of the electron configuration of the adsorbate, and (e) presence of unpaired electrons and π electrons.

Suhrmann's interpretation of the results of hydrogen adsorption on nickel were questioned by Sachtler.[24] Suhrmann and others had found that hydrogen adsorption on platinum foil and tungsten caused a decrease in the work function and that hydrogen adsorption on aged nickel films caused a decrease in resistance. This is contrary to what would be expected of an electronegative adsorbate. However, Suhrmann found that hydrogen adsorbed on fresh nickel films produced the expected increase in resistance and work function. He interpreted the difference between fresh and aged films as being due to a different degree of order in the films. Sachtler did similar experiments under varying vacuum conditions and concluded that the difference in behaviour of fresh and aged films was due to different degrees of surface contamination.

Suhrmann has also investigated carbon monoxide, oxygen, and hydrogen adsorbed on nickel and bismuth films.[10] He found that carbon monoxide on nickel films caused an increase in resistance. He attributed this to metal electrons being displaced towards the CO molecule, since the electron affinity of the CO molecule is greater than that of the nickel surface. However, carbon monoxide on bismuth films caused a decrease in resistance even though the work function of bismuth is 0.65 volts less than that of nickel. It is known that bismuth has a low concentration of electrons in its conduction band. Suhrmann interpreted this to mean that electron concentration, as well as the work function, plays an important role in governing the electron affinity of a metal surface and hence in the electronic interaction at the surface. The results with oxygen and hydrogen bore out this conclusion.

More recently Zweitering et al.[4] and Suhrmann et al.[25] have been able to give a quantitative interpretation of conductivity measurements with regard to the sharing of conduction electrons in the chemisorption

process. In order to do this, the number of molecules adsorbed and either the weight or surface area of the film must be known in addition to the measured change in conductivity. The data are plotted as fractional change in conductivity versus the number of adsorbed molecules per unit weight of film. This plot gave a straight line for low coverages in all cases investigated by Zweitering. Figure 2 shows an example of these data. A constant α is then determined from the slope as follows:

$$\text{slope} = -\frac{\Delta\lambda/\lambda_o}{n}$$

$$\alpha = \frac{\text{slope}}{\text{atomic wt. of metal}} = -\frac{\Delta\lambda/\lambda_o}{n}\,\frac{N}{W} = -\frac{\Delta\lambda/\lambda_o}{n_a/N}$$

where $\Delta\lambda$ = change in conductivity, λ_o = initial conductivity, N = total number of metal atoms in film, W = weight of film, n = number of adsorbed molecules/unit film weight, and n_a = total number of molecules adsorbed. The value of α was found by Zweitering to be of the order of unity for the systems he studied, namely, H_2, CO, and C_2H_4 adsorbed on Ti, Ni, and Fe. He interpreted this to mean that in chemisorption the fractional decrease in electrical conductivity roughly equals the fraction of the total number of metal atoms involved in the formation of the chemisorption bond.

More qualitative conclusions can be drawn from the data by the introduction of two new constants, X and γ. X is the number of chemical bonds formed per adsorbed molecule. γ is the effective valency of the metal atom or, in the free electron model, the number of conduction electrons contributed by the atom. So if γ chemical bonds are made with a metal atom, then its contribution to the conductivity of the film is completely cancelled. Therefore, by assuming that each metal atom contributes equally to conduction, α can also be written as

