AN ULTRAHIGH VACUUM SYSTEM

by

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ABSTRACT

An ultrahigh vacuum system has been constructed for the purpose of filling discharge tubes with gases without introduction of impurities. An ultimate pressure of 6×10^{-10} mm. of Hg. has been reached before filling. Two tubes have been constructed and filled with Neon without critical contamination.

ACKNOWLEDGMENT

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INTRODUCTION

It is well known that the presence of small amounts of impurity greatly affects the spectroscopic emission of most gases and vapors. It is generally observed that the introduction of a foreign gas may drastically reduce both the intensity of resonance radiation and the coefficient of absorption for many electronic transitions (1). The extent to which the impurity affects the gas under study depends on the amount and the nature of the impurity (2). Also, a particular impurity will affect one transition more than another.

In this laboratory, experiments performed on the absorption properties of Neon showed that the coefficient of absorption from excited states is critically dependent on the purity level of the Neon gas. With the existing facilities for the preparation of a Neon discharge tube it was not possible to prevent serious contamination of the Neon. For this reason it was decided that an ultra - high vacuum system would be built which could be used for the preparation of gas discharge tubes. This thesis deals with the apparatus and techniques involved in the construction and operation of such a system. Some aspects of ultra - high vacuum theory are also discussed. The project described served as a link in a chain of experiments performed in this laboratory in order to measure transition probabilities in excited Neon.

One possible reason for the decrease of intensity of resonance lines in the presence of a foreign gas is the depopulation of excited energy states of atoms of the major constituent because of collisions with the foreign gas atoms or molecules. Instead of giving up its energy in radiation, the excited atom transfers some or all of its excitation energy to the foreign gas, which carries it off as kinetic energy. The probability for this to

occur is obviously related to the probability that a collision will occur
between the two atoms. Hence those states with long lifetimes are more
easily depopulated than those with very short lifetimes, and correspondingly
the effect of the foreign gas on the transitions from very shortlived states
is smaller than on those from states with a relatively long lifetime, for
states with the same collision cross section.

The absorption properties of a gas are of course similarly affected by
impurities. The effect may be particularly severe in the case of absorption
taking place from a metastable state to a higher state. The metastable
states have a lifetime of the order of milliseconds or more, and the proba-
bility for a collision to occur is very high. Hence the population density
of metastable states may be lowered to such an extent by the contaminant
that the absorption becomes very weak indeed. Meissner (3) reports in a
paper on the absorption of excited Neon that even the smallest traces of
Hydrogen present in the Neon discharge decreased the absorption drastically.
Ladenburg (4) in a paper on the anomolous dispersion of excited Neon confirms
this and shows that only under extremely pure conditions is one able to
observe effects dependent on sufficient population of metastable states,
such as absorption and anomolous dispersion involving transitions from these
states.

The experimental arrangement formerly used in this laboratory for
absorption measurements was as follows. A discharge tube with windows on
the ends was permanently attached to a conventional vacuum system served by
an oil diffusion pump. The system was pumped down to a pressure of approxi-
mately 10^{-6} mm. of Hg. after which it was filled with Neon to a pressure of
a few millimeters. Powdered Uranium was employed as a Hydrogen getter. A

potential difference of about a kilovolt was applied across the electrodes of the discharge tube to give a steady orange glow of Neon. A continuum flash background source was used and the absorption of this light by the Neon discharge photographed on a spectograph. Since absorption lines of excited Neon failed to appear in sufficient intensity on the spectrograph under the most varied experimental conditions, it was suggested that although the greatest care was taken to avoid contamination of the Neon, the system used was not sufficiently pure for the measurements required. This was further confirmed by the fact that upon continued use, the color of the discharge began to deteriorate. Balmer lines of Hydrogen were also clearly visible on the spectrograph whenever a picture of the Neon discharge by itself was taken. With the use of ultrahigh vacuum techniques it was hoped that these difficulties could be avoided.

The Neon used in this project was the purest available commercially and was reported to have the following impurities present:

Helium	80 parts per million
Oxygen	50 " " "
Nitrogen	10 " " "
Hydrogen	10 " " "
Water	1 " " "

Hence the quality of the system used had to be such that the level of impurity did not rise significantly above the quoted values due to the transfer of the Neon to the discharge tube and its subsequent use. As will become apparent in the rest of this thesis, this requirement necessitated the use of ultra high vacuum techniques.

CHAPTER I

THEORY

Introduction

There exist many mechanisms which may be responsible for the change in pressure in a particular system making use of the removal or introduction of matter in the gas phase. The most important ones are the following, assuming leaks have been eliminated:

a. Pumping with rotary or diffusion type pumps.

b. Backstreaming from the pumping units.

c. Adsorption of molecules to the walls of the container.

d. Desorption of molecules from the walls of the container.

e. Diffusion of molecules from the interior of the walls of the container.

f. Permeation of molecules through the walls of the container.

g. Electrostatic entrapment of ions.

There are a number of ways in which these processes may be classified; external pumping, adsorption and ion entrapment are mechanisms leading to a decrease in pressure, while the others all tend to increase the pressure in the system; whereas one may at any time choose to turn off the pumps, the other processes go on at all times and can not be simply controlled. Pumping and backstreaming always occur at the same time, and adsorption and desorption likewise. Desorption, diffusion, and permeation together are usually referred to as "outgassing".

In any particular system, not all these processes are equally important. The relative importance of the different mechanisms generally depends on many parameters of the system, such as the pumping speed of the external pumps, the temperature, the geometry of the wall material (e.g. surface to volume ratio),

and the nature and condition of the surfaces exposed to the vacuum. Because many of the processes invariably occur at the same time it is often difficult to distinguish one from the other, and therefore not much quantitative information is available which would enable one to predict the behavior of a vacuum system accurately. The difficulty in predicting the system's behavior is increased by the fact that no one system is identical to another as far as its reactions to adsorption, desorption, diffusion, and permeation is concerned. These mechanisms are always a function of the previous history of the wall material of the system. However, simple calculations based on data obtained experimentally under more or less controlled conditions can give a fairly good estimate of the relative order of magnitude of the different processes in any particular experimental situation. In what follows these processes will be discussed in some detail in turn. For each of the processes an expression will be derived which gives the rate of change of pressure as a function of time if only that particular process were in operation. After that the processes will be combined in one equation giving the pressure as a function of time, in terms of all the different parameters connected with the separate mechanisms. It must be emphasized, however, that all the calculations only serve to at best give a semiquantitative picture of the behavior of a vacuum system. References can be found in any standard book on vacuum technique. (See for example (5) or (6). For the adsorption and outgassing processes, which are particularly of importance for ultrahigh vacuum technique, a good reference is (7) and also (8)). The latter two also describe the general requirements for ultrahigh vacuum.

1. Mechanisms Causing Pressure Change.

a. Pumping with External Pumps.

The process of pumping with an external pump is nothing more than the

coming to equilibrium of a gas which has an externally maintained pressure gradient set up in it. Consider therefore the following idealized system.
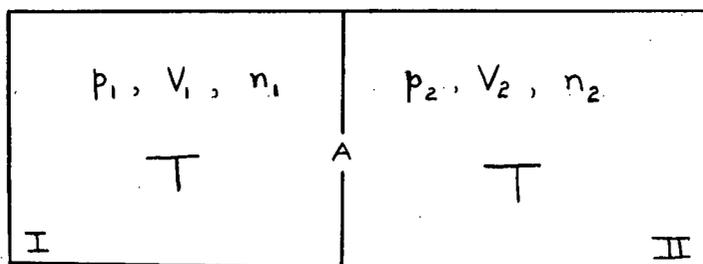
Enclosures I and II (with volumes V_1 and V_2, pressures p_1 and p_2, number densities n_1 and n_2), characterized by temperature T, are joined by an aperture of area A. The stepfunction pressure gradient of height $p_2 - p_1$ appears at A. We assume that $p_2 > p_1$.

From the Kinetic Theory, for a gas of density n molecules per cc., the number of molecules striking unit area of a wall per unit time is given by

$$\nu = n \sqrt{\frac{kT}{2\pi m}} \tag{1}$$

where k is Boltzmann's constant, m is the mass of one molecule, and T is the absolute Temperature.

Hence we can say in the above model that the net number of molecules, ν_{21}, coming through the aperture A per unit time in the preferred direction (II to I) is given by

$$\nu_{21} = (n_2 - n_1) A \sqrt{\frac{kT}{2\pi m}}$$

We define the Conductance C of the aperture as the net number of molecules traveling through the aperture in the preferred direction per unit time

per unit density difference. Thus

$$C = \frac{\nu_{21}}{n_2 - n_1} = A\sqrt{\frac{kT}{2\pi m}} \tag{2}$$

The dimensions of C are easily seen to be $\dfrac{[L^3]}{[t]}$

We now derive an expression for C in terms of p_1, p_2, V_1, and V_2. From the elementary gas laws,

$$p = nkT \tag{3}$$

so that, at constant Temperature,

$$\frac{dp}{dt} = kT\frac{dn}{dt}$$

As defined,

$$C = \frac{\nu_{21}}{n_2 - n_1}$$

ν_{21} is the number of molecules traveling from II to I per second; hence it is equal to the rate at which molecules leave II minus the rate at which molecules enter II; that is

$$\nu_{21} = -\frac{d}{dt}\left[n_2 V_2\right] + \frac{d}{dt}\left[n_1 V_1\right]$$

$$= +V_1\frac{dn_1}{dt} + V_2\frac{dn_2}{dt} + n_1\frac{dV_1}{dt} - n_2\frac{dV_2}{dt}$$

$$= -V_2\frac{dn_2}{dt} + V_1\frac{dn_1}{dt} \qquad (V \text{ is constant})$$

$$= \frac{V_1\frac{dp_1}{dt} - V_2\frac{dp_2}{dt}}{kT}$$

By equation (3), the difference in densities, $n_2 - n_1$, is given by

$$n_2 - n_1 = \frac{1}{kT}(p_2 - p_1)$$

Hence,

$$C = \frac{\nu_{21}}{n_2 - n_1} = \frac{V_1 \frac{dp_1}{dt} - V_2 \frac{dp_2}{dt}}{p_2 - p_1}$$

We now specialize this model to the case of pumping by defining enclosure I to be an ideal pump, having the properties that $p_1 \equiv 0$ and $\frac{dp_1}{dt} \equiv 0$ This defines C as the pumping speed S, and we have

$$S = \frac{-V_2 \frac{dp_2}{dt}}{p_2}$$

From this we obtain the equation for the pressure rate of change due to pumping in enclosure II, dropping the subscripts,

$$\frac{dp}{dt} = -\frac{S}{V} p \tag{4}$$

The idea of pumping speed can be very naturally extended to include all mechanisms for the removal of gas out of or influx of gas into a system; it is then defined by the equation

$$Q = S p \tag{5}$$

where Q is a measure of the flow of gas into or out of the system; the dimensions of Q are pV per unit time. In this thesis we shall use the rather

convenient pV unit of mm. of Hg. - liters, abbreviated mm. - liters. Thus an influx of gas Q of 10 mm. - liters per second means that for a one liter system the pressure will rise 10 mm. in one second. This quantity Q is particularly useful if the rate of gas influx into a system is constant.

We note from this derivation that the rate of evacuation for any type of pump involving the kinetic flow of gas through an orifice is directly proportional to the quantity $\sqrt{\dfrac{T}{m}}$. This means, for example, that Hydrogen is pumped five times as fast as Nitrogen. We also see that the minimum cross-sectional area of the system opening on the pumping side sets an upper limit to the pumping speed of the system; for Oxygen at room temperature this value is approximately

$$11 \; A_{min} \text{ liters/sec.;} \qquad A_{min} \text{ in cm}^2$$

Equation (4) is of course only true for an ideal pump. We have neglected the drag introduced by the walls of the tubing to the pump, and also the backstreaming which is always present to some extent in every pump. The first effect is not so important for our purposes; this merely changes the effective pumping speed at any particular point in the system. The second effect will be discussed in the next section.

b. <u>Backstreaming from External Pumps</u>.

No practical pumps satisfy the defining requirement of the ideal pump, viz. $p_1 = 0$, and $\dfrac{dp_1}{dt} = 0$. In practice, a steady flow of gas is present going from the pump to the system. This flow is generally constant in time and independent of the pressure in the system. We must consequently rewrite equation (4) as follows:

$$\frac{dp}{dt} = -\frac{S}{V} p + \frac{Q_b}{V} \qquad (6)$$

Where Q_b is the quantity of gas flowing back in units of pV/t. An equivalent way of expressing this is by writing

$$\frac{dp}{dt} = -\frac{S}{V}\left(p - p_u\right)$$

Here p_u must be defined as $\frac{Q_b}{S}$, and can be seen to be the ultimate pressure attainable with any particular pumping speed S and backstreaming influx Q_b. Once again we emphasize that this is only applicable to a system in which one may ignore all other effects (e.g. mechanisms c-f, page 1). Often this is not the case in practice, and the ultimate pressure lies considerably higher than p_u.

c. Adsorption.

One of the most important phenomena occuring in ultrahigh vacuum systems is adsorption of gases to the walls of the system. Generally the distinction is made between physical adsorption, where gas molecules are held to the wall material by relatively weak Van der Waals type forces, and chemical adsorption, where molecules combine chemically with the wall material. The latter process is often accompanied by dissociation of gas molecules, and the bonds between the gas and wall material are usually much stronger than those of physical adsorption. In this thesis we shall treat physical and chemical adsorption in the same general way, although strictly speaking it is not correct to do so, since as mentioned, chemical adsorption is often a more than one step process. Since this would involve us in too many details and special cases at the expense of clarity, and since the assumption is not critical, we shall assume that physical and chemical adsorption occur in the same manner, the only difference between them being the energy of adsorption. The assumption appears justified for calculating orders of magnitude.

