

1972

The potential energy of interaction between non-polar molecules and a gold surface

John F. Bohland
Lehigh University

Follow this and additional works at: <https://preserve.lehigh.edu/etd>

 Part of the [Materials Science and Engineering Commons](#)

Recommended Citation

Bohland, John F., "The potential energy of interaction between non-polar molecules and a gold surface" (1972). *Theses and Dissertations*. 4057.
<https://preserve.lehigh.edu/etd/4057>

This Thesis is brought to you for free and open access by Lehigh Preserve. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Lehigh Preserve. For more information, please contact preserve@lehigh.edu.

THE POTENTIAL ENERGY OF INTERACTION BETWEEN
NON-POLAR MOLECULES AND A GOLD SURFACE

by

John Francis Bohland Jr.

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Metallurgy and Materials Science

Lehigh University

1972

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment
of the requirements for the degree of Master of Science.

5 May 1972
(date)

Walter C. Hahn, Jr.
Professor in Charge

G. P. Conrad
Chairman, Department of
Metallurgy and Materials
Science

ACKNOWLEDGEMENTS

The author appreciates the guidance provided by Dr. W. C. Hahn in completing this thesis. Special thanks are due to Dr. David Lando of the Western Electric Engineering Research Center who generously shared his valuable experience.

The author gratefully acknowledges Western Electric Company, Inc. for sponsoring his graduate studies.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	1
I Introduction	3
II Theory	5
III The Quartz Crystal Microbalance	9
IV Experimental	
A. Apparatus	13
1. The Quartz Crystal Microbalance	13
2. The Adsorption and Reference Cells	21
3. Pressure Measurement	21
4. Vacuum Pumping System	21
5. Temperature Control	24
6. Sample Gas Supply	24
7. Hardware	24
B. Procedure	25
1. Cleaning the System	25
2. Loading the Adsorbate	26
3. Measurements	26
V Results and Discussion	28
VI Conclusions and Suggestions for Further Studies	46
Appendix I Frequency Change as a Function of Pressure for Non-Adsorbing Gases	47
Appendix II Adsorption Isotherm Data	52
References	58
Vita	60

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Values of n in the Equation $\ln \frac{P}{P_0} = \frac{C'C}{(-\Delta f)^n}$	32
II	Values of the Constants in the Interaction Equation	43
III	Physical Properties of Adsorbates	44

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Adsorption Measurement System	14
2	Schematic Representation of Adsorption Measurement System	16
3	Block Diagram of Electronics	18
4	Adsorption and Reference Cells	22
5	$-\text{LN}(\text{P}_0/\text{P})$ vs $\text{LN}(-\Delta f)$ for Benzene, Carbon Tetrachloride, Cyclohexane, and Octane	30
6	$1/(-\Delta f)^2$ vs $-\text{LN}(\text{P}/\text{P}_0)$ for Benzene	34
7	$1/(\Delta f)^2$ vs $-\text{LN}(\text{P}/\text{P}_0)$ for Carbon Tetrachloride	36
8	$1/(\Delta f)^2$ vs $-\text{LN}(\text{P}/\text{P}_0)$ for Cyclohexane	38
9	$1/(\Delta f)^2$ vs $-\text{LN}(\text{P}/\text{P}_0)$ for Octane	40

ABSTRACT

Recently developed techniques are used to measure the high coverage portions (5 to 31 molecular layers) of the adsorption isotherms of benzene, carbon tetrachloride, cyclohexane, and octane physically adsorbed onto a single crystal gold film.

The Frenkel-Halsey-Hill equation is used to relate the adsorption isotherms to the potential energy of interaction between the gold surface and the molecules. The interaction energy is found to be inversely proportional to the square of the molecule to metal distance and directly proportional to the polarizability of the molecule.

The potential constants are calculated and compared with those found by an earlier investigator who also studied long range interactions with metals. The results are found to compare favorably with those of the other investigator. The present work is significant in that it extends the applicability of the interaction equation to molecules with more complex shapes than those previously studied. This study presents results for molecules with tetrahedral, ring, and chain configurations.

The difficulties involved in measuring very high coverage isotherms are discussed, and the features of the apparatus which minimize these problems are described. The problems in characterizing an adsorbent surface are discussed with emphasis on the ambiguous results which are obtained when the composition

and structure of the surface are not carefully controlled.

I INTRODUCTION

There has been considerable interest for many years in the nature of gas-metal interactions¹⁻⁷. Experimental support for the proposed theories, however, is limited by the difficulty of obtaining reliable data. Recently, Lando⁸⁻¹⁰ and Slutsky^{9,10} utilized new techniques to obtain highly reliable information on the form of the gas-metal interaction equation. They studied the interaction between a gold surface and several different non-polar, organic molecules and found the potential energy of interaction to be a function of the inverse square of the molecule to metal distance. The purpose of this project was to determine the analytical behavior of the interaction potential of several non-polar molecules which were not studied by Lando and Slutsky.

A classical method for determining interaction potentials is through the measurement of the adsorption isotherm which measures the amount of gas molecules sorbed on a surface at a given vapor pressure. The following relationship which was derived by Halsey¹¹ has proven very successful in describing the high coverage portions of such adsorption isotherms¹².

$$\ln \frac{P}{P_0} = \frac{C}{\theta^n}, \quad (1)$$

where P is the vapor pressure of the adsorbed film, P_0 is the saturation vapor pressure of the adsorbate, C and n are constants,

and θ is the number of molecular layers adsorbed. The relative vapor pressure of an adsorbed film is related to the molecular interaction energy through the Frenkel¹³ - Halsey¹¹ - Hill¹⁴⁻¹⁶ equation;

$$\frac{U(Z)-U'(Z)}{kT} = \ln \frac{P}{P_0}, \quad (2)$$

where $U(Z)$ is the potential energy of interaction of an adsorbate molecule at distance Z from the adsorbent surface, $U'(Z)$ is the interaction energy of an adsorbate molecule at distance Z from its bulk liquid, k is Boltzmann's constant, and T is the absolute temperature. At high coverages where the adsorbed film is continuous, θ is proportional to Z . A knowledge of the adsorption isotherm coupled with equations (1) and (2) can then be used to find the interaction energy as a function of distance.

The measurement of adsorption isotherms at high coverages is difficult using the conventional volumetric or gravimetric techniques. The work of Lando⁸⁻¹⁰ and Slutsky^{9,10}, however, indicates that high coverage isotherms can be obtained gravimetrically on low surface area samples by taking advantage of the high mass sensitivity of a resonating quartz crystal microbalance.

II THEORY

Lennard-Jones¹ treated the interaction of non-polar atoms with metals by considering metals to be perfectly polarizable. He then calculated the energy of interaction between the atom and its electrical image in the metal to be

$$U(Z) = - \frac{e^2 \overline{r^2}}{12Z^3},$$

where e is the charge on an electron, $\overline{r^2}$ is the mean square position of the electrons relative to the center of charge, and Z is the distance from the atom to the metal surface.

Bardeen², by including the effects of the self interaction of electrons in the metal, predicted a lower interaction potential;

$$U(Z) = - \frac{e^2 \overline{r^2}}{12Z^3} \frac{C e^2 / 2r_s \Delta}{1 + C e^2 / 2r_s \Delta},$$

where C is a constant with a value of about 2.6, r_s is the radius of a sphere whose volume is equal to the volume occupied by an electron in the metal, and Δ is the average difference in energy between the normal atom and the atom in its excited states.

Margenau and Pollard³ pointed out that the atoms and molecules which had been investigated had resonance frequencies in the ultraviolet region and that at these frequencies metals could not be considered perfectly polarizable. They considered the electrons in the metal to have a finite relaxation time and found the inter-

action energy to be

$$U(Z) = - \frac{1}{8Z^3} \left[\frac{e^2 \hbar}{m} A \frac{f}{\nu} + \alpha \Delta \right]$$

where A is the volume polarizability of the metal at the resonance frequency of the molecule ν , f is the oscillator strength of the resonance transition having frequency ν , and α is the static polarizability of the molecule.

Prosen and Sachs⁴ employed the state functions of the metal directly and applied second order perturbation theory to arrive at a solution. When they included the effects of electron degeneracy they found the interaction energy to be

$$U(Z) = - \frac{\alpha e^2 \pi k_m^2}{(2\pi)^3} \frac{\log(2k_m Z)}{Z^2}$$

where $k_m = (3\pi^2\rho)^{1/3}$, ρ being the electron density in the metal. They pointed out that because they neglected electron-electron interactions their equation was only applicable for values of Z of the order of magnitude of the Bohr radius.

Casimir and Polder⁵, using quantum electrodynamics, considered the effect of retardation on the interaction between a molecule and a perfectly conducting surface. They found that a correction factor must be used in the interaction relation to account for these effects if the molecule to metal distance is large compared to the wavelengths corresponding to the atomic frequencies. The

corrected interaction energy is then proportional to Z^{-4} . When the molecule to metal distance is small, the effect of retardation on the interaction relation is negligible.

Dzyaloshinskii, Lifshitz, and Pitaevskii⁶ considered van-der-Waals forces to be due to a fluctuating electromagnetic field. The interaction energy they obtained is

$$U(Z) = \frac{3 \hbar c \alpha}{8 \pi Z^4} \frac{\epsilon - 1}{\epsilon + 1} \varphi(\epsilon),$$

where φ is a complicated function of the dielectric constant of the solid. For a perfectly conducting metal $\epsilon = \infty$, and the interaction energy reduces to

$$U(Z) = \frac{3 \hbar c \alpha}{8 \pi Z^4}.$$

This is the same as the Casimir and Polder relation.

