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FEASIBILITY STUDY OF TECHNIQUES
TO PROTECT MECHANISMS OPERATING
IN SPACE FROM MALFUNCTION

PART II - EXPERIMENTAL RESULTS AND
RECOMMENDATIONS

January, 1965

Mechanical Engineering Division
IIT Research Institute
Technology Center
Chicago, Illinois 60616

Technical Summary Report - K6055

FEASIBILITY STUDY OF TECHNIQUES TO PROTECT

MECHANISMS OPERATING IN SPACE FROM MALFUNCTION

PART II - EXPERIMENTAL RESULTS AND RECOMMENDATIONS

28 June 1963 - 27 June 1964

by

W. E. Jamison

Prepared for the

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

January, 1965

FOREWORD

This technical summary report on IITRI Project No. K6055, "Feasibility Study of Techniques to Protect Mechanisms Operating in Space From Malfunction," covers the work performed during the period June 28, 1963 to June 27, 1964. The work was sponsored by the National Aeronautics and Space Administration, George C. Marshall Space Flight Center under contract NAS8-11014, with Dr. W. R. Eulitz acting as the contracting officer's technical representative.

This work was performed by the Fluid Systems and Lubrication Section of the Mechanical Engineering Division under the management of Mr. F. Iwatsuki. Principal investigator was Mr. W. E. Jamison. Support was provided by Drs. C. Riesz and A. Dravnieks and Mr. H. Weber of the Chemistry Research Division for the contact potential measurements and by Drs. P.R.V. Evans and R. Elliott and Mr. D. Warwick of the Metals Research Division in the preparation and analysis of the experimental materials.

IIT RESEARCH INSTITUTE

K6055
Final Report

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

K6055
Final Report

LIST OF TABLES

FEASIBILITY STUDY OF TECHNIQUES TO PROTECT
MECHANISMS OPERATING IN SPACE FROM MALFUNCTION

I. INTRODUCTION

The point of view adopted here, that further advances in understanding and controlling friction must be derived through fundamental studies conducted on a molecular level, requires clarification and definition for complete understanding.

Friction, defined as the macroscopic resistance to motion of two bodies in loaded contact, can no longer be viewed as a materials property on a molecular level. This is so because the phase boundaries, or "surfaces" of the solids exist in a state profoundly different from that of the bulk material. In addition, the "surface" exists on a different plane and the "surface state" encompasses a different volume according to a chemical, physical, or electromagnetic point of view. The situation is complicated by the inevitable contamination which arises from surface adsorption.

For the discussion which follows, we define "a friction interface" which consists of a volume encompassing the region in which relative motion occurs, and which includes all of the molecules in both solid phases which participate in the friction process. The differences between this interface and the classical picture of a friction interface are illustrated in Fig. 1. Basically, the classical picture charts the physical distribution of molecular species. The new interface picture, however, can be interpreted equally well in the physical, chemical, or electromagnetic sense. The region of motion is seen to be a volume which, in the ideal case, would contain a plane of zero shear strength. In this picture, no assumptions are made concerning the distribution of molecules, their states, or their interactions, although the difference which is known

K6055
Final Report

Fig. 1 FRICTION INTERFACE

CLASSICAL FRICTION INTERFACE

NEW FRICTION INTERFACE

PLANE OF SLIDING

REGION OF BULK MATERIAL INFLUENCE

INTERFACIAL VOLUME

BULK MATERIAL

BULK MATERIAL

SURFACE FILM

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K6055
Final Report
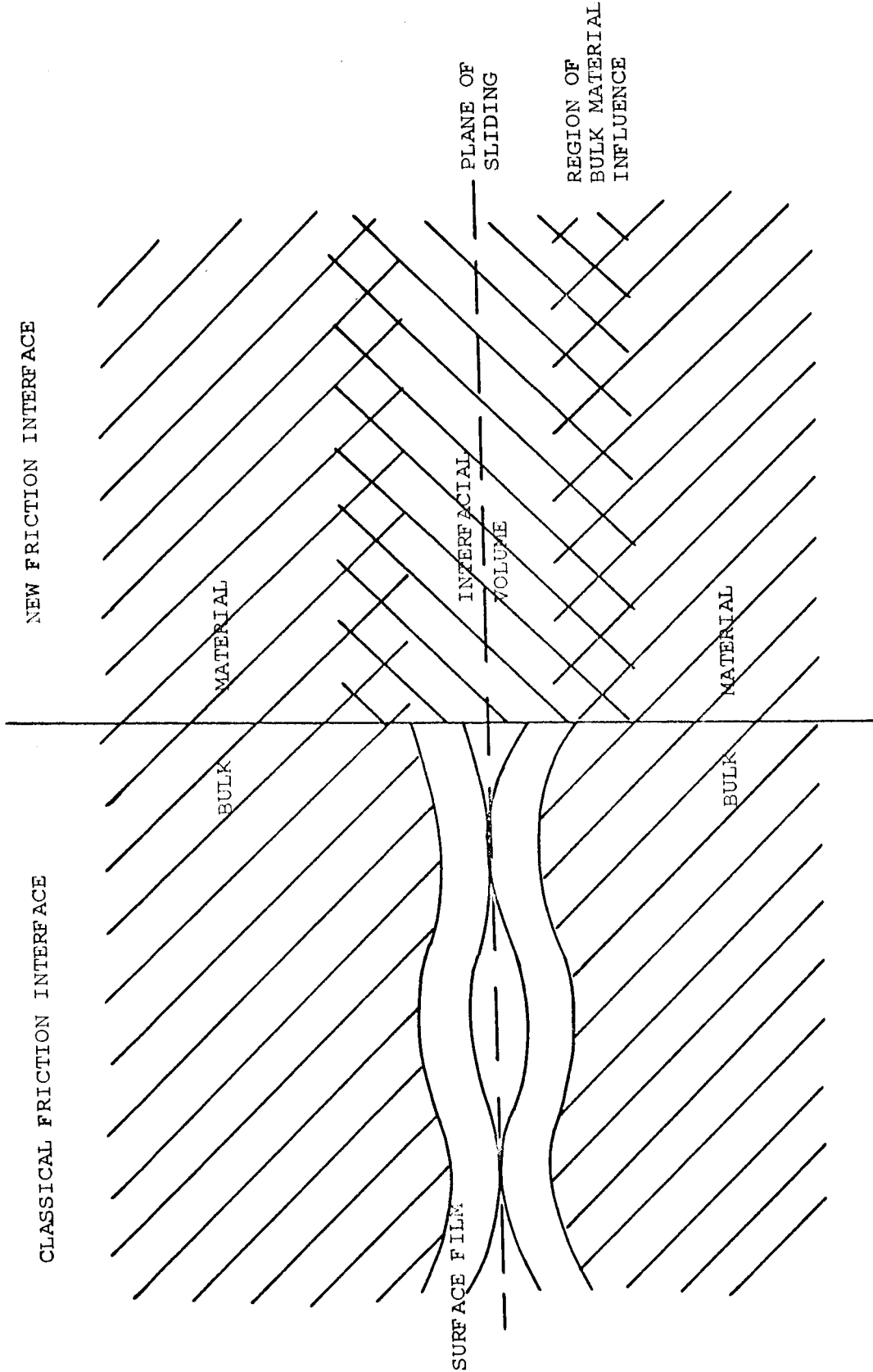
to exist between bulk and surface states is acknowledged.

Although this generalization of the friction interface may at first seem arbitrary and superfluous, it has been found necessary to deviate from the classical picture to allow for the definition of the electrical and chemical interactions whose influence on friction will be revealed as our knowledge of the fundamental friction processes progresses, and to define the "ideal" friction interface in all senses.

It can be seen that the "friction interface," as defined above, can exist within a single solid phase. When a single solid material is sheared, it contains the regions of undeformed bulk material, the region of relative motion, and volumes of molecules on both sides which undergo no macroscopic relative motion but which participate in the friction process through bulk distortion. The observed friction in this case is the force required to shear the material. Clearly, this is a non-ideal friction interface which points to the importance of surface states in determining friction properties.

II. RECOMMENDED METHODS FOR MEETING SPACE ANTI-FRICTION REQUIREMENTS

A. A Summary Statement of the Space Friction Situation

It was established in Part I of this report that current lubrication practices show little promise of meeting anti-friction requirements for space applications. This is largely due to the empirical development of lubrication technology. Historically, anti-friction devices (bearings, gears, etc.) were designed to operate with ordinary materials (metals and lubricants) and thus relied on naturally occurring phenomena to provide acceptable friction and wear performance. Since the level of sliding friction with natural materials was too high for many applications, rolling element bearings were developed to reduce frictional torque. While these devices have provided satisfactory service for most earth-bound applications, aerospace requirements have exceeded their capabilities. As requirements changed and operational environments increased in variety and severity, bulk materials properties were altered in attempts to provide satisfactory interfacial conditions while still employing the same basic mechanisms. The environments have now become so extreme that materials development has not succeeded in keeping pace with the requirements. This has occurred because the naturally occurring phenomena leading to friction and wear are not sufficiently understood to enable researchers to develop the necessary interface properties. This situation has also inhibited the development of anti-friction techniques based on artificially induced phenomena; i.e., artificially induced interface conditions can probably produce friction performance superior to that found in nature, but without a complete understanding of the molecular interactions involved in friction, even the requirements for such an interface cannot be fully stated. It is clear, however, that one requirement, zero shear strength along a predetermined plane, must be fulfilled for ultimate performance. Once this

IIT RESEARCH INSTITUTE

4

requirement is met, such complex devices as rolling element bearings can be discarded in favor of simpler mechanisms.

B.   Recommendations for Meeting Current Requirements

It is recognized that many friction and lubrication problems are of immediate concern to designers, and that solutions must be found within a reasonably short period of time. For these situations it is recommended that the designers concentrate on efficient application of current space lubrication technology, and limit their experimental efforts to "application testing." Large scale materials screening programs and development of new lubricants for specific applications have generally been unsuccessful in either solving the immediate problems or contributing to the basic understanding of friction.

C.   Recommendations for Meeting Future Requirements

The space friction problem is seen to be primarily an interface problem. Its solution is thus the development of new materials and surfaces or the modification of old materials and surfaces to provide the necessary interfacial conditions to produce good friction and other operational characteristics. It is clear, then, that a basic understanding of how surface properties affect friction is required. This has not yet been achieved. Since surfaces must be modified or manufactured through molecular interactions, it seems logical that friction, also, must be understood on the same scale. Our current knowledge of friction is generally related only to the macroscopic properties of materials.

It is therefore recommended that a major effort be made to obtain a better understanding of the molecular interactions which comprise friction and to establish a control over these interactions through adjustments in surface composition and treatment. Two methods are seen for accomplishing this. The first is to theoretically establish the desired properties and then, based on a knowledge of the laws of atomic and molecular

interactions, to formulate interfaces with the required properties. Numerous examples of the success of this approach can be found in bio and polymer chemistry and solid state physics.

The second method is to investigate those materials existing in nature which exhibit certain desired properties. These properties can then be induced in other materials which may be more suitable for the particular application. For example, if the molecular interactions which provide lubricity with graphite and adsorbed organic monolayers can be understood, then these interactions can be promoted in the surface layers of materials whose structural properties are satisfactory for bearing manufacture. A preliminary investigation of this latter approach was conducted in the experimental portion of this program. This work is discussed in detail in Section IV. Specific recommendations for research on both approaches are discussed in Section III.

III. RECOMMENDATIONS FOR FURTHER RESEARCH

It was stated in Section II that the required understanding of the molecular nature of friction can be obtained through two methods of investigation: a theoretical approach and an experimental approach. Specific programs for these investigations are outlined below.

