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## HIGH VACUA

## Principles, Production, and Measurement

By

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To

## His Highness S̃ri Maharaja

Sir Narendra Saha Bahadur, K.C.S.I., LL.D.
Ruling Chief, Tehri-Garbwal State, India
as a token of affection

## FOREWORD

At the beginning of the twentieth century the highest vacuum attainable by air pumps was of the order of $10^{-4} \mathrm{~mm}$ of mercury. In the following brief period of some 45 years the limiting vacuum obtainable has not only been pushed to a much lower pressure but, especially, the speed of pumping has been enormously increased, the simplicity and ease of the pumping operation have been greatly advanced, and many investigations are now brought into the realm of practicality which four decades ago were quite impossible. In short, a very large portion of modern research owes its existence and impetus to the development of methods of obtaining high vacua rapidly and in enclosed spaces of considerable volume.

The literature regarding the theory and development of vacuum pumps, like other material on new lines of investigation, has been widespread, both as to time and as to journals of scientific publications. Although there have been, in the past, a few good expositions of theory and practice in the production of high vacua, there is now a distinct need for an up-to-date and thorough treatise on the subject.

Dr. Jnanananda has made an extended study of the different types and varieties of vacuum pumps, not only with respect to their historical development, but also with regard to their relative performances in operation. He has arranged the material in such a way that the reader may readily find the description of any particular pump on which he desires information. At the same time he will find mention of variations and modifications intended to increase the efficiency of the pump and render it more suitable for the operator's purpose.

Preceding the discussion of the pumps is found a fundamental treatment of the theory of gases, especially as it is applied to the operation of vacuum pumps. Throughout are many illustrations of the pumps described, so that the reader may more easily follow the explanation.

Closely associated with the production of high yacua is the
ability to measure the vacuum obtained. In Chapter III we have an exhaustive discussion of practically all the various types of gauges which have been used in vacuum work, with comments on their range of application and their relative merits.

The final step in removing gases from an enclosure usually consists in the action of certain materials which are capable of absorbing gases strongly. When a stage is reached at which relatively few molecules are left in the space to be evacuated these agents are able to improve the vacuum to a remarkable degree, thus continuing the process after the pumps have reached their limit. Chapter V treats of the employment of the principal materials used for this purpose, together with valuable suggestions for the attainment of successful operating conditions.

The work supplies a real need for collected and organized information on the techniques of the production of high vacua and should be a valuable reference for the worker in that field.

George A. Lindsay
Ann Arbor, Michigan
July, 1947

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## CHAPTER 1

## KINETIC GAS THEORY AS THE BASIS OF THE SCIENCE OF HIGH VACUA

## Sdection I. Introduction.

1-1. Definition of High Vacuum.-High vacuum may be defined as the state of any space-or, strictly speaking, of any enclosurefrom which air or any gas is evacuated to a pressure of not more than one dyne per square centimeter, which would be sufficient to support a mercury column 0.000750 mm . high. Since the vapor tension of mercury at the normal temperature is approximately of this order, and as mercury has been up to this time often used in vacuum gauges, as well as in certain kinds of vacuum pumps, it can be said that a high vacuum is one which requires a device or an appliance by which the pressure of a gas, or that of the vapor of any liquid, is either maintained at the mercury vapor pressure at normal temperature or lowered beyond the vapor saturation pressure of mercury. Since mercury is the common agent used in high-vacuum gauges and in many pumps, it is not possible to free entirely the high vacuum from the presence of mercury vapor. Consequently the vapor tension of mercury at any particular temperature will naturally be the limit of high vacuum obtained at that temperature. In order to obtain a high vacuum whose pressure is lower than the vapor tension of mercury, it is necessary to lower this vapor pressure, or use, in the vacuum pumps and gauges, liquids whose vapor tension is lower than that of mercury vapor. Hence, either those liquids whose vapor tension is less than that of mercury vapor at normal temperature, such as Apiezon oils, or those whose boiling point at normal pressure is comparatively high and whose vapor tension at normal temperature is comparatively low, are used in the vacuum pumps and gauges.
From the consideration of electrical discharge in vacua, however, high vacuum is defined as the state of any enclosed space-or
any enclosure-from which is evacuated any gas or vapor to such an extent that the remaining molecules of gas or vapor do not retard " space charge." If the pressure of any obtained vacuum be comparatively high, the positive ions, caused by the ionization of the residual gas, compensate either partly or wholly the " space charge " or completely prevent it. This definition, which is originally due to Langmuir, is of great importance even from purely theoretical considerations.

1-2. Units of Pressure.-The magnitude of every physical quantity is measured and expressed in terms of some unit arbitrarily taken as a standard. The unit is more or less a matter of convention. The pressure of high vacuum is usually measured in terms of the height of a column of mercury or of some other suitable liquid, supported by the pressure of high vacuum. In the absolute metric system of units, the unit of pressure is a pressure exerted by a force of one dyne uniformly distributed over an area of one square centimeter, and it is expressed dimensionally thus:

$$
\begin{equation*}
\frac{L M}{T^{2} L^{2}}=M T^{-2} L^{-1} \tag{1-1}
\end{equation*}
$$

The measurement of pressure in any system of units is a matter of convention. Meteorologists measure the atmospheric pressure in terms of a unit called "bar," which is equivalent to $10^{6}$ absolute units of pressure or 1 megadyne/cm. ${ }^{2}$. In this sense, therefore, the absolute unit of pressure, 1 dyne $/ \mathrm{cm}^{2}$, can be called a " microbar." Formerly the absolute unit of pressure was sometimes called a " bar," though this usage is no longer in vogue. To avoid any ambiguity we shall use the unit bar to denote 1 megadyne/ $\mathrm{cm} .^{2}$, while one " barye" will be used to signify the absolute unit of pressure, 1 dyne $/ \mathrm{cm}^{2}{ }^{2}$, or one microbar.

In practice, the standard atmospheric pressure is taken to be the standard unit pressure. This is a pressure which supports a column of mercury 760 mm . high at a temperature of $0^{\circ} \mathrm{C}$. under the gravitational constant $g=980.665 \mathrm{~cm} . / \mathrm{sec} .^{2}$. The specific gravity of mercury at $0^{\circ} \mathrm{C}$. is 13.595 . For practical purposes the pressure of high vacuum is expressed in 1 mm . of mercury, the unit being called a Tor, after Torricelli.

From the relation between the atmospheric pressure and height of the column of mercury with the known specific gravity, and taking $g$ as $980.665 \mathrm{~cm} . / \mathrm{sec} .^{2}$, the standard atmospheric pressure can be expressed in terms of the absolute units of pressure thus:

$$
\begin{equation*}
h \cdot s p_{g} \cdot G=1,013,240 \text { dynes } / \mathrm{cm} .^{2}, \tag{1-2}
\end{equation*}
$$

where $h$ is the height of the mercury column, $s p_{g}$ is the specific gravity of mercury, and $G$ is the gravitational constant. For convenient reference some practical units and their equivalents in absolute units are given in Table 1-1.

## Tabie 1-1

> Height of mercury column

Absolute units of pressure dyne/cm. ${ }^{2}=$ " barye" $=$ $10^{-6}$ "bar"

$1,013,240$ dynes $/ \mathrm{cm} .{ }^{2}$
1 atmosphere.
$750.07 \mathrm{~mm} \ldots \ldots \ldots \ldots .{ }^{10}$ dynes $/ \mathrm{cm}^{2}{ }^{2}=1$ bar $=10^{6}$ barye
1 mm . or 1 Tor. . . . . . . . . 1,333 dynes $/ \mathrm{cm} .{ }^{2}$
$0.1 \mathrm{~mm} . . . . . . . . . . . . . . . .133 .3$ dynes $/ \mathrm{cm}^{2}{ }^{2}$
$0.01 \mathrm{~mm} . . . . . . . . . . . . . . .13 .33$ dynes $/ \mathrm{cm}^{2}{ }^{2}$
0.001 mm . ( 1 micron).... 1.333 dynes $/ \mathrm{cm}^{2}{ }^{2}$
$10^{-6} \mathrm{~mm} .(1 / \mu \mu) \ldots \ldots . .1 .333 \times 10^{-8}$ dynes $/ \mathrm{cm}^{2}{ }^{2}$
$0.00075007 \mathrm{~mm} . . . . . . . .1$ microbar $=$ (barye)
0.75007 micron.

1 dyne/cm. ${ }^{2}=$ (barye)
1-3. Limit of High Vacuum and Limiting Pressure.-The construction and improvement of the systems of high-vacuum generators should be based upon physical and technical laws. Also proper material must be employed in their construction. Each one of these systems is capable of exhausting a gas enclosure to a certain maximum limit depending upon its type and construction. The optimum vacuum which may be attained by such a system is the limit of high vacuum or the limiting vacuum of the system. The pressure of limiting vacuum is called the limiting pressure.

1-4. Relation between Kinetic Theory of Gases and Techniques of High Vacua.-Production of high vacua is a process of continuous decrement of gaseous pressure. A system of high-vacuum generators functions in transporting the gas molecules at normal atmospheric preasure as well as those at the pressures of high vacua. The conditions for the transport of the gas molecules at
normal pressure should be different from those of the transport of gas molecules at the pressures of high vacua, because in the former case, the flow of gas molecules is mainly influenced by viscosity, while in the latter case viscosity is vanishingly small and does not affect the flow. It is therefore natural to expect that the laws, the intermolecular relations and their corresponding expressions for the gas molecules at the pressures of high vacua differ from those of the gas molecules at normal atmospheric pressure. Efficient production and measurement of high vacua are based upon a careful consideration and thorough realization of the molecular laws of gases under normal pressure as well as pressures of high vacua. Hence the science and the technique of the production and measurement of high vacua should be preceded by a study of the science of gaseous molecules. Inasmuch as the laws of the kinetic theory of gases form the foundation of the science and the technique of high vacua, the following sections of this chapter deal mainly with a simple exposition of the elements of the kinetic theory of gases in so far as they bear upon the science and the technique of high vacua.

## Section II. Gases and Velocities of Gas Molecules

1-5. Fundamentals of the Kinetic Theory of Gases.-Let there be an enclosure with rigid walls containing a gas. If a certain amount of gas from outside be pumped into the enclosure, the original gas permits the added amount to share the enclosure. Now the total amount of gas continues to occupy the same enclosure, of course exerting a pressure on its walls greater than before. Again, if the same enclosure be partially exhausted, the remaining gas continues to occupy the enclosure, exerting a pressure on its walls less than before exhaustion. These facts can be explained by assuming that gases in general are discontinuous systems, consisting of very minute particles called molecules, or, in other words, they are molecular in structure.

This conception of the molecular structure of gases has been extended by the further assumption that all molecules of the same gas are identical as regards mass, etc., but differ in their motion, and that heat is identical with the energy of the molecules. These ideas, which were originally mere assumptions, were subsequently
supported by experimental evidence, and now form the basis of the kinetic theory of gases.

1-6. The Ideal or Perfect Gas.-In connection with the experimental observations on an enclosed gas, it has been pointed out that the gas exerts pressure on the walls of the enclosure. This property is interpreted as arising from the constant motion of the molecules, and it is on this basis that a quantitative expression for pressure can be obtained. To deduce this expression for the pressure, as well as other expressions of relations between the various phenomena, a gas is assumed to have certain ideal characteristics. Such an ideal or perfect gas is defined as one in which the gas molecules are elastic mass points, having practically no forces between them. Its molecules fill no appreciable portion of the space it occupies, or, in other words, the dimensions of the molecules are negligible compared with the free space in which they move. Also, it is tentatively assumed that the molecules move about at random with various velocities and collide with one another, thereby having their velocities altered both in magnitude and direction; that in a steady state, the molecular collisions do not affect the molecular density of the gas; that the motion of a molecule between two of its consecutive collisions is rectilinear, obeying Newton's laws of motion; and that the duration of a collision is negligible compared with the interval between two successive collisions.
1-7. Gaseous Pressure as a Function of Kinetic Energy of Gas Molecules.-Let a gas, such as the one defined above, be enclosed in a cube, each side of which is one centimeter long. Then, as the gas molecules are in motion with the three degrees of freedom associated with motion of translation, it may be supposed that a group of molecules moving with the same velocity in a direction, say $O X$, perpendicular to one of the walls, collide against the same" wall of the enclosure. Inasmuch as the molecules are taken to be perfectly elastic and in consequence sustain no loss of energy by their collisions with the rigid wall, it may be considered that each one of this group of molecules striking against the wall with a velocity $v_{x}$ rebounds with the same velocity. By the law of aetion and reaction, the surface of the wall imparts an equal and opposite momentum to the gas molecule. Hence the change of momentum which the molecule experiences during collision is
$2 m v_{x}$, where $m$ is the mass and $v_{x}$ the velocity of the molecule in the direction $O X$, while its velocities in the other two directions $O Y$ and $O Z$, perpendicular to $O X$, are $v_{y}$ and $v_{z}$ respectively. Now, as the molecule collides with that particular surface $v_{x} / 2$ times per second, the change of momentum experienced by this molecule in one second must be $2 m v_{x} \cdot v_{x} / 2=m v_{x}^{2}$. Since force is equal to change of momentum per second, the total force imparted to the entire surface of that particular wall is $\sum m v_{x}^{2}$, where the summation extends over all the molecules having the velocity component $v_{a}$. This total force here is the same as the pressure $P_{x}$ exerted on the surface of the wall because its area is $1 \mathrm{~cm} .^{2}$. Hence $P_{x}=\sum m v_{x}{ }^{2}$. In this case, since all the molecules of the same gas have the same mass, the mass $m$ may be removed from the summation so that

$$
\begin{equation*}
P_{x}=m \sum v_{x}^{2} . \tag{1-3}
\end{equation*}
$$

Now $\sum v_{x}^{2}=n \overline{v_{x}^{2}}$, where $n$ is the total number of molecules per unit volume contained in the enclosure, and $\overline{v_{x}^{2}}$ denotes the average of $v_{x}^{2}$ for all these molecules. Therefore,

$$
\begin{equation*}
P_{x}=m n \overline{v_{x}^{2}} \tag{1-4a}
\end{equation*}
$$

or,

$$
\begin{equation*}
P_{x}=\rho \overline{v_{x}^{2}} \tag{1-4b}
\end{equation*}
$$

where $\rho=m n$, is the density of the gas.
If $\overline{v_{y}{ }^{2}}, \overline{v_{z}{ }^{2}}$ denote the mean square velocity of the motion of the gas molecules in the two other directions $O Y$ and $O Z$, normal to the direction $O X$, then

$$
\begin{equation*}
\overline{v_{x}^{2}}=\overline{v_{y}^{2}}=\overline{v_{z}^{2}}, \tag{1-4c}
\end{equation*}
$$

since the molecules are in continual motion without tending to accumulate in any part.

Again, since the resultant mean square velocity $\overline{v^{2}}$ is the sum of the squares of the velocities in the three directions,

$$
\begin{equation*}
\overline{v_{x}^{2}}+\overline{v_{y}^{2}}+\overline{v_{x}^{2}}=\overline{v^{2}}=3 \overline{v_{x}^{2}}=3 \overline{v_{y}^{2}}=3 \overline{v_{z}^{2}} . \tag{1-4d}
\end{equation*}
$$

Hence equations $1-4 a$ and $1-4 b$ may be written in either of the forms,

$$
\begin{equation*}
P=\frac{1}{3} m n \overline{v^{2}}=\frac{1}{3} P \overline{v^{2}}, \quad P \bar{V}=\frac{1}{3} \overline{v^{2}}, \tag{1-5a,b}
\end{equation*}
$$

where $\overline{\boldsymbol{V}}$ is specific volume of the gas, standing for the volume of a gram.

To proceed a step further, it may be noted that the kinetic energy of translation of a group of molecules of mass $m$ is $\sum \frac{1}{2} m v^{2}=$ $\frac{1}{2} m n v^{2}$. Now by substituting the relation expressed in this equation for the total kinetic energy of translation in equation 1-5a, an alternative expression for the pressure as a function of the total kinetic energy of translation is obtained. Thus,

$$
P=\frac{1}{3} m n \overline{v^{2}},
$$

or,

$$
\begin{equation*}
\frac{8}{2} P=\frac{1}{2} m n v^{2}=E . \tag{1-8a}
\end{equation*}
$$

Therefore,

$$
\begin{equation*}
P=\frac{8}{3} E \text {, } \tag{1-6b}
\end{equation*}
$$

where $E=\frac{1}{2} m n \bar{v}^{2}$, the total kinetic energy of translation of gas molecules per unit volume.

1-8. Elementary Laws of Perfect Gases.-From the foregoing considerations of gases, it may now be shown how the elementary laws of perfect gases can be derived.
(I) Daiton's Law: Let a number of perfect gases of densities $\rho_{1}, \rho_{2}, \rho_{3}, \cdots \rho_{n}$ and average square velocities $\overline{v_{1}{ }^{2}, \overline{v_{2}{ }^{2}}, \overline{v_{3}{ }^{2}}, \ldots \overline{v_{n}{ }^{2}},{ }^{2},}$ be mixed in an enclosure of a certain volume. Then an expression for the resultant pressure of the mixture in relation to the partial pressures exerted by the different types of molecules may be deduced thus:

$$
P=\frac{1}{3} \rho_{1} \overline{v_{1}{ }^{2}}+\frac{1}{3} \rho_{2} \overline{v_{2}^{2}}+\frac{1}{3} \rho_{3} \overline{v_{3}^{2}}+\cdots+\frac{1}{3} \rho_{n} \overline{v_{n}^{2}}
$$

or

$$
\begin{equation*}
P=p_{1}+p_{2}+p_{3}+\cdots+p_{n} . \tag{1-7}
\end{equation*}
$$

To express this in words, the resultant total pressure of a mixture of a number of perfect gases is simply the sum of the pressures. exerted by its components, if each occupied the same volume by itself. This is Dalton's law of partial pressures and is known experimentally to be true at sufficiently low densities.
(II) Avooadro's Law: If there be a number of perfect gases of masses $m_{1}, m_{2}, m_{3}, \cdots m_{n}$, of molecules $n_{1}, n_{2}, n_{3}, \cdots n_{n}$ per unit volume and of mean square velocities $\overline{v_{1}{ }^{2}}, \overline{v_{3}{ }^{2}}, \overline{v_{3}{ }^{2}}, \ldots \overline{v_{n}{ }^{2}}$, at the same given pressure $P$, we have, by equation 1-5a,

$$
\begin{equation*}
P=\frac{1}{3} m_{1} n_{1} \overline{v_{1}^{2}}=\frac{1}{3} m_{2} n_{2} \overline{v_{2}^{2}}=\frac{1}{3} m_{3} n_{8} \overline{v_{3}^{2}}=\cdots=\frac{1}{3} m_{n} n_{n} \overline{v_{n}^{2}} . \tag{1-8}
\end{equation*}
$$

Again, if all these gases are at the same given temperature, on mixing them together, there will be no transfer of thermal energy from one to the other. Now, according to a theorem of statistical mechanics in a limited form, the mean kinetic energy associated with each degree of freedom of a mechanical system in statistical equilibrium has the same value. So in the gases in equilibrium at the same given temperature, the average translatory kinetic energy of all molecules must have the same value. Hence it follows that

$$
\begin{equation*}
\frac{1}{2} m_{1} \overline{v_{1}^{2}}=\frac{1}{2} m_{2} \overline{v_{2}^{2}}=\frac{1}{2} m_{3} \overline{v_{3}^{2}}=\cdots=\frac{1}{2} m_{n} \overline{v_{n}^{2}} . \tag{1-9}
\end{equation*}
$$

Now, on dividing equation 1-8 by 1-9 and simplifying, we have

$$
\begin{equation*}
n_{1}=n_{2}=n_{3}=\cdots=n_{n} . \tag{1-10}
\end{equation*}
$$

From the considerations of the kinetic theory of gases we thus arrive at the very important conclusion that all perfect gases at the same pressure and temperature contain the same number of molecules per unit volume. This deduction, which was proposed as a hypothesis by Avogadro, is known as Avogadro's law.
(III) Boyle's Law: In a state of thermal equilibrium, especially at low pressures, the mean square velocity $\overline{v^{2}}$ for each type of molecules is independent of density and therefore a function only of the temperature. Hence for any perfect gas the resultant mean square velocity $\overline{v^{2}}$ is constant provided its temperature is constant. It follows by equation $1-5 a$ that when the temperature remains constant the pressure of a gas is directly proportional to its density or inversely proportional to its volume $V$, or, in other words, $P V$ is constant, $V$ being the volume of a given mass of gas. This last statement, obtained as a deduction from the kinetic theory of gases, is Boyle's law, and it may be written symbolically thus:

$$
\begin{equation*}
P V=A \text { constant, } T \text { constant. } \tag{1-11}
\end{equation*}
$$

(IV) Gay-Lussac's Law: From equation 1-6a, it is evident that the total kinetic energy of translation per unit volume of a gas is a linear function of pressure. On multiplying both sides of the expression 1-6a by $V$, the given volume of a gas, we obtain an expression for the total kinetic energy of translation of gas molocules contained in the given volume as a function of the product
of pressure and volume of the same gas, which may be written,

$$
\begin{equation*}
\frac{1}{2} m n \overline{v^{2}} \cdot V=\frac{3}{2} P V, \tag{1-12}
\end{equation*}
$$

where $V$ is simply the given volume of the gas.
If the gas under consideration be a rarefied one in thermal equilibrium, $\overline{v^{2}}$ the mean square velocity of translation for the given gas molecule is only a function of temperature. We may therefore write

$$
\begin{equation*}
\frac{1}{2} m n \overline{v^{2}}=\frac{3}{2} P=\frac{3}{2} n k T, \tag{1-13}
\end{equation*}
$$

where $k$ is a constant and $T$ is the absolute temperature.
Now, as $P V$ in expression 1-12 is proportional to the product of volume and the kinetic energy of translation per unit volume, it can further be assumed that $P V$ varies according to temperature so that from the expressions $1-12$ and $1-13$ we may derive an equation, expressing the perfect gas law of Gay-Lussac, which is

$$
\begin{equation*}
P V=n k T \tag{1-14a}
\end{equation*}
$$

which may be written in the usual form,

$$
\begin{equation*}
P \bar{V}=\bar{R} T \tag{1-14b}
\end{equation*}
$$

where $\bar{R}$ is the gas constant for a gram.
1-9. Volume of a " Mole" $\bar{V}$, Volume $\bar{\nabla}$ of a Gram, Density of the Same Gas at $0^{\circ} \mathbf{C}$. and a Pressure of 1 Standard Atmosphere.From Avogadro's law, it follows that the densities of different ideal gases at the same temperature and pressure are proportional to their molecular weights. If $\bar{V}$ be the volume of a $\operatorname{gram}(\bar{V}=$ $1 / m n=1 / \rho$ ), the values of the product $P \bar{V}$ are inversely proportional to the molecular weights. If $\breve{V}$, however, be the volume of a gram molecule or "Mole" which is defined as the number of grams equal to the molecular weight, then $\bar{V}$ is the same for all gases at any given temperature and pressure. This volume $\breve{V}$ occupied by a mole of an ideal gas under standard conditions is a universal constant and its accepted value at $0^{\circ} \mathrm{C}$. and standard staospheric pressure is

$$
\begin{equation*}
\breve{V}=22414 \mathrm{~cm}^{3}{ }^{3} . \tag{1-15}
\end{equation*}
$$

Then the volume $\bar{\eta}$ of a gram of gas, whose molecules have the molecular weight $M$, is given by

$$
\begin{equation*}
\nabla=\frac{1}{m n}=\frac{1}{\rho}=\frac{\breve{V}}{M}, \tag{1-16a}
\end{equation*}
$$

while its density at $0^{\circ} \mathrm{C}$. and a pressure of one standard atmosphere is given by

$$
\begin{equation*}
\rho=\frac{M}{\breve{V}}=4.461 \times 10^{-5} M \mathrm{~g} . / \mathrm{cm}^{8} \tag{1-16b}
\end{equation*}
$$

1-10. Root Mean Square Velocity.-Equation 1-5a gives us a direct expression for the square root of the mean square velocity $v_{s}=\left(\overline{v^{2}}\right)^{3 / 2}$ of the molecules of a perfect gas at a temperature of $0^{\circ} \mathrm{C}$. and a pressure of one standard atmosphere, which may be written,

$$
\begin{equation*}
v_{\mathrm{s}}=\sqrt{\hat{v^{2}}}=\sqrt{\frac{3 P}{\rho}} \mathrm{~cm} . / \mathrm{sec} \tag{1-17}
\end{equation*}
$$

Now, on introducing the value of the density of a perfect gas from $1-16 b$ in the expression 1-17, the value of $v_{s}$, the root of the mean square velocity of the molecules of the same gas under standard conditions, is obtained. Again, in the usual gas equation 1-14b, if $\bar{V}$ stands for the volume of a gram, $\bar{V}=1 / m n=1 / \rho$, then from the equations $1-5 b$ and $1-14 b$ we have

$$
\begin{equation*}
v_{s}=\left(\overline{v^{2}}\right)^{3 / 2}=\sqrt{3 \bar{R} T} \tag{1-18}
\end{equation*}
$$

If, on the other hand, the volume be that of one gram molecule, then equation $1-5 b$ takes the form,

$$
\begin{equation*}
P \breve{V}=\frac{1}{3} M \overline{v^{2}} \tag{1-19}
\end{equation*}
$$

where $M$ is the molecular weight of the gas. From the equations $1-14 b$ and 1-19, we obtain another expression for the root of the mean square velocity which may be written,

$$
\begin{equation*}
v_{s}=\left(\overline{v^{2}}\right)^{1 / 2}=\sqrt{\frac{3 \stackrel{R}{ }}{M}} \tag{1-20}
\end{equation*}
$$

Therefore we have

$$
\begin{equation*}
v_{s}=\left(\overline{v^{2}}\right)^{3 / 2}=\sqrt{3 \bar{R} T}=\sqrt{\frac{3 \bar{R} T}{M}} \tag{1-21}
\end{equation*}
$$

where $\bar{R}$ is the gas constant for a gram and $\breve{R}$ is the universal gas constant.

It follows that the root of the mean square velocity varies directly as the square root of the absolute temperature, and for different gases inversely as the square root of the molecular weight. At any given temperature the rate of the flow of different gases, especially at low pressures, through a given tube system, therefore, must be inversely proportional to the square root of the molecular weights of different gases. Hence it is easier to evacuate the gases of lower molecular weights from a given enclosure than to evacuate the gases of higher molecular weights. A consideration of this fact may sometimes be found useful in the adjustment of the evacuating system according to the gas. The data given in Table 1-2 will be useful for similar considerations in the science and technique of the production and measurement of high vacua.

1-11. Number and Mass Constants of Gas Molecules.-A consideration of the elements of the kinetic theory of gases indicates a method of calculating the density $\rho$, of a gas. However, the kinetic theory of gases by itself does not enable us to calculate $m$ and $n$ separately. It is only from experimental evidence that these values have been derived. The following methods give the best values.

It has been found from direct experimental observation that the electric charge $E$ carried by a gram of a monovalent element is 96,489 abcoulombs and each atom carries the same numerical charge as the electron. Millikan calculated the charge of an electron from his oil-drop results and his calculated value of the charge of an electron was $4.774 \times 10^{-10}$ e.s.u This value, however, was subsequently found to be too low because of an inaccurate value of the coefficient of viscosity. If Millikan's value be corrected by using Kellström's determination of the viscosity coefficient, ${ }^{1}$ the more accurate value of the charge of the electron is in agreement with the value calculated from $x$-ray wave lengths as measured by means of a grating. The accepted value at present is
$e=4.8029 \times 10^{-10}$ e.s.u. or $\frac{4.8029 \times 10^{-10}}{2.9979 \times 10^{9}}$ abcoulombs. (1-22)
${ }^{1}$ G. Kelletröm, Phys. Rev. 50, 100 (1936).

Now, on dividing the value of the charge $E$ of one gram atom or gram molecule by the charge of a single atom $e$ which is equivalent to that of an electron, the number of atoms in a gram atom or of molecules in a mole, called Avogadro's number or Avogadro's constant $N_{A}$, is obtained thus:

$$
\begin{equation*}
\frac{E}{e}=\frac{96489}{1.6017885 \times 10^{-19}}=N_{A}=6.02383 \times 10^{23} . \tag{1-23}
\end{equation*}
$$

Since Avogadro's number $N_{A}$ is the number of molecules contained in a volume $\breve{V}=22414$ cc. of a gram molecule, the number of molecules $n_{L}$, called Loschmidt number, contained in a unit volume of a perfect gas at a temperature of $0^{\circ} \mathrm{C}$. and the standard atmospheric pressure is

$$
\begin{equation*}
n_{L}=\frac{N_{A}}{\widetilde{V}}=\frac{6.02383 \times 10^{23}}{22414}=2.6875 \times 10^{19} . \tag{1-24}
\end{equation*}
$$

Loschmidt number $n_{L}$ is also called the molecular density. The reciprocal of the value $N_{A}$ from 1-23 gives the mass $m_{\circ}$ of an imaginary molecule whose molecular weight is unity and it is

$$
m_{0}=\frac{1}{N_{A}}=\frac{1}{6.02383 \times 10^{23}}=1.6607 \times 10^{-24} \mathrm{gram}
$$

or nearly

$$
\begin{equation*}
1.661 \times 10^{-24} \mathrm{gram} \tag{1-25}
\end{equation*}
$$

Now on multiplying this value by the molecular weight $M$ of a perfect gas, we obtain the actual mass $m_{a}$ of a single molecule of the same gas thus:

$$
\begin{equation*}
m_{a}=m_{o} \times M=\left(1.661 \times 10^{-24} \times M\right) \text { gram } \tag{1-26}
\end{equation*}
$$

Some of the data, such as molecular weights, masses of molecules, the square roots of the average square velocities, and the average speeds of gas molecules (at $20^{\circ} \mathrm{C}$. and a pressure of 760 mm .) of some of the gases are given in Table 1-2. From this table it is obvious that the mean average speeds of gas molecules are higher than most of the speeds which human ingenuity through technical and engineering skill has so far produced. These high values of the average velocities of the gas molecules and the enormous mag-
nitudes of $N_{A}$ or $n_{L}$ serve to explain, on the one hand, what it would mean if a gas enclosure were to be evacuated and, on the other, why a gas behaves in so many ways as if it were continuously distributed.

Table 1-2

| Gas or Vapor | Molecular Weight M | $\begin{gathered} \text { Mass } \\ m \\ \left(10^{-24} \mathrm{~g} .\right) \end{gathered}$ | $\begin{gathered} R \\ \left(10^{3} \mathrm{crg}\right. \\ \text { per deg. }) \end{gathered}$ | $\left(\begin{array}{c} v_{\varepsilon} \\ \left(10^{3} \mathrm{~cm} / / \mathrm{sec} .\right) \\ \left(293.14^{\circ} \mathrm{Abs} . \mathrm{T} .\right) \end{array}\right.$ | $\begin{gathered} v_{m} \\ \left(10^{3} \mathrm{~cm} .\right. \\ \text { per sec. } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Hydrogen, $\mathrm{H}_{2}$ | 2.016 | 3.349 | 4125 | 190.90 | 175.47 |
| Helium, He | 4.002 | 6.648 | 20.78 | 135.49 | 124.54 |
| Water, $\mathrm{H}_{2} \mathrm{O}$ | 18.016 | 29.93 | 4.615 | 63.71 | 58.69 |
| Neon, Ne | 20.18 | 33.52 | 4.120 | 60.19 | 55.46 |
| Carbon monoxide, CO | 28.00 | 46.508 | 2.9696 | 51.10 | 47.08 |
| Nitrogen, $\mathrm{N}_{2}$ | 28.02 | 46.54 | 2.968 | 51.09 | 47.07 |
| Oxygen, $\mathrm{O}_{2}$ | 32.00 | 53.16 | 2.598 | 47.80 | 44.04 |
| Argon, A | 39.94 | 66.34 | 2.082 | 42.79 | 39.42 |
| Carbon dioxide, $\mathrm{CO}_{2}$ | 44.00 | 73.09 | 1.890 | 40.77 | 37.56 |
| Krypton, Kr | 82.9 | 137.7 | 1.0030 | 29.70 | 27.36 |
| Xenon, Xe | 130.2 | 216.3 | 0.6386 | 2370 | 21.83 |
| Mercury, Hg | 200.6 | 333.2 | 0.4145 | 19.09 | 17.60 |
| Air | 28.96 | 48.11 | 2.871 | 50.25 | 46.30 |

1-12. Maxwell's Law of Distribution of Molecular Velocities.The pressure and temperature of perfect gases are related to the mean square velocity of gas molecules. Because of this, a study of the pressure and temperature of a gas has led us to the knowledge of the mean square velocity of the gas molecules. This study, however, has not enabled us to understand the manner in which the velocities of the molecules vary among themselves, inasmuch as the pressure and temperature are independent of it. But the molecular free path and the transport phenomena of gases are to a certain extent based upon the actual distribution of molecular velocities. Since a consideration of the molecular free path and the transport phenomena of gases is necessary in the science and the technique of high vacua; it is essential to have an elementary survey of the distribution of molecular velocities. In other words, we should know how many molecules of a gas in equitibrium poesess any particular speed. It is self-evident that
in a given volume all the molecules of a gas cannot have the same speed, for even if it be assumed that all the molecules have the same speed at any instant, the collisions of the next moment raise the speed of some and lower that of the others. So at any given moment the individual molecules of the given volume of the gas in equilibrium are moving in all directions and with speeds varying all the way from zero up to values many times as great as the average. A law which governs the distribution of molecular velocities was deduced by Clerk Maxwell ${ }^{2}$ purely from considerations of probability.
-If a quantity of gas in an enclosure be in a state of equilibrium, the density $\rho$ remains constant, being uninfluenced by collisions, and the molecules on the average have the same velocity in all directions. The velocity of each molecule may be resolved in three perpendicular directions. Let these velocity components, which may be assumed to be independent, be denoted, by $v_{x}, v_{y}$, and $v_{z}$ and their resultant by $\gamma$. Then from the theorem of probabilities, the probability that the velocity components of a molecule lie between $v_{x}$ and $v_{x}+d v_{x}, v_{y}$ and $v_{y}+d v_{y}$, and $v_{z}$ and $v_{z}+d v_{z}$ must be

$$
\begin{equation*}
f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right) d v_{x} d v_{y} d v_{z} . \tag{1-27}
\end{equation*}
$$

Now the number of velocity vectors having their end points in the volume $d v_{x} d v_{y} d v_{z}$ is

$$
\begin{equation*}
n f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right) d v_{x} d v_{y} d v_{z}, \tag{1-27a}
\end{equation*}
$$

depending, because of isotropy, on the resultant $\gamma$ and being from probability considerations taken to be equal to $n F(\gamma) d v_{x} d v_{y} d v_{s}$. If all those $v_{x}, v_{y}, v_{z}$ be considered so that the square of the resultant of the velocity components is equal to the sum of the squares of the components, we have $\gamma^{2}=\left(v_{x}{ }^{2}+v_{y}{ }^{2}+v_{z}{ }^{2}\right)$, or $v_{x}{ }^{2}+v_{y}{ }^{2}+$ $v_{z}^{2}-\gamma^{2}=0$. Hence
$n f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right)=n F(\gamma)=n \phi\left(\gamma^{2}\right)=n \phi\left(v_{x}^{2}+v_{y}^{2}+v_{z}^{2}\right)$.
Since for a particular value of $\gamma, \phi\left(\gamma^{2}\right)$ is a constant,

$$
\begin{equation*}
d\left\{\phi\left(\gamma^{2}\right)\right\}=d\left\{f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right)\right\}=0 \tag{1-29a}
\end{equation*}
$$

${ }^{2}$ J. C. Maxwell Phil. Mag. 19, No. 124, 19-32 (1860); 20, No. 130, 21-87 (1880).
and therefore,

$$
\begin{align*}
& f^{\prime}\left(v_{x}\right) d v_{x} f\left(v_{y}\right) f\left(v_{z}\right)+f^{\prime}\left(v_{y}\right) d v_{y} f\left(v_{x}\right) f\left(v_{z}\right)+ \\
& f^{\prime}\left(v_{z}\right) d v_{z} f\left(v_{x}\right) f\left(v_{y}\right)=0 \tag{1-29b}
\end{align*}
$$

which, on dividing by $f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{s}\right)$, has the form:

$$
\begin{equation*}
\frac{f^{\prime}\left(v_{x}\right)}{f\left(v_{x}\right)} d v_{x}+\frac{f^{\prime}\left(v_{y}\right)}{f\left(v_{y}\right)} d v_{y}+\frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)} d v_{z}=0 \tag{1-29c}
\end{equation*}
$$

In the case under consideration $v_{x}{ }^{2}+v_{\nu}{ }^{2}+v_{z}{ }^{2}=\gamma^{2}$, and hence as $\boldsymbol{\gamma}$ is maintained as a constant the variables $d v_{x} d v_{y} d v_{z}$ are connected by the relation,

$$
\begin{equation*}
v_{x} d v_{z}+v_{y} d v_{y}+v_{x} d v_{z}=0 \tag{1-30a}
\end{equation*}
$$

so that

$$
\begin{equation*}
d v_{z}=-\frac{v_{x} d v_{x}+v_{y} d v_{y}}{v_{z}} \tag{1-30b}
\end{equation*}
$$

Now, on substituting this expression in equation 1-29c, we obtain

$$
\begin{equation*}
\left[\frac{f^{\prime}\left(v_{x}\right)}{f\left(v_{x}\right)}-\frac{v_{x}}{v_{z}} \frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)}\right] d v_{x}+\left[\frac{f^{\prime}\left(v_{y}\right)}{f\left(v_{y}\right)}-\frac{v_{y}}{v_{z}} \frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)}\right] d v_{y}=0 . \tag{1-31}
\end{equation*}
$$

Hence

$$
\begin{align*}
& \frac{f^{\prime}\left(v_{x}\right)}{f\left(v_{x}\right)}=\frac{v_{x}}{v_{z}} \frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)},  \tag{1-31a}\\
& \frac{f^{\prime}\left(v_{y}\right)}{f\left(v_{y}\right)}=\frac{v_{y}}{v_{z}} \frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)} . \tag{1-31b}
\end{align*}
$$

On multiplying by the factors $1 / v_{x}$, etc., we have

$$
\begin{equation*}
\frac{1}{v_{x}} \frac{f^{\prime}\left(v_{x}\right)}{f\left(v_{x}\right)}=\frac{1}{v_{y}} \frac{f^{\prime}\left(v_{y}\right)}{f\left(v_{y}\right)}=\frac{1}{v_{z}} \frac{f^{\prime}\left(v_{z}\right)}{f\left(v_{z}\right)}=-\beta \tag{1-32}
\end{equation*}
$$

where $-\beta$ is a constant independent of $v_{x}, v_{y}, v_{z}$. Therefore
$\frac{f^{\prime}\left(v_{x}\right)}{f\left(v_{x}\right)}=-\beta v_{x}$ or $\log f\left(v_{x}\right)=\frac{\beta v_{x}^{2}}{2}+\log a$ or $f\left(v_{x}\right)=a e^{-b v_{x}^{2}}$,
and similarly

$$
\begin{equation*}
f\left(v_{y}\right)=a e^{-b v_{y}^{2}}, \quad f\left(v_{s}\right)=a e^{-b v_{z}^{2}} \tag{1-33a}
\end{equation*}
$$

where $a, b$ are constants. Hence

$$
\begin{equation*}
f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right)=a^{3} e^{-b\left(v_{z}^{2}+v_{y}^{2}+v_{z}\right)} . \tag{1-34}
\end{equation*}
$$

To determine $a$, let the number of molecules per cc. be $n$, so that

$$
\begin{equation*}
n \iiint f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{z}\right) d v_{x} d v_{y} d v_{z}=n \tag{1-35}
\end{equation*}
$$

where for each variable the integration is from $-\infty$ to $+\infty$. If the value of the function be substituted we have

$$
\iiint_{-\infty}^{+\infty} a^{3} e^{-b\left(v_{x}^{2}+v_{y}^{2}+v_{x}\right)} d v_{x} d v_{y} d v_{z}=1
$$

giving

$$
a^{3} \sqrt{\left(\frac{\pi}{b}\right)^{3}}=1
$$

Therefore

$$
\begin{equation*}
a=\sqrt{\frac{b}{\pi}} . \tag{1-36}
\end{equation*}
$$

Now, to determine $b$, let the volume actually occupied by the molecules, compared with the volume occupied by the gas, be negligible. The molecules colliding against a plane of unit area in a time $d t$ with a velocity $v$ may be supposed to be contained in a solid tube of the length $v d t$, normal to the plane. As the numberof molecules $n$ per unit volume with component of velocity normal to the plane varying between $v$ and $v+d v$ is

$$
n a e^{-b v^{2}} \cdot d v
$$

the number in the solid tube of the length vadt must be

$$
n a e^{-b v^{2}} \cdot v d v \cdot d t
$$

and the pressure exerted by these molecules, which is equal to the total change of momentum per unit time, is

$$
\begin{equation*}
\int_{0}^{\infty} n a e^{-b v^{e}} \cdot v d v \cdot 2 m v, \tag{1-87}
\end{equation*}
$$

where $2 m v$ is the change in momentum suffered by each of the molecules in the imaginary " solid tube" of gas during collision against the surface of the plane and the integration being from 0
to $\infty$, since the molecules considered are taken to be only with positive velocity. Therefore,

$$
P=n k T=2 a \cdot m n \cdot \frac{1}{4} \sqrt{\frac{\pi}{b^{3}}},
$$

or, on substituting the value of $a$ given in (1-36),

$$
n k T=\frac{m n}{2 b}
$$

Hence

$$
\begin{equation*}
b=\frac{m}{2 k T} \tag{1-38}
\end{equation*}
$$

Now, therefore, the number $d n$ of molecules with velocities whose components lie between $v_{x}$ and $v_{x}+d v_{x}, v_{y}$ and $v_{y}+d v_{y}$, and $v_{z}$ and $v_{z}+d v_{z}$ is

$$
\begin{array}{r}
d n=n\left\{f\left(v_{x}\right) f\left(v_{y}\right) f\left(v_{x}\right)\right\} d v_{x} d v_{y} d v_{z}= \\
n a^{3} e^{-b\left(v_{x}+v_{y}+v_{x}\right)} d v_{x} d v_{y} d v_{z} . \tag{1-39a}
\end{array}
$$

Since from (1-36) and (1-38) $a=\sqrt{b / \pi}$, and $b=m / 2 k T$, equation 1-39a may finally be written in the form,

$$
d n=n\left(\frac{m}{2 \pi k T}\right)^{3 / 2} \cdot e^{-m \frac{\left(v_{x} 2+v_{y}^{2}+v_{x}\right)}{2 k T}} \cdot d v_{x} d v_{y} d v_{z} .-(1-39 b)
$$

This is Maxwell's law of the velocity distribution for a gas in equilibrium.

Now, to find the number of molecules having speeds between $v$ and $v+d v$ irrespective of directions, let the element of the volume $d v_{x} d v_{y} d v_{s}$ of the $v_{x} v_{y} v_{z}$ representative space be replaced by the volume included between spheres of radii $v$ and $v+d v$, that is, since $d v$ is an infinitesimal, by $4 \pi v^{2} d v$. Then $1-39 b$ becomes

$$
\begin{equation*}
d n_{v}=4 \pi n a^{3} e^{-b v^{2}} \cdot v^{2} d v \tag{1-40}
\end{equation*}
$$

Again, if $h$ be put for $h=1 / 2 k T$, then the relation given in 1-39b may be expressed in terms of $h$ thus:

$$
\begin{equation*}
d n=n\left(\frac{h m}{\pi}\right)^{3 / 4} e^{-h m\left(v_{x}^{2}+v_{y}^{2}+v_{s}\right)} \cdot d v_{x} d v_{y} d v_{z} \tag{1-41}
\end{equation*}
$$

and similarly expression 1-40 may be written in terms of $h$ thus:

$$
\begin{equation*}
d n_{v}=4 n \sqrt{\frac{h^{3} m^{3}}{\pi}} e^{-\lambda m v^{2} v^{2} d v .} \tag{1-42}
\end{equation*}
$$

## 1. KINETIC GAS THEORY

From the relation between $d n$ and $v$, expressed in equation 1the curve shown in figure 1-1 is obtained by plotting $d n$ against The most probable speed comes at the highest point of the cur The curve has zero ordinate at the origin, and after passing throu its maximum, it comes down asymptotically to the $v$-axis. Hen the whole gas for some purposes may be approximately taken possess the most probable speed.