Mavroyannis⁷, using the techniques of Dzyaloshinskii, obtained an interaction equation similar to Bardeen's equation for distances at which retardation is not important;

$$U(Z) = - \frac{1}{12 Z^3} \sum_n |\epsilon_{on}|^2 \frac{\hbar \omega / \sqrt{2}}{E_{no} + \hbar \omega / \sqrt{2}},$$

where E_{no} is the ionization potential of the molecule, ω is the characteristic resonance frequency of absorption of electrons in the metal, $\hat{q} = -e \sum_i \hat{r}_i$ is the electric dipole operator with \hat{r}_i

being the displacement of the i^{th} electron from the center of charge.

With the exception of the Prosen and Sachs theory, all of the above theories predict that the potential energy of interaction between a gas molecule and a metallic surface will vary with the inverse cube of the molecule to metal distance in the region where retardation effects are small. Lando⁸⁻¹⁰ and Slutsky^{9,10} empirically determined the interaction to be an inverse square relation for a gold surface. The need for more experimental information on the long range interactions between molecules and metals was the impetus behind the present work.

III THE QUARTZ CRYSTAL MICROBALANCE

In the restricted circumstances which allow their use, resonating quartz crystals are capable of measuring very small changes in mass. Commercial units are extensively used to monitor the thickness of vapor deposited films. The use of the quartz crystal microbalance for adsorption studies has, however, been limited. Wade and Slutsky¹⁷ determined isotherms for materials adsorbed directly on the resonating quartz surface and Lando⁸⁻¹⁰ and Slutsky^{9,10} determined isotherms for materials adsorbed on a thin film of gold which had been evaporated onto the quartz surface.

Sauerbrey¹⁸ showed that for an AT-cut crystal resonating in the thickness-shear mode the frequency change due to mass added to the antinodal surfaces is given by

$$-\frac{\Delta f}{f} = \frac{\Delta m}{m}, \quad (3)$$

where Δf is the change in frequency, f is the initial frequency, Δm is the mass added to the surface of the crystal, and m is the mass of the crystal. In order for this equation to be valid, the added mass must be uniformly distributed on the crystal surface.

The mass sensitivity of the system used in this work can be calculated from equation (3) by substituting in the minimum detectable frequency change for Δf (0.1 Hz), the resonant

frequency f , and the mass m of the crystal. The sensitivity calculated in this manner is approximately a nanogram per cm^2 .

In addition to mass, the resonant frequency of a quartz crystal is sensitive to temperature changes, and when the crystal is immersed in a fluid, the frequency is affected by hydrostatic pressure and aerodynamic loading. It is necessary to consider these effects when attempting to measure mass with a quartz crystal microbalance.

The temperature coefficients of frequency for the crystals used in this work have been measured to be approximately 0.3 Hz/C. Since the crystals are thermostated to within a few thousandths of a degree Centigrade during the adsorption measurements, frequency changes due to temperature changes are not considered a problem.

The effects of hydrostatic pressure and aerodynamic loading on the resonant frequencies of quartz crystals have been extensively studied by Stockbridge¹⁹. He found that when quartz crystals are immersed in gases, the frequency increases linearly with the hydrostatic pressure due to the changes in elastic moduli of the quartz and decreases linearly with the square root of pressure due to aerodynamic loading.

Lando⁸ measured the hydrostatic pressure and aerodynamic loading effects on 5 MHz crystals and related the effects to the properties of the gas. When measuring adsorption, he was

then able to correct the frequency changes so that they would only reflect the effects of added mass. Except at very low pressures, Lando's correction formula is of the form

$$\Delta f_c = k_1 P - k_2 \sqrt{W \eta} \sqrt{P}, \quad (4)$$

where Δf_c is the net frequency change due to hydrostatic pressure and aerodynamic loading, P is the gas pressure, W is the molecular weight of the gas, η is the viscosity of the gas, and k_1 and k_2 are constants.

An attempt was made to experimentally determine a correction formula for pressure effects to be used in this work. Non-adsorbing gases were admitted in small pressure increments to the cell containing the crystal while the frequency changes were monitored. The data were fitted to equation (4) but instead of being constant, k_1 and k_2 were found to be different for different gases. It was, therefore, not possible to obtain a correction formula for hydrostatic pressure and aerodynamic loading. The data collected for non-adsorbing gases are tabulated in appendix I.

The inability to correct for gas pressure restricts the useful portion of the adsorption isotherms to the high coverage regions. In this region the correction is nearly constant, and it is small compared to the frequency change due to adsorbed mass. Since the very high coverage portions of the isotherms are the regions of interest for this project, the lack of an

ambient gas correction formula does not directly cause a problem.

Unfortunately, the low coverage portions of the isotherms are necessary in order to calculate a roughness factor for the gold surface. The roughness factor is defined as the ratio of the actual surface area to the geometrical area. The BET (Brunauer, Emmett, Teller)²⁰ method of determining the actual surface area requires adsorption data in the vicinity of a monolayer of coverage. At this low coverage the gas pressure corrections are significant. As explained later, however, only a small error in the interaction potential constants results if the roughness factor is assumed to be one.

IV EXPERIMENTAL

A. Apparatus

The experimental apparatus consists of a mass measurement system, a pressure measurement system, a temperature control system, a vacuum pumping system, and a sample gas supply system. The apparatus which was specially designed and constructed for this project is shown in Figure 1. In the foreground of the photograph the upper temperature control bath containing the valving system and the differential manometer can be seen. The vacuum pumping system and the sample gas supply system is located behind the upper temperature control bath. The reference cell and the adsorption cell are suspended below the upper temperature control bath. When the system is in operation, the cells are immersed in the lower temperature control bath. Figure 2 is a schematic representation of the system. V1, V2, V3, V4, and V5 are valves used during the necessary gas transfer procedures.

1. The Quartz Crystal Microbalance

The quartz crystal microbalance consists of a crystal mounted in the adsorption cell, an oscillator to drive the crystal, a frequency counter, a digital to analog converter, and a strip chart recorder. A block diagram of these components is shown in Figure 3.

The AT-cut crystals used in this work are cut to resonate at 5 MHz in the fundamental thickness-shear mode. The precise