The pumping action due to adsorption depends on three things in general:

- Pressure. (This determines the rate at which molecules strike the wall.)
- Surface area of the wall.
- Sticking probability. (The probability that on striking the wall a molecule will be adsorbed.)

We can thus write for the number of molecules adsorbed per second,

$$\frac{dN}{dt} = c \, \nu(p) \, A \tag{7}$$

Where c is the sticking probability, A is the available surface area, and

$$\nu(p) = n(p) \sqrt{\frac{kT}{2\pi m}} \qquad \text{(See equation (1))}$$

is the number of molecules striking a unit area per unit time. Hence, using equation (3), we obtain,

$$\frac{dp}{dt} = - \frac{kT}{V} \frac{dN}{dt} = - \frac{kT}{V} c \, \nu(p) \, A$$

It is convenient to express ν in terms of the pressure; using the gas law we obtain

$$\nu(p) = \frac{p}{kT} \sqrt{\frac{kT}{2\pi m}}$$

and therefore

$$\frac{dp}{dt} = - \frac{1}{V} \left(c A \sqrt{\frac{kT}{2\pi m}} \right) p = - \frac{S_a}{V} p \tag{8}$$

The quantity $cA\sqrt{\dfrac{kT}{2\pi m}}$ is a pumping speed, (c.f. equation (4))which we call

S_a. Although its form is quite similar to the pumping speed derived for

external pumps, it differs from the latter in two important respects. First

of all, the area A here refers to the effective surface area of the wall

material, whereas for the external pump A stands for the smallest crossec-

tional area of orifice to the pump. The former is usually several orders of

magnitude larger than the latter. The other difference is the sticking

probability factor c. This quantity is difficult to determine for a particu-

lar system. It depends first of all on the gas-wall material combination.

Furthermore, as can be expected for an adsorption process, it depends on the

surface coverage of the wall material. Measurements have been made by Foner

et al. (9), Schafer and Gerstacker, (10), and Becker (11). The latter deals

specifically with chemical adsorption. The results can be generalized by

saying that for a clean surface c is of the order of 1 for most combinations,

varies directly as the percentage of the surface not yet covered during the

formation of the first monolayer, and drops rather rapidly for second and

higher order monolayers. For a clean surface it can be seen that S_a repre-

sents a very formidable pumping speed. However, systems being pumped down

from atmospheric pressure do not have clean surfaces in the above sense, and

the pumping action is therefore of little or no significance. In most unbaked

systems, on the other hand, as we shall see in the next section, the reverse

process of desorption is then more prevalent. In a baked system adsorption

pumping can play a very important role. This will be discussed in more detail

later in connection with the other processes.

To give an idea of the numbers involved in adsorption, the following

table has been prepared. We assume that in an equilibrium situation at any

pressure a monolayer of gas is adsorbed; this corresponds to a surface density

of molecules of the order of 5×10^{14} molecules per cm.^{2}. The last column then gives the ratio of molecules in the adsorbed phase (Na) to those in the gas phase (Ng), for a spherical container. The large ratios at low pressures should serve to convince any sceptic of the importance of the surface effects in ultrahigh vacuum technology. If one were to liberate one monolayer of gas

TABLE I

p mm. Hg	N_g mol./cc.	N_a mol./cm^2	N_a/N_g
1	3.3×10^{16}	5×10^{14}	7.5×10^{-3}
10^{-6}	3.3×10^{10}	5×10^{14}	7.5×10^{3}
10^{-11}	3.3×10^{5}	5×10^{14}	7.5×10^{8}

from the surface of a one liter sphere into a perfect vacuum, the pressure would rise to 7.5×10^{-3} torr (1 torr = 1 mm. of Hg.). It is therefore of great importance to study the process of desorption as well as adsorption. This will be done next.

d. Desorption.

As indicated above, the process of adsorption is always accompanied by spontaneous desorption of molecules from the surface of the wall material. The average time that an adsorbed molecule remains on a surface is given approximately by

$$t_a = t_o \, e^{\frac{E_d}{RT}} \tag{9}$$

where E_d is the energy of activation, corresponding to the gas-wall material combination, T is the absolute temperature, and t_o is the period of thermal oscillation of the adsorbed molecule normal to the surface. Normally t_o is about 10^{-13} seconds. It follows from the above equation that the rate at

which molecules leave the surface on the average is given by

$$\frac{dN_a}{dt} = -\frac{N_a(t)}{t_a} = -\frac{N_a(t)}{t_o} e^{-\left(\frac{E_d}{RT}\right)} \quad (10)$$

where $N_a(t)$ is the number of molecules per square centimeter adsorbed to the surface at any time t. In terms of changes in pressure, we obtain

$$\frac{dp}{dt} = \frac{kT}{V}\left(-A\frac{dN_a}{dt}\right) = \frac{kT}{V}\frac{N_a(t)A}{t_o} e^{-\frac{E_d}{RT}} \quad (11)$$

It should be noted at this point that the rate of rise in pressure due to desorption depends exponentially on the quantity E_d/T. To give an idea of the orders of magnitude involved Table II has been prepared, which gives the rate of rise in pressure for a one liter spherical system (due to desorption only) as a function of activation energy, at room temperature, when the surface coverage is equal to one monolayer of gas, which is approximately 5 x 10^{14} molecules/cm^2.

TABLE II

E_d Kcal./mole.	$\frac{dp}{dt}$ mm./second.
1	1.42 x 10^7
5	1.83 x 10^4
10	4.20
15	1.05 x 10^{-3}
20	2.6 x 10^{-7}

The importance of the temperature and activation energy in the desorption process is clearly brought out by this table. Typical values for E_d in practice are: Physical adsorption (inert gases - glass e.g.) 1 - 10 kcal. per

mole; chemical adsorption (Oxygen, Hydrogen - metals e.g.) 10 - 50 kcal per
mole.

e. <u>Diffusion.</u>

The diffusion process is also of great importance in ultrahigh vacuum
work. The mechanism is as follows. Gases entrapped in the interior of the
glass or metal during manufacture or absorbed on long storage diffuse out of
the material and into the vacuum system, thereby causing a change in the
pressure. A good general reference to the diffusion process is Barrer (14).
Much early work on this subject was performed by Sherwood (12) and more
recently by Todd (13). The latter did extensive measurements on the diffu-
sion out of glass and found that the principal constituent given off by the
glass was water vapor at a rate which varies as the inverse square root of
the time:

$$\frac{d Q_d}{dt} = k_d \, t^{-\frac{1}{2}} \tag{12}$$

Here Q_d is the amount of water vapor given off by the diffusion process in
units of pV. The point t = 0 corresponds to the glass or metal being exposed
to the atmosphere. The quantity k_d is related to the diffusion coefficient
by the relation

$$k_d = C_o \, D^{1/2} \tag{13}$$

where C_o is the initial concentration of the gas in the solid, and D is the
diffusion coefficient of the particular gas-solid combination. D is a
function of temperature:

$$D = D_o \, e^{-\frac{Q}{RT}} \tag{13a}$$

where D_0 is a constant and Q is the heat of diffusion in cal./mole.

We can combine equations (13) and (13a) and write in general

$$k_d = K_0 e^{-\frac{E}{RT}}$$

where K_0, E are constants associated with the gas-solid combination. Todd (13) gives for diffusion of water vapor out of borosilicate glass the values

$$K_0 = 4 \times 10^{-5} mm. l./cm^2 \sqrt{sec}; \quad E = 9020 \ cal/mole$$

Corresponding to the diffusion process, the rate of rise in pressure is given by the relation

$$\frac{dp}{dt} = \frac{A}{V} k_d t^{-\frac{1}{2}} \tag{14}$$

Again an order of magnitude calculation will show the importance of the temperature in the diffusion process. Suppose an unbaked system is pumped down for 4 hours and closed off from the pumps. The pressure rise at room temperature during the next 4 hours due to diffusion using the above equations would correspond to 2×10^{-6} torr. We assume a one liter spherical system. Now suppose that while pumping the system down we had baked the entire system at 750° K. for 4 hours, and upon cooling had closed the system off from the pumps. During the next 4 hours, the pressure would rise by only 2×10^{-10} torr due to diffusion. The figures speak for themselves. Because the slope of the $\frac{dp}{dt}$ versus $t^{1/2}$ curve is so much steeper at 750° K. than at 300° K., 4 hours of out gassing at baking temperature has the same effect as approximately 10^8 hours at room temperature. This corresponds to about 1000 years! Another aspect of diffusion worth considering is the fact that it goes on for

a very long time; Todd (13) reports that the diffusion follows the $t^{1/2}$ law for the order of a year even at 800° K.

f. Permeation.

The permeation of gases through solids is of fundamental importance in that it usually sets the limit on the vacuum obtainable for any particular system. The phenomenon has been extensively studied by Norton (15). The process involves several steps and is a combination of the last three mechanisms discussed (adsorption, desorption, and diffusion). Atmospheric gases are adsorbed to the exterior surface of the walls where they dissolve into the wall material. They are then diffused through the wall material, and subsequently desorbed into the vacuum. In some cases the gas dissociates on adsorption (e.g. Hydrogen permeation through steel), and the permeation then takes place in the atomic state. In such cases the permeation rate varies as the square root of the pressure difference. In the case of permeation through glass, no dissociation generally takes place. The permeation rate is then given by the emperical relation,

$$\frac{dQ_p}{dt} = k_p A \frac{(p_1 - p_2)}{d} \tag{15}$$

k_p is a constant depending both on the material of the walls and the temperature. It varies with temperature according to the relation

$$k_p = C e^{-\frac{Q}{RT}} \tag{16}$$

where Q is the Heat of permeation. Equation (15) is analogous to the well known heat transfer equation; p_1 is the partial pressure outside the system (atmospheric) while p_2 is the vacuum pressure, A the surface area, and d the

thickness of the wall material. In normal situations, $p_2 \ll p_1$, while p_1 is constant. Hence the rate of influx is constant to a very good approximation. We have a corresponding rate of change of pressure given by

$$\frac{dp}{dt} = \frac{1}{V} \frac{dQ_p}{dt} = k_p \frac{A}{V} \frac{p_1}{d} \qquad (17)$$

It turns out that of the atmospheric gases, Helium permeates most rapidly through glass. This is not only borne out by the measurements of Norton (15) but Alpert and Buritz showed in a very interesting experiment (16) that the ultimate lower limit on the pressure in a ultrahigh vacuum system is set by the permeation rate of Helium through glass, which they measured to be approximately 5×10^{-13} mm. liters/sec. This is still a very small rate, but important for very high vacuum work.

g. Ion pumping.

Ion pumping in a vacuum system is achieved in the following manner. Electrons from a source are caused to accelerate in an electric field until they have enough energy to ionize atoms and molecules. The positive ions thus formed are then collected on a negatively charged electrode. Special pumps have been designed utilizing ion pumping, but they were not used in this project. However, even an ionization gauge acts like a pump because its operation depends on the collection of ions on a negatively charged electrode. The construction and operation of the ionization gauge will be discussed in detail later, and therefore we shall not go into the details of the pumping mechanism now. The decrease in pressure due to the ion pumping can be described by an equation very similar to equation (4)

$$\frac{dp}{dt} = -\frac{S_i}{V} p \qquad (18)$$

where S_i is the pumping speed due to ion pumping. An expression for S_i in terms of the parameters of the gauge will be derived later. It should be noted that there is little backstreaming in an ion pumping arrangement such as the ionization gauge. Hence the gauge lowers the pressure until the outgassing rate of the system is equal to the pumping rate of the gauge. This is of particular importance in well baked systems for which the outgassing rate is small.

2. Pressure Equation.

Having briefly discussed each of the important mechanisms in the evacuation process, we shall now make a quantitative estimation of a vacuum system's behavior, by combining these mechanisms into one set of equations. We obtain the following:

$$
\frac{dp}{dt} = \frac{1}{V} \left\{ -(S + S_a + S_i) p(t) + A \left(\frac{N_a(t)}{t_0} kT e^{-\frac{E_d}{RT}} + k_d t^{-\frac{1}{2}} + k_p \frac{p_{AT}}{d} \right) + Q_b \right\}
$$

$$
\frac{dN_a}{dt} = \frac{N_a(t)}{t_0} e^{-\frac{E_d}{RT}} + \frac{c(N_a)}{kT} \sqrt{\frac{kT}{2\pi m}} \, p(t)
$$

$$
S_a = c(N_a) A \sqrt{\frac{kT}{2\pi m}}
$$

(19)

A summary of the symbols used is given below.

   V is the volume of the system.

   S is the pumping speed of the external pumps.

S_a is the pumping speed due to adsorption.

S_i is the pumping speed of the ion pumps.

A is the area exposed to the vacuum.

t_o is the period of oscillation of adsorbed molecules in a direction

normal to the surface.

$N_a(t)$ is the number of adsorbed molecules per cm.^{2} of surface area.

k is Boltzmann's constant.

T is the absolute temperature.

m is the mass of one molecule of gas.

E_d is the energy of adsorption.

k_d is the constant associated with diffusion (equation 13, 13a.)

k_p is the constant associated with permeation (equation 16.)

c is the sticking probability (equation 7.)

P_{at} is the partial pressure outside of the system of the permeating gas.

d is the thickness of the wall material.