Fig. 1-1. Maxwell's distribution law.
1-13. Most Probable and Average Speeds.-The most probable velocity $s$ is the speed which a specified molecule is most likely tc possess. It can be seen as an extension of expression 1-42, that the probability that a molecule has a speed between $v$ and $v+d v$ is

$$
\bar{\delta}=\frac{d n}{n}=4 \sqrt{\frac{h^{3} m^{3}}{\pi}} e^{-h m v^{2} v^{2} d v}
$$

and that therefore the condition for maximum probability is

$$
\frac{d \overline{8}}{d v}=4 \sqrt{\frac{h^{3} m^{3}}{\pi}}\left\{-2 h m v^{3} e^{-h m v^{2}}+2 v e^{-h m v^{2}}\right\} d v=0
$$

and the most probability $s$ is given by

$$
\begin{equation*}
S=\frac{1}{\sqrt{h m}} \text { in terms of } h \tag{1-43a}
\end{equation*}
$$

or, since $h=1 / 2 k T$,

$$
\begin{equation*}
S=\sqrt{\frac{2 k T}{m}} \text { in terms of } T \tag{1-43b}
\end{equation*}
$$

The physical phenomena, such as pressure, depend upon the mean square velocity $\overline{v^{2}}$, from which $v_{s}$ has been derived as the square root. The square root $v_{s}$ of the mean square velocity is such that its square is the average of the squares of the velocities of the molecules. Thus we have,

$$
\overline{v^{2}}=v_{s}^{2}=\frac{1}{n} \int_{0}^{\infty} v^{2} d n=4 \sqrt{\frac{h^{3} m^{3}}{\pi}} \int_{0}^{\infty} e^{-h m v^{2} v^{4}} d v
$$

which, on integrating by parts, reduces and finally becomes,

$$
\begin{equation*}
\overline{v^{2}}=v_{0}^{2}=\frac{3}{2 h m} \tag{1-44}
\end{equation*}
$$

Hence

$$
\begin{equation*}
v_{0}=\sqrt{\frac{3}{2 h m}} \text { in terms of } h \tag{1-45a}
\end{equation*}
$$

and, therefore,

$$
\begin{equation*}
v_{s}=\sqrt{\frac{3 k T}{m}} \text { in terms of } T \tag{1-45b}
\end{equation*}
$$

Certain other phenomena of gases, however, may be described more simply by the use of the mean velocity $v_{m}$ rather than by $v_{s}$. For such purposes, therefore, the arithmetic mean velocity $v_{m}$ is essential, and to find it,

$$
\begin{aligned}
v_{m}=\frac{1}{n} \int_{0}^{\infty} v d n & =4 \sqrt{\frac{h^{3} m^{3}}{\pi}} \int_{0}^{\infty} e^{-h m v^{3}} v^{3} d v \\
& =2 \sqrt{\frac{h^{3} m^{3}}{\pi}} \int_{0}^{\infty} e^{-h m x} x d x
\end{aligned}
$$

The change of variable from $v$ to $x$ is made by writing $v^{2}=x$. The equation thus finally reduces to

$$
\begin{equation*}
v_{m}=\frac{2}{\sqrt{\pi h m}} \text { in terms of } h \tag{1-46a}
\end{equation*}
$$

or,

$$
\begin{equation*}
=\sqrt{\frac{8 k T}{m \pi}} \text { in terms of } T \tag{1-46b}
\end{equation*}
$$

In 1-43ab, 1-45ab and 1-46ab we have

$$
\begin{aligned}
& S=\frac{1}{\sqrt{h m}}=\sqrt{\frac{2 k T}{m}} \\
& v_{m}=\frac{2}{\sqrt{\pi h m}}=\sqrt{\frac{8 k T}{m \pi}} \\
& v_{s}=\sqrt{\frac{3}{2 h m}}=\sqrt{\frac{3 k T}{m}}
\end{aligned}
$$

and therefore,

$$
\begin{equation*}
S: v_{m}: v_{s}=\sqrt{\frac{2}{3}}: \sqrt{\frac{8}{3 \pi}}: 1=0.8165: 0.9213: 1 \tag{1-47}
\end{equation*}
$$

the most probable speed $S$ being the smallest in value. Each of these three velocities is indicated in the curve (figure 1-1) from which it is obvious also that $v_{m}$ exceeds $S$ slightly because the curve for $f(v)$ is unsymmetrical about the ordinate at $S$, while $v_{s}$, the root of the mean square velocity, exceeds $v_{m}$ because the squares of larger values of $v$ contribute heavily to $\overline{v^{2}}$.

1-14A. Number of Molecules Striking a Unit Surface per Second.-The deductions of gaseous pressure and molecular velocity are in a way based upon the assumption of gaseous molecular chaos. According to this assumption, for the molecules of an enclosed gas in equilibrium and in the absence of external forces, all positions in the enclosure and all directions of velocity are equally probable. Because of this, and of the enormous number of molecules contained in a unit volume, the ceaselessly moving molecules in traversing an enclosed space incessantly strike against the surface of the walls of the containing enclosure.

As will be shown later, it becomes important to estimate the number of molecules that strike a unit surface per second. Now to determine this, consider a square centimeter of surface with $n$ molecules per cubic centimeter in the space above it, and let the molecules be treated as if they were all moving with the mean velocity $v_{m}$. From the deductions of probability of directions of velocity, it can be shown that of these molecules, the probability that any one molecule has a velocity whose direction makes an angle between $\theta$ and $\theta+d \theta$ with the normal to the surface is pro-
portional to $\sin \theta d \theta / 2$. Out of the $n$ molecules, only those which lie in a parallelepiped $v_{m} \mathrm{~cm}$. long and orthogonal section $1 \times \cos \theta$ $\mathrm{cm} .{ }^{2}$ may strike the unit surface in one second, since those further away, going with a velocity $v_{m} \mathrm{~cm}$., will not reach the surface in the unit time interval; and only those that lie in the cylinder whose orthogonal section has the area normal to the direction of motion can strike the surface at an angle $\theta$ with the normal. So


Fig. 1-2. Parallelepiped $V_{m} \mathrm{~cm}$. long and orthogonal section $1 \times \cos \theta \mathrm{cm} .{ }^{2}$.
only the number $n v_{m} \cos \theta$ of molecules in the volume $v_{m} \times 1 \times$ $\cos \theta \mathrm{cm} .^{3}$, illustrated in figure 1-2, will be capable of striking the surface, and again, only the fraction $\sin \theta d \theta / 2$ of these molecules will have the chance of striking the surface at an angle between $\theta+d \theta$. Therefore the number $d n_{\theta}$ of molecules striking the surface of unit area at an angle between $\theta$ and $\theta+d \theta$ is

$$
d n_{\theta}=\frac{1}{2} n v_{m} \cos \theta \sin \theta d \theta .
$$

Now, on integrating from 0 to $\pi / 2$ to cover the total space above the surface, we obtain the number $n_{\square}$ of molecules which strike the entire unit surface in one second,

$$
\begin{equation*}
n_{\square}=\int d n_{0}=\frac{1}{2} n v_{m} \int_{0}^{\pi / 2} \sin \theta \cos \theta d \theta=\frac{1}{4} n v_{m} \tag{1-48a}
\end{equation*}
$$

1-14B. Vapor Pressure of Highly Refractory Metals from the Rate of Evaporation.-Evaporation in high vacua takes place at the same rate as it occurs in the presence of the saturated vapor so that equilibrium is a balance between the rate of evaporation and that of condensation. The rate at which saturated vapor comes into contact with the unit surface of a solid may be derived from expression 1-48a, thus:

If the mass of a single molecule be $m$, the product of the number $n_{\square}$ and $m$ gives the mass $w$ of molecules striking a unit surface per second which amounts to the rate of evaporation and which may be written,

$$
\begin{equation*}
w=n_{\square} m=\frac{1}{4} n m v_{m}=\frac{1}{4} \rho v_{m}, \tag{1-48b}
\end{equation*}
$$

where $m n$ is the density $\rho$, which by expression $1-16 b$ is equal to $M / \breve{V}=M p / p \breve{V}$ and by $1-14 b=M p / \overparen{R} T, p$ being the pressure and $M$ the mass of one mole. Therefore,

$$
\begin{equation*}
w=\frac{1}{4} \frac{M p}{\breve{R} T} v_{m} \tag{1-48c}
\end{equation*}
$$

which, by the relation given in the equation 1-46b, becomes

$$
\begin{equation*}
w=\frac{1}{4} \frac{M p}{\breve{R} T} \sqrt{\frac{8 \breve{R} T}{\pi M}}=p \sqrt{\frac{M}{2 \pi \breve{R} T}} \tag{1-48d}
\end{equation*}
$$

where $w$ is the weight in grams striking each square centimeter per second, $p$ the vapor pressure in dynes per square centimeter, $M$ the molecular mass, $T$ the absolute temperature, and $\breve{R}$ the universal gas constant. On the assumption that every atom or molecule of vapor condenses on striking the surface of a solid, equation $1-48 d$ gives the relation between the vapor pressure $p$ and the maximum rate of evaporation $w$ in a vacuum at the absolute temperature $T$, so that the vapor pressure $p$ may be written as

$$
\begin{equation*}
p=w \sqrt{\frac{2 \pi \check{R} T}{M}} \tag{1-48e}
\end{equation*}
$$

$p$ being in dynes per square centimeter.
Langmuir ${ }^{3}$ made use of expression 1-48e for calculating vapor pressure of tungsten from the rate of evaporation, experimentally determined in the following way:
${ }^{8}$ I. Langmuir, Phys. Rev. 2, 327 (1913).

A fine tungsten filament of about 0.1 mm . diameter and about 105 mm . in length, carefully weighed on a delicate micro balance, is supported in the form of a loop inside a bulb with electric leads, which is exhausted to a pressure below $10^{-3} \mathrm{~mm} . \mathrm{Hg}$. The filament is heated to a definite temperature which is kept constant for a time $t$ by maintaining the product $V \sqrt[3]{i}$ constant ( $V$ being the

> Table 1-3. Rate of Evaporation and Vapor Presbure or Tungsten

| Abeolute temperature ( ${ }^{\circ}$ ) | Evaporation (g. per cm. ${ }^{2}$ per sec.) ( $W$ ) | Vapor pressure (mm. of Hg ) |
| :---: | :---: | :---: |
| 2000 | 114. $\times 10^{-15}$ | $6.45 \times 10^{-12}$ |
| 2100 | $1.44 \times 10^{-12}$ | $83.2 \times 10^{-12}$ |
| 2200 | $14.4 \times 10^{-12}$ | 849. $\times 10^{-12}$ |
| 2300 | $116.7 \times 10^{-12}$ | $7.05 \times 10^{-9}$ |
| 2400 | 798. $\times 10^{-12}$ | $49.2 \times 10^{-9}$ |
| 2500 | $4.67 \times 10^{-9}$ | $294 . \times 10^{-0}$ |
| 2600 | $23.6 \times 10^{-9}$ | $1.51 \times 10^{-6}$ |
| 2700 | 106. $\times 10^{-9}$ | $6.95 \times 10^{-6}$ |
| 2800 | 429. $\times 10^{-9}$ | $286 \times 10^{-6}$ |
| 2900 | $1.57 \times 10^{-6}$ | 106. $\times 10^{-6}$ |
| 3000 | $5.23 \times 10^{-6}$ | 0.000362 |
| 3100 | $163 \times 10^{-6}$ | 0.00114 |
| 3200 | $46.7 \times 10^{-6}$ | 0.00333 |
| 3300 | 126. $\times 10^{-6}$ | 0.00910 |
| 3400 | 320. $\times 10^{-6}$ | 0.0234 |
| 3500 | $769 . \times 10^{-6}$ | 0.0572 |
| 3540 | 0.00107 | 0.080 |
| 5100 |  | 760 mm . |

voltage and $i$ the current) during the period $t$. The temperature of the filament is determined by comparing the color of the light emitted from the filament with that from a standard lamp observed through a special blue glass. While heating, the tungsten atoms are emitted as vapor from the filament and, the mean free path at low pressures being great, they strike the walls of the bulb and form a deposit there. Then the heating of the filament is stopped, the bulb is opened, and the rate of evaporation is determined by measuring the decrease in weight of the filament on the micro balance or finding the increase in electrical resistance. Langmuir's results obtained in this way are given in Table 1-3.

Subsequently Langmuir and Mackay ${ }^{4}$ determined in a similar manner the rates of evaporation and the saturation vapor pressures of platinum and molybdenum at various temperatures.

## Section III. Free Path Phenomena

1-15. Free Paths and Collisions.-In the preceding section, in the study of pressures exerted by gases, we were led to an estimation of the high values of the molecular velocities at the normal temperature without any consideration whatever of the actual dimensions of the molecules. In considering the ceaseless motion of molecules as the basis of gaseous pressure, the assumption that


Fig. 1-3. Track of a brownian particle. the size of the molecules, being small in comparison with their average distance apart, could reasonably be neglected, is even valuable for the simplification of the pressure laws.

There are, however, other features of motions which do not permit us to neglect the size of the molecules. Certainphenomena of gases may be explained only by assuming that the molecules have small, yet finite, dimensions. They must also be assumed to exert no mutual forces on each other except when very near together. Molecules of this sort, in a finite limited region, are to be looked upon as spherical small-field molecules with radius $a$. Then as they move forward, when two centers reach a separation as small as $2 a$ a collision occurs, which alters completely the velocities and the directions of the motion. Thus the path of the center of mass of each one of the small-field molecules must be an irregular one, as illustrated in figure 1-3. The individual lengths of these straight free paths vary widely. If the course of a molecule be followed until it has traversed very many free paths, the average of their lengths, called the mean free path, has a definite value. Similarly, the collisions are quite irregularly distributed in time, but if a series of collisions which extends over a considerable time be considered, then there are on the average a definite number of

[^0]collisions in each second and this number is called the collision frequency. The relation between collision frequency and mean free path is obvious. These correlated definite features of the free path phenomena, which form the distinctive qualities of each gas at a specific temperature and pressure, are quite important in understanding actual mechanism of the transport phenomena and thus in deducing their respective laws. Since the production and the measurement of high vacua and the construction of the necessary appliances are to some extent based on the laws of the transport phenomena and those of the molecular streaming, a study of the collision frequency and the mean free path of gas molecules is useful for the science of high vacua.


Fia. 1-4. (A) Gas-kinetic effective cross section and the cross section of the sphere of influence. (B) Cylinder described by the sphere of influence in a time $t$ when the molecule is moving with a velocity $v$.

1-16. Collision Frequency and Mean Free Path.-Let us consider a molecule, which is tentatively taken to be a rigid sphere, of radius $a$, traversing the gas with velocity $v$. Then the center of the molecule cannot come within a distance $\sigma=2 a$ of the center of another molecule without colliding. In a collision, therefore, the centers of mass of two equal molecules cannot come nearer than the distance $\sigma$. The sphere of radius $\sigma$ described about the center of the molecule is known as the sphere of influence. A plane which cuts the sphere of influence right through its center is the cross section of the sphere of influence, illustrated in figure 1-4. As the molecule is moving with the velocity $v$, its sphere of influence describes, in the time $t$, a cylinder of length ot and cross section $\pi_{0}^{2}$. The volume of this cylinder is $\pi \sigma^{2} v t$. As a preliminary step toward the treatment of the actual case, if all other molecules, whose centers lie in the cylinder, be supposed to be at rest, they
will be struck by the original molecule. As the cylinder encloses $\pi \sigma^{2} v t n$ centers of molecules, the number of collisions of the given moving molecule in time $t$ must be $\pi \sigma^{2} n v t$. Hence the number of collisions of the given molecule per second, which is termed collision frequency and denoted by $\nu$, is

$$
\begin{equation*}
\nu=\pi \sigma^{2} n v . \tag{1-49}
\end{equation*}
$$

In deriving the simple and approximate expression 1-49, we have assumed as a mere hypothesis that while the given molecule is moving with the velocity $v$, all the molecules collided with are at rest. In actuality, the molecules are, however, in motion. Hence it is necessary to consider the cylinder described by the sphere of influence of the molecule under consideration as it passes through the gas due to its velocity relative to the molecules collided with. If $v$ be the velocity of the given molecule and $v^{\prime}$ be that of the molecules collided with, the relative velocity of approach, denoted by $v_{r}$, of the two molecules is

$$
\begin{equation*}
v_{r}=\sqrt{v^{2}+v^{\prime 2}-2 v v^{\prime} \cos \theta} \tag{1-50}
\end{equation*}
$$

$\theta$ being the angle between the directions of motion of the two molecules, and the molecules struck in time $t$ are those whose centers lie in a cylinder of the volume $\pi \sigma^{2} v_{r} t$. Hence the collision frequency,

$$
\begin{equation*}
\nu=\pi \sigma^{2} n v_{r} . \tag{1-51}
\end{equation*}
$$

Following Clausius, when the molecules are treated as if they were all moving with the mean velocity $v_{m}$ in all directions which are equally probable, we have,

$$
\begin{equation*}
v=v^{\prime}=v_{m} \tag{1-52}
\end{equation*}
$$

Under these conditions, the speed of the first molecule, relative to one of the others, varies only with the angle between their respective directions of motion. It is known from the kinetic gas theory that among the other molecules which will be moving in all directions, only a fraction $\frac{1}{2} \sin \theta d \theta$ of them will be moving in a direction inclined to the direction of the motion of the original molecule by angle between $\theta$ and $\theta+d \theta$. Hence the value of $v_{r}$ is to beaveraged over the fraction of those whose directions make an angle between $\theta$ and $\theta+d \theta$ with the direction of the velocity of the molecule under consideration. Since the average $\overline{v_{r}}$ is a function of the integral of
the products of the $v_{r}$ and the fraction of those whose velocity directions lie within the solid angle between $\theta$ and $\theta+d \theta$, we have

$$
\begin{equation*}
\bar{v}_{r}=\int_{0}^{\pi} v_{r} \cdot \frac{1}{2} \sin \theta d \theta=\frac{1}{2} \int_{0}^{\pi} v_{r} \cdot \sin \theta d \theta . \tag{1-53a}
\end{equation*}
$$

If in expression 1-53a, we replace $v_{r}$ by its value given in equation $1-50$, we obtain for the mean relative velocity an alternative expression,

$$
\begin{align*}
\overline{v_{r^{\prime}}} & =\frac{1}{2} \int_{0}^{\pi}\left(v^{2}+v^{\prime 2}-2 v v^{\prime} \cos \theta\right)^{3 / 3} \cdot \sin \theta d \theta \\
& =\frac{1}{6 v v^{\prime}}\left[-\left(v-v^{\prime}\right)^{3}+\left(v+v^{\prime}\right)^{3}\right] . \tag{1-53b}
\end{align*}
$$

The mean relative velocity $\overline{v_{r}}$ of the molecules having the velocity $v$ with respect to the molecules of velocity $v^{\prime}$ given in expression $1-53 b$ should be positive whatever be the actual values of $v$ and $v^{\prime}$. Consequently, on introducing the limits of integration, the case when $v$ is greater than $v^{\prime}$ is distinguished from the case of its contrary. Hence,

$$
\begin{align*}
& \overline{v_{r^{\prime}}}=\frac{3 v^{2}+v^{\prime 2}}{3 v} \text { if } v>v^{\prime},  \tag{1-53c}\\
& \overline{v_{r^{\prime}}}=\frac{3 v^{\prime 2}+v^{2}}{3 v^{\prime}} \text { if } v<v^{\prime} . \tag{1-53d}
\end{align*}
$$

In the case of a "homogeneous gas" whose molecular velocities are the same as given in expression 1-52, the relative velocity given in expressions $1-53 \mathrm{~cd}$ reduces to

$$
\begin{equation*}
\overline{v_{r}}=\frac{4}{3} v_{m}, \tag{1-53e}
\end{equation*}
$$

$v_{m}$ being, as stated, the mean velocity of a gas molecule. Hence the mean relative velocity is obviously $\frac{4}{3}$ times the mean velocity of gas molecules.
Now, on introducing in expression 1-51, the value of the mean relative velocity $\bar{\delta}_{r}$ in terms of the mean velocity of the molecules given in equation 1-53c, we obtain the Clausius expression for the colligion frequency,

$$
\begin{equation*}
\nu=\pi \sigma^{2} n \frac{f_{s}}{s} v_{m}, \tag{1-54}
\end{equation*}
$$

which can be valid only on the condition that all molecules move with the same average speed $v_{m}$. It has been pointed out in section $1-12$, of this chapter that the molecules of a gas in equilibrium, however, have speeds ranging all the way from zero up to values many times as great as the average. Hence Clausius' assumption cannot be justified, and his expression 1-53e for $\bar{v}_{r}$ in terms of the average speed $v_{m}$, and consequently his equation $1-54$ for the collision frequency, cannot be rigorous.

Actually, however, since $v^{\prime} \neq v \neq v_{m}$, it is required to determine the probable mean relative velocity $\overline{v_{r}}$ of the molecules of the velocity $v$ with respect to the molecules of the velocity $v^{\prime}$ from the probabilities of the velocities $v$ and $v^{\prime}$ taken from the law of distribution of velocities. From the consideration of this law given in expression 1-40, it is obvious that the probability that the velocity of a molecule lies between $v^{\prime}$ and $v^{\prime}+d v^{\prime}$ is

$$
\begin{equation*}
P_{\bar{v}^{\prime}}=4 \pi a^{3} c^{-b v^{\prime}} v^{\prime 2} d v^{\prime} \tag{1-55a}
\end{equation*}
$$

and likewise the probability that the velocity lies between $v$ and $v+d v$ is

$$
\begin{equation*}
P_{₹}=4 \pi a^{3} e^{-b v^{2}} v^{2} d v . \tag{1-55b}
\end{equation*}
$$

The mean relative velocity in fact depends on both $v$ and $v^{\prime}$ and on their relative magnitudes. Hence, as a first step in proceeding to the actual case, let us consider the variation of $v^{\prime}$. The average relative velocity $v_{7 v}$, of the molecules of the velocity $v$ with respect to the rest is

$$
\begin{equation*}
v_{\bar{r} v^{\prime}}=\int_{0}^{\infty} v_{r} \cdot 4 \pi a^{3} e^{-\delta v^{\prime 2}} v^{\prime 2} d v^{\prime} \tag{1-56}
\end{equation*}
$$

$v_{r}$ has two different values depending upon whether $v^{\prime}$ is greater than $v$ or not. Therefore, on replacing $v_{r}$ by both of its values given in $1-53 c d$ in expression 1-56, we obtain

$$
\begin{align*}
& v_{\mp v^{\prime}}=\int_{0}^{0} \frac{3 v^{2}+v^{\prime 2}}{3 v} \cdot 4 \pi a^{3} e^{-b v^{\prime 2}} v^{\prime 2} d v^{\prime} \\
&+\int_{v}^{\infty} \frac{3 v^{\prime 2}+v^{2}}{3 v^{\prime}} \cdot 4 \pi a^{8} e^{-b v^{\prime \prime}} v^{\prime 2} d v^{\prime} \tag{1-57}
\end{align*}
$$

We have still to introduce the probability $P_{8}$ given in 1-55b. The product $v_{F v}$ and $P_{\eta}$ gives the actual average relative velocity $\bar{v}_{r}$ of
any molecule with respect to all others. Hence we have

$$
\begin{align*}
\sigma_{r} & =\int_{0}^{\infty} 4 \pi a^{3} e^{-b v^{2} v^{2} d v} \int_{0}^{\infty} \frac{3 v^{2}+v^{\prime 2}}{3 v} \cdot 4 \pi a^{3} e^{-b v^{\prime} v^{\prime}} d v^{\prime} \\
& +\int_{0}^{\infty} 4 \pi a^{3} e^{-b v^{2} v^{2} d v} \int_{v}^{\infty} \frac{3 v^{\prime 2}+v^{2}}{3 v^{\prime}} \cdot 4 \pi a^{3} e^{-b v^{\prime} v^{\prime 2}} d v^{\prime} \\
= & 16 \pi^{2} a^{6}\left\{\phi_{1}+\phi_{2}\right\}, \tag{1-58}
\end{align*}
$$

where $\quad \phi_{1}=\int_{0}^{\infty} v^{2} e^{-b v^{2}} d v \int_{0}^{v} \frac{3 v^{2}+v^{\prime 2}}{3 v} \cdot v^{2} e^{-b v^{\prime 2}} d v^{\prime}$,

$$
\phi_{2}=\int_{0}^{\infty} v^{2} e^{-b v^{2}} d v \int_{0}^{\infty} \frac{3 v^{\prime 2}+v^{2}}{3 v^{\prime}} \cdot v^{\prime 2} e^{-b v^{\prime 2}} d v^{\prime}
$$

Since it can be shown that

$$
\begin{align*}
& \phi_{1}=\phi_{2}=\frac{1}{8 \sqrt{2}} \sqrt{\frac{\pi}{b^{7}}} \\
& \bar{v}_{r}=\frac{4}{\sqrt{2 b \pi}}=4 \sqrt{\frac{k T}{m \pi}} . \tag{1-59}
\end{align*}
$$

Since the average velocity of a molecule (1-46b), $v_{m}=4 \sqrt{k T / 2 \pi m}$, we have Maxwell's expression for $\overline{v_{r}}$ in terms of the mean velocity $v_{m}$ :

$$
\begin{equation*}
\bar{v}_{r}=\sqrt{2} \cdot v_{m} \tag{1-60}
\end{equation*}
$$

Hence the actual mean relative velocity $\overline{v_{r}}$ for collisions between molecules of all possible velocities is $\sqrt{2}$ times the average velocity $\boldsymbol{v}_{m}$.

Now, if we introduce in equation 1-51 the value of the mean relative velocity in terms of the mean velocity given in equation $1-60$, we have Maxwell's expression for the collision frequency,

$$
\begin{equation*}
\nu=\sqrt{2} v_{m} \pi \sigma^{2} n . \tag{1-61}
\end{equation*}
$$

As the molecules of an ideal gas are free from mutual force action, or in other words, as there are no attractions or repulsions between the molecules of a perfect gas, each molecule moves in a straight line between collisions. The course which a single molecule traverses for a considerable time is, as already mentioned, a sigzag of many straight free paths of irregular lengths. The mean
free path is the average of the individual lengths of a very large number of free paths. If $\lambda_{1}, \lambda_{2}, \lambda_{3}, \cdots \lambda_{n}$ be such free paths described during the time intervals $t_{1}, t_{2}, t_{3}, \cdots t_{n}$ where $t_{1}+$ $t_{2}+t_{3}+\cdots+t_{n}=1$ second, with velocities $v_{1}, v_{2}, v_{3}, \cdots v_{n}$ respectively, then the mean free path, denoted by $\lambda$, is expressed

$$
\begin{equation*}
\lambda=\frac{\lambda_{1}+\lambda_{2}+\lambda_{3}+\cdots+\lambda_{n}}{\nu}=\frac{v_{1} t_{1}+v_{2} t_{2}+v_{3} t_{3}+\cdots+v_{n} t_{n}}{\nu}=\frac{v_{m}}{\nu} \tag{1-62a}
\end{equation*}
$$

inasmuch as the velocity of a single molecule averaged over a long period of time is equal to the average velocity of a large number of molecules at a single instant.

If we now introduce in expression 1-62a, the Clausius value for the collision frequency $\nu$, given in 1-54, we obtain the Clausius equation for the mean free path $\lambda$,

$$
\begin{equation*}
\lambda=\frac{3}{4 \pi \sigma^{2} n} \tag{1-62b}
\end{equation*}
$$

If Maxwell's more accurate value for $\nu$ given in equation 1-61 be used, Maxwell's more rigorous expression for the mean free path $\lambda$ is obtained:

$$
\begin{equation*}
\lambda=\frac{1}{\sqrt{2 \pi} \sigma^{2} n} \tag{1-62c}
\end{equation*}
$$

Now, expressions $1-54$ and $1-62 b$, as well as $1-60$ and $1-62 c$, imply that the collision frequency is directly proportional to the density and also to the square root of the absolute temperature, since $v_{m} \propto \sqrt{T}$, while the mean free path on the other hand varies only with the density and is inversely proportional to it, being, therefore, at a given temperature, inversely proportional to the pressure. The facts that $\nu$ is directly and $\lambda$ inversely proportional to the density of a gas, which are also obvious from Tables 1-4 and 1-5, are of fundamental importance, for it is with the consideration of these that vacuum generating and measuring devices are designed.

1-17. Distribution of Free Paths.-The course which a single gas molecule takes during a considerable time is a zigzag of many free paths of irregular lengths, generally differing from the mean
Table 1-4. Molecular Data for Nitrogen at $20^{\circ}$ C. at the Pressures Given Below

| Pressure in mm. Hg | 760 | 1 | $10^{-3}$ | $10^{-6}$ | $10^{-7}$ | $10^{-9}$ | $10^{-11}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Number of molecules per cm. ${ }^{\text {² }}$ | $2.503 \cdot 10^{19}$ | $3.293 \cdot 10^{16}$ | $3.293 \cdot 10^{18}$ | $3.293 \cdot 10^{11}$ | $3.293 \cdot 10^{9}$ | 3.293-10 ${ }^{7}$ | 3.293-10 ${ }^{5}$ |
| Density gm. $/ \mathrm{cm} .^{3}$ | $1.165 \cdot 10^{-3}$ | $1.536 \cdot 10^{-6}$ | $1.536 \cdot 10^{-9}$ | $1.536 \cdot 10^{-11}$ | $1.536 \cdot 10^{-13}$ | $1.536 \cdot 10^{-15}$ | $1.536 \cdot 10^{-17}$ |
| Collision frequency | $5.17 \cdot 10^{9}$ | $6.82 \cdot 10^{6}$ | $6.82 \cdot 10^{3}$ | 6.82-10 | $6.82 \cdot 10^{-1}$ | $6.82 \cdot 10^{-3}$ | $6.82 \cdot 10^{-5}$ |
| Mean free path in cm. | $9.09 \cdot 10^{-6}$ | $6.91 \cdot 10^{-3}$ | 6.91 | $6.91 \cdot 10^{2}$ | 6.91-104 | $6.91 \cdot 10^{6}$ | $\mathbf{6 . 9 1} \cdot 10^{8}$ |

Table 1-5. Monecular Data for Gases at a Temperature of $20^{\circ} \mathrm{C}$.

| Gas or vapor | Pressure $760 \mathrm{~mm} . \mathbf{H g}$ |  |  | Pressure $10^{-6} \mathrm{~mm} . \mathrm{Hg}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\rho$-density <br> g. $/ \mathrm{cm} .^{3}$ | v-collision frequency | $\lambda$-mean free path in cm. | $\rho$-density <br> g. $/ \mathrm{cm} .^{3}$ | n-collision frequency | $\lambda$-mean free path in cm. |
| Hydrogen | $0.0838 \cdot 10^{-3}$ | $14.86 \cdot 10^{9}$ | $11.80 \cdot 10^{-6}$ | $0.110 \cdot 10^{-12}$ | 19.60 | $8.97 \cdot 10^{3}$ |
| Helium | $0.166 \cdot 10^{-3}$ | $7.33 \cdot 10^{9}$ | $17.00 \cdot 10^{-6}$ | $0.220 \cdot 10^{-12}$ | 9.64 | $12.90 \cdot 10^{3}$ |
| Water vapor | $0.749 \cdot 10^{-3}$ | $10.44 \cdot 10^{9}$ | $5.62 \cdot 10^{-6}$ | $0.986 \cdot 10^{-12}$ | 13.74 | $4.27 \cdot 10^{2}$ |
| Neon | $0.839 \cdot 10^{-3}$ | $3.85 \cdot 10^{9}$ | $14.40 \cdot 10^{-6}$ | $1.10 \cdot 10^{-12}$ | 5.07 | $10.90 \cdot 10^{8}$ |
| Carbon monoxide | $1.16 \cdot 10^{-3}$ | $10.84 \cdot 10^{9}$ | $4.34 \cdot 10^{-6}$ | $1.53 \cdot 10^{-12}$ | 14.26 | $3.30 \cdot 10^{3}$ |
| Nitrogen | $1.17 \cdot 10^{-3}$ | $5.17 \cdot 10^{9}$ | $9.09 \cdot 10^{-6}$ | $1.54 \cdot 10^{-12}$ | 6.82 | $6.91 \cdot 10^{3}$ |
| Air | $1.20 \cdot 10^{-3}$ | $7.12 \cdot 10^{9}$ | $6.50 \cdot 10^{-6}$ | $1.58 \cdot 10^{-12}$ | 9.37 | $4.94 \cdot 10^{3}$ |
| Oxygen | $1.33 \cdot 10^{-3}$ | $4.14 \cdot 10^{9}$ | $10.65 \cdot 10^{-6}$ | $1.75 \cdot 10^{-12}$ | 5.44 | $8.09 \cdot 10^{3}$ |
| Argon | $1.66 \cdot 10^{-8}$ | $3.69 \cdot 10^{9}$ | $10.69 \cdot 10^{-6}$ | $2.19 \cdot 10^{-12}$ | 4.85 | $8.13 \cdot 10^{3}$ |
| Carbon dioxide | $1.83 \cdot 10^{-3}$ | $8.80 \cdot 10^{9}$ | $4.63 \cdot 10^{-6}$ | $2.41 \cdot 10^{-12}$ | 11.58 | $3.24 \cdot 10^{3}$ |
| Krypton | $3.45 \cdot 10^{-3}$ | $3.00 \cdot 10^{9}$ | $9.12 \cdot 10^{-6}$ | $4.53 \cdot 10^{-12}$ | 3.95 | $6.93 \cdot 10^{3}$ |
| Xenon | $5.41 \cdot 10^{-3}$ | $2.84 \cdot 10^{9}$ | $7.69 \cdot 10^{-6}$ | $7.12 \cdot 10^{-12}$ | 3.74 | $5.84 \cdot 10^{3}$ |
| Mercury vapor | $8.34 \cdot 10^{-3}$ | $2.004 \cdot 10^{9}$ | $8.78 \cdot 10^{-6}$ | $10.70 \cdot 10^{-12}$ | 2.64 | $6.67 \cdot 10^{3}$ |

path $\lambda$. They are, however, distributed about the mean path; and the law which governs the distribution of the free paths may be derived from the probability considerations as follows: It can be reasonably supposed that the molecules which have traversed a distance $x$ have all equal chances of covering a further length $d x$ without suffering collision. The probability of suffering no collision in the path $x+d x$ comprises, on the one hand, the probability of suffering no collision in the path $x$, denoted by $f(x)$, and on the other, that of experiencing no collision in the path $d x$, denoted by the expression $1-\alpha d x, \alpha$ being a constant, because the probability of collision in $d x$ is proportional to this small distance. Therefore the probability that it will suffer no collision as it traverses the distance $x+d x$, denoted by $f(x+d x)$, being the product of the two factors, may be written as

$$
f(x+d x)=f(x)(1-\alpha d x)
$$

or

$$
f^{\prime}(x) d x=-f(x) \alpha d x
$$

Therefore,

$$
f^{\prime}(x)=-\alpha f(x)
$$

which, by integration, becomes

$$
\begin{equation*}
f(x)=\beta e^{-\alpha x} \tag{1-63a}
\end{equation*}
$$

Now, if the path traversed is taken to be zero, the probability of a path without collision becomes an absolute certainty, so that for $x=0, f(x)$ reduces to unity, and therefore $\beta=1$. In order to obtain a meaning for the constant $\alpha$, it may be noted that as the collision frequency, or the number of collisions which a molecule experiences in one second, is $\nu$, the number of free paths of the molecule per second must be $\nu$. Of these $\nu$ free paths, those which exceed $x$ may be written as

$$
\nu f(x)=\nu e^{-\alpha x},
$$

and those which exceed $x+d x$ as

$$
\nu f(x+d x)=\nu e^{-\alpha(x+d x)},
$$

so that the number of those which extend between $x$ and $x+d x$ is given by

$$
\nu f(x)-\nu f(x+d x)=\nu e^{-\alpha x}-\nu e^{-\alpha(x+d x)},
$$

which, on using the expansion of $e^{-\alpha d x}$ in the power series of $x$ and neglecting powers higher than the first, becomes

$$
\nu e^{-\alpha x}\left(1-e^{-\alpha d x}\right)=\nu \alpha d x e^{-\alpha x}
$$

In this case, the probable length of each free path being $x$, the sum of their lengths is

$$
\nu \alpha x d x e^{-\alpha x}
$$

and if the summation is extended to all the free paths traversed in one second, we obtain the velocity of the molecule:

$$
v=\nu \alpha \int_{0}^{\infty} e^{-\alpha x} x d x=\frac{\nu}{\alpha} .
$$

Since the mean free path $\lambda=v / v$, the constant $\alpha=1 / \lambda$.
Now, on introducing the values $\beta=1$ and $\alpha=1 / \lambda$ in expression 1-63a, we obtain the probability of a molecule having a free path equal to or greater than $x$; this may be written as

$$
\begin{equation*}
f(x)=e^{-x / \lambda} \tag{1-63b}
\end{equation*}
$$



Fig. 1-6. Born's arrangement for the direct determination of mean free path.
1-18. Determination of Mean Free Path.-On the basis of the definition of the mean free path by the exponential law, expressed in equation $1-63 b$, Born ${ }^{5}$ directly determined it by measuring the attenuation of a beam of silver atoms on passage through a gas which is at rest. This was achieved by the device illustrated in figuxe 1-5. This apparatus consists of a quarte tube $Q$ in which silver is heated at the reservoir $S$ by an electric oven. The vapor,
${ }^{5}$ Max Born, Phye. Zeits. 21, 578 (1920).
which the heated silver gives out, escaping through the narrow slit $R$, passes through a circular perforation in each of the four brass disks $P_{1}, P_{2}, P_{3}, P_{4}$, which are placed 1 cm . apart. Each of these disks is provided with a glass quadrant $G$ whose apex lies at the center of the hole, and each quadrant is displaced through a right angle relative to the adjoining one. By this arrangement each quadrant receives only a quarter of the incident leam of the silver vapor, and the disks being cooled by a mixture of solid carbon dioxide and salt, the silver atoms deposit on the quadrants. The whole body of the apparatus is exhausted by means of a highvacuum pump, and the pressure is measured by suitable absolute

Table 1-6

| Gas | Pressure in $\mathrm{mm} . \mathrm{Hg}$ | Mean free path in cm. |
| :---: | :---: | :---: |
| Air | $58 \times 10^{-8}$ | 1.7 |
| Air | $45 \times 10^{-8}$ | 2.4 |

manometers. The relative amounts of silver deposited on the quadrants are obtained by a photometric comparison of the density of the deposit, first when the quadrants are under the pressures of the highest attainable vacuum, and next when a certain quantity of gas or air is admitted into the body so as to have an appreciable effect on the free-path phenomena. Now if $D_{1}{ }^{\prime}$ be the density of the layer of silver on the first quadrant at the pressure of the highest attainable vacuum, $D_{1}$ that of the silver layer on the same quadrant when the mean free path is $\lambda$, and $x_{1}$ be the distance of the first disk from the source of the beam of silver atoms, we have, by equation 1-63b,

$$
\begin{equation*}
D_{1}=D_{1}^{\prime} e^{-x_{1} / \lambda} \tag{1-64a}
\end{equation*}
$$

and similarly for the second disk

$$
\begin{equation*}
D_{2}=D_{2}{ }^{\prime} e^{-x_{3} / \lambda} \tag{1-64b}
\end{equation*}
$$

Therefore,

$$
\begin{equation*}
\lambda=\frac{x_{2}-x_{1}}{\log \left(\frac{D_{1}}{D_{2}} \cdot \frac{D_{2}{ }^{\prime}}{D_{1}^{\prime}}\right)} \tag{1-65}
\end{equation*}
$$

In this way Born measured directly the mean free path $\boldsymbol{\lambda}$, simul-
taneously verifying the law of distribution of free paths; his values of the mean free path at pressures indicated are given in Table 1-6.

## Section IV. Transport Phenomena

1-19. Introduction.-In the preceding section our study of the gaseous phenomena was limited to cases of gases in equilibrium. There we dealt with the phenomena of gases whose different parts are all alike as regards momentum, energy distribution, and constitution. If each of these three singly, or all the three conjointly, of any one part of a gas be unlike that or those of another part, the gas exhibits a different set of phenomena. When a gas in an enclosure is set in motion, the motion will be dissipated gradually until the pressure and the temperature become uniform throughout and the gas attains a state of internal equilibrium. This gradual process of the dissipation of the internal motion of a gas is due to viscosity. If the different parts of a gas in an enclosure be at different temperatures, the heat from the regions at higher temperature is transferred to the regions of lower temperature until temperature equilibrium is attained. The transference of heat, from molecule to molecule due to molecular random motion from the regions at higher temperature to those at lower temperature until there is uniformity of temperature throughout the gas, is known as conduction. A gas is not in equilibrium if its constitution be different in its different parts. In this case the molecules of the different constituent gases distribute themselves, as a result of chaotic random heat motion of the molecules, in such a way that the composition finally becomes uniform, thereby attaining equilibrium. This gradual process of distribution is called diffusion. These three phenomena-viscosity, conduction, and diffusion-represent the transfer of momentum, energy, and mass, respectively, and they are referred to under the name of transport phenomena. A simple view of the mechanism of the fundamentals of transport phenomena forms the basis of certain considerations of the science and technique of high vacua. Hence we shall treat each main item of the transport phenomena only as far as necessary for the study of the science of high vacua.

1-20A. Viscosity.-Suppose a gas is streaming in the $x$-direction in such a manner that different layers have a velocity the same in
direction but varying in magnitude from layer to layer, and this variation in magnitude is most rapid in a certain direction perpendicular to that of the velocity, while over a plane perpendicular to the direction of maximum variation, the velocity is constant. In this case the maximum rate of variation is known as the velocity gradient. If $v_{x}$ be the mass velocity of the gas in the $x$-direction and $d v_{x} / d y$ the velocity gradient lying along the $y$-axis, the shearing component of stress in the $y$-direction which tends to equalize the velocities at the two adjacent layers considered is given by

$$
\begin{equation*}
F_{x y}=-\eta \frac{d v_{x}}{d y} \tag{1-66}
\end{equation*}
$$

where $\eta$ is a constant of proportionality characteristic of the gas, called the coefficient of viscosity. Viscosity occurs when the faster-moving molecules in the upper layers pass down into the lower layers of molecules, which are thereby accelerated, and the slower molecules in the lower layers pass into the upper layers of molecules, which are thereby retarded, until the gas attains a state of internal equilibrium. In this process of the passage of molecules from layer to layer, there is obviously a transfer of momentum from the faster layer to the adjacent slower layer throughout the gas, thereby leading to the establishment of the velocity gradient from layer to layer.

Owing to the relation between the transfer of momentum and the velocity gradient, on the one hand, and to the close association of the latter with the coefficient of viscosity in equation 1-66, on the other, an analysis of the process of the transfer of momentum would render it possible to derive an expression for the coefficient of viscosity. As from the second law of Newton it follows that force is equal to the time rate of increase of momentum, the shearing component of stress $F_{x y}$ must be equal to the velocity component of momentum which is transferred across a unit area perpendicular to the $y$-axis in unit time. To study further this component of momentum and thus to know the mechanism of viscosity, let it be assumed that the thermal velocities of all the molecules are the same and are considered to be equal to the mean velocity $v_{m}$, as in the case of the derivation of the Clausius expression for the collision frequency. If we consider only adjacent layers of a gas a distance $y$ apart, we find that the molecules in the
upper layers have, besides the thermal velocity $v_{m}$, an additional streaming velocity $v_{x}+\left(d v_{x} / d y\right) \cdot y$, while the molecules in the lower layers have the translational velocity $v_{x}-\left(d v_{x} / d y\right) \cdot y$.

Assume a unit area perpendicular to the $y$-axis across which the $x$-component of momentum is transferred by the passage of gas molecules from the upper layer, and let the origin be at the center of this unit area as shown in figure 1-6. Take a volume element $d x d y d z$ at $P$, a distance $r$ from the origin, having $n$ molecules per


Fig. 1-6.
cubic centimeter, and consider the molecules whose free paths begin in this volume element. The $n d x d y d z$ of molecules contained in the volume element experience $n \nu d x d y d z$ collisions per unit time. So in each second $n v d x d y d z$ molecules start new paths leaving the volume element, and of these $e^{-r / \lambda} \nu n d x d y d z$ molecules go the distance $r$ or more without colliding. As all directions are equally probable, and as the unit area at $O$ subtends a solid angle $\cos \theta / r^{2}$, the fraction $\cos \theta \cdot 1 / 4 \pi r^{2}$ of these is directed so as to pass through the unit area at $O$. Consequently a number of

$$
\frac{m \cos \theta}{4 \pi r^{2}} \cdot e^{-r / \lambda} d x d y d z,
$$

molecules whose free paths originate in the volume element during unit time pass through the unit area before suffering a collision.