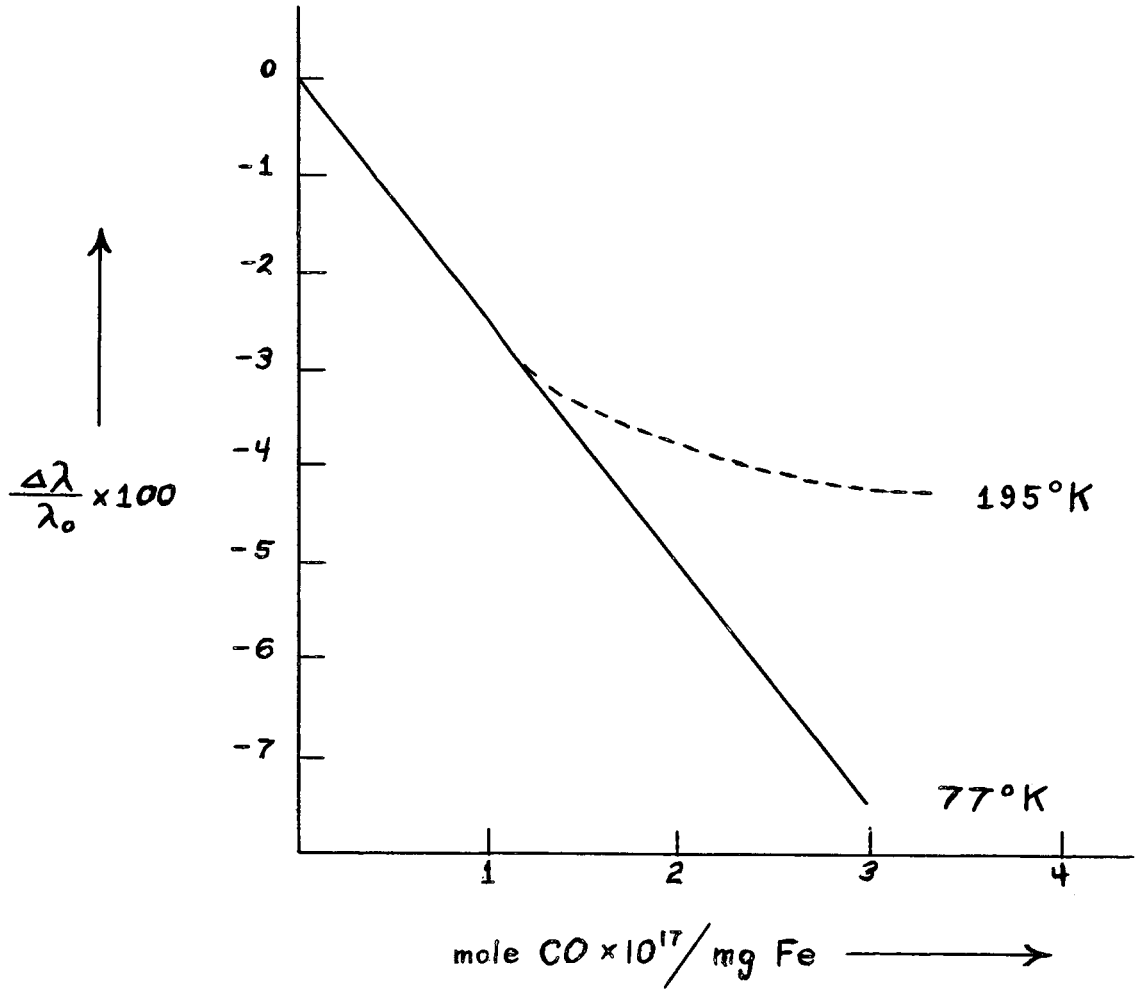

Figure 2: Adsorption of carbon monoxide on iron film.

$$\alpha = \frac{X}{\gamma}$$

Since α is experimentally determined, if either X or γ is known, the other can be calculated. For instance, Zweitering considered X for hydrogen to be two, since he assumed that hydrogen dissociates in adsorption and that each atom then forms one bond. He then determined γ values for Ti, Fe, and Ni to be 1.9, 0.9 and 0.75 respectively. He then in turn determined X for CO and C_2H_4 to be approximately 2.5 and 4.0 respectively.

Suhrmann does not consider X to be simply the number of bonds formed per adsorbed molecule. He takes it instead to be a constant factor which contains the influence of one chemisorbed molecule on the mobility of conduction electrons as well as on their number. However, he does not separate these two effects.

Suhrmann analyzed his data of hydrogen adsorption on palladium films by this method. He found two modes of hydrogen adsorption. Initially the dissociated hydrogen atoms strongly bind the conduction electrons and form a negative layer. At higher coverages, however, the hydrogen atoms dissociate into electrons and protons which may diffuse into the metal. The electrons fill holes in the d-band and so the number of conduction electrons is not increased. Changes in magnetization of the palladium, which might be expected on the basis of this explanation, were not investigated. The protons, on the other hand, act as impurities in the lattice and therefore cause the resistance to increase. This is substantially the same as Suhrmann's earlier findings for the adsorption of hydrogen on nickel films.

Ehrlich[26] has pointed out some difficulties in the above method of interpreting conductivity effects due to adsorption, and he emphasises that an understanding of these effects is a prerequisite to the use

of such measurements for the exploration of the chemical bond involved in adsorption. He proposes three mechanisms by which adsorption may contribute to observed resistance increases.

He assumes a film structure of metallic aggregates connected by conducting bridges. The resistance of the film is increased because the atoms adsorbed on the bridge reduce the number of charge carriers in the bridge. While adsorption takes place on the aggregates as well, this does not affect the conduction of the film. Ehrlich defines a constant α_B as

$$\frac{\Delta\lambda}{\lambda} = - \alpha_B \frac{n_B}{N_B}$$

where n_B = number of atoms adsorbed on the bridge, and N_B = total number of atoms in the bridge. This is related to Zweitering's α by

$$\alpha = \alpha_B \frac{A_B}{V_B}$$

where A_B = fraction of total surface on bridges, and V_B = fraction of total volume in bridges. Thus, on Ehrlich's model of a film, α_B is less than unity. He considers Zweitering's small integral values for α to be fortuitous and the conclusions he draws regarding the chemical bond to be invalid.

The second mechanism for resistance change is that the adsorbed molecules alter the surface stresses of the film, which it is known have an effect on its resistance. However, Ehrlich believes it unlikely that this mechanism makes more than a small contribution.

If the gaps between metal aggregates in the film are small, and at the same time the bridges are thin, then electron tunneling between aggregates may contribute to the total current carried by the film. The extent to which this actually occurs in films is not known. Adsorbed gas which increases the surface potential will therefore decrease the amount of electron tunneling. Ehrich believes that this last mechanism provides the major contribution to the resistance change.