Q_b is the backstreaming rate.

Equations (19) cannot be solved simply as they stand; if $N_a(t)$ is eliminated,
we obtain a second order equation in p which is nonlinear. The nonlinearity
is the result of the fact that the pumping action of the walls is dependent
on both the pressure and the number of atoms already adsorbed. The importance
of this process varies with the condition of the vacuum. It cannot be neg-
lected when in some way the wall surfaces are made free of adsorbed gas for
a short period of time and then left to adsorb molecules from the gas phase of
the system. This occurs when the system is heated to some temperature above
room temperature and then left to cool. Later considerations will bear this
out. However, when the system is pumped down from atmospheric pressure and
has not been baked, the walls are not likely to do any pumping because many

monolayers of gas are already adsorbed and the sticking probability c is therefore small. Hence in such a case it is justifiable to neglect the terms associated with adsorption pumping. This will be done in our calculation, which applies to pumping on a system starting from atmospheric pressure. We shall also neglect the $t^{-\frac{1}{2}}$ dependence in the diffusion term, and assume the diffusion to be constant in time. The reason for this is that a solution in closed form can not be obtained if the $t^{-\frac{1}{2}}$ dependence is left in. The importance of this term is not in the time dependence but rather the temperature dependence, as is borne out by the sample calculation on page (16).

Hence we write the following equations instead of equation (19)

$$\frac{dp}{dt} = \frac{1}{V} \left\{ -(S+S_i)p(t) + A\left(\frac{N_a(t)}{t_0} kT e^{-\frac{E_d}{RT}} \right.\right.$$
$$\left.\left. + k_d + k_p \frac{p_{AT}}{d}\right) + Q_b \right\} \tag{20}$$

$$\frac{dN_a}{dt} = -\frac{N_a(t)}{t_0} e^{-\frac{E_d}{RT}} \tag{21}$$

Solving (21) for $N_a(t)$, we obtain

$$N_a(t) = N_a(0) \exp\left\{-\frac{t}{t_0} e^{-\frac{E_d}{RT}}\right\} \tag{22}$$

We define the following quantities:

$$\alpha \equiv \frac{1}{V}(S + S_i)$$

$$\beta \equiv \frac{A}{V} kT \frac{N_a(0)}{t_0} \exp\left(-\frac{E_d}{RT}\right)$$

$$\gamma \equiv \frac{A}{V}\left(k_d + k_p \frac{p_{AT}}{d}\right) + \frac{Q_b}{V}$$

$$\lambda \equiv \frac{1}{t_0} e^{-\frac{E_d}{RT}}$$

We then obtain, substituting (22) in (20), using the above definition,

$$\frac{dp}{dt} = -\alpha p + \beta e^{-\lambda t} + \gamma \qquad (23)$$

We now solve this equation with the initial condition

$$p(0) = p_0$$

We rearrange equation (23) and multiply by $e^{\alpha t}$. This gives

$$\frac{dp}{dt} e^{\alpha t} + \alpha p e^{\alpha t} = \beta e^{-(\lambda - \alpha)t} + \gamma e^{\alpha t}$$

Then

$$\frac{d}{dt}\left(p e^{\alpha t}\right) = \beta e^{-(\lambda - \alpha)t} + \gamma e^{\alpha t}$$

So that

$$p e^{\alpha t} = \beta \int e^{-(\lambda - \alpha)t} + \gamma \int e^{\alpha t}$$

$$= \frac{-\beta}{\lambda - \alpha} e^{-(\lambda - \alpha)t} + \frac{\gamma}{\alpha} e^{\alpha t} + C_0$$

Hence

$$p(t) = \frac{-\beta}{\lambda - \alpha} e^{-\lambda t} + \frac{\gamma}{\alpha} + C_0 e^{-\alpha t}$$

$$p(0) = p_0 \; ; \quad \therefore \; p_0 = \frac{-\beta}{\lambda - \alpha} + \frac{\gamma}{\alpha} + C_0$$

$$\therefore \; C_0 = p_0 + \frac{\beta}{\lambda - \alpha} - \frac{\gamma}{\alpha}$$

Hence the solution is

$$p(t) = \frac{\beta}{\lambda - \alpha}\left(e^{-\alpha t} - e^{-\lambda t}\right) + \left(p_0 - \frac{\gamma}{\alpha}\right)e^{-\alpha t} + \frac{\gamma}{\alpha} \quad (24)$$

As can be seen from this equation, the time independent part , $\frac{\gamma}{\alpha}$, determines the ultimate pressure. γ is a measure of the influx of gas due to diffusion and permeation, while α is a measure of the pumping speed of the system. γ can take on many different values depending on the material of the vacuum chamber. In the system used for this project, the wall material was mostly glass, although metal valves were used. For the purposes of calculation we shall assume that we have a one liter glass system of surface area 1000 cm^2. Later we shall see how the presence of metal parts changes the situation. We shall also assume that we are pumping on this system with a pumping speed of one liter per second at a temperature of 300° K (approximately room temperature). We first determine

$$\gamma = \left(k_d + k_p \frac{p_{AT}}{d}\right)\frac{A}{V} + \frac{Q_b}{V}$$

From Todd's measurements (13) on Pyrex glass, we have initially, (t = 1 sec)

$$k_d = 1.4 \times 10^{-11} \text{ mm. liters/cm}^2 \text{ sec.}$$

$$(300 °K.)$$

According to experiments of Alpert, Buritz, and Rogers (17), the major influx of gas due to permeation of glass is in the form of atmospheric Helium, and from measurements of Norton (15) we calculate

$$k_p = 9 \times 10^{-14} \text{ mm liters/cm}^2 \text{sec}$$

for unit pressure difference and thickness 1 mm. Again, Q_b is very much a paramater of the system used; here we shall assume that Q_b is very small compared to the diffusion and permeation influxes. In practice this is not true, certainly not at room temperature, unless very efficient traps are used. However, assuming Q_b to be small does show up other limitations of the vacuum system that are not so obvious.

The partial pressure of Helium in the atmospher is 5 x 10⁻³ mm. so we get

$$\gamma = \left(1.4 \times 10^{-11} + 4.5 \times 10^{-16}\right) \frac{A}{V} \text{ mm. l./sec.}$$

For a one liter system with surface area 1000 cm² then, we obtain

$$\gamma = 1.4 \times 10^{-8} + 4.5 \times 10^{-13} \text{. mm. l./sec}$$

The permeation rate is much smaller then the diffusion rate for an un-baked system and can be neglected at this stage. Once the system has been baked, however, the diffusion rate is much smaller (see page   ), and then

the permeation rate is much more important.

Since $\frac{\gamma}{\alpha}$ is the pressure at $t = \infty$, we shall call it p_u, the ultimate

pressure. Since $\alpha = 1$ for our sample system, we have

$$p_u = 1.4 \times 10^{-8} \text{ mm. of Hg.}$$

Several points should be noted at this stage. First of all, no mention

was made of any nongaseous contaminants which may be on the glass, such as

grease or oil films deposited while the glass was being handled. These con-

taminants may have a very high vapor pressure compared to the value of p_u

quoted above, and set a corresponding limit on the pressure that can be

achieved. Considerable amounts of gas may also be trapped in the contaminat-

ing film and the release of this gas, which is not necessarily governed by

one of the described processes, can cause the pressure to stay high for con-

siderable length of time. Our figures are therefore applicable only to

systems which are not contaminated beyond having been exposed to the atmos-

phere for some time. A second point is that while p_u sets a limit on the

pressure that can be achieved, we do not know how long it takes to reach this

pressure until we have evaluated the time dependent part of equation (24).

This may in fact be a very long time, depending on the values of β and λ.

In order to give an idea of the time dependence of the pressure in the

system, a table has been prepared giving the value of the pressure as predicted

by equation (24) at times $t = 15$ minutes, $t = 24$ hours and $t = 10$ days for the

sample system used above. The parameter which is varied is E_d, the energy of

desorption. The reason for doing this is that E_d varies for different gas-

solid combinations. Measured values range from 20 cal. per mole (the heat of

vaporization of liquid Helium) to several hundred thousand cal. per mole (e.g.

the activation energy of oxygen on Titanium is 236 kcal. per mole.) Not much

quantitative data is available for glass-gas systems. Tuzi and Okamoto (18)

report E_d for water on glass in high vacuum apparatus to be between 13 and 40

kcal. per mole. Because the values of E_d for the various gases and vapors in

the system are not well known, we have calculated the pressure time dependence

for various values of E_d, in order to see for which values of E_d the desorp-

tion process is important from the point of view of reaching high vacuum

quickly.

One difficulty in computing the values of the table is the choice of a

suitable initial value of N_a, the number of molecules adsorbed. Briggs (19)

gives a figure for water vapor on glass of the order of 5×10^{16} molecules/cm^2

while the number of Nitrogen molecules per cm^2 is given as 5×10^{14} mol./cm^2.

This is in agreement with observations by Todd (13), who reports that 99% of

the gas desorbed from glass on heating is water. Hence we have taken Na(0) to

be 5×10^{16}. The table is given on page (27).

The results of the calculations show that if our assumptions are correct,

there exists a definite range of desorption energies for which the outgassing

process impedes the speedy production of high vacuum. This range lies between

20 and 30 kcal. per mole for the p_u calculated above. If the p_u happens to

be lower, this range is correspondingly extended. Qualitatively, these results

mean that for low energies of desorption, the molecules are pumped off the

walls in a very short time because they are bound by very weak forces. For

high energies, on the other hand, the molecules are so tightly bound that no

appreciable desorption takes place. It is for the middle range of energies

that desorption takes place at a rate which keeps the vacuum of low quality

for long times. It is likely that water vapor and other active atmospheric

TABLE (III)

E_d	p (t = 15 min.) (mm. of Hg.)	p (t = 24 hrs.) (mm. of Hg.)	p (t = 10 days))mm. of Hg.)
1 kcal./mole	p_u	p_u	p_u
10 kcal./mole	p_u	p_u	p_u
20 kcal./mole	p_u	p_u	p_u
21 kcal./mole	1.8×10^{-4}	p_u	p_u
22 kcal./mole	4.0×10^{-4}	p_u	p_u
23 kcal./mole	2.0×10^{-4}	p_u	p_u
24 kcal./mole	6.0×10^{-5}	1.1×10^{-6}	p_u
25 kcal./mole	1.5×10^{-5}	6.0×10^{-6}	p_u
26 kcal./mole	2.4×10^{-6}	2.0×10^{-6}	4.1×10^{-7}
27 kcal./mole	4.5×10^{-7}	4.5×10^{-7}	3.3×10^{-7}
28 kcal./mole	8.9×10^{-8}	8.9×10^{-8}	8.9×10^{-8}
29 kcal./mole	2.5×10^{-8}	2.5×10^{-8}	2.5×10^{-8}
30 kcal./mole	1.7×10^{-8}	1.7×10^{-8}	1.7×10^{-8}
31 kcal./mole	p_u	p_u	p_u

Table showing the time dependence of the pressure as a function of E_d, the energy of desorption, for a glass vacuum system at 300° K., Volume 1 liter, surface area 1000 cm^2, initial surface coverage 5×10^{16} mol./cm^2, with a pumping speed of 1 liter/sec. p_u is the ultimate pressure under these conditions and is equal to 1.4×10^{-8} mm. of Hg.

gases are bound to the glass with energies in this middle range.

The calculations show the importance of the parameter E_d in high vacuum work. If we know E_d for a particular gas, we can see whether this gas is going to be present to any extent in the residual gas once high vacuum has been reached. It may be, for example, that in a particular system all atmospheric gases are desorbed rapidly except one, say Hydrogen. The residual gas may then be 90% Hydrogen, while in the atmosphere Hydrogen is only present in very small amounts. While this is not likely for glass systems, and probably not to such a large extent in most systems, it must nevertheless be realized that "selective" pumping can occur in this manner, and that the composition of the residual gas is not governed so much by the composition of the gas before pumping commenced, but rather by the mechanisms involved in the pumping process. Because so little quantitative data is available that can be applied in general to a vacuum system, it is very difficult to predict what the composition of the residual gas will be. It is needless to say that such a prediction would have been of some interest for our system.

We shall next discuss what happens when the system as a whole is heated by means of an oven. This process, called "baking" is one of the most effective ways of reaching pressures which are less than 10^{-8} mm. of Hg. (ultra-high vacuum). We can no longer solve equation (24) in the simple manner as before, because the temperature is now also a function of time. However, in order to see why the vacuum improves, it is sufficient to analyze what happens qualitatively during and after baking. First of all, the term $\frac{\gamma}{\alpha}$ becomes several orders of magnitude smaller, as was shown on page (16). The high temperature causes so much water vapor to diffuse out of the glass, that the diffusion rate at subsequent lower temperatures becomes

negligible compared to the permeation rate. The latter, which also changes
with temperature, comes back to its original value on cooling rather than a
lower value, because it does not depend on how much gas is _in_ the glass mate-
rial, but rather on how much can go through the material.