FIGURE 1

Adsorption Measurement System

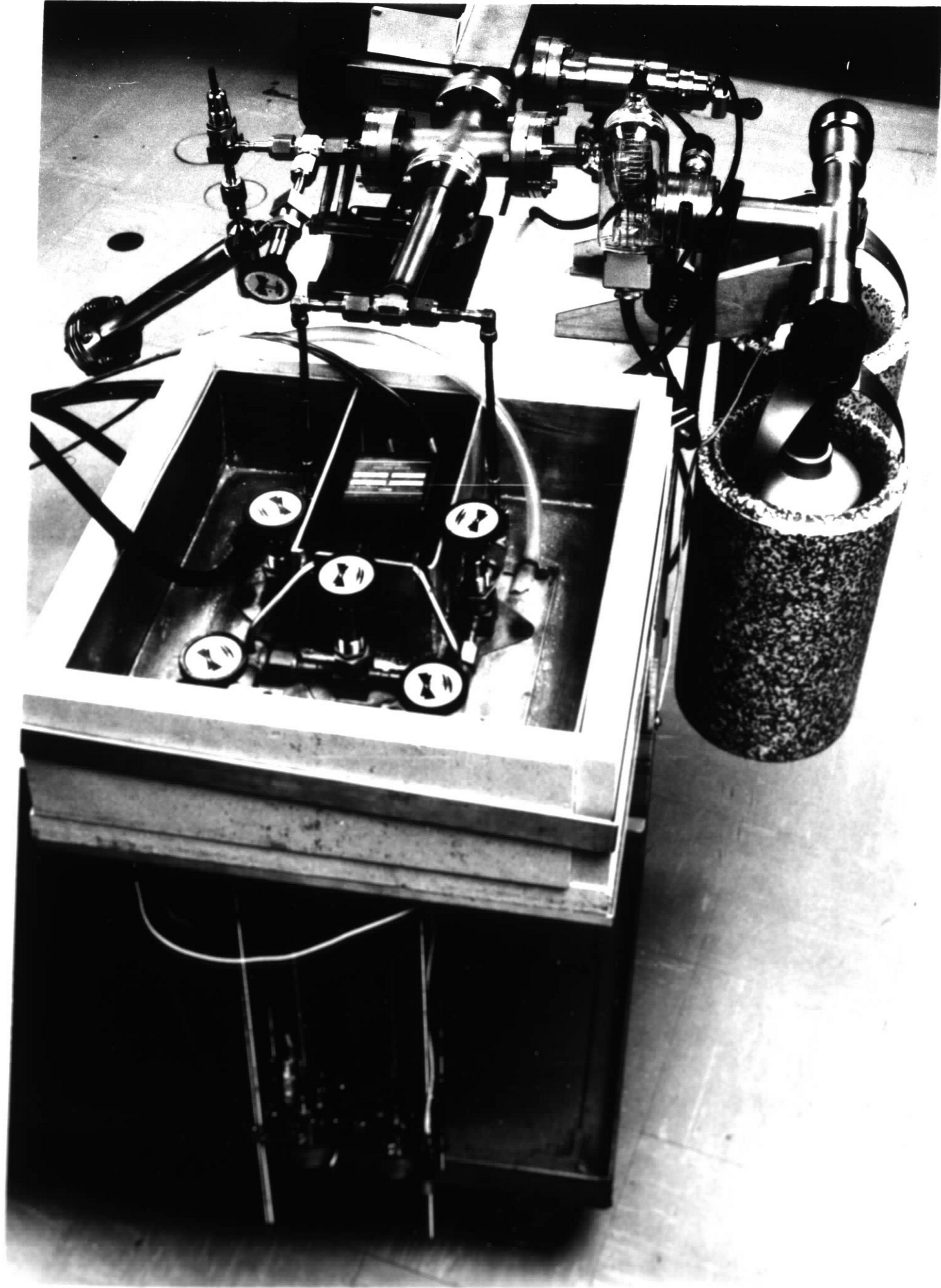
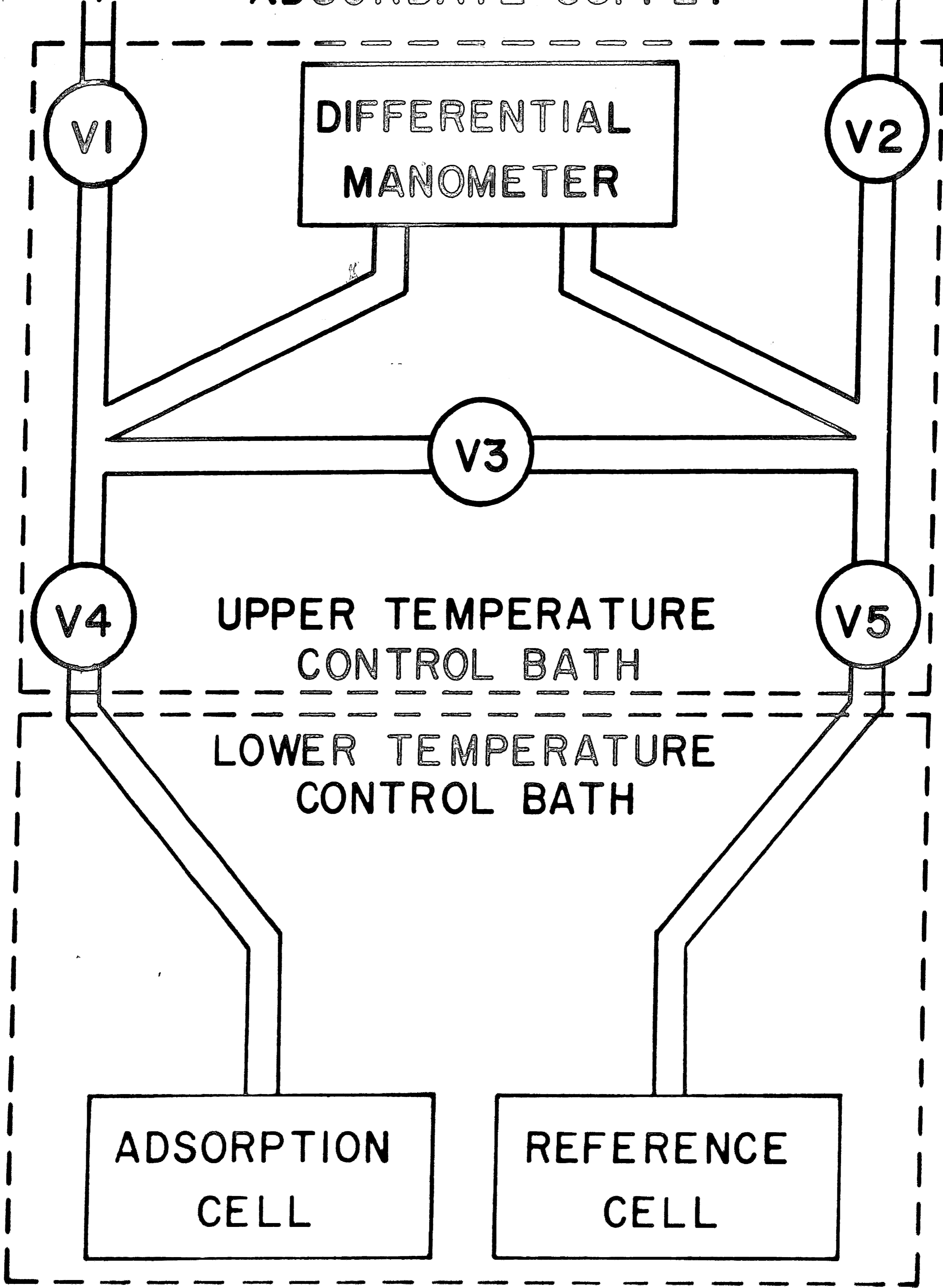


FIGURE 2

Schematic Representation of Adsorption Measurement System

TO VACUUM PUMPS AND
ADSORBATE SUPPLY



V1

V2

DIFFERENTIAL
MANOMETER

V3

V4

V5

UPPER TEMPERATURE
CONTROL BATH

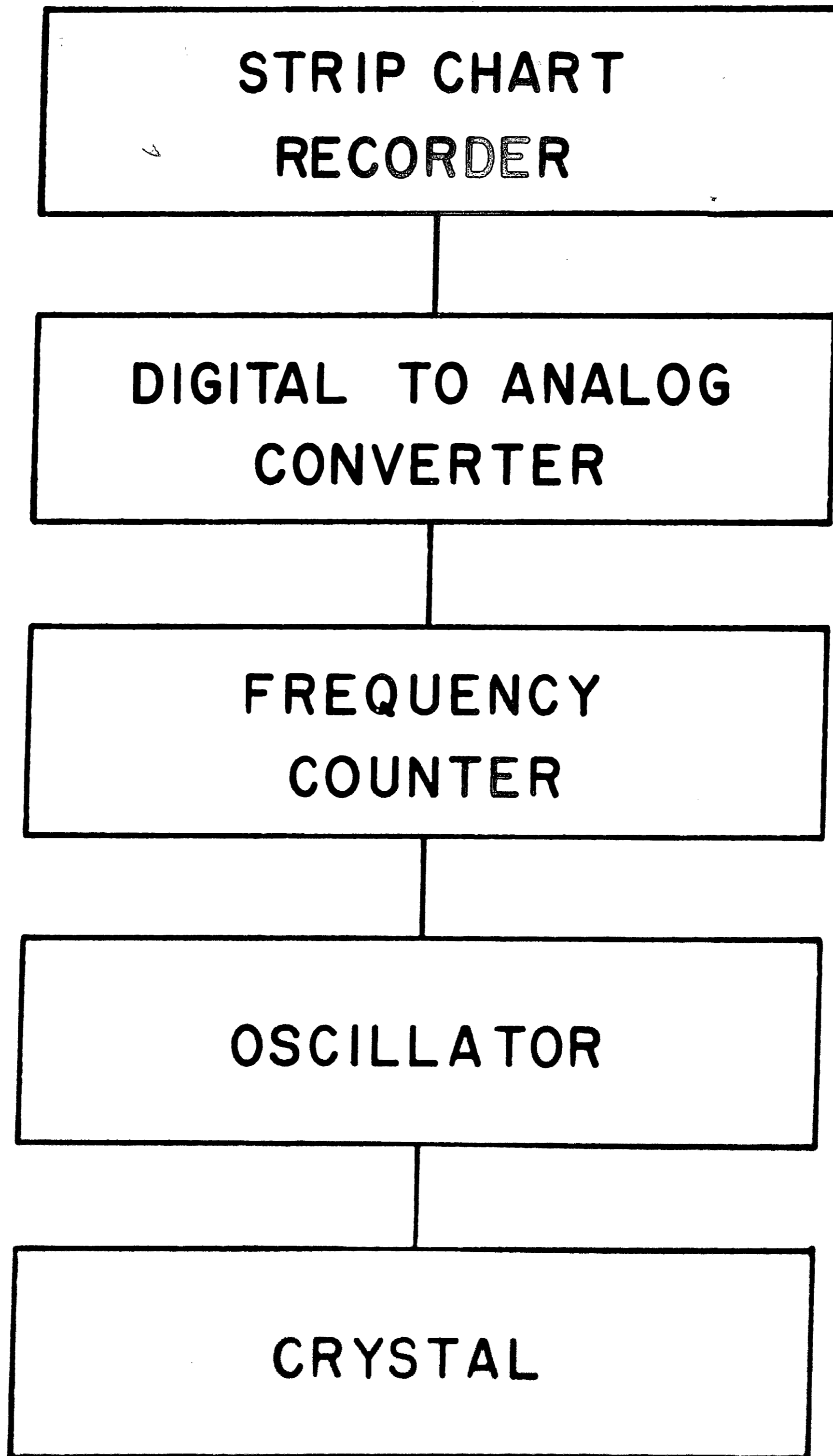
LOWER TEMPERATURE
CONTROL BATH

ADSORPTION
CELL

REFERENCE
CELL

FIGURE 3

Block Diagram of Electronics



angle of cut within the AT-cut range is chosen to give a zero temperature coefficient of frequency at 25°C. The crystals are in the form of circular plates 1.498 cm in diameter and 0.0334 cm thick. The major surfaces of the crystals have been polished to within a half wavelength of sodium light. The cutting, polishing, and plating of the crystals was done by Bliley Electric Company.