A.   Theoretical Approach

It has been established that the forces of interaction between atoms are ultimately electrical in origin. Furthermore, these interactions can be mathematically described through the use of quantum mechanical theory. Calculations of this nature have been extremely successful in describing such physical phenomena as adsorption[1], interlayer binding energies in lamellar materials[2], and the directional properties of chemical valence bonds[3,4].

An investigative program based on this approach can proceed in a logical fashion. The structure of solid surfaces must be defined before the molecular interactions leading to friction can be thoroughly understood. When this is accomplished, the ideal friction interface (see Fig. 1) can be established as two plane surfaces with well defined properties separated by a volume encompassing a plane of zero shear strength. The basic steps in achieving the desired conditions are listed below:

1.   Definition of ideal surfaces at 0°K

2.   Definition of the interactions of individual molecules with ideal surfaces at 0°K

3.   Definition of the interactions between groups of molecules (lateral interactions) on ideal surfaces at 0°K.

4.   Definition of the thermal effects on the interactions at real temperatures

5.   Definition of the effects caused by non-ideal surfaces

   a.   Dislocations and crystalline imperfections

IIT RESEARCH INSTITUTE

b. Crystalline impurities

c. Adsorbed impurities

6. Definition of the interactions caused by the lateral transport of individual molecules and assemblages of molecules across the surface

7. Mathematical formulation of molecules with ideal properties. That is, once the molecular interactions which lead to friction between surfaces have been mathematically expressed (in terms of electron orbits, etc.) then it should be possible to mathematically formulate a molecular assemblage with ideal interface properties (zero friction)

8. Physical synthesization of the materials with the ideal properties

Two gross problems are apparent in the conduct of such an investigation. First, our present knowledge and mathematical capabilities limit studies of surfaces to only the simplest cases. Second, the scope of work outlined above would require a mammoth expenditure of effort for completion. However, much of the ground work is already done and the required investigative tools are presently being developed.

The structure of solid surfaces is being studied at laboratories throughout the world. In addition to providing the required background technology, this research provides a supply of man-power already well versed in the investigative techniques. Also, the breadth of the problem can be considerably narrowed by considerations of the ultimate objectives. That is, by considering the physical requirements specifically for anti-friction system, constraints can be stated which narrow the conditions which need to be studied.

Significant benefits will be derived from even partial completion of the proposed investigation. Any results which further the understanding of surface phenomena will immediately contribute to the experimental solution of the friction problem. The knowledge gained will also apply to many current research problems in other fields.

K6055
Final Report

Since the laws of nature are universal, the basic understanding of the molecular nature of friction will eventually be developed through research in other disciplines. However, if the results are to be of value in providing working components for space vehicles now in the design concept stage, an organized program such as that outlined above should be started without delay.

B. Experimental Approach

Experimental studies can contribute to our understanding of friction in two ways: verification of the hypotheses developed theoretically, and disclosure of unknown relationships occurring in nature. The former becomes obvious as the theoretical approach is pursued. The latter form an infinite set. The programs suggested below are investigations which seem to offer potential in the latter manner based on our current knowledge.

1. Investigations of the Influence on Friction of Surface Roughness, Surface Energy and Molecular Distribution

The surface of an engineering material may be characterized as a three dimensional array of atoms and molecules which deviates physically from a plane by distances manifoldly greater than the intermolecular spacings, and which exists in an energy state far different from that of the bulk material. In addition, a surface differs from the bulk in molecular composition through the mechanisms of diffusion, chemical reaction and adsorption; such differences being often controlled by the external environment. Surface conditions govern, in a large part, the observed friction of the unlubricated materials and the effectiveness of lubricants in reducing friction. It seems necessary, then, to adequately define how surface conditions affect friction before durable low friction interfaces can be generated.

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Both surface roughness and surface energy are implicitly interrelated with the distribution of atoms and molecules within the interfacial volume. These relationships are discussed below and research is suggested for further elucidation of their effects on friction and for development of techniques to produce low friction surfaces.

In the study of low friction systems involving solid surfaces, it has been found that the ploughing, or deformation, aspect of friction is often negligible, and that frictional forces arise mainly through molecular adhesion. The roughness which exists on engineering surfaces thus affects friction in three manners: (a) alteration of the contact area between surfaces, (b) imposition of surface shear strains, and (c) variation of the surface energy available to form adhesive bonds.

Although the effects of roughness on friction have been qualitatively stated in some detail[5.6,7,8], and elegant experimental techniques have been devised for surface examination, useful quantitative relationships have not been established. This is due, in a large part, to the complex forms which roughness can assume and to the variable effects of contamination of surfaces in impure environments.

Surface energy, surface tension, and surface stress are terms describing variations which arise when a bulk material terminates in a boundary. Surface free energy of a solid surface is the reversible work of formation of a unit area of surface from interior molecules[9]. On the other hand, surface tension is the force per unit distance which is required to overcome lateral interactions between molecules[5]. That is, surface energy describes conditions on a plane parallel to the surface and surface tension involves molecular interactions on a plane perpendicular to the surface.

The existence of roughness testifies to the ability of solid surfaces to withstand stress without undergoing flow.

This implies that the surface energy need not be the lowest possible for that material and is not necessarily uniform. It also implies that a correspondence need not exist between free surface energy and surface tension. Because neither of these quantities is accessible to direct experimental measurement and theoretical predictions for engineering surfaces composed of various crystal lattice planes, grain boundaries, imperfections anc contaminant species are practically impossible, studies of their effects on friction have thus been limited to near perfect crystals[10,11,12,13, 14]. It has been established that the lowest surface energy corresponds to crystalline planes having the closest molecular packing (maximum number of nearest neighbors)[9]. It should be expected, then, that frictional anisotropy should be observed in crystalline solids. Bowden[10] has shown that the friction along the octahedral face,(111) plane, of diamond (5.4 $\overset{\circ}{A}{}^2$ per atom-surface energy $\simeq$ 5000 ergs/cm^2) is 2 to 3 times lower than along the cube face,(100) plane (6 $\overset{\circ}{A}{}^2$ per atom-surface energy $\simeq$ 8000 ergs/cm^2). However, covalently bonded structures such as diamond show strong directionality in bond formation, and these relationships are not directly transferable to ionic or metallic materials.

These observations suggest investigation of the effects of surface energy, surface tension, and molecular distribution on the friction of metallic engineering surfaces. Gwathmey[14] reports that the static friction coefficient between oriented, oxide-free single crystals of copper is four times higher on the (100) face than on the (111) face. Rabinowicz[15] has found a correlation between surface energy (and surface tension) and the size of wear particles generated in sliding metal systems. The influence of lubricants and environmental contaminants in reducing adhesive bonding through lowering of surface energy has been experimentally demonstrated[16]. It is expected that similar quantitative relationships between kinetic friction, surface energy, and molecular distribution can be disclosed.

Experiments should logically utilize metallic surfaces which are as uniform and compositionally homogeneous as possible. The plasticity of metals complicates the study and use of the various crystalline planes in sliding systems and the large influence of microcontamination imposes severe experimental practical limitations.

Certain techniques of mechanical polishing can produce metallic surfaces of high flatness, smoothness, and uniformity. Such surfaces contain a Bielby[17] layer of amorphous material which has flowed under the polishing action. This Bielby surface can then be used as a normalized substrate for investigating the effects on friction of various surface treatments.

a. Adsorbed Organic Films

Since the time of Hardy[18], the lowering of friction between solids by monomolecular films of organic compounds has received considerable study[19]. Recently, Zisman[20] has performed a careful and systematic study of the action of monolayers of the various polar-nonpolar compounds of varying chain lengths. Friction coefficients are readily reduced to values on the order of 0.05 and are apparently independent of load. The mechanism by which friction is reduced is not clearly understood; however, several factors show definite influence.

The monolayers adsorb with their polar ends attached to the substrate and tend to orient in a two dimensional lattice dictated by the polar group and the crystallinity of the substrate. For homologous series, the surface tension (as described by contact angle measurements) decreases with increasing molecular weight (increasing chain length) and reaches a limiting value which corresponds to a close packed array of the unattached terminal groups. Friction also decreases with increasing molecular weight and reaches a limiting value at approximately the same weight. The limiting value of friction depends both on the type of exposed end group and on the nature

of the attached polar group. This has been attributed[21] in part to the difference in size between the two terminal groups, which prevents the exposed surface from reaching a closely packed configuration (e.g., in the case of fatty acids the polar acid groups each occupy ~ 21 sq $\overset{\circ}{A}$ and the nonpolar methyl groups occupy only 18 sq $\overset{\circ}{A}$). The effect of substituting fluorine atoms for hydrogen atoms in the end group increases the diameter of the group and decreases the surface tension as predicted by theory, but does not reduce friction as might be expected.

Zisman[20,22] has shown that such monolayers may be regarded as solids and can support loads of 70 kg/mm^2 (107,000 psi) without penetration. However, the durability and wear life are low under dynamic conditions. Recent developments of similar silicone compounds for lubricating aluminum[23] show that adsorbed monolayers can be utilized to provide low friction for extended periods in highly loaded mechanisms.

It is suggested that research be conducted to investigate the application of adsorbed organic monolayers for space mechanisms. Smith[24,25] has shown that adsorbtion can be activated by mechanically working the substrate surfaces (the Kramer effect) under solutions of the adsorbates. Production of monolayers on Bielby surfaces in this manner will provide friction interfaces approaching the ideal. Investigations may then be performed of the effects on friction of surface energy, surface tension, and molecular distribution by varying the molecular species and packing in the terminal groups. Other investigations should be performed of the effects of cross linking and otherwise modifying the bulk characteristics of the monolayers.

b. Thin Metal Films

The advantages of using metal films for producing low friction in space applications lie in their thermal stability

and low volatility. In previous investigations, metals such as gallium[26], indium and lead[27], and gold[28]; and alloys such as Wood's metal[29], Bismuth-lead[30], and gallium-indium-tin eutectics[31] have provided effective lubrication under certain operating conditions. The lowest friction is derived with films of 10^{-5} to 10^{-3} cm thickness which wet the substrate surface and which are operated at a temperature corresponding to a minimum shear strength. Effectiveness is lost as films are displaced or worn through, or when they react with atmospheric components or substrate constituents.

However, limited evidence exists which indicates that even lower friction may be obtained with thin metal films by an entirely different mechanism. The mechanism is not clearly understood, but is thought to arise from electrical influences at the film-substrate interface. Silver films deposited on certain crystals have exhibited a mobility corresponding to a shear strength well below that commonly associated with boundary lubrication[32]. Barium films vacuum deposited on ball bearings containing certain metals in their structure have provided lower friction than could be predicted from their physical properties and better lubrication than films of other metals with lower shear strength and melting points[33]. The films readily migrated over the bearing surface and acted as if in a liquid state.

It is suggested that investigations be undertaken to elucidate this mechanism for possible application to space bearings. The Bielby surface can be logically used to provide a smooth, homogeneous substrate. Possibly, thin metal films may be replenished by incorporating the metal in the substrate structure or in porous secondary members of mechanisms.

c.   Crystalline Surfaces

Materials with layer lamellar crystal structures, such as graphite, MoS_2, talc, etc., have long been used as lubricating

materials. Normally, they are employed as fine particles (crystallites) and retention in the load bearing area has been the major problem in their use. The recent search for space lubricants has improved their utility through development of improved binders and application techniques, but has done little toward revealing the mechanism by which friction is reduced. Current theories ascribe them with a low tendency to form cohesive or adhesive bonds on their basal planes due to utilization of all available bonding electrons to form the structure or to saturation of bonds through adsorption of atmospheric components.