Now, since the thermal velocity throughout the gas is taken to be the same, and the translatory velocity at $P$ is

$$
v_{x}+\frac{d v_{x}}{d y} r \cos \theta
$$

and that at $P^{\prime}$ of the lower layers is

$$
v_{x}-\frac{d v_{x}}{d y} r \cos \theta
$$

the momentum carried per second by each molecule through the unit square under consideration from the volume element at $P$ is

$$
m\left(v_{x}+\frac{d v_{x}}{d y} r \cos \theta\right)
$$

and that from the volume element at $P^{\prime}$ is

$$
m\left(v_{x}-\frac{d v_{x}}{d y} r \cos \theta\right)
$$

Hence the momentum transfer from higher values of $y$ to lower values of $y$ is

$$
-\frac{n m v_{x} \nu}{4 \pi} \frac{\cos \theta}{r^{2}} e^{-r / \lambda} d x d y d z-n m r \cos ^{2} \theta \frac{d v_{x}}{d y} e^{-r / \lambda} \nu d x d y d z
$$

On integrating this value of the momentum transfer from $r=0$ to $r=\infty$ and also on integrating it so that the volume element covers all the space above the $x z$-plane, we obtain the momentum per second going downward from the above layers through the unit area at $O$, thus:

$$
\begin{aligned}
x_{\square} \downarrow=-\frac{n m \nu}{4 \pi}\left(v_{x}\right. & \int_{0}^{\infty} e^{-r / \lambda} d r \int_{0}^{\pi / 2} \cos \theta \sin \theta d \theta \int_{0}^{2 \pi} d \phi \\
& \left.+\frac{d v_{x}}{d y} \int_{0}^{\infty} r e^{-r / \lambda} d r \int_{0}^{\pi / 2} \cos ^{2} \theta \sin \theta d \theta \int_{0}^{2 \pi} d \phi\right),
\end{aligned}
$$

where $d x d y d z$ is replaced by $d r(r \sin \theta d \phi)(r d \theta)$ and $\theta$ is integrated from 0 to $\pi / 2$ and $\phi$ from 0 to $2 \pi$.

Now, keeping in mind the translatory velocity below the xzplane and the corresponding momentum carried by the molecules,
the momentum transfer from below $x z$-plane upward from the volume element at $P^{\prime}$ may similarly be written,

$$
\begin{aligned}
x_{\square} \uparrow=\frac{n m \nu}{4 \pi}\left(v_{x}\right. & \int_{0}^{\infty} e^{-r / \lambda} d r \int_{0}^{\pi / 2} \cos \theta \sin \theta d \theta \int_{0}^{2 \pi} d \phi \\
& \left.-\frac{d v_{x}}{d y} \int_{0}^{\infty} r e^{-r / \lambda} d r \int_{0}^{\pi / 2} \cos ^{2} \theta \sin \theta d \theta \int_{0}^{2 \pi} d \phi\right) .
\end{aligned}
$$

On adding these two terms $\chi_{\square} \downarrow$ and $\chi_{\square} \uparrow$ and integrating for the total transfer of momentum we obtain,

$$
\begin{equation*}
x_{\square} \downarrow \uparrow=-\frac{4 \pi n m \nu \lambda^{2}}{3(4 \pi)} \frac{d v_{x}}{d y}=-\frac{1}{3} n m \lambda v_{m} \frac{d v_{x}}{d y}, \tag{1-67}
\end{equation*}
$$

since $\nu=v_{m} / \lambda$. This total transfer of momentum through unit area per second is equal to the shearing stress. Hence from (1-66) and (1-67)

$$
\begin{equation*}
-\eta \frac{d v_{x}}{d y}=-\frac{1}{3} n m \lambda v_{m} \frac{d v_{x}}{d y} . \tag{1-68}
\end{equation*}
$$

Therefore the coefficient of viscosity is

$$
\begin{equation*}
\eta=\frac{1}{3} n m \lambda v_{m}=\frac{1}{3} \rho \lambda v_{m}, \tag{1-69}
\end{equation*}
$$

since $m n$ is the density $\rho$.
In deriving expression 1-69 for the coefficient of viscosity, the integration was carried out on the assumption that the free path is the same for molecules moving with all speeds. In reality, however, the faster-moving molecules have longer free paths and carry greater momentum. Hence the relation expressed in the equation cannot be quite rigorous. Applying Maxwell's velocity distribution law in the calculation for the viscosity coefficient, the following expression is derived which replaces equation 1-69:

$$
\begin{equation*}
\eta=0.3502 \rho \lambda v_{m} . \tag{1-70}
\end{equation*}
$$

This calculation contains another error. In deriving this expression, the collision frequency is maintained as constant, whereas it really varies during the passage of the molecule because of the variation in the translatory velocity of the gas through which the molecule is passing. After the necessary calculation to allow for this effect, the resulting expression for the coefficient of viscosity is

$$
\begin{equation*}
\eta=0.310 \rho \lambda v_{\mathrm{m}} . \tag{1-71}
\end{equation*}
$$

Equation 1-71 contains still another error, inasmuch as its calculation is based on the assumption that Maxwell's velocitydistribution law holds even in the case of molecules that have just collided at any point. It can be justly considered that in such cases the molecules exhibit some departure from Maxwellian distribution. Molecules which have come from a region of higher translatory velocity have an average excess of velocity in that direction and after colliding they might retain some of this excess, so that the transfer of momentum would be greater than that found in the previous calculations. So the expression may further be corrected for the persistence of velocity after collision. Keeping this fact in view, Chapman ${ }^{6}$ and also Enskog, ${ }^{7}$ after following a rigorous method of analysis by means of successive approximations, give an expression for the coefficient of viscosity,

$$
\begin{equation*}
\eta=0.499 \rho \lambda v_{m}, \tag{1-72a}
\end{equation*}
$$

where $\rho$ as usual is the density in grams per cubic centimeter, $\lambda$ the mean free path, and $v_{m}$ the mean molecular speed. This equation is probably to be regarded as a correct expression for a homogeneous gas of elastic spherical molecules at ordinary pressures.

1-20B. Viscosity, Density, and Temperature.-If the value of the mean free path given in equation $1-62 c$ be introduced in the formula 1-72a, we obtain an alternative expression for the coefficient of viscosity which may be written,

$$
\begin{equation*}
\eta=\frac{0.499}{\sqrt{2}} \frac{m v_{m}}{\pi \sigma^{2}} \tag{1-72b}
\end{equation*}
$$

where $m$ is the mass of a gas molecule and $\sigma$ the molecular diameter. From this equation $1-72 b$ it is obvious that if the temperature of a gas be constant, the viscosity of a gas is independent of its density. It was experimentally found by Meyer, ${ }^{8}$ Maxwell, ${ }^{9}$ and subsequently by others, that this law held quite true for a gas at pres-

[^1]sures between 760 mm . and 10 mm . of mercury. It fails, however, at higher densities since the intermolecular forces then have a noticeable influence upon the transference of momentum. Again at the pressures of high vacua, when the mean free path becomes comparable with the spatial dimensions of the container, the law fails, as might be expected. In either case when the number of intermolecular collisions is almost vanishingly small, the effects of individual molecules must be simply additive and the viscosity should then be proportional to the density and therefore to the pressure. It may be noted that this dependence of the viscosity upon the pressure is utilized in the viscosity gauges (described in the fourth section of chapter 4) for measuring the pressures in high vacua.

The molecular mean velocity $v_{m}$ appears in the viscosity equations. Now since $v_{m}$, as shown in equation $1-46 b$, is inversely proportional to $\sqrt{m}$, the viscosity for different gases should be a linear function of $\sqrt{m}$; and this is found to be approximately true. Again, it can be noted that the molecular mean velocity $v_{m}$ is proportional to the square root of absolute temperature. Hence the viscosity should vary as the square root of the absolute temperature, but it is actually found to vary much more rapidly. To eliminate this discrepancy, Sutherland ${ }^{10}$ worked out a theory on the assumption that the molecules are hard spheres having a weak attraction between them, falling off rapidly with distance. Such an attraction acts in two ways to produce shortening of the mean free path. In the first place, the molecules which pass near each other at close range without actually striking against each other experience a deflection. Secondly, this deflection may actually cause some molecules to collide when they would otherwise have passed by each other without touching, thereby increasing the collision frequency. Of these two effects, Sutherland, ignoring the first, gave prominence to the second. After the necessary calculation to allow for this effect, Sutherland deduced an expression for the molecular effective cross section $S$ :

$$
\begin{equation*}
S=S_{0}\left[1-4 \frac{\omega(\sigma)}{m v^{2}}\right] \tag{1-73}
\end{equation*}
$$

where $\omega$ is the intensity of the force field and $S_{0}$ is the cross section
for the zero field. Now, on substituting the value of $S$ from equation 1-73 in Maxwell's expression for the free path 1-62c, we obtain Sutherland's mean free path expression, which becomes the function of temperature given by

$$
\begin{equation*}
\lambda_{s}=\frac{\lambda_{m}}{1+\frac{c}{T}} . \tag{1-74}
\end{equation*}
$$

In equation 1-74 $\lambda_{m}=1 / \sqrt{2} n \pi \sigma^{2} ; \pi \sigma^{2}=S_{0} ; c=-4 \omega \sigma T / m v^{2}=$ a constant and $T$ is the absolute temperature.

If the term $\lambda$ in the viscosity expression 1-72a be replaced by the value of $\lambda_{s}$ given in equation 1-74, we have an expression for the viscosity of a gas whose molecules are influenced by mutual force action in the form

$$
\begin{equation*}
\eta_{s}=0.499 p v_{m} \frac{\lambda_{m}}{1+\frac{c}{T}}, \tag{1-75a}
\end{equation*}
$$

or

$$
\begin{equation*}
\eta_{s}=0.499 \rho v_{m} \frac{1}{\left(1+\frac{c}{T}\right) \sqrt{2 \pi n \sigma^{2}}} . \tag{1.75b}
\end{equation*}
$$

If the coefficient of viscosity $\eta_{s}$ at $273.14^{\circ}$ absolute scale of temperature be denoted by $\eta_{s o}$ and that at $273.14+t=T$ by $\eta_{s t}$, the respective values of $\eta_{s t}$ and $\eta_{s o}$ are in the ratio of

$$
\begin{equation*}
\frac{\eta_{s t}}{\eta_{s o}}=\frac{0.499 \rho v_{m t}\left\{\frac{T}{(T+c) \sqrt{2} \pi n \sigma^{2}}\right\}}{0.499 \rho v_{m 0}\left\{\frac{273.14}{(273.14+c) \sqrt{2} \pi n \sigma^{2}}\right\}}, \tag{1-76a}
\end{equation*}
$$

which on simplification becomes

$$
\begin{equation*}
\frac{\eta_{s t}}{\eta_{s o}}=\frac{v_{m t}}{v_{m 0}} \cdot \frac{T(273.14+c)}{273.14(T+c)} \tag{1-76b}
\end{equation*}
$$

and since from 1-46b $v_{m}=\sqrt{s k T / m \pi}$ and consequently $v_{m t} / v_{m 0}=$
$\sqrt{T / 273.14}, \eta_{\Delta t}$ may be expressed in terms of $\eta_{s o}$ thus:

$$
\begin{equation*}
\eta_{s t}=\eta_{s o}\left\{\sqrt{\frac{T}{273.14}} \cdot \frac{T(273.14+c)}{273.14(T+c)}\right\} \tag{1-76c}
\end{equation*}
$$

or,

$$
\begin{equation*}
\eta_{a t}=\eta_{\Delta o}\left(\frac{273.14+c}{T+c}\right)\left(\frac{T}{273.14}\right)^{3 / 2} . \tag{1-76d}
\end{equation*}
$$

From these expressions it is obvious that the viscosity of a gas depends upon the temperature. If the coefficient of viscosity of a gas at a particular temperature be measured and the value of the constant $c$ be known, its viscosity at any other temperature can be computed from the relations given in the expression $1-76 c$ or 1-76d.

1-20C. Determination of Mean Free Path and Molecular Diameter of Gas Molecules from Viscosity Measurements.-The coefficient of viscosity $\eta_{s t}$ of a gas with intermolecular attraction at a temperature $T$ can be measured by either the method based on the measurement of the rate of gaseous flow through a capillary tube, or by any one of those methods which are based on the measurement of the damping on the oscillations of a pendulum, a constant deflecting force of a cylinder in the rotating mass of gas and the fall of small spheres through a gas. If the measured values of the viscosity, the density, and the molecular mean velocity $v_{m t}$ of a gas at a temperature $T$ be introduced in the equation

$$
\begin{equation*}
\lambda_{s t}=\frac{\lambda_{m}}{1+\frac{c}{T}}=\frac{\eta_{s t}}{0.499 \rho v_{m t}}, \tag{1-77}
\end{equation*}
$$

which is derived from expressions 1-74 and 1-75a, the value of the mean free path $\lambda_{s t}$ of hard spherical molecules with intermolecular attraction at a temperature $T$ is obtained.

If equation $1-75 b$ be solved for the effective molecular diameter $\sigma$, we get

$$
\begin{equation*}
\sigma_{s t}=\sqrt{\frac{0.499 \rho v_{m t}}{2 \pi n \eta_{s t}}} \tag{1-78}
\end{equation*}
$$

and on introducing the values of the viscosity coefficient $\eta_{s t}$, the number $n$ of molecules and the molecular mean velocity $v_{m t}$ in
expression 1-78, the value of the effective diameter of gaseous molecules at a temperature $T$ is obtained. In deriving expression 1-78 for the determination of the molecular diameter, the persistence of translatory velocity, the temperature, and the Maxwellian distribution of thermal velocities, as well as the intermolecular attraction, are taken into account.

1-21A. Thermal Conduction.-Consider a gas which is not at a uniform temperature throughout. Some parts of the gas are at a higher temperature than the rest. The heat is transferred from the regions at a higher temperature to those at a lower one by molecular action due to the chaotic random motion of the gas molecules. This process, known as conduction, which is different from convection involving mass motion, is independent of radiation. The heat flows in the direction in which the temperature falls most rapidly. The maximum rate of temperature decrement is called temperature gradient. If the temperature gradient be assumed to be uniform over any distance at least equal in length to the mean free path, then the amount of heat conducted in a given time is empirically known to be proportional to the temperature gradient. So the quantity of heat $Q$ transferred per unit time across unit area in the $X Z$-plane, taken normal to the temperature gradient along $y$-axis, is given by

$$
\begin{equation*}
Q=-K \frac{d T}{d y} \tag{1-79}
\end{equation*}
$$

where $K$ is the constant of proportionality, characteristic of the gas, known as the coefficient of thermal conduction, $T$ the temperature, and $d T / d y$ the temperature gradient along the $y$-axis.

Owing to the temperature inequalities that exist in the gas, there is a transfer of energy from the layers of molecules at higher temperature across the plane of unit area under consideration to the layers of lower temperature, and similarly from the layers of lower temperature across the same plane of unit area to the layers of higher temperature, until equilibrium of temperature is attained. The method of analysis of this transfer of energy is quite analogous to that of transfer of momentum in the derivation of the viscosity expression. Therefore if a method of argument similar to that leading up to the total momentum expression $1-67$ be followed, the
net transfer of energy due to the gas molecules will be found to be

$$
\begin{equation*}
\bar{Q}=-\frac{1}{3} n m v_{m} \lambda C_{v} \frac{d T}{d y} \tag{1-80}
\end{equation*}
$$

$n$, as usual, being the number of gas molecules per unit volume, $m$ the mass of each molecule, $v_{m}$ the molecular mean velocity, $\lambda$ the mean free path, and $C_{v}$ the molecular specific heat at constant volume.

The total transfer of heat through unit area per unit time given by equation 1-79 is equal to the net transfer of energy due to gas molecules through unit cross section per unit time given by 1-80. Therefore,

$$
\begin{equation*}
Q=\bar{Q}=-K \frac{d T}{d y}=-\frac{1}{3} n m v_{m} \lambda C_{v} \frac{d T}{d y} \tag{1-81}
\end{equation*}
$$

Hence the coefficient of thermal conduction $K$, which is the quantity of heat passing through a unit cross section in unit time per unit temperature gradient, is given by

$$
\begin{equation*}
K=\frac{1}{3} n m v_{m} \lambda C_{v}=\frac{1}{3} \rho v_{m} \lambda C_{v}, \tag{1-82a}
\end{equation*}
$$

$n m$ being the density $\rho$, or, expressing the same in terms of the coefficient of viscosity,

$$
\begin{equation*}
K=\eta C_{v} \tag{1-82b}
\end{equation*}
$$

where $\eta$ is the coefficient of viscosity and $C_{v}$ is the molecular specific heat at constant volume expressed in heat units.

The relation expressed in equations $1-82 a$ or $1-82 b$ was, however, found to be at variance with the actual experimental facts. This sort of discrepancy could be expected, because their derivation, strictly speaking, was not rigorous. In this derivation it is assumed that the density is uniform throughout, while, since there is no mass motion in the gas, the density actually is a variable on account of the variation of temperature. Second, it is assumed that the molecular mean velocity is a constant, but it varies with the temperature. Third, in this derivation Maxwell's velocity distribution law of gases in equilibrium is assumed, while heat conduction, in fact, is not an equilibrium phenomenon. With these facts in view, Meyer, ${ }^{11}$ after the necessary analysis to allow for
${ }^{11}$ O. E. Meyer, "Kinetic Theory of Gases," Mathematical Appendices Nos. 55, 56, 57, p. 461. (Longmans, Green \& Co., 1899.)
some of the mentioned effects, deduced an expression for the coefficient of thermal conduction, which may be written

$$
\begin{equation*}
K=1.53 \eta C_{v} . \tag{1-83}
\end{equation*}
$$

In the derivation of expression 1-83 the variation of collision frequency and the persistence of velocities were not taken into consideration. Jeans, ${ }^{12}$ having included certain terms expressing the variation of collision frequency and persistence of velocities in his analysis, has given the coefficient of thermal conduction,

$$
\begin{equation*}
K=1.497 \eta C_{v} . \tag{1-84}
\end{equation*}
$$

By a rigorous deduction one finds the numerical factor to be equal to the $\eta C_{v}$, part of the coefficient of conduction $K$ which is obviously greater then unity. If this factor which is equal to $K / \eta C_{v}$ be denoted by $\epsilon$, then we have for the coefficient of conduction a general expression,

$$
\begin{equation*}
K=\epsilon \eta C_{v} . \tag{1-85}
\end{equation*}
$$

Again Chapman ${ }^{13}$ and Enskog, ${ }^{14}$ each following a different line of argument and with due consideration for the intermolecular forces together with other factors, derived the following values:

$$
\epsilon=2.5 \text { for monatomic gases }
$$

and

$$
\epsilon=1.9 \text { for diatomic gases. }
$$

Therefore the coefficient of thermal conduction in the case of monatomic gases is

$$
\begin{equation*}
K=2.5 \eta C_{v} \tag{1-86}
\end{equation*}
$$

and that in the case of diatomic gases is

$$
\begin{equation*}
K=1.9 \eta C_{v} . \tag{1-87}
\end{equation*}
$$

These two equations $1-86$ and $1-87$ probably are to be regarded as the most accurate expressions for the coefficient of thermal conduction.

[^2]
## 1-21B. CONDUCTION, PRESSURE, TEMPERATURE

1-21B. Conduction, Pressure, and Temperature.-The expressions for the coefficient of conduction mainly constitute the two terms $\eta$ and $C_{v}$ which respectively express viscosity and molecular specific heat at constant volume. It is pointed out in the section on viscosity that viscosity in a certain range of pressure is independent of the pressure. Therefore $K$, the coefficient of conduction at a given temperature, should be independent of pressure to the extent $\eta$ and $C_{v}$ are independent. This law was found to hold from the pressure at which convection ceased down to the pressure of 1 mm . of mercury. It is, however, not expected to hold at high pressures, and positively fails when the mean free path is comparable to distances in which the temperature gradient varies appreciably. As Kennard ${ }^{15}$ points out, the range of pressure allowed by such conditions is sufficient to make the fact of importance in some types of vacuum work. As an example he states that in a $10-\mathrm{cm}$. bulb containing air, the pressure is to be reduced to less than 0.001 mm . in order to obtain the advantage of the diminished loss of heat by conduction through air.
At the range of pressures of high vacua, the thermal conduction coefficient $K$ varies with the pressure; this is due to the fact that at these pressures, when the mean free path becomes comparable to the dimensions of the space under consideration and the number of molecular collisions is negligible, the effects of individual molecules, as in the case of viscosity, are additive. This variation of thermal conduction with the pressure is utilized as a means of pressure measurement of high vacua in the thermal conductivity gauges of the Pirani-Hale type described in the third section of chapter 4.
If $C_{v}$ be assumed constant, the coefficient of thermal conduction, from certain theoretical considerations, is expected to be proportional to the square root of the absolute temperature. $K$ actually varies, however, more rapidly than $\sqrt{T}$, as in the case of viscosity. The qualities of conduction with respect to pressure and temperature have, in a way, a parallelism with those of viscosity with respect to pressure and temperature, so that the coefficient of conduction $K_{T}$ at a temperature $T=\left(273.14+t^{\circ}\right)$ can be expressed in terms of that at a temperature of $273.14^{\circ}$ absolute, as in the
${ }^{\boldsymbol{u}}$ E. H. Kennard, Kinetic Theory of Gases, Edition I, 182. McGraw-Hill Book Co., New York (1938).
case of viscosity, thus:

$$
\begin{equation*}
K_{T}=K_{273.14}\left(\frac{c+273.14}{C+T}\right)\left(\frac{T}{273.14}\right)^{2 / 6} \tag{1-88}
\end{equation*}
$$

1-21C. Conduction Coefficient, Mean Free Path, and Molecular Diameter.-From the direct measurements of the coefficient of thermal conduction, it may be possible to compute the mean free path $\lambda$ by means of the conduction expression 1-85 and thence the molecular diameter $\sigma$ by means of 1-62c. Measurements of $K$ in gases are, on the whole, inaccurate because of the difficulty in eliminating convection and radiation. Also a certain degree of uncertainty exists in the value of $\epsilon$ of the conduction coefficient expression. Therefore it is not worth while to make use of this coefficient in determining the mean free path and the molecular diameter.


Fia. 1-7.
1-22. Diffusion.-Suppose a tube $A B$ (figure 1-7) contains two different gases whose relative densities vary from point to point. In consequence of thermal agitation, more molecules of each one of the two kinds flow from the regions rich in that kind to the regions of their scarcity than travel in the reverse direction, thereby tending to smooth the inequalities of distribution. This process by which the inequalities of composition diminish until uniformity of the molecular distribution of the composition is attained is called diffusion. In diffusion the net flow of each kind of molecules occurs in the direction in which the density decreases most rapidly. The
maximum rate of such a variation of density is called density gradient. If the density gradient be assumed to be steady the number of molecules $\Gamma_{1}$ of the gas from the $B$-end of the tube and the number of molecules $\Gamma_{2}$ from the $A$-end of the tube, diffusing through unit area in unit time may be expressed by the relations

$$
\begin{equation*}
-\Gamma_{1}=-D \frac{d n_{1}}{d x}=\Gamma_{2}=-D \frac{d n_{2}}{d x}, \tag{1-89}
\end{equation*}
$$

where $d n_{1} / d x$ and $d n_{2} / d x$ are the density gradients of gas 1 and gas 2 respectively along the $x$-axis, and $D$ is the constant of proportionality, known as the coefficient of diffusion characteristic of the gas in question.

The density gradients $d n_{1} / d x$ and $d n_{2} / d x$ which cause the process of diffusion are proportional to the pressure gradients $d p_{1} / d x$ and $d p_{2} / d x$ respectively. The coefficient of diffusion depends obviously on the rate at which molecules move across unit area as a result of the gradients of partial pressures caused by molecular thermal agitation. The determination of the coefficient of diffusion, therefore, reduces itself to one of finding the quantitative expression for the net number $\Gamma$ of molecules moving across unit area in unit time under the density gradient. Let $p_{1}$ be the partial pressure and $n_{1}$ the number of molecules per unit volume of gas 1 , and $p_{2}$ and $n_{2}$ the corresponding quantities for gas 2 . If the two gases are in equilibrium as regards pressure and temperature, the pressure $p$ at any point $P$ by Dalton's law of partial pressures must be

$$
\begin{equation*}
p=p_{1}+p_{2} \tag{1-90}
\end{equation*}
$$

and the number $n$ of molecules per unit volume at any point $P$, by Avogadro's law, must be

$$
\begin{equation*}
n=n_{1}+n_{2} . \tag{1-91}
\end{equation*}
$$

Similarly we have

$$
\frac{d n_{1}}{d x}=-\frac{d n_{2}}{d x} ;\left(\frac{1}{m_{1}}\right)\left(\frac{d \rho_{1}}{d x}\right)=-\left(\frac{1}{m_{2}}\right)\left(\frac{d \rho_{2}}{d x}\right), \quad(1-92 a b)
$$

where $m_{1}$ is the molecular mass, $\rho_{1}$ the density of gas 1 , and $m_{2}$, $p_{2}$ the corresponding quantities for gas 2 .
Now, let $p_{0}$ be the partial pressure and $n_{0}$ the number of molecules per unit volume of gas 1 at the origin 0 . Then, as the
density gradient is uniform throughout the tube, the pressure $p_{1}$ and the number $n_{1}$ at any point $P$ distant $x$ from the origin are given by

$$
\begin{align*}
& p_{1}=p_{0}+\frac{d p_{1}}{d x} x=p_{0}+\frac{d p_{1}}{d x} r \cos \theta  \tag{1-93a}\\
& n_{1}=n_{0}+\frac{d n_{1}}{d x} x=n_{0}+\frac{d n_{1}}{d x} r \cos \theta \tag{1-93b}
\end{align*}
$$

Let the molecules of gas 1 and those of gas 2 be treated as if all the molecules of each type were moving with the molecular mean velocity $v_{m 1}$ and $v_{m 2}$ respectively at the temperature of the mixture. If there be a unit cross section of the tube at $O$, the number of molecules of gas 1 coming from the volume element $d x d y d z$ at $P$ and passing through a unit cross section at $O$ in unit time, as seen from the discussion on viscosity, must be

$$
\begin{align*}
& \frac{\nu_{1} n_{1}}{4 \pi r^{2}} e^{-r / \lambda_{1}} \cos \theta d x d y d z= \\
& \frac{\nu_{1}}{2} e^{-r / \lambda_{1}}\left(n_{0}+\frac{d n_{1}}{d x} r \cos \theta\right) \cos \theta \sin \theta d \theta d r . \tag{1-94}
\end{align*}
$$

The integration of expression 1-94 over all space gives the excess of number of molecules crossing from right to left over those crossing from left to right, thus:

$$
\begin{align*}
\frac{\nu_{1}}{2} \int_{0}^{\infty} e^{-r / \lambda_{1}} d r \int_{0}^{\pi}\left(n_{0}+\frac{d n_{1}}{d x}\right. & r \cos \theta) \cos \theta \sin \theta d \theta \\
& =\frac{1}{3} \nu_{1} \lambda_{1}{ }^{2} \frac{d n_{1}}{d x}=\frac{1}{3} v_{m 1} \lambda_{1} \frac{d n_{1}}{d x} \tag{1-95}
\end{align*}
$$

Similarly for gas 2, by Avogadro's relation expressed in 1-91 and $1-92 a b$, the excess of the number of molecules passing through the unit cross section of the tube from right to left over those from left to right must be

$$
\begin{equation*}
\frac{1}{3} \nu_{2} \lambda_{2}{ }^{2} \frac{d n_{2}}{d x}=\frac{1}{3} v_{m 2} \lambda_{2} \frac{d n_{2}}{d x}=-\frac{1}{3} v_{m 2} \lambda_{2} \frac{d n_{1}}{d x} . \tag{1-96}
\end{equation*}
$$

From expressions 1-95 and 1-96, it is obvious that the number of molecules of both the gases taken together, passing from right to
left through unit cross section in unit time due to chaotic molecular agitation, is given by

$$
\begin{equation*}
\frac{1}{3}\left(v_{m 1} \lambda_{1}-v_{m 2} \lambda_{2}\right) \frac{d n_{1}}{d x} \tag{1-97}
\end{equation*}
$$

The passage of the number of molecules given in expression 1-97, causes inequality of pressure. Consequently equal numbers of molecules of the two constituents of the composition cross from left to right, and these numbers are given by

$$
\frac{1}{3}\left(v_{m 1} \lambda_{1}-v_{m 2} \lambda_{2}\right) \frac{d n_{1}}{d x} \frac{n_{1}}{n}, \quad \text { and } \quad \frac{1}{3}\left(v_{m 1} \lambda_{1}-v_{m 2} \lambda_{2}\right) \frac{d n_{1}}{d x} \frac{n_{2}}{n}
$$

molecules of gas 1 and gas 2 respectively. Hence the total number of molecules of gas 1 which cross a unit area in unit time from right to left is

$$
\begin{align*}
-\Gamma_{1} & =-\left\{\frac{1}{3} v_{m 1} \lambda_{1} \frac{d n_{1}}{d x}-\frac{1}{3}\left(v_{m 1} \lambda_{1}-v_{m 2} \lambda_{2}\right) \frac{n_{1}}{n} \frac{d n_{1}}{d x}\right\} \\
& =-\left\{\frac{1}{3}\left(\frac{n_{2} v_{m 1} \lambda_{1}}{n_{1}}+\frac{n_{1} v_{m 2} \lambda_{2}}{n_{2}}\right) \frac{d n_{1}}{d x}\right\} \tag{1-98}
\end{align*}
$$

and an equal number of molecules of gas 2 cross from left to right.
Now on comparing equation 1-89 with 1-98, we have the expression for the coefficient of mutual diffusion

$$
\begin{equation*}
D=\frac{1}{3}\left(\frac{n_{2}}{n_{1}} v_{m 1} \lambda_{1}+\frac{n_{1}}{n_{2}} v_{m 2} \lambda_{2}\right) . \tag{1-99}
\end{equation*}
$$

In the derivation of expression 1-99, if the correction for Maxwell's law be included, we have $\pi / 8$ instead of $\frac{1}{3}$.

In the determination of the coefficient of self-diffusion, we must consider that the two types of gas molecules treated in the derivation of expression 1-99 are identical in every respect. Then expression 1-98 has the form

$$
\begin{equation*}
-\Gamma=-\frac{1}{3} \lambda v_{m} \frac{d n}{d x} \tag{1-100}
\end{equation*}
$$

and on comparing this with equation 1-85, we obtain an expression for the coefficient of self-diffusion,

$$
\begin{equation*}
D=\frac{1}{3} v_{m} \lambda \tag{1-101}
\end{equation*}
$$

Table 1-7. Coefficients of Viscosity, Thermal Conductivity, and Diffusion

| Gas or Vapor | Viscosities |  | Thermal Conductivities |  | Diffusion Coefficients $\mathrm{cm} .{ }^{2} / \mathrm{sec}$. at $0^{\circ} \mathrm{C}$. and $760 \mathrm{~mm} . \mathrm{Hg}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Temp. ${ }^{\circ} \mathrm{C}$. | $\eta \times 10^{7}$ c.g.s. | Temp. ${ }^{\circ} \mathrm{C}$. | $K \times 10^{-3} \mathrm{cal}$. |  |  |
|  |  |  |  | cal. /cm. sec. deg. | in $\mathrm{H}_{2}$ | in air |
| $\mathrm{H}_{2}$ | 19.4 | 875 | 0 | 0406 | 1285 | $\ldots$ |
| He | 14.0 | 1943 | 0 | 0336 | . | .... |
| $\mathrm{NH}_{8}$ | 15 | 1005 | 0 | 0.0513 | $\ldots$ | 0.198 |
| $\mathrm{H}_{2} \mathrm{O}$ | 20 | 937 | 46 | 0.0458 | 0.687 | 0.198 |
| Ne | 15 | 3076 | 0 | 0.1104 | 0.687 | .... |
| CO | 15.1 | 1730 | 0 | 0.0563 | 0.649 | .... |
| $\mathrm{N}_{2}$ | 0 | 1665 | 0 | 0.0580 | . . . . | $\ldots$ |
| 0 | 14.2 | 1973 | 0 | 0.0589 | 0.68 | $\ldots$ |
| A | 15.4 | 2196 | 0 | 00388 | .... | $\ldots$ |
| $\mathrm{CO}_{2}$ | 0 | 1382 | 0 | 0.0343 | 0.538 | 0.142 |
| Cl | 15.6 | 1294 | 0 | 0.0183 | .... | .... |
| $\mathbf{K r}$ | 0 | 2327 | . | .... | $\ldots$ | $\ldots$ |
| $\mathbf{X e}$ | 15 | 2236 | . | . | .... | ... |
| Hg | 281 | 5310 | 203 | 00185 | ... |  |
| Air | 0 | 1809 | 0 | 00583 | $\ldots$ | . |

## 1-24. VAN DER WAALS' EQUATION OF STATE 53

or, since the coefficient of viscosity is given by $\eta=\frac{1}{3} v_{m} \lambda \rho$, the expression for the coefficient of self-diffusion may be written in the form

$$
\begin{equation*}
D=\frac{1}{3} \frac{\eta}{\rho} \tag{1-102a}
\end{equation*}
$$

If a more rigorous analysis be followed, introducing factors to allow for the effects of certain omissions and improper assumptions which lead to expression 1-102a, we obtain, as in the case of viscosity and conduction, numerical factors greater than unity which are in general denoted by $\epsilon$. So, on replacing $\frac{1}{3}$ by $\epsilon$ in equation $1-102 a$, we have the general expression for the coefficient of self diffusion,

$$
\begin{equation*}
D=\epsilon \frac{\eta}{\rho}, \tag{1-102b}
\end{equation*}
$$

$\eta$ being the coefficient of viscosity and $\rho$ the density of the gas.

## Section V. The Equation of State

1-23. Definition.-As a result of certain experiences with the physical characteristics of gases in equilibrium, it is known that there exists a general relation between the volume, the pressure, and the temperature of a gas. An equation expressing this relation is called the equation of state and is of fundamental importance to the theory of gases as well as to the science of high vacua. For an ideal or perfect gas the simple equation of state $p V=R T$ has been found, and it is obvious from this that the physical state of a given mass of gas in equilibrium is fixed when definite values are assigned to any two of the three variables. The equation in this form holds only when the gas is at high temperature and low density. As the density is raised and the temperature is lowered toward condensation, this form of the equation given by Boyle-Gay-Lussac fails.

1-24. Van der Waals' Equation of State.-The law of ideal gases is based on the assumptions that (1) the molecules have negligible dimensions and that (2) no operative forces exist between the gas molecules except when they are in collision. These assumptions, however, are not true for an actual gas, since the molecules are of finite sive and intermolecular forces do exist which act on one an-
other even when the molecules are not in contact. With these points of view, corrections to the equation of perfect gases may be introduced in order to render it an equation of state of real gases. In this way Van der Waals derived an equation of state which for all practical purposes represents the actual properties of gases.

To study the method of derivation of this equation, consider that the molecules are of finite dimensions, being spheres of finite diameter $\sigma$. Let a sphere of radius $\sigma$ be concentrically drawn about each molecule. Within this sphere, the sphere of influence of a given molecule, no other molecule can penetrate. In other words, it is impossible for the center of any one molecule to lie within the sphere of influence of the molecule. If $V$, the total gas volume, be equal to the volume of a gram-molecule or mole, and $N$ the number of molecules equal to the Avogadro's constant, then each molecule carries with it in its motion a sphere of influence of volume $\frac{4_{3}}{3} \pi \sigma^{3}$, so that the volume excluded for the center of a given molecule is $\frac{4}{3} \pi \sigma^{3}(N-1)$, which may be written $\frac{4}{3} \pi \sigma^{3} N$, since $N$ is a very great number. Then the space outside the spheres of influence which may be available for the center of a given molecule is $V-\frac{4}{3} \pi \sigma^{3} N$. Therefore the probability of the center of the given molecule being found inside a specified volume $d V$ of the available space is

$$
\begin{equation*}
\frac{d V}{V-\frac{4}{3} \pi \sigma^{3} N} . \tag{1-103}
\end{equation*}
$$

If the molecule under consideration be moving with a velocity of components $v_{x}, v_{y}, v_{z}$, of which $v_{x}$ is normal to a given region $d_{s}$ of the wall, it will hit $d s$ within a small interval of time $d t$, provided that at the beginning of this interval the center of this molecule lies within a small volume element $d s v_{z} d t$ lying at a distance of $\frac{1}{2} \sigma$ from the wall. (See figure 1-8). Let this element of volume be identified with $d V$ in the expression 1-103.
Now let a plane which passes through the center of each sphere be parallel to $d s$. Any point on the farther hemisphere is farther from $d s$ than the center of the Sphere. Therefore such a point in the farther hemisphere cannot be at a distance less than $\frac{1}{2} \sigma$ from ds. Because the element of volume is $\frac{1}{2} \sigma$ from the wall, it is obviously excluded from one of the hemispheres farther from the wall, but all points in the nearer hemispheres are open to it. The

1-24. VAN DER WAALS' EQUATION OF STATE 55
total volume of the farther hemispheres is $\frac{2}{8} \pi \sigma^{3}(N-1)$, which by disregarding the difference between $N$ and $N-1$ becomes $\frac{2}{3} \pi \sigma^{3} N$. Therefore the probabilities of $d V$ being and not being inside are respectively given by

$$
\begin{equation*}
\frac{\frac{2}{3} \pi \sigma^{3} N}{V} \tag{1-103a}
\end{equation*}
$$

and

$$
\begin{equation*}
\frac{V-\frac{2}{3} \pi \sigma^{3} N}{V} \tag{1-103b}
\end{equation*}
$$

In the former no collision is probable, while in the latter, prob-


Fig. 1-8.
ability of collision within a time $d t$, from expression 1-103, is

$$
\begin{equation*}
\frac{N d V}{V-\frac{4}{3} \pi \sigma^{3} N} \tag{1-103c}
\end{equation*}
$$

so that the value of probability of a collision, which is a product of the values of the probabilities, given by $1-103 b$ and $1-103 c$, is

$$
\begin{equation*}
\frac{N d V}{V} \frac{V-b}{V-2 b} \tag{1-103d}
\end{equation*}
$$

where $b=\frac{2}{3} \pi \sigma^{3} N$. If we assume $V \gg b$, then powers of $b / V$
higher than the first may be neglected and so equation 1-103d may be reduced to

$$
\begin{equation*}
\frac{N d V}{V-b} \tag{1-103e}
\end{equation*}
$$

When the total volume of $N$ molecules is small compared with the volume $V$, the gas behaves as if its volume $V$ were diminished by $b$. Hence the effect of finite size of the molecules is sufficiently allowed for if $V-b$ is substituted for $V$ in the law of ideal gases. So we have

$$
\begin{equation*}
p(V-b)=\breve{R} T \tag{1-103f}
\end{equation*}
$$

where $\breve{R}$ is the universal gas constant and $b$ is the "co-volume," which is four times as large as the total volume of all the molecules of the gas.

It is also necessary to introduce a second correction in order to allow for intermolecular forces of cohesion. These forces are central forces of attraction acting from each molecule over fairly large distances, and they are of the same nature as those which give the phenomenon of surface tension in liquids. The mean effect of the forces acting on a molecule remote from the wall is zero, since those which vary continually in direction and magnitude are likely to cancel out when averaged over a sufficient interval of time. So the pressure at internal points given by $1-103 f$ is unaffected by this correction. But it is not so near the wall, and in this region these forces must be taken into account in order to calculate the pressure of the gas.

The molecules of the gas in the region of the wall are acted upon by an average force of attraction directed to the internal points at right angles to the wall along with the forces of action of the wall. These forces set up a permanent field acting upon each molecule and exerting a steady inward drag upon the molecules at and near the wall. The magnitude of the drag is proportional to the number of molecules per unit area of the molecular layer near the wall and to the intensity of the normal component which in turn are jointly proportional to $C \rho^{2}$. Taking $C \rho^{2}=C m^{2} N^{2} / V^{2}$, where $\rho$ is the density of the gas, $C$ a constant depending on the nature of the gas, $N$ the Avogadro's constant, $m$ the mass of the molecule, and $V$ the volume of a gram-molecule, and putting
$C N^{2} m^{2}=a$, equation 1-103f may further be corrected and be written in the forms:

$$
\begin{equation*}
\left(p^{2}+C \rho^{2}\right)(V-b)=\widetilde{R} T \tag{1-103g}
\end{equation*}
$$

and

$$
\begin{equation*}
\left(p^{2}+\frac{a}{V^{2}}\right)(V-b)=\breve{R} T \tag{1-103h}
\end{equation*}
$$

This is Van der Waals' equation of state of real gases expressing the relation between $p, V$, and $T$.

1-25. Molecular Diameter from Van der Waals' Equation. The molecular diameter may be determined from the constant $b$ in equation $1-103 h$. In order to find the relation between this constant and the molecular diameter, it is assumed that the simultaneous collisions of more than a pair of molecules are so rare that there will not be appreciable error in proceeding as if all collisions occur between two molecules. If two molecules collide, their centers get no nearer than the distance $\sigma$. So a space $\frac{4}{3} \pi \sigma^{3}$ has to be omitted from the volume $V$ on account of a pair of colliding molecules, or $\frac{2}{3} \pi \sigma^{3}$ for each molecule. Therefore, if $N$ be the Avogadro's number of molecules, we have

$$
\begin{equation*}
b=\frac{2}{3} \pi \sigma^{3} N! \tag{1-104}
\end{equation*}
$$

Hence

$$
\begin{equation*}
\sigma^{3}=\frac{3 b}{2 \pi N} \tag{1-105}
\end{equation*}
$$

On introducing the value of the constant $b$-determined by the method of the pressure and volume coefficients of expansion, or by the constant-volume method, or by the isothermal method, or from critical data-in expression 1-105, the value of the molecular diameter is obtained.

1-25A. Molecular Diameters by Different Methods.-The kinetic theory of gases thus gives different methods by which molecular diameter $\sigma$ is determined. It may be calculated from the measurements of the coefficients of viscosity, thermal conduction, and self-diffusion, as well as from the measurement of the constant $b$ in Van der Waals' equation. The values of the molecular dismeters of different gases, determined by the mentioned methods, are compiled in Table 1-8 from the data given by Jeans (Dymamical Theory of Gases, 4th ed., p. 329).

Table 1-8. Molecular Diameters of Different Gaseb, Determined by the Different Methods Given in $10^{-8} \mathrm{~cm}$.

| Gas | Viscosity <br> $\sigma$ | Thermal Conduction <br> $\sigma$ | Diffusion <br> $\sigma$ | Constant " $b$ " <br> $\sigma$ |
| :--- | :---: | :---: | :---: | :---: |
| Hydrogen | 2.72 | 2.72 | 2.72 | 2.54 |
| Helium | 2.18 | 2.20 | - | 1.98 |
| Nitrogen | 3.78 | 378 | 3.84 | 356 |
| Oxygen | 3.62 | 3.62 | 3.64 | 2.90 |
| Carbon |  |  |  |  |
| $\quad$ Dioxide | 4.62 | 4.84 | 4.38 | 3.42 |
| Air | 3.74 | 3.74 | 3.74 | 3.32 |

## Section VI. Free Molecular Behavior of Gases

1-26A. Introduction.-The study of transport phenomena is mainly restricted to discussion of the properties of a gas at such densities that the mean free path is very small compared with the dimensions of its container. It is shown that under such conditions the behavior of the gas depends essentially upon the frequency of the intermolecular collisions, the mean space-interval between them, and the molecular diameter characteristic of each gas. If the pressure, however, is lowered to the range of high vacua, the intermolecular collisions become rare compared with the collisions of the gas molecules with the walls of the container. Then each one of the molecules acts independently of all the others in giving rise to the properties of the gas. The gas in this condition is said to be of free molecular behavior.

Laws governing the phenomena of gases of ordinary behavior differ from those of the phenomena exhibited by gases of free molecular behavior. The viscosity and the thermal conduction coefficients of gases of ordinary behavior which are independent of pressure through a considerable pressure range are, as pointed out, by no means so in the case of gases of free molecular behavior.