The gold electrodes on the crystal, which serve as the adsorbent surface, were vacuum deposited to a thickness of about 3000 Å and cover an area of about 1 cm².

The oscillator circuit is a solid state modified Pierce circuit which has been used successfully for mass measurement by Lando⁸. A feedback loop in this circuit maintains a constant crystal current despite the changes in crystal resistance which result from loading. Lando⁸ found the frequency of this oscillator circuit to be insensitive to temperature changes provided that the remote crystal was maintained at a constant temperature.

The frequency of the oscillator output signal is measured to eight significant digits (0.1 Hz) by a General Radio 1191B counter. The two least significant digits measured by the counter are converted to an analog signal by a General Radio 1136A digital to analog converter and recorded on a Varian strip chart recorder.

2. The Adsorption and Reference Cells

The adsorption and reference cells are shown in Figure 4. Each cell was formed by connecting a Varian viewing port with a glass window to an Ultek 7-pin electrical feedthrough. The feedthroughs were modified by Ultek for this system by replacing the center conductors with a length of stainless steel vacuum tubing. A quartz crystal is mounted in each of the cells on a pair of the feedthrough conductors. Since the cells are identical, the reference cell and the adsorption cell are interchangeable.

When in operation, the copper block seen below the cells in the photograph is mounted on the four supporting rods so that it covers both cells. The purpose of the block is to minimize thermal gradients between the cells.

3. Pressure Measurement

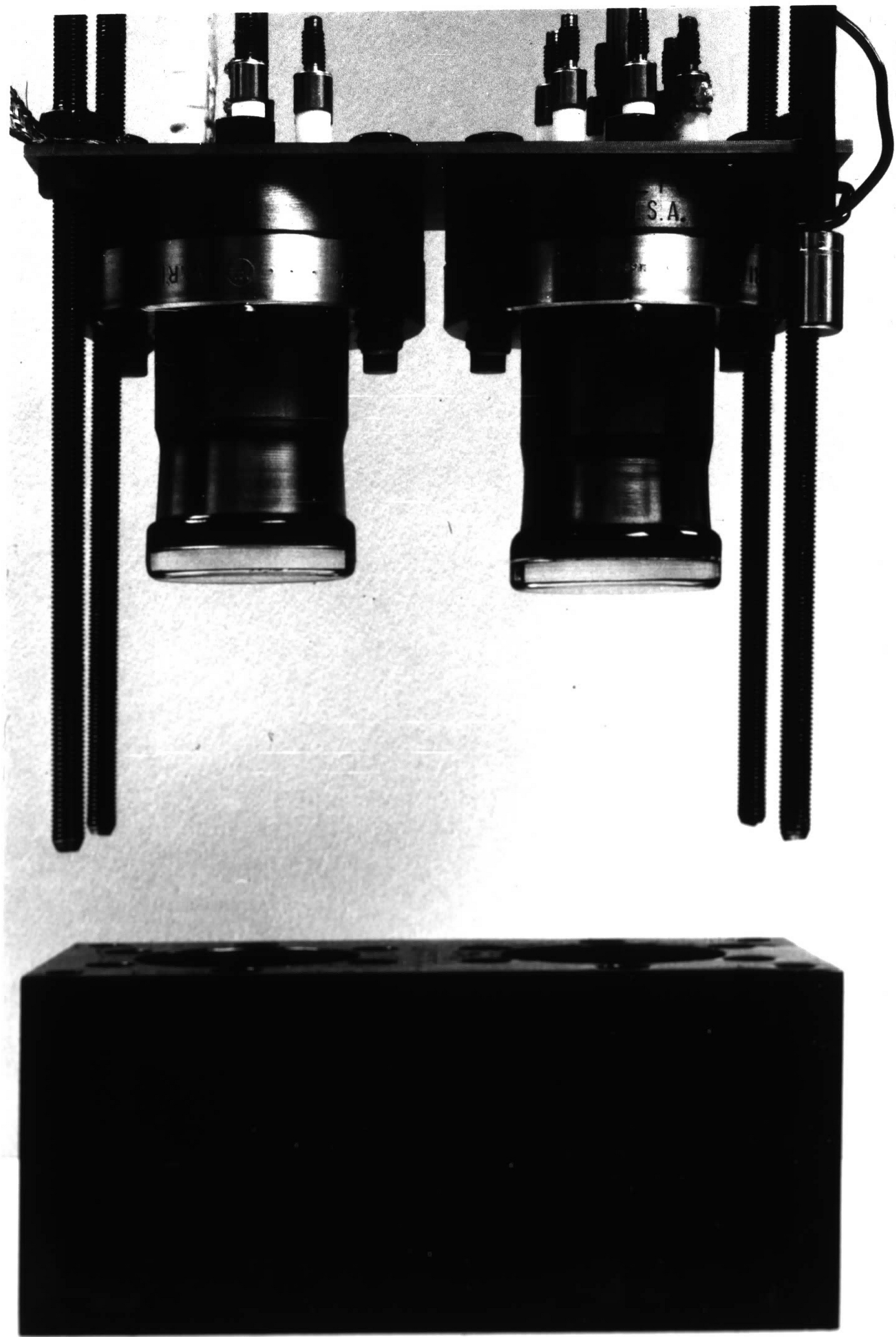
A Datametrics 1014A differential capacitance manometer is used to measure the adsorbate pressure in the adsorption cell relative to its saturation vapor pressure in the reference cell. Pressure differences can be measured from 0.0001 to 100 mmHg. For all but the lowest pressure measurements, three significant figures can be read.

4. Vacuum Pumping System

In adsorption studies it is important to prevent contamination from the pumping system; therefore mechanical pumps and diffusion pumps must be thoroughly trapped if they are used.

FIGURE 4

Adsorption and Reference Cells



In order to avoid these problems in this system, two Varian sorption pumps are used for rough pumping and an Ultek 20 l/s ion pump is used for high vacuum pumping.

5. Temperature Control

The upper temperature control bath is designed to contain the valving system and the differential pressure transducer. A compartment within the bath protects the transducer from the bath medium. The temperature of the upper bath is controlled by a commercial Lauda constant temperature circulator.

The lower temperature control bath contains the adsorption and reference cells and the copper block in which they are mounted. A Hewlett Packard quartz crystal thermometer is mounted alongside the copper block. The Hallikainen Model 1392 bath when operated with a water medium is able to maintain a constant temperature at the quartz thermometer within a few thousandths of a degree centigrade for at least several days.

6. Sample Gas Supply

The system is designed so that a sample can be introduced without atmospheric contamination. A cylinder designed to accommodate a sample ampoule contains a steel sphere which can break the ampoule upon impact. A hand held magnet outside the system can be used to drive the sphere into the ampoule and break it.

7. Hardware

The tubing and fittings used in the system are standard

stainless steel vacuum components. All of the flanges and valves used in the high vacuum portion of the system are sealed by copper gaskets. The valves used in the upper bath and the adsorbate supply system are Nupro bellows-type valves which are bakeable to 450°C. All permanent joints are either heliarc welded or brazed with low vapor pressure fillers.

B. Procedure

1. Cleaning the System

Since the objective of this work is to determine the interaction potential between certain molecules and a gold surface, it is important not only that the material being adsorbed is very pure but that the gold surface be pure and clean. The gold surface is cleaned by heating the crystal in a high vacuum for an extended period of time. Typically, a vacuum of 10^{-8} mmHg is maintained while the crystal is heated in excess of 200°C for at least 48 hrs. Since the crystal returns to approximately the same frequency after each vacuum bake cycle, it is felt that this procedure effectively removes most of the physically adsorbed species from the surface.

The remainder of the system is also cleaned by vacuum baking to remove any volatile contaminants. The system is considered sufficiently clean when a vacuum of 10^{-9} mmHg can be maintained with the ion pump operating. Whenever the system is opened to the atmosphere, it is followed by a thorough baking

to eliminate water vapor which will strongly adsorb on the internal surfaces.

2. Loading the Adsorbate

The materials for which experimental data are obtained are purchased in the highest purity grade available. The materials are received in sealed glass ampoules under an argon atmosphere. The ampoule is placed, intact, into a cylinder which is designed to accommodate it. The cylinder is then connected to the system and evacuated. When the pressure is down to approximately 10^{-8} mmHg, the ampoule is broken with a magnetically controlled steel sphere. The adsorbate is then distilled into another cylinder for the degassing procedure. The distillation is accomplished by cooling the receiving vessel with ice water while maintaining the source vessel at room temperature.

Several freeze-pump-thaw cycles are used to remove the argon gas under which the sample material is packaged. The repetition of this cycle also allows the removal of dissolved argon. The sample material is then distilled into the reference cell.

3. Measurements

The lower temperature control bath is stabilized at the desired adsorption temperature. The temperature fluctuations as indicated by the quartz crystal thermometer are less than 0.003°C . The upper temperature control bath is stabilized at

a temperature a few degrees above the lower temperature control bath to prevent condensation of the adsorbate in the valve system and the pressure transducer.

After thermal equilibrium is reached, the initial measurements are made. The frequency of the crystal is monitored for a short period of time to check its stability and this value is recorded as f_0 . With valves V1, V2, and V3 closed and V5 open the saturation vapor pressure of the adsorbate is measured. This value is recorded as P_0 .