It is suggested that friction interfaces incorporating these materials be studied to determine the mechanism by which low friction is produced. Such information may be utilized in producing low friction interfaces in actual bearing systems.

2. Investigations of the Influence on Friction of Surface Electric Effects

It has been established that friction arises from the same forces which bind atoms together and that these forces result from the interaction of the electric fields formed by the electrons and protons within the atoms. Surfaces form electrical discontinuities, just as they do physical discontinuities, and electrical phenomena exist at surfaces which are forbidden in the bulk. Quite often natural phenomena act to increase friction. However, a better understanding of the electrical interactions can facilitate the production of low friction interfaces.

A relationship has been established between the friction, surface tension, and interfacial potential of metals in electrolytes[34]. For minimum friction and surface tension, the interfacial potential is adjusted to attract positive or negative ions to the surfaces. The mutual repulsion in the layer of ions on the surface reduces the surface tension. Additional

ions of opposite charge accumulate in the vicinity of the surface, producing the well known "double diffuse layer". Two such layers tend to repel each other at relatively large distances, probably accounting for the reduced friction. Similar double layers are induced through adsorption on surfaces in vacua. Application of an electrostatic potential gradient parallel to the interface promotes ion movement[5] and could presumably further reduce friction.

The development of laser action, anisotropically conductive semiconductors, and superconducting materials points to additional techniques for modifying the energy levels and charge accumulations at friction interfaces.

A permanent polarization can be effected in certain dielectrics[35]. This polarization induces surface electric charges as high as 3×10^{-5} coulombs/m^2 in waxes and 1.5×10^{-4} coulombs/m^2 in certain plastics. When induced in a friction interface, these surface charges could provide bearing supports of 100 n/m^2 (0.015 psi) and 2560 n/m^2 (0.38 psi) respectively. This compares favorably with an existing gyroscope electric support[36] of 1500 n/m^2 (0.22 psi). In addition, the surface electric field reflects an orderly distribution of electric dipoles which could be used to promote adsorption of molecular species to further reduce friction.

It is suggested that investigations be undertaken of friction reduction through modification of surface electrical properties. In particular, the accumulation of selected molecular species at the friction interface through dipole attraction, and the modification of surfaces to reduce the electrical forces giving rise to friction seem most promising.

IV.　EXPERIMENTAL INVESTIGATION OF VACUUM FRICTION

A.　Objective

The objective of the experimental investigations conducted in this program was to establish techniques for providing a composite view of the friction interface. Previous fundamental investigations of friction have been concerned with physical, chemical, or electrical phenomena at the interface, but seldom have all three been investigated simultaneously. It is thought that a composite picture is required for complete understanding of the friction process.

B.　Experimental Procedures and Equipment

The limited time and funds for this portion of the program restricted both the number of techniques which could be utilized and the types of friction interfaces which could be investigated. It was decided that interfaces of materials with known low friction properties should be investigated to derive an understanding of the interactions producing low friction. Materials of layer lamellar crystal structure were utilized in the form of thin films physically applied to metal substrates.

The friction interfaces were studied in an ultra high vacuum friction apparatus (Fig. 2). Experimental techniques which were employed included X-ray diffraction, contact potential measurements, and residual gas mass spectrometry. The parameters which were investigated for their effect on friction were: (1) interfacial molecular composition, (2) crystal lattice spacing, and (3) surface contact potential as affected by sliding and by adsorption of gaseous species.

The test specimen geometry was that of a sphere on a flat, as shown in Fig. 3. A 9.5 mm (3/8 in.) diameter sphere was loaded onto the flat substrate containing the surface film of material under study. The spheres were standard 440C
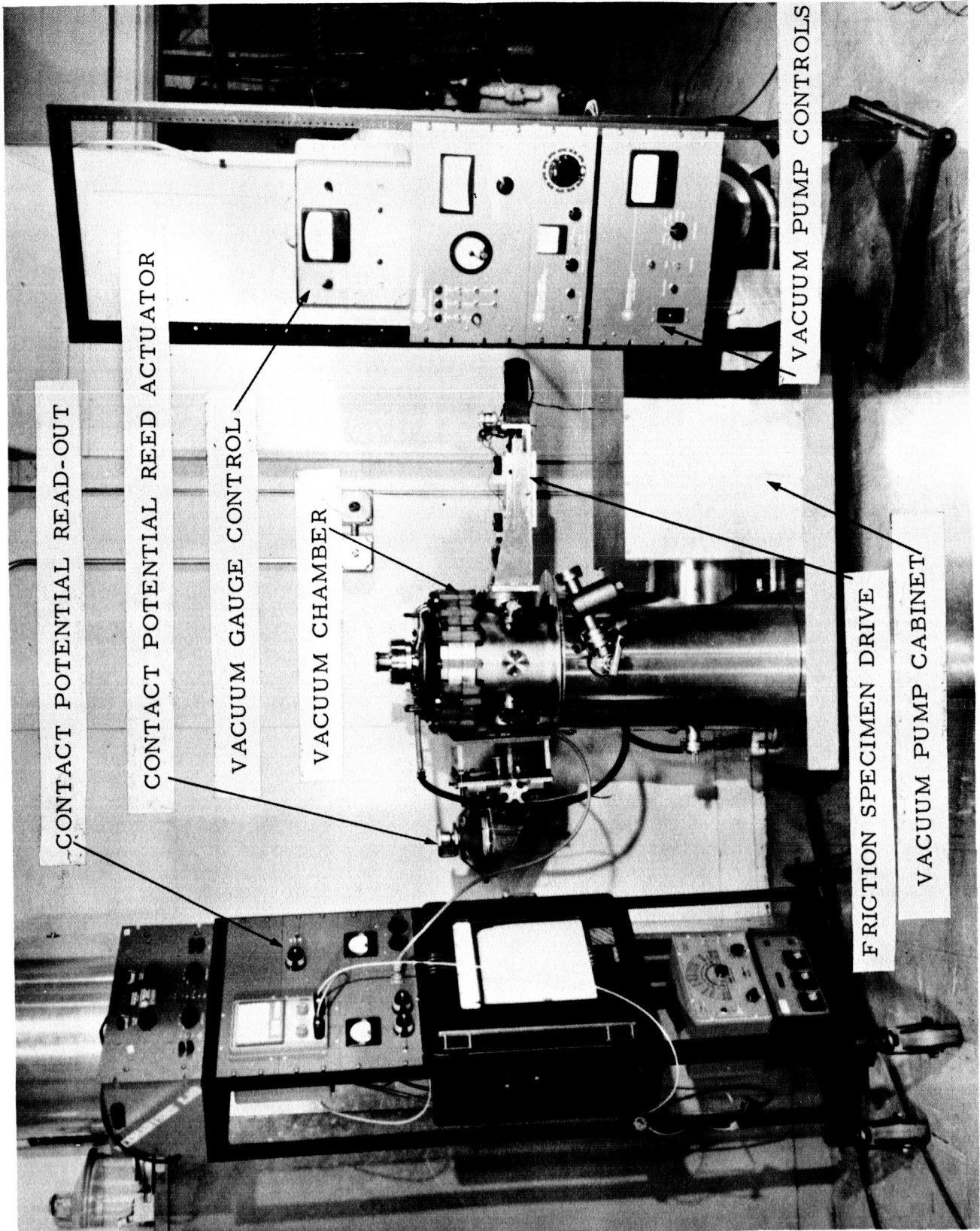
IIT RESEARCH INSTITUTE

　　　　　K6055
Final Report

CONTACT POTENTIAL READ-OUT

CONTACT POTENTIAL REED ACTUATOR

VACUUM GAUGE CONTROL

VACUUM CHAMBER

VACUUM PUMP CONTROLS

FRICTION SPECIMEN DRIVE

VACUUM PUMP CABINET
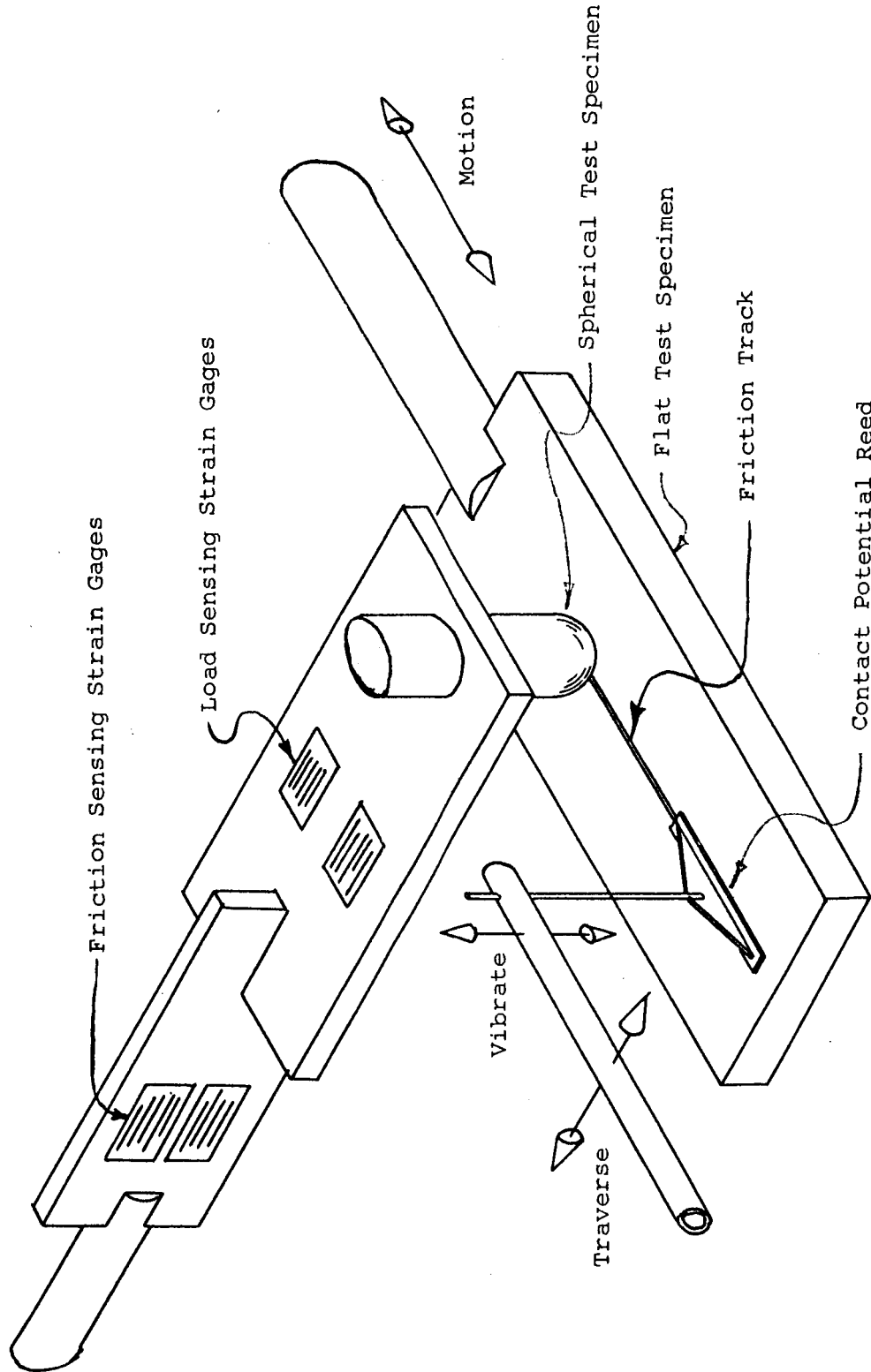
Figure 2 VACUUM FRICTION APPARATUS.