SECTION III

EXPERIMENTAL METHOD

I. DESCRIPTION OF APPARATUS

General Description

If the ideal apparatus were to be built for the purpose of acquiring the most meaningful data on the change of electrical resistance of metal thin films with the adsorption of gases, it would have to meet the following requirements:

First of all, it should allow the controlled deposition of thin metal films. The various parameters which determine the structure and properties of the film should, ideally, all be variable so that their effect on the ultimate data could be observed. Those parameters which must be controlled have already been mentioned and are as follows. The substrate should be controlled with respect to material, temperature, and preparation. The evaporation source should be controlled as to type of source, temperature, and distance from the substrate. The vacuum environment should be controlled as to degree of vacuum and type of residual gas present. In particular, the vacuum must be maintained at less than 10^{-8} torr (at which pressure a monolayer of gas will form on an exposed surface in ~ 20 min.) during and after the deposition.

In addition to this the ideal apparatus should allow for annealing and temperature control of the film after deposition. The thickness of the film should be uniform and measurable, and both the weight of the film and its area should be known.

The adsorbate gas should be controlled as to leak rate and ultimate pressures reached. There should also be a method of determining the amount of gas adsorbed on the film.

Associated with the apparatus should be a device for continuous measurement of the resistance of the film with sufficient sensitivity to detect changes of the order of 1%. Contact should be made with the film in such a manner that conduction path through the film is known.

The actual apparatus built for this work is shown in block diagram form in Figure 3. It provided for controlling the temperature of the substrate, maintaining a vacuum of less than 10^{-8} torr, and holding all other deposition parameters constant. The nature of the residual gas was unknown. Neither the thickness, nor the weight or area of the film was measurable. The pressure of the carbon monoxide used as the adsorbate gas could be well controlled, but no method was provided to measure the amount adsorbed. A method of continuous resistance measurement of sufficient sensitivity was incorporated in the system; however, the conduction path through the film was unknown. A more detailed description of the apparatus is given in the next section.

Vacuum system

The principal parts of the vacuum system are shown in Figure 3. The mechanical pump is a Welch Duo-Seal 1400 pump with a pumping speed of 1/3 liters per second for free air which is capable of producing a vacuum of less than 10^{-3} torr. A sorbent trap, using Linde type 13X molecular sieve pellets, was placed between the mechanical pump and the main system. Further pumping was done by a Varian 8 liter/second Vac-Ion pump. This was turned on after the pressure in the system was below 10^{-3} torr. The Granville-Phillips Type C ultra-high vacuum valve was then closed, isolating the system from the mechanical pump, and the VacIon pump proceeded to pump down to an ultimate pressure of 1×10^{-9} torr. A titanium getter was also installed on the system to give increased pumping speed; however, it proved to be of doubtful value.