1-26B. Flow of a Gas Through Capillary Tube.-It will now be seen that the flow of a gas of free molecular behavior through a capillary tube of a diameter small compared with the mean free path, has laws which differ from those of the flow of a gas whose mean free path is quite small compared with the diameter of the capillary tube through which it flows. If the capillary tube be
long with a bore of circular cross section of a diameter large compared with the mean free path, the amount of gas that passes per second measured in terms of its $p V$ value, which is inversely proportional to the viscosity coefficient of a gas of ordinary gaseous behavior, is given by Poisseuille's law for the steady capillary flow of a gas at high pressures,

$$
\begin{equation*}
Q_{p V}=\frac{\pi r^{4} p}{8 \eta L}\left(p_{1}-p_{2}\right) \tag{1-106a}
\end{equation*}
$$

where $r$ and $L$ respectively denote the radius and the length of the tube, $p$ the pressure at which $Q_{p V}$ is measured, $\eta$ the viscosity coefficient of the gas, and $p_{1} p_{2}$ respectively represent the entrance and exit pressures. Since twice the radius is the diameter, $(2 r=D)$, equation 1-106a may be written in the form,

$$
\begin{equation*}
Q_{p V}=\frac{\pi D^{4} p}{128 \eta L}\left(p_{1}-p_{2}\right) \tag{1-106b}
\end{equation*}
$$

In deriving Poisseuille's law, the speed of flow at high pressures is taken to vary from a maximum in the center of the tube to a minimum verging to the value of zero at the walls. Thus the mass-velocity of the gas at high pressures in contact with the walls of the tube is assumed to be zero.

If a gas at low pressure be flowing down a capillary tube, as a result of pressure difference, $p_{1}-p_{2}$, the quantity of gas $Q_{p V}$ that flows per second is, as found by Kundt and Warburg, ${ }^{16}$ actually greater than that given by Poisseuille's law. This discrepancy could be expected when the pressure is so low that the mean free path $\lambda$ of the molecules is no longer negligible as compared with the diameter of the capillary. If $\lambda$ is comparable to the diameter of the tube, the molecules which impinge on the walls of the tube, instead of wholly coming to rest, are reflected with the normal component of velocity changed in sign. In this way the gaseous mass seems to slip past the walls of the tube with a certain fraction of the speed of incidence. This fraction is equal to the numerical value of the ratio of the coefficient of viscosity to the coefficient of gaseous friction against the walls of the tube. The numerical value of this ratio, represented symbolically by $\zeta=\eta / \epsilon$, is known as the coefficient of slip. For the steady flow of a gas at low pres-

[^3]sures through a capillary tube, Poisseuille's law is extended so as to allow for the influence of the coefficient of slip on the flow of the gaseous mass, and the law after the necessary extension has the form
\[

$$
\begin{equation*}
Q_{p V}=\frac{\pi D^{4} p}{128 \eta L}\left(p_{1}-p_{2}\right)\left(1+8 \frac{\zeta}{D}\right) \tag{1-107}
\end{equation*}
$$

\]

$\zeta$ being the coefficient of slip and $D$ the diameter of the capillary tube. As the gaseous pressure increases the value of the correction term for slip correspondingly decreases, so that in the case of high pressures the correction term for slip becomes unity in numerical value and equation 1-107 reduces itself to Poisseuille's law as given in expression 1-106. If, however, the gaseous pressure be so low that the mean free path of the gas is of the order of the diameter of the capillary, the correction term for the slip becomes relatively large, thereby increasing the value of the term $Q_{p} \nabla$. Thus in this region of low pressures $Q_{p \nabla}$ increases as a result of the advantageous effects of slip.

1-27A. Molecular Streaming.-If the gaseous pressure be lowered down to the range of pressures of high vacua, the mean free path becomes large compared to the diameter of the capillary tube and the viscosity effects become vanishingly small, so that the gaseous flow in this condition does not obey the law given in expression 1-107. The flow of a gas of free molecular behavior, known as molecular streaming, in contrast to the other kinds of flow should therefore have a different analysis for the derivation of the law governing its phenomena. A theory which comprises the analysis and the derivation of the law of molecular streaming has been given by Knudsen. ${ }^{17}$ He starts with the assumption that the number of molecules that strike a unit area of the surface of the walls of the tube per second by equation $1-48 a$ is $\frac{1}{4} n v_{m}$, where $v_{m}$ is the mean molecular velocity. If there are $n$ molecules per cubic centimeter, the number $d n$ of molecules with velocity components between $v$ and $v+d v$ is given, by equation 1-40, as

$$
\begin{equation*}
d n=4 n \pi a^{3} e^{-b v^{2}} v^{2} d v \tag{1-108a}
\end{equation*}
$$

Of these molecules, the number that strike a square centimeter

[^4]surface of the walls of the tube per second may therefore be written as
\[

$$
\begin{equation*}
\frac{1}{4} d n v=n \pi a^{3} e^{-b v^{2}} v^{3} d v \tag{1-108b}
\end{equation*}
$$

\]

Now, consider that the mean component of velocity of translation of the molecules parallel to the wall is $u$, and that the molecules striking the wall are absorbed by it and are re-emitted in all directions which are equally probable. If $u$, expressed in terms of the molecular velocity $v$, be $u=c v$, where $c$ is a proportionality constant for all values of $v$, the momentum transfer to the wall by the $d n$ molecules may be taken as

$$
\begin{equation*}
\frac{1}{4} d n m c v^{2} . \tag{1-109}
\end{equation*}
$$

The momentum $B$ imparted to the unit area of the wall per second by molecules of all velocities is therefore given by

$$
\begin{equation*}
B=\int \frac{1}{4} d n m c v^{2} \tag{1-110a}
\end{equation*}
$$

Since from 1-45b $v^{2}=3 k T / m, 1-110 a$ may be written in the form,

$$
\begin{align*}
B & =\int \frac{1}{4} d n \cdot m c \frac{3 k T}{m} \\
& =\frac{3}{4} c k T \int d n \\
& =\frac{3}{4} n c k T . \tag{1-110b}
\end{align*}
$$

Since from 1-46b $T=v_{m}{ }^{2} m \pi / 8 k$, equation 1-110b can be expressed in terms of the mean molecular velocity $v_{m}$, thus:

$$
\begin{align*}
B & =\frac{3}{4} n c k \frac{v_{m}^{2} m \pi}{8 k} \\
& =\frac{3}{32} \pi n m c v_{m}^{2} \tag{1-111}
\end{align*}
$$

As $v_{m}=\sum v / n, c v_{m}=\sum c v / n=\sum u / n=\check{v}$, where $\check{v}$ is the velocity of the gas flowing down the tube. In the region of free molecular behavior, $y$ can be assumed with justification to be constant across the tube. Therefore $B$, in terms of the velocity of translation of the gas $\delta$, has the form:

$$
\begin{equation*}
B=\frac{3 \pi}{32} n m v_{m} \delta=\frac{3 \pi}{32} \rho v_{m} \delta . \tag{1-112}
\end{equation*}
$$

Again, since $v_{m}=\sqrt{8 k T / m \pi}, v_{s}=\sqrt{3 k T / m}$ and $3 p=m n v_{s}, B$, in terms of the pressure $p$, is

$$
\begin{equation*}
B=\frac{3 \pi}{32} \rho \breve{v} \sqrt{\frac{8}{\pi} \cdot \frac{p}{\rho}}=\frac{3 \rho \breve{v}}{32} \sqrt{\frac{\pi 8 p}{\rho}} . \tag{1-113}
\end{equation*}
$$

If the tube is approximately cylindrical in form with length $L$ and diameter of cross section $D$, then the momentum received per second by the small element of length $d L$ of the tube due to the molecular impacts is given by

$$
\begin{equation*}
\pi D d L \frac{3 \rho \breve{v}}{32} \sqrt{\frac{\pi 8 p}{\rho}} \tag{1-114}
\end{equation*}
$$

This momentum is imparted as a result of the pressure drop across the length of the tube, which is given by

$$
-\frac{d p}{d L} \frac{\pi D^{2}}{4} d L
$$

Since this pressure drop must be equal to the momentum received by the length $d L$ of the tube due to molecular impacts, we have

$$
\begin{equation*}
-\frac{d p}{d L} \frac{\pi D^{2}}{4} d L=\pi D d L \cdot \frac{3 \rho \check{v}}{32} \sqrt{\frac{\pi 8 p}{\rho}} \tag{1-115}
\end{equation*}
$$

Therefore

$$
\begin{equation*}
-\frac{d p}{d L}=\frac{3 \rho \breve{v}}{8} \cdot \frac{1}{D} \sqrt{\frac{\pi 8 p}{\rho}} . \tag{1-116}
\end{equation*}
$$

Now, since $\check{v}$ is the velocity of translation of the gas down the tube, $\pi\left(D^{2} / 4\right)$ the area of the cross section of the tube, and $\rho$ the density of the gas, the gaseous mass $G$ flowing down the tube per second is given by

$$
\begin{equation*}
G=\frac{\pi D^{2}}{4} \rho \check{\nu} . \tag{1-117}
\end{equation*}
$$

If $\breve{v}$ is replaced by its value derived from equation 1-116, expression 1-117 has the form,

$$
\begin{equation*}
G=\frac{\pi D^{2}}{4} \rho \frac{8 D \sqrt{\rho}}{3 \rho \sqrt{\pi 8 p}} \cdot \frac{d p}{L}=\frac{\sqrt{2 \pi} D^{3}}{6 L} \sqrt{\frac{\rho}{p}} \cdot\left(p_{1}-p_{2}\right) \tag{1-118}
\end{equation*}
$$

If the term $\sqrt{2 \pi} D^{3} / 6 L$ be denoted by $1 / W$, expression $1-118$ has the form

$$
\begin{equation*}
G=\sqrt{\frac{\rho}{p}} \cdot \frac{p_{1}-p_{2}}{W} \tag{1-119}
\end{equation*}
$$

This law of molecular streaming, expressed by equation $1-119$, is of a very practical importance, for it can be applied with advantage for determining vapor pressures of certain materials in vacua. Knudsen ${ }^{18}$ made use of this law in his method of molecular streaming for determining saturation vapor pressure of mercury at temperatures from $0^{\circ} \mathrm{C}$. to about $40^{\circ} \mathrm{C}$.

The volume $Q$ of a gas at a uniform temperature flowing out measured at a pressure of 1 dyne $/ \mathrm{cm}^{2}$ may be derived from 1-119. It is

$$
\begin{equation*}
Q=\frac{G}{\rho_{1}}=\frac{p_{1}-p_{2}}{W \sqrt{\rho_{1}}} \tag{1-120}
\end{equation*}
$$

where $\rho_{1}$ is the density of the gas at a uniform temperature of the tube and a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ and $W$ is the "resistance" of the walls of the tube to the flow of the gas. $W$ is analogous to electrical resistance. The " resistance" may be expressed

$$
\begin{equation*}
W=\frac{6}{\sqrt{2 \pi}} \cdot \frac{L}{D^{3}} \tag{1-121}
\end{equation*}
$$

where $D$, as before, is the diameter of the cross section of the tube and $L$ its length. If the tube be of different diameters $D_{n}$ and of different lengths $L_{n}$, the net resistance is the sum of resistances of the whole tube system of different cross sections with different lengths as in the case of electrical resistance in series.

If the end of the tube be circular with diameter $D^{\prime}$, the volume $Q^{\prime}$ of gas that flows out of the opening alone at a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ can be written in analogy with equation $1-120$

$$
\begin{equation*}
Q^{\prime}=\frac{p_{1}-p_{2}}{W^{\prime} \sqrt{\rho_{1}}} \tag{1-122}
\end{equation*}
$$

where $W^{\prime}=\sqrt{2 / \pi} / D^{\prime 2}=3.192 / D^{\prime 2}$ and acts as "resistance" of the end opening of the tube. It is obvious that the cross section of

[^5]diameter $D$ and length $L$ of the tube and the end of the tube with circular opening of the diameter $D^{\prime}$ constitute two resistances in series. Hence the total resistance $W_{r}$ of the tube, together with the influence of the end opening, is given by
\[

$$
\begin{equation*}
W_{r}=W+W^{\prime}=\frac{6 L}{\sqrt{2 \pi} D^{3}}+\frac{3.192}{D^{\prime 2}} \tag{1-123}
\end{equation*}
$$

\]

Therefore the volume of gas at a pressure of 1 dyne $/ \mathrm{cm}^{2}$ flowing through the tube with the influence of its end opening is

$$
\begin{equation*}
Q_{r}=Q+Q^{\prime}=\frac{p_{1}-p_{2}}{W_{r} \sqrt{\rho_{1}}} \tag{1-124}
\end{equation*}
$$

1-27B. "Conductivity" and "Resistance" of Tubes.-In the practical and experimental fields of the science of high vacua, it is quite essential to determine the "conductivity" $F$ or the rate of flow of gas in cubic centimeters per second per unit pressure difference. From expression 1-124, $F$ is seen to be

$$
\begin{equation*}
F=\frac{Q_{r}}{p_{1}-p_{2}}=\frac{1}{W_{r} \sqrt{\rho_{1}}} \tag{1-125}
\end{equation*}
$$

where $W_{r}$ is the total resistance of the tube together with the influence of the end opening, $\rho_{1}$ the density of the gas at normal temperature and a pressure of 1 dyne $/ \mathrm{cm}^{2}, W_{r} \sqrt{\rho_{1}}$ the combined " resistance" to molecular streaming at a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ offered by the tube, and $p_{1}, p_{2}$ are the entrance and exit pressures respectively. It is obvious that "conductivity " is the reciprocal of the combined " resistance" to molecular streaming at a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ offered by the tube. Hence

$$
\begin{align*}
\frac{1}{F} & =\left(W+W^{\prime}\right) \sqrt{\rho_{1}}=W_{r} \sqrt{\rho_{1}} \\
& =\left(\frac{2.394 L}{D^{3}}+\frac{3.192}{D^{\prime 2}}\right) \sqrt{\rho_{1}} \tag{1-126a}
\end{align*}
$$

It follows from the gas laws that the density $\rho_{1}$ at a pressure of 1 dyne/cm. ${ }^{2}$ is

$$
\rho_{1}=\frac{M}{\mathscr{h} \cdot T}
$$

## 1-27B. "CONDUCTIVITY" AND "RESISTANCE" 65

where $M$ is the molecular weight, $\breve{R}$ the universal gas constant, and $T$ the temperature on the absolute scale. Therefore equation 1-126a may be written in the form

$$
\begin{equation*}
\frac{1}{F}=W_{r} \sqrt{\rho_{1}}=\left(\frac{2.394 L}{D^{3}}+\frac{3.192}{D^{\prime 2}}\right) \sqrt{\frac{M}{\breve{R} T}} \tag{1-126b}
\end{equation*}
$$

It is obvious that the total "resistance" to molecular streaming $W_{r} \sqrt{\rho_{1}}$ is proportional to $\sqrt{M}$ and inversely proportional to $\sqrt{T}$. The term $L$ as numerator and the terms $D^{3}$ and $D^{\prime 2}$ as denominators indicate the influences of the length and the diameters of the tube and its end opening respectively on $W_{r} \sqrt{\rho_{1}}$ and consequently on $F$. Expressions $1-126 a, b$ are of great importance to the practical science of high vacua, for with the application of either one of these expressions, the pumping speed of a high-vacuum generator can be precisely determined.

It may be noted that expressions $1-126 a, b$ hold only when the ratio of the diameter of the tube $D$ to the mean free path $\lambda$ is very small. The values for $W_{r} \sqrt{\rho_{1}}$ calculated from 1-126a would, as shown by Knudsen, never be more than 5 per cent in error even if the numerical value of $D / \lambda$ were as much as 0.4 , so that, if this equation is to hold, $D / \lambda$ should be smaller than 0.4 and, therefore, the limiting diameters of the tubes for the flow of various gases, each at a temperature of $20^{\circ} \mathrm{C}$. and a pressure of 1 dyne $/ \mathrm{cm} .^{2}$, must be less than the values given in Table 1-9.

## Table 1-9

| Gas | Air | $\mathrm{H}_{2}$ | He | $\mathrm{N}_{2}$ | $\mathrm{O}_{2}$ | A | CO | $\mathrm{CO}_{2}$ | $\mathrm{NH}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | mm. | mm. | mm. | mm. | mm. | mm. | mm. | mm. | mm. |
| D $<\ldots$ | 37.5 | 69.9 | 109.8 | 37.2 | 39.7 | 39.5 | 36.9 | 24.6 | 26.4 |

If the diameter of the tube be 1 cm ., the value of $W_{r} \sqrt{\rho}$ for air, obtained from equation 1-126a, has a precision of 5 per cent for any range of high vacuum till the pressure rises to 3.76 dynes $/ \mathrm{cm} .^{2}$ If the pressure is higher than this, the total resistance of streaming increases with the increasing pressure to a certain maximum and then begins to decrease. It is thus obvious that this law does not hold for high pressures.

The rate of flow of gases of ordinary gaseous behavior differs from that of gases of free molecular behavior. An expression for the " conductivity," which necessarily differs from expression 1-125 for gases of free molecular behavior, can be derived from Poisseuille's law given in equations $1-106 a, b$. Since the "conductivity " $F=Q /\left(p_{1}-p_{2}\right)$, we obtain from Poisseuille's law for $F$ of gases of ordinary gaseous behavior an expression which may be written as

$$
\begin{equation*}
F=\frac{Q}{p_{1}-p_{2}}=\frac{\pi D^{4} p}{128 \eta L} \tag{1-127}
\end{equation*}
$$

where $D$ and $L$ respectively represent the diameter and the length of the tube, $\eta$ the coefficient of viscosity, and $p$ the pressure at which $F$ is measured. Since the reciprocal value of $F$ is taken to be the total " resistance" to the gaseous flow offered by the tube system, we have an expression for the resistance in the case of high pressures which may be written

$$
\begin{equation*}
\frac{1}{F}=\frac{128 \eta L}{\pi D^{4} p} \tag{1-128}
\end{equation*}
$$

Equations 1-127 and 1-128 which express respectively the conductivity of and the total resistance to the gaseous flow hold only in the case of gases of ordinary gaseous behavior, while expressions $1-125$ and $1-126 a, b$ for the conductivity of and resistance to molecular streaming hold only in the case of gases of free molecular behavior.

Knudsen, partly on the basis of his experimental results on the " conductivity " of different gases at different pressures and partly on the basis of certain theoretical considerations, derived an expression for the "conductivity" of gases which holds for all pressures. It may be written in the form

$$
\begin{equation*}
F=\frac{\pi D^{4} p}{128 \eta L}+\frac{D}{2.394 L} \frac{1}{\sqrt{\rho_{1}}} \cdot \frac{1+\frac{\sqrt{\rho_{1}}}{\eta} D p}{1+1.235 \frac{\rho_{1}}{\eta} D p} \tag{1-129a}
\end{equation*}
$$

In the derivation of equation $1-129 a$ the influence of the opening at the end is not taken into account. To allow for the influence

## 1-27B. "CONDUCTIVITY" AND " RESISTANCE" 67

of the opening of the diameter $D^{\prime}$, if $W_{r}$ be introduced instead of $W$ in equation 1-129a, we obtain an expression of the form

$$
\begin{align*}
F= & \frac{\pi D^{4} p}{128 \eta L} \\
& +\left\{\left(\frac{D^{3}}{2.394 L}+\frac{D^{\prime 2}}{3.192}\right) \frac{1}{\sqrt{\rho_{1}}}\right\} \frac{1+\frac{\sqrt{\rho_{1}}}{\eta} D p}{1+1.235 \frac{\sqrt{\rho_{1}}}{\eta} D p} \tag{1-120b}
\end{align*}
$$

In equation 1-129b the first term corresponds to the law for the flow of a gas through a tube, when its diameter is large compared with the mean free path given by Poisseuille's expression 1-127. The fraction at the end of the second term corresponds to the transition stage between viscous flow and free molecular flow. If the mean pressure $\bar{p}$ be quite small, the fraction becomes unity and therefore the equation reduces to the reciprocal value of the expression 1-125, or $1-126 b$, given by

$$
\begin{aligned}
F=\frac{1}{W_{r} \sqrt{\rho_{1}}}=\left(\frac{D^{3}}{2.394 L}+\frac{D^{\prime 2}}{3.192}\right) \frac{1}{\sqrt{\rho_{1}}} & \\
& =\left(\frac{D^{3}}{2.394 L}+\frac{D^{\prime 2}}{3.192}\right) \sqrt{\frac{R T}{M}}
\end{aligned}
$$

Therefore the semi-empirical equation, $1-129 a$ or $b$, unlike expressions $1-125,1-126 a, b$ on the one hand and 1-127, 1-128 on the other, can be said to be of universal application inasmuch as it holds for all pressures. H. Ebert ${ }^{19}$ has experimentally verified it, and his results agree with the calculated values, thereby confirming the validity of the general law given in expression 1-129a. This equation is of great importance for the science of high vacua in determining the "conductivity" $F$ and the " resistance" of the system. With its aid, Dushman ${ }^{20}$ calculated the rates of flow of air and hydrogen at $20^{\circ} \mathrm{C}$. and at pressures low enough that $\lambda \geq D$. His calculated values are as follows:
${ }^{19}$ H. Ebert, Phys. Zeits. 33, No. 4, 145-151 (1932).
${ }^{30} \mathrm{~g}$. Dushman, Production and Measurement of High Vacuum, p. 235, (Gen. Elec. Co., N. Y., 1922).

Table 1-10

| $L$ <br> $(\mathrm{~cm})$. | $D$ <br> $(\mathrm{~cm})$. | $W$ | $F$ (Air) | $F$ (Hydrogen) |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 5.58 | 5,204 | 19,710 |
| 10 | 1 | 27.12 | 1,070 | 4,053 |
| 1 | 0.1 | $2,712.4$ | 10.70 | 40.53 |
| 10 | 0.1 | 24,258 | 1.196 | 3.60 |

1-28A. Thermal Efflux or Transpiration.-It has been already shown that when a gas in a tube is subjected to a pressure difference, the gas flows from the terminal at higher pressure to that at lower pressure even in the absence of a temperature gradient. In this type of flow, the tube and the gas are assumed to be at a uniform temperature. If it be assumed, however, that the initial pressure of the gas is uniform throughout and that one of the end; of the flow tube is kept at a higher temperature, while the other is at a lower one, so as to establish a temperature gradient, another type of the phenomena of gaseous flow presents itself in the tube. This type, mainly due to temperature difference-which differs in many respects from the type of gaseous flow effected only by driving pressure difference-is called thermal efflux or transpiration.

Let the study of the phenomena of thermal transpiration be begun with the consideration of the type which was originally investigated by Osborne Reynolds ${ }^{21}$. Consider a cylindrical tube $A B$ in which a porous plug of earthenware or stucco or meerschaum, from 1.5 to 2 mm . thick, is inserted at $C$ in the middle of the tube (figure 1-9). Each end of the tube is provided with a suitable jacket so that either steam or cold water could circulate. Thus the steam-jacketed end is maintained at higher temperature than the other end whose temperature is kept low by the cold-water jacket. Let these temperatures of the hot and the cold ends be denoted by $T_{1}$ and $T_{2}$ respectively on the absolute scale of temperature. Each part of the tube, separated by the porous plug, is connected with a separate manometer to take the total gaseous pressure readings of each part separately. Before establishing temperature difference, the initial gaseous pressure in both the

[^6]parts is uniform. After establishing temperature difference between the two parts of the tube, it can be observed that a differential flow will continue until the gaseous densities become so adjusted that the final equilibrium pressures are related by
\[

$$
\begin{equation*}
\frac{p_{1}}{p_{2}}=\sqrt{\frac{T_{1}}{T_{2}}} \tag{1-130}
\end{equation*}
$$

\]

where $T_{1}, T_{2}$ are absolute temperatures, $T_{1}>T_{2}$, and $p_{1}, p_{2}$ are the gaseous pressures at $T_{1}$ and $T_{2}$ respectively. This law holds


Fig. 1-9. "Thermo-diffusiometer."
when the mean free path is large compared with the diameters of the pores of the porous plug.

From the considerations of the kinetic theory of gases, ${ }^{22}$ it will be obvious that even if the porous plug between the heated and the cold parts be removed, the law given in expression 1-130 should hold, provided the mean free path is large compared with the diameter of the tube. In order to ascertain this, let it be supposed that the tube $A B$ (figure 1-9) is a capillary connecting two vacuum enclosures, initially at a uniform pressure, that the plug at $C$ is removed, and that there is discontinuity of temperature at the section $C$, so that the temperature of the gas throughout the heated part up to section $C$ is $T_{1}$ and that of the gas throughout the cold part up to the section $C$ on the other side is $T_{2}$. If $m$ be the mass of each single gas molecule, $n_{1}$ and $n_{2}$ the number of molecules per cubic centimeter in the hot and the cold parts respectively, and
${ }^{22}$ M. Knudsen, " Thermal molecular streaming," Ann. d. phys. 31, 205-229, 633-680 (1910).
$v_{m 1}$ and $v_{m 2}$ the mean molecular velocities corresponding to $T_{1}$ and $\boldsymbol{T}_{\mathbf{2}}$, then the pressures $p_{1}$ and $p_{2}$ are given by

$$
p_{1}=\frac{\pi}{8} n_{1} m v_{m 1}^{2}=\frac{\pi}{8} n_{1} m \frac{8 k T_{1}}{m \pi}
$$

and

$$
p_{2}=\frac{\pi}{8} n_{2} m v_{m 2}^{2}=\frac{\pi}{8} n_{2} m \frac{8 k T_{2}}{m \pi} .
$$

When a temperature difference is established, differential flow sets in and the density of the gas in each part becomes adjusted in such a way that $(\pi / 8) \rho_{1} v_{m 1}{ }^{2}$ or $(\pi / 8) \rho_{1}\left(8 k T_{1} / m \pi\right)$ counterpoises $(\pi / 8) \rho_{2} v_{m 2}{ }^{2}$ or $(\pi / 8) \rho_{2}\left(8 k T_{2} / m \pi\right)$ for the attainment of equilibrium. Hence we have

$$
\frac{\pi}{8} \rho_{1} v_{m 1}{ }^{2}=\frac{\pi}{8} \rho_{2} v_{m 2}^{2}
$$

or

$$
\frac{\pi}{8} \rho_{1} \frac{8 k T_{1}}{m \pi}=\frac{\pi}{8} \rho_{2} \frac{8 k T_{2}}{m \pi} .
$$

Therefore

$$
\frac{\rho_{1}}{\rho_{2}}=\frac{n_{1} m}{n_{2} m}=\frac{v_{m 2}{ }^{2}}{v_{m 1}{ }^{2}}=\frac{T_{2}}{T_{1}} .
$$

Equilibrium is attained by the establishment of the equality of the quantities of gas which flow from the cold to the warm parts


Fig. 1-10.
and, vice versa, from the warm to the cold part, across the cross section at $C$, instead of by the equalization of pressures. With high pressures, the mean free path is small compared to the diameter of the tube; as a result of temperature difference, the gas flows in two streams-the outer layers, surrounding the wall of the tube, moving from the cold to the warm region, and the more central layers, surrounding the axial line of the tube, moving in the opposite direction as shown in figure 1-10. But with low
pressures, when the mean free path is great compared to the diameter of the tube, the gas flows only in one stream, because of the molecular impacts on the walls of the tube which are great in number compared with the intermolecular collisions. In this region of pressures, as a consequence of the transference of molecules because of temperature difference, the numbers of molecules traversing unit area of the cross section of the tube in one second in opposite directions are

$$
\frac{1}{4} n_{1} v_{m 1} \quad \text { and } \quad \frac{1}{4} n_{2} v_{m 2} .
$$

Then the equality of numbers of molecules traversing the cross section in opposite directions is thus expressed by

$$
n_{1} v_{m 1}=n_{2} v_{m 2}
$$

so that the differential flow ceases to continue when the pressure ratio becomes

$$
\frac{p_{1}}{p_{2}}=\frac{n_{1} m v_{m 1}^{2}}{n_{2} m v_{m 2}{ }^{2}}=\frac{v_{m 1}}{v_{m 2}}=\sqrt{\frac{T_{1}}{T_{2}}}
$$

and the density ratio is

$$
\frac{\rho_{1}}{\rho_{2}}=\frac{n_{1} m}{n_{2} m}=\frac{v_{m 2}}{v_{m 1}}=\sqrt{\frac{T_{2}}{T_{1}}} .
$$

In deriving this relation it is assumed for simplicity that there is discontinuity of temperature at the cross section $C$. Even for the case of constant temperature gradient along the length of the tube which connects the two bulbs, the pressure and the density ratios adjust themselves so as to arrest the gaseous flow. Thus expression 1-130 holds in the case of thermal efflux of a gas at such low pressures that the mean free path is large compared with the diameter of a fine capillary tube, or, in other words, when $D / \lambda$ is quite small and the flow is not in double currents.

The law given in equation 1-130 does not apply to gases at high pressures where the ratio of the diameter of the tube to the mean free path, $D / \lambda$, is very large and the pressure differences produced are small and quite complicated by the flow in double streams, one along the wall and the other, the return stream, along the axial line of the tube. For thermal flux at higher pressures, Maxwell's
theory and that of Knudsen give similar forms of expressions for the pressure gradient. Knudsen's form is given by

$$
\begin{equation*}
\frac{d p}{d T}=\frac{0.0139 \frac{1+\frac{C}{273.14}}{1+\frac{C}{T}} \frac{\eta_{0}}{\sqrt{\rho_{0}}} k_{1}}{\frac{D}{2}+25.98 \frac{\sqrt{\rho_{0}}}{\eta_{0}} \cdot \frac{1+\frac{C}{T}}{1+\frac{C}{273.14}} \frac{D^{2}}{4} \cdot \frac{p}{T}} \tag{1-131}
\end{equation*}
$$

where $D$ is the diameter of the tube, $\eta_{0}$ the viscosity at $0^{\circ} \mathrm{C} ., \rho_{0}$ the density of the gas at $0^{\circ} \mathrm{C}$. and a pressure of 1 dyne $/ \mathrm{cm} .^{2}, C$ the Sutherland's constant for the change of viscosity with temperature, and $k_{1}$ a coefficient whose value depends on the form of the isothermal surfaces in the tube.

The law expressed in equation 1-131 does not hold for the flow of a gas at the pressure where $D / \lambda$ is neither very large nor very small. The derivation of this expression is based on the assumption that the molecules which collide with an element of the surface have speeds corresponding to the temperature of the surface element. This assumption is, however, not valid for the case where $D / \lambda$ is neither large nor small, for the molecules which reach the surface element come from regions which are so far away from it that their respective temperatures, and consequently the molecular velocities corresponding to them, cannot be taken to be identical. Allowing for such differences between the mean molecular velocities corresponding to different temperatures at different regions, Knudsen has given an expression for the pressure gradient for this case; it is

$$
\begin{equation*}
\frac{d p}{p}=\frac{3}{4} k \frac{1}{1+\frac{D}{\lambda}} \frac{d v_{m}}{v_{m}} \tag{1-132a}
\end{equation*}
$$

where $D$ is the diameter of the tube, $\lambda$ the mean free path, $v_{m}$ the mean molecular velocity, and $k$ the coefficient varying with the ratio $D / \lambda$. Since $d v_{m} / v_{m}=\frac{1}{2} d T / T$, the pressure gradient may be
expressed in terms of temperature gradient. Therefore expression 1-132a may be written in the form

$$
\begin{equation*}
\frac{d p}{p}=\frac{3}{8} k \frac{1}{1+\frac{D}{\lambda}} \frac{d T}{T} . \tag{1-132b}
\end{equation*}
$$

The numerical value of the coefficient $k$ varies with the ratio $D / \lambda$ and approaches the value $\frac{4}{3}$ as $D / \lambda$ approaches zero. If $k=\frac{4}{3}$, expression $1-132 b$ reduces to

$$
\frac{d p}{p}=\frac{1}{2} \times \frac{d T}{T},
$$

whence we have expression 1-130

$$
\frac{p_{1}}{p_{2}}=\sqrt{\frac{T_{1}}{T_{2}}} .
$$

1-28B. Thermal Efflux Correction of Pressure Measurement.This equation 1-130 is, in fact, important to the science of. high vacua, for it enables us to determine the true gaseous pressure in a vacuum enclosure from the manometric reading. It often happens that the temperature of a gas is quite different from that of the gauge. In this case a correction must be applied to the reading of the manometer. For example, the pressure in a vacuum enclosure, maintained at $80^{\circ}$ Abs. by means of a liquid-air bath, as indicated by a gauge which is at $293^{\circ} \mathrm{Abs}$., is $15.13 \times 10^{-6} \mathrm{~mm}$. Hg . Then by equation 1-130, the true pressure $p_{\text {r80 }} \mathrm{Ab}^{\mathrm{Ab}}$ in the vacuum enclosure at $80^{\circ} \mathrm{Abs}$. from this manometric reading is given by

$$
p_{\text {r80 Abe }}=15.13 \times 10^{-6} \mathrm{~mm} . \sqrt{\frac{80^{\circ}}{293}}=7.91 \times 10^{-6} \mathrm{~mm} . \mathrm{Hg} .
$$

As another example, the saturation vapor pressure of mercury at $298^{\circ}$ Abs. as indicated by a gauge filled with phlegmatic liquid which is kept at $216^{\circ}$ Abs. by cooling with solid carbon dioxide is $1.49 \times 10^{-3} \mathrm{~mm} . \mathrm{Hg}$, while the true value of the saturation vapor pressure of mercury at $298^{\circ} \mathrm{Abs}$., $p_{\text {r298 }}$ Abs. would be

$$
p_{\mathrm{r} 298_{\mathrm{Abe}}}=1.49 \times 10^{-3} \mathrm{~mm} . \mathrm{Hg} \sqrt{\frac{293}{216}}=1.75 \cdot 10^{-3} \mathrm{~mm} . \mathrm{Hg} .
$$

## CHAPTER 2

## VACUUM PUMPS OR GENERATORS

## Section I. Introduction

2-1. Vacuum Pumps-Characteristics and Classification.-A vacuum pump is a device by which any gas is evacuated from an enclosure. It is characterized by (1) the initial pressure from which it functions, (2) the limiting vacuum it generates, and (3) the speed of exhaust or evacuation.

From the view of the initial pressure from which vacuum pumps work, they can be brought into two principal groups: those which, abstracting the gas from an enclosure, eject it directly into the atmosphere; and those whose function is practicable only when they can eject it into a vessel at reduced pressure. So a pump of the latter group works only in conjunction with one of the former group.

The pumps of the first group are by themselves not sufficiently capable of generating high vacua. There are, however, certain new models which can produce vacuum to a pressure as low as nearly $10^{-5} \mathrm{~mm}$. of mercury. A pump of the second group operates efficiently only against a small difference of pressures at pressures less than a few tenths of a millimeter of mercury. It needs an auxiliary supporting pump, one of the first group, to make its functioning possible. This group of pumps, requiring a suitable fore-vacuum support, is the actual group of high-vacuum pumps which can exhaust to the limiting pressure of the highest attainable vacuum with great speed.
2-2A. Speed of Exhaust or Pumping Speed.-Speed of exhaust is one of the characteristics of a vacuum pump. The pumping speed at any given pressure is the volume or the mass of gas abstracted per unit time, measured at that pressure, from an enclosure containing gas at the same mean pressure. This definition, which is due to $W$. Gaede, thus confines itself to the speed at a given pressure instead of the pump speed in general for
all pressures. This restriction is proper, for in many of the pumps the speed of exhaust varies with the variation of pressure. For example, the speed of exhaust of all mechanical rotary pumps, as a rule, decreases with decrease in pressure.

In accordance with the above definition, the speed of exhaust $S$ may be given a precise expression. If the volume $d v$ of a gas at a given pressure be abstracted in a time $d t$ from an enclosure at the mean pressure equal to the said given pressure, the speed $S$ may be written in the form,

$$
\begin{equation*}
S=\frac{d v}{d t} \tag{2-1}
\end{equation*}
$$

Pumping speed can be measured by the method of constant pressure calculated by Gaede, in which the relation given in expression $2-1$ is applied. This method depends upon the regulated admission of gas into an enclosure which is being continuously exhausted by a pump in such a way that the pressure in the enclosure remains constant. The speed of exhaust at constant pressure is measured by the following device: A fine needle valve or any other valve which can be closely regulated is arranged so that air or any gas at barometric pressure may be admitted to the enclosure to maintain the pressure in the enclosure constant. It is thus possible to measure the volume rate at which gas is to be supplied to the enclosure to counterbalance the working of the evacuating pump and so maintain a constant pressure. If the volume of gas at the barometric pressure $b$ enters the enclosure which is maintained at a constant pressure $p$ during the time $t$ be $v$, then the pumping speed $S$ can be expressed, from the consideration of Boyle's law, thus:

$$
\begin{equation*}
v b=\operatorname{Stp} \tag{2-2a}
\end{equation*}
$$

or

$$
\begin{equation*}
S=\frac{b v}{p t} . \tag{2-2b}
\end{equation*}
$$

This method is practicable for measuring the speed of exhaust of very high-speed vacuum pumps.

In practice, however, it is necessary, while conducting speed tests, to make measurements over an appreciable pressure range.

In order to do this, it is essential to join the vacuum pump to a vacuum gauge by means of a connecting tube of suitable dimensions so that the pressure reading at any instant represents the actual pressure on the low-pressure side of the pump. The pump is thus joined to the enclosure of volume $v$ with the gauge connected to it. If $p_{1}$ and $p_{2}$ be the pressures obtained in the enclosure at times $t_{1}$ and $t_{2}$, then the pressure range in which the speed of the pump may be taken to be constant is $p_{1}-p_{2}$. If the original pressure in the enclosure be $p$, and the pressure of the limiting vacuum of the pump be $p_{0}$, the pressure decrease $d p$ due to evacuation for a time $d t$ is proportional to the total range of pressure which is the difference between the original pressure $p$ in the enclosure and the pressure $p_{0}$ of the limiting vacuum. So the rate of pressure decrease in the vacuum enclosure may be expressed in the form

$$
\begin{equation*}
-\frac{d p}{d t}=K\left(p-p_{0}\right) \tag{2-3a}
\end{equation*}
$$

$K$ being the constant characteristic of the volume of the enclosure and of the pumping speed. The pressure decrease is inversely proportional to the volume $v$ of the vacuum system. Hence, the rate at which the pressure is reduced in the vacuum enclosure, as determined by the pumping speed $S$, the volume $v$ of the vacuum enclosure, and the limiting pressure $p_{0}$, is given by

$$
\begin{equation*}
-\frac{d p}{d t}=\frac{S}{v}\left(p-p_{0}\right) . \tag{2-3b}
\end{equation*}
$$

From this an expression for the speed of exhaust $S$ is derived by

$$
\begin{equation*}
S=\frac{v}{t_{2}-t_{1}} \int_{0}^{p} \frac{d p}{p_{1}-p_{2}}=\frac{v}{t_{2}-t_{1}} \log _{\epsilon}\left[\frac{p_{1}-p_{2}}{p_{2}-p_{0}}\right] \tag{2-4}
\end{equation*}
$$

where $t_{2}-t_{1}$ is the time interval in which the pressure $p_{1}$ falls to $p_{2}$ by evacuation. Expression $2-4$ is used with advantage only in the case of those pumps whose limiting pressure is very small. If $p_{0}$ is, however, treated as negligible compared with $p_{1}$ and $p_{2}$, expression 2-4 becomes

$$
\begin{equation*}
S^{\prime}=\frac{v}{t_{2}-t_{1}} \log \frac{p_{1}}{p_{2}} \text { or } \frac{p_{2}}{p_{1}}=\frac{\epsilon^{-S\left(t_{2}-t_{1}\right)}}{v} . \tag{2-5}
\end{equation*}
$$

Then $S$ and $S^{\prime}$ are equal. Even expression 2-5 serves as a form of definition of the speed of exhaust, and it does not differ essentially from the definition of the pumping speed expressed by equation 2-1 or $2-2 a$ because even in this case the speed is not mere rate of change of pressure in the volume $v$ but is the rate of change of volume of the gas in the enclosure at any instant, the volume being measured under the pressure attained by the pump at that instant. Thus the intrinsic pumping speed is measured in terms of volume per unit time and is numerically equal to the volume (volume of the vacuum system together with that of the pump) in which the reduction of pressure by the pump in one second is such that the difference between the instantaneous pressure and the limiting pressure will be $1 / \epsilon$ of the difference between the initial pressure and the limiting pressure; or, in other words, the difference between the instantaneous and the limiting pressure will be 36.78 per cent of the difference between the initial pressure and the limiting pressure. This follows because, if in equation 2-4 the terms $t_{2}-t_{1}=1$ second, and $\log _{e}\left(p_{1}-p_{0}\right) /\left(p_{2}-p_{0}\right)=1$ or $\left(p_{2}-p_{0}\right) /\left(p_{1}-p_{0}\right)=1 / \epsilon$, then the pumping speed $S$ is numerically equal to the volume $v$ of the vacuum system, i.e., $S=v$.

2-2B. Influence of Connecting-Tube System upon Speed of Exhaust.-The equipment of a high-vacuum generator system usually consists of a vacuum pump, a connecting system of tubes, and a suitable enclosure. As a result of "resistance" of the tube system encountered by the gaseous flow, the actual speed of exhaust $E$ depends not only upon the intrinsic pumping speed $S$ but also upon the " conductivity" $F$. The pressure $p$ at the lower pressure terminus of the pump therefore differs from the pressure $p_{1}$ in the vacuum enclosure. The pressure gradient set up between $p$ and $p_{1}$ establishes a flow of gas from the enclosure to the pump, and the " conductivity " or rate of flow $F$ is given by expression 1-125 (see chapter 1, section VI, 1-27B, page 64) and may be rewritten in the form,

$$
\begin{align*}
F=\frac{Q}{p-p_{1}}=\frac{1}{W_{r} \sqrt{\rho_{1}}}= & \left\{\left(\frac{D^{3}}{2.394 L}+\frac{D^{\prime 2}}{3.192}\right) \frac{1}{\sqrt{\rho_{1}}}\right\} \\
& =\left\{\left(\frac{D^{3}}{2.394 L}+\frac{D^{\prime 2}}{3.192}\right) \sqrt{\frac{\breve{R} T}{M}}\right\}, \tag{2-6}
\end{align*}
$$

where $L$ and $D$ represent the length and the diameter of the tube, respectively, while $Q$ denotes the volume of gas at a uniform temperature flowing out, measured at a pressure of 1 dyne $/ \mathrm{cm}^{2}{ }^{2}$, $W_{r} \sqrt{\rho_{1}}$ the resistance of the tube together with the influence of the opening at the end encountered by the gaseous flow, $\rho_{1}$ the density of the gas at a pressure of 1 dyne/cm. ${ }^{2}, M$ the molecular weight,


Fig. 2-1. Rate of flow of air through a tube at $20^{\circ} \mathrm{C}$. in $\mathrm{cm} .^{3}$ at one barye.
and $T$ the absolute temperature. This equation shows that for small values of $D$ and large values of $L$, the "conductivity" $F$ varies approximately directly as $D^{3}$ and inversely as $L$. For a clear comprehension of this relation, Payne's ${ }^{1}$ graphical representation is reproduced below (figure 2-1). The curves in the graph representing plots of equation 2-6, applied to air at $20^{\circ} \mathrm{C}$. drawn on log-log scale, give the " conductivity " $F$ as a function of $L$ for different values of $D$ indicated at the bottom of the graph (figure 2-1).

Since from equation 2-6 it follows that for the same dimensions of the tube, the rates of flow of the gases at the same temperature are proportional to the square roots of their respective molecular ${ }^{1}$ J. Franklin Inst., 211, No. 6, 689-750 (1931).
weights, the values of $F$ of any gas at $20^{\circ} \mathrm{C}$. can be easily derived from the values of $F$ of the flow of air at the same temperature given in Payne's graph.