18

Fig. 3 SCHEMATIC OF VACUUM FRICTION APPARATUS

19

stainless steel balls of the type used in ball bearings. The flat copper substrates were polished with crocus cloth and had a Vickers hardness of 77 (100 g load). The flat was reciprocated under the sphere with sliding speeds of 420 and 8.5 microns per second. The sphere was loaded and contrained from outside the vacuum vessel, and the friction and load were measured inside the vessel with electrical resistance type strain gauges (suitably modified for UHV use).

Contact potential measurement was selected as a means of characterizing the electrical state of the friction interface. Contact potential is the potential difference that is established between the two phases when they are electrically connected. Basically, it describes the work required to bring a small amount of charged species from infinity to a point deep within the phase. It reflects a number of effects, including extraction of electrons from the phase (electronic work function) and the electrostatic effect of the Dipole Sheath (double layer) existing at the surface. Measurements of contact potential were made by the vibrating capacitor technique. In using this technique, the reed shown in Fig. 3 was held close to the friction surface and vibrated normal to the surface with a small amplitude at 170 cps. The vibration was supplied by a loud-speaker mounted externally to the vacuum vessel. The basic measurement technique is shown schematically in Fig. 4.
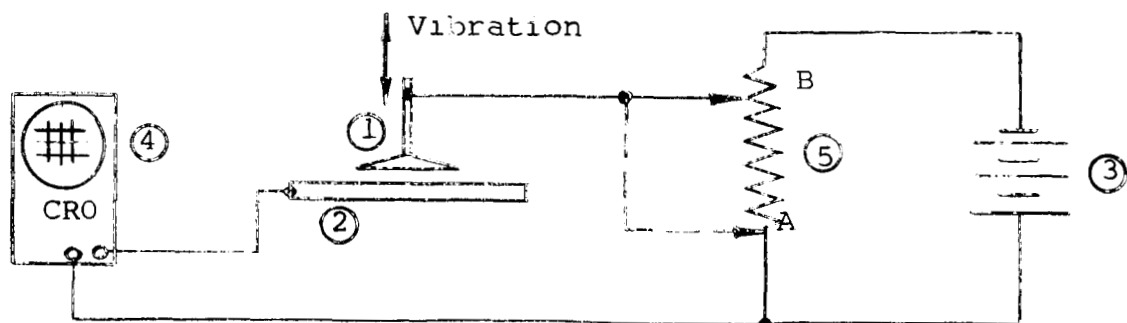

Fig. 4 SCHEMATIC OF CONTACT POTENTIAL APPARATUS

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K6055
Final Report

The vibrating reed (1) and the friction surface (2) are electrically connected in the circuit shown. A source of voltage (3) is supplied to cancel out the naturally occurring real potential between the two surfaces. This real potential is measured on the oscilloscope (4) with variable resistor (5) positioned at "A". The reed and friction surface form two plates of a capacitor, and, when vibration is present, impose an AC signal on the oscilloscope. By adjusting the variable resistor to "B", the potential difference between the plates is nulled and the AC signal disappears. The contact potential is then read as the voltage difference between "A" and "B". A contact potential scan of the friction surface can be made by moving the reed parallel to the surface in a direction normal to the friction track.

The vacuum system employed both sputter-ion pumping and getter pumping from evaporated titanium films. The pumping speeds were nominally 500 1/sec for the ion pump, which diminished to a very low value at pressures below 1×10^{-10} torr, and approximately 2000 1/sec for the getter pump. The total chamber pressure was measured with a Redhead Magnetron ionization gauge. Partial pressures of gases in the system were determined with an ultra high vacuum mass spectrometer of the 60 degree sector field type.

C.   Experimental Techniques

Preliminary experiments in air showed that reproducible test specimens could be produced by hand rubbing powders of the materials being studied onto metal substrates. Although the durability of the films was limited, the friction level remained at a low, constant value characteristic of the material itself for a period much longer than that required for the vacuum tests. In addition, contact potential measurements gave values which were reproducible for the various film materials and which were independent of the substrate materials.

IIT RESEARCH INSTITUTE

K6055
Final Report

No attempt was made to further optimize or refine the test specimen preparation, since all the work accomplished here was considered preliminary.

Samples of micron-size powders of MoS_2 refined from natural molybdenite were obtained from two suppliers. No difference in measurable properties was noted between the samples. Samples of synthetic powders of WS_2, WSe_2, WTe_2, $MoSe_2$, and $MoTe_2$ were also obtained[*].

The studies of crystal lattice spacing effects on friction consisted of alloying mixtures of these powders to produce crystals with expanded interlamellar distances, and comparing the frictional properties of films of these alloys with those of the unalloyed materials. It was originally theorized that if materials with similar crystal structure could be alloyed, then the differences in atom sizes would produce a distorted crystal; e.g., if WSe_2 could be alloyed into WS_2, then the larger selenium atoms would produce a lattice expansion in the WS_2 crystal. It was also theorized that if crystal lattice spacing is important in determining friction, then these materials with expanded interlamellar distances should exhibit lower friction than either of the unalloyed materials.

Various mixtures of the powders were compacted into pellets which were heat treated in glass vials in argon atmospheres. The effects of the treatments were measured by X-ray diffraction and the lattice constants were determined both by plots on a Hull-Davy chart and by computer analysis. It was determined by preliminary experimentation that alloying could be accomplished and that the lattice was expanded with several different mixtures of the materials. Optimum results

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[*] Initial samples of WSe_2, WTe_2, $MoSe_2$ and $MoTe_2$ were supplied by Dr. Himes, Battelle Memorial Institute.

K6055
Final Report

were achieved with a 1000°C heat treatment for 24 hours. Summary data for the individual powders and the best alloys are presented in Table 1.

The materials, as received from the supplier, contained considerable crystal distortion, probably incurred in the pulverizing process. In some cases, the materials required annealing before sharp X-ray diffraction patterns could be obtained. The annealing of the pure powders was done under the same conditions as the alloying of the mixtures.

The investigation of the effects of adsorption on friction was accomplished by measuring the friction and contact potential of the friction specimens after various procedures of vacuum exposure and thermal degassing. Mass spectrometric analyses of the residual gases in the vacuum vessel were made before and during the friction process to monitor frictional desorption from the solid films. Oxygen and methane were admitted to the chamber to determine the effects of adsorption of these gases on the friction and contact potential of MoS_2.

The friction apparatus was equipped to provide sliding speeds in the range of 8.5 to 420 microns per second. These slow speeds were selected to avoid changes in surface properties due to frictional heating. No measurable differences in friction level were noted between 8.5 and 420 microns per second. Therefore, all experiments were conducted at the higher speed to facilitate data recording, except as noted hereafter.

D.   Effects of Material Composition and Lattice Spacing on Friction

Materials whose lattice structure had been most noticeably modified by alloying (see Table 1) were evaluated for frictional performance in air and in ultra high vacua. Friction testing was accomplished by initially applying a light load (2-5g), sliding the specimen under the ball and measuring the friction

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TABLE 1- LATTICE CONSTANTS OF MATERIALS FROM DETERMINATIONS ON THIS PROGRAM

Material	Condition	Lattice Constants (Angstrom Units)		c/a	
		a=b	c	Computer	Chart
MoS_2	Heat Treated(1)	--	--	--	3.88
$MoSe_2$	Heat Treated(1)	3.3990	13.5642	3.9906	3.94
$MoTe_2$	As Received	3.5184	13.9400	3.9614	3.93
$2/3MoTe_2$ + $1/3MoSe_2$	Heat Treated	3.4161	13.6959	4.0092	4.02
$2/3MoTe_2$ + $1/3MoSe_2$	Heat Treated	3.2916	12.9582	3.9369	4.02
WS_2	Heat Treated(1)	3.1610	12.3678	3.9126	3.92
WSe_2	Heat Treated(1)	3.2868	12.9649	3.9445	3.95
WTe_2		(2)	(2)	(2)	(2)
$2/3WSe_2$ + $1/3WS_2$	Heat Treated	3.1928	13.1396	4.1154	4.00
$2/3WSe_2$ + $1/3WS_2$	Heat Treated	3.2283	12.8131	3.9689	3.96

(1) Heat treatment required to obtain accurate lattice constant determination

(2) Not indexed, since structure is orthorhombic. Values obtained from literature give a=14.028 Å, b=3.495 Å, c=6.270 Å.

in both sliding directions. The load was incrementally in-creased to a maximum of 250 g. In most cases, the friction was also measured in the same track as the load was decreased. In these tests, no difference in friction was noted between the increasing application of load and the decreasing one.

The results of the friction tests with modified lattice materials are shown in Fig. 5. Although the two materials studied had almost identical crystal structure, the friction performance of the molybdenum alloy was poor, while that of the tungsten alloy was good. However, the performance of the tungsten alloy was not superior to that of pure powders of WS_2 and WSe_2. Although the results of such limited testing cannot be considered conclusive, the indications are that lattice spacing does not play a predominant role in promoting low friction with materials of this type.

The effect of annealing on the vacuum friction of MoS_2 is shown on Fig. 6. It was originally thought that the lower friction exhibited by the annealed MoS_2 could be attributed to the relaxation of the crystal distortions produced by the manufacturing process. However, the friction differences were later explained as adsorption phenomena. Similarly, the re-duction in friction with the "as received" powder upon diminish-ing load was originally attributed to orientation of the MoS_2 crystallites in the friction track by the friction process. However, this was also shown to be an adsorption effect.