Valve V3 is used to admit the adsorbate to the adsorption cell in small pressure increments. After each such introduction of gas the system is allowed to come to equilibrium, and the frequency of the crystal and the pressure difference between the adsorption and reference cells are recorded. Desorption measurements are made in a similar manner by drawing the adsorbate out through valve V1 in small pressure increments.

After completion of the desorption measurements, the saturation vapor pressure of the sample material and the frequency of the crystal are measured for comparison with the initial values.

V RESULTS AND DISCUSSION

At high coverages where the thickness of the adsorbed film is proportional to the number of molecular layers, the Halsey isotherm (equation (1)) may be written as

$$\ln \frac{P}{P_0} = \frac{C}{Z^n} \quad (5)$$

The molecule to metal distance Z can then be related to the measured frequency changes through equation (3).

$$-\frac{\Delta f}{f} = \frac{\Delta m}{m} = \frac{\rho_A 2A_A Z}{\rho_q A_q t_q} = \frac{2 \rho_A kZ}{\rho_q t_q}, \quad (6)$$

where ρ_A is the density of the adsorbate, A_A is the area available for adsorption on one of the gold electrodes, $\rho_q = 2.65 \text{ gm/cm}^3$ is the density of quartz, A_q is the area of the quartz crystal, $t_q = 0.0334 \text{ cm}$ is the thickness of the quartz, and $k = A_A/A_q$ is the roughness factor of the gold film. Substitution of equation (6) into equation (5) gives

$$\ln \frac{P}{P_0} = \frac{C'C}{(-\Delta f)^n}, \quad (7)$$

where $C' = \left(\frac{2 \rho_A k f}{\rho_q t_q} \right)^n = \text{constant}$. Taking the logarithm of both

sides of equation (7) gives

$$\ln \ln \frac{P_0}{P} = \ln(-C^*C) - n \ln(-\Delta f). \quad (8)$$

When $-\ln \ln(P_0/P)$ is plotted versus $\ln(-\Delta f)$, the constant n is equal to the slope of the resulting straight line. The data are plotted in this manner in Figure 5. Straight lines are fitted to the data points by the method of least squares, and the slopes of these lines are listed in Table I. The data plotted are selected from the tables in Appendix II. Some of the data at the highest relative pressures are not plotted because the pressure readings are in error by an amount equal to the partial pressure of argon which was not completely removed by the degassing procedure. The amount of argon present is small, but at very high relative pressures it becomes a significant part of the measured pressure difference.

If the values of n in Table I are compared with their corresponding ranges of coverage, it is apparent that the two materials for which the widest ranges of coverage are given yield values of n closest to two. It is also seen that the data obtained for these two materials are at higher coverages than the other data. It is felt therefore, that $n = 2$ accurately describes long-range interactions with metals.

The deviations from $n = 2$ can be explained by the degree of cleanliness of the gold surface. Some measurements were made in which the crystal was not sufficiently baked, and n was found to

FIGURE 5

$-\text{LN}(\text{LN}(P_0/P))$ versus $\text{LN}(-\Delta f)$ for Benzene, Carbon Tetrachloride, Cyclohexane, and Octane

- ▽ Benzene
- Carbon Tetrachloride
- × Cyclohexane
- △ Octane

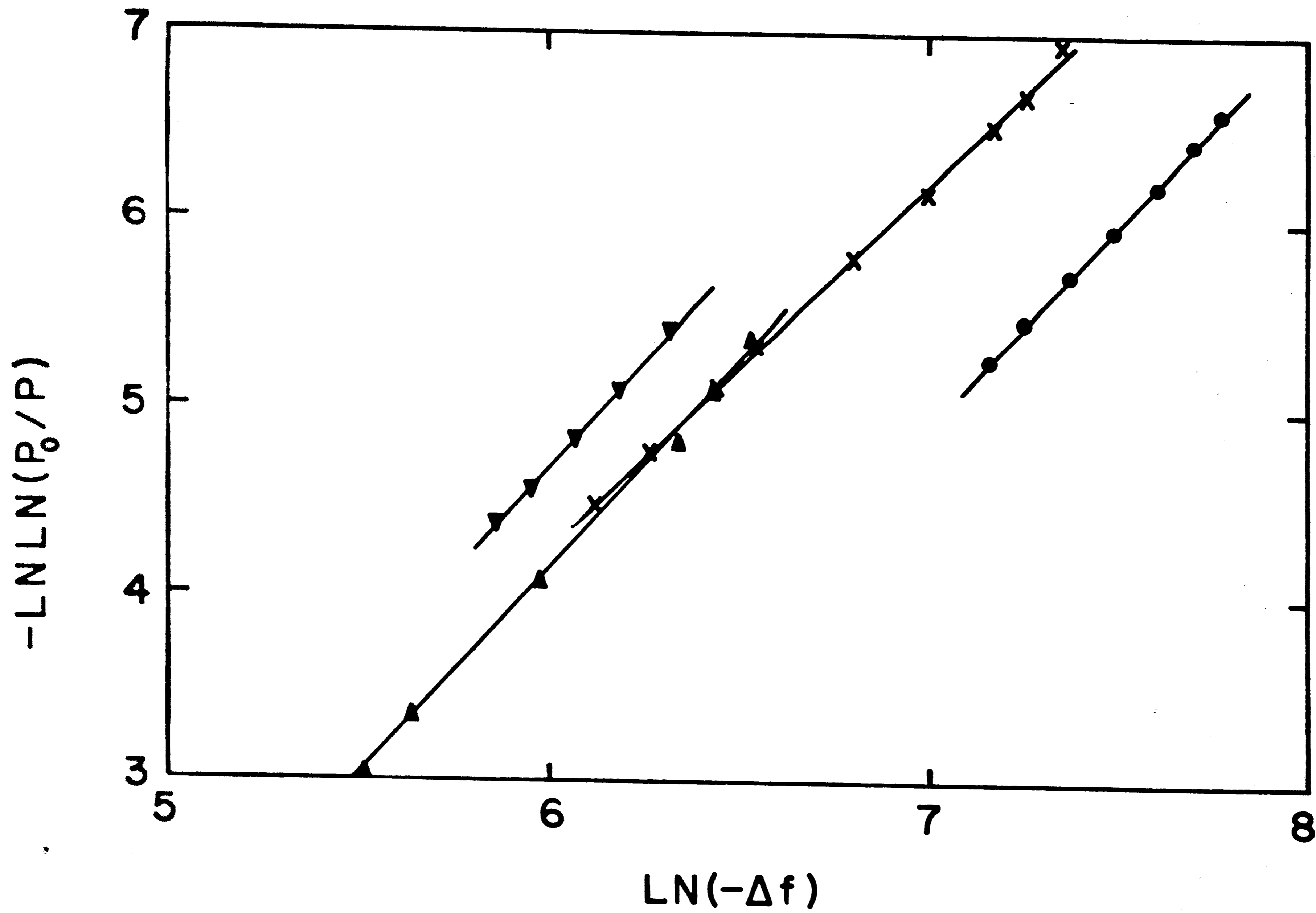


TABLE I

Values of n in the Equation $\ln \frac{P}{P_0} = \frac{C'C}{(-\Delta f)^n}$

<u>Substance</u>	<u>Temperature (°C)</u>	<u>Coverage (Å)</u>	<u># of Points</u>	<u>n</u>
Benzene	25.0	35.3-55.8	5	2.26
Carbon Tetrachloride	21.8	71.6-133.0	7	2.12
Cyclohexane	25.0	51.5-176.2	9	1.94
Octane	25.0	31.0-86.2	6	2.22

range between 1.36 and 2.86. The ranges of n shown in Table I are obtained with the more thorough baking described in the experimental section. The deviations from $n = 2$ are therefore attributed to interactions with at least a partial layer of foreign material adsorbed on the gold surface.

With $n = 2$, equation (7) becomes

$$\ln \frac{P}{P_0} = \frac{C'C}{(-\Delta f)^2}, \text{ with } C' = \frac{2 \rho_A k f}{\rho_q t_q}.$$

The value of $C'C$ can be calculated from the slope of a plot of $1/(\Delta f)^2$ versus $\ln P/P_0$. In figures 6-9 these plots are presented for the substances studied. Straight lines are fitted to the data by the least squares method.

The constant C' can be calculated if the roughness factor k is known. As explained earlier, no measured value of the roughness factor is available for the adsorbent surfaces used. Lando and Slutsky⁹, however, were able to measure k for the evaporated electrodes on their quartz crystals, and they found k to be equal to one within the experimental error. The value of k for these calculations is assumed to be one. An error in k does not affect the value obtained for n , but it does affect the value calculated for the potential constant C .