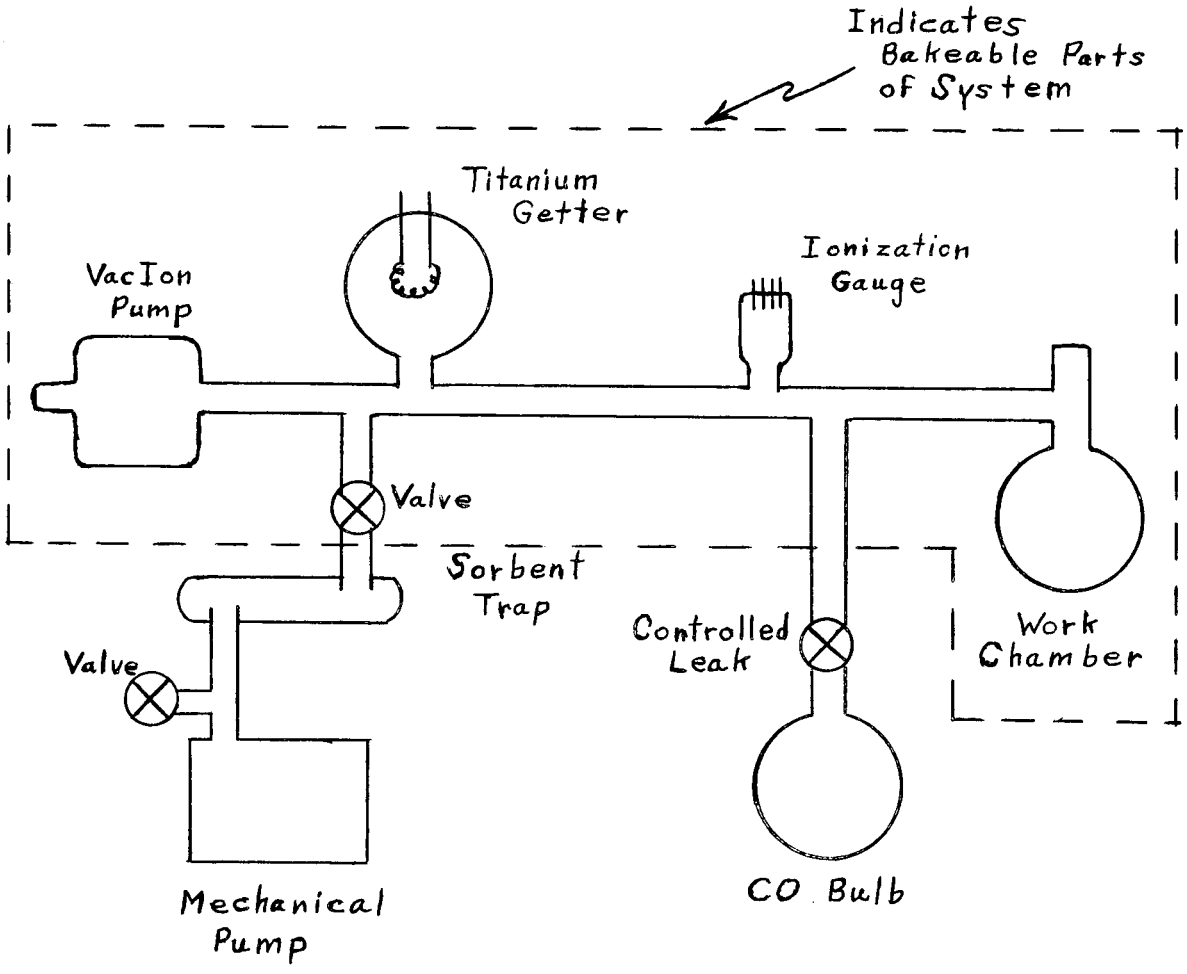

Figure 38 Diagram of apparatus for the deposition of thin films.

A Veeco type RG-75 Bayard-Alpert type ionization gauge capable of measuring pressures down to 10^{-10} torr was used. The carbon monoxide used as the adsorbate gas was let into the system through a Granville-Phillips type C valve equipped with a low-torque driver.

Film Deposition

The molybdenum films were deposited on the inside of a glass bulb, approximately 10 cm in diameter, whose temperature was regulated by immersion in a constant temperature bath. Details of the bulb are shown in Figure 4. The substrate surface for the first two films was cleaned by acid, rinsed with distilled water, and then rinsed with acetone. For the third film the cleaning procedure was changed to detergent cleaning, acid cleaning, NH_4OH rinse, and distilled water rinse with distilled water rinse between all steps.

The film material was evaporated directly from a filament of 0.012 inch diameter molybdenum wire heated by passing a current of 7 amperes through it. The purity of the wire was unknown. Before installing it in the system, the filament was heated under vacuum to the sublimation point.

Resistance Measurement

Electrical contact with the film was made through two spring clips making contact with two strips of silver conducting paint on the sides of the bulb. A direct current of 1 milliampere, provided by a 6 volt battery in series with a 6000 ohm variable resistance, was passed through the film. The resulting voltage across the film was measured and recorded by a Sargent model SR recorder. By this method resistance of the film could be measured to within 0.5 ohm.