E.   Effects of Gas Adsorption on Friction

Generally, the effect of gas adsorption on MoS_2 and related materials is one of increased friction. This effect, which has been observed by others, was confirmed in these experiments and is in direct contrast to the case of graphite which requires adsorbed gas species for low friction. This effect can be seen in Fig. 5, in which the friction of the tungsten alloy is lower in vacua than in air, and in Figs. 7 and 8 which show the
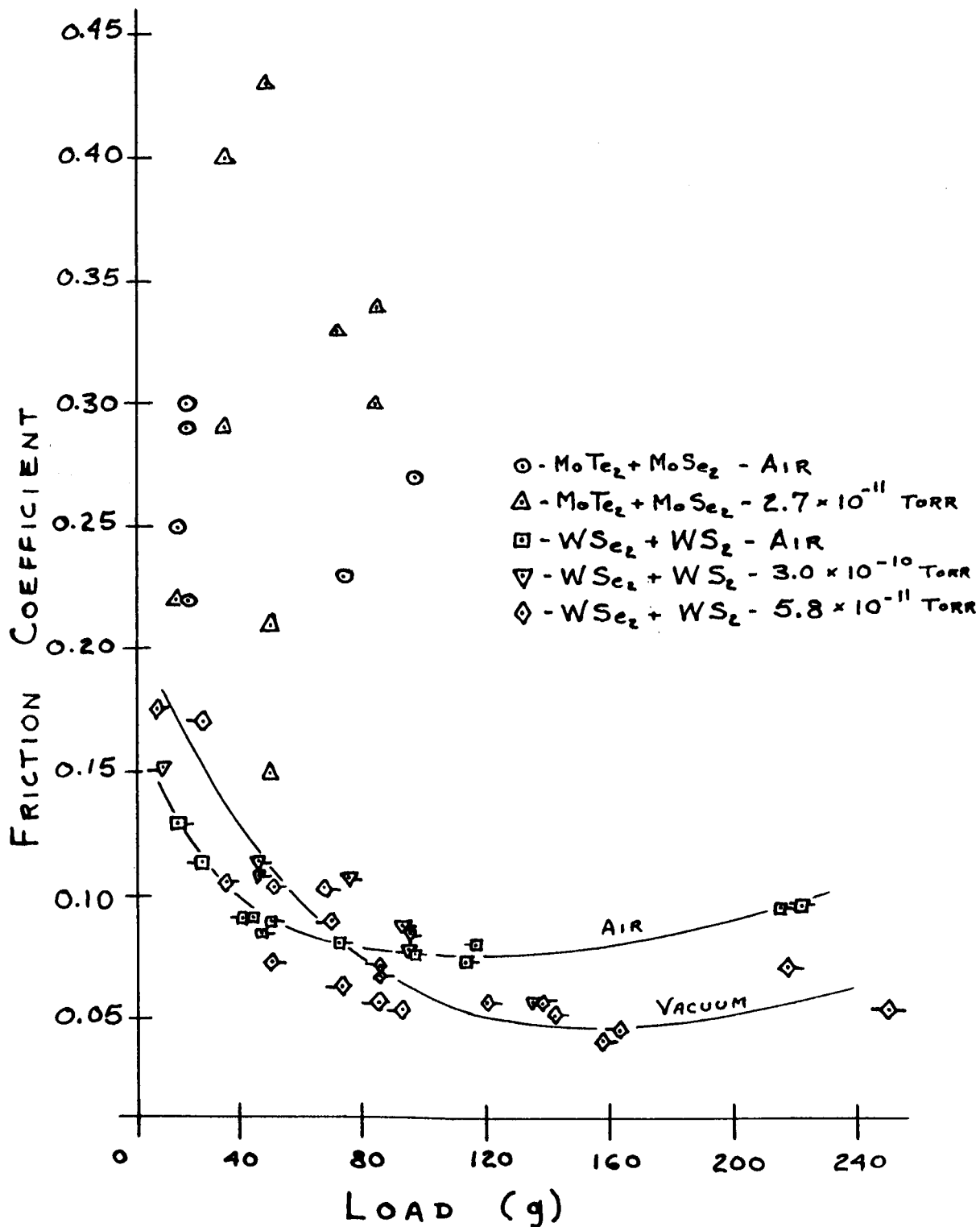
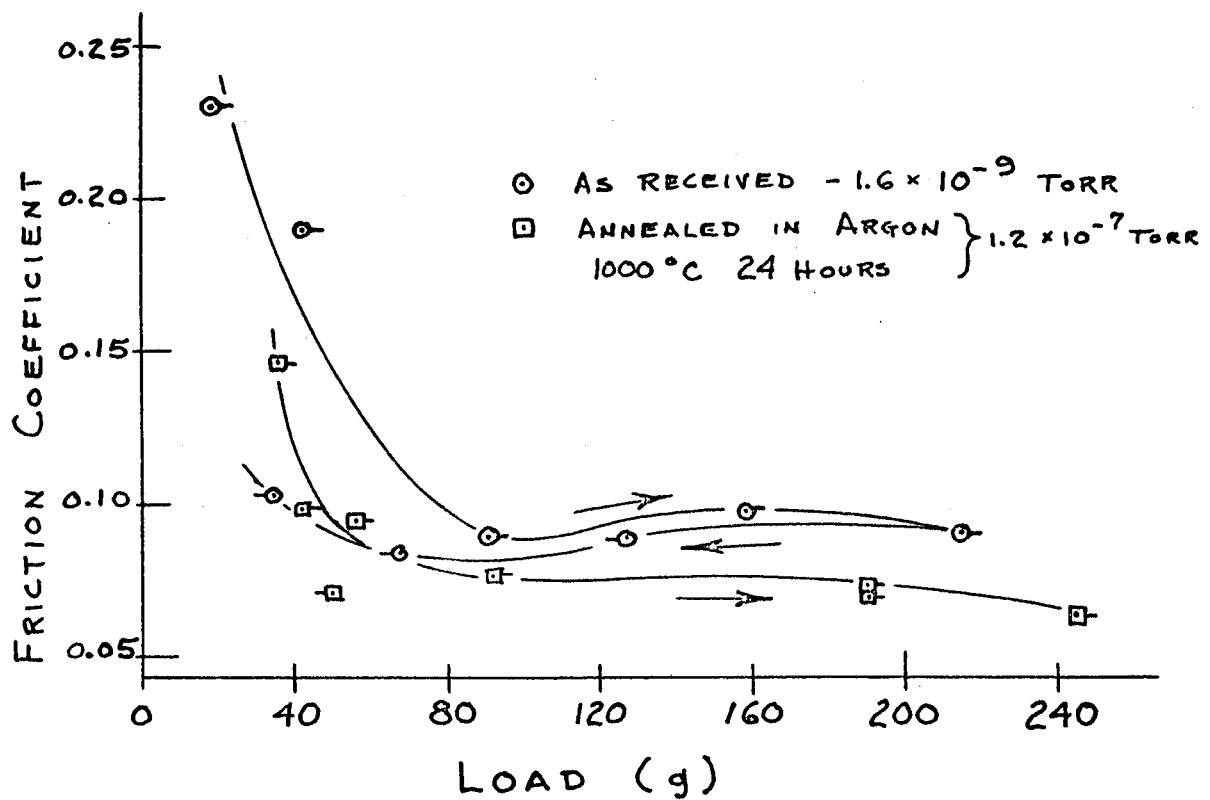Fig. 5 FRICTION OF MODIFIED CRYSTAL STRUCTURE
MATERIALS

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26

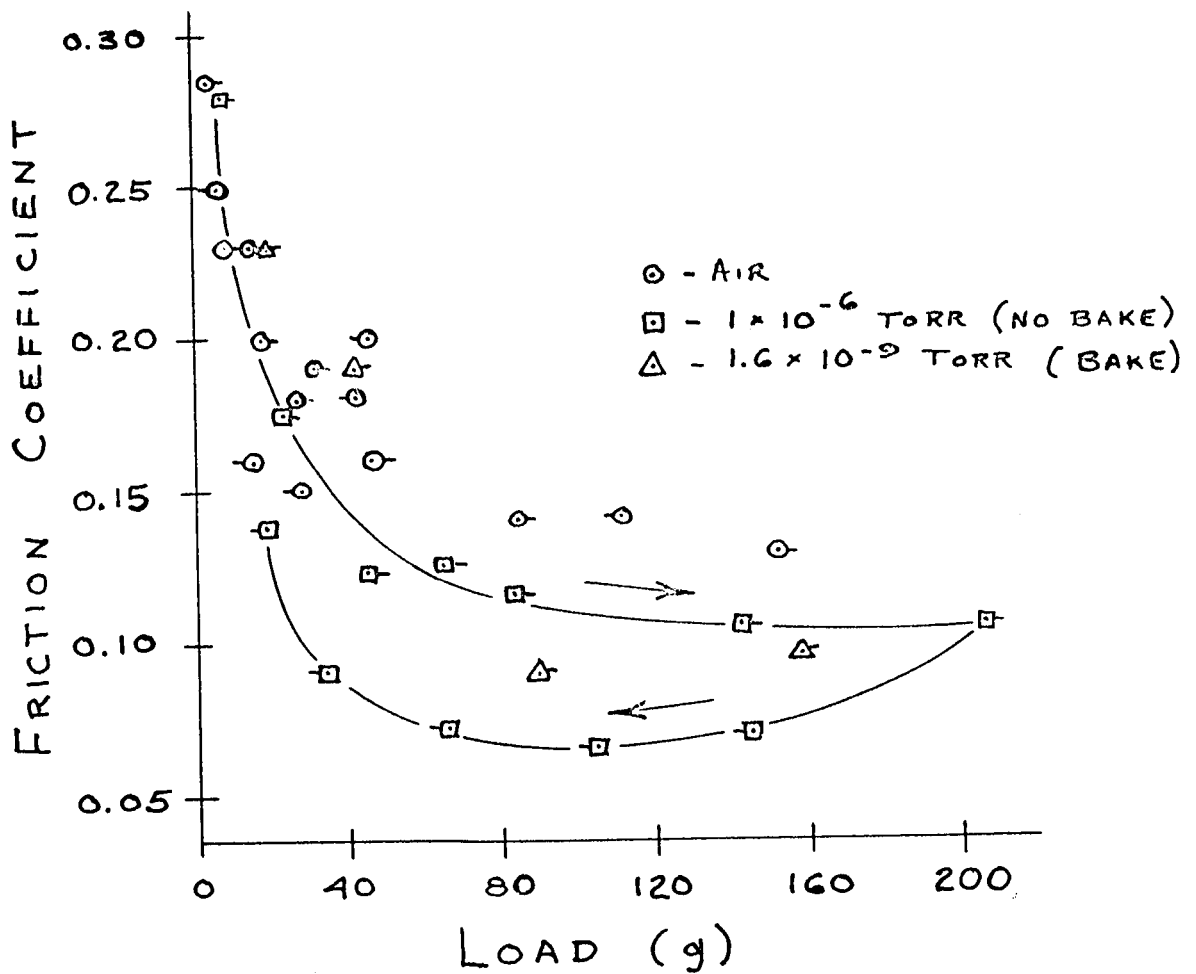Fig. 6 FRICTION OF ANNEALED AND "AS RECEIVED" (NONANNEALED)
MoS$_2$ IN VACUA

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Fig. 7 FRICTION OF "AS RECEIVED" MoS$_2$ AT VARIOUS ENVIRONMENTAL
PRESSURES
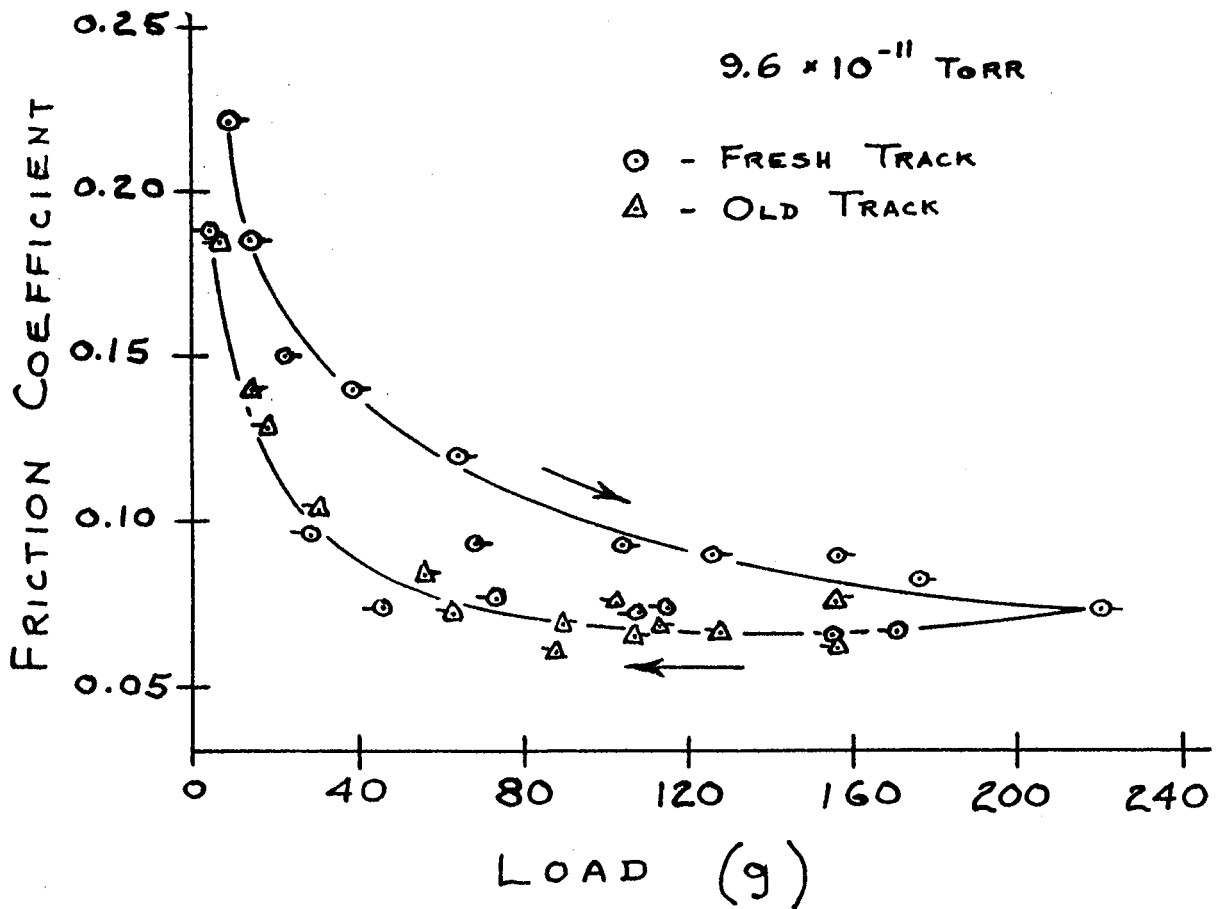
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Fig. **8** FRICTION OF "AS RECEIVED" MoS$_2$ IN ULTRA HIGH VACUUM