The values of C are calculated by dividing $C'C$ by C' . These constants used with equations (5) and (7) give the potential energy difference between an adsorbed molecule and a molecule in the

FIGURE 6

$1/(\Delta f)^2$ versus $-\ln(P/P_0)$ for Benzene

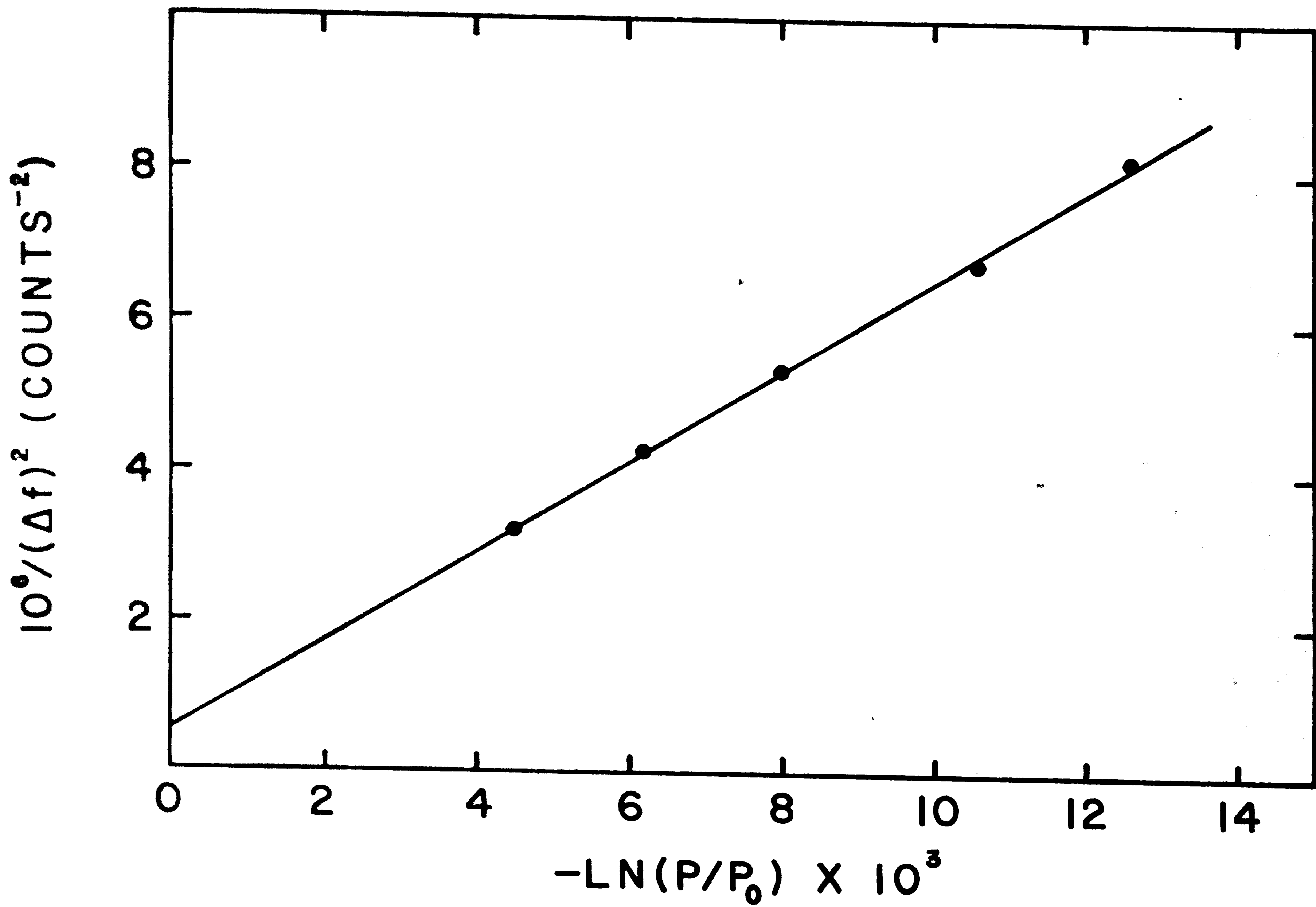


FIGURE 7

$1/(\Delta f)^2$ versus $-\ln(P/P_0)$ for Carbon Tetrachloride

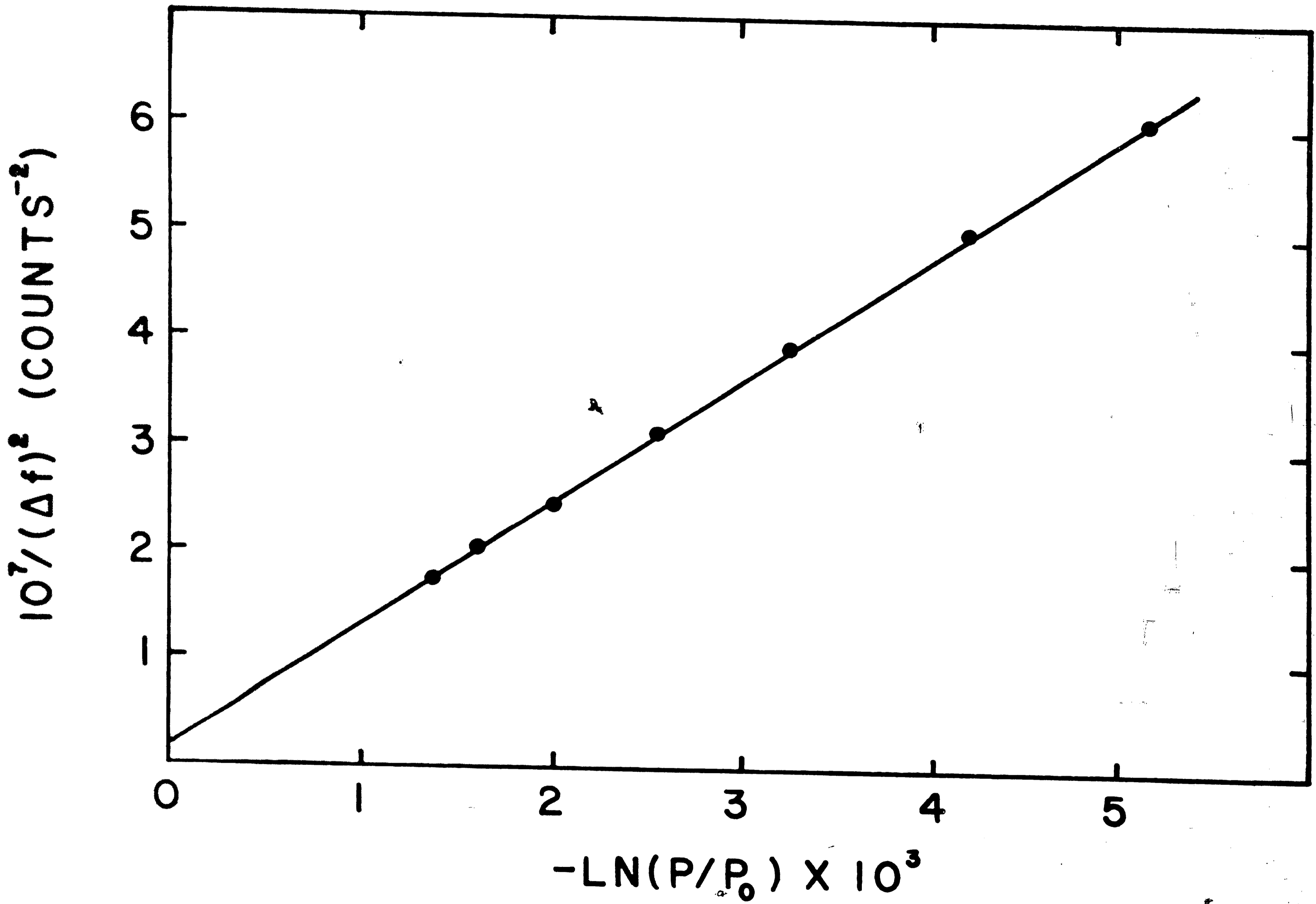


FIGURE 8

$1/(\Delta f)^2$ versus $-\ln(P/P_0)$ for Cyclohexane

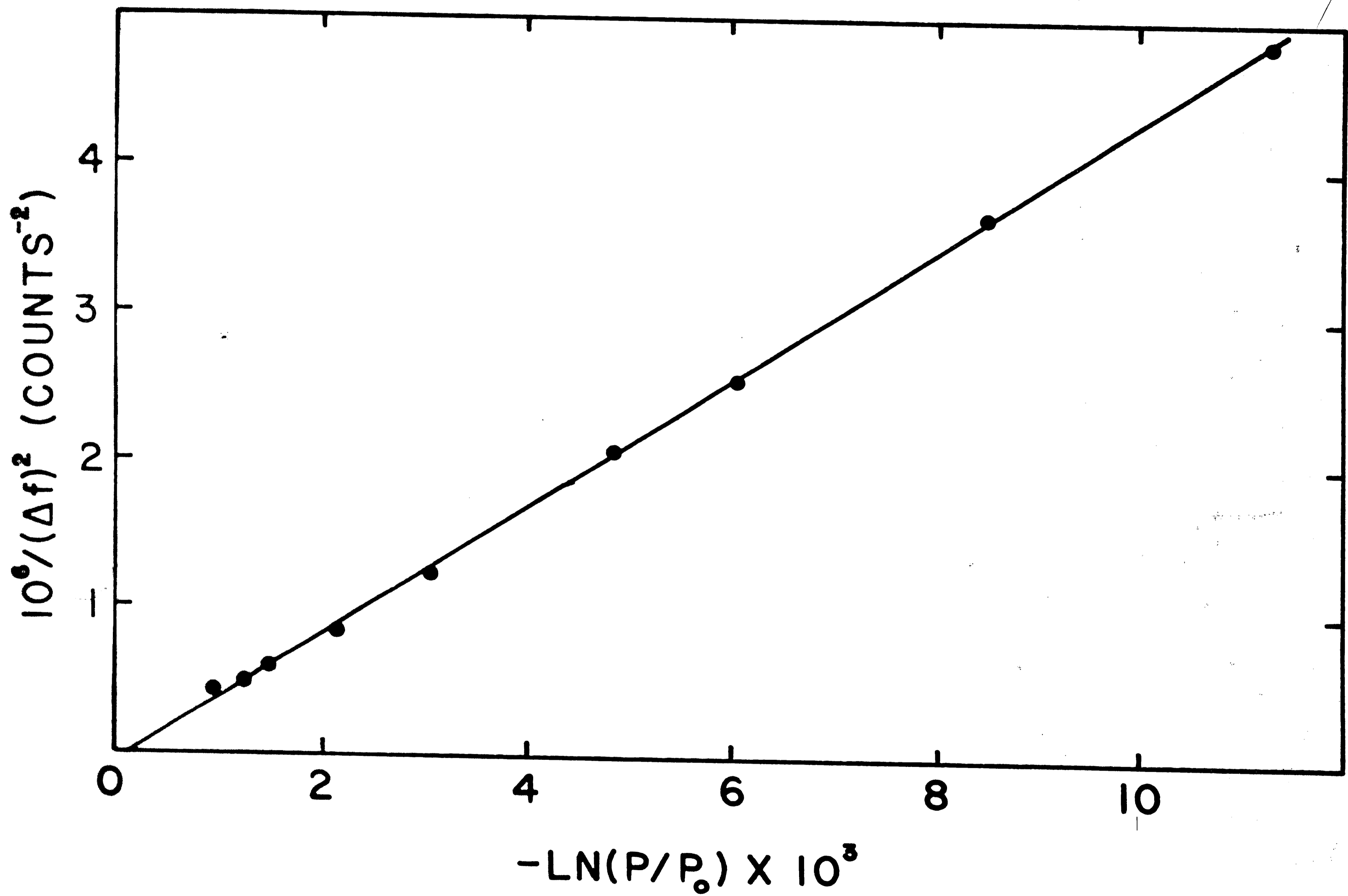
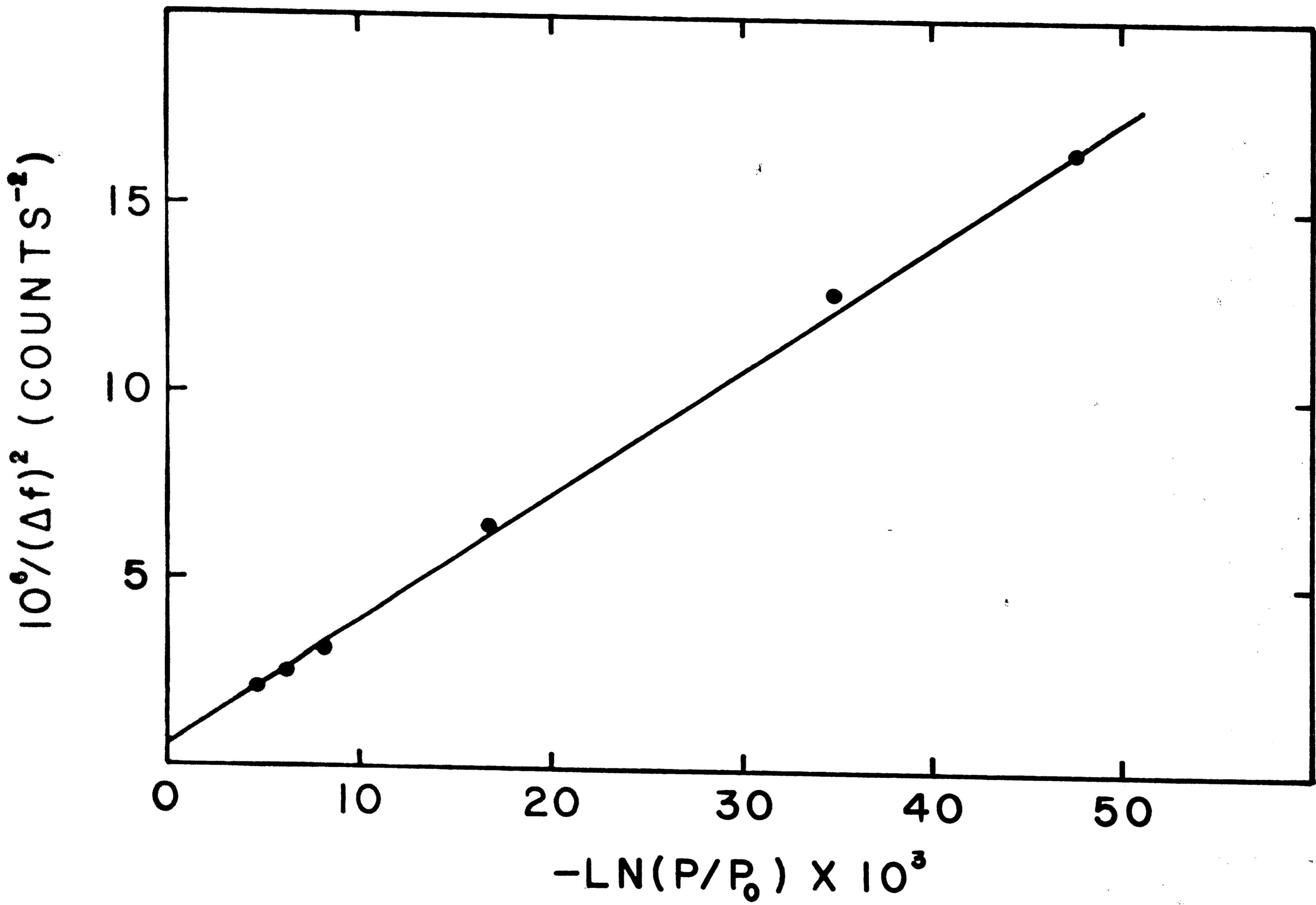


FIGURE 9

$1/(\Delta f)^2$ versus $-\ln(P/P_0)$ for Octane



bulk liquid;

$$U(z) - U'(z) = \frac{kTC}{z^2} \quad (9)$$

Wade and Slutsky¹⁷ used a similar approach to determine the interaction energy between heptane and quartz. They obtained an inverse cube relationship with distance; this is expected for a nonmetallic adsorbent. Comparing the results for metallic and nonmetallic adsorbents leads to the conclusion that the interaction with the bulk liquid U' is an inverse cube function and that at high coverages it is small compared with the inverse square interaction with the metal. Therefore, at high coverages equation (9) becomes

$$U(z) = \frac{kTC}{z^2} \quad (10)$$

The values of kTC for the substances studied are listed in Table II. In order to obtain a general interaction equation, the polarizabilities of the molecules are considered. Since the interaction energy is expected to vary directly with the molecular polarizability, equation (10) may be written as

$$U(z) = \frac{B \alpha}{z^2},$$

where $B = kTC$ and α is the molecular polarizability of the gas molecule. The values obtained for B are listed in Table II.

The physical properties of the materials studied are listed in Table III.

TABLE II

Values of the Constants in the Interaction Equation

$$U(Z) = \frac{kTC}{Z^2} = \frac{B\alpha}{Z^2}$$

<u>SUBSTANCE</u>	<u>kTC x 10²⁸ (erg cm²)</u>	<u>B x 10⁴ (erg/cm)</u>