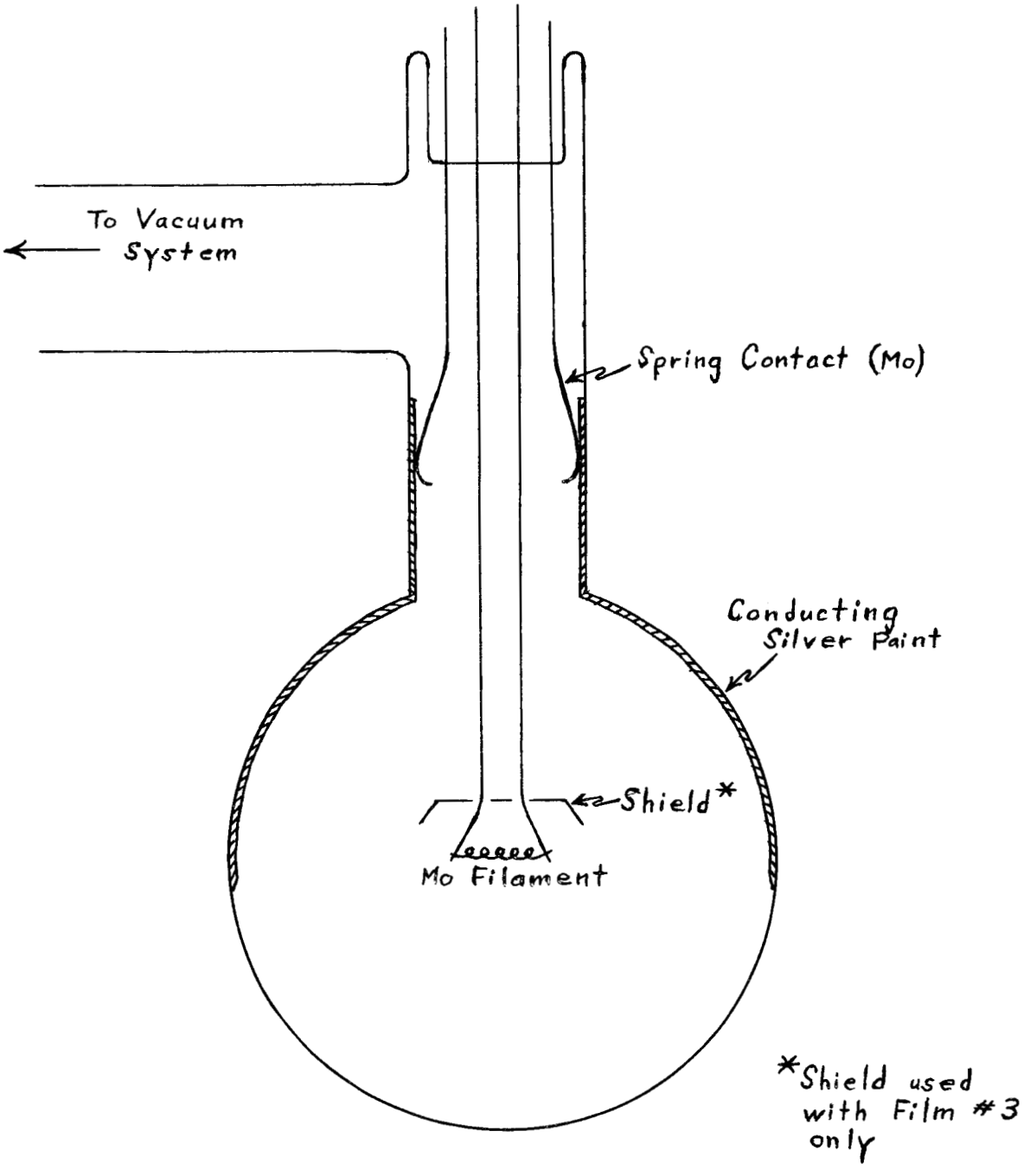

Figure 4. Bulb for the deposition and measurement of resistance of molybdenum films.

II. PROCEDURE

The procedure used in the deposition of the molybdenum films and the subsequent measurement of resistance was as follows:

1. The Mo filament was outgassed just below the evaporation point, and a dry ice and acetone bath (-78°C) was placed around the bulb.
2. The filament was evaporated until a film of approximately 100 ohms was produced. The resistance was then monitored for ten minutes.
3. The dry ice bath was removed, and boiling water (100°C) was placed around the bulb. The film was annealed at this temperature until no further resistance change was noted. The dry ice bath was then put back in place.
4. Carbon monoxide was let into the system to a pressure of 10^{-8} torr. The film resistance was monitored until no further resistance change was noted. The carbon monoxide was then pumped off.
5. Step 4 was repeated using carbon monoxide at pressures of 10^{-6}, 10^{-5}, and 10^{-4} torr.
6. The temperature of the film was cycled between -78°C and 100°C several times while the resistance was recorded in order to give a basis for calculating the temperature coefficient of resistance.

SECTION IV

RESULTS AND DISCUSSION

Three molybdenum films were produced and their resistance measured as carbon monoxide was let into the system at various pressures according to the procedure outlined in the preceding section. The first two films were deposited over the entire bulb (see Figure 4), while for the third film a shield was placed over the filament so that molybdenum was deposited only over the lower half of the bulb. This meant that effectively a larger area of film was contributing to the measured resistance.

The thickness of the films in all three cases was estimated on the basis of appearance to be of the order of 200-500 Å. The data are given in Figures 5-7 and are summarized in Table I.

Several qualitative comments can be made on the basis of these data.

1. The apparatus as constructed is capable of depositing and measuring the resistance of molybdenum films. Pressure can be maintained at less than 10^{-8} torr while evaporation is taking place. The resistance of the films showed qualitatively expected results. Resistance decreased as initial annealing took place and increased as adsorption took place. After annealing, the films showed a positive temperature coefficient of resistance. The fact that the pressure did not show an appreciable rise as evaporation started indicates that the filament was well outgassed. The favorable vacuum conditions during evaporation plus the positive temperature coefficient make it reasonably safe to assume that the films were metallic molybdenum.

When the dry ice bath was removed and the annealing bath put on (step 3 of procedure), the pressure in the system rose to about 1×10^{-7} torr. Upon replacing the dry ice bath after completion of the anneal (approximately 10 min.), the pressure fell again to 5×10^{-9} torr. Similar observations are reported by Roberts[28], but he offers no explanation for them.

2. The increase of resistance of all three films was approximately 4.5%. This is of the same order of magnitude as that observed in previous work with carbon monoxide on nickel films.[3,4] Quantitative measurements, such as those described by Zweitering[4], which would have made possible the determination of the number of electrons per molybdenum atom involved in the bond were not carried out. This would be desirable in future experiments.