friction of MoS_2 at various levels of vacua. The results are explained as follows: A contaminant species is present either as an absorbant into the crystal lattice or as an adsorbed layer on the crystallites surface. The contaminant can be desorbed both mechanically by the friction process and thermally by vacuum bake and by the heat treatment in argon. Upon standing in vacua for extended periods, the surfaces become recontaminated. Evidence supporting this explanation is seen in the figures. In Fig. 7, it can be seen that the friction of unbaked "as received" MoS_2 is somewhat lower at 1×10^{-6} than at atmospheric pressure. In addition, the friction in vacuum shows a dependence on sliding history which is not noted in air. Upon initial increase in load, the friction coefficient decreases uniformly. Decreasing the load in air causes the friction coefficient to retrace the original curve. The vacuum friction coefficient, however, traces a new curve with lower values upon decreasing the load. (The flags on the data points indicate the direction of load change). This effect is interpreted as frictional desorption of contaminant gases.

Upon baking of the vacuum system at 250°C, the pressure was reduced to the 10^{-9} torr range, and the friction in the same track increased to a higher level. However, it is noted that sufficient time elapsed for the surface to become recontaminated, even at these reduced pressure levels.

Upon further baking and pumping, the pressure was decreased to the 10^{-11} torr range. Friction in a new track exhibited the same initial load direction sensitivity, as shown by the curve in Fig. 8. However, at these pressures, the time required for recontamination is extended, and subsequent friction measurements in this track retraced the lower curve (within experimental error).

Contact potential and mass spectrometric residual gas measurements provided additional insight into the adsorption phenomena. Measurements in air of undisturbed heavy MoS_2 films on various metal substrates gave contact potential values

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of +0.390 $\pm$ 0.010 volts[*]. Subsequent measurements in vacua gave values of +0.130 $\pm$ 0.050 with some dependence on history (pressure level, vacuum exposure time, temperature histroy). Contact potential scans across the specimen surface at various times after friction tests are shown in Fig. 9. Curve A shows the contact potential of the surface after 43 hours exposure to high vacuum subsequent to the friction test shown in Fig. 7. Curve B shows the contact potential following the first friction test shown in Fig. 8. Eighteen hours after this latter track was made, a third friction test was made in a new track adjacent to the first. The tracks are about 0.25 mm wide and are spaced about 1 mm apart. The remaining curves show the subsequent contact potential changes as a function of time between friction test and contact potential measurement.

It is noted that the peak contact potential of the left hand track diminished only 50 millivolts during the 18 hours between the second and third friction tests, but decayed at a much faster rate after the right hand track was run. It appears that contaminant species were desorbed by friction on the right track and subsequently contaminated the left track to produce the noted results.

Figure 10 shows similar contact potential scans for the molybdenum alloy which exhibited poor friction performance characteristics. The contact potential of this surface decreased immediately following friction and then increased to a much higher value after vacuum exposure. It is seen that the adsorption effects are much greater with this material than with MoS_2.

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[*] All values are referred to the gold reference surface. Electronic work functions of the surfaces may be obtained by adding or subtracting the contact potential values to the work function of gold (+ 4.46 volts) as indicated by the sign.
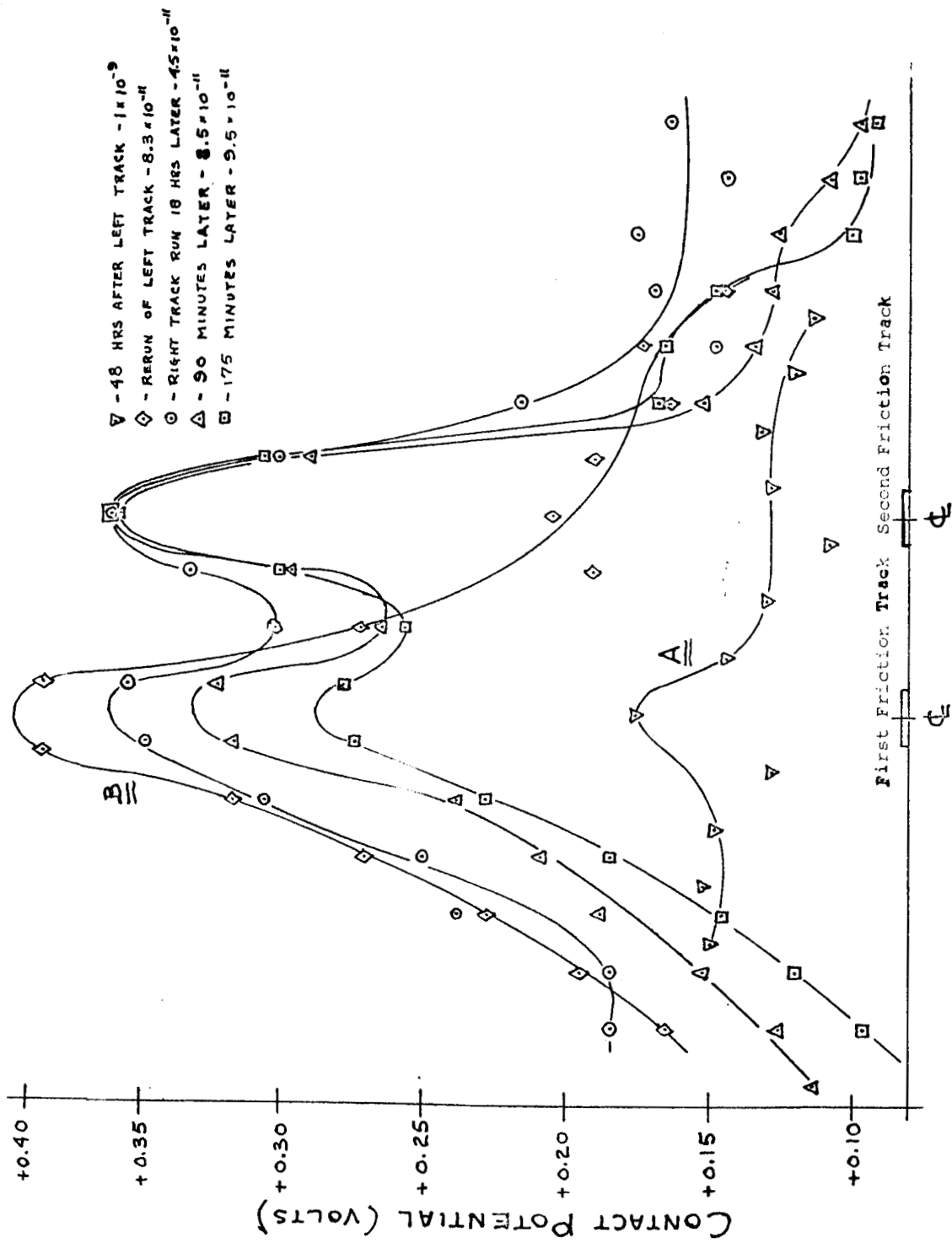
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Fig. 9 CONTACT POTENTIAL OF MoS$_2$ FRICTION SURFACE IN VACUA AT VARIOUS STAGES OF EXPERIMENTATION

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32   K6055
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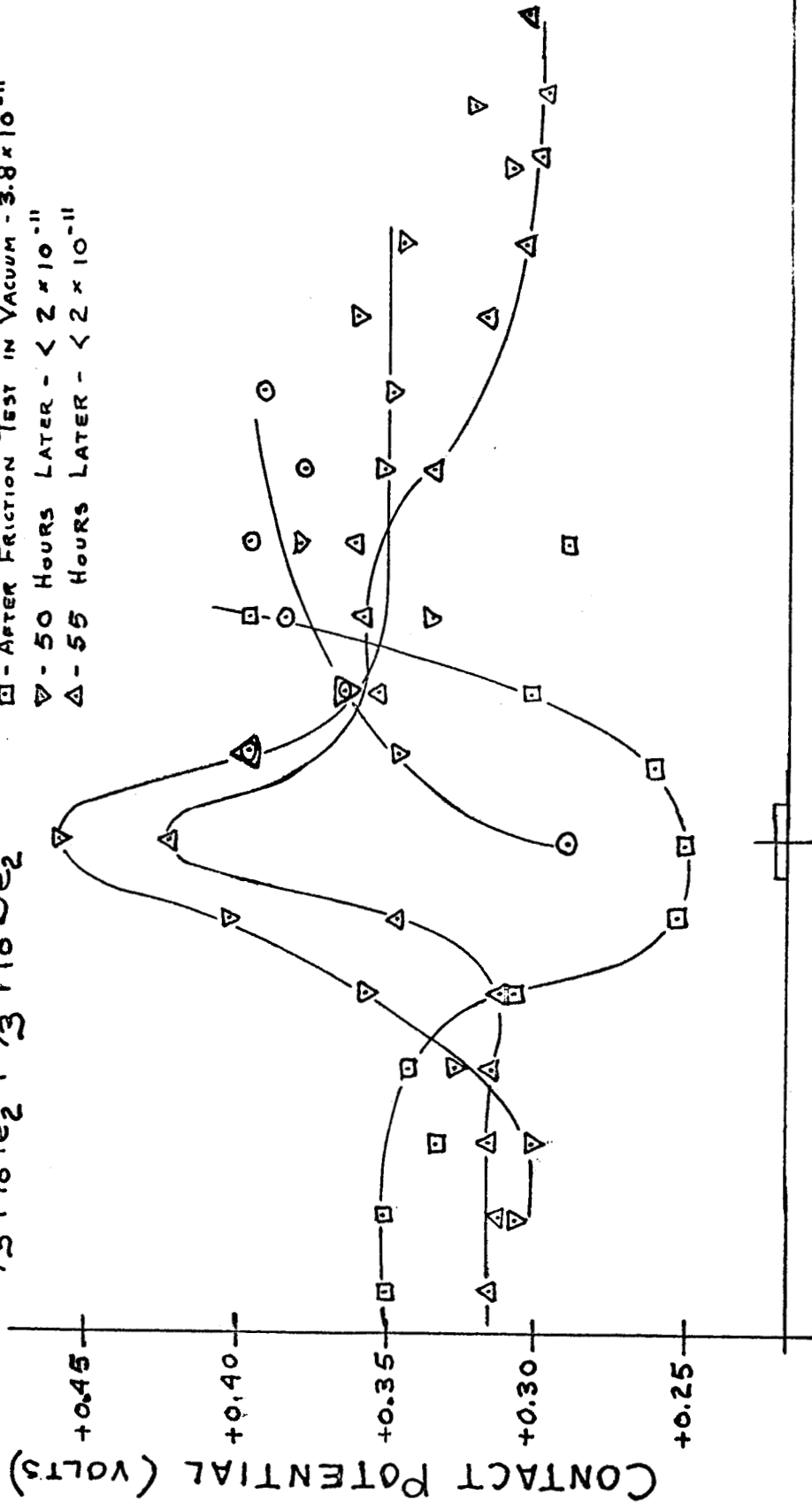
Fig. 10 CONTACT POTENTIAL OF 2/3 MoTe2 + 1/3 MoSe2 ALLOY FRICTION SURFACE