Suppose we bake for six hours at 700° K. Upon cooling k_d, the constant
associated with diffusion from inside the glass, is calculated to be 2×10^{-17}
mm.liters/cm^2 sec. k_p is unchanged, and equal to 9×10^{-14} mm.liters/cm^{2}sec.
for He as before. Hence p_u, the ultimate pressure is given by

$$p_u = \frac{\gamma}{\alpha} = \frac{1}{\alpha} \left(k_d + k_p \frac{p_{AT}(He)}{d} \right) \frac{A}{V} + \frac{Q_b}{\alpha V} =$$

$$2 \times 10^{-14} + 4 \times 10^{-13} + \frac{Q_b}{\alpha} \quad m.m.$$

We can at this stage not neglect Q_b; no matter how well we trap the back-
streaming oil, Q_b is bound to be larger than 4×10^{-13} mm. liters/sec.
Alpert (20) shows that exposure to the pumps eventually destroys the ultra-
high vacuum rather than maintain it. Hence the system is usually closed upon
cooling and ion pumping used to obtain and maintain an ultrahigh vacuum. The
process of ion pumping will be described in a later section, but we can say
now that the backstreaming rate from an ion pump is much smaller than that of
a diffusion pump, so that again we can neglect Q_b, compared to the influx due
to permeation. This was experimentally shown by Alpert and Buritz (16).

Thus the permeation process is now the most important, and sets the
fundamental limit on the vacuum.

The surface gases, which for unbaked systems caused slow net pumping
speeds, are rapidly desorbed at the baking temperature. The range of values

of E_d, which will cause difficulties in pumping at 700° K. is now shifted to 45 kcal. $<$ E_d $<$ 70 kcal. Hence any gas or vapor with value of E_d in the troublesome range between 20 and 30 kcal./mole. will be rapidly desorbed at such a high temperature. Although on cooling some gas will be readsorbed, much of the desorbed gas will be pumped away while the system is still warm and hence the surface coverage after cooling will be several orders of magnitude smaller than before, with a corresponding lower pressure.

The presence of metals in the vacuum system can alter the behavior significantly. The desorption process is not much different from that associated with glass, although, as mentioned before, metals tend to have more nongaseous contaminants on them, which may alter the desorption. The diffusion out of metals is of more importance, however. Gases dissolve in the metal in large quantities when the metal is cast, and when exposed to a vacuum these gases diffuse out. Again, the rates of diffusion vary greatly with the particular glass metal combination. An extensive account of diffusion of gases in solids is given by Barrer (14), and it would not do the subject any justice to discuss it in this thesis. We can say in general, however, that the lighter gases (Hydrogen, Helium) diffuse the fastest, and particularly at elevated temperatures this diffusion may cause serious influx of gas. In order to illustrate these points we use equation (13) and (13a) to compute k_d (see equation (14)), for some gas-metal combinations at room temperature, before baking. Data for the different gas-metal combinations are taken out of Barrer (14). We must choose a typical value for C_o, the initial concentration of gas dissolved in the metal. Since this varies for different samples, we take C_o to be .1 cc(NTP)/cc. of metal. This gives a rough upper limit to k_d. Typically C_o is between 10^{-5} cc/cc and .1 cc/cc (see (7), p. 356). We then obtain:

TABLE IV

Gas metal Combination	k_d (upper limit) (mm. liters/cm^{2}sec)
N - Fe	1×10^{-14}
H$_2$ - Ni	3×10^{-6}
H$_2$ - Fe	6×10^{-6}
H$_2$ - P$_d$	4×10^{-5}

For comparison, the value obtained for diffusion of water vapor out of pyrex glass was 1.4×10^{-11} mm. liters/cm^2 sec. The results show that if sizable pieces of metal are in the system, the diffusion of Hydrogen out of these metals may be of importance. It must be remembered that the values of k_d quoted are an upper limit, and that actual values may be lower, depending on the concentration of the gas in the metal. Baking will lower the value of k_d by several orders of magnitude, as shown before.

CHAPTER II

APPARATUS

The apparatus used for the production of ultrahigh vacuum will be described next. A schematic diagram of the general arrangement of the system is given in figure (1).

1. Pumps.

a. Mechanical backing Pump.

A two stage rotary vane pump of pumping speed 1½ liter per second was used to bring the pressure down to about 10 microns of Hg. The reason for having this type of mechanical pump is to provide a suitable backing pressure for the diffusion pump (see below), which will not operate at pressures above 100 microns of Hg.

b. Diffusion Pump.

The diffusion pump is one of the most widely used instruments for the production of ultrahigh vacuum. Generally the distinction is made between two types, the mercury diffusion pump and the oil diffusion pump. Both types have certain advantages and disadvantages. The principal advantages of the mercury pumps are: a) the pump fluid can be easily trapped at liquid Nitrogen temperature, thereby reducing the backstreaming rate, and b) the pump fluid is stable; i.e. no products are produced by thermal breakdown. However, oil diffusion pumps are more widely used in spite of the fact that they do not have the above-mentioned advantages because the pump fluid is less dangerous. Also, recent development of low vapor pressure oils and efficient trapping systems have greatly reduced the backstreaming problems. In this project, an oil diffusion pump was used. Its mode of operation will be described briefly.

Figure (2) illustrates the design of the oil diffusion pump used. The casing is water cooled and an electric heater for the evaporation of oil is installed in the base. The jet system consists of three concentric tubes terminating in nozzles, together with an annular nozzle system as shown. The oil vapor rises in the tubes and issues from the nozzles at supersonic speeds. The gases from the vacuum chamber diffuse into the jet of oil vapor and are trapped by the oil droplets. The oil subsequently condenses on the water-cooled walls of the pump, where the trapped air is liberated and pumped off by the backing pump. The umbrella shaped jet of oil vapor issuing from the nozzles acts as a diaphragm in that it keeps gas molecules in the high pressure area below the jet from escaping back into the vacuum system. For a more complete account of the physics involved in the operation of the diffusion pump see for example Dushman (5).

In order to reduce the backstreaming from this pump a specially designed baffle was installed at the vacuum side of the pump which utilized water cooling to condense any vapors that escaped from the pumping unit into the vacuum system. Although such a baffle lowers the pumping speed of the pump, its use is essential in order that the system will not be contaminated with oil from the pump. The ultimate pressure attainable with the pump is also lowered because of the reduced backstreaming. Figure (3) shows the design of the baffle.

Even though the backstreaming is reduced by means of the water-cooled baffle, small quantities of oil vapor will still find their way into the vacuum system. As was shown by an experiment performed by Alpert (20), prolonged pumping with a diffusion pump, even though properly baffled, will ultimately deteriorate the vacuum in a baked system because of small deposits

of oil on the walls of the vacuum chamber. In order to minimize this effect a trap was built into the system near the pumps, which was filled with pellets of alkali metal alumino-silicate, more commonly known as Zeolite. This substance is porous and acts as a very effective pump for oil vapor. Biondi (21) reports on the use of this material as an oil trap and gives some data on its use for ultrahigh vacuum applications. The Zeolite may be degassed and reactivated at 400° C. Other kinds of traps, although not used for this project, can be very efficient in removing backstreaming oil. One simple design is the copper foil trap (see for example (8), page 656). Clean copper has an efficient adsorbing surface for backstreaming oil vapor even at room temperature. The efficiency of nearly all traps is increased by cooling, for instance with liquid Nitrogen; while this may be of great advantage in obtaining a lower pressure, cold traps have the drawback that they must be kept cold at all times. If the trap is allowed to warm up the evolved gas may spoil the clean surface conditions of the chamber obtained with baking. For this reason no liquid air traps were used in this project.

2. Valves.

Because the vacuum system had to be baked in its entirety, no greased stop cocks could be used to isolate the various compartments of the system. Not only does the grease melt at elevated temperatures, but also the vapor pressure of the best vacuum grease is usually well above the ultrahigh vacuum range at room temperature. Consequently bakeable metal valves were used which employ no grease in the sealing process. These valves, manufactured by the Granville Philips Co., are designed to withstand temperatures up to 450° C. and can be closed to a leak rate of less than 1×10^{-14} mm.1./sec. Briefly, their design is as follows. The seal is produced by a $\frac{1}{2}$ inch diameter monel nosepiece carrying a very small carefully machined silver

gasket which seats in a specially shaped groove in the monel valve body.
The nose piece, mounted in the center of a flexible nickel diaphragm is moved
in and out of the sealing groove by a driver mechanism which is designed to
apply the high forces required for a metal to metal seal. Metals in contact
with the vacuum are monel, nickel, silver, Kovar and very low vapor pressure
brazing alloys containing gold, nickel, silver and copper. A diagram of the
exterior of the valve is given in figure (6). Relatively large torques are
required to seal the valve; therefore the valve brackets were ridgidly
mounted on a steel bar which in turn was fastened to the oven base. Because
the valves were ridgidly mounted, allowance had to be made for the fact that
with heating or cooling stresses might develop in the glass tubing which
could cause breakage of the glass. In order to avoid this each valve was
fitted with flexible glass bellows in order to reduce any stress.

When baked, the valves had to be open in order to prevent fusing of the
sealing gaskets. For this purpose the driving screw was taken off and a
special clamp attached to keep the valve open during bakeout. Figure (7)
gives a graph of the leak rate versus closing torque for the valves used.

3. Vacuum gauges.

Four types of vacuum pressure gauges were used in this project.

a) The McLeod gauge (1×10^{-2} - 1×10^{-5} mm. of Hg.)

b) The Ionization gauge (1×10^{-4} - 1×10^{-10} mm. of Hg.)

c) A relaxation oscillator type discharge gauge (1-10 mm. of Hg.)

d) An oil manometer (.1 - 10 mm. Hg.)

These gauges will be described in turn.

a) McLeod Gauge.

This gauge was put on the system initially for the purpose of testing

the behavior of the system before baking. The gauge uses Mercury to measure pressures between .1 and 10^{-6} mm. of Hg: For a discription of the design and operation of the McLeod gauge see (6) page 77.

Several points should be realized in connection with this gauge. Its chief advantage is that it gives an absolute measure of the pressure over a considerable range; for this reason it is very widely used for the calibration of other gauges. On the other hand, it reads pressure of noncondensible vapors only, since any gas that condenses easily at room temperature is removed from the gas phase during the reading. Also, the instrument is not very convenient if many readings are to be taken in a short period of time, since it takes a minute or so to let the mercury rise and fall. For the same reason leak testing, which is very conveniently done with electrically operated gauges (such as the Pirani or Ionization gauge), is very difficult with the McLeod gauge. A liquid air trap must always be used together with the McLeod gauge in order to prevent Mercury vapor from contaminating the system.

b) Ionization Gauge.

The ionization gauge, hereafter abbreviated ion gauge, is the most widely used instrument for the measurement of pressures of less than 10^{-4} mm. of Hg. In order to understand the design of the ionization gauge as used today, it is instructive to review some earlier designs, and to see why they had to be modified. The ionization gauge used before 1950 resembles a triode. The filament, placed in the center of a cylindrically symmetric arrangement, serves as a source of electrons which travel to a positively charged grid (about 200 volts). On their way to the grid these electrons are capable of ionizing gas atoms and molecules. These ions in turn are collected by the cylindrical outer electrode, which encloses the entire

electrode structure and is negatively charged to about 50 volts. The number

of ions produced per unit electron current is assumed to be proportional to

the gas density, and hence the current to the ion collector is used as an

indication of the pressure. Thus for a constant electron accelerating

voltage, (which must be in excess of the ionization potential of the gas

molecules), the number of positive ions formed should vary linearly with

pressure according to the relation.

$$i_c = k\, i_g\, p \implies p = \frac{i_c / i_g}{k} \tag{25}$$

where i_c is the ion current, i_g is the electron current to the grid, and p is

the pressure in mm. of Hg. The constant varies with different gases; a

typical value for k is 10 (mm. of Hg.)$^{-1}$. A normal operating electron

current is 10 milliamps; hence the ion current at a pressure of 10^{-8} mm. Hg.

is about 10^{-9} amps.

Prior to 1948 no one had recorded a pressure of less than 10^{-8} mm. with

an ion gauge of the design described above. There is good reason to believe,

however, that pressures well below this value had been obtained, even though

the gauge read a higher pressure(22). A theory to account for this lower

limit of the gauge was first proposed by Nottingham (23), and later substan-

tiated by the experimental work of Bayard and Alpert (24), Lander (25), and

Metson (26). The explanation was as follows. It was suggested that there

exists a residual current to the collector of the ion gauge which is complete-

ly independent of pressure. This current is caused by soft X-rays which are

created when the electrons strike the grid. The X-rays, being intercepted by

the collector, in turn cause photoelectrons to be released from the collector.

These photoelectrons travel to the positively biased grid, and hence

constitute a current of the same sign as the ion current. This X-ray current

at normal operating voltages is about 1 to 2 x 10^{-7} amps; hence a reading of

less than 10^{-8} mm. of Hg. would be impossible to obtain. In order to over-

come this difficulty the Bayard - Alpert type gauge was developed. This

gauge is now almost exclusively used, and was used for this project.

The design of the Bayard - Alpert type ion gauge grew out of experiments

to prove the X-ray hypothesis of Nottingham. A design was needed in which

the collector would not intercept as many of the X-rays that were emitted

from the grid. Hence the electrode structure was inverted; the collector was

made a thin wire in the center, with the grid around it, and the filament on

the very outside. In this way the solid angle which the ion collector pres-

ents to the X-rays from the grid is at least one hundred times as small as

that for the earlier design. By making the wire of extremely small cross-

section this can be still improved. Gauges are now manufactured which are

linear down to approximately 10^{-11} mm. Hg. The linearity of the ion gauge

was clearly shown in experiments carried out by Alpert and Buritz (16).

One of the features of the ion gauge, besides its capability of measur-

ing pressure,is that it removes gases from the gas phase of the system while

in operation. This pumping action, briefly mentioned earlier in this thesis,

(see page (18)), has both advantages and disadvantages in ultrahigh vacuum

work. If one wishes to obtain the lowest possible pressures in the system,

the pumping action of the gauge is of great advantage. At the point where

backstreaming from the diffusion pump becomes important, the system can be

closed and further evacuated utilizing the pumping action of the ion gauge.