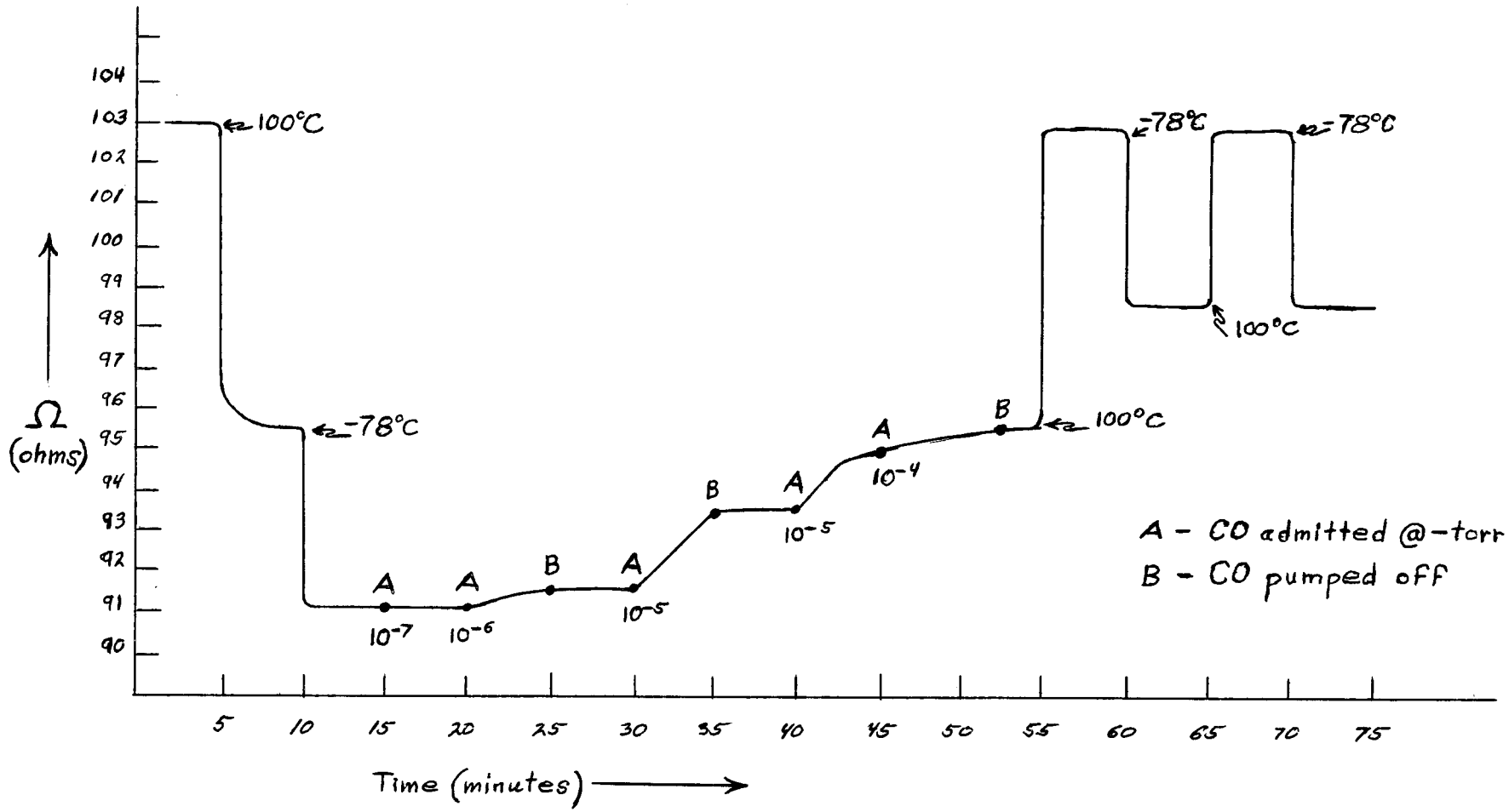

Figure 5: Resistance changes of molybdenum Film #1 on the adsorption of carbon monoxide.