In the case of evacuation by means of a pump, the quantity of gas $Q$ taken out by the pump must be the same as that which flows through the connecting tube system from the enclosure. Therefore

$$
\begin{equation*}
Q=F\left(p_{1}-p\right)=S p=E p_{1} \tag{2-7}
\end{equation*}
$$

On eliminating $p$ and $p_{1}$ from this expression 2-7, an equation, expressing the relation between the intrinsic pump speed $S$, the " conductivity " $F$, and the actual speed of exhaust $E$, is obtained:

$$
\begin{equation*}
\frac{1}{E}=\frac{1}{S}+\frac{1}{F} \tag{2-8a}
\end{equation*}
$$

or

$$
\begin{equation*}
E=\frac{S F}{S+F} . \tag{2-8b}
\end{equation*}
$$

Equation $2-8 a$ or $b$ shows the influence of the connecting tube system upon the speed of exhaust and how the speed of exhaust differs from the intrinsic pumping speed. To grasp clearly the extent of the influence of the connecting tube upon the speed of exhaust from concrete examples, let a pump with an intrinsic pumping speed $S=1500 \mathrm{~cm} .3 / \mathrm{sec}$. be connected to an enclosure by means of a connecting tube 50 cm . long with a diameter of 2 cm . The actual speed of exhaust $E$ attained by this evacuating system is the result of the intrinsic pumping speed $S$ as modified by $F$. If the molecular weight of air, the value of $20^{\circ}$ on the absolute scale of temperature, the length of the tube $L=50 \mathrm{~cm}$., and its diameter $D=2 \mathrm{~cm}$., be introduced in equation $2-6$, we obtain the value of the conductivity

$$
F=1800 \mathrm{~cm} .^{3} / \mathrm{sec} . \text { approximately } .
$$

Now, on introducing the value of the intrinsic pumping speed $S=1500 \mathrm{~cm} .3 / \mathrm{sec}$. and that of $F=1800 \mathrm{~cm} .{ }^{3} / \mathrm{sec}$. in equation 2-8, the actual speed of exhaust $E$ of this evacuating system is obtained thus:

$$
\frac{1}{E}=\frac{1}{1500}+\frac{1}{1800} \text { or } E=\frac{1500 \times 1800}{1500+1800}=820 \mathrm{~cm} .8 / \mathrm{sec} .
$$

In this case, the speed of exhaust $\dot{E}$ and the intrinsic pumping speed
$S$ are in the ratio of approximately $8: 15$, i.e., $E: S:: 8: 15$. It is obvious that in this case the speed of exhaust $E$ of the evacuating system may be taken to be roughly about half of the value of the intrinsic pumping speed $S$. As another example, let a pump with an intrinsic speed $S=15,000 \mathrm{~cm} .^{3} / \mathrm{sec}$. be joined to an enclosure by means of a connecting tube whose dimensions are quite the same as those of the connecting tube of the former evacuating system.

Table 2-1. Speeds of Exhaust $E$ for Different Values of $F$ with Pumping Speeds $S$ of Different Values

| $F$ | Speed of Exhaust $E\left(\mathrm{~cm} .^{8} / \mathrm{sec}\right)$ |  |  |  |
| ---: | :---: | :---: | :---: | :---: |
|  | $S=5000$ | $S=10,000$ | $S=20,000$ | $S=50,000$ |
| $\infty$ | 5,000 | 10,000 | 20,000 | 50,000 |
| 20,000 | 4,000 | 6,667 | 10,000 | 14,286 |
| 10,000 | 3,333 | 5,000 | 6,667 | 8,333 |
| 5,000 | 2,500 | 3,333 | 4,000 | 4,545 |
| 2,500 | 1,667 | 2,000 | 2,222 | 2,381 |
| 1,000 | 833 | 909 | 952 | 980 |
| 500 | 454 | 476 | 488 | 495 |

Temperature and other conditions remaining constant and quite similar to those of the former example, the actual speed of exhaust in this latter case must be

$$
\frac{1}{E}=\frac{1}{15,000}+\frac{1}{1800} \text { or } E=\frac{15,000 \times 1800}{15,000+1800}=1610 \mathrm{~cm} .^{3} / \mathrm{sec}
$$

Here $E$ and $S$ are in the ratio of approximately $8: 75$ or $E: S:: 8: 75$ approximately. Though the pumping speed $S$ of this second case is ten times greater than that of the first, the speed of exhaust $E$ here is not even twice the value of $E$ of the first evacuating system. These examples, which represent very ordinary cases of evacuating systems, enable one to appreciate how and to what extent the connecting tubes of an evacuating system influence the speed of exhaust $E$.

Speeds of exhaust for different values of $F$ with pumps of different speeds, calculated from equation 2-8 as shown above are given in Table 2-1.

The results of the examples, as well as the data given in Table 2-1, indicate that the effect of a large value of $S$ becomes more and
more inappreciable as $F$ is decreased, so that for low values of $F$, the value of $E$ becomes well-nigh independent of $S$ and approaches the value of $F$. It is therefore important for an efficient utilization of the maximum speed of a pump that the dimensions of the connecting tube be so chosen that $F$ is made as large as practicable. If the dimensions of the tube system were, however, to be determined by other considerations, so that $F$ is not of sufficiently large magnitude, it would be futile to make use of a pump of high intrinsic speed. As the data given in Table 2-1 indicate, for $F=$ 500 ( $L=23 \mathrm{~cm}$., $D=1 \mathrm{~cm}$.), a pump with a pumping speed $S=5000$ is almost as good as one for which the speed $S=20,000$ or even one for which the speed $S=50,000 \mathrm{cc}$. $/ \mathrm{sec}$. These considerations are of great importance in the adjustment of an efficient evacuating system.

2-3. Methods of Exhaust.-Limiting vacuum in an enclosure, generated by a working pump system, is maintained by continued pumping. It can be maintained at the same limiting pressure so long as the vacuum enclosure is connected to the operating pump system. If the vacuum enclosure, after being thoroughly evacuated to the limiting vacuum, be sealed off from the evacuating pump system, however, the vacuum does not remain at the obtained limiting pressure, because the connecting tube, during the process of sealing off the enclosure from the working pump, gives out a certain quantity of gas because of the chemical action that takes place by thermal activity. Such sealed vacuum enclosures thus contain quantities of gases in excess of the limiting vacuum. These sealed enclosures which contain traces of such liberated gases can, however, be re-exhausted to the limiting pressure by methods other than continued pumping. These methods-which involve the use of peculiar devices called "getters" (see chapter VI, pp. 287 ff .) -not only remove the residual gases, but also maintain the vacuum at the same low pressure against the deteriorating effects. Before describing the getters, the action of various types of pumps will be considered.

## Section II. Pumps with Pistons

2-4A. Solid-Piston Pump of Von Guericke.-The first, simplest, and most elementary contrivance for removing a gas from an enclosure is a piston pump, originally designed and constructed by

Von Guericke. This type of pump, whose design is shown in figure 2-2, consists of a cylinder, which forms the body, having valves opening upward, one at its upper end and the other at the lower. Within this body is a piston having a valve which also opens upward. The lower end of the pump's body is connected by


Fic. 2-2. Von Guericke's type of solid piston pump. a pipe with a vessel to be exhausted of air.

The piston and the valves are carefully constructed to be as airtight as possible.

The operation of the pump consists of repeated up-anddown strokes of the piston. Consider that the operation of the pump commences when the piston is at the lower end of the body. As the piston is drawn upward, a partial vacuum is formed between it and thelower end of the cylinder. The pressure of the air below the lower end opens the lower valve, and the air from the jar and the tube follows the piston, while the air above the piston becomes compressed, opens the upper valve of the cylinder, and passes into the atmosphere.
When the piston reaches the upper end of the cylinder it is given a downward stroke so that the air between it and the lower end of the cylinder becomes compressed, shuts the valve at the lower end, and opens the valve in the piston. Then the air that was between the piston and the lower end of the cylinder passes through the piston valve and occupies the space above the piston.

Thus in one complete stroke a quantity of air from the vessel and the tube below the lower end of the body has been removed, while with each succeeding stroke the same volume of air, but at a diminished pressure, is abstracted, until the pressure of the residual air is insufficient to raise the valves.

Because of the valve at the upper end of the pump body, the pressure of the air above the piston, during the downward stroke, becomes much less than the atmospheric pressure, so that the piston valve is more easily raised than would otherwise be the case. Also, the piston can be drawn upward with considerable ease.

Let $V$ be the volume of the vessel to be exhausted and the connecting tube, $m$ the mass of air when the piston is at the bottom stroke, and $v$ the volume of the cylinder between its upper and lower valves. At the end of the upward stroke, the volume of the mass $m$ of air will be $V+v$. Of this volume, a volume $v$ of air will be expelled at the downward stroke, and a volume $V$ of air will be left in the apparatus, of course with a density lower than before. At the end of the first stroke, the mass of air left in the instrument is $\left(\frac{V}{V+v}\right) m$. If the strokes are repeated $n$ times, then the mass of air after $n$ strokes is $\left(\frac{V}{V+v}\right)^{n} m$. Inasmuch as this mass of air now occupies the volume $V$, it follows that its density is $\left(\frac{V}{V+v}\right)^{n} \cdot \frac{m}{V}$, while the original density was $m / V$. Therefore, the density of the air left in the instrument after $n$ strokes is $\left(\frac{V}{V+v}\right)^{n}$ times the original density. From this expression, it is obvious that the density of the air in the instrument cannot be made zero unless the number of strokes $n$ is infinite. If the original pressure within the enclosure is $p$, then after $n$ strokes it will be $\left(\frac{V}{V+v}\right)^{n} \cdot p$. In practice, however, it is not possible to obtain a very low pressure with this solid-piston cylinder pump, because of the weight of the valves, the leakage around the piston, and the fact that the piston, when at the bottom of its stroke, does not expel all the air in the cylinder.

2-4B. Oil-Sealed Solid-Piston Cylinder Pump.-The original model of the piston cylinder pump of Von Guericke was subsequently improved by Gaede, ${ }^{2}$ Fleuss, and others. In the form in which it was given by Gaede when the piston is at the compressed stroke, the intervening space between the piston and the cylinder

[^7]which usually reserves gas molecules is entirely removed. In the pump designed by Fleuss, the piston, the valves, and the intervening space between the piston and the cylinder are oil-sealed, so that the pump is fairly airtight in all


Fig. 2-3. directions. The details of the construction of this pump having the piston with its leather cup at the bottom end of the stroke is shown in figure 2-3. A pool of oil above the piston moves up and down with it so as to provide a perfect seal for both the piston and its valve. In the upward stroke, as the piston approaches the top, the spring-controlled valve in the head gives way under the pressure, and the entrapped gas and some of the oil are projected through the valve and the oil seal above it. The transported oil thus actually functions as the piston, and consequently no difficulties arise from dead space in the cylinder head. The release of the head valve aids in preventing the gas from sticking to the walls at low pressures. On the return stroke the head valve cannot close until sufficient oil has run through to provide the oil seal for the piston. The Ushaped tube connected to the pump at its base relieves the pressure on the piston during the first few strokes in pumping from atmospheric pressure. A threaded plug is provided so that oil may be replenished or surplus oil removed. The success of the oilsealed mechanical piston pump depends only upon the purity of the oil, and on its being maintained free from dissolved liquids and gases, including air. A single pump of this type in good condition can reduce the pressure to about 0.05 to $0.02 \mathrm{~mm} . \mathrm{Hg}$. But when two or three of these pumps are combined so as to form a two- or three-stage pump, it can exhaust an enclosure to a pressure as low
as $2 \cdot 10^{-4} \mathrm{~mm}$. Hg. The oil-sealed piston pump, consisting of four pumps in series worked by a common piston-rod in the same vertical cylinder, designed by Gaede, when working from atmospheric pressure was stated to have given a pressure of $5 \times 10^{-5}$ $\mathrm{mm} . \mathrm{Hg}$. These piston-cylinder pumps are usually operated by means of simple hand machines.

2-5. Oil-Sealed Rotary-Piston Pumps.-Among the piston pumps, those which are of greater importance and of much practical use for the rarefication of gases are the pumps with rotatory


Fia. 2-4.
solid pistons, known as rotary pumps. The process of evacuation of gases from an enclosure by means of the rotary pumps is similar to the compression of gases with rotary compressors or compressing pumps. Oil is used for sealing and filling up dead space in these rotary pumps, making them airtight. These pumps, are therefore called oil-sealed rotary pumps.

A rotary pump was first designed and constructed by Siemens and Schuokert and K. T. Fischer. ${ }^{3}$ The principle and the design of this pump are illustrated in figure 2-4. The pump as shown consists principally of one cylindrical casing, closed on either side with airtight disks and supporting eccentrically the axis of a cylinder, which can freely rotate on it. The eccentricity is such that the cylinder is in close contact with the inner wall of the casing
${ }^{8}$ K. T. Fischer: Ben. Phys. Ges., 7, 383 (1905); Phys. Zeits. 6, No. 24, 868 (1905).
over the area between an inlet and an outlet port. Two vanes sliding within a diametrical slot in the rotating cylinder are kept continuously pressed by coiled springs against the inner surface of the wall of the casing as they rotate with the cylinder. The effect is to press out air continuously from the inlet port to the outlet port, where a metal valve is mounted. It is essential that sufficient pure and non-volatile oil should always be present to serve


Fig. 2-5. not only for lubrication, but also for sealing possible leaks and filling up any dead space.

Almost all the modern rotary pumps, including that of Gaede, are constructed on this " scraping-vane " principle. The Gaede rotary pump is among the best at the present time. This model, with many modifications, is being manufactured by Trimount and Central Scientific Co. in America, Fysma in Czechoslovakia, Hilger \& Co. in England, Gaiffe-Gallot and Pilon Company in France, and Leybold \& Co. in Germany. The construction and the manner of operation of one of the modern models are shown in figure 2-5.
The pump has an airtight outer casing containing its entire mechanism. The outer casing is provided with outlet and inlet tubes, and an opening on the top through which the pump is fed with oil. The mechanism consists of an airtight cylindrical exhausting chamber having an inlet port joined to the inlet tube, an outlet port fitted with a valve, and a cylindrical rotor which turns on an eccentric axis, having a diametrical slot with two steel sliders pressed by means of steel springs against the inner walls of the exhausting chamber. The pump is fed with oil so as to keep the exhausting chamber submerged in the oil.

As the cylindrical piston rotates on its axis, air is drawn into the exhausting chamber. The vanes conduct the air from the inletport side to the outlet-port side of the chamber, and finally press it out the outlet-port valve into the body of the outer casing. Hence the air escapes through the outlet tube. One of the sides of the outer casing is provided with two orifices to conduct the necessary amount of oil to seal the valve. A small channel leads oil into the exhausting chamber not only to lubricate the inner rotary
mechanism but also to form a continuous layer covering the inner walls of the exhausting chamber against which the vanes slide. This oil layer keeps the walls of the chamber smooth for easy sliding of the vanes on the one hand, and on the other seals the dead space between the slides and the surface of the walls. A special device continuously drops oil onto the axle in order to keep air from leaking along it.

The Cenco "hyvac" rotary pump, constructed by the Central Scientific Co. of America (U.S.A.), is a special type of scraping vane pump, driven by an electric motor. The cylinder of this pump, which rotateseccentrically aboutan axis, coinciding with the center of the casing, has no diametrical slot with vanes, such as those of Gaede pumps. The inlet and outlet are close together, separated only by


Fig. 2-6. a single scraping vane passing through the casing, which is kept under pressure by a spring device, as shown in figure 2-6. The entire pump is submerged in oil, which makes all the connected parts quite airtight.


Fig. 2-7.
Another interesting and elaborate rotary pump is that of Trimount, shown diagrammatically in figure 2-7. The rotating cylinder is in close contact with the casing over half its circumference
and is provided with eight laminated vanes separating the exhausting chamber into compartments. The sliding vanes are regulated by means of special devices $B$ and $G$. By this arrangement, the whole apparatus is kept perfectly airtight. This pump functions, in a way, like the multi-stage rotary vacuum pump.

A pump is said to be a two- or multi-stage pump if two or more' pumps are connected in series so as to form a single system. A


Fig. 2-8.
diagram of a two-stage pump is shown in figure 2-8. The principle of connecting the rotary pumps, as indicated in figure 2-8, is the same as that of connecting pumps of any other sort. Several companies manufacture multiple-stage pumps. The pumps are connected together either in series to obtain a higher limiting vacuum, or in parallel to obtain a greater speed of evacuation. Table 2-2 shows the efficiency and the speed of a two-stage pump.

The data given in Table 2-2 are for a pump having 300 revolutions per second, with a special kind of oil for sealing. The limiting vacuum of this type of two-stage rotary pumps is $10^{-5} \mathrm{~mm}$. Hg. The pressures given in Table 2-2 are measured when the pump is connected with a measuring gauge by a short connecting tube, or when the measuring gauge is directly connected to the cones of the high-vacuum arms of the pump.

The limiting vacuum of a rotary-piston pump is dependent upon the precision of construction of each part and upon the general design and the technical arrangement as a whole.

The speed of exhaust in the region of high pressures of a rotarypiston pump may be taken as the product of the volume of the exhausting chamber and the number of revolutions of the rotatory cylindrical piston per second.

Rotary pumps with great speed of exhaust are often used for evacuating systems in large labora ories and workshops but they

Table 2-2

| Time of exhaust <br> $t$ (sec.) | Pressure obtained <br> $p$ (mm. Hg.) | Speed of exhaust <br> $S$ (lit. /sec.) |
| :---: | :---: | :---: |
| 0 | 740 | 0.7 |
| 30 | 24 | 0.75 |
| 60 | 1.0 | 0.55 |
| 90 | 0.15 | 0.35 |
| 120 | 0.025 | 0.25 |
| 180 | 0.004 | 0.2 |
| 240 | 0.001 | 0.15 |
| 300 | 0.00025 | 0.1 |
| 360 | 0.0001 | 0.1 |
| 420 | 0.00004 | 0.1 |

yield a comparatively low limiting vacuum of 1 to $2 \mathrm{~mm} . \mathrm{Hg}$. It is therefore not advisable to make use of such a central supply when high vacua are required. It is not safe to connect rotary pumps of any make directly to a vacuum enclosure in which chemicals are being distilled without inserting some device for absorbing the vapors of the chemicals between the vacuum enclosure and the pump. If such provision is not made the vapors given out by the chemicals during the distillation process are easily absorbed by the oil, forming a sort of emulsion, thereby increasing the vapor pressure, and so bringing down the limiting vacuum. Kanik and Sandera devised an arrangement for removing such absorbed volatile chemicals from the oil. Before commencing to pump, the conducting tube connected to the vacuum enclosure is closed and the outlet is connected to a water-jet pump, and the whole of the pumping apparatus is heated to a temperature of $100^{\circ} \mathrm{C}$. The heat vaporizes the absorbed chemicals, and the
vapors thus given out are drawn out by an aspirator. Consequently the oil of the pump is freed from all the absorbed chemicals which damage the vacuum. Then the pump is cooled to normal temperature and it is ready to function properly. This process is particularly useful in case the oil of the pump is contaminated by water.

Rotary pumps cannot be said to be high-vacuum pumps, for their pumping speed decreases considerably as the pumps reach the limiting vacuum. They can, however, be used as backing pumps for high-vacuum pumps. The limiting vacuum of these pumps, which is usually 0.1 to $0.02 \mathrm{~mm} . \mathrm{Hg}$, is quite sufficient for the operation of all high-vacuum pumps.

Rotary pumps are used as backing pumps not only for the oildiffusion pumps, but also for mercury-diffusion and condensation high-vacuum pumps. Rotary ptmps are invariably constructed of cast iron, for in addition to being airtight, it is unaffected by mercury.

Two rotary pumps may be connected either in series or in parallel, according to necessity. A two-stage rotary pump, arranged in series, can yield a limiting vacuum with a pressure as low as $10^{-5} \mathrm{~mm} . \mathrm{Hg}$. Contrary to what one might expect, there is no advantage in increasing further the number of stages. These twostage rotary pumps are submerged in oil to keep every part air tight.

The outlet of the rotary-piston pump is open to the surrounding atmosphere. The pump ejects the gas into the outside air of normal atmospheric pressure, which is very high in comparison with the pressure within. Consequently a certain amount of air from the surrounding atmosphere becomes dissolved in the sealing oil of the pump. This dissolved air is released in the vacuum. Thus a small amount of air enters the vacuum, and is partly expelled again by the pump till a sort of equilibrium is attained. With a two-stage pump, arranged in series, the absorbed air does not affect the vacuum as much as in the single-stage pump. In order to avoid undesirable absorption of gases or air, it is essential that the oil come in contact with the outside air as little as possible when the pump is not in operation. Every pump of this type takes a certain time before it begins to function properly. The time before proper operation depends upon the quantity of air absorbed by the oil. During this period, the pump gradually exhausts to a
great extent the air absorbed in the oil. Some of the latest models of these pumps require only a relatively short time before satisfactory operation.

It is remarkable that at normal temperature the vapor pressure of the oil which is generally used in the rotary pumps is 0.015 mm . Hg , while the pressure of the limiting vacuum obtained by these pumps, which is only $0.01 \mathrm{~mm} . \mathrm{Hg}$, is obviously much lower than the vapor pressure of the oil. This fact indicates that the pump speed is greater than the speed of the vaporization of the oil. Therefore, in the vacuum, an equilibrium of the gas molecules is obtained at a pressure lower than the pressure of the vapor of the oil used in the pump. Usually the temperature of the oil is increased during the operation of the pump. This temperature rise increases the vapor pressure of the oil. To minimize the vapor pressure and obtain the highest possible limiting vacuum of these rotary pumps, it is usual to cool them. It is, however, advisable to use an oil which has a low vapor pressure even at higher temperatures.

For low vacuum with one-stage rotary pumps it may be sufficient to use motor oil such as " Penzoil" (motor oil S.A.E. 70), while for obtaining good limiting vacuum with two- or multi-stage pumps, it is better to use an oil such as "Cenco" vacuum pump oil which has a low vapor pressure. For satisfactory operation of these pumps it is advisable to clean and refill them from time to time with fresh oil. Beyond this they do not demand any special care.

2-6. Electromagnetic-Piston Pumps.-An electro-magnetic-piston pump is similar in its form and de-


Fig. 2-9A. sign to the common cylinder piston pump. The piston of this pump, unlike that of the ordinary cylinder piston pump, is given its alternate up-and-down strokes by alternating electromagnetic induction. This pump was designed and constructed by Porter, Bardwell, and Lind. ${ }^{4}$ The pump, shown in figure 2-9A, consists of a main glass cylinder with two ball-and-socket valves, one in the upper and the other in the lower
${ }^{4}$ Induatrial and Eng. Chem. 18, 1086 (1916).

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part, in which is placed a glass piston, having a tube fitted with a soft iron rod 5 cm . long and 0.3 cm . in diameter. The piston also has a ball-and-socket valve which allows the passage of any gas in the same direction as the valves of the cylinder. The entire piston is moved up and down by means of the solenoid that surrounds the cylindrical jacket of the pump. The solenoid is actuated by a current of 0.5 amp . interrupted three times a second by an oscillating relay. A 50 -watt 100 -volt lamp is connected across


Fig. 2-9B.
the break, so that the current is never completely interrupted, but oscillates between 0.5 and 0.3 amps . The piston therefore does not fall to the bottom of the tube.

The electromagnet raises the piston to the upper part of the pump against gravitation, thereby increasing the volume of the lower part of the pump, which causes the air from the receiver to be drawn into the cylinder through the lower valve. In the interrupted interval of the electromagnetic force, the gravitational force gives a downward stroke to the piston, thereby causing the air in the lower part to pass upward through the valve of the piston. On the upward stroke the air above the piston is forced out through the upper valve of the cylinder. Thus by the repetition of this process the receiver is exhausted. This pump exhausts to a pressure of about $0.2 \mathrm{~mm} . \mathrm{Hg}$, with a pumping speed of about 7 liters per hour.

Recently the design of this pump has been modified, especially
in the arrangement of the electromagnets for the operation of the piston. Funnel and Hower ${ }^{5}$ have modified the pump in such a way that the glass cylinder is arranged in a horizontal position with four valves instead of in the usual vertical position with only two valves. This modified pump, shown in figure $2-9 B$, is operated by two electromagnets instead of one. The current in these electromagnets is interrupted 78 times per minute. With this arrangement, the pump works more steadily and efficiently. There are certain disadvantages. The piston in its horizontal position moves on the lower part of the horizontal cylinder with considerable friction.

Livingstone ${ }^{6}$ avoided this friction by placing the cylinder with its four valves in a vertical position as shown in figure 2-9C.

The cylinder of Livingstone's electromagnetic-piston pump is 35 cm . long with an internal diameter of


Fig. 2-9C. 1 cm . The glass piston is 10 cm . long, and has a bundle of soft iron wires as its core. The electromagnets are 7.5 cm . long. The piston makes sixty complete strokes a minute, and the pump has a speed of $1000 \mathrm{~cm} .^{3}$ per minute. This speed holds for both dry and moist gases if with the latter the valves are kept at a temperature of about $40^{\circ} \mathrm{C}$.
In some of these pumps the piston hangs upon an elastic spiral. The motion of the piston is controlled by two electromagnets, in

[^8]which the current is regularly interrupted by a pendulum arrangement.
The electromagnetic-piston pumps are not oil sealed as the rotary-piston pumps are, since they are designed for producing vacua uncontaminated by oil vapor. Such vacua are sometimes of considerable importance to certain branches of industrial and engineeing chemistry.
2-7. Liquid-Piston Pumps. (A) General Remarks.-Liquidpiston pumps were the first devices with which high vacua were originally obtained. With these pumps, which are in some use even today, it is only under favorable conditions that a high vacuum may be efficiently produced. Their speed is also very low, and, consequently, it takes considerably longer to produce a high vacuum by means of these pumps. Nowadays, when there are pumps whose pumping speed is much higher, and which are of greater efficiency than the liquid-piston pumps, these are not used except for certain special purposes. The water-jet pump is often used only as a backing pump, especially if vacuum enclosures contain volatile fluids whose vapors would contaminate the sealing oil of the oil pumps. But the mercury-piston pumps, the Töpler pump, and the Sprengel pump can be used to advantage for the production of high vacua, especially if the volume of vacuum enclosure is small and if the exhausted gas is pure and is to be carefully conserved as in the case of rare gases, though their pumping speed is very low.

There are, however, certain liquid-piston pumps which may be termed high-speed high-vacuum pumps. The rotary mercurypiston pump of Kaufmann, and that of Gaede, may be placed in such a class. Since the discovery of the more efficient and much simpler pumps with greater pumping speed, these two kinds of rotary mercury-piston pumps have become obsolete. They are briefly described here only for their historical interest.
(B) Water-Jet Pump or Aspirator.-The water-jet pump or aspirator is of ancient design; its construction was based upon the principle of fluid ejectors, often used for propelling liquids or gases. These pumps are still extensively used either as filter pumps or for pumping out vapors which would contaminate oil in the oil-sealed pumps. These pumps are of many designs, of which one efficient type is shown in figure 2-10.

A stream of water flows through a jet tube, then into a suitable choke tube. At the entrance of the choke tube the water jet from the nozzle drags along with it the surrounding air. As it enters the mouth of the choke tube, air forms, as it were, a sheath around the jet. Then with the divergent jet the air sheath grows thinner, and, becoming entangled with the jet, is carried out with the water.


Fig. 2-10.


Fig. 2-11.

A water-jet pump of Hanf Buest Co. evacuates a volume of 2000 cc. from normal pressure to $12 \mathrm{~mm} . \mathrm{Hg}$ in 61 seconds, while one made in the Spectroscopical Institute at Prague, similar to the one illustrated in figure 2-10, evacuates the same volume of gas at normal pressure to a pressure of $12 \mathrm{~mm} . \mathrm{Hg}$ in 48.5 seconds.

B(1) Modifird Aspirator.-The speed and efficiency of the water-jet pump have been raised by allowing the water to enter through a short tube, slightly curved to impart a whirling motion to the water as it falls through the pump and enters the choke tube. The modification is shown in figures 2-11 ard 2-12. From

Tables 2-3 and 2-4 and the graph of figure 2-13 it is plain that this improved design is in every way superior to those of the Hanf Buest Co. and of the Spectroscopical Institute.

Number 1 is the Hanf Buest pump, No. 2 an ordinary aspirator, and No. 3 the modified type just described. The data were obtained by evaruating a vessel of 2000 cc . capacity.


Fig. 2-12.


Fig. 2-13.

The limiting pressure of these pumps can be made lower than the saturation pressure of water vapor at normal temperature by introducing drying agents between the aspirator and the vacuum enclosure. With this aid the limiting vacuum of the aspirator is said to be approximately $7 \mathrm{~mm} . \mathrm{Hg}$ with a speed of 20 cc . to 50 cc . per second.

For a proper working of a water-jet pump, the water pressure must be constant. If the water supply is temporarily arrested or substantially diminished the direction of suction is reversed in the exhaust tube, with damaging consequences. If the pressure of the water supply is not steady and constant, a valve or a large water trap should be inserted between the apparatus and the pump, in order to prevent water from entering the apparatus.

Table 2-3

| Aspirator No. | 760 mm. | 120 mm. | 60 mm. | 20 mm. | $12 \mathrm{~mm} . \mathrm{Hg}$ |
| :---: | :---: | :---: | :--- | :--- | :--- |
| No. 1 | 0 | 20 sec. | 28.5 sec. | 44.5 sec. | 61.0 sec. |
| No. 2 | 0 | 15 | 22.0 | 36.0 | 48.5 |
| No. 3 | 0 | 10 | 15.5 | 24.0 | 35.0 |

(C) Töpler Pump.-Töpler invented a mercury-piston pump in the year 1862 and obtained high vacuum with it. This pump was the earliest one with which high vacuum was successfully produced. In time this pump underwent many modifications, although the underlying principle remained the same. This pump is made of glass. A modified form is shown in figure 2-14.

Table 2-4

| Aspirator No. | Amount of water required in <br> liters for exhausting 2000 cc. <br> at normal pressure to a pres- <br> sure of 20 mm . at normal temp. | Amount of water <br> required in liters <br> in one hour |
| :---: | :---: | :---: |
| No. 1 | 12.4 | 1000 |
| No. 2 | 11.6 | 1030 |
| No. 3 | 7.7 | 1160 |

The pump consists of a glass bulb $A$, with a side tube $B$ to the lower end of which, an exhaust tube CH is attached. Sometimes a glass float valve is inserted in the lower part of the exhaust tube to exclude mercury. A fall tube $D$, about 80 cm . long, with a diameter of about 1 mm ., and with its lower end turned upward in order to facilitate the collection of the expelled gas, if it should be desired, is attached to the top of the bulb $A$. Another tube $E$, about the same length as the fall tube, is attached to the bottom
of the bulb. The lower end of the tube $E$ is connected to a reservoir $K$, containing pure mercury, by a length of strong rubber tubing $F$, to permit raising or lowering of the reservoir. If the reservoir $K$ is raised, the mercury column rises into the tube $E$, and cuts off the connection between the bulb $A$ and the exhaust


Fig. 2-14. tube $C H$ at the joint $C$. The reservoir $K$ is raised till the mercury completely fills the bulb $A$ and flows out to the tube $D$, driving the air that was in the bulb before this operation. Mercury does not rise into the exhaust tube when the pressure is high, but at low pressures, the mercury tends to enter the exhaust tube. It is prevented from doing so by means of a glass float valve. If the reservoir $K$ is lowered, so as to bring down the mercury to a length more than that of the barometric height below the joint between the side tube and the exhaust tube, the mercury in the bulb $A$ and the tube $D$ will fall to the barometric height leaving Torricellian vacuum in the bulb. When the mercury in the tube $E$ has fallen below $C$, the exhaust tube $C H$ will be connected to this vacuum in $A$. Hence the air in the exhaust tube and the enclosure attached to it will rush into the bulb. By raising the reservoir, the air enclosed in the bulb $A$, being cut off by the rising mercury from the exhaust tube, is forced out of the apparatus at the lower curved end of the fall tube, and on lowering the mercury reservoir, a vacuum will again be left in the bulb $A$. In this pump mercury plays the part of a piston moving up and down the bulb $A$ and constitutes its own valves. By repeating this process the enclosure is exhausted to the range of pressures of high vacuum.

The operation of the Töpler pump by hand is extremely tedious and the pumping speed is very low. So far no attempts to render the Töpler pump automatic have met with success. The pump is often used for transferring gas from one vessel to the other. In all forms of Töpler pumps, the mercury reservoir must be raised very slowly when the vacuum becomes high; otherwise, near the
end of the stroke, the mercury will give a hard blow to the top of the bulb and fracture it. At the end of the rubber tubing where it is connected to the tube $E$, it is usual to insert a trap to prevent air, which occludes through the rubber tubing, from entering the pump.
(D) Sprengel Pump.-The Sprengel pump had its origin in the study of water-jet pumps for producing compressed air. It had many improvements, but its underlying principle remained unchanged. One of the improved models of theSprengel pump is shown in figure 2-15.

The pump consists of a bent tube $A$ connected to a reservoir of pure mercury $B$ by a tube with a stopcock, and to an exhaust tube $D$ attached at $E$. Flow of mercury from the reservoir $B$ is restricted by the stopcock so that it falls only in drops down the tube which is of narrow bore, of barometric length, and is bent at the end in a basin $G$. Each pellet of mercury that drops down the tube entraps a small quantity of air or gas, which it drives down the fall tube and out at the open end, thereby acting as a small piston. The mercury thus


Fig. 2-15. collected in $G$ is transferred from time to time back into the reservoir. Thus the air is gradually removed from the vessel to be exhausted. When the pressure is quite low, each mercury pellet, as it falls down the tube, strikes the top of the mercury column with a clinking sound, but when the pressure is high, the pump is quiet.

As the pressure falls, the gas bubbles become small and it is rather difficult to expel them, as in the Töpler pump. But when a rough vacuum is applied to the end of the fall tube, the length of the fall tube may be reduced and compression on the trapped air
bubbles is diminished. Consequently the small bubbles at low pressures may be expelled with greater ease. The speed of the Sprengel pump is low but may be proportionately increased by using several fall tubes fed by the same reservoir of mercury. The limiting pressure is lowered by gentle heating.

Attempts to render the Sprengel pump automatic were successful. Guichard ${ }^{7}$ designed an automatic Sprengel pump which is simple in its construction and is quite useful. Waran ${ }^{8}$ also devised an automatic type which collects the exhaust gas. It is therefore used more as a circulator than as a means for the production of high vacua.


Fig. 2-16. ( $F$ rom High Vacua, G. W. C. Kaye, Longmans Green \& Co., London, 1927.)
(E) Kaufmann Rotary Mercury-Piston Pump.-The rotary mercury-piston pump of Kaufmann and that of Gaede marked a great advance in high-vacuum pumps. The Kaufmann rotary mercury-piston pump is shown in figure 2-16.

Kaufmann designed and constructed his pump in the year 1905. Although at the time the pump was considered a high-speed one,
${ }^{7}$ Guichard, Bull. Scientifque Tremestriel 3, (1911).
${ }^{8}$ Waran, Proc. Phys. Soc. 34, Part 3, 120 (1922).
its pumping speed is very low compared with that of modern highvacuum pumps. In the same year Gaede ${ }^{9}$ brought out his rotary mercury-piston pump, which, being superior to that of Kaufmann, superseded it. The Kaufmann rotary mercury-piston pump never came into extensive use.
(F) Gaede Rotary Mercury-Piston Pump.-Gaede ${ }^{9}$ originally designed and constructed his mercury-piston pump in 1905, and it is now nearly obsolete. It was modified, and the pump


Vertical Section


Diagrammatic View

Fig. 2-17. Gaede rotary mercury pump.
in the final form is diagrammatically shown in figure $2-17$. This pump consists of a hollow iron drum, capable of rotating coaxially within an iron cylindrical casing, somewhat more than half filled with mercury. The drum is divided into two chambers, the major and the minor situated side by side. The major chamber is divided into three equal compartments by three approximately radial partitions which stop short of the center of the chamber. The wall of each of the compartments of the major chamber is provided with an inlet having communication with the minor chamber of the drum, and finally with the U-shaped exhaust tube which passes out of the pump through the center of one face of the cylindrical casing, as shown in figure 2-17. The outlet of each compartment has a channel which passes halfway around the periphery of the drum and finally emerges on the outside.
${ }^{9}$ Gaede, Phys. Zeits. 6, 758 (1905).

The rotation of the drum causes each one of its compartments to be filled with mercury and emptied once in each revolution. Thus air is drawn in from the exhaust tube and is expelled through a channel to the rough vacuum above the mercury in the outer casing, whence it is removed by an auxiliary pump. The backing pressure is about 10 to $20 \mathrm{~mm} . \mathrm{Hg}$. The exhaust tube is fitted with a by-pass, controlled by an automatic mercury cutoff. The by-pass allows the fore pump initially to exhaust simultaneously both the mercury pump and the vacuum enclosure, until the cutoff operates and further exhaustion is carried on by the rotary mer-cury-piston pump backed by the fore pump. The speed of the Gaede rotary-piston pump was between 100 and 150 cc. per second for backing pressures ranging from 10 to $0.01 \mathrm{~mm} . \mathrm{Hg}$. As such speeds are very low compared with those of the present day, this pump is now almost out of use.

## Section III. Molecular Pumps

## (Pistonless High-Vacuum Pumps)

2-8. Theory of Molecular Pump.-If the molecules of a gas which have no motion other than thermal agitation, strike a fixed boundary, they rebound at random; in other words, the motion after impact is independent of the velocity before impact as regards magnitude and direction, so long as they do not react with the material of the boundary. The action of impact and that of rebound are equivalent to condensation on the walls and subsequent evaporation. If this boundary be given a motion of translation in its own plane, all the molecules proceeding from the boundary will be given a velocity component equal and parallel to the velocity of the boundary. It is on these principles of the kinetic theory of gases that the action of molecular pumps depends.

Suppose a drum, contained in a cylindrical casing, is rotating in the direction indicated by the arrow in figure 2-18. Owing to the momentum given to the molecules by the boundary of the drum, the molecules move from $m$ to $n$. Hence, the density of the gas at $n$ is greater than that at $m$, so that a difference of pressure $p_{n}-p_{m}$, which may be termed " excess-pressure," is established between
$m$ and $n$. This " excess-pressure," which can be measured by the vacuum gauge $G$, is a constant for a given speed of the boundary of the drum.
If the mean free path of the gas molecules be small compared to the distance between the boundary of the drum and the inner walls of the casing, the "excess-pressure" depends on the peripheral speed of the cylinder, the dimensions of the clearance channel, and the viscosity of the gas. So the "excess-pressure" from a consideration of the kinetic theory of gases may be written,

$$
\begin{equation*}
p_{n}-p_{m}=\frac{6 m v x}{D^{2}}, \tag{2-9}
\end{equation*}
$$

where $\eta$ is the viscosity of the gas, $v$ the velocity of the rotating drum, $x$ the distance between $m$ and $n$, and $D$ the distance between the boundary of the drum and the inner walls of the casing. As pointed out in chapter 1, section IV, p. 40 , since the viscosity is independent of density and therefore of pressure, the " excess-pressure" is independent of the mean pressure at the entrance of


Fig. 2-18. the clearance channel. It was actually found that the "excess-pressure" was $10 \mathrm{~mm} . \mathrm{Hg}$ in both cases when the backing pressure was 760 mm . and $500 \mathrm{~mm} . \mathrm{Hg}$.

If the gas pressure be sufficiently reduced so that the mean free path of the molecules is large compared with the distance $D$, the molecular collisions are very few, and the viscosity is almost negligible, then the relation given in expression 2-9 does not apply. In this case, the ratio of the pressures $p_{m}$ and $p_{n}$ is, according to Knudsen and Gaede, ${ }^{10}$ independent of the average pressure. This follows from the law of molecular streaming that the output $Q$, which is a product of the mean pressure and the volume removed per second, under a pressure difference of 1 dyne $/ \mathrm{cm} .^{2}$, is a constant. The volume is here measured under the pressure $p$. If $\tau$ be this constant, $A$ the cross-sectional area of the clearance space, $v$ the

[^9]drift velocity, and $p$ the mean pressure of gas along the clearance space,
\[

$$
\begin{equation*}
Q=\tau=\frac{A p v}{p_{n}-p_{m}} \tag{2-10}
\end{equation*}
$$

\]

where

$$
p=\frac{p_{m}+p_{n}}{2}
$$

$$
\begin{equation*}
\frac{p_{m}}{p_{n}}=\frac{1-A v / 2 \tau}{1+A v / 2 \tau}=\frac{1-A v / 2 Q}{1+A v / 2 Q} \tag{2-12}
\end{equation*}
$$

and

$$
\begin{equation*}
\frac{p_{n}+p_{m}}{p_{n}-p_{m}}=\frac{2 \tau}{A v}=\frac{2 Q}{A v} \tag{2-11}
\end{equation*}
$$

The ratio of the pressures at $m$ and $n$ is thus independent of the mean pressure. The stream velocity of gas molecules increases with the speed of the rotating drum. Hence the pressure ratio can be made comparatively small. If the velocity of the boundary, however, were even slightly greater than the mean velocity of the molecules, a very small number of molecules would, after impact, have a velocity component in the direction $n m$. So it is futile to give the boundary such high velocities as to cause some molecules to have a velocity component in the opposite direction. In order to lower the limiting pressure, similar systems may be joined in series instead of trying to impart high speeds to the surface of the rotating drum.

For speeds of the moving surface of the rotating drum which do not exceed the mean velocity of the molecules, every collision of the molecules with the moving surface of the drum contributes motion to the molecules in the direction of peripheral speed. This fact indicates that to increase the efficiency of driving the gas molecules from the inlet at $n$ to the outlet at $m$, it is essential to make the width $D$ of the clearance space as small as practicable so as to force the maximum number of collisions of the gas molecules with the moving surface of the rotary drum. It can be seen that the efficiency and the speed of a pump depend upon the width of the clearance channel from the fact that when $D$ is increased from 0.02 to 0.05 mm . the pumping speed is reduced by 50 per cent.

2-9. Gaede Molecular Pump.-Gaede ${ }^{11}$ was the first to design and construct a pump whose function was based on the principle of the drag exerted on a gas by a rapidly rotating drum. To increase the efficiency of the pump he subsequently modified the original design. This modified form, shown in figure 2-19, consists of a cylinder with a series of circumferential grooves of different depths and dimensions, the largest being at the center of the


Front View


Side View

Fig. 2-19. Gaede molecular pump.
cylinder, the rest being gradually reduced in the dimensions toward the sides, and each one of the grooves being connected with the succeeding one in the series by means of narrow channels. The casing is provided with a set of toothlike projections which protrude into the grooves and closely fit within them with a clearance of 0.1 mm . The dimensions of the grooves are so chosen as to suit the mean free path of gas molecules at the possible pressures in different positions of the pump. In the central part, where there is an inlet, the gas pressure is naturally lower than that at either side of the pump. The gas molecules at the central largest groove which have the longest mean free path are gradually led from groove to groove through the connecting narrow channels to the smallest grooves on either side, where the pressure is greater
${ }^{11}$ W. Gaede, Phys. Zeits. 13, 864-870 (1912); Verh. d. deut. Phys. Ges. 14, 775-787 (1912); Ann. d. Phys. 41, 337-380 (1913).
than that at the center, and thence through a connecting tube and outlet to the pump. Owing to the slow rate of diffusion of rarefied gases through the narrow slitlike openings between the teeth and the sides of the grooves, and between the casing and the cylindrical drum, the gas, that passes from the fore-vacuum side grooves to the grooves on the high-vacuum side, is negligible.

With this pump the maximum output reaches $1400 \mathrm{~cm} .^{3}$ per second at a pressure of $10^{-2} \mathrm{~mm} . \mathrm{Hg}$. It was the best among the high-speed high-vacuum pumps in the days when it was first constructed. The construction of the Gaede molecular pump demands great technical skill-in constructing the motor which causes the cylinder to rotate at 8000 revolutions per minute, in making the pump perfectly airtight, in adjusting extremely small clearance, and, finally, in cutting the grooves and the toothlike projections to the proper dimensions. In practice, the satisfactory operation of the pump is found to be quite difficult. Hence the Gaede molecular pump is almost entirely out of use.

2-10. Holweck Molecular Pump.-It is very difficult to construct a perfect Gaede molecular pump. To avoid certain diffculties in its construction as well as to increase the efficiency and the pumping speed, Holweck ${ }^{12}$ made some material improvements. In the Holweck molecular pump, shown in figure 2-20, the cylinder is made of duralumin and its surface, unlike that of the Gaede pump cylinder, is smooth. The cylinder rotates within a closely fitting stationary bronze casing, provided with an inlet at the middle, the peripheral clearance not exceeding 0.05 mm . In the inner face of the casing and on either side of the inlet, a helical groove is cut in such a way that on one side it is right-handed and on the other is left-handed, the depth of the grooves gradually increasing from about 0.5 mm . at the ends to 5 mm . or more at the central port, connected with a backing pump. The interior of the ends of the pump casing and the space around the rotor are opened to the channel in the body of the casing and consequently they are also subjected to backing-pump pressure which obviates any chance of leakage through the joints to the region of high vacuum. The depths of the grooves are cut according to the mean free path of the gas molecules at different possible pressures at different positions of the clearance. This design of the pump with helical

[^10]grooves eliminates the tedious process of cutting the leading channels from groove to groove, as in the Gaede molecular pump.

When the cylinder rotates, gas molecules in the helical grooves are pressed out from the center of the casing to the two ends, whence they are drawn out through the communicating channel and outlet by the backing pump. The cylinder is provided with


Fig. 2-20.
ball bearings to minimize friction and to permit smooth, free, and rapid rotation. The cylinder is maintained in rotation by an induction motor, the rotor of which is on the shaft of the cylinder within an exterior enclosure of the pump casing, the stator being outside. The enclosing case of the rotor is made of a special material which largely prevents heating from eddy currents. The stator is supplied with a two-phase alternating current furnished by a small rotary converter.