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33

Liberation of gas from MoS_2 by friction has been observed by this writer[37] in previous experiments and by others[38] as an increase in vacuum chamber pressure during sliding, and attempts have been made to define the gaseous species by mass spectrometric means[39]. No increase in total chamber pressure was observed in any of the friction experiments conducted on this program, probably because the extremely slow sliding speeds desorbed gases at too slow a rate. However, frictional desorption was definitely indicated in both friction and contact potential measurements, so a sensitive mass spectrometer gas analyzer was attached to the vacuum system to monitor the vacuum chamber gases during the friction process. Mass spectrometer traces were taken during friction experiments with MoS_2 and with the expanded lattice alloys under sliding at 8.5 and 420 microns per second. The mass peak heights which changed significantly during friction are shown in Fig. 11. The peak heights are shown in pressure units (torr) and the most probable gas species associated with each peak are indicated. Since the mass spectrometer was new, no cracking patterns had been established for the unit and thus no accurate determination of partial pressures of individual gas species could be made. It is noted, however, that the major changes occurred with peaks associated with atmospheric gases and low molecular weight hydrocarbons.

Tests were then programmed in which contaminant gases were deliberately introduced into the vacuum vessel during friction experiments. Because of time limitations, only tests with oxygen and methane contamination were accomplished. The results are shown in Figs. 12 and 13. After measuring the friction and contact potential of MoS_2 in a fresh track at 1.5×10^{-10} torr, oxygen was admitted to the vacuum vessel to a pressure of 9.2×10^{-9}. Mass spectrometer traces indicated that the oxygen partial pressure was thus increased by a factor

Fig 10a – MoS_2 (Annealed)

□   No Sliding – 1.4×10^{-7} torr
▨   8.5 μ/sec – 1.2×10^{-7} torr
▦   420 μ/sec – 1.2×10^{-7} torr

Fig 10b – MoS_2 ("As Received")

□   No Sliding – 1.4×10^{-10}
▨   8.5 μ/sec – 1.5×10^{-10}
▦   420 μ/sec – 1.8×10^{-10}
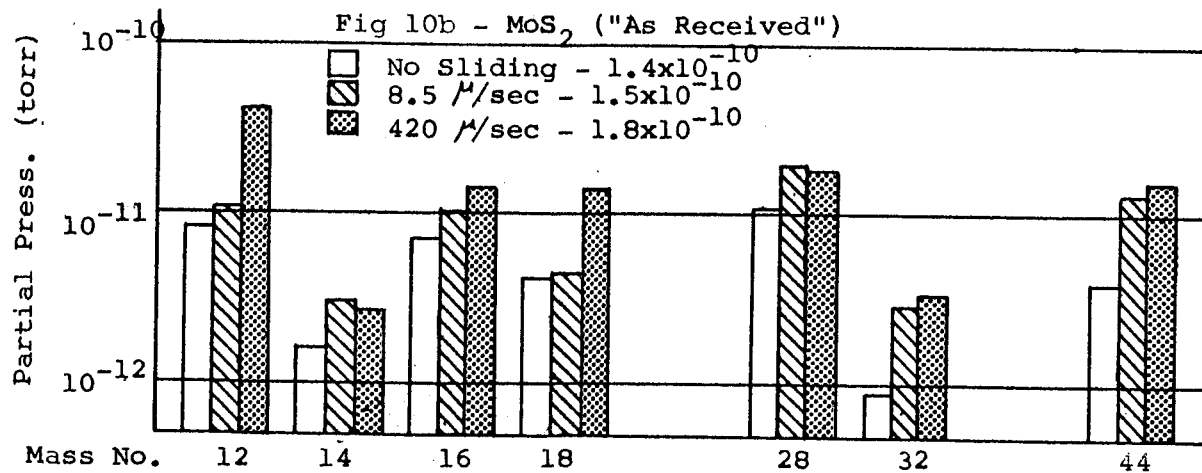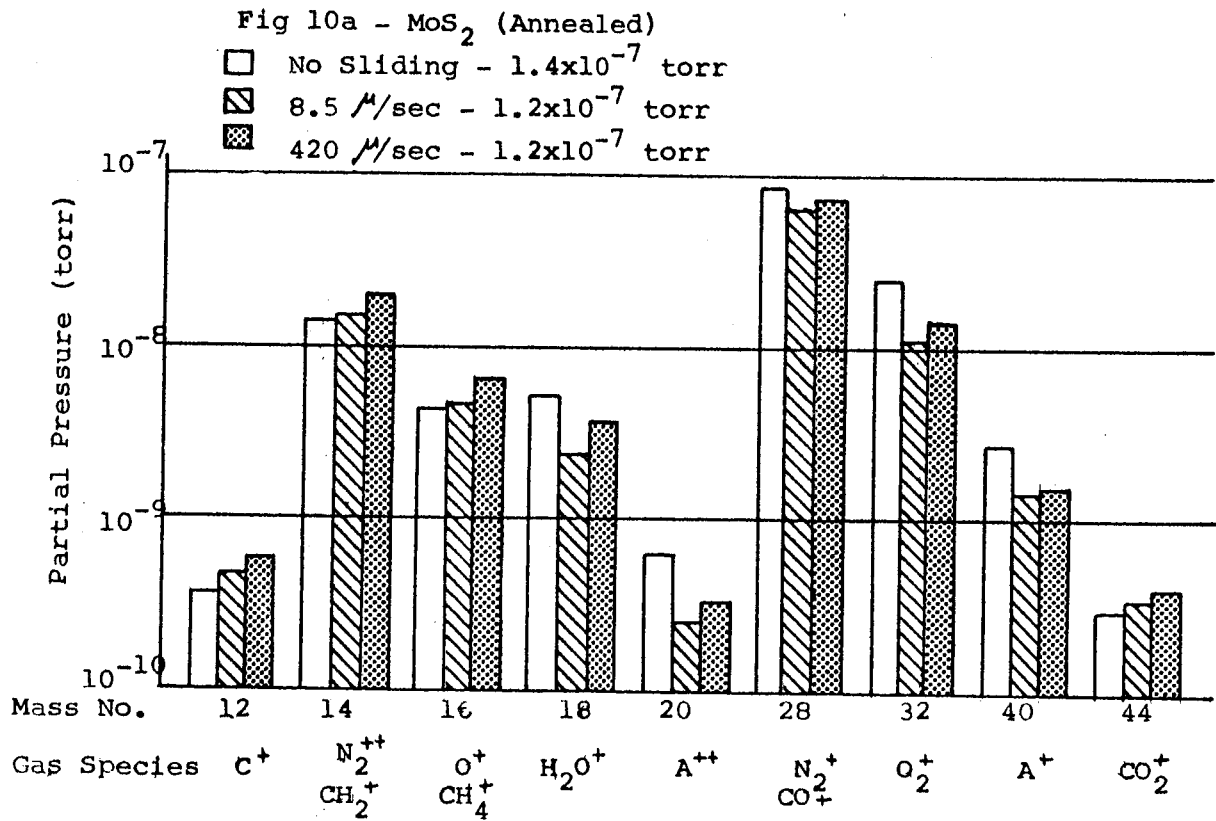
Fig. 11 GAS SPECIES PRESENT IN VACUUM CHAMBER DURING FRICTION TESTING

Fig 10c – $MoSe_2 + MoTe_2$
☐ No Sliding – 3.8×10^{-11}
▨ 420 M/sec – 2.6×10^{-11}

Mass No.   12   14   16   18   28   32   44   77

Gas Species: C^+ N_2^{++} O^+ H_2O^+ N_2^+ O_2^+ CO_2^+
                    CH_2^+ CH_4^+ CO^+

Fig 10d – $WSe_2 + WS_2$
☐ No Sliding – 3×10^{-10}
▨ 420 M/sec – 3×10^{-10}

Mass No.   12   14   16   18   20   28   32   40   44

Fig. 11 (CONTINUED)