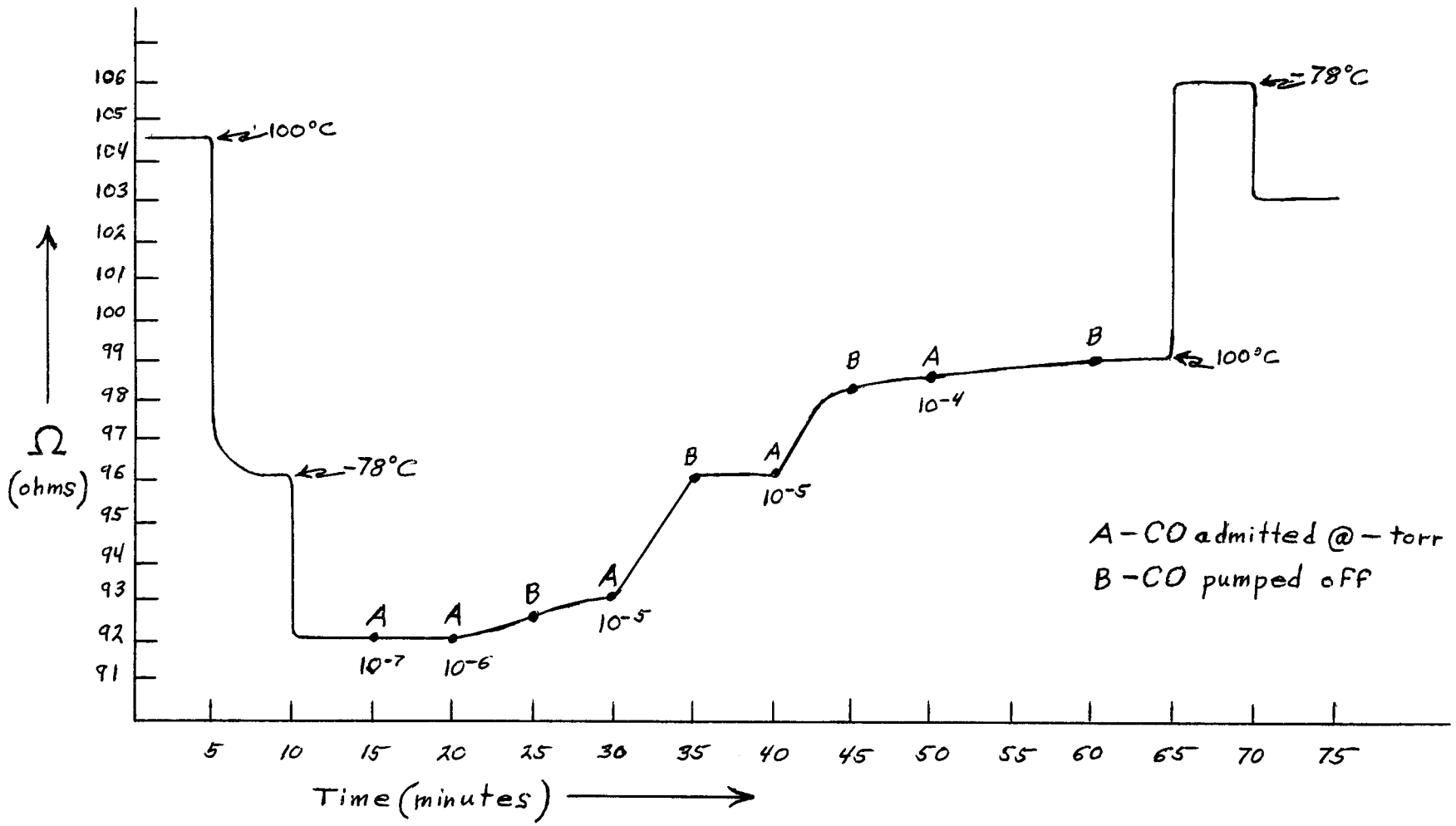

Figure 6: Resistance changes of molybdenum Film #2 on the adsorption of carbon monoxide.

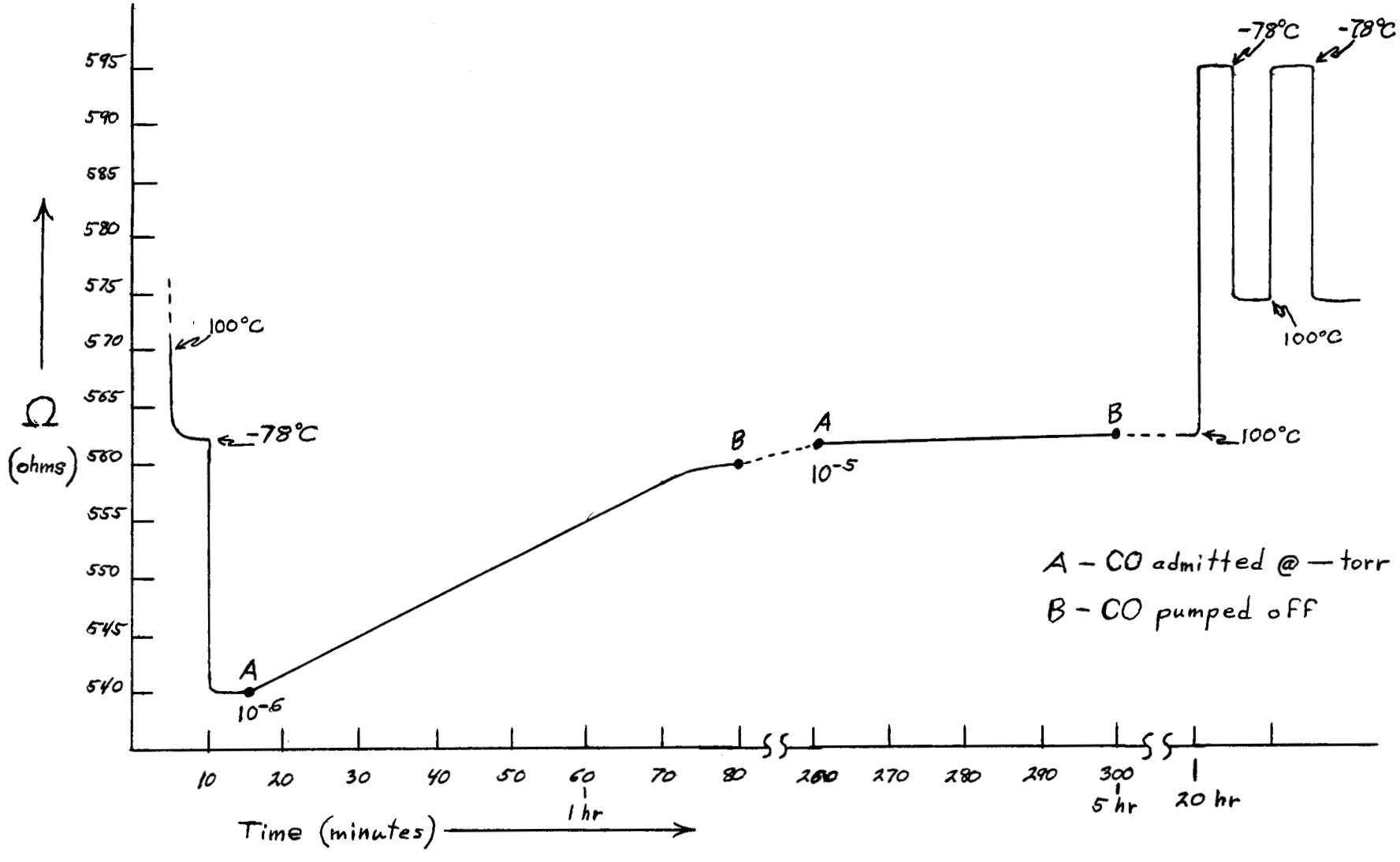

Figure 7: Resistance changes of molybdenum Film #3 on the adsorption of carbon monoxide.