The Holweck molecular pump is simpler, more economical and more efficient than the Gaede molecular pump. This pump, like other molecular pumps, pumps not only gases, but also vapors,
and does not require any vapor trap. In order to keep the pump in its best working condition, it is important that water or grease be kept from coming in contact with the high-vacuum region.

2-11. Siegbahn Molecular Pump.-Siegbahn designed and constructed a modified and improved form of molecular pump. ${ }^{13}$ It proved to be both reliable and convenient in use. The pump ${ }^{14}$


Fig. 2-21. Schematic diagram of a molecular pump of the ordinary Siegbann type. Diameter of disk 22 cm .
shown in figure 2-21, differs somewhat from those of Gaede ${ }^{15}$ and Holweck. ${ }^{16}$ It is provided with a circular steel disk (1) which rotates inside a metal container, consisting of the two shields (3) with a clearance of a few hundredths of a millimeter between the sides of the disk and the shields.

Helical grooves are cut in the shields, deep at the periphery and gradually decreasing in depth toward the center. At the outer end of each groove, its cross section is a square $10 \times 10 \mathrm{~mm}$., while near the axis it is $10 \times 1 \mathrm{~mm}$.

[^11]The joint between the shields is made vacuum-tight by a rubber gasket on the high-vacuum side and by paper gaskets on the lowvacuum side. The disk is mounted on ball bearings and rotates at $4000-10,000$ revolutions per minute. A means of connection between the pulley (7) and the shaft (2) of the disk with the maintenance of a fore vacuum inside is provided by a long journal bearing for the shaft. A flexible coupling is provided between (6) and (2).
The peripheral space within the container is connected to a passage which leads to the inlet. If the disk rotates, the molecules from the inlet strike the disk and acquire a velocity component down the helical groove toward the axis, whence they are pumped out through the channels (8) by means of a fore-vacuum pump. The inlet passage is provided with a needle valve.
A large model of the Siegbahn molecular pump ${ }^{17}$; shown in figure 2-22, differs in some respects from the one described above. The diameter of the disk is 54 cm . In each shield three helical grooves (I, II, III) are cut, and each one of the grooves starts at the periphery and ends near the center so that the pump serves as three pumps connected in parallel inside a common case. The individual grooves, in this model, are 22 mm . wide with a depth varying between 22 and 1 mm .
The channels in the pieces (4) join the peripheral ends of the grooves to wide metal tubes (9) which have a common inlet (10) connecting the apparatus to be evacuated. The joints between the pieces (4) and the pump have gaskets made of blotting paper soaked in Apiezon grease. The arrangements at the low-vacuum end do not differ much from those of the smaller model. In this large model, the load from the belt drive is taken off the shaft (6) by means of ball bearings which support the pulley (7) and the flexible coupling (5) at the outer end of the axis.
This pump is driven by a 1 -hp. d.c. motor. The pump can work against a pressure of a few millimeters. The normal backing pressure applied to the pump is about $0.05 \mathrm{~mm} . \mathrm{Hg}$. The speed at $10^{-3} \mathrm{~mm} . \mathrm{Hg}$ is $73,000 \mathrm{cc} . / \mathrm{sec}$. at $3700 \mathrm{r} . \mathrm{p} . \mathrm{m}$. The limiting pressure of the pump is $6 \times 10^{-7} \mathrm{~mm}$. Hg without refrigerant or drying agent, and this limit is possibly set by the presence of Apiezon
${ }^{17}$ S. von Friesen, Rev. Sci. Inst. 11, No. 11, 364 (1940).
grease which has a vapor tension of about $5 \times 10^{-7} \mathrm{~mm} . \mathrm{Hg}$ at normal room temperature. ${ }^{18}$

Among all types of molecular pumps Siegbahn's large model is the most efficient. Since the working speed of the cylinder is much lower, this pump works for a longer time without being


Fig. 2-22. Schematic diagram of a molecular pump with high pumping speed. Diameter of disk 54 cm
unduly heated. Hence it has a longer working life than any other of its kind. Molecular pumps are usually very costly but are inexpensive to run. They are somewhat noisy, and are liable to mechanical troubles.

Other high-vacuum pumps which are free from such liability are developed on the principles of diffusion, ejection, and condensation of vapors of pumping media in vacuum. These, which are actually much simpler in construction and in many respects fairly efficient, are described in the following sections.
${ }^{18}$ G. Seydel, Zeits. f. tech. Physik 16, 107 (1935).

## Section IV A. Pistonless High-Vacuum Pumps with Mercury as Pumping Medium

(Single-Stage Pumps)
2-12. Preliminary Remarks.-Among the pistonless highvacuum pumps, vapor pumps are the latest in origin. There are two types of vapor pumps, known as diffusion pumps and condensation pumps. Of the contrivances for the production of high vacua, vapor pumps may be considered the most important, because the highest limiting vacuum may he obtained only with their aid. In this field, also, Gaede ${ }^{19}$ is the pioneer. He designed and constructed the first mercury-vapor pump, basing his design upon the law of diffusion at low pressures. He considered that penetration of gas molecules into a mercury-vapor stream was due to diffusion. If an enclosure containing a gas is opened by means of a suitable aperture to a stream of mercury vapor, the gas molecules diffuse into the stream of mercury vapor, as the partial pressure of the gas is higher than that of mercury vapor. They are then driven by the stream of mercury-vapor molecules to the region of condensation, whence they may be drawn out by a fore-vacuum pump.

Shortly after the announcement of the construction of the Gaede diffusion pump, Langmuir ${ }^{20}$ made a similar type. In his arrangement he could realize a steady and continuous cyclic process of condensation and revaporization of mercury so as to maintain a regular stream of mercury vapor. This vapor stream draws in and collects gas molecules into the region of condensation, whence they may be evacuated by means of a fore-vacuum pump. By this process Langmuir could obtain a speed of exhaust about 50 times greater than that of the Gaede diffusion pump. Hence the Langmuir condensation pump soon came into extensive use in scientific research and industry.

The operation of the Langmuir mercury-vapor pump consists in the transference of the kinetic energy of the mercury-vapor molecules to the gas molecules which diffuse into the vapor stream. The greater the velocity of the vapor stream the greater will be the pumping speed. Thus the molecules of the diffusing gas,

[^12]which are given a velocity component in the direction of the vapor stream, move toward the outlet.

In the operation of the Gaede diffusion pump and the vapor pump of Langmuir, the processes of both diffusion and condensation take place in the evacuation of gases. Gaede gave prominence to the principles of diffusion and he designed his vapor pump in order to satisfy the conditions governing diffusion of gas molecules into those of mercury vapor. Langmuir gave greater importance to condensation than to diffusion, though he could not disregard the latter altogether. He arranged his pump so as to obtain very rapid condensation. The vapor pump of Gaede, therefore, is called the Gaede diffusion pump, while the latter is called the Langmuir condensation pump.

2-13A. Theory of the Gaede Diffusion Pump. When an enclosure containing a gas is connected to a tube, through which passes a stream of mercury vapor, the gas molecules migrate into the stream of mercury vapor by laws of diffusion. Gaede showed theoretically and also established experimentally that the optimum diffusion of gas molecules takes place only when the width of the aperture is comparable with their mean free path. In the construction of an efficient diffusion pump the essential condition, according to Gaede, is to provide a diffusion aperture of proper width. If this condition is fulfilled, the pumping speed is not affected by the pressure of air in the enclosure. It is influenced, however, by the pressure of mercury vapor and the backing pressure. If the vapor pressure is too high, vapor molecules retard the flow of air from the enclosure. If, on the other hand, the vapor pressure is too low, air molecules diffuse back from the fore-vacuum part of the tube. Hence they cannot be removed by the fore-vacuum pump. The conditions, therefore, for the successful operation of a diffusion pump, are not easily attained.

If a gas diffuses into vapor in a tube of diameter $D$ and length $L$ under such pressure that the mean free path is of the order of the diameter $D$, the volume of gas diffusing per second across a cross section of the tube, measured under the mean pressure of the gas, is independent of this pressure. This relation is given by Gaede's expression ${ }^{21}$

$$
V=k \pi \frac{D^{3}}{L}
$$

${ }^{21}$ Grede, Ann. d. Phys. 46, 357-392 (1915).
where $k$ is a constant depending on the nature of the gas and that of the vapor. The rate of diffusion is identical with the speed $S^{\prime}$ given in expression 2-5. The Gaede diffusion pump and the Langmuir condensation pump are theoretically expected to have a very low limiting pressure, approaching zero, and a constant speed of exhaust.

2-13B. Operation of Gaede Diffusion Pump. - One of Gaede's glass diffusion pumps is shown in figure 2-23. It contains a steel cylinder having a diffusion aperture which can be regulated according to the requirements. This cylinder separates the high vacuum from fore vacuum. The lower end of the steel tube is made air-tight by a small column of mercury. In the top of the cylinder is a thermometer, so that the pressure of mercury vapor may be determined by means of the indicated temperature. Pure mercury in the boiler, is heated and the vapor passes from the boiler through the space between the steel cylinder and the inner conducting cylinder, filling the region of thediffusion aperture. The gas molecules from the enclosure gradually diffuse through the aperture


Fig. 2-23. into the stream of mercury vapor and flow through the inner conducting tube to the condenser, which is connected with a backing pump. The mercury vapor thus transports the diffused gas molecules to the condenser. There the mercury vapor becomes condensed and falls back into the boiler, while the transported gas molecules are drawn out by the backing pump.

The mean free path of gas molecules in saturated mercury vapor at $100^{\circ} \mathrm{C}$. is about 0.023 cm ., and Gaede considered that the width of the diffusion aperture should be about half of this value. It was found experimentally that an increase in the temperature of the mercury vapor did not increase the pumping speed, indicating that the essential principle of the pump is diffusion and not ejection. The speed of exhaust of the original Gaede diffusion pump,
with mercury-vapor pressure corresponding to $100^{\circ} \mathrm{C}$., was only 80 cc. per second.

The construction of the Gaede pump is complicated, the conditions for successful operation are rather exacting, and the speed of exhaust is not very high. For these reasons the pump is now obsolete.

2-14A. Langmuir Condensation Pumps.-Langmuir, in his study of the Gaede diffusion pump, found the diffusion to be too slow for the speedy production of high vacua. He thought that,


Fig. 2-24. apart from diffusion, the increase of the speed of vaporization would cause a corresponding increase of the kinetic energy, which would be transmitted to the gas molecules, thus giving them greater speed in the region of condensation. If proper arrangements were not made for speedy vaporization and for correspondingly brisk and active condensation, the flow of gas molecules to the region of the condenser, connected to the backing pump, would be very slow. Langmuir was, therefore, led to think that the principal agent which would cause high speed of evacuation was condensation, and on this basis he constructed a pump known as the Langmuir condensation pump, shown in figure 2-24.

The original Langmuir condensation pump was made of glass. The boiler of the pump (figure 2-24) is drawn out into a cylindrical tube to conduct an upward mercury-vapor jet upward into the region of condensation. The upper end of the jet tube is very close to the lower end of the condenser where there is an annular diffusion space. The region of the annular diffusion aperture is surrounded by a jacket connected to the high-vacuum enclosure. The condenser is provided with a water jacket into which cold water is regularly circulated. Thus the walls of the condenser are continuously kept at a low temperature. One or
two tubes are fitted to the condenser so as to let the condensed mercury fall back into the boiler. The upper part of the condenser (see figure 2-24) is connected to the backing pump to draw out the accumulating gas molecules.

With the increase of the kinetic energy of the vapor molecules and the correspondingly increased condensation, this pump was found to have fifty times greater speed of exhaust than the Gaede diffusion pump.


Fig. 2-25.
2-14B. Langmuir Modified Condensation Pump. -As already stated, Langmuir considered that active vaporization, with correspondingly suitable condensation, would be the real source of speedy evacuation. Unlike Gaede, he thought that it was not necessary to use diffusion phenomena for the attainment of efficient and speedy functioning of the pump. His first model of the condensation pump, however, shows a tendency to retain the slit arrangement of the Gaede diffusion pump. But in the modified Langmuir condensation pump, illustrated in figure 2-25, the slit arrangement has been removed.

A fairly flat-bottomed flask about a quarter-liter in capacity may form the boiler of the pump. The neck of the boiler is drawn out and bent over at the top, so that the height of the boiler to the end of the top bend is about twice the height of the water jacket of the condenser. The entire boiler and most of the drawn-out and bent neck are thermally insulated. The end of the bent neck forms an orifice surrounded by a water jacket which is fused to the bent neck. The upper end of the condensing space communicates with the vacuum enclosure through a vapor trap. The width of the annular space between the end of the neck tube and the condenser may vary from about 2 mm . up to about 12 mm ., according to the size of the diameter of the orifice at the end of the bent neck. The level of the orifice at the end of the bent neck should be below the level of the water in the water jacket of the condenser in order to facilitate rapid condensation. The length of the condenser should be nearly eight times its diameter. It is best to have the orifice about one-third of the way along the condenser. The lower end of the condenser is drawn out into a narrow bent tube which joins the boiler. The bend of this narrow tube forms a cutoff between the vapor in the boiler and the condenser. On one side of the lower part of the condenser, just below the lower end of the water jacket, there is an outlet connected to the fore-vacuum pump.

The boiler is heated electrically, with an energy input of about 220 watts for a pump having an orifice 22 mm . in diameter. The mercury vapor from the boiler streams forth through the orifice, forming a downward jet. This jet of mercury vapor draws in gas molecules from the receptacle and presses them down to the outlet whence they are drawn out by the fore-vacuum pump, while mercury vapor becomes condensed on the walls of the condenser. The condensed mercury, slipping down the walls of the condenser, finally finds its way into the boiler. The trap between the condenser and the vacuum enclosure prevents mercury vapor from entering the high-vacuum enclosure. Since different parts of the pump are subjected to greatly different temperatures, pyrex glass should be used.

The speed of evacuation of this pump varies with the diameter of the orifice from 400 cc . to 1500 cc . per second. It varies relatively slowly with the rate of vaporization and the condensation corresponding to it. The power input may vary from 220 watts up
to 550 watts with very little change in the output of the pump. The speed of vaporization affects the fore-vacuum pressure necessary to attain the maximum efficiency. In practice it is found that the pump with an orifice diameter of 22 mm . works efficiently with an energy input of 220 watts and an auxiliary pressure of $3 \times 10^{-2} \mathrm{~mm}$. Hg. If the energy input is increased to 550 watts the pump works equally well with a fore-vacuum pressure of about $0.6 \mathrm{~mm} . \mathrm{Hg}$.

2-14C. Langmuir Metal Condensation Pump.-Langmuir also designed and constructed a metal condensation pump. This pump consists of one main cast-iron or steel cylinder, having two ports, one on the top for connecting with the high-vacuum enclosure, and the other on the side opened to the fore-vacuum pump. The boiler at the bottom of the cylinder is surrounded by a tube. This tube conducts mercury vapor from the boiler to the cap deflector which is provided on the top of the tube for turning the direction of the mercury vapor so as to form a downward annular jet. The diffusion


Fig. 2-26. Langmuir condensation pump, metal form. annulus and the jet are each about 1 cm . in width. The main cylinder is fitted with a cooling spiral tube through which cold water regularly flows. The cooling spiral starts almost above the top of the body of the boiler and extends to the top of the cap deflector, as shown in figure 2-26.

By the downward vapor jet, the gas molecules are driven from the upper inlet to the outlet pipe in the side of the pump. Thereafter the gas molecules are drawn out by the fore-vacuum pump. The mercury vapor, coming in contact with the cool region of the condenser, becomes condensed, while the kinetic energy of the vapor molecules is transferred to the gas molecules. The condensate drops through small holes down into the boiler,

A Langmuir metal condensation pump, with diameters of main cylinder and inner tube 7 cm . and 3 cm . respectively, has a pumping speed of 3000 to 4000 cc . per second, when the backing pressure is 0.2 to 0.5 mm . Hg. Limiting pressures down to about $10^{-6} \mathrm{~mm}$. Hg can be obtained when the pump has a backing pressure of $0.01 \mathrm{~mm} . \mathrm{Hg}$.

The joints of the pump are welded so as to make it airtight. Access to the interior of the pump is, therefore, not readily possible and consequently repair and cleaning of the internal parts are somewhat difficult.

A modification of the Langmuir single-stage pump (metal form) shown in figure $2-26 A$, was developed by McGraw. ${ }^{22}$ It has a pumping speed of 5000 to $6000 \mathrm{~cm} .^{3}$ per second and operates against a back pressure of about $0.1 \mathrm{~mm} . \mathrm{Hg}$.

2-15. G.G.P. Steel Condensation Pump.-An interesting pump whose function is based upon the principles of condensation and whose performance is, in fact, similar to that of the Langmuir metal condensation pump, is the G.G.P. steel condensation pump, manufactured by Gaiffe-Gallot and Pilon of Paris. The special feature of this design is the water-cooled central tube. This water-cooled tube is a condenser, and it forms the highvacuum side of the pump. A large cup and a deflector which are supported from the lower end of this tube, as shown in figure 2-27, protect against penetration of mercury vapor into the central tube of the high-vacuum side.

Through the clearance between the cup and the walls of the pump mercury vapor streams upward from the boiler. The annular space between the walls of the central tube and the cup serves as a diffusion aperture through which gas molecules from the high-vacuum enclosure and the central conducting tube dif-

[^13]fuse into the vapor stream. The fuither operation of the pump is similar to that of the Langmuir condensation pump.

The large joint at the top of the pump is completed by a rubber gasket which is subjected to the fore vacuum. This arrangement obviously makes it easy to take the pump to pieces for cleaning and refilling the boiler with pure mercury.


Fig. 2-27.


Fig. 2-28A. Crawford's form of mercury-vapor jet pump, vertical type.

2-16. Crawford Mercury-Vapor Jet Pumps.-The type of pump whose operation is based on the ejection principle came into the field after the Gaede diffusion pump and the Langmuir condensation pump. The steam injector, used in the production of vacuum in the condenser of a steam engine, has been turned to account in connection with this type of pump, known as the vapor jet pump. Crawford ${ }^{23}$ introduced this type of pump, shown in figures $2-28 A, B$. In either of these forms the end of the conducting tube
${ }^{23}$ W. W. Crawford, Phys. Rev. 10, 557 (1917).
from the boiler is formed into a nozzle so as to produce a stream of mercury vapor in which the molecules move in parallel paths with equal velocities. When such a jet is directed vertically, as in figure $2-28 A$, or horizontally as in figure $2-28 B$, into a tube whose diameter is of the same order as that of the jet, pumping takes place around the diffusion annulus. The special feature of these models is that the nozzles from which vapor comes are not inside the condenser as in the Gaede diffusion pump or the Langmuir condensation pump. The operation of the pump is not


Fig. 2-28B. Crawford's form of mercury-vapor jet pump, horizontal type.
impaired when the tube is heated. In designing these pumps no special attention is given to either diffusion or condensation. Of course in both forms the condensers are air-cooled, though in the vertical model additional cooling may be provided behind the jet.

The maximum speed of exhaust of these pumps is about 600 $\mathrm{cm} .^{3}$ per second at $10^{-3} \mathrm{~mm} . \mathrm{Hg}$ when the condensers are only aircooled. With the vertical model, having additional cooling behind the jet, the boiler pressure may be increased from 12 mm . to 108 mm . and a maximum speed of $1300 \mathrm{~cm} .^{3}$ per second at $10^{-8} \mathrm{~mm}$. Hg with a backing pressure of $5 \times 10^{-2} \mathrm{~mm}$. may be obtained.

2-16A. Upward Parallel Jet Pump.-A glass upward parallel jet pump, shown in figure 2-29A, was designed by Volmer. The neck of the boiler is long and its mouth is drawn out into a jet tube. When the mercury in the boiler is heated, mercury vapor streams through the jet tube. The mercury-vapor jet is received by a
choke tube opening to the inlet port. The upper end of the choke tube is connected to a condenser leading to the fore vacuum. The condenser and the annular space about the jet are surrounded by a water jacket. This Volmer parallel jet pump can produce a vacuum of about $10^{-3} \mathrm{~mm} . \mathrm{Hg}$ with a fore vacuum of a few mm . pressure.


Fig. 2-29

2-16B. Downward Annular Jet Pump.-At about the same time Volmer also designed a downward annular jet pump of glass. This pump, shown in figure 2-29B, has a cylindrical body with its lower end forming the boiler. It contains also an inner tube, the lower end of which ends in the mercury in the boiler. The tube whose top opening forms the inlet is sealed into the body in such a way that its lower end enters the upper opening of the inner tube so as to form an annular entrance between them. The pump is provided with an internal water cooler situated along the central axis in the inner tube and extending above the middle of the upper
tube. Mercury vapor from the boiler streams through the annular nozzle, forming an annular downward jet. The gas molecules enter the vapor stream by diffusion and are then pressed down to the outlet, whence they are drawn out by the fore pump, while the vapor is condensed and falls back into the boiler.

An upward parallel jet pump and a down ward annular jet pump


Fig. 2-30. of Volmer may be joined in series as the first- and second-stage pumps, respectively, to form a two-stage pump. If the backing pressure is $1 \mathrm{~mm} . \mathrm{Hg}$, such a combination, as Ebert ${ }^{24}$ pointed out, has a speed of about $1700 \mathrm{~cm} .^{3}$ per second at a pressure of $7 \cdot 10^{-3} \mathrm{~mm} . \mathrm{Hg}$, and about 500 $\mathrm{cm} .^{3}$ per second at $2 \cdot 10^{-6} \mathrm{~mm} . \mathrm{Hg}$ pressure.

2-16C. Modified Downward Annular Jet Pump.-Figure 2-30 is an illustration of a modified downward annular jet pump, manufactured by Leybold. The entire pump is made of glass. The principle on which it functions is quite similar to that of the pump of paragraph $2-26 B$. Some of the complications of the original Volmer pump are removed in this design. Hence this form may be regarded as a simplified type. It operates most satisfactorily when it is subjected to backing pressures not greater than $0.1 \mathrm{~mm} . \mathrm{Hg}$. With this backing pressure the limiting vacuum is of a high order. It is said to have a pump speed of $600 \mathrm{~cm} .^{3}$ per second.
2-17. Steel Mercury-Vapor Pump (Thomson). -The pump illustrated in figure 2-31 is made of plate metal in the form of a bottle. It is a very simple design of a mercury-vapor pump and may be used with advantage in the production of vacuum for industrial purposes. The pump consists of a bottle-shaped body with a drawn-out tube on the top forming the outlet and another tube branching out in the side close above the boiler-part at the bottom to serve as an inlet. The whole pump, including the major
${ }^{4}$ H. Ebert, Zeits. f. Phys. 19, 206 (1923).
part of the inlet and the lower part of the outlet pipe, excepting the boiler-part, is water-cooled. The entrance of the side tube is at a considerable distance from the boiling mercury.

This pump requires a fore vacuum of about $0.01 \mathrm{~mm} . \mathrm{Hg}$ pressure. With this fore vacuum, and pumping common air, the pumping speed is said to be 1500 cc . per second. The actual pump speed is, however, conditioned by the dimensions of the inlet tube.

2-18A. Convergent Jet Pump (Waran).-Waran ${ }^{25}$ designed two glass pumps, one with a parallel jet and the other with a convergent jet. The convergent jet pump, illustrated in figure $2-32 A$, has a boiler whose mouth is drawn out into a bent tube ending in a nozzle. The jet tube is sealed into a horizontal and slightly inclined tube constricted in the region of the jet issuing from the nozzle. The inlet is provided behind the jet at the top of the choke tube which


Fig. 2-31. is enclosed for almost its entire length in a water jacket. The other end of the choke tube ends in a $T$, the upper branch being the outlet. The lower branch tube is joined to the lower part of the boiler by means of a connecting tube. The lower part of the boiler, together with the mercury conducting tube, is filled with pure mercury so that the mercury level in the boiler stands above the bore-level of the mercury conducting tube from the condenser. Mercury vapor from the boiler streams forth through the jet tube in the form of a convergent jet. The sides of the boiler are usually covered with asbestos. This pump can produce a pressure of about $0.1 \mathrm{~mm} . \mathrm{Hg}$ when backed by a filter pump.
${ }^{25}$ H. P. Waran. Jour. Sci. Inst. 1, 51 (1923).

2-18B. Parallel Jet Pump (Waran).-This pump was designed by Waran along with his convergent jet pump. The general form and structure of this pump (figure $2-32 B$ ) are similar to those of the convergent jet pump, but differ somewhat from the latter. The form of the nozzle is such that the mercury vapor which streams


Fic. 2-32.
through it forms a parallel jet. This jet of mercury vapor is received by a tube condenser whose diameter is equal to the diameter of the parallel jet. The operation of this pump is similar to that of the convergent jet pump. This pump, with a parallel jet of 8 mm . diameter, is expected to produce the highest vacua with a fore vacuum ranging from 0.5 mm . to 0.1 mm . Hg.

These two models of Waran may be joined as the first- and second-stage pumps respectively with great advantage to form a two-stage glass pump.

## 2-19. DOWNWARD ANNULAR PUMP (KAYE) 125

2-19. Downward Annular Jet Pump (Kaye).-A design of a steel mercury-vapor pump of the downward annular jet type, which may be attributed to Kaye, is shown in figure 2-33. The body of the pump is of solid drawn-steel tubing of about 1.5 mm . wall thickness, with a plate of the same thickness welded to the walls at the bottom. The lower part of the tubing, having a welded bottom, serves as the boiler of the pump. The top of the boiler is capable of being withdrawn when required from the other part of the pump. The upper main joint is made airtight by mercury seal. An inner cylindrical tube opens at its lower end to the mercury boiler. This tube has two deflectors at its top, one over the other, with a short interval between them. The tube has holes in the interval between the two deflectors. The two deflectors are molded so as to enclose an annular aperture of about 0.8 mm . width. The narrow annular space, between the projecting lip of the upper deflector and the inner wall of the external casing, which is of the same width as the annular ap-


Fia. 2-33. erture, forms a diffusion annulus. The chamber between the inner tube and the casing forms the condenser. An outlet tube is provided in the lower part of the condenser. A narrow tube is fitted to the bottom of the condenser, which runs into the mercury and extends nearly to the bottom of the boiler. The part of the main casing of the

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 2. VACUUM PUMPS OR GENERATORSpump beginning at the bottom of the condenser and extending to some distance above the jet, is surrounded by a closed water jacket through which cold water circulates. To increase the efficiency of cooling, a helix of copper tape, which causes a swirling motion, is placed in the water jacket. The upper end of the pump is closed by a steel cap, and the joint is sealed by mercury to render it airtight. The cap carries an inlet tube with a tapering ground joint which forms the connection between the pump and the vacuumenclosing apparatus.

Some 50 cc. of mercury are poured in the boiler. The pump is heated either electrically or by gas. Vapor from the boiling mercury passes up through the central tube and through the holes in the tube between the deflectors, whence it issues as a downward annular jet and entrains gas from the diffusion annulus. The entrained gas molecules are pressed to the outlet, whence they are drawn out by a fore-vacuum pump. The mercury vapor in the condenser becomes condensed and falls back into the boiler through a small conducting tube which is kept relatively cool. Similarly, the top of the boiler is also kept cool to prevent re-vaporization of condensed mercury. This pump can produce high vacua with a backing pressure of $1.5 \mathrm{~mm} . \mathrm{Hg}$, and it has a pumping speed of 7000 cc. per second.

The outer walls of the inner cylindrical tube and the bottom of the condenser are thermally insulated by baked steatite, while the outer walls of the boiler are covered with asbestos.

## Section IV B. Pistonless High-Vacuum Pumps with Mercury as Pumping Medium

## (Multiple-Stage Mercury-Vapor Pumps)

2-20. Two-Stage Mercury-Vapor Pump (Kraus).-The difference between the pressure of the limiting vacuum of a highvacuum pump and that of an auxiliary pump can be much increased by joining two or more pumps of the same type or of different types in series as in the case of the arrangement in series of two or more rotary pumps. For the arrangement of vapor pumps in series, the mercury-vapor stream forms two or more jets in one unit of the pumping system. Kraus ${ }^{26}$ joined two condensation pumps in
${ }^{26}$ Kraus, J. Am. Chem. Soc. 39, 2183 (1917).
series and obtained a two-stage condensation pump. He used as a backing pump an ordinary aspirator, which gives a pressure of about $12 \mathrm{~mm} . \mathrm{Hg}$. With this backing pressure he was able to exhaust a volume of some 1500 cc. to less than $10^{-4} \mathrm{~mm} . \mathrm{Hg}$ in about ten minutes.

2-21. Two-Stage MercuryVapor Pump (Stimson).-A twostage pump in which the two stages are connected in series and fed from a common boiler, was designed by Stimson. ${ }^{27}$ This pump, illustrated in figure 2-34, is made of glass. Mercury vapor passes from the boiler through the main veitical tube which divides in the upper part. The main mercury-vapor stream is thus made into two branch streams and these flow onward in parallel through two jets. One, a convergent jet with a choke tube forming the first stage, is backed by an ordinary aspirator, and the other, a parallel jet, forming the second stage, is open to the inlet. The two jets of the pump are enclosed by cooling jackets in which cold water circulates. The condensed mercury vapor falls back in parallel into the boiler. In this process, the gas molecules are drawn from the inlet and are finally expelled through the outlet connected to a backing pump.
2-22A. Two-Stage Mercury-Vapor Pump (Volmer).-A twostage pump of silica, originally designed by Volmer, is manufactured by Leybold. This pump consists of a boiler with a long cylindrical neck, bent at its upper end into an inverted U-shape, so that the other limb runs downward parallel to the neck, as ${ }^{27}$ H. F. Stimson, J. Wash, Acad, Sci. 7, 477 (1917).
illustrated in figure 2-35. The second limb forms the cold-water jacket which surrounds the condenser. Two stages are mounted in series one over the other in the same condenser. The upper one, which forms the second stage, is an annular jet, and the lower one, which is a convergent jet with a choke tube, forms the first stage of


Frg. 2-35. the pump. Part of the mercury vapor, passing from the boiler through the main tube, issues as an annular jet, entraining gas molecules from the inlet situated above the jet. The rest of the vapor passing through the central tube, issues as a convergent jet into the choke tube. The entrained gas molecules are finally pressed to the outlet, whence they are drawn out by a fore-vacuum pump. This pump is said to have a pumping speed of about 300 cc . per second.

2-22B. Three-Stage Mercury-Vapor Pump (Volmer).-It is possible to produce high vacua even from considerable backing pressures when a third stage is added. Leybold manufactures the three-stage vapor pump in glass, shown in figure 2-36. The pump can produce high vacua even with backing pressure as high as 20 mm . Hg. The pump has a boiler which feeds all three stages. In its design and construction this pump is similar to the twostage pump manufactured by the same firm. In this pump, the three stages are mounted one above the other in a common vertical condenser, the uppermost and the middle being annular jets and the lowest being a convergent jet. The upper annular jet constitutes the third stage, opened to the inlet, while the lower annular jet forms the second stage. The convergent jet is the first stage of the pump. An outlet is provided just below the first stage of the pump, as shown.

Electric or gas heating may be employed for boiling the mercury. The operation of this pump is similar to that of the two-stage one designed by Volmer. The sides of the boiler and those of the long
cylindrical neck of the boiler are usually covered with asbestos. The pump has a speed of 300 cc . per second, when subjected to a backing pressure of $20 \mathrm{~mm} . \mathrm{Hg}$.

2-23. Two-Stage Mercury-Vapor Pump (Dunoyer).-Dunoyer ${ }^{28}$ has designed a two-stage mercury-vapor pump in glass, as shown in figure 2-37. The two stages are arranged within a common inclined condenser, enclosed by a


Fig. 2-36. water jacket. Mercury vapor is supplied from a single boiler through a common vapor tube. The inlet is at the very commencement of the central vapor tube behind the second-stage vapor jet. A portion


Fig. 2-37.
of the mercury vapor passes through the holes of the central vapor tube, issuing in an annular jet which constitutes the second stage of the pump. As the annular jet streams forth into the condenser, gas molecules are entrained from the inlet into the broader part of the condenser, while the condensate falls back into the boiler through the first branch of the mercury conducting tube. The rest of the mercury vapor, flowing farther through the central tube, issues at the end a convergent jet which forms the first stage of the pump. As the first-stage jet streams into the narrower part of the condenser,

[^14]gas molecules are drawn from the broader part of the condenser through the annular space into the narrower part of the condenser, and are pressed to the outlet, whence they are drawn out by the fore-vacuum pump. The mercury vapor, coming in contact with the walls of the condenser, becomes condensed and the condensate


Fig. 2-38. falls into the boiler through the other branch of the mercuryconducting tube. This pump is said to have a speed of about 370 cc. per second.

2-24. Gaede Two-Stage Mer-cury-Vapor Pump.-Gaede has brought out a number of mer-cury-vapor jet pumps of one, two, threc, and four stages. His two-stage pump is of the annular jet type. It works with a backing pressure of about $6 \mathrm{~mm} . \mathrm{Hg}$, producing very high vacua. It has a speed of about $10,000 \mathrm{cc}$. per second at a pressure of $10^{-3}$ $\mathrm{mm} . \mathrm{Hg}$.

2-25A. Gaede Three-Stage Mercury-Vapor Pump.-The three-stage pump of Gaede functionsagainst back pressuresup to 20 mm. Hg. The body of the pump, illustrated in figure 2-38, is a vertical steel tube about 65 to 70 cm . long, with a diameter of 5 to 6 cm . The bottom of the tubing is welded to the walls. The lower part of the tube, having the welded bottom, about 14 to 15 cm . long, forms the boiler of the pump, while the major part of the remainder, which is water-jacketed, constitutes the condenser, common to all the three stages. The condenser is divided into three separate compartments, one over the other. They are separated by disks which are made airtight by mercury-sealed leather cups. One of the three stages is contained in each one of these compartments, situated one over the other in the common condenser.

A central vapor tube from the boiler, passing right through the disks that separate the compartments, feeds all the three stages. An umbrella-shaped deflector is mounted on the upper end of the vapor tube just over the vapor supplying aperture. The deflector is so shaped as to form a large annular jet expanding downward, which forms the third stage of the pump. In the lower part of the uppermost compartment, the vapor tube has a small opening in order to supply mercury vapor to the second stage, which is a plain jet of slightly expanding form. This jet is directed downward into a choke tube. The body of this choke is a disk, which separates the uppermost compartment from the middle one. Similarly, in the lower part of the the middle compartment, the first stage is fed with mercury vapor from the central vapor tube through an orifice. This first stage is a downward, slightly divergent jet. The jet is received by a choke tube, which is a part of the disk separating the middle compartment from the lowermost one.

In each stage, special trapping devices are employed to permit the return of condensed mercury into the boiler without sustaining loss of vacuum. The prevention of re-evaporation of mercury going back through the return tube to the boiler is achieved by thermally insulating the outer walls of the return tube by baked steatite and by fitting a cooling rod to the part of the return tube in the first stage and the boiler. It is advisable to cover the outer walls of the vapor tube with some thermal insulating material.

An outlet is provided on the side of the main body just below the first stage, and a conducting tube fitted to the outlet passes through the water jacket. The outer end of this tube is connected to the fore-vacuum pump. The upper end of the pump is closed with a steel cap having an inlet. This joint is mercury-sealed, and is subjected to rough vacuum, to make it perfectly gastight. The steel cap with the inlet has a tapering ground joint which forms the connection between the inlet in the steel cap and the connecting tube of the apparatus to be exhausted.

Either gas or electrical heating is employed for boiling the mercury. Mercury vapor from the boiler passing through the vapor tube and apertures issues in three jets. Gas molecules from the inlet enter by diffusion into the vapor jets successively one after the other. They are then driven to the outlet whence they are drawn out by the fore-vacuum pump, while the mercury vapor
from each one of the stages, becomes condensed and is caught in the specially devised traps. The trapped condensate falls into the boiler.

The Gaede three-stage pump reaches a speed of 15,000 cc. per second at $10^{-4} \mathrm{~mm} . \mathrm{Hg}$ (for air). For electrical heating, the power


Fig. 2-39. required is 1 kw , while for gas heating, about 12 liters of coal gas per minute are required.

2-25B. Gaede Four-Stage MercuryVapor Pump.-Gaede has also designed a high-speed high-vacuum four-stage pump, shown in figure 2-39. The design and construction are similar to those of the three-stage pump, except for an additional stage. This additional stage is similar to the stage near the fore vacuum of the three-stage pump. It works with a backing pressure of $40 \mathrm{~mm} . \mathrm{Hg}$. It has a pumping speed of about $16,000 \mathrm{~cm} .^{3}$ of air per second at a pressure of $10^{-4}$ $\mathrm{mm} . \mathrm{Hg}$.

## 2-26. Three-Stage Mercury-Vapor

 Pump.-A three-stage mercury-vapor pump in glass, illustrated in figure 2-40, is produced by the research laboratories of General Electric Co. (England). The pump has only one boiler which supplies mercury vapor to all the three stages. The main vapor tube from the boiler divides into two branches, of which one feeds the first stage with its convergent jet and choke tube and the other feeds the second and the third stages. Each of the second and the third stages consists of a downward annular jet formed by a glass cap-deflector, mounted immediately over the holes in the central vapor tube. The cap deflector of the third stage is so made as to form a large expanding annular jet. The first stage has its own condenser, while the other two have a separate condenser common to both. Both the con-densers are jacketed with cold, running water. The first stage is connected with the second stage by a glass tube which serves a double purpose. The condensate from the first stage returns down the tube in one direction and falls in the boiler, while gas molecules


Fig. 2-40.
pass through it from the second to the first stage in the opposite direction.

This pump works with a backing pressure of $20 \mathrm{~mm} . \mathrm{Hg}$, and can produce vacua of a high order. It is said to be fast enough for the work of exhausting the largest thermionic tubes. It is advisable to cover the walls of the boiler, the main vapor tube, and the lower part of the walls of the branch vapor tubes with asbestos.

2-27. Two-Stage Mercury Condensation Pump (Kurth-Ruggles).-A two-stage mercury condensation pump, shown in figure 2-41, has been described by Kurth. It is a variation of the construction designed by Ruggles ${ }^{29}$ and is made of pyrex. The mercury boiler shown at $M$ is heated by a standard radiant heater. Mercury vapor from the boiler, which is led through the thermally insulated tube to the two sets of nozzles, one at the


Fig. 2-41. Two-stage mercury vapor pump, glass form.


Fig. 2-42. Two-stage marcury condensation pump (Payne design).
upper part of the leading tube near the high-vacuum side, and the other set at the very terminus of the leading tube near the fore-
${ }^{29}$ See S. Dushman, J. Franklin Inst. 211, No. 6, 707 (1931).
vacuum side, streams out in two jets. The return tube is bent at $T$ to hold a column of mercury which serves as a baffle. The condenser is cooled by circulating water.
This pump has the advantage that the glass blowing is not very difficult. The speed of exhaust ranges from $3000 \mathrm{~cm} .^{3}$ to $4000 \mathrm{~cm} .^{3}$ per second.

2-28. Two-Stage Mercury Condensation Pump (Payne).-A two-stage mercury condensation pump, designed by Payne, ${ }^{30}$ is made of steel (figure 2-42). The boiler is heated by an electric heater and the mercury vapor, which is led through the chimney to the nozzles at the top and the middle part of the chimney, streams forth in two annular jets. Gas molecules from the vacuum system, connected at the very top of the pump, diffusing through the annular spaces, enter first into the jet of the lower-pressure stage and then that of the higher-pressure stage. Thus gas molecules are transported to the outlet which is connected to the fore-vacuum pump by means of a spiral tube.

This pump, with an input of 550 watts and a backing pressure of 1 mm . to $2 \mathrm{~mm} . \mathrm{Hg}$, has a speed of from 12,000 to $15,000 \mathrm{~cm} .^{3}$.

> Section V. Pistonless High-Vacuum Pumps with Oils or Paraffins or High-Boiling Organic (Phlegmatic) Liquids as Pumping Media

2-29. Introduction.-In the last sections, IVA and $B$, we have dealt with pumps in which mercury is used as a pumping medium. The vapor pressure of mercury is so high that traps are required to prevent it from diffusing into the vacuum enclosure and increasing the pressure there. As the traps exert high resistance to the flow of gas, the pump is throttled and the effective speed of exhaust becomes very low. Because of this considerable disadvantage, mercury as a pumping medium is being replaced by others whose vapor pressure is as much as a thousand times lower than that of mercury. The substitutes for mercury which can be and are used as pumping media with advantage are oils, or paraffins, and certain kinds of high-boiling organic (phlegmatic) liquids. The oils used for this purpose are specially refined petroleum products of the

[^15]napthene type, such as Apiezon oil as developed by C. R. Burch, ${ }^{31}$ or certain kinds of heavy paraffins with high boiling points, purified and freed from volatile components by the process of fractional distillation in vacuum, or organic compounds such as butyl phthalate developed by Hickman and Sanford. Another synthetic organic preparation, such as Octoil, ${ }^{32}$ whose vapor pressure is lower than that of butyl phthalate, is used in some of the pumps in America. There are also oils similar to Apiezon oil yielding pressures below $10^{-6} \mathrm{~mm} . \mathrm{Hg}$.

Pumps using oils or paraffins or high-boiling organic (phlegmatic) liquids as pumping media, unlike those using mercury, have the advantage of yielding considerably lower pressures without the use of traps. Oil pumps without traps do not give quite as low a limiting pressure as trapped mercury pumps, although their speed is many times greater than the latter. In oil pumps, baked-out charcoal tubes at normal temperature are as effective as liquid-air traps. The use of the total-obstruction charcoal trap naturally sacrifices the higher exhaust speed of an oil pump. Efficient operation of oil pumps requires a slightly lower backing pressure than that of mercury pumps. It is advisable to use two or more oil pumps in series, or to use two- or more-stage oil pumps with a sufficiently low backing pressure.

Oil pumps may be made of steel or of brass and copper or iron, whereas metal mercury pumps can be constructed only of steel with welded joints. The assemblage of brass and copper pumps can be effected with soft solder, except for the boiler and the chimney, where the use of silver solder is more efficient.

Oil pumps are similar in many respects to mercury pumps. Both types have the same elements-a boiler to vaporize the fluid, a chimney for conducting the vapor to the jet, and a condenser to condense the vapor. They are also similar in operation. The vapor jet projected from the nozzle across the throat of the pump, ejecting the gas molecules from the inlet to the outlet, condenses on the walls of the condenser which form the outer boundary of the throat. The condensed fluid flows down from the condensing surface back to the boiler. The vapor jet of an oil or paraffin pump, like that of a mercury pump, may be arranged in several

[^16]ways. It may be directed upward, as in the upward jet pumps; it may be directed downward, as in the downward annular jet pump; or it may be projected laterally, as in the lateral parallel jet pump. Although the two types have the same elements, they differ in constructional details. In this section we describe some of the pumps in which oils or paraffins or certain high-boiling organic (phlegmatic) fluids are used as pumping media.


Fig. 2-43.

## 2-30. Multiple-Nozzle Figh-Speed Oil-Diffusion Pump (Zabel).

 -This pump consists of a boiler containing Apiezon B oil, a tube leading to the nozzles, an inlet tube which ends in a chamber surrounding the last part of the tube leading to the nozzles, and a condenser with two tubes at the end. One of these tubes is connected to the fore pump and the other is joined to the boiler so as to let the condensate flow back to the boiler as shown in figure 2-43. This pump, designed by Zabel, ${ }^{33}$ includes the following advantages: a short, wide tube from the boiler to the nozzles, thus assuring an ample vapor stream without requiring a high vapor pressure in the[^17]boiler, which might decompose the oil; elimination of the hot tube through the condensation chamber; high pumping speed; and ease of construction. The condenser and the lower part of the inlet tube are wound with thin-walled rubber tubing through which cold water is circulated for cooling. Zabel constructs these pumps in two sizes, the smaller


Fig. 2-44. with four nozzles and the larger with seven nozzles. The required input of the former is of the order of 200 watts and of the latter, 300 watts. Table $2-5$ gives the speeds of the two pumps for air at various pressures when operated on Apiezon Boil, measured by the constantflow method approximately 7.5 cm . above the nozzles.

Since the annular clearance space is sufficiently broad to permit high speed of exhaust, it is necessary to use comparatively low backing pressure to obtain the maximum limiting vacuum. It is advisable to use a heavy coating of asbestos over the boiler and the tube leading to the nozzles to reduce the necessary heat input to the oil. In case the large pump is to be operated against a leak, it is best to wind an auxiliary heating coil around the boiler. In some of these pumps, an ordinary electric oven is replaced by a Bearden type heater (helix of Nichrome wire immersed in oil), in order to boil the oil.