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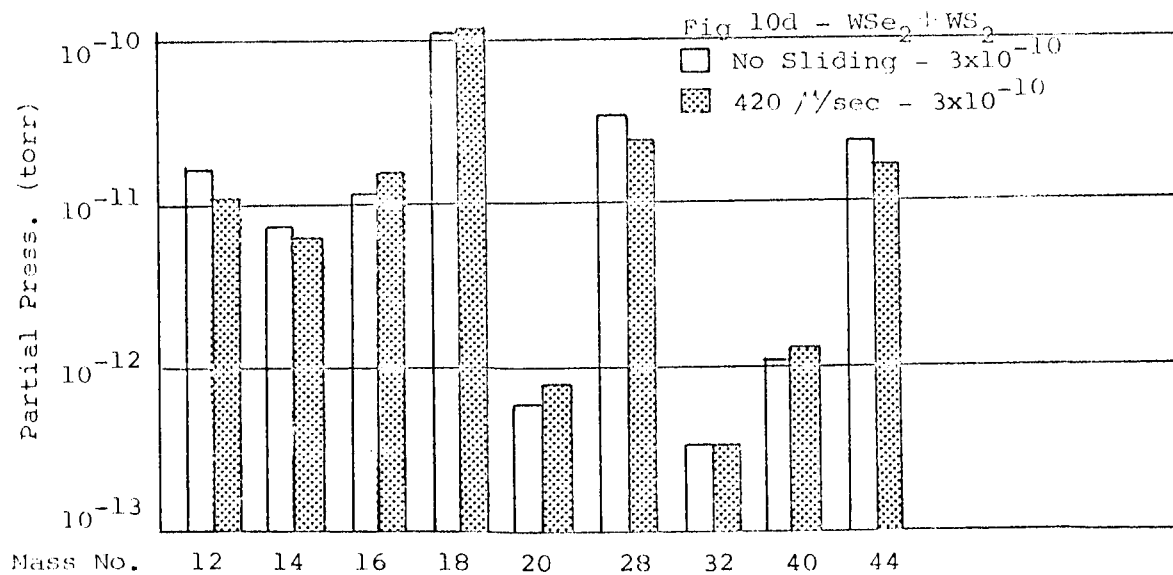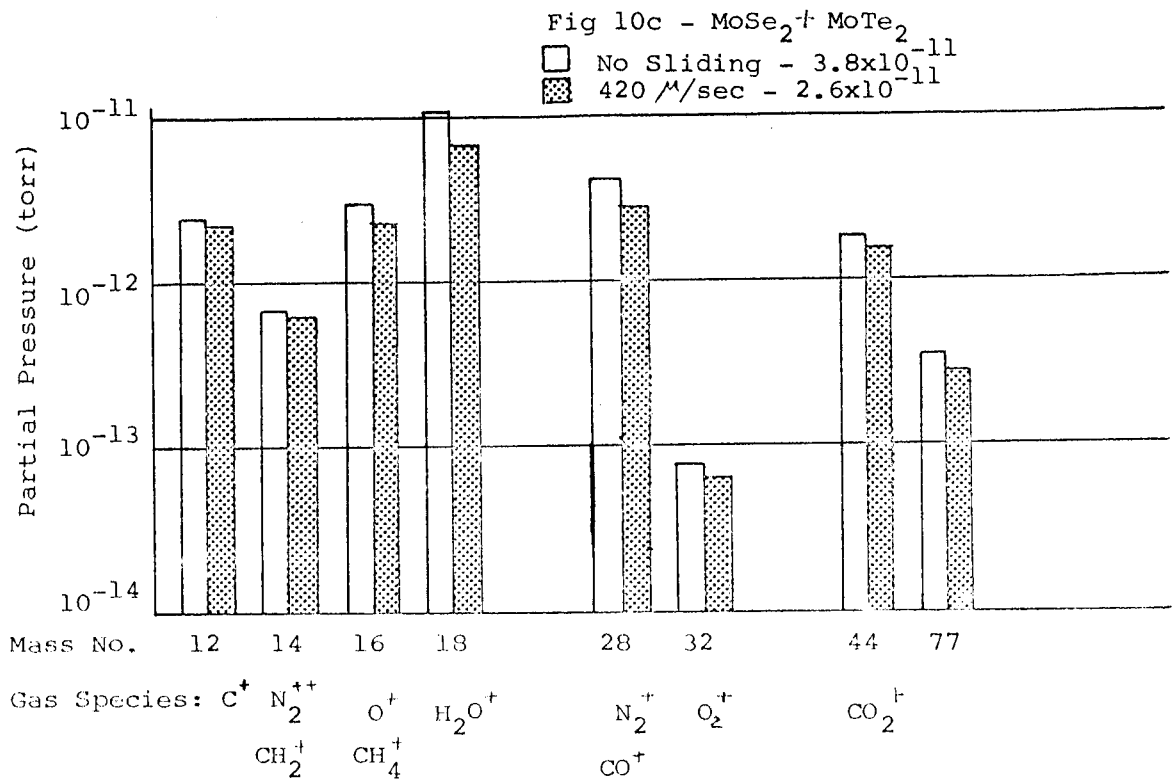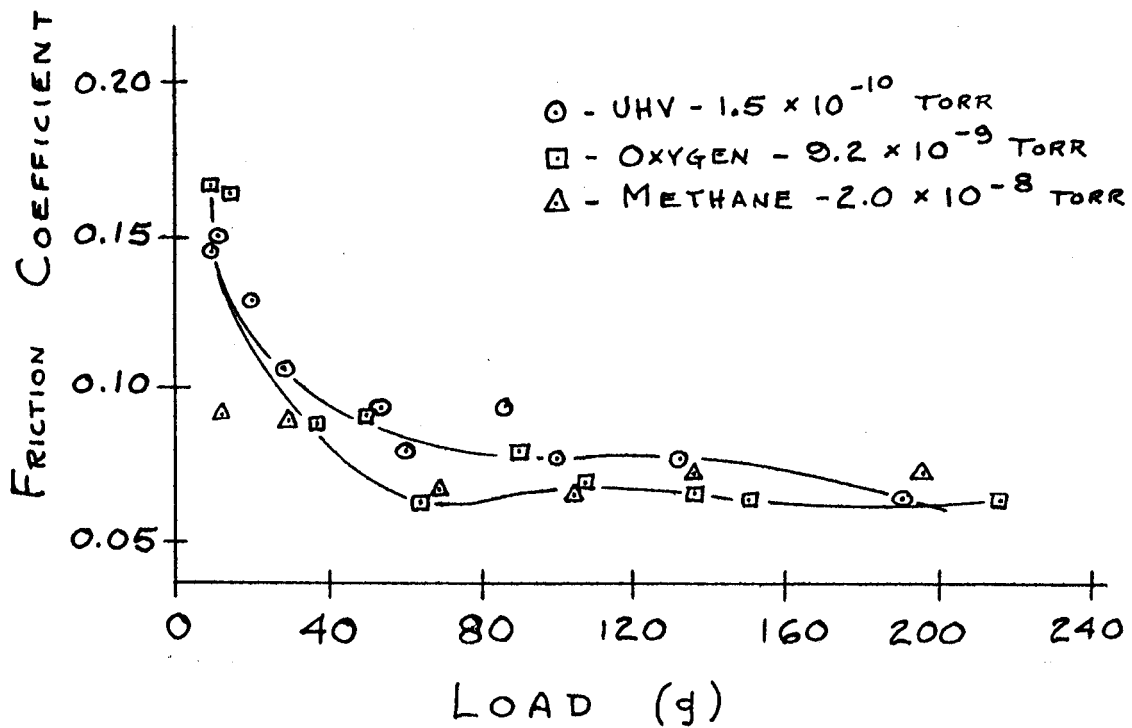
Fig. 12 FRICTION OF MoS$_2$ IN ULTRA HIGH VACUUM AND IN
CONTAMINATING ATMOSPHERES

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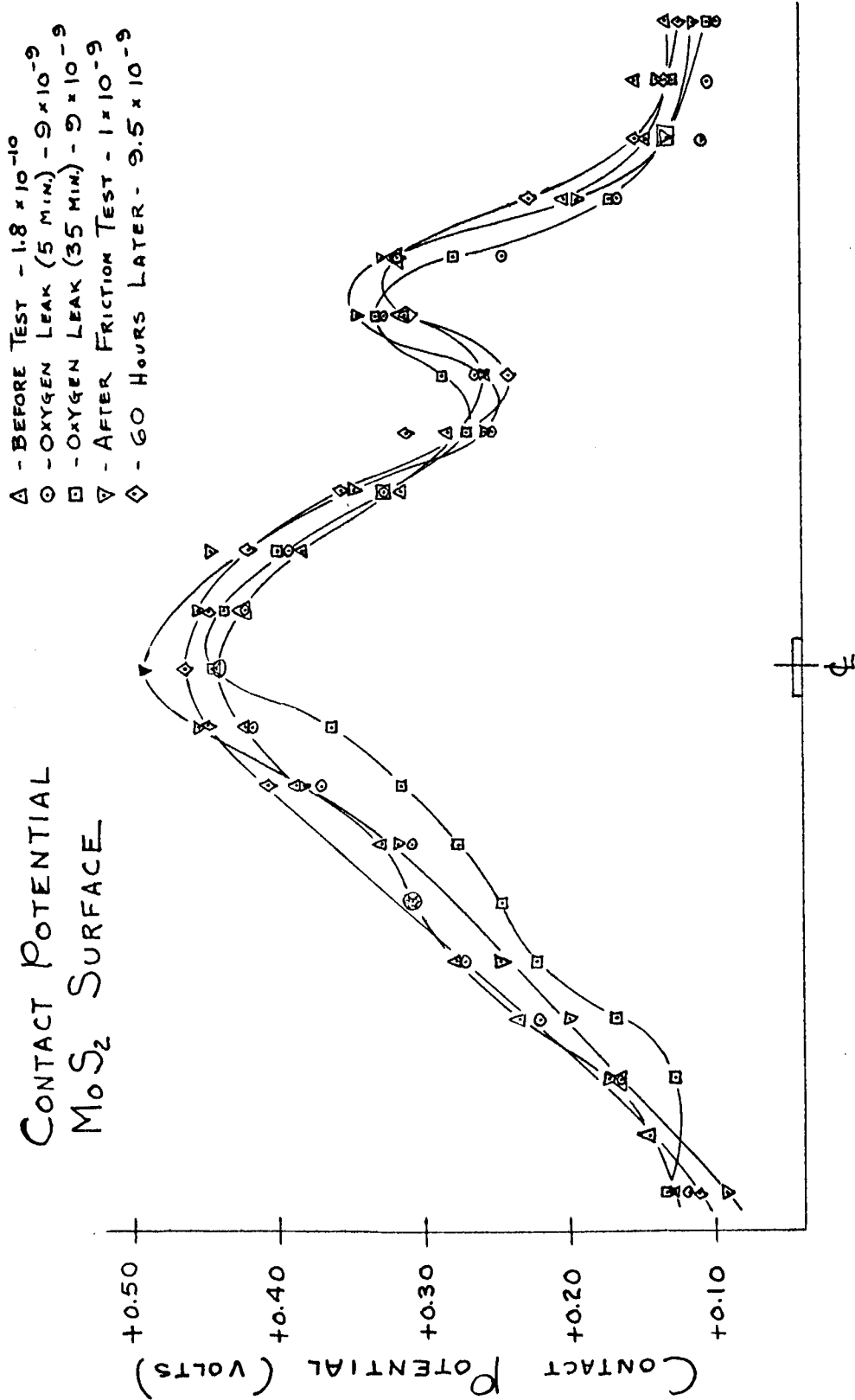
Fig. 13 CONTACT POTENTIAL OF MoS₂ FRICTION SURFACE IN ULTRA HIGH VACUUM AND IN ATMOSPHERES

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of approximately 350. Friction and contact potential measurements were made in the same track after 35 minutes exposure to this environment.

The chamber was than reevacuated to a pressure of 7.2×10^{-10} torr and methane admitted to raise the pressure to 2.0×10^{-8} torr, thus increasing the methane concentration by a factor of 30. Friction and contact potential were again measured in the same track after a similar exposure period. The friction of MoS_2 showed a slight decrease with the introduction of oxygen and methane, rather than the expected increase. However, the contact potential remained virtually unchanged during the entire contamination experiment, as shown in Fig. 13[*]. The measurements made during methane contamination are omitted from the figure for clarity, but are essentially the same. Even after 60 hours subsequent exposure to the vacuum environment, the contact potential was unaltered.

F. Conclusions

The specific conclusions reached from the experiments conducted on this program are:

1. The low friction observed with some materials with layer lamellar hexagonal crystal structures is not an inherent characteristic of this class

2. Expansion of the crystal lattices of hexagonal layer lamellar materials does not appreciably alter their frictional properties

3. Both natural and synthetic materials of this class contain contaminant adsorbed or absorbed species which increase their friction. Such species are either very low concentrations of atmospheric gases or are materials which will condense in a vacuum system before reaching a mass spectrometer tube

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[*] The minor peak to the right in the figure is associated with an earlier friction experiment with the same specimen.

4. Molybdenum disulfide surfaces show a remarkable insensitivity to external contamination by oxygen, methane, and residual gases in vacuum systems (as determined by contact potential measurements), although they can be self-contaminated if the material is not thoroughly degassed

5. Contact potential measurements can be effectively used in vacuum friction studies to characterize the electrical state of friction surfaces and to observe adsorption phenomena

No conclusions have been formed from these experiments concerning the molecular nature of friction or the molecular interactions which comprise it. Such limited experimentation does not allow for this. It is believed, however, that the low inherent friction of MoS_2 and related substances can be attributed to a saturation of the available bonding forces within the molecular structure, leaving only weak attractive forces to hold the crystal together and to promote friction upon sliding. It is also believed that the variance in measured friction levels between the two different alloys studied on this program can also be attributed to the availability of bonding mechanisms at the crystallite surfaces. This same bond availability probably controls adsorption of gases which, in turn, further affect friction.

It has been shown that the techniques used in these studies can contribute significantly to the understanding of the fundamental processes involved in friction, and to the development of interfaces with low friction properties. Specifically, the use of ultra high vacua extends the time available for measurements of gas-surface interactions to permit careful, quantitative studies; contact potential measurements provide a convenient, speedy means for characterizing the electrical state of friction surfaces and for quantitatively defining adsorption processes (when used in conjunction with partial pressure measurements).

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K6055
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Additional techniques which have formerly been laboratory
curiosities are being developed into useful research tools
which can be productively employed in understanding friction
on a molecular scale. These techniques include low energy
electron diffraction, secondary electron emission, and field
emission microscopy.

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