This pumping action is a disadvantage when a steady state is required; unless

measurements are taken in very small time intervals, the operation of the

ion gauge will alter the condition of the vacuum. This is further compli-
cated by the fact that immediately after the gauge is turned on a small amount
of gas is desorbed from the gauge filament which also momentarily may change
the condition of the vacuum. Because these effects are of importance in many
applications, the pumping action will be discussed briefly in what follows.

The removal of gases from the system with the ion gauge predominantly
takes place in any of the following three ways:

a) The surfaces of the electrodes may remove gases by physical or
chemical processes. For example, the hot filament may interact with chemi-
cally active gases resulting in gas removal. Such a process accounts for the
rapid removal of oxygen, which forms oxides of Tungsten at the hot filament.

b) The negatively charged collector will trap the ions which account
for the pressure measuring ion current. This mechanism is the predominant
one for inert gases and also important for most molecular gases.

c) The electrons traveling to the grid will dissociate molecules and
the resulting "active" atoms may be removed from the gas phase by attachment
or combination at the walls of the gauge.

For all three mechanisms, the rate of pressure reduction is expected to
be proportional to the pressure; hence we write for any particular mechanism

$$\frac{dp}{dt} = - \frac{S_i}{V} p \quad ; \tag{26}$$

S_i is the pumping speed for the ith mechanism. We have then for the three
mechanisms going on at the same time:

$$p = p_0 \, \exp\left(- \frac{(S_a + S_b + S_c)}{V} t\right)$$

Let $S = \left(S_a + S_b + S_c\right)$ It is convenient to define τ , the characteristic pumping time

$$\tau = \frac{V}{S} \implies \frac{1}{\tau} = \frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c}$$

Thus

$$p = p_0 \, exp\left(-\frac{t}{\tau}\right)$$

We must evaluate the different τ's in order to get an estimate of the importance of the pumping action. (a) is essentially a process as described under adsorption earlier; an upper limit to the pumping speed is given by

$$S_a = 11 \text{ A liters/sec.} \qquad \text{(see Equation (2))}$$

where A is surface area of electrode in cm^2. For a typical gauge, this surface area is approximately 0.2 cm^2. Hence the pumping speed for this mechanism is limited to 2 liters per second. In practice the pumping speed is lower because not all molecules incident on the electrode react and are captured. The probability for reaction is usually much less than unity. For Tungsten at 2300° C. the probability for reaction with an oxygen molecule is about one tenth so that the pumping speed for this mechanism is of the order of 0.2 liters per second.

For the ion entrapment at the collector (b), a first approximation of the ion pumping speed can be made by assuming that all the ions incident on the collector are permanently removed from the volume. The ion pumping speed can be found in the following manner. We write equation (26) in terms of the molecular density

$$\frac{dN}{dt} = -\frac{S_b}{V}n$$

Since $V\frac{dn}{dt}$ is the total removal rate of molecules, $\frac{dN}{dt}$, we have

$$S_b = \frac{dN/dt}{n}$$

But $\frac{dN}{dt}$ is related to the ion current i_c

$$\frac{dN}{dt} = a\,i_c$$

where a is the number of ions/unit i_c. Hence using equation (25), rewriting it in terms of n, we obtain

$$S_b = \frac{a\,i_c}{n} = \frac{a\,i_g\,k\,p}{n}$$

$$= \frac{a}{b}\,\frac{i_g\,k\,n}{n} = \frac{a}{b}\,i_g\,k$$

where b is the number of molecules/unit pressure per liter at room temperature. If p is in mm. Hg., k in (mm. Hg.)$^{-1}$, and i_g in amperes, then we have

$$S_b = 0.2\,i_g\,k \quad \text{liters/sec.}$$

Thus at a normal operating current of 10 milliamps, with k equal to 10, we get a maximum pumping speed for ion pumping:

$$S_b = .02 \quad \text{liters/sec.}$$

Considerably higher pumping speeds due to ion pumping have been observed. According to Alpert (20) this is due to the ionization of gas outside the accelarating grid, with subsequent collection of the ions at the negatively charged walls of the gauge. This may increase the above pumping speed by as much as a factor of ten.

Not much quantitative data is known about (c), the removal of dissociated atoms. Generally the crossections for dissociation of molecules due to electron impact are smaller than those for ionization, so that we may conclude that the pumping speed is correspondingly lower. The first two processes seem to be the more important ones.

The characteristic pumping times associated with these two are respectively for chemical removal $\left(\tau_a\right)$ 1 second, and for ion pumping $\left(\tau_b\right)$ 10 seconds. It is therefore clear that during measurements of this order of time the condition of the vacuum will change appreciably. The characteristic time associated with chemical removal can be lengthened by operating at a lower filament temperature, while the time τ_b corresponding to ion pumping is lengthened by operating at a smaller grid current. Hence if accurate instantaneous values of the pressure are required it is recommended that one operate at a grid current of say 0.1 milliamp with as low as possible filament emission. By taking the pumping speeds into account, one can make fairly accurate instantaneous measurements, and if necessary, using the above equations, corrections to the measurements can be made to account for gauge pumping. In this connection it should be mentioned that a continuously recording instrument for measuring the ion current simplifies the estimation of instantaneous pressure. By observing the shape of the pressure versus time curve as traced out by the instrument, one can estimate the total pumping speed of the

ion gauge quite accurately if the system is closed. Such an instrument was used for this project.

Of course one cannot continue lowering the pressure indefinitely by means of ion gauge pumping in a closed system; after a certain time the rate of reduction of pressure is balanced by the rate of rise of pressure due to outgassing of the system or re-emission of the ionically pumped gases. For a particularly clean system the ultimate pressure that can be attained is limited by the permeation of Helium through the walls of the system, and this process coupled with the pumping action of the gauge for a typical small system leads to an ultimate pressure of about 10^{-11} mm. of Hg. (16). The transition from 10^{-8} mm. to 10^{-11} mm. is generally accomplished only after baking, with the system closed from the pumps and the ion gauge or other ion pump operating continuously.

c. Discharge Gauge.

The Neon which was to be used in the preparation of the absorption tube had to be inserted to a known pressure in the 1 to 10 mm. range. It was very important in the measurement of this Neon pressure that the gas not be contaminated by the pressure measuring device. For this reason it was not desirable to use a mercury type gauge because this would necessarily introduce small amounts of mercury vapor into the Neon, thereby contaminating it. Not many pressure gauges exist which are capable of measuring pressure accurately in this range without introduction of impurities into the system. One type of gauge often used is the so called capacitance manometer (20), but bakeable commercially made gauges of this type are very expensive. Glass gauges which utilize the flexibility of glass for the measurement of pressure differences are also used. This type of gauge was not thought to be very suitable for this project since it had to withstand atmospheric pressure and

at the same time be capable of measuring small pressure differences in the

millimeter range. These two requirements together make the design of such a

gauge difficult.

Hirsch (27) reports on an alternating discharge gauge of relatively simple

design which seemed to be very suitable for our purposes. The gauge works on

the principle that the difference between the firing voltage and extinction

voltage of a D.C. discharge is a function of the pressure. Its design and

operation will be described briefly.

Figure (8) shows a schematic diagram of the gauge together with the

circuit necessary for operation. A potential difference of about 1000 volts

is applied which charges the capacitor C through the resistor R. The capaci-

tor will charge until it has reached a voltage V_f which is sufficient to

start a discharge in the small discharge tube. This causes the capacitor to

discharge until it has reached a potential difference V_e which is no longer

sufficient to maintain the discharge. The capacitor is then recharged through

R from the power supply and the cycle repeats itself. The signal from this

relaxation type oscillator is picked up from the small resistor r and fed to

a counter or oscilloscope so that its frequency may be observed.

Curves of striking and extinction voltage versus pressure for a typical

discharge tube filled with air are given in figure (9). It can be seen

qualitatively that the frequency of the signal is in some way proportional to

the difference of the striking and extinction voltage. During the charging

part of the cycle, the voltage on the capacitor and hence across the discharge

tube is given by the relation

$$V = V_0 \left(1 - \exp \frac{-t}{RC} \right)$$

so that we may write

$$V_f = V_0 \left(1 - \exp \frac{-t_f}{RC}\right) \; ; \; V_e = V_0 \left(1 - \exp -\frac{t_e}{RC}\right)$$

and

$$(t_f - t_e) = RC \, \ln \left(\frac{V_0 - V_e}{V_0 - V_f}\right)$$

During the discharge, we assume that the resistance of the discharge tube is constant and equal to R_i, and that the capacitance of the tube is negligible compared to C; we then have the voltage across the capacitor governed by the relation

$$V = V_f \exp \frac{-t}{(R_i + r)C} \Rightarrow t_{disch.} = (R_i + r) C \, \ln \frac{V_f}{V_e}$$

so that hence the total time taken by one cycle is given by

$$t_D + (t_f - t_e) = C \left\{ R \ln \left(\frac{V_0 - V_e}{V_0 - V_f}\right) + (R_i + r) \ln \frac{V_f}{V_e} \right\}$$

Rewriting this in terms of $\triangle$, which we define as V_f - V_e, we get for the frequency of oscillation

$$f = \left[C \left\{ R \ln \left(1 + \frac{\triangle}{V_0 - V_f}\right) + (R_i + r) \ln \left(1 + \frac{\triangle}{V_e}\right) \right\} \right]^{-1} \quad (27)$$

At low pressures, when $\triangle$ becomes very small, the frequency no longer
follows the simple logarithmic dependence as predicted by equation (27).
This is due to the fact that the internal resistance of the discharge tube on
firing is no longer constant but rises considerably, while the capacitance of
the discharge tube also increases. Hence the gauge should not be used to its
ultimate lower limit. The departure from equation (27) manifests itself in a
sharp drop in frequency where a logarithmic rise would be expected.

The range of pressures that can be measured with a discharge gauge of
the kind described above is determined by the geometry of the tube, the
nature of the gas, the voltage applied, and the values of the components in
the circuit. The lower limit of the gauge is reached when for a particular
gauge geometry the firing voltage and extinction voltage of the gas under
consideration are equal, while the upper limit is reached when the firing
voltage exceeds the applied voltage. By decreasing the width of the dis-
charge gap, the gauge will be able to measure higher pressures using a given
applied voltage because the firing voltage is lowered. Similarly the range
is also extended by increasing the applied voltage.

Calibration curves for the discharge gauge used in this project are given
for air and Neon in figures (10, 11). It should be mentioned that while the
calibration for air was quite reproducible, the Neon calibration could not be
reproduced unless the strictest purity conditions were fulfilled. This can
be attributed to the fact that the firing and extinction voltages of the noble
gases change considerably with very small amounts of impurity present. The
design of the discharge tube used is illustrated in figure (8). This design
is different from the one used by Hirsch (27), who used cylindrically sym-
metric electrodes. It seemed to work equally well and is a lot simpler. The
inter-electrode capacity of this design is also smaller than the cylindrical

design of Hirsch. This fact should increase the useful range of the gauge.

Because electromagnetic noise from the lines influenced the operation of the gauge significantly, a small aluminum box was used to shield it. This was especially important when Neon pressure was to be measured.

d) Oil Manometer.

A simple U tube type oil manometer was used for the calibration of the discharge gauge. This manometer utilized low vapor pressure oil (n-butyll phthalate) to measure pressures between .1 and 10 mm. Hg. A zeolite trap was used to prevent the oil from contaminating the system. The U tube was initially evacuated at both ends and then sealed off at one end. Figure (4) shows the oil manometer.

4) Gas Handling System.

Figure (1) shows a schematic diagram of the gas handling system. The glass part of the apparatus, which formed the central part of the vacuum system, was divided into four main compartments by the metal valves and contained vacuum gauges, the gas supply, and the large discharge tube which was to be prepared for the spectroscopy experiment. (In order to avoid confusion, the latter will be called the discharge tube from here on; the small discharge tube used to measure pressure will be called the discharge gauge.) The design of this part of the system was such as to leave the system as versatile as possible so that later it could be adapted to prepare other gas tubes, possibly with mixtures of gases in them. The essential features of the system will be discussed in what follows.

The Neon bottle was attached to the system at compartment IV. The manufacturer had supplied the bottle with one breakseal which could be opened after evacuation by dropping a steel ball on the seal, thereby breaking it.

This is the usual method for the introduction of gas into a vacuum system; the steel ball is moved from a small compartment above the seal by means of a magnet and is then allowed to drop on the seal. In this way, however, the Neon bottle could be used only once between bakings because the metal valves could only be baked while they were open. Therefore several additional break-seals were installed in parallel in the manner shown in figure (5). The bottle could be closed later by closing a constriction in the glass above the seal with a hot flame. In this way the Neon bottle could be used several times over, each time using a different breakseal. The bottle itself was not baked in order not to introduce further impurities into the Neon. The pressure inside the Neon bottle would also become too high. The bottle was therefore suspended by its glass outlet tube underneath the oven base.

The discharge tube was attached to volume III, so that any mixing could be done if necessary in volume II or I. Before the discharge tube was attached, the McLeod gauge was attached to volume III for testing of the vacuum system at pressures in excess of 10^{-6} mm. This gauge was later removed before the first bakeout.