2-31. Metal Oil-Diffusion Pump (Multiple-Nozzle Type).This pump, constructed by Amdur (see figure 2-44), ${ }^{34}$ has a body of $1 / 16$-inch stainless steel cylindrical tubing with a plate welded at its bottom by atomic hydrogen welding. A tube of

[^18]copper which leads vapor to the nozzles is mounted in the body so that its lower end rests on the bottom of the body. The closed upper end of the chimney is provided with ten small branch tubes of equal size each bent downward and ending in a divergent orifice. About $70 \mathrm{~cm} .^{3}$ of Apiezon B oil are placed in the pump and heated

Table 2-5. Speed of Evacuation of Multiple-Nozzle Pumps

| Pressure in mm. Hg | Speed of the 4-nozzle <br> pump in liters per sec. | Speed of the 7-nozzle <br> pump in liters per sec. |
| :---: | :---: | :---: |
| $0.5 \times 10^{-4}$ | 41 | 76 |
| 1 | 40 | 69 |
| 3 | 40 | 63 |
| 8 | 37 | 60 |
| 20 | 30 | - |

from the outside with a flat circular heater. Oil vapor which is led to the nozzles through the chimney is forced downward as divergent jets. The baffle disk prevents the ascent of hot oil vapor from outside the boiler into the condenser.

Speed tests were run with hydrogen gas giving the following results (Table 2-6):

## Table 2-6

| Speed at $10^{-4} \mathrm{~m}$ | 250 liters per second |
| :---: | :---: |
| Maximum fore-vacuum pressure. | 0.03 mm . |
| Heat input.... | . 630 watts |

The speed of the pump is high but it needs a very good forevacuum pump.

2-32. Apiezon Oil-Diffusion Pump (Metal).-A metal pump in which Apiezon B oil is used as the pumping medium was originally developed by the Metropolitan Vickers Company in England. A simplified form of this model is illustrated in figure 2-45. The outer body, 5 cm . in diameter, consists of a water-jacketed brass cylinder with a copper plate silver-soldered to its lower end. In the cavity beneath is placed an electric heater which boils Apiezon oil at less than $200^{\circ} \mathrm{C}$. In the chamber above, a chimney is fixed over the boiler and a spun-copper, umbrella-shaped deflector is mounted on a stand which passes through the chimney. The
clearance between the edge of the deflector and the wall of the condenser is about 7 mm . Gas molecules from the inlet diffuse through the annular clearance and enter into the downward annular jet. They are then pressed down to the outlet tube,


Fig. 2-45.
whence they are drawn out by the fore pump, while the oil vapor is condensed and returns to the boiler. The lower baffle plate prevents the rise of oil vapor from the roof of the boiler into the condenser. A glass heat-shield is mounted around the chimney to prevent the condensate from coming in contact with the hot chimney. The two baffles above the deflector prevent the escape of oil vapor directly into the enclosure which is being evacuated.

This baffle system reduces the speed of the pump by more than 50 per cent, so that its over-all speed is $30,000 \mathrm{cc}$. per second. It produces a limiting pressure of $10^{-5} \mathrm{~mm} . \mathrm{Hg}$.

It is advisable to use two pumps of this type, joined in series, to increase the efficiency of the system with relatively high backing pressure. In this case the annular clearance space between the edge of the deflector and the condenser of the pump directly connected to the fore-vacuum pump should be relatively smaller than that of the other pump, so that the oil is less likely to deteriorate.

2-33. High-Speed Oil-Diffusion Pump.-This pump, shown in figure 2-46, was designed and constructed by Hiram W. Edwards. ${ }^{35}$ Its outer shell consists of a thinwalled cylindrical tube of brass or steel about 20 inches long and 3 inches inside diameter. The lower end is closed by a circular plate of copper, silversoldered in position. A special oil, prepared by Edwards, is put in the cylinder so that its lower edge rests immersed in the oil on the bottom plate of the cylinder. Beneath the bottom is placed an electric heater to boil the oil. A deflector is mounted on a


Fig. 2-46. stand, which is fixed to the bottom plate and electric-heater holder, and passes through the middle of the chimney. The clearance between its outer edge and the pump wall is about 7.5 mm ., while the vertical clearance between the upper edge of the chimney and the under surface of the deflector is about 6 mm . A small-angle conical baffle system is mounted on the upper end of the deflector stand to prevent vapor from entering the vacuum system, without, however, greatly impeding the flow of gas from the vacuum enclosure. A
${ }^{85}$ H. W. Edwards, Rev. Sci. Inst. 6, No. 5, 145 (1935).
baffle is placed at the lower edge of the cylindrical part of the chimney which leads the oil vapor from the boiler to the deflector. This lower baffle allows the condensed oil from the condenser to flow down into the boiler and prevents the vapor from the boiler from entering directly into the condenser.


Fig. 2-47. Two-stage oil diffusion pump of glass.
The part of the cylindrical main body from just above the outlet port up to the central part of the upper baffle system is waterjacketed to keep the condenser cool.

The oil vapor from the boiler passes through the chimney to the deflector. The vapor stream then is deflected downward, forming a downward annular jet.

This pump with the conical baffle system has a pumping speed of about $50,000 \mathrm{cc}$., at a pressure of $10^{-4} \mathrm{~mm} . \mathrm{Hg}$. It obviously needs a high-speed fore pump with a limiting pressure as low as 0.01 to 0.02 mm. Hg. As the upper baffle system is directly
connected to the hot deflector stand, it is easily heated. The hot baffle system is less advantageous than the cold baffle system in preventing vapor from entering the vacuum chamber.

2-34. Two-Stage Oil-Diffusion Pump of Glass.-A two-stage oil-diffusion pump of glass, designed by Henderson, ${ }^{36}$ utilizes the advantages of oil such as Apiezon B without requiring an unusually good auxiliary fore pump. The operation of this pump is indicated by the details of construction shown in figure 2-47.

With Apiezon B oil, and with a fore vacuum of nearly 0.2 mm . and without drying agents, it is capable of producing a vacuum of nearly $10^{-6} \mathrm{~mm} . \mathrm{Hg}$. Using a carbon trap of Becker and Jaycox, pressures of the order of $10^{-7} \mathrm{~mm}$. were readily obtained and with thorough outgassing of the equipment and baking of the charcoal, this value was lowered to $2 \cdot 10^{-8} \mathrm{~mm} . \mathrm{Hg}$.

2-35. Two-Stage Oil-Diffusion Pump of Metal.-The pump shown in figure 2-48, has an outer shell consisting of a cylindrical brass tube 5 cm . in diameter, closed at its lower end by a plate attached with silver solder. Apiezon oil is put into the lower end of the tube which forms the boiler


Fig. 2-48. and is heated electrically. A copper chimney, like that of figure 2-45, rests on the bottom of the boiler. A copper deflector surmounts the chimney. Part of the oil-vapor stream from the boiler passes through the chimney to the deflector at the top, where it is turned downward as an annular jet. About one-third of the way down a slitlike opening in the chimney is overhung by a second deflector. Part of the oil vapor passes

[^19]through this opening. These two downward, annular vapor jets, one over the other, fed through the same chimney, constitute the two stages of the pump. The annular space between the edge of the upper deflector and the walls of the body is comparatively wider than the annular space between the edge of the lower deflector and the walls of the body.


Fig. 2-49. The upper end of the cylindrical tube is connected with the vacuum enclosure. The cylinder has an outlet tube on one side connected to the fore pump. Above this outlet is the cooling water jacket.

A system of baffle plates between the boiler and the condenser prevents the rise of oil vapor through this region, but allows the condensed liquid to move downward. A baffle above the upper deflector prevents vaporsfromentering the vacuum enclosure.

This pump, with a fore vacuum of 0.1 mm ., is capable of reducing the pressure to about $10^{-6}$ $\mathrm{mm} . \mathrm{Hg}$. With this baffle arrangement it has a speed of nearly $30,000 \mathrm{cc}$. per second.
2-36. Butyl Benzyl Phthalate Condensation Pump (Hickman). -This pump, designed by Hickman, ${ }^{37}$ is one of the compact forms of high-vacuum pumps in which butyl benzyl phthalate is used as the pumping medium. It is advantageous over many other forms when compactness and the elimination of water-cooling arrangements are of importance. It consists, as shown in figure 2-49, of a flat-bottomed flask 5.5 cm . in diameter to serve as a boiler, with its neck thrust into, and sealed to, the base chamber of a chimneyshaped condenser provided with a copper radiator. The upper end of the condenser is connected to an outlet tube joined to the
${ }^{37}$ K. C. D. Hickman, J. Phys. Chem. 34, No. 3, 648 (1930).

## 2-37. FRACTIONATING OIL-DIFFUSION PUMP

fore pump. The base chamber is fitted with an inlet tube joined to the vacuum system and with a single-coiled tube, the other end of which is connected to the boiler.

The vapor of butyl benzyl phthalate from the boiler is led through the throat of the boiler and is directed as an upward parallel jet into the condenser, which is kept cool by the copper radiator. Gas molecules from the vacuum system which diffuse into the jet are ejected by it to the outlet tube, whence they are drawn out by the fore pump. The vapor, coming in contact with the cooler regions of the condenser, becomes condensed, and the condensate returns to the boiler through the single coiled tube. The coil of the return tube retains a column of the fluid which serves as a baffle to prevent the vapor from the boiler from entering the base chamber of the condenser.

The pump reaches a limiting


R- Reservoir For Removal of Volatile Components of oil Formed in the Boiler.

Fig. 2-50. vacuum at a pressure of $10^{-6} \mathrm{~mm}$. Hg , and has a speed of about 50 ce. per second at a pressure of $10^{-3} \mathrm{~mm}$. of Hg. If the boiler is enlarged and the dimensions increased, the pump attains much higher speeds.

2-37. Two-Stage Fractionating Oil-Diffusion Pump (Vertical Type).-Synthetic oils which are used as pumping media are not homogeneous in nature and even less homogeneous after some decomposition has taken place because of cracking in the course of heating, due to strong heat, high boiler pressure, and sudden change of pressure by accidental leaks. The products of decomposition are more volatile and have greater saturation pressure than the pure and undecomposed oils used as pumping media. Pumps with oils as pumping media lose their efficiency if the oils have volatile components. For efficient operation of such a pump it is advisable to isolate such volatile components from the medium and keep it continually pure during the operation of the pump. A pump designed to fulfill these conditions is shown in figure 2-50.

This pump consists of a boiler with a long, drawn neck having a branch tube connected at the lower part of the neck near the boiler to serve as an outlet leading to the fore pump, a bi-column chimney having a nozzle at the upper end of each column, and an overhanging deflector placed in the throat of the pump. The exhaust limb has a fractionating column to isolate more volatile constituents, with a side tube for their removal into the reservoir. The stand of the chimney resting on the top of the boiler serves as a baffle system. When the pumping medium boils, the vapor, led through the chimney to the nozzle opening, is deflected by the two deflectors, forming two downward annular jets which are directed across the throat. The baffle system, on the one hand, permits the condensed fluid to flow freely into the boiler, and on the other hand prevents the vapor from the boiler from escaping into the condenser.

The vapors of the volatile constituents which enter the outlet tube, coming in contact with the cooler region of the outlet tube above the fractionating column, become condensed on the walls of the tube. They then flow down into the fractionating column, collect, and fall into a reservoir. In this way the pumping medium is automatically kept free from volatile constituents whose vapors would otherwise impair the vacuum.

It is desirable to cover the sides of the boiler with asbestos, and the lower part of the neck and the outlet tube as far as the fractionating column, with cotton. The condenser is cooled by air jets.
This pump, with Octoil as pumping medium, and with a fore vacuum of about 0.2 mm . and without drying agents, is capable of reaching a pressure of $10^{-7} \mathrm{~mm} . \mathrm{Hg}$ at a temperature of nearly $20^{\circ} \mathrm{C}$. with a pumping speed of about 5000 cc . per second at a pressure of $0.5 \times 10^{-3} \mathrm{~mm}$. Hg.
It is advisable to use an electric heater, with fine regulation, for heating the boiler. Strong and irregular heating induces the synthetic organic oils to crack easily and thus lowers the efficiency of the pump.
2-38. Self-Fractionating Oil-Diffusion Pump.-Fluids obtained by vacuum distillation of natural petroleums, or those of synthetic nature which constitute extremely satisfactory pumping media, are not homogeneous. The boiling point of the different components varies. On the basis of the assumption that high vapor
pressures will, in general, be associated with lower boiling points, Hickman has connected a number of glass pumps in such a way that the condensate formed in each pump is returned to the reservoir farthest from the high vacuum. The reservoir of the pump farthest removed from the high vacuum is connected to that of the succeeding one by a tube of narrow bore. In this way the condensate is subjected to a continuous distillation action whereby the highest vapor-pressure fractions are confined to the first of the series, and the lowest vapor-pressure fraction finally works its way into the pump which is directly connected to high vacuum.

Malter and Marcuvitz ${ }^{38}$ have constructed a metal pump, as shown in figure 2-51, based on this self-fractionating principle. In the vertical arrangement of the three stages, downward annular jets are employed to pump out gases by successive stages to the outlet port, whence they are drawn out by the fore pump. The modifications of the pump lie in the bottom stage and in


Fig. 2-51. the introduction of two fractionating cylinders $B$ and $C$. In the course of operation the condensed vapor, issuing from the separate stages, collects in the region surrounding the lower end of the outer cylinder. It is prevented from immediately entering the region between the two cylinders by the small size of the apertures. The lowest boiling fractions are boiled off before the remaining fluid passes into the region. Similarly, further low boiling-point fractions are boiled off in that region, with the result that the highest boiling-point fraction or the fraction with the lowest vapor pressure finally works its way into the inner-

[^20]
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 2. VACUUM PUMPS OR GENERATORSmost region, whence the vapor issues to the stage nearest high vacuum. The form of the stage near the fore vacuum is such as to permit the operation of the pump at relatively higher backing pressure.

The pressures of limiting vacuums of the pump with and without the two fractionating cylinders present, using different


Fig. 2-52. Hickman fractionating oil-diffusion pump (two jet model).
fluids as pumping media, were measured under similar conditions by means of an ionization gauge calibrated with air. The results are given in Table 2-7.

Table 2-7

|  | Octoil | Burned Octoil | Apiezon B |
| :--- | :---: | :---: | :---: |
| Fractionating cylinders in | $8 \times 10^{-8} \mathrm{~mm}$. | $2.0 \times 10^{-7} \mathrm{~mm}$. | $2.4 \times 10^{-7}$ |
| Fractionating cylinders removed | $4 \times 10^{-7} \mathrm{~mm}$. | $9.0 \times 10^{-7} \mathrm{~mm}$. | $1.0 \times 10^{-6}$ |

The pumping speed without the oil baffle present varied between

70 and 80 liters per second over a pressure range of $10^{-3}$ to $10^{-4}$ $\mathrm{mm} . \mathrm{Hg}$.

2-39. Fractionating Oil-Diffusion Pumps (Hickman).-Hickman $^{39}$ designed and constructed fractionating oil-diffusion pumps of glass, including two or three jet models of horizontal type. The two-jet model, illustrated in figure 2-52, consists of three independent boilers, each containing a heater wire immersed directly in the operating liquid.
The neck of the boiler on the right is inserted and fused into a horizontal tube so that its circular opening on the top leads to a vertical column of lobes. The space between the rim of the boiler's opening and the inner walls of the base of the vertical column of lobes forms the first-stage diffusion annulus. The vapor from this boiler issues as an upward parallel jet, representing the first stage. An outlet, which is connected to a fore pump, is located at the upper part of the chimney over the column of lobes. Volatile contaminations of the operating liquid are trapped by the lobes and thus are prevented from falling back into the pump.
The neck of the second boiler is inserted and fused in the central part of the horizontal tube and provided with a funnel-shaped opening. The space between the rim of this opening and the walls of the horizontal tube forms the high-vacuum stage diffusion annulus. The vapor from the boiler issues as a divergent horizontal jet, representing the high-vacuum stage of this two-stage pump.
The third boiler is a sink of nonvolatiles, tars, and polymerized products, and any proper liquid present in the sink is returned to the first-stage boiler and the relatively purer liquid to the highvacuum stage boiler through the respective return tubes.
The opening at the end of the horizontal tube is an inlet connecting the apparatus to be evacuated. Gas molecules from the apparatus diffuse through the second-stage annulus into the vapor stream of the second-stage jet, and are forced toward the diffusion annulus of the first stage. These gas molecules passing through the first-stage diffusion annulus enter the vapor stream of the upward parallel jet of the first stage. They are then transported to the outlet whence they are pumped out by the fore pump.
Hickman constructed a three-stage pump similar in design and construction to the two-stage pump, except for the addition of an

[^21]intermediate jet-stage of the divergent type. The condensers of these pumps are usually air-cooled, though some are provided with water cooling.
The horizontal design is better than the vertical one, since the boiler area is independent of the jet diameter, and the heat input to each boiler can be regulated with precision.

Oils used as operating liquids of these diffusion pumps and the performances of the pumps from pump fluids at $25^{\circ} \mathrm{C}$. are as follows:

Table 2-8

| Chemical name | Trade name | Max. backing <br> pressure <br> (mm.) | Limiting vacuum, <br> trap at $25^{\circ} \mathrm{C}$. <br> (mm. Hg ) |
| :--- | :---: | :---: | :---: |
| Butyl sebacate | $\ldots$ | $1.5 \times 10^{-1}$ | $10^{-5}$ |
| Amyl sebacate | Amoil-S | $1.7 \times 10^{-1}$ | $2 \times 10^{-6}$ |
| 2-ethyl hexyl phthalate | Octoil | $2.5 \times 10^{-1}$ | $2 \times 10^{-7}$ |
| 2-hexyl sebacate | Octoil-S | $2 \times 10^{-1}$ | $5 \times 10^{-8}$ |
| Butyl phthalate | $\ldots .0$ | 1.0 | $10^{-8}$ |

To maintain a good pumping speed, the oil must be heated properly. The temperature is critical, and the oil must not be heated at a pressure greater than $1 \mathrm{~mm} . \mathrm{Hg}$, as otherwise the operating fluid may crack, with serious consequences to the performance of the pump.
2-40. Three-Stage Paraffin Condensation Pump (DolejSek).This pump, shown in figure 2-53, ${ }^{40}$ is a product of the Spectroscopic Institute Laboratory at Prague. It is used for evacuating x -ray tubes and x -ray vacuum spectrographs and is found to be more efficient than some of the pumps in which oils have been used as operating liquids. The pump body consists of waterjacketed cylindrical brass tubing, 4 cm . in diameter and 26 cm . long, with its lower end closed by a copper plate attached by silver solder. Into the tube are poured about 50 grams of a kind of heavy paraffin, specially prepared and purified for the purpose. The lighter ingredients are removed by Dobiavosky's method of fractional distillation. The remaining purified and heavy part of paraffin has a very low vapor tension. An electric heater is placed beneath the bottom plate of the cylinder to boil the paraffin above.

[^22]A chimney is placed in the body so that its lower end rests submerged in the paraffin on the bottom plate of the cylinder. The chimney has nozzles on the sides at the topmost part and at two other equidistant intermediate places between the boiler and the top of the chimney. The three sets of nozzles are overhung by deflectors with their edges inclined to the walls of the cylinder. The vapor from the boiler, issuing from the nozzles, is deflected downward in annular jets.

The annular clearance between the uppermost deflector and condenser is about 2 mm . Although the other two clearances at the second and the first stages are kept at the same dimensions, they become effectively narrower because of the layer of liquid paraffin flowing down the walls. Thus the uppermost clearance is the widest and the lowest is the narrowest of all, as it should be, for the free path of the gas molecules near thehigh vacuum is considerably greater than at the first stage near the fore vacuum, where the pressure is much higher than at the final stage.

Just above the boiler on the baffle plate glass balls are placed in two or three layers so that they form an effective baffle system which prevents the vapor from the boiler from reaching to the condenser without, however, preventing the condensate from flowing down into the boiler.

Gas molecules from the vacuum enclosure diffusing through the uppermost clearance


Frg. 2-53. into the uppermost vapor jet, are pressed down by the vapor molecules to the second clearance. They again diffuse through the second clearance into the second annular jet. At this stage also the gas molecules are pressed again to the lowest clearance, through which they again diffuse and enter the lowest vapor jet. Finally these molecules are pressed down to the outlet, whence they are drawn out by the fore pump.

Thispumphasan intrinsic speed of nearly $2000 \mathrm{~cm} .^{3}$ at a pressure of $10^{-8} \mathrm{~mm} . \mathrm{Hg}$. Since the clearance at the first stage is rather small, it works at the fairly high backing pressure of nearly 1 mm .

Hg. The pump is capable of producing a vacuum better than $10^{-6}$ $\mathrm{mm} . \mathrm{Hg}$ without the use of any trap. The pumping medium must not be heated at a pressure greater than $1 \mathrm{~mm} . \mathrm{Hg}$, as the paraffin will be decomposed into constituents heaving a higher vapor tension.

## Section VI. Vacuum Pumps and Their Performances

Table 2-9A

|  | Limiting vacuum (mm.) | Pumping speed (cm. ${ }^{3} / \mathrm{sec}$.) |
| :---: | :---: | :---: |
| Aspirator | 12-15 | 10-30 |
| Modified aspirator | 12-15 | 25-55 |
| Rotary mercury pumps | Backing pressure (mm.) | Pumping speed (cm. ${ }^{3} / \mathrm{sec}$.) |
| Gaede | 10-0.01 | 100-150 |

Table 2-9B

| Oil-sealed rotary <br> pumps | r.p.m. | Displacement <br> (cm. $^{3} / \mathrm{sec}$. | Limiting vacuum <br> (mm.) |
| :--- | :---: | :---: | :---: |
| Gaede small (single- |  |  |  |
| stage) | 400 | 250 | 0.1 |
| Gaede iron (single-stage) | 400 | 550 | 0.002 |
| Hyvac (two-stage) | 450 | 210 | 0.001 |
| Edwards type $\mathrm{B}_{2}$ | $\ldots$ | 3470 | 0.0001 |
| Hypervac (two-stage) | 450 | 3500 | 0.00005 |
| Gaede iron (two-stage) | 400 | 550 | 0.00001 |

Table 2-9c

| Molecular <br> pumps of | r.p.m. | Speed of exhaust <br> (cm. ${ }^{8} / \mathrm{sec}$.) | Limiting vacuum <br> (mm.) |
| :--- | :---: | :---: | :---: |
| Grede | 8,000 | 1,400 at $10^{-3}$ | $10^{-5}$ |
| Siegbahn | 6,000 | 3,000 at $10^{-3}$ | $10^{-5}$ |
| Holweck | 4,000 | 2,300 at $10^{-3}$ | $10^{-5}$ |
| Siegbahn (arge type) | 3,500 | 73,000 at $10^{-3}$ | $6 \times 10^{-7}$ |

Table 2-9d

| Mercury-vapor pumps | Backing pressure <br> (mm.) | Speed of exhaust <br> (cm. ${ }^{3} / \mathrm{sec}$.) |
| :--- | :---: | :---: |
| Original Gaede diffusion pump | 0.1 | 100 |
| Langmuir glass condensaton pump | 0.1 | $3,000-4,000$ |
| Langmuir metal condensation pump | 0.01 | $3,000-4,000$ |
| Thomson stcel pump | 0.01 | $1,500-2,000$ |
| Kaye single-stage stee' pump | 1.5 | $5,000-7,000$ |
| Gaede two-stage " B" | 8.0 | 10,000 |
| Gaede three-stage " E " | 20.0 | 15,000 |
| Gaede four-stage " D" | 40.0 | $15,000-16,000$ |
| Kaye four-stage type IV | 0.15 | 20,000 |
| Kaye four-stage IV 3F | 2.0 | 20,000 |

Table 2-9e

| Oil and paraffin |
| :--- | :---: | :---: | :---: |
| vapor pumps |$\quad$| Backing |
| :---: |
| p:essure |
| (mm.) |$\quad$| Speed of exhaust |
| :---: |
| (cm. ${ }^{3} / \mathrm{sec}$.) |$\quad$| Limiting |
| :---: |
| pressure |
| (mm.) |

## CHAPTER 3

## MEASUREMENT OF PRESSURES OF HIGH VACUA

## Section I. Classification of Pressure Gauges

3-1. Introduction.-High vacua are produced by various types of pumps. The principles of these have been dealt with in chapter 2. Each pump has a particular speed of exhaust and limiting pressure. To determine these characteristics, it is necessary to measure the pressures of vacua, in order to compare the characteristics of pumps of one design and construction with those of another and thus to estimate their relative efficiencies. Since high vacua desired in application cannot be of arbitrary value, it is necessary to have a good means of measuring the pressures of high vacua if these are to be used for scientific, technical, or industrial purposes. It is also necessary to know the pressures of high vacua used in the study of rarefied gases.

A device or an instrument with which the pressures of high vacua are measured is called a manometer, or a high-vacuum gauge. Because of its great utility and importance, the highvacuum gauge has been the object of special study. Consequently, a large number of manometers have been designed and constructed, but of these only a few have been found to be of practical value.

3-2. Kinds of Gauges.-These instruments, which are of practical use for measuring low pressures, belong to two different categories. The principle of operation of the manometers of the first category, depends on comparison of the unknown pressure with a known pressure, usually by the difference of level of liquid columns. The McLeod ${ }^{1}$ manometer, with all its variations, and the oil manometers, which are of more recent origin, such as the DolejsekKunzl ${ }^{2}$ oil manometer or the oil manometer of Backovsky-Slavik, ${ }^{3}$ belong to this class. This comparison may be effected by ob-

[^23]serving the bending of an elastic membrane which separates the gas at known pressure from that at the unknown pressure. The manometers belonging to the second category or class make use of the different properties of gases which are functions of the pressure, especially in the region of high vacua. This latter class of manometers may be brought under four groups, each group utilizing a distinct property of the gas which varies according to pressure. The four groups are:
(1) Gauges, such as the radiometer gauge of Knudsen, ${ }^{4}$ which measure the force of impact of gas molecules due to temperature difference.
(2) Gauges, such as the Pirani ${ }^{5}$-Hale ${ }^{6}$ gauge, which depend on the thermal conductivity of a gas which varies by pressure only in the region of high vacua.
(3) Gauges, such as the Langmuir ${ }^{7}$-Dushman ${ }^{8}$ molecular gauge, depending upon the transfer of momentum between two surfaces by gas molecules which decreases with the pressure, only when the mean free path is large compared with the distances between the surfaces.
(4) Gauges, such as the Dushman-Found ionization gauge, ${ }^{9}$ which are based upon the relation between ionization current and pressure.

Among the gauges which work on the comparison of the unknown pressure with a known pressure, the McLeod manometer is the oldest and the one most used for low-pressure absolute measurements. Mercury was chosen as the manometric liquid of this gauge owing to its comparatively low vapor pressure. Also, it would not wet the container and gases would not dissolve in it. Mercury introduces vapor into the gauge, which makes the readings of the manometer somewhat uncertain. This can be greatly remedied by a liquid-air trap. This gauge can be used only for gases which obey Boyle's law.

Certain mercury-filled gauges are specially designed for instantaneous reading or for continuous registration. Rayleigh ${ }^{10}$

[^24]designed and constructed a mercury gauge, shown in figure 3-1, for instantaneous reading. With this instrument, measurements could be made by having a mirror fixed to the manometer and measuring the angle through which the manometer had to be turned, in order to bring the surfaces into contact with the glass points. This gauge could be used to measure steady pressure


Fig. 3-2. Optical lever manometer.
differences ranging between 1.5 mm . and $10^{-3} \mathrm{~mm}$. Shrader and Ryder ${ }^{11}$ have constructed a mercury gauge, shown in figure 3-2, which is suitable for continuous registration. This gauge has two mercury limbs with a central cutoff. This central cutoff is used to establish common pressure before use. Afterward, in order to use the gauge, the connection is broken and the variation of pressure in the limb, in which there is an optical-lever, results in a change in level of the mercury column. On the surface of the column of mercury is a small glass float. This is fitted to the end of an optical-lever, the axis of rotation of which is fixed to the sides of
${ }^{11}$ J. E. Shrader and H. M. Ryder, Phys. Rev. 13, 321 (1919).
the tube, the entire optical-lever being inside the limb. The lever is provided with a mirror. With the alteration of the level of the mercury column, the lever is tilted to an extent which can be measured by a beam of light, reflected by the mirror attached to the lever. The sensitivity of this gauge is of the order of $10^{-3} \mathrm{~mm}$. Hg. The limiting sensitivity of the Rayleigh gauge or the ShraderRyder optical-lever gauge does not exceed $10^{-3} \mathrm{~mm}$. Hence, neither of these two gauges can be used for the measurement of pressures of high vacua.

Among high-vacuum gauges, with liquids as gauge-filling fluids, the McLeod gauge, as mentioned, is incapable of indicating the pressures of vapors. There are, however, some gauges of comparatively recent origin, such as the Backovsky-Slavik gauge, ${ }^{12}$ having phlegmatic fluids as gauge-filling liquids, which are capable of measuring vapor pressures, ${ }^{13}$ such as that of mercury; these will be dealt with hereafter.

## Section II A. Mercury-Filled Gauges-McLeod Manometers

3-3. Original Form of McLeod Gauge.-Low-pressure measurement of a gas is possible by isolating a known volume $V$ of the gas at an unknown pressure $p$ and compressing this gas into a small volume $v$ at which the pressure $P$ is measured. Since, according to Boyle's law, the product of pressure and volume is constant at constant temperature, the low pressure $p$ can be determined from the relation expressed in the following equation:

$$
\begin{equation*}
p V=P v \quad \text { or, } \quad p=P \frac{v}{V} \tag{3-1}
\end{equation*}
$$

In order to use this principle for measuring low pressures of gases, McLeod designed a device by which a gas, the pressure of which is to be determined, is isolated into a bulb of known volume $V$ and is then compressed into a capillary tube of known volume $v$, the pressure $P$ required being measured. This gauge, illustrated in

12 J. M. Backovsky and J. B. Slavik, Casopis pro p. math. a fy. 66, 1, 72 (1936).
${ }^{13}$ Swami Jnanananda, Casopis pro p. math. a fy. 69, (1939).
figure 3-3, consists of a bulb with a compression capillary tube at its top. This capillary has a uniform bore, having a diameter usually of 0.5 mm . Its upper end is closed and sealed off airtight by fusion as fatly, as uniformly, and as abruptly as possible. The bottom of the bulb is drawn into a tube. This fall tube at its lower end is joined to a reservoir by means of a suitable flexible rubber tube. The reservoir is filled with very pure and dry mercury. Another capillary tube with a uniform


Fig. 3-3. bore, having the same diameter as the compression capillary, is joined to the fall tube just below the bottom of the bulb. This serves not only as a comparison tube but also as a means of establishing communication between the vacuum apparatus and the gauge.

The upper end of the comparison capillary is connected to the vacuum apparatus, the residual gas pressure of which is to be measured. When the level of the mercury column is brought just below the juncture of the fall tube and the comparison capillary, equalization of pressures is established between the vacuum apparatus on the one hand and the bulb with the compression capillary on the other. Then the mercury reservoir is slowly lifted until the level of mercury rises just above the juncture of the fall tube and the comparison capillary leading to the apparatus, so as to isolate the gas in the bulb and the compression capillary from that of the comparison capillary and the apparatus.

The gas in the bulb and the compression capillary is cut off, and its volume $V$ is the volume of the bulb together with that of the compression capillary, which is carefully measured before adjusting the manometer. The compression of this isolated gas is achieved by further lifting the mercury reservoir until the mercury level reaches the graduation on the compression capillary tube, filling the entire bulb and the part of the compression capillary to the graduation. The volume $v$ of the gas after compression is the volume between the top of the compression capillary and the graduation on it, which is also carefully measured before the ad-
justment of the gauge. When the level of mercury reaches the graduation on the compression capillary, the mercury will rise to a higher level in the comparison capillary leading to the vacuum apparatus. Since both the capillary tubes have the same diameter, the difference of these levels measures the pressure $P$ to which the gas is compressed, so long as the initial pressure is very small compared with the pressure $P$ of the gas after the compression.

Now on introducing the measured values of the volume $V$ of the gas before the compression, of the volume $v$ of the gas after compression, and of the pressure $P$ to which the gas is compressed in equation $3-1$, the initial pressure of the gas is determined. This gauge, with a suitably long comparison capillary, covers a working range from a few millimeters up to nearly $10^{-5} \mathrm{~mm}$. with a probable error of about 1 per cent, especially at higher pressures. Since this gauge is slow in action, it is unsuitable for the measurement of rapid variations of pressure.

In the model of the McLeod manometer described above, the comparison capillary serves also as a means to establish connection between the gauge and the apparatus. Since the bore of the capillary is comparatively small, the connection is not free and time is needed for equalization of pressures of the gauge and the vacuum apparatus.

The use of a flexible rubber tube for raising and lowering the mercury reservoir is objectionable for various reasons. Air is easily occluded through the rubber tube. The occluded air may be prevented from entering the gauge by inserting a trap; however, it contaminates the mercury. Mercury contamination also occurs from its contact with the rubber; this condition can be remedied to some extent by thoroughly cleaning the rubber tube by immersion in a boiling dilute solution of caustic soda for a number of hours, washing it with distilled water and alcohol, and finally drying it by passing a rapid current of dry and dust-free air through it. Thus sulphur dust and other impurities are eliminated. The contamination of mercury by a gas occluded through the rubber tube, how-. ever, cannot be avoided by this cleansing process. Further, after being used for some time the rubber tube may crack and give way because of the weight of the mercury.

3-4. Modified McLeod Manometer.-The McLeod gauge has been modified and improved so as to eliminate defects described
above. In one of these modified forms, illustrated in figure 3-4, an additional wide by-pass tube is attached to the comparison capillary, in order to establish a freer and easier connection between the vacuum apparatus and the gauge. By this arrangement, the equilization of pressures takes place without loss of much time.


Fig. 3-4.


Fig. 3-5.

In this form of the gauge, the rubber tube used in the original forms for raising and lowering the mercury column is removed. In this arrangement, the reservoir of mercury has a side tube, joined through an air trap and fused on to the fall tube of the gauge. Through the small side tube, the mercury reservoir can either be exhausted by a vacuum pump or connected to the atmosphere. A needle valve, with a thread cut on the needle, which works in the rubber bung, closing the top of the mercury reservoir, as illustrated in figure 3-4, or a two-way stopcock as shown in figure 3-5, is arranged between the mercury reservoir and the gauge. In the
former arrangement the valve is opened and the side tube is communicated to the atmosphere so as to raise the mercury into the gauge; when the mercury column reaches the desired position in the compressed tube, the valve is closed in order to stop further rising of the mercury column. After readings are taken, the mercury column is lowered by evacuating the bulb of the mercury reservoir through the side tube and opening the valve. Note that in this arrangement, if the valve is not closed, th? reservoir will be emptied of mercury, and air will rush in violently through the gauge, endangering the tube system, which may, in such cases, be easily damaged.

In this form of the gauge, a needle valve is better than a stopcock because the stopcock grease contaminates the mercury and hardens, so that the whole gauge has to be taken down, which is usually a source of much inconvenience. It is also more advantageous than a stopcock in that it allows a wider passage for the mercury to flow through and thus permits a quicker operation of the instrument. In either one of the arrangements the mercury must always pass into an air trap to remove the air bubbles carried along with the mercury. This form of the gauge is, in some respects, better than the previously described form of the McLeod gauge. Its working range, however, is as much limited as that-of the older forms.

3-5. McLeod Multiple Manometer.-This gauge is an improvement on the original types of McLeod gauges for extending the working range. In this instrument, two or more bulbs of different sizes, each with its appropriate capillaries, are mounted in parallel on the common fall tube of suitable dimensions, as illustrated in figure 3-5. Each compression capillary with its comparison capillary is provided with a graduated scale in millimeters and half millimeters.

The lower end of the fall tube passes through the mercury to the very bottom of the mercury reservoir. The reservoir is provided with a side tube on the upper part above the topmost limit of the mercury level in the reservoir. The side tube can be opened either to the exhaust pump or to the atmosphere by means of a two-way stopcock or by an arrangement with a needle valve. The stopcock, when opened to the exhaust pump simultaneously closes the outlet to the atmosphere. By opening the stopcock to the atmos-
phere, while it simultaneously closes to the exhaust pump, the mercury can be raised in the gauge until its level reaches the mark on the compression capillary. After closing the stopcock both to the atmosphere and the exhaust pump, when the level of the mercury column remains steady at the mark on the compression capillary, the vacuum is measured. After readings are taken, the stopcock is opened to the exhaust pump but left closed to the atmosphere. By this means the mercury column is lowered until its level falls below the joint between the fall tube and the tube which establishes connection between the vacuum apparatus and the gauge, so that the gauge is ready for fresh operation for pressure measurements.

This arrangement overcomes, to a considerable extent, the limitation of the working range. But it is not convenient to mount a number of bulbs, each with its compression capillary and comparison tube, on a common fall tube. The arrangement of several bulbs, each with its compression capillary and comparison tube, greatly complicates the design. Precise calibration of many bulbs is rather a tedious affair, and the surface-tension correction for so many compression capillaries, especially when their corresponding comparison capillaries are not of equal diameter, is equally cumbersome.

3-6. Modified McLeod Multiple Manometer.-This gauge, a modified form of the McLeod multiple manometer, is a useful elaboration of the older forms to overcome the limitation of working range. In this instrument, the number of bulbs required by the multiple manometer is dispensed with. This gauge is provided with only one main compression bulb on which a series of four capillaries of decreasing diameter, fused together, are mounted, the widest and the longest compression capillary being directly joined to the bulb. The other three, with diameters of descending order and of the same length, are joined together in series and mounted on the widest capillary, as illustrated in figure 3-6. These tubes are joined and fused in such a way that the diameter at the joints is least affected. The sizes of the capillaries must be arranged so that the chosen marks are far from the joints. With this arrangement the diameters at the marks will remain unaffected when the joints are made.

A set of comparison tubes of diameters and number equal to
those of the series of compression capillaries is so mounted that each comparison capillary is parallel to its compression capillary with corresponding diameter. Each tube of this set is marked, and the mark of each is level with the mark in the corresponding part of the same diameter of the compression chamber. In the operation of the gauge, the level of mercury reaches the mark on one of the portions of the compression chamber. From the mark on the corresponding parallel tube of the same diameter, the difference of level can be directly read in fractions of $1 \mathrm{~mm} . \mathrm{Hg}$ in order to determine the vacuum pressure.

This instrument eliminates the need of applying a surface-tension correction to the measurement. The use of a number of parallel tubes somewhat complicates the design of this instrument. In order to avoid this complication, this instrument is sometimes arranged with only a single parallel comparison tube with a diameter which is equal to that of the widest portion of the series of the compression capillaries. Inasmuch as the surface tension varies from portion to portion of the compression chamber, some discrepancy actually enters into the pressure measurements made with the manometer having a single comparison tube. Therefore, surface-tension corrections of the rest of the portions of the compression chamber, found by preliminary experiment, must be applied to the measurements of pressure. As the


Fig. 3-6. corrections for surface tension are not constant, this arrangement, though simpler in construction, is less useful than the other.

This manometer, with comparison tubes communicating to the vacuum system of proper dimensions and sensitivity, has a working range from pressures of a few millimeters down to the lower limit of an ordinary mercury manometer.

3-7. Glass-Steel McLeod Gauge.-The McLeod gauge is constructed also in other forms. Whatever the design of the gauge, it is usually made of glass. The bulbs have to support considerable weights of mercury during the measurements. Glass being fragile, the instrument is likely to break under the weight of mercury. To avoid this, W. Edwards \& Co. have constructed a McLeod gauge, as shown in figure 3-7, in which


Fia. 3-7. the glasswork is replaced by steel except for the glass bulb, capillaries, and by-pass, which are compactly arranged and are attached to the fall tube by means of a ground joint. The mercury reservoir is also of steel and is arranged so that it may readily be raised or lowered to any desired position.

3-8. Accurate McLeod Gauge.-Gaede attempted to increase the sensitivity, precision, and accuracy of a McLeod gauge by using a large volume and fine capillaries. His efforts do not seem, however, to have met with success. This failure may be attributed to the following experimental difficulties: (1) uneven and unreliable motion of the fine mercury threads, variable capillarity, and mercury sticking to the walls while traveling through the narrow capillaries; (2) non-uniformity of the cross-section of the capillary bores; (3) errors due to the distortion of the capillary bore which occurs when closing the top end of the compression capillary, and errors in reading the position of the top end of the closed bore. To realize a very large compression ratio, it is necessary to have large apparatus in which masses of mercury must be handled and supported in large glass vessels which are usually fragile.

Paul Rosenberg ${ }^{14}$ has constructed a large McLeod gauge in which these difficulties are overcome, and his gauge achieves sensitivity, precision, and accuracy which are comparable to the gauge's compression ratio of $2.4 \times 10^{-7}$. It is important to realize such high accuracy in the McLeod gauge measurements, for in
${ }^{14}$ Paul Rosenberg, Rev. Sci. Inst. 10, No. 4, 131 (1939).
practice most of the useful vacuum gauges depend upon the McLeod gauge for calibration. This gauge, shown in figure 3-8, consists of a bulb $A$, having a volume of $1300 \mathrm{~cm} .^{3}$, and a reservoir $B$ of about $2500 \mathrm{~cm} .^{3}$, containing approximately 60 lbs . of pure mercury. Both of these are thick-walled glass vessels, mounted on the two plaster of Paris blocks $P$ and $Q$. The gauge is made entirely of pyrex except for the two capillaries, which are of Jena KPG round precisionbore glass tubing, joined to the pyrex with uranium seals. The capillaries, which are of uniform cross section, have an internal diameter of 0.63 mm ., and each of them is about 18 cm . long.

The bores of the capillary tubes are given a rough and ground finish so as to diminish sticking and breaking off of mercury threads while moving in capillaries. Sticking is successfully eliminated by thorough outgassing of the gauge by heat treatment while exhausting it with a high-vacuum pumping system, and by continuously maintaining cleanliness and vacuum in the gauge. Consequently the motion of the mercury threads in this gauge is uniform and reliable. To prevent contamination of the gauge by vapors which are sometimespresent in the main vacuum systems, the gauge is to be opened to the rest of the vacuum apparatus only with a refrigerant in an intervening trap. To prevent external-source contamination of mercury, the air is dried and filtered before it enters the


Fig. 3-8. reservoir $B$ through $T$ to raise the mercury.

In most of the McLeod gauges in which mercury sticks to the walls of the capillaries, and in those which have variable capillarity and non-uniform bores, the "Linear Scale" method of gauge reading is used with justification. In this method the mercury is always brought to a fixed mark in the closed capillary and is allowed to rise high in the open capillary. In this gauge, however, since these defects are eliminated and since it is possible to read the level of the top of the compression capillary, the higher-precision "Squared Scale" method of gauge reading can be used with advantage. In this method the mercury meniscus in the open
capillary is always brought level with the top of the closed capillary bore. In this instrument, the positions of the mercury menisci and the level of the top of the closed capillary are read by observing their images in a vertical mirror which is fitted directly behind the capillaries and upon whose face the rulings of a millimeter scale are engraved.

This gauge may be found useful for the calibration of most of the other gauges in use. The large volume of the bulb makes the time of its operation very long. When the pressure is low it is necessary to allow some time for the equalization of pressure. Because of the long time required for its operation, the gauge is not suitable for following changes of variable pressures.

3-9. Selection of Dimensions; Calibration.-The sens tivity or the low limit of pressure of high vacuum which can be obtained accurately by a common McLeod gauge depends on the ratio of $V$, the volume of the main chamber of the gauge, to $v$, the volume of the compression capillary between the graduation and the upper end. So the larger the ratio $V: v$ of the gauge, the lower the pressure it could measure. The ratio may be enlarged by increasing the $V$ of the bulb and decreasing $v$ of the compression capillary. But $V$ cannot be increased indefinitely because the time of operation becomes very long, making it impossible to follow the variations of pressure. To avoid this difficulty, $V$ is usually not made greater than 250 cc . But $V$ could be made as large as 500 cc . or even much larger only in gauges intended to serve as standard and accurate instruments for calibrating other gauges, for in such cases where the pressure is constant, tedium and slowness of readings are not of primary concern.
It is not possible to reduce $v$ indefinitely. If the diameter of the compression capillary is too small, mercury, no matter how clean and dry, moves in jerks and it is difficult to bring the surface of the column to the mark. If its diameter is less than 0.5 mm ., even the slightest trace of impurity on the surface of the mercury column, or the contamination of the mercury surface by oxygen or some other gases, makes it stick easily to the walls of the compression capillary, thereby closing the bore. The volume $v$ of the compression capillary cannot be reduced by marking the graduation too near the end, because the error due to imperfection in the flatness of the end, possible during the sealing process, enters com-
paratively magnified in the measurements. Thus, for practical use, a gauge with $V=250 \mathrm{cc}$. and a compression capillary of 0.5 mm . to 0.8 mm . diameter and 5 cm . long would be quite convenient for the measurement of pressures.