Benzene	0.695	0.0673
Carbon Tetrachloride	1.11	0.106
Cyclohexane	1.25	0.112
Octane	1.93	0.123

TABLE III

Physical Properties of the Adsorbates

<u>SUBSTANCE</u>	<u>FORMULA</u>	<u>MOL. WT.</u>	<u>STRUCTURE</u>	<u>DENSITY</u>	<u>$\alpha \times 10^{25} (\text{cm}^3)$</u>
Benzene	C_6H_6	78	ring	0.879	103.2
Carbon Tetrachloride	CCl_4	154	tetrahedron	1.59	105
Cyclohexane	C_6H_{12}	84	ring	0.779	109
Octane	C_8H_{18}	114	chain	0.703	154.4

Using the average values of B from Table II the general interaction equation is

$$U(z) = \frac{.102 \times 10^{-4} \alpha}{z^2} \frac{\text{erg}}{\text{cm}}$$

This compares favorably with the results of Lando and Slutsky⁹ who obtained a constant of $.174 \times 10^{-4}$ erg/cm. The difference between this value and the one obtained in the present work can be explained by the roughness factor k of the gold surface. Lando and Slutsky determined a roughness factor of $k = 1.1 \pm .2$ but it was not possible to obtain a roughness factor for the present work. Since C' is a function of the square of the roughness factor, the error in the determination of the roughness factor is sufficient to explain the moderate lack of agreement of the present results with those of Lando and Slutsky.

VI CONCLUSIONS AND SUGGESTIONS FOR FURTHER EXPERIMENTS

The long-range potential energy of interaction between non-polar molecules and a metal surface is a function of the inverse square of the molecule to metal distance. This relationship which was first observed by Lando⁸⁻¹⁰ and Slutsky^{9,10} has now been independently confirmed. These results do not agree with the various theories which have been proposed to describe molecule-metal interactions. The proposed theories predict an inverse cube relationship. The assumptions which have been made by the theoreticians in order to make the problem more manageable apparently lead to an incorrect form for the interaction equation.