5. Oven.

The oven used to bake the system was made in the form of a double walled 16" x 32" x 16" hood which fitted over an asbestos plate base on which the vacuum system was mounted. The walls of the oven were 1/16 th inch aluminum plate separated by asbestos spacers. Glass wool was used as insulation between the inner and outer walls. Four 750 watt elements were mounted inside the oven on its walls. The hood could be raised and lowered by means of a wheel and axle system mounted above the apparatus. The wiring inside the oven consisted of stranded nickel wire wrapped in asbestos ribbon for insulation. The temperature inside the oven was controlled by a Fenwall Thermoswitch which

operated a relay to turn the oven power off and on. After equilibrium had been established this switch controlled the temperature to within a few centigrade degrees at 400° C. The duty cycle of the oven at this temperature was about 30 seconds on to one minute off. The temperature was monitored by a 100 - 500° C. thermometer inserted through a small hole in the side of the oven. The asbestos plate base was reenforced by means of a 1/16 th inch aluminum sheet with the whole base mounted firmly to a dexion table. The oven hood enclosed virtually all of the system when lowered; the parts enclosed are indicated by the dotted line on figure (1.).

6. Electronics.

The control unit for the ionization gauge is shown in figure (12). The unit is designed to deliver all the necessary voltages to the electrodes, and to control these such as to keep the grid current constant at any set level independent of the pressure in the tube. This is done by means of a feed - back network which reflects any changes in the grid current as a change in the opposite direction in the filament emission. The very minute collector current is amplified and read on a continuously recording ammeter. This ion current amplifier is shown in figure (13).

CHAPTER III

EXPERIMENTAL PROCEDURES AND RESULTS

In this section the general procedure for attaining ultrahigh vacuum will be described, together with some remarks on general high vacuum techniques.

After the vacuum system has been assembled and built, the first job is to test for large leaks. For this purpose it is convenient to have a manometer in the micron to millimeter range since usually pinhole leaks in solder joints or glassware show up in this region of pressure. A leak in the glassware can be most easily detected using a Tesla coil; the discharge produced in the partial vacuum will show a very bright spot at the location of the leak. Several leaks in the glassware of our system were located in this way. Leaks in metal sections of the system are much harder to detect. If the system has various compartments, the leak can usually be traced to one general area. The parts of the system under suspicion in that area (usually joints) can then be tested in the following manner. If elsewhere in the system a visible glow discharge can be maintained, a change of colour in the discharge will be observed when some acetone is sprayed on the metal in the vicinity of the leak. In this way the leak can be traced to a very small area on the metal, by careful use of the acetone. If an electrically operated gauge is used, such as a pirani gauge (6, page 81) or ion gauge, the organic vapor introduced into the leak will cause a sudden change in the reading, so that it is not necessary to observe the colour of a discharge. The ion gauge can of course only be used if the leak is quite small, since it should not be operated at pressures in excess of 10^{-3} mm. Hg.

It should be emphasized that a rise in pressure occuring after the pumps are isolated from the system does not always indicate a leak. This should be clear from the considerations put forth in the early part of this thesis;

desorption, diffusion and permeation take place at all times. Often it is difficult to distinguish a real leak from a rise in pressure due to the above processes. One way of telling is by plotting a pressure versus time curve. If there is a leak, the pressure should rise linearly for an indefinite period of time after the system is closed. Outgassing, on the other hand, should show signs of saturation. Eventually, the desorption process will be balanced by adsorption, and then the only significant rise in pressure will be due to diffusion, which follows a $t^{\frac{1}{2}}$ law. Hence the pressure versus time curve will level off for the outgassing processes. One may nevertheless have to wait a long time before this leveling off occurs, particularly for a "dirty" system which has not been baked.

With the system free of all leaks, the following procedure was used to reach ultrahigh vacuum. The system was evacuated to about 6×10^{-3} mm. Hg. by means of the rotary backing pump, and the diffusion pump turned on. After about twenty minutes the diffusion pump would be warm and the pressure would fall rapidly to about 10^{-6} mm. During this warmup time the bakeout clamps (see figure 6) were put on the valves. The clamps serve to keep the valves open at all times during bakeout. The system was then checked with a Tesla coil to make sure that the pressure was low enough for the ion gauge to be turned on. This precaution had to be taken in order to avoid oxidation of the ion gauge filament. After the ion gauge was turned on the pressure would rise initially and come to an equilibrium value of approximately 5×10^{-5} mm. of Hg. This high pressure is the result of the fact that for the unbaked system the ion gauge electrodes and envelope liberate large quantities of gas. The pressure in the unbaked system could be improved by carefully outgassing the gauge (this process will be described later), but since the whole system was going to be baked anyway this was generally not done at this stage.

After a few minutes the ion gauge was turned off again, the wires removed from the oven area, and the oven hood lowered over the system. In order to avoid strains in the glassware caused by too rapid heating, it was necessary to raise the temperature inside the oven slowly. Therefore the thermoswitch was always set at its lowest value (about 50° C.) before the oven elements were first switched on. The temperature inside the oven was then raised slowly by periodically setting the thermoswitch at a higher switching temperature. Usually the transition from room temperature to 400° C. was made in about ten steps over a period of about $1\frac{1}{2}$ to 2 hours. During this time and subsequent bakeout the pumps were left running. The system was usually left to bake for three or four hours, although once it was baked for seven hours to make sure all surface gases had been desorbed. The system was then left to cool with the oven lid in place until a temperature of about two hundred degrees was reached. This usually took about two hours. The oven lid was then raised a little at the time and after some twenty minutes removed all-together. A fan would be placed near the system to speed up the final cooling. While the system was still warm to the touch but sufficiently cool to be handled, the ion gauge was connected to the control circuit and the pressure would drop to about 2×10^{-8} mm. The grid of the ion gauge would then be outgassed by passing 10 amperes through it for some ten minutes. The pressure would then drop another factor of five to about 4×10^{-9} mm. Hg. Repeated outgassing of the grid in some cases lowered the pressure a little more. During all this time the fan was blowing onto the system, thereby keeping the ionization gauge envelope cool. If the fan was removed, the pressure would rise by about a factor of two. If at this point valve # 1 was closed, the pressure would drop quite rapidly and level off at about 1×10^{-9}, generally. The best vacuum obtained with valve # 1 closed was 6×10^{-10} mm.

of Hg. Due to possible errors in calibration this value could be out by a factor of two either way, but certainly no more.

It is possible to spoil the vacuum temporarily or permanently in many ways. Outgassing of the grid for too long a period or at too high a temperature will liberate material from the grid itself which will raise the pressure. The best way to outgas the grid is to do it for short periods of time (say five minutes) with the valve to the pumps open and to close this valve as soon as the grid has cooled down. In this way the grid surface has no time to adsorb any backstreaming oil vapor from the pumps. Leaving the system exposed to the pumps for long periods of time after it has cooled also deteriorates the vacuum. For this reason the system was never left to cool off overnight, in spite of the fact that the cooling process is quite lengthy.

After the lowest possible pressures had been reached, Neon was introduced into the system with the valve to the pumps closed. The Neon could be let into the system by breaking the breakseal on the bottle (see figure (5)). Usually valve 4 was closed before the seal was broken; in this way the Neon would only expand into the small volume IV. By opening valve 4 very carefully, the Neon could be leaked into the other parts of the system very slowly. After enough Neon had been leaked in to maintain a discharge on the large discharge tube, the electrodes of the tube were outgassed by passing a larger than usual discharge current through them. This undoubtedly contaminated the Neon, but since valve 4 was closed at this stage, this dirty Neon could be pumped off, and fresh pure Neon leaked in as before via valve 4. A striking characteristic of the Neon gas was that it did not stick to the walls of the system like air does; even though the Neon pressures were as high as 10 mm. Hg., it was always possible to reach ultrahigh vacuum again

without baking, by pumping the Neon off and outgassing the grid.

The gauge which was intended for the measurement of Neon pressure after the tube had been filled had to be calibrated in Neon before it could be used. Because the calibration had to take place under the same purity conditions as the filling of the tube (see apparatus description page (16)), this posed a problem, since any other gauge used for calibration would introduce impurities. It was finally suggested that the minimum amount of impurity would be introduced if an oil manometer were used, filled with very low vapor pressure oil, and connected to the system via a tube filled with Ziolite pellets.

After the oil manometer was put on the performance of the vacuum system changed slightly. The lowest pressure ever attained with the oil manometer in the system was of the order of 1×10^{-9} mm. Hg. In general the system performed quite well in spite of the presence of the oil. The manometer was placed outside the oven area, which meant that a part of the system was not baked.

The calibration curves for the discharge gauge are given in figures (11, 10). The calibration was found to change slightly if the Neon were left in the oil-containing part of the system for any length of time (say over-night). Therefore it was deemed best to measure the pressure of the Neon as soon as possible after the leaking in, and to seal the tube immediately afterwards. In this way the contamination of the Neon was kept to a minimum. The second tube of Neon was prepared after calibration of the discharge gauge with the oil manometer still in the system, to provide a check on the pressure. The pressure at which the tube was sealed off was 1.3 mm. Hg. This was the optimum pressure for the absorption experiment (see Ladenburg (4)).

For both tubes prepared, the pressure before filling was in the 10^{-9} range.

The tubes prepared were both used in the absorption experiment and showed much improvement over the system used before. The absorption lines, which were nearly nonexistent with the old system, showed up stronger and also in greater number. The H_α line was barely visible when emission spectra of the Neon were taken, indicating that traces of Hydrogen were still present. However, it was very much weaker for the prepared tubes than it had ever been under similar conditions with the old system, indicating that the Hydrogen content of the discharge tube was much less than before. This Hydrogen is probably that which was in the Neon initially (see page (3)). The experiments with the absorption tubes are still in progress, and therefore it cannot be said with certainty at this stage whether the Neon was pure enough for our purposes. Indications are, however, that this is the case.

There are, of course, ways in which the system can be improved. It seems likely that with careful experimentation the ultimate pressure can be lowered somewhat, particularly when the oil manometer is removed again. This manometer was left on for the time being to check the calibration of the discharge gauge at some later time. If in the preparation of more discharge tubes it appears that the limitation on the purity is not in the ultimate pressure attainable, but rather in the manufactured Neon bottle itself, various methods of further purification could be built into the system. One such method which seems particularly promising is purification by cataphoresis (28). The removal of Hydrogen utilizing Uranium powder as described by Dieke (29) could also be tried.

In the series of experiments carried out in this laboratory for the measurement of transition probabilities in excited gases, it is likely that

many tubes of the kind described above will have to be prepared, not only

filled with Neon, but also with other gases. It is hoped that the system

built for this project, together with the experience gained, will be of some

use for this purpose and in the general interest of scientific endeavor in

the future.

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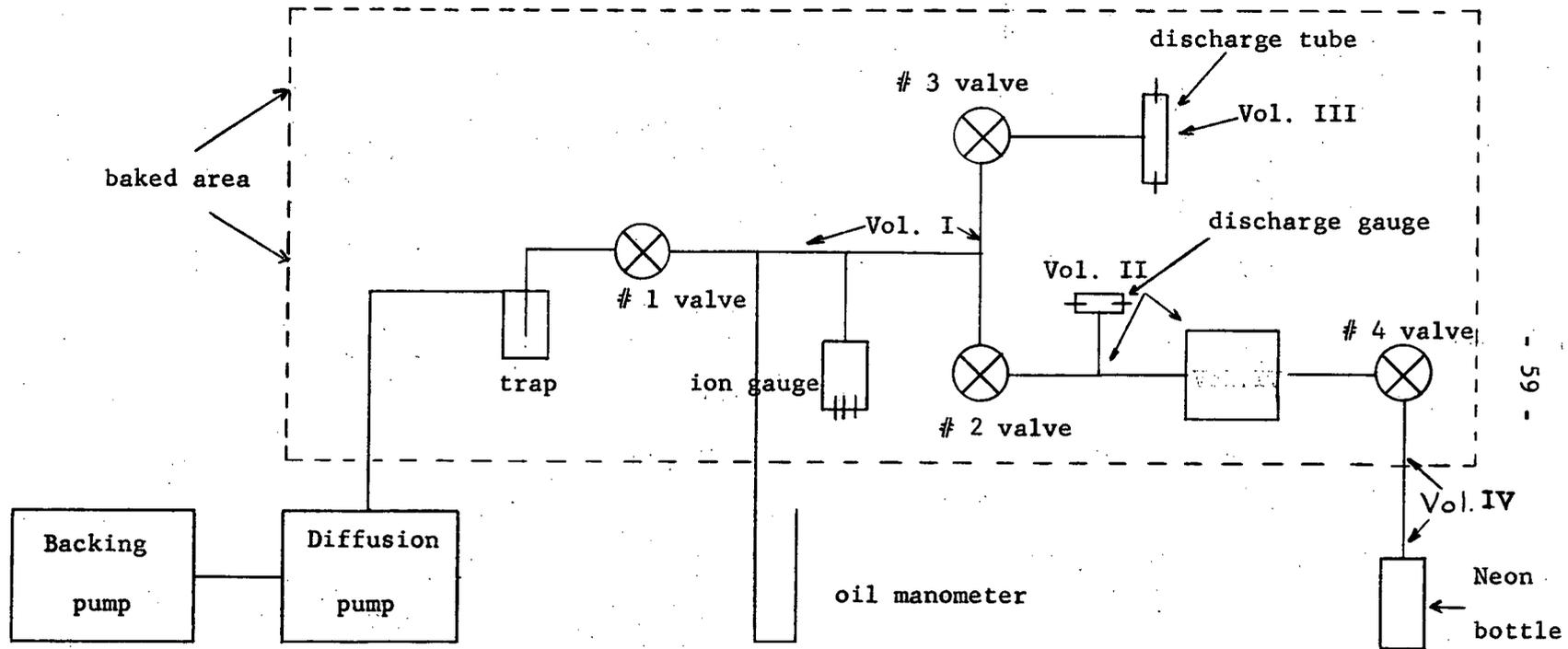
FIGURE 1