A McLeod gauge having a bulb of 250 cc. and a compression capillary of 0.8 mm . diameter and 5 cm . long, with a comparison capillary of the same diameter and 40 cm . long, could be used to great advantage to measure pressures between $10^{-5}$ and 1.6 mm . Hg. The lower limit may be extended to some extent by enlarging further the ratio $V / v$, but the accuracy of the measurement of even a pressure of $10^{-5} \mathrm{~mm} . \mathrm{Hg}$ is, if special arrangements are not made, by no means quite certain. Any attempt, therefore, to extend the lower limit down below this pressure by simply enlarging the ratio is ordinarily not very practicable. The limitation of the working range is, however, overcome by extending the upper limit as in the McLeod modified multiple manometer and the lower limit by increasing the ratio as in Rosenberg's accurate McLeod gauge.

It is necessary to determine precisely the volumes of the bulb and the compression capillary up to the chosen graduation. This is done before the gauge is fused to the air trap. The gauge is turned upside down and is clamped to a suitable stand. The end of the communicating by-pass is joined to a fore-vacuum pump; then, through a tap, temporarily fused to the fall tube just a couple of centimeters below the juncture of the fall tube and the communicating by-pass, clean and dry mercury is let in until the gauge is filled up to the point where the communicating by-pass is joined to it. Then the mercury is drawn out and carefully weighed to determine precisely the volume $V$ of the bulb. Again, when the gauge is being exhausted by the fore-vacuum pump, mercury is poured in and brought to fill the compression capillary up to the graduation. The mercury is then drawn out and weighed in order to determine the volume $v$ of the compression capillary. The same method is used also in determining the volume of the bulb and the volumes of the different capillaries in the series of the compression capillaries of the modified McLeod multiple manometer.

The bulb and the compression capillary of a McLeod gauge are calibrated when upside down. Pressures are measured, however, when the gauge is right side up. Therefore, a correction for meniscus curvature may be necessary. When an amount of
mercury, whose volume is exactly equal to the volume $v$ of the gas in the compression capillary, is poured in to the compression capillary, it occupies some volume, say MENI, as illustrated in figure 3-9. But the graduation, in fact, ought to be at $E^{\prime}$, and it is such that if the gauge were to be turned right side up, as in the


Fig. 3-9. case of measurement of pressure, the volume of $M^{\prime} E^{\prime} N^{\prime} I^{\prime}$ would be equal to the volume of $M E N I$. Suppose the surface MEN of the convex meniscus curvature of themercury column $M E N I$ is depressed and receded down in such a way that it forms the concave meniscus $M^{\prime \prime} E^{\prime \prime} N^{\prime \prime}$. The quantity of mercury being the same in either case, $M^{\prime \prime} E^{\prime \prime} N^{\prime \prime} I$ must be equal in volume to MENI and, therefore, to $M^{\prime} E^{\prime} N^{\prime} I^{\prime}$. Now, the volume of the portion of the sphere of the convex meniscus cut off at the plane $M N$, and the volume between this plane and the surface $M^{\prime \prime} E^{\prime \prime} N^{\prime \prime}$ of the concave meniscus, represented by the shading in the diagram, are equal to one another.

Now, let $\epsilon$ be the height of the meniscus, $\alpha$ the radius of the tube, and $\gamma$ the distance of the graduation from the plane $M N$. From figure 3-9 it is obvious that

$$
M N E=M N N^{\prime \prime} E^{\prime \prime} M^{\prime \prime}=\frac{1}{2} M \dot{N} N^{\prime \prime} M^{\prime \prime}
$$

and

$$
\begin{equation*}
\frac{1}{2} M N N^{\prime \prime} M^{\prime \prime}=\frac{1}{2} \pi \alpha^{2}(\epsilon+\gamma)=M N E \tag{3-2}
\end{equation*}
$$

$$
M N E=\frac{1}{2} \pi \alpha^{2} \epsilon+\frac{4}{3} \pi\left(\frac{\epsilon}{2}\right)^{3}
$$

$$
\begin{equation*}
=\frac{1}{6} \pi \epsilon\left(3 \alpha^{2}+\epsilon^{2}\right) . \tag{3-3}
\end{equation*}
$$

From 3-2 and 3-3 we have

$$
\begin{aligned}
& \frac{1}{2} \pi \alpha^{2}(\epsilon+\gamma)=\frac{1}{6} \pi \epsilon\left(3 \alpha^{2}+\epsilon^{2}\right) \\
& 3 \alpha^{2} \epsilon+3 \alpha^{2} \gamma=3 \alpha^{2} \epsilon+\epsilon^{3} .
\end{aligned}
$$

Therefore

$$
\begin{equation*}
\gamma=\frac{\epsilon^{3}}{3 \alpha^{2}} \tag{3-4}
\end{equation*}
$$

Now,

$$
\begin{align*}
\alpha^{2} & =\epsilon(2 R-\epsilon),  \tag{3-5a}\\
\epsilon & =R-R \sin \varphi
\end{align*}
$$

whence

$$
R=\frac{\epsilon}{1-\sin \varphi}
$$

Therefore,

$$
\begin{align*}
\alpha^{2} & =\epsilon\left(\frac{2 \epsilon}{1-\sin \varphi}-\epsilon\right) \\
& =\epsilon^{2} \frac{2-1+\sin \varphi}{1-\sin \varphi}=\epsilon^{2} \frac{1+\sin \varphi}{1-\sin \varphi} . \tag{3-5b}
\end{align*}
$$

Hence $\quad \epsilon^{2}=\alpha^{2} \frac{1-\sin \varphi}{1+\sin \varphi}$
or

$$
\begin{equation*}
\epsilon=\alpha\left(\frac{1-\sin \varphi}{1+\sin \varphi}\right)^{1 / 2} \tag{3-6}
\end{equation*}
$$

Now, from the relations expressed in equations 3-4 and $3-5 b, \gamma$ may be expressed in terms of $\epsilon$ thus:

$$
\begin{equation*}
\gamma=\frac{\epsilon^{3}}{3 \epsilon^{2} \frac{1+\sin \varphi}{1-\sin \varphi}}=\frac{\epsilon(1-\sin \varphi)}{3(1+\sin \varphi)} \tag{3-7}
\end{equation*}
$$

And from expressions 3-4 and 3-6 we have

$$
\begin{equation*}
\gamma=\frac{\alpha^{3}(1-\sin \varphi)^{3 / 2}}{3 \alpha^{2}(1+\sin \varphi)^{3 / 2}}=\frac{\alpha}{3}\left(\frac{1-\sin \varphi}{1+\sin \varphi}\right)^{3 / 2} . \tag{3-8}
\end{equation*}
$$

If $\varphi$ is taken roughly to be $45^{\circ}$,

$$
\begin{aligned}
\frac{1-\sin \varphi}{1+\sin \varphi} & =\frac{1-\frac{\sqrt{2}}{2}}{1+\frac{\sqrt{2}}{2}}=\frac{2-\sqrt{2}}{2+\sqrt{2}}=\frac{(2-\sqrt{2})^{2}}{4-2} \\
& =\frac{4-4 \sqrt{2}+2}{2}=3-2 \times \sqrt{2}
\end{aligned}
$$

Hence

$$
\gamma=\frac{\epsilon}{3}(3-2 \sqrt{2})=\frac{\epsilon}{3}(3-2 \times 1.41421)
$$

or

$$
\left.\gamma=\frac{\alpha}{3}(3-2 \sqrt{2})^{3 / 2}=\frac{\alpha}{3} \sqrt{(3-2 \sqrt{2}}\right)^{3} .
$$

Therefore

$$
\gamma=\frac{\epsilon}{3}(3-2.82842)=\frac{\epsilon}{3} \times 0.17158=\epsilon \times 0.0572
$$

or

$$
\gamma=\alpha \times 0.0237
$$

Therefore

$$
\gamma=0.0572 \epsilon \text { or } 0.0237 \alpha
$$

So the graduation should be just a little nearer the curvature than the base of the meniscus when the gauge is upside down. The value of $\epsilon$ can be calculated by actual measurement, and on introducing this value in the above equation, the exact position of the graduation above the base $M N$ is obtained. In practice, however, this calculation is not looked upon as an essentially valuable item in the calibration of the gauge. For all practical purposes, the mark made at the level of the ring of contact of mercury and glass when the gauge is reversed is taken to be sufficiently precise.

Only after calibration can the McLeod gauge be used advantageously for absolute measurements of pressure. This gauge depends upon the validity of Boyle's law at low pressures, when the pressure ratio used is about, 10,000 or 100,000 to 1 . This will not apply to easily condensable vapors or to the gases which do not obey Boyle's law in the region of high vacua. The traces of these vapors render the results obtained with permanent gases quite wrong. If the gas be not quite dry, the results are by no means correct. In order to secure correct results with a new gauge, it must be thoroughly freed from the gases and vapors which may be sticking to the walls of the gauge even after evacuation as well
as from the organic vapors which are transported from the organic substances present in certain kinds of pumps. Before taking the readings, a preliminary sweep-through of the mercury by alternately raising and lowering the column will be found to be advantageous.

## Section II B. Non-volatile and Phlegmatic Liquidfilled Gauges

3-10. Introduction.-Mercury as a gauge liquid has certain disadvantages. Its vapor pressure being rather high (above 0.001 mm . at normal temperature), a powerful refrigerant must be used for high-vacuum work between the mercury-filled gauge and the vacuum system. Since mercury has a very high surface tension, it does not form a definite reproducible meniscus and the column may stick in the glass tubes. To eliminate this difficulty the bores of the capillaries must be skillfully treated so as to give a rough and ground finish to the walls. If the manometer column is required to conduct electricity, the metallic vapor may be objectionable.

In consideration of the disadvantages associated with the use of mercury as a gauge liquid, certain kinds of non-volatile liquids or phlegmatic organic liquids may be substituted for mercury as gauge-filling liquids with certain advantages. The saturation vapor pressures of some of these liquids are as much as 1000 or more times lower than that of mercury. These liquids have very low surface tension, compared to that of mercury, and their density being low ( 1.05 in the case of $n$-di-butyl phthalate), the readings of a non-volatile liquid-filled gauge are multiplied by a factor of nearly 13, which permits greater accuracy of readings than those of a mercury-filled gauge. Having studied these advantages, Hickman and Weyerts ${ }^{15}$ were the first to use these liquids as gauge-filling fluids. The use of the non-volatile organic liquids has, however, one serious defect, for they are ready solvents for many gases. Gas therefore dissolves in the gauge-filling liquid on the high-pressure side and, diffusing through the liquid, eventually accumulates in the closed end. If any gas molecules are present in the closed end, the manometer readings will not indicate the actual gaseous pressure on the open side. Hence, the closed
${ }^{15}$ K. C. D. Hickman and Weyerts, J. Am. Chem. Soc. 52, 4714 (1930).
end should contain only the vapor of the gauge-filling liquid at a pressure corresponding to the surrounding temperature. This difficulty, however, can be surmounted by keeping the vacuum side continuously exhausted by a high-vacuum pump.

3-11. Hickman-Weyerts Phlegmatic Liquid-Filled Gauge.Hickman and Weyerts have constructed a butyl phthalate-filled gauge, shown in figure 3-10, in which the reference vacuum side is


Fig. 3-10.


Fig. 3-11.
continuously exhausted by a high-vacuum pump. This arrangement gives fairly reliable readings but it has certain disadvantages. From the illustration it is obvious that vapors eliminated at one place in the cycle partly dissolve at another, thereby causing a slight deterioration of the reference vacuum. Secondly, a sudden or accidental admission of air would drive the contents of the manometer into the condensation pump and it would take much time to recondition.

3-12. Malmberg-Nicholas Phlegmatic Liquid-Filled Gauge.As a substitute for the Hickman-Weyerts gauge Malmberg and Nicholas ${ }^{16}$ have designed and constructed a simple form of nonvolatile liquid-filled gauge, shown in figure 3-11, in which the removal of gas from the liquid and from the reference-vacuum limb is quickly and effectively accomplished.
${ }^{16}$ Malmberg and Nicholas, Rev. Sci. Inst. 3, No. 8, 440 (1932).

This manometer consists of a U-tube (1, 2), the (2) being the closed limb and the (1) limb being opened to the exit tube (4) and to the bulb (3), having the ebullition tube right on the top. Some gauge-filling liquid such as $n$-di-butyl phthalate is put in through the side tube, which is subsequently sealed off. The exit tube is connected to a vacuum pump. After the manometer is exhausted to as good a vacuum as is convenient, it is rotated clockwise until the liquid runs into the bulb. It is necessary to adjust the exit tube in such a way that it will prevent any flow of liquid to the pump during this operation. Liquid in bulb (3) is carefully heated until the dissolved gas is all evolved. Then the gauge is rotated counterclockwise until the liquid flows back and fills the closed limb (2). If a gas bubble be present in the liquid owing to an appreciable gas pressure, the manometer is rotated further and the bubble escapes into the open limb. Then the gauge is rotated clockwise until it comes to its erect position as shown in figure 3-11. The ebullition tube prevents bumping. After the exit tube is closed by turning the stopcock, the pump is disconnected and the gauge is joined to the vacuum system. Now the gauge is ready for a pressure measurement. This manometer gives pressure readings of the order of $0.1 \mathrm{~mm} . \mathrm{Hg}$.

3-13. Dolejšek-Kunzl Phlegmatic Liquid-Filled Gauge.-The Malmberg and Nicholas gauge is simple and reliable but its working range is very much limited. After the gauge and its contents have been primed and degassed, the degassed liquid is brought to the closed limb in order to remove the residual gas bubble and thus to secure a good reference vacuum in the closed limb. The removal of the residual gas bubble from the closed limbs and the isolation of the liquid column from the top of the closed limb present considerable difficulty.

The difficulty of conditioning is surmounted in the form of construction of Dolejsek and Kunzl. ${ }^{17}$ In the Dolejšek-Kunzl gauge, shown in figure 3-12, the closed limb is bent and a mercury pellet is introduced to enable easy removal of the residual gas bubble and effect a quick separation of the liquid column from the top of the closed limb to the working position.

This gauge is of approximately the same sensitivity as the Malm-berg-Nicholas gauge. Its readings, however, are not expected
${ }^{17}$ Records of The Spectroscopic Institute, Charles University, Prague.
to be so accurate, for mercury reacts upon the gauge-filling liquid and makes the latter apt to decompose and give out small quantities of gases which destroy the reference vacuum and render the readings somewhat uncertain.

3-14. Hickman Organic Liquid-Filled Gauge.-Hickman ${ }^{18}$ has designed and constructed a gauge in which phlegmatic liquid is used. This gauge, shown in figure 3-13, allows priming while in


Fig. 3-12.


Fia. 3-13.
use and without change of position. It avoids the difficulties connected with the non-volatile liquid-filled gauges. The gauge, though not simple in construction, is simple to fill, condition, and use for pressure measurements of vacua. Many of the defects associated with the non-volatile liquid-filled gauges already described are eliminated.

The priming of the gauge is done in the following manner. The barrel of the stopcock $B$ is removed and the boiler $A$ is charged with sufficient pure $n$-di-butyl phthalate and is warmed by the electric heater $H$ (30-50 watts). The stopcocks $B$ (the barrel being returned to position) and $C$ are fully opened and the tube $D$ is joined to a rotary oil pump, capable of reducing the pressure to less than 0.1 mm . Hg. The tube $B$, which is heavily lagged with
${ }^{18}$ K. C. D. Hickman, Rev. Sci. Inst. 5, No. 4, 162 (1934).
absorbent cotton, covered on the outside with bright metallized paper, conveys the vapor of phthalate and volatiles to the condenser $F$. The condensate on the walls of $F$ passes downward against the vapor stream and any residual gases or volatiles redissolving at the upper region are blown out by the hot vapor before it enters the pipe $G$. Here it flows through the coiling $K$ into the constant-level bulb $L$ and finally finds its way into the manometer limbs $M_{1}$ and $M_{2}$. The excess flows through the Sprengel tube $N$ to the pump $P$, whence it returns to the boiler $A$. During the passage of the liquid through the constant-level bulb it gradually dissolves or entraps gases and within a short time ( 20 minutes) of starting, the bubbles passing down $N$ collapse entirely at the bottom, giving visible assurance that the gauge is perfectly primed and ready for pressure measurements.

The stopcock $B$ is then closed and the vacuum apparatus whose pressure is to be measured is joined to the gauge through the tube $D$. The level of the liquid column $M_{2}$ sinks while that of the other remains constant, the excess having flowed down the pump tube. If the pressure, however, falls, the limb $M_{2}$ is replenished from the reservoir $L$ which is, in turn, quickly brought back to repletion by the inflow of phthalate. It will, for this reason, suffice to take readings from only one limb.

The gauge gives pressure readings as low as $0.001 \mathrm{~mm} . \mathrm{Hg}$. The construction of the instrument is not simple. Since the instrument is a complicated one, there may be some difficulty in mounting it near and joining it to the apparatus for pressure measurement.

3-15. Beeck Oil Micromanometer.-Otto Beeck ${ }^{19}$ has designed a simple oil micromanometer which combines appropriately the use of oil and mercury, and the principle of volume transfer into a capillary for the purpose of magnification. This manometer, shown in figure 3-14, consists of a fairly wide U-tube filled with an oil of low vapor pressure, such as Apiezon B oil, up to a mark formed by a sharp, platinized glass pointer $T$, pointing upward in the center of the tube within the oil. For good degassing, the oil is distilled directly in the gauge under high vacuum. The glass pointer in the center of the tube enables the oil meniscus in the branch tube to be set very accurately at the same position with ${ }^{19}$ Otto Beeck, Rev. Sci. Inst. 6, No. 12, 399 (1935).
the aid of a suitable magnification glass. The two manometer arms can be connected by means of the stopcock $B$, while the arm $a$ can be continuously connected with a high vacuum by the stopcock $A$. The oil column rests on a mercury column of appropriate length, so as to maintain the mercury level $L$ near the lower


Fig. 3-14. end of the capillary $C$, when both the arms above the oil column are at the pressure of high vacuum and the oil meniscus is set on the fixed pointer $T$. The bulb at the lower end of the capillary $C$ should have a capacity of at least the total volume of the capillary to assure that no air be carried over into the main arm of the gauge by the mercury.

For a pressure measurement, the oil column is kept at the pressure of high vacuum while the pressure to be measured is applied to the branch $b$. Then the oil meniscus is set again on the fixed pointer by means of rough vacuum applied on the upper end of the capillary $C$. The fine adjustment is made by the screw arrangement of the plunger, $P$. The lowering of the oil column and the raising of the mercury column are inversely proportional to their cross sections. The gauge may be calibrated directly by a careful choice and calibration of the tubes, or indirectly by comparison with a McLeod gauge using a permanent gas. For great accuracy and highest precision, the whole gauge must be immersed in a thermostatically controlled temperature bath. In that case, the mercury level may be read by means of a cathetometer. With Beeck's construction, the gauge constant, measured in centimeters of mercury column per $1 \mathrm{~mm} . \mathrm{Hg}$ pressure at $15^{\circ} \mathrm{C}$. in the manom-
eter proper, has been found to be 33.5 cm . as compared to the more reliable value 34.5 cm ., obtained by comparing the gauge with a good McLeod gauge. The precision of the actual manometric readings, which is about 0.1 mm ., corresponds to a pressure of about $3 \times 10^{-4} \mathrm{~mm}$. Hg.

This gauge has certain advantages over the McLeod gauge. Unlike the McLeod gauge, it operates without the exposure of mercury to the vacuum system. It also measures small pressures of easily condensable vapors. The limit of its precision is not far from that of a good McLeod gauge. The only objectionable feature is the combination of Apiezon oil and mercury, inasmuch as the oil is decomposed by mercury and the high vacuum is degenerated by the products of decomposition.

3-16A. Backovsky-Slavik Phlegmatic Liquid-Filled Gauge.This manometer, shown in figure 3-15, has been designed by Backovsky and Slavik. ${ }^{20}$ The gauge consists of a glass U-tube whose bore is very precisely uniform and whose closed end is provided with a cylindrical bulb and the open end with a double spherical chambered bulb. The curved end of a bent tube, having a vacuum-tight stopcock, is inserted into the upper chamber and the tube is sealed to it. This tube can be joined to the vacuum apparatus to admit an unknown pressure into the gauge for measurement. The U-tube at its upper part, just below the juncture of the limbs and the bulbs, is slightly bent at the same height from the bottom of the U-tube.

The gauge is primed through a small tube, situated on the top of the cylindrical bulb, with pure butyl-benzyl phthalate. This liquid is entirely freed from volatile components by fractional distillation under high vacuum. Any other pure non-volatile liquid, treated in the same way, may be used as the gauge-filling liquid. After priming, the small tube, on the top of the cylindrical bulb, is sealed by fusion.

Since the gauge-filling liquid has a low viscosity and low surface tension, the gauge permits an inclined position in its adjustment. Such an inclination in the adjustment of the gauge enables the displacements of the meniscus of the liquid column caused by the pressure variation to be read by means of a microscope. This

[^25]kind of measuring procedure permits greater sensitivity, precision, and accuracy than is possible in the usual measurement in a vertical position. The manometer can be inclined to an angle of about $1^{\circ}$ from the horizontal plane, and in this case, the accuracy


Fig. 3-15.
of the readings is not limited by the capillary forces but by the uniformity of the bore.

The difficulties encountered in degassing the instrument and the gauge-filling liquids are overcome by directly heating the liquid in the bulb of the closed limb under high vacuum and distilling out the liquid into the limbs. During the process of the distillation of the liquid from the bulb into the limbs, the vapor drives the residual
gas out of the closed limb and the condensate seals this closed limb so as to maintain it free from all traces of gases. In this way the closed limb obtains the highest possible vacuum, which is limited only by the vapor tension of the used liquid. During the distillation process it often happens that the suddenly liberated occluded and absorbed gases are apt to blow the distilled liquid from the limbs of the gauge. The curved tube inserted and sealed into the upper chamber of the bulb of the open limb, however, prevents the liquid from being blown out of the gauge.

When the gauge is inclined to the required slope, the small bends at the upper parts of the limbs prevent the liquid from flowing into the bulbs. They also serve to keep the liquid column, when inclined, at such a level that the passage between the closed and open limbs remains closed and the closed limb of the gauge is thereby maintained vacuum tight. Now the instrument is ready for pressure measurement.

3-16B. Use of Backovsky-Slavik Gauge to Measure Vapor Tension of Mercury.-Two phlegmatic liquid-filled gauges which will be simultaneously used for pressure measurement to minimize accidental errors in the readings are joined to each one of the chambers of a double-chambered vacuum enclosure as shown in figure 3-16. When required, this enclosure can easily be converted into a mercury-vapor reservoir by opening it to the activated and functioning sources of mercury vapor. Before converting the enclosure into a mercury-vapor reservoir, it is exhausted to a pressure below $10^{-6} \mathrm{~mm} . \mathrm{Hg}$ by means of a paraffin condensation pump, backed by a fore-vacuum rotary pump.

The two gauges, one filled with butyl-benzyl phthalate and the other with tri-o-creoylphosphate and each having a small mirror at the upper part, are laid in a perfectly horizontal plane each on a separate stand. Each one of the mirrors of the gauges in the horizontal plane is brought into the focus of a small telescope which is at a distance of nearly 200 cm . from the mirror of each one of the gauges. An illuminated scale is mounted vertically near the telescope in such a way that its reflection in each of the mirrors can be observed through the telescope. The telescope is adjusted so that one of the scale divisions from each of the reflections coincides with the horizontal one of the cross wires of the telescope. Then the readings of the scale divisions from each of the mirrors at
the precisely horizontal position of each one of the gauges are carefully taken. After these readings are taken in the horizontal position, the gauge stands are gently lowered in such a way that either one of the gauges comes to a slanting position with an angle of inclination of about $1^{\circ}$ from the horizontal plane. Then the stands are fixed so that the gauges remain firm in that position.


Fia. 3-16.
The readings of the scale divisions from each of the mirrors which coincide with the horizontal one of the cross wires of the telescope are taken when the gauges are in the fixed position. If the reading of the scale division when the gauge is in the horizontal plane be $h_{x}$, and the reading of the scale division when the gauge is in standing position be $h_{y}, h_{x}-h_{y}=d h$ is the height to which the gauge is inclined at a distance $L, L$ being the distance between the mirrors of the gauges and the telescope. Then the angle of inclination $\alpha$ is obtained from the expression,

$$
\begin{equation*}
\tan 2 \alpha=\frac{d h}{L} \tag{3-9}
\end{equation*}
$$

After adjusting the gauges in inclined positions and thus determining the angle of inclination of each one of the gauges, a microscope having a measuring scale is mounted and is focused on the meniscus of the liquid column in the open limb of each one of the gauges. As long as the vacuum remains uniform and constant, the meniscus of each of the gauges remains stationary, provided the temperature of the vacuum chamber is constant. If, however, the temperature of the vacuum enclosure be changed, the readings of the meniscus of each of the gauges vary even when other conditions are kept constant. So, to record such changes in the readings of each one of the gauges, the temperature of the vacuum enclosure is lowered from $25^{\circ} \mathrm{C}$. down to $7^{\circ} \mathrm{C}$. and raised again from $7^{\circ} \mathrm{C}$. back to $25^{\circ} \mathrm{C}$., and at each degree of rise or fall the manometric readings of each of the gauges are recorded. If the manometric readings be plotted against the temperature, a fairly straight curve which gives the zero positions of each of the manometers for the temperatures between $7^{\circ} \mathrm{C}$. and $25^{\circ} \mathrm{C}$. is obtained.

After thus determining the zero positions of the gauges for the required range of temperature, the vacuum chamber is filled to saturation with mercury vapor by opening it to the activated sources of mercury vapor. Then the temperature of the mercuryvapor reservoir is lowered from $25^{\circ} \mathrm{C}$. to $7^{\circ} \mathrm{C}$. and is raised again from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$., and at each degree of rise or fall of its temperature manometric readings are again recorded. If these readings be also plotted against the temperature on the graph of zero positions, a temperature-manometric reading curve of the mercury vapor from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$. is obtained.

The difference of divisions between the zero position curve and the temperature-manometeric reading curve of the vapor tension of mercury at each degree of temperature gives the number of divisions of the manometric readings for each degree of temperature which correspond to the vapor tension of mercury for that temperature. Now, each division $d$ of the manometric readings taken on the scale of the microscope may be expressed in terms of pressure $p$ in millimeters of mercury from the relation,

$$
\begin{equation*}
d \sim p=\beta \frac{S}{S_{\mathrm{Hg}}} \sin \alpha \tag{3-10}
\end{equation*}
$$

where $d$ is the division of the gauge reading on the scale of the

## 3. MEASUREMENT OF PRESSURES

microscope, $\beta$ the value of the division on the microscope scale in terms of a millimeter, $S, S_{\mathrm{Hg}}$ the specific gravities of the gaugefilling liquid and mercury respectively, and $\alpha$ the angle of inclina-

## + Motecular streaming methad - MeAsurements with phlegmaticliquid gauges



Fig. 3-17.
tion. Therefore the difference of divisions, $n d$, between the manometric zero curve and the temperature-manometric reading curve for each degree of temperature from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$. gives the vapor tension of mercury for that range of temperatures.

Measurements of vapor tension ${ }^{21}$ taken in this way by the two gauges, one filled with tri-o-creoylphosphate and the other filled with butyl-benzyl phthalate, from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$., are given in Tables 3-1A,B and 3-2. The vapor tension-temperature relation is recorded by plotting the logarithms of the pressures against the

## Table 3-1a. Butyl-benzyl Pethalate-Filled Gauat

(Saturation vapor pressure of mercury from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$. measured in the unit $10^{-8} \mathrm{~mm}$. Hg by the manometer 1.)

| Temperature, ${ }^{\circ} \mathrm{C}$. | Divisions* | Measured <br> pressure | True <br> pressure |
| :---: | :---: | :---: | :---: |
| 7.1 | $\ldots$. | 0.350 | 0.360 |
| 8.0 | $\ldots$. | $\ldots$. | $\ldots$. |
| 10.0 | 5.8 | 0.502 | 0.511 |
| 11.0 | 5.9 | 0.511 | 0.521 |
| 12.0 | 6.5 | 0.563 | 0.575 |
| 13.0 | 7.0 | 0.606 | 0.620 |
| 14.0 | 7.5 | 0.650 | 0.667 |
| 15.0 | 8.7 | 0.754 | 0.774 |
| 16.0 | 9.5 | 0.823 | 0.847 |
| 17.0 | 10.0 | 0.866 | 0.893 |
| 18.0 | 11.9 | 1.031 | 1.064 |
| 19.0 | 13.3 | 1.152 | 1.191 |
| 20.0 | 13.5 | 1.169 | 1.211 |
| 21.0 | 14.8 | 1.282 | 1.330 |
| 22.0 | 15.5 | 1.342 | 1.395 |
| 23.0 | 16.5 | 1.429 | 1.488 |
| 24.0 | 17.5 | 1506 | 1.571 |
| 25.0 | 19.0 | 1.646 | 1.720 |

* 1 division $=8.661 \times 10^{-5} \mathrm{~mm} . \mathrm{I}_{5}{ }_{5}$.
inverse values of absolute temperatures as shown in figure 3-17. From these data it may be observed that the measurements, and the calculated and extrapolated values from these measurements, agree remarkably well with the values obtained by Knudsen ${ }^{22}$ with his method of molecular streaming. Knudsen's measurements are not direct but they are very accurate. The measurements obtained by these liquid-filled gauges are not only absolute

[^26]but also direct and accurate. The Backovsky-Slavik gauge, used in the method indicated above, would be an absolute, sensitive, and accurate instrument. If it be filled with a non-volatile liquid of a very low vapor pressure, such as Octoil, this instrument may be used for measuring pressures from 1 mm . up to $10^{-7} \mathrm{~mm} . \mathrm{Hg}$.

Table 3-1b. Tri-o-creoylphosphate Filled Gauge
(Saturation vapor pressure of mercury from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$. measured in the unit $10^{-3} \mathrm{~mm} . \mathrm{Hg}$ by the manometer 2. )

| Temperature, ${ }^{\circ} \mathrm{C}$. | Divisions* | Measured <br> pressure | True <br> pressure |
| :---: | :---: | :---: | :---: |
| 7.1 | $\ldots .$. | 0.336 | 0.345 |
| 8.0 | $\ldots$. | 0.409 | 0.420 |
| 10.0 | 4.8 | 0.432 | 0.440 |
| 11.0 | 5.9 | 0.531 | 0.543 |
| 12.0 | 6.4 | 0.575 | 0.589 |
| 13.0 | 7.5 | 0.674 | 0.690 |
| 14.0 | 7.2 | 0.634 | 0.648 |
| 15.0 | 7.9 | 0.712 | 0.731 |
| 16.0 | 9.2 | 0.827 | 0.852 |
| 17.0 | 9.6 | 0.863 | 0.890 |
| 18.0 | 11.0 | 0.989 | 1.021 |
| 19.0 | 11.5 | 1.034 | 1.070 |
| 20.0 | 12.5 | 1.124 | 1.166 |
| 21.0 | 13.5 | 1.214 | 1.262 |
| 22.0 | 14.5 | 1.304 | 1.358 |
| 23.0 | 15.6 | 1.403 | 1.463 |
| 24.0 | 17.0 | 1.529 | 1.598 |
| 25.0 | 18.3 | 1.646 | 1.723 |

$* 1$ division $=8.992 \times 10^{-5} \mathrm{~mm} . \mathrm{Hg}$.
The instrument is simple, and its priming and conditioning are equally simple. It is very sensitive and gives instantaneous and continuous registration of steady as well as varying pressures. Unlike the McLeod gauge, it gives pressure readings of both gases and vapors. During measurement it is necessary to maintain both the limbs of the manometer at the same constant temperature, and the position of the gauge must on no account be disturbed during the measurements. If, for any reason, the position is altered, the angle of inclination must be redetermined for further use of the instrument.

Table 3-2
(Mean values of the vapor tension of mercury from $7^{\circ} \mathrm{C}$. to $25^{\circ} \mathrm{C}$., given in the unit $10^{-3} \mathrm{~mm} . \mathrm{Hg}$.)

| Temperature, ${ }^{\circ} \mathrm{C}$. | By gauge I | By gauge II | Mean <br> pressure |
| :---: | :---: | :---: | :---: |
| 7.1 | 0.360 | 0.345 | 0.353 |
| 80 | $\ldots .$. | 0.420 | 0.420 |
| 10.0 | 0.511 | 0.440 | 0.476 |
| 11.0 | 0.521 | 0.543 | 0.537 |
| 12.0 | 0.575 | 0.589 | 0.582 |
| 13.0 | 0620 | 0.690 | 0.655 |
| 14.0 | 0.667 | 0.648 | 0.658 |
| 15.0 | 0.774 | 0.731 | 0.753 |
| 16.0 | 0.847 | 0.852 | 0.850 |
| 17.0 | 0.893 | 0.890 | 0.892 |
| 18.0 | 1.061 | 1.021 | 1.042 |
| 19.0 | 1.191 | 1.070 | 1.130 |
| 20.0 | 1.211 | 1.166 | 1.188 |
| 21.0 | 1.330 | 1.262 | 1.296 |
| 22.0 | 1.395 | 1.358 | 1.376 |
| 23.0 | 1.488 | 1.463 | 1.475 |
| 24.0 | 1.571 | 1.598 | 1.584 |
| 25.0 | 1.720 | 1.723 | 1.722 |

## Section III. High-Vacuum Gauges Depending on the Principle of Radiometric Action

3-17. Introduction.-A group of high-vacuum gauges operates on the principle of radiometric action. Knudsen ${ }^{23}$ realized this as a result of his investigation on the change of the velocity of gas molecules due to their impact against a fixed wall which differs in temperature from the gas. This actually occurs in the radiometer, invented by Crookes. This apparatus has four vanes of mica, each covered on one side with lampblack. They are mounted on the arms of a horizontal cross, free to spin round on a pivot. An equal number of gas molecules strikes each of the faces of the vanes in a like manner, but the molecules which impinge against the blackened faces are thrown with greater velocity than those that bombard clear faces, inasmuch as the blackened faces have higher
${ }^{23}$ M. Knudsen, Ann. d. Phys. 31, 207 (1910).
temperatures due to greater heat absorption. Consequently the vanes revolve with their clear faces turned forward.

Knudsen chose a case for which the theory could be adequately developed. He took two plate systems $A$ and $B$ (figure 3-18),


Fig. 3-18.
immersed in a strongly rarefied gas and placed at a distance from each other which is small compared with the mean free path of gas molecules. The plate $A$, heated electrically, has a temperature $T_{1}$ while $B$ is at a lower temperature $T_{2}$, so that the plates exert upon each other a repelling force. The force is a function of the pressure. The pressure can therefore be determined by measuring the repelling force either as a torque or by a direct deflection, which gives the principle for constructing two main classes of this group of manometers. Knudsen gave an expression for the relation between the pressure $p, R$ the repelling force per unit area of the plate, and $T_{1}$ and $T_{2}$ the absolute temperatures of the hot- and the cold-plate systems respectively. Knudsen's expression may be derived from the following simple gaseous kinetic theory considerations.

Let it be assumed that the gas molecules, on their impact with the plate, acquire its temperature, so that the molecules leaving the plate $A$ have the velocity distribution corresponding to $T_{1}$ while those leaving the plate $B$ have the velocity distribution corresponding to $T_{2}$. Assume that the number of molecules per
cubic centimeter having velocity components directed toward $B$ from $A$ is $n_{1}$, and that the average and the mean square velocities of these molecules are $v_{m 1}$ and $\overline{v_{1}{ }^{2}}$ respectively at the absolute temperature $T_{1}$. Similarly, the number of molecules that have velocity components directed toward $A$ from $B$ is $n_{2}$, while their average and the mean square velocities are $v_{m 2}$ and $\overline{v_{2}{ }^{2}}$ respectively at the absolute temperature $T_{2}$. Then the pressure exerted on the surface of the plate $B$ facing $A$ by the former molecules is $\frac{1}{3} m n_{1} \overline{v_{1}{ }^{2}}$ and that by the latter is $\frac{1}{3} m n_{2} \overline{v_{2}}{ }^{2}$. Therefore the pressure $\bar{p}$ on the surface of the plate $B$, due to the molecules in the gap between the plates being the sum of these two, is given by

$$
\begin{equation*}
\tilde{p}=\frac{1}{3} m\left(n_{1} v_{1}^{2}+n_{2} \overline{v_{2}{ }^{2}}\right) . \tag{3-11}
\end{equation*}
$$

Again, if the two plates be surrounded by $n$ number of molecules per cubic centimeter at average and mean square velocities of $v_{m}$ and $\overline{v^{2}}$ respectively, then the pressure, $p=\frac{1}{3} m n \bar{v}^{2}$, outside the gap surrounding the plates, exerts such a force on $B$ that it is pressed toward $A$, so that the resulting force $R$ per unit area acting on the plate $B$, being the difference between the total pressure due to the molecules between the plates and that due to the molecules outside the gap of the plates, is given by

$$
\begin{equation*}
R=\bar{p}-p=\left[\left\{\frac{1}{3} m\left(n_{1} \overline{v_{1}^{2}}+n_{2} \overline{v_{2}^{2}}\right)\right\}-p\right] . \tag{3-12}
\end{equation*}
$$

If the number of molecules between the plates going in one way be $n_{1}$ and that of the molecules going in the other way $n_{2}$, their respective densities will be $2 n_{1}$ and $2 n_{2}$. Then by $(1-48 a)$ the number of the former striking unit area is given by $\frac{1}{2} n_{1} v_{m 1}$ and that of the latter striking unit area by $\frac{1}{2} n_{2} v_{m 2}$. Because of chaotic molecular agitation, the molecules do not accumulate at any place between the plates. Therefore, when equilibrium is established and no molecules escape from the gap between the plates, the number of molecules per cubic centimeter between the plates, moving in one direction, must be equal to that of the molecules moving in the other direction. Hence,

$$
\begin{equation*}
\frac{1}{2} n_{1} v_{m 1}=\frac{1}{2} n_{2} v_{m 2} . \tag{3-13}
\end{equation*}
$$

In order that the pressure between the plates remain constant, the number of molecules $\frac{1}{2} n_{1} v_{m 1}+\frac{1}{2} n_{2} v_{m 2}$ crossing a surface per-
pendicular to the plates outward from inside must equal the number $\frac{1}{4} n v_{m}$ crossing the same inward from outside. Therefore,

$$
\begin{equation*}
\frac{1}{4} n_{1} v_{m 1}+\frac{1}{4} n_{2} v_{m 2}=\frac{1}{4} n v_{m} \tag{3-14a}
\end{equation*}
$$

or

$$
2 n_{1} v_{m 1}=n v_{m}
$$

whence

$$
\begin{equation*}
n_{1} v_{m 1}=n_{2} v_{m 2}=\frac{1}{2} n v_{m} \tag{3-14b}
\end{equation*}
$$

Since the average molecular velocity $v_{m}$ and the root of the mean square velocity $\left(\overline{v^{2}}\right)^{1 / 2}=v_{s}$ are by equation $1-47$ proportional, expression $3-14 b$ may be written,

$$
\begin{equation*}
n_{1} v_{s 1}=n_{2} v_{s 2}=\frac{1}{2} n v_{s} \tag{3-15}
\end{equation*}
$$

Now, on introducing the values of the terms given in expression $3-15$ into equation $3-12$, we obtain an alternative expression for the repelling force $R$, which may be written

$$
\begin{align*}
R & =\frac{1}{3} m n \frac{1}{2} v_{s}\left(v_{s 1}+v_{s 2}\right)-p  \tag{3-16a}\\
& =\frac{1}{2} p\left(\frac{v_{s 1}+v_{s 2}}{v_{s}}\right)-p \tag{3-16b}
\end{align*}
$$

If the cold-plate system $B$ is maintained at the temperature of the gas surrounding the plates (i.e., $T_{2}=T$ ) then $v_{s 1}=v_{s}$. Therefore,

$$
\begin{equation*}
R=\frac{1}{2} p\left(\frac{v_{s 1}}{v_{s 2}}-1\right) \tag{3-17}
\end{equation*}
$$

Again, since by equation $1-45 b, v_{s}=(3 k T / m)^{3 / 2}$, the repelling force $R$ given in equation 3-17 may be expressed in terms of the absolute temperatures $T_{1}$ and $T_{2}$ of the hot- and the cold-plate systems, and is

$$
\begin{equation*}
R=\frac{1}{2} p\left(\sqrt{\frac{T_{1}}{T_{2}}}-1\right) \tag{3-18}
\end{equation*}
$$

Hence the pressure $p$ of the gas in the chamber enclosing the hotand the cold-plate systems is

$$
\begin{equation*}
p=\frac{2 R}{\left[\left(T_{1} / T_{2}\right)^{3 / 2}-1\right]} \text { dynes } / \mathrm{cm}^{2} \tag{3-19}
\end{equation*}
$$

For small temperature differences (i.e., when $T_{1}-T_{2}<250^{\circ}$ C.) the equation reduces to the simple form

$$
\begin{equation*}
p=4 R \frac{T_{2}}{T_{1}-T_{2}} \text { dynes } / \mathrm{cm} .^{2} \tag{3-19a}
\end{equation*}
$$

which, on introducing the characteristic magnitudes of the instrument and the measuring lamp and scale devices, becomes

$$
\begin{equation*}
p=\frac{8 \pi^{2} \gamma \beta}{D \alpha t^{2} l} \cdot \frac{T_{2}}{T_{1}-T_{2}} \text { dynes } / \mathrm{cm} .^{2} \tag{3-19b}
\end{equation*}
$$

where $\gamma$ is the moment of inertia of the suspended plate system $B$, $D$ its mean diameter, $\alpha$ the area of its one side, $t$ the period of oscillation, $\beta$ the scale deflection, and $l$ the distance of the scale from the mirror attached to the suspension of the cold-plate system $B$.

If the hot-platinum-plate system $A$ be heated electrically, $T_{1}-T_{2}$ may be expressed in terms of the electrical resistance of the hot-plate system at $0^{\circ} \mathrm{C} ., T_{1}{ }^{\circ}$, and $T_{2}{ }^{\circ}$ respectively by $T_{1}$ -$T_{2}=r_{1}-r_{2} / r_{0 \varphi}, r_{0}, r_{1}$, and $r_{2}$ being the resistances at $0^{\circ} \mathrm{C}, T_{1}{ }^{\circ}$, and $T_{2}{ }^{\circ}$ respectively, and $\varphi$ the temperature coefficient of platinum. Hence expression 3-19b for pressure $p$ in terms of these electrical resistances may be written as

$$
\begin{equation*}
p=\frac{T_{2} 8 \pi^{2} \gamma \beta}{D \alpha t^{2} l} \cdot \frac{r_{1}-r_{2}}{r_{0 \varphi}} . \tag{3-19c}
\end{equation*}
$$

Now, in order to measure $R, T_{1}$, and $T_{2}$ and to substitute their values in the manometric equation 3-19 for computing therefrom the value of $p$, Knudsen and subsequently others have constructed manometers which are of great value for the science and the technique of high vacua.

3-18. Knudsen Absolute Gauge.-This gauge is capable of giving absolute values of pressures which are independent of the nature of the gas. The instrument, illustrated in figure 3-18, consists of a system of two stationary plates $A A^{\prime}$ and a suspended system of two plates $B B^{\prime}$. The pair of movable plates is suspended from a quartz fiber carrying a mirror and is capable of rotation. The relative positions of the fixed and the movable systems of
plates are such that the distance between the two systems is much smaller than the mean free path of gas molecules at low pressures. The system of fixed plates, made of platinum, is electrically heated and its temperature is either measured by a thermometer attached to it or determined from the measurement of electrical resistance. The temperature of the cold-plate system is measured by a thermometer attached to it, and that of the surrounding gas by a separate thermometer. These principal parts are enclosed in an airtight chamber of glass connected through a communicating tube with the vacuum system.
If the obtained pressure $p$ is such that the mean free path is much longer than the distance between the system of fixed plates and that of movable plates, repulsion of the system of cold plates takes place to an extent which is directly proportional to the pressure. Gas molecules impinge on both the systems of plates in a like manner but those proceeding from the hot-plate system are of greater velocity than those proceeding from the cold-plate system. The cold-plate system is repelled by the impingement of the gas molecules proceeding from the hot-plate system on the suspended cold-plate system. The