An interesting experiment which naturally follows the work presented here is the measurement of the energy of interaction with a nonmetallic surface using the same techniques. The more manageable theory of interactions with nonmetals predicts an inverse cube relationship with distance²¹. If this can be shown experimentally using apparatus of the type employed in this work, it will serve two purposes. First, potential constants will be obtained for the interactions, and second, the basic differences between interactions with metals and interactions with nonmetals will be demonstrated.

APPENDIX I

Frequency Change as a Function of Pressure
for Non-Adsorbing Gases

Frequency Change as a Function of Pressure for Helium

<u>Pressure (mmHg)</u>	<u>Frequency Change (Counts)</u>
1.02	1
5.00	2
10.0	4
15.0	6
20.0	7
25.2	8
29.5	9
34.1	11
40.0	12
45.5	13
51.8	14
55.8	14
61.6	15
65.0	16
71.9	17
75.8	17
80.8	18
85.0	19
92.1	19
100.0	20
109.7	20
120.7	21
128.9	22
140.1	22
152.1	23
161.9	24
172.0	24
180.0	25
190.0	26
200.6	27
210.1	27
221.5	28
230.7	28
240.1	29

Frequency Change as a Function of Pressure for Argon

<u>Pressure (mmHg)</u>	<u>Frequency Change (Counts)</u>
3.22	2
5.70	4
9.80	7
15.0	10
20.1	12
24.8	14
29.7	17
40.5	21
50.8	24
60.9	27
70.8	30
79.4	32
91.7	35
102.3	37
113.4	40
122.7	42
132.3	43
142.2	45
153.1	47
163.3	48
172.2	50
182.8	51
192.0	52
203.2	54
212.7	55
222.7	56
232.6	57
242.4	58
252.8	60
262.4	61
266.4	61
240.9	58
216.4	55
191.2	52
166.4	49
130.9	45
114.4	40
89.3	35
65.9	30
40.0	21
16.1	11

Frequency Change as a Function of Pressure for Nitrogen

<u>Pressure (mmHg)</u>	<u>Frequency Change (Counts)</u>
2.37	2
5.21	3
10.1	5
15.2	7
19.8	9
30.2	12
40.3	14
49.9	16
59.8	18
70.0	20
80.7	20
90.0	22
93.1	23
104.3	24
113.6	25
122.7	25
132.6	26
142.6	27
154.3	28
162.7	28
172.5	29
184.7	30
193.8	30
204.4	31
214.3	31
224.5	31
234.7	32
243.3	32
253.0	32
262.2	32
267.0	33
244.8	32
220.0	32
194.7	30
168.3	29
144.7	27
120.7	25
93.3	23
65.1	19
38.8	14
15.7	8

Frequency Change as a Function of Pressure for Krypton

<u>Pressure (mmHg)</u>	<u>Frequency Change (Counts)</u>
4.97	5
10.1	10
15.1	15
19.9	19
25.2	23
30.3	26
40.4	33
50.3	38
59.8	43
69.7	47
80.7	52
90.0	55
99.8	59
110.7	63
119.9	66
129.8	69
139.5	72
150.0	75
159.5	78
169.0	81
179.7	84
188.7	86
199.6	89
210.0	91
219.6	93
229.8	96
239.7	98
249.7	100
259.3	102
268.8	104
273.5	105
247.8	100
224.2	95
200.1	90
174.1	84
149.9	77
123.5	69
103.2	62
86.0	55
59.0	44
34.5	31

APPENDIX II

Adsorption Isotherm Data

Frequency Change as a Function of Relative Pressure
for the Adsorption of Benzene

$$P_0 = 95.1 \text{ mmHg}$$

$$T = 25.0^\circ\text{C}$$

<u>Relative Pressure</u>	<u>Frequency Change (Counts)</u>
0.0967	14
0.1956	26
0.3134	39
0.4343	52
0.5478	67
0.6877	88
0.8097	115
0.8906	147
0.9201	168
0.9475	198
0.9636	230
0.9753	267
0.9875	350
0.9895	384
0.9920	432
0.9938	484
0.9955	554
0.9972	656
0.9983	743
0.9988	775
0.9961	578
0.9939	483
0.9913	414
0.9746	269
0.9339	185
0.8612	136
0.6772	88
0.4616	60
0.2482	37

Frequency Change as a Function of Relative Pressure
for the Adsorption of Carbon Tetrachloride

$$P_0 = 99.7 \text{ mmHg}$$

$$T = 21.8^\circ\text{C}$$

<u>Relative Pressure</u>	<u>Frequency Change (Counts)</u>
0.0381	11
0.0812	23
0.1545	42
0.2297	59
0.3109	77
0.3862	95
0.4714	117
0.5657	144
0.6590	173
0.7302	202
0.7914	234
0.8325	263
0.8786	307
0.9146	361
0.9259	387
0.9458	443
0.9686	567
0.9796	693
0.9882	881
0.9949	1286
0.9958	1411
0.9967	1595
0.9974	1787
0.9980	2015
0.9984	2213
0.9986	2387
0.9989	2562
0.9985	2328
0.9979	1998
0.9970	1621
0.9947	1196
0.9926	1019
0.9876	806
0.9746	593
0.9528	469
0.9270	395
0.8596	302
0.7472	228

<u>Relative Pressure</u>	<u>Frequency Change (Counts)</u>
0.6179	178
0.4814	138
0.3300	99
0.2006	68
0.0843	38

Frequency Change as a Function of Relative Pressure
for the Adsorption of Cyclohexane

$$P_0 = 97.8 \text{ mmHg}$$

$$T = 25.0^\circ\text{C}$$

<u>Relative Pressure</u>	<u>Frequency Change (Counts)</u>
0.0706	10
0.1697	21
0.2822	34
0.3814	45
0.4898	58
0.5961	74
0.6871	90
0.7924	116
0.8967	167
0.9146	181
0.9396	212
0.9585	251
0.9783	332
0.9888	453
0.9915	522
0.9940	624
0.9952	693
0.9970	897
0.9979	1090
0.9985	1293
0.9987	1413
0.9990	1550
0.9981	1147
0.9970	849
0.9951	631
0.9815	330
0.9363	196
0.8712	142
0.6851	86
0.4642	54
0.2648	31
0.0695	7

Frequency Change as a Function of Relative Pressure
for the Adsorption of Octane

$$P_0 = 14.1 \text{ mmHg}$$

$$T = 25.0^\circ\text{C}$$

<u>Relative Pressure</u>	<u>Frequency Change (Counts)</u>
0.0922	11
0.1773	20
0.2837	33
0.3702	42
0.5000	58
0.5957	72
0.6830	87
0.7624	106
0.8461	138
0.9142	186
0.9316	205
0.9534	246
0.9657	280
0.9834	392
0.9921	562
0.9939	621
0.9953	685
0.9965	746
0.9978	853
0.9957	647
0.9928	506
0.9733	278
0.9463	203
0.9149	165
0.7865	101
0.6918	71
0.4943	48
0.3574	33
0.1773	14

REFERENCES

1. J.E. Lennard-Jones, *Trans. Faraday Soc.* 28, 333(1932).
2. J. Bardeen, *Phys. Rev.* 58, 727(1940).
3. H. Margenau and W. G. Pollard, *Phys. Rev.* 60, 128(1941).
4. E.S.R. Prosen and R.G. Sachs, *Phys. Rev.* 61, 65(1942).
5. H.B.G. Casimir and D. Polder, *Phys. Rev.* 73, 360(1948).
6. I. Ye Dzyaloshinskii, I.M. Lifshitz, and L.P. Pitaevskii, *Advan. Phys.* 10, 165(1961).
7. C. Mavroyannis, *Mol. Phys.* 7, 593(1963).
8. D.J. Lando, Doctoral Dissertation, University of Washington, Seattle, 1969.
9. D. Lando and L. J. Slutsky, *Phys. Rev. B*, 2, 2863(1970).
10. D. Lando and L. J. Slutsky, *J. Chem. Phys.* 52, (1970).
11. G.D. Halsey, *J. Chem. Phys.* 16, 931(1948).
12. D.M. Young and A.D. Crowell, Physical Adsorption of Gases, Butterworths, Washington (1962).
13. J. Frenkel, Kinetic Theory of Liquids. Clarendon Press, Oxford (1946).
14. T.L. Hill, *J. Chem. Phys.* 17, 590(1949).
15. T.L. Hill, *J. Chem. Phys.* 17, 668(1949).
16. T.L. Hill, *J. Phys. Chem.* 54, 1186(1950).
17. W.H. Wade and L. J. Slutsky, *J. Chem. Phys.* 40, 3994(1964).
18. G. Sauerbrey, *Z. Physik*, 155, 206(1959).
19. C.D. Stockbridge, Vacuum Microbalance Techniques, Plenum, New York (1966).

REFERENCES (cont)

20. S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc. 60, 309(1938).
21. A. Muller, Proc. Roy. Soc. (London) A154, 624(1936).

VITA

John Francis Bohland Jr., was born on February 22, 1944 in Hackensack, N. J. to Mr. John F. and Mrs. Dorothy R. Bohland.

He attended Western Carolina College from September, 1962 to June, 1963. In September, 1963 he transferred to North Carolina State University where in June, 1967 he earned a B.S. Degree in Mechanical Engineering. Following graduation he was employed by Western Electric Company as an engineer. He began graduate work at Lehigh University in September, 1970.