General arrangement of the system (schematic)

cooling water
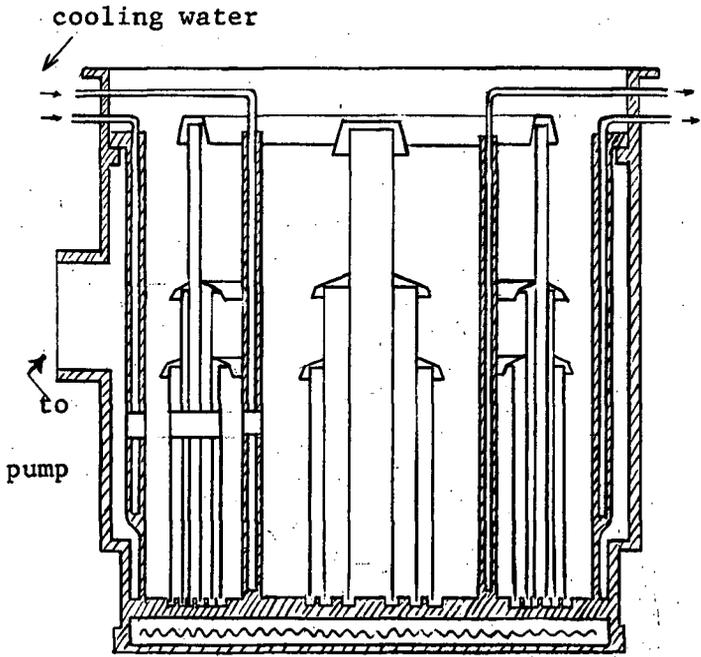
to system

FIGURE 2

Diffusion pump (schematic diagram)
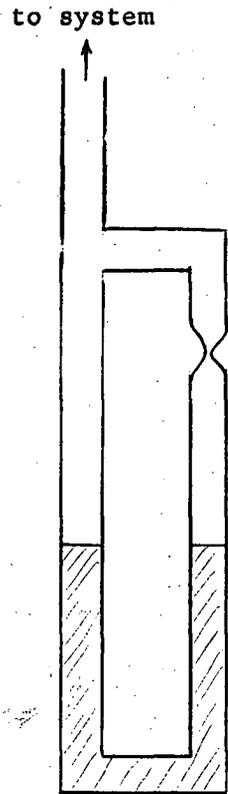
FIGURE 4

U tube oil manometer

to

pump
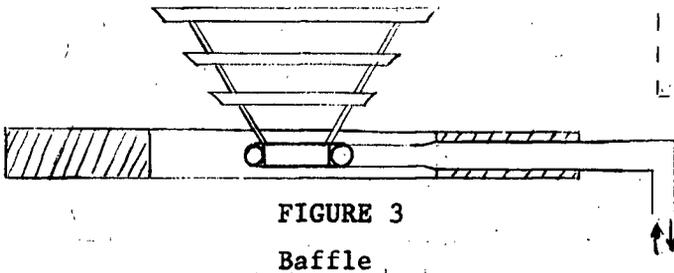
FIGURE 3

Baffle

cooling water
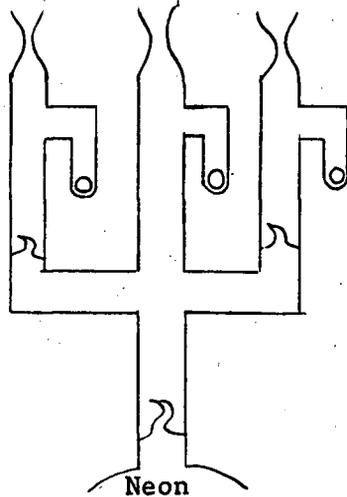
Neon

FIGURE 5   Schematic of Neon filling system
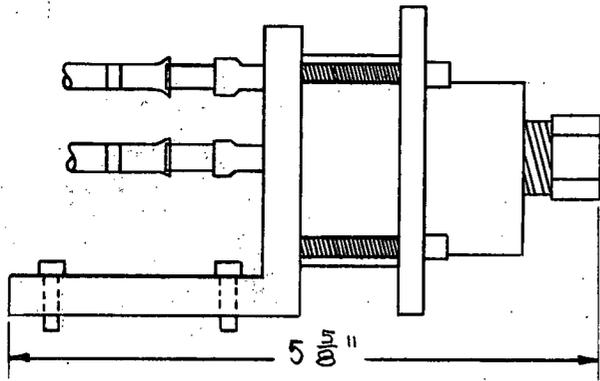
FIGURE 6

Valve with driver
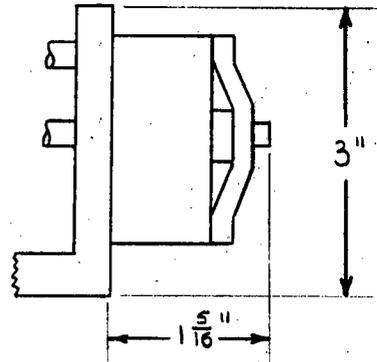
Valve with bakeout clamp

Torque in ft. lbs.
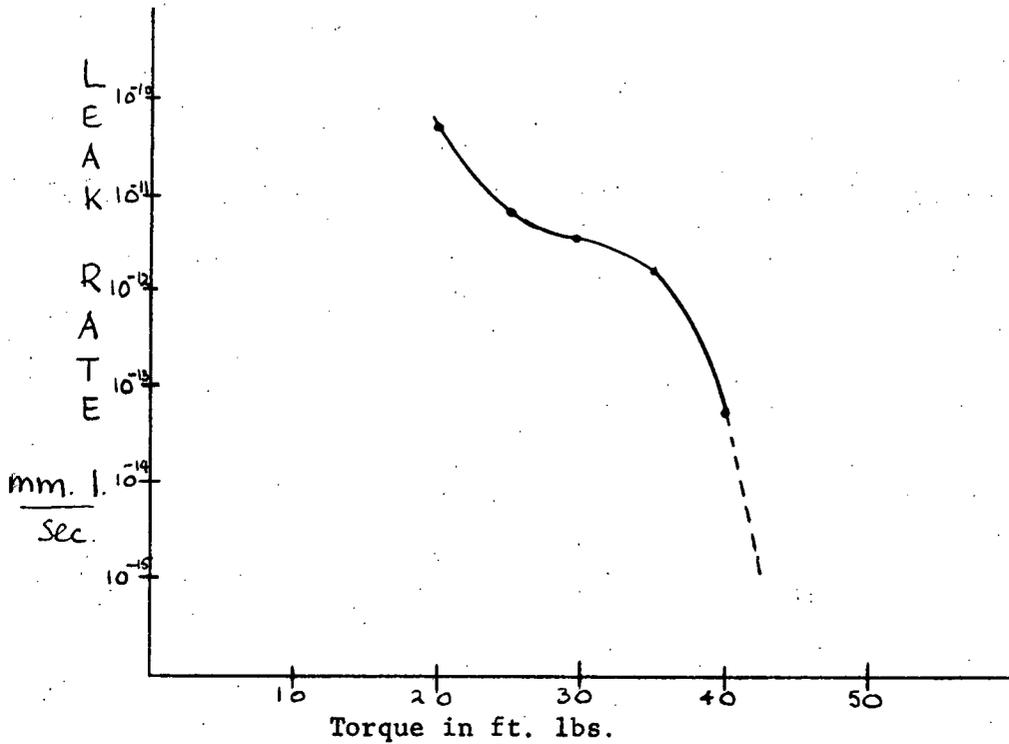
FIGURE 7

Graph of closing torque versus leak rate for the all metal valves
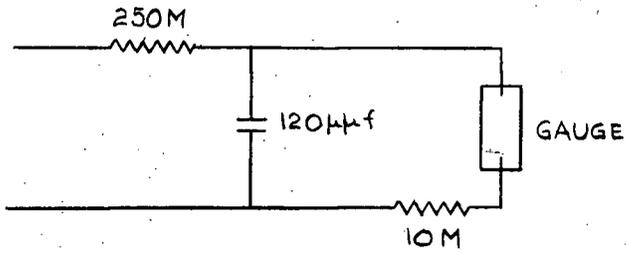
FIGURE 8

Discharge gauge circuit
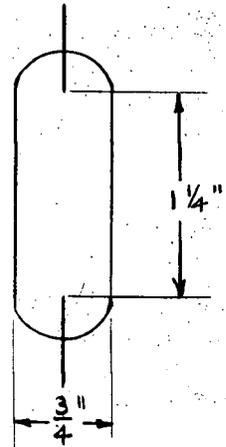
gauge geometry
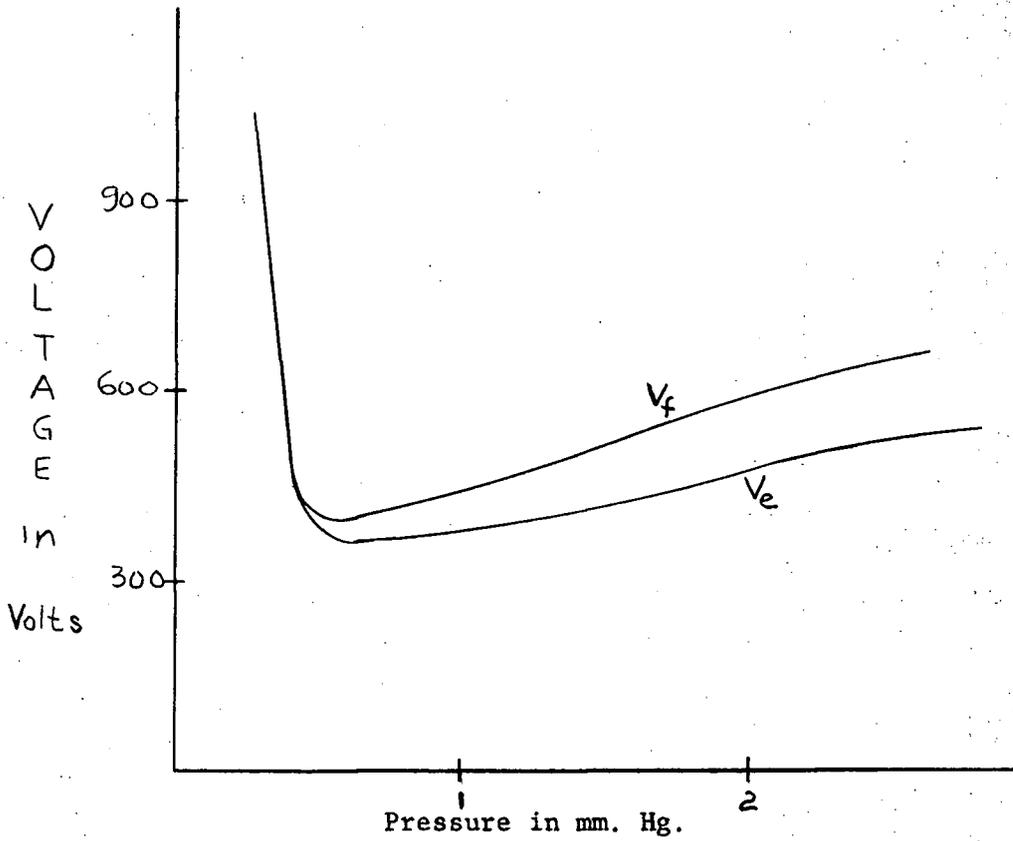
FIGURE 9