TABLE I

RESISTANCE OF MOLYBDENUM FILMS AS A

FUNCTION OF CARBON MONOXIDE PRESSURE

CO pressure (torr)	Film number	Resistance (ohms)	% Change in Resistance	Time exposed to CO (min)
	1	91	0	5
10^{-7}	2	92	0	5
	3	-	-	-
	1	91.5	0.55	5
10^{-6}	2	92.5	0.54	5
	3	562	4.1	65
	1	95	4.4	10
10^{-5}	2	97.5	6.0	10
	3	565	4.6	50
	1	95.5	4.9	10
10^{-4}	2	98.5	7.0	12
	3	-	-	-

3. The resistance of the third film was monitored for 15 hours after the carbon monoxide had been pumped off and no decrease in resistance was noted. This indicates that the adsorption is not reversible since, on the basis of the present theory, desorption would cause a decrease in resistance. This is also in agreement with previous work using carbon monoxide as the adsorbate.(3)

4. After the resistance measurements (at -78°C) were completed, the film temperature was cycled between 100°C and -78°C several times. Resistance was measured at the two temperatures. The first heating to 100°C produced an irreversible increase in resistance. Upon subsequent cooling to -78°C the resistance was 2% higher than the previously measured resistance at that temperature. This was observed for all three films. Further temperature cycling produced no additional irreversible effects. The system pressure increased somewhat during the heating of the film.

No explanation is offered for this irreversible temperature effect. Two possible results of increasing the film temperature, desorption of the carbon monixide and further annealing of the film structure, would both be expected to produce a decrease in resistance, whereas just the opposite occurred.

5. The temperature coefficient of resistance of the films was calculated as

$$\alpha = \frac{2}{R_1+R_2} \frac{R_2-R_1}{T_2-T_1}$$

where R_1 = total resistance at T_1, and R_2 = total resistance at T_2. The values of α for two of the films are given in Table II. These values are of the order of $10^{-4}/C°$ as compared to values of the order of $10^{-3}/C°$

TABLE II

TEMPERATURE COEFFICIENT OF RESISTANCE OF THE MOLYBDENUM FILMS

	$\frac{R_1 + R_2}{2}$	α
film 1	100	2.5×10^{-4}
film 3	583	2.1×10^{-4}
bulk metal[29] value		3.5×10^{-3}

for bulk molybdenum.[29] The lower temperature coefficient may indicate a more disordered structure in the films than in the bulk metal.

6. With all three films an apparent saturation level was reached at a certain pressure of carbon monoxide. This was indicated by the fact that no further increase of resistance was noted as the carbon monoxide pressure was increased above the saturation-level pressure. For the first two films this saturation pressure was 10^{-5} torr, while for the third film it was 10^{-6} torr. The time required to reach saturation at the given pressure was less than 10 minutes for the first two films, but on the order of 70 minutes for the third film. This difference by nearly a factor of 10 in the times corresponds to the factor of 10 difference in the pressure at which the adsorption was taking place.

The time required for a monolayer of a gas to form on a surface at a given pressure can be calculated on the basis of simple kinetic theory from a knowledge of the number of molecules striking a surface per unit time and the number of sites available on the surface. Assuming a sticking coefficient of one, the time is one second and ten seconds for pressures of 10^{-5} and 10^{-6} torr respectively.

The times required to reach the saturation level were of the order of 500 times as great as these calculated times. There are three possible explanations for this. The adsorbed gas may be more than a monolayer; the sticking coefficient may be much less than one; or not all of the adsorption sites may be directly exposed to the gas. The first of these is unlikely on the basis of what is already known about chemisorption. The sticking coefficient has been determined for carbon monoxide on tungsten by the flash filament technique to be about 0.5[30] and so is almost certainly not of the order of 10^{-3} for carbon monoxide on molybdenum.

The third suggestion has recently been put forward by Roberts[28]. He found the probability of carbon monoxide adsorption on molybdenum films to be about 5×10^{-3} at -80°C for about 90% of the adsorption. The probability of adsorption is defined as the ratio of number of molecules adsorbed to number striking the surface. This probability was found to be temperature dependent, but independent of gas pressure, film thickness, or annealing temperature of the film. He proposed a porous film model to explain this. The gas "sees" only the outer surface of the film and rapidly forms a monolayer on it. The molecules from the outer surface can then become adsorbed on the much greater inner surface, and this is then a kind of rate determining step and accounts for the low constant probability of adsorption observed.

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