Graph of striking and extinction voltage versus pressure
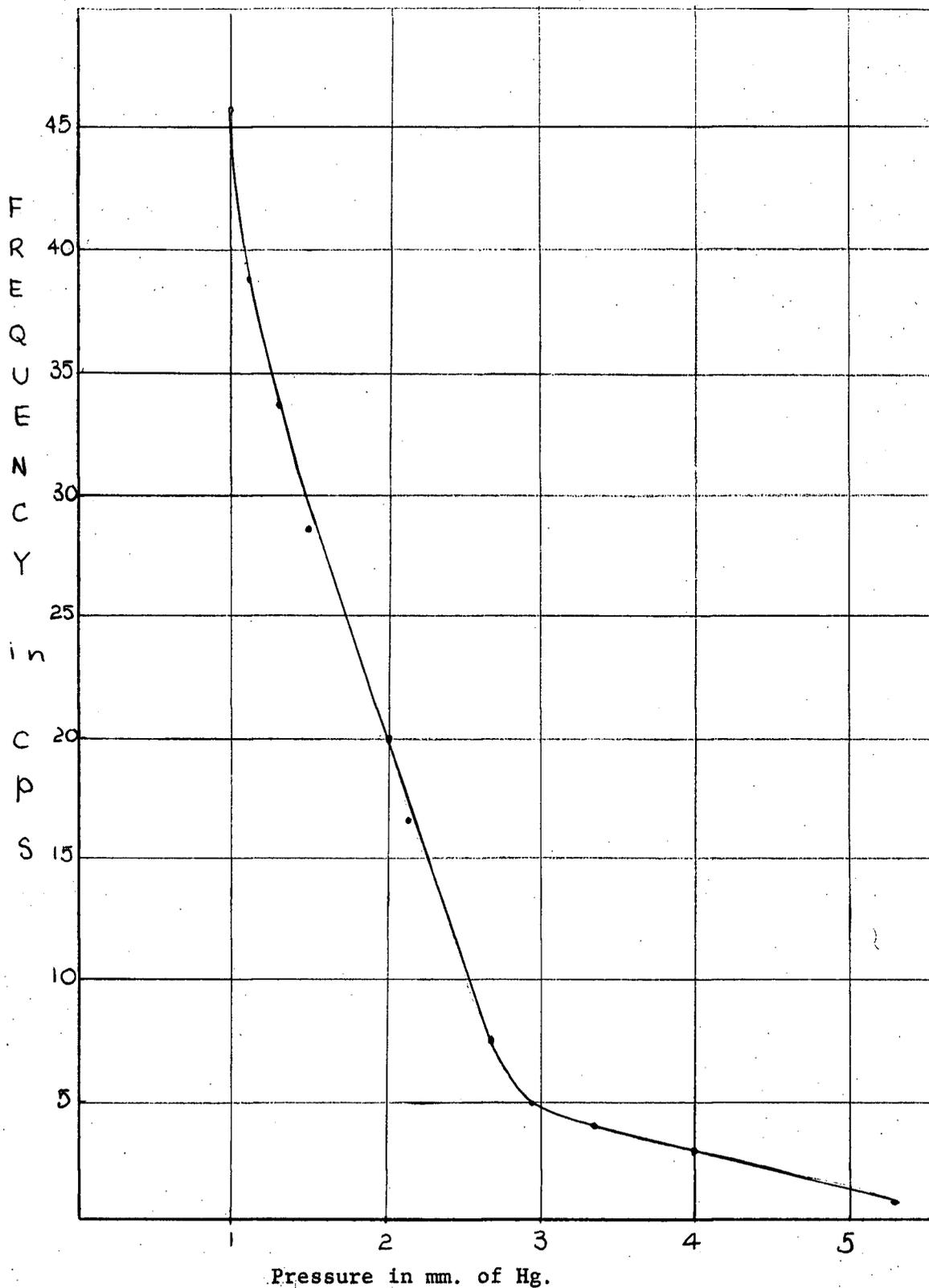
FIGURE 10

Calibration of the discharge gauge; V_o = 500 V. (Neon)
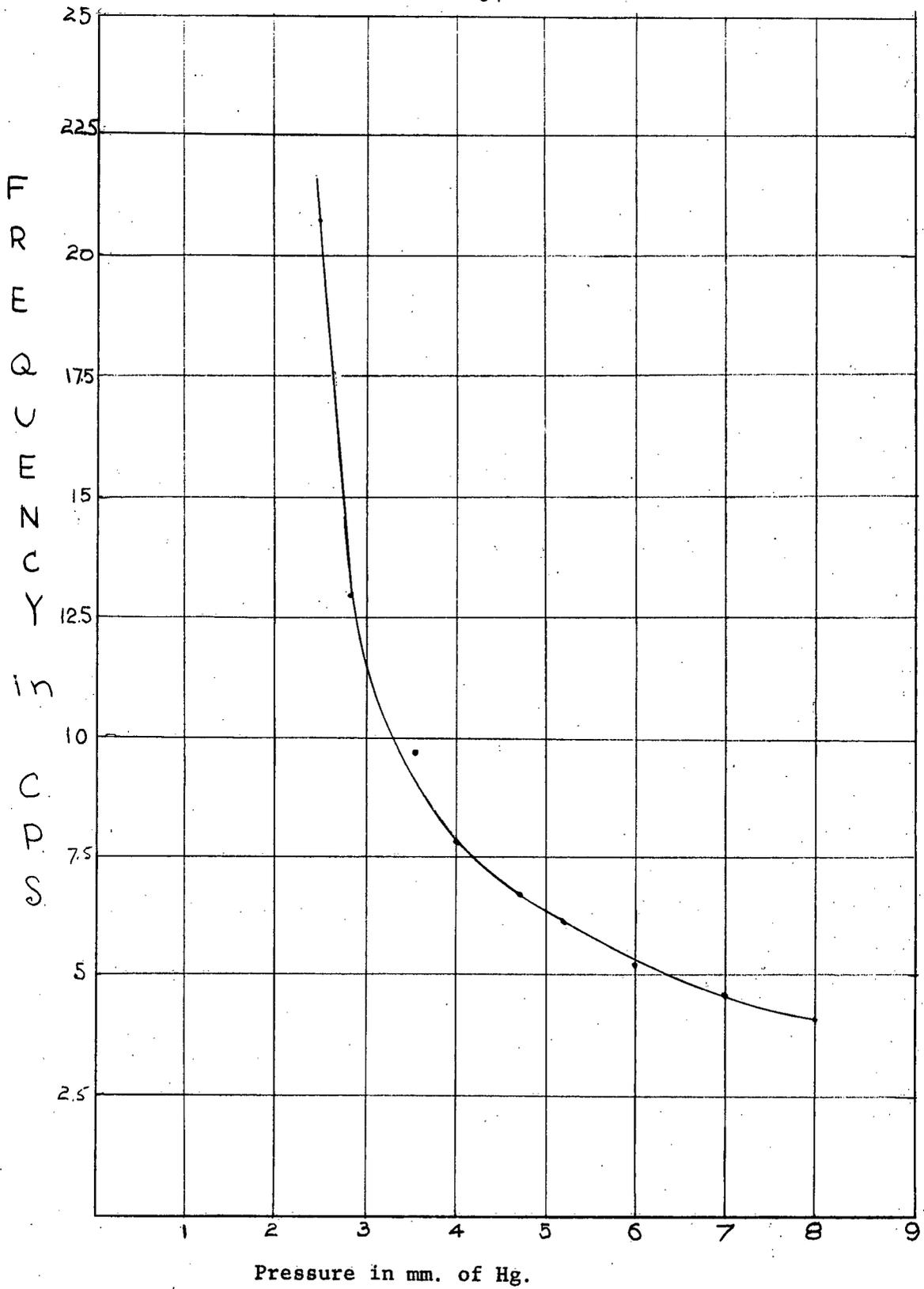
FIGURE 11

Calibration curve for the discharge gauge; V_0 = 600 V. (NEON)
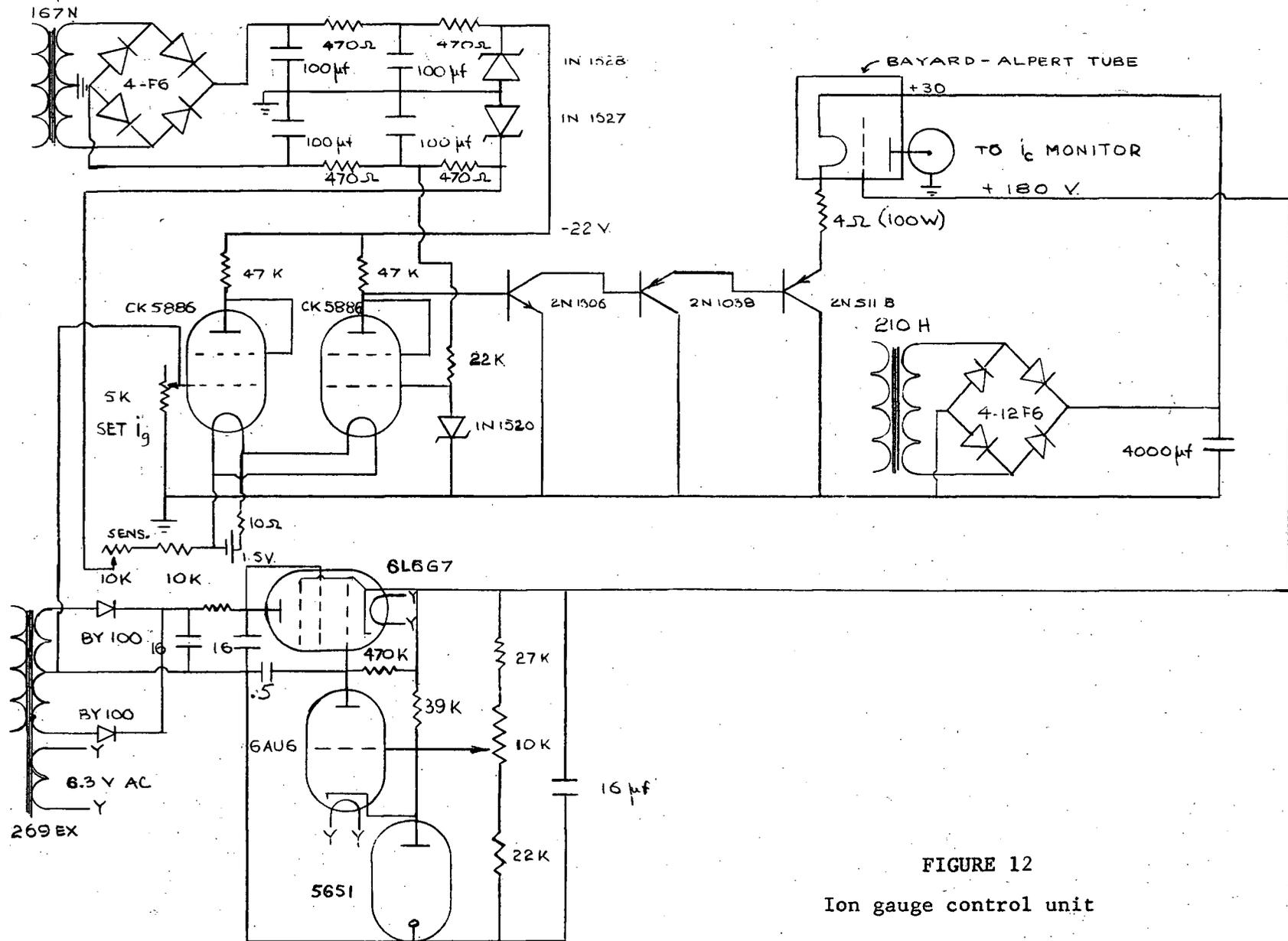
FIGURE 12

Ion gauge control unit
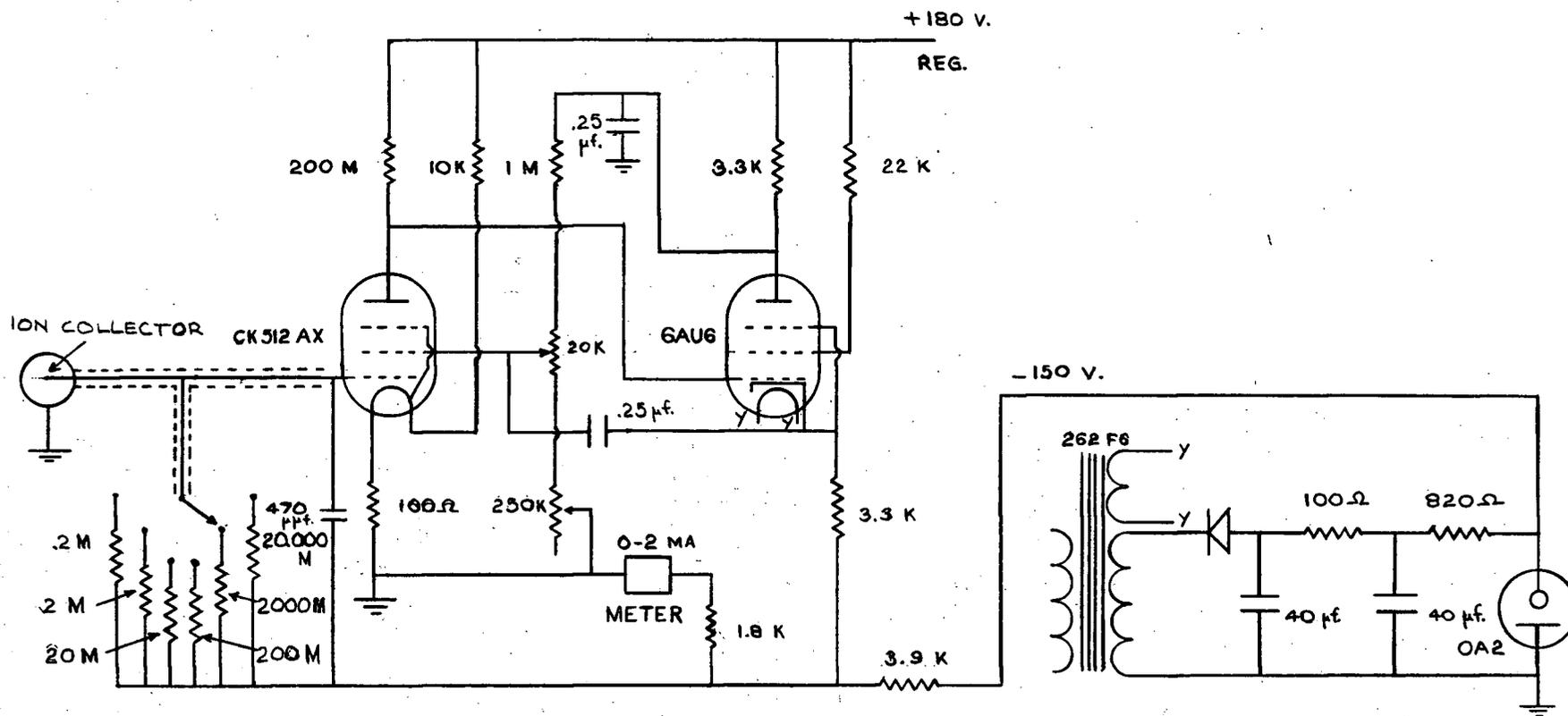
FIGURE 13

Ion current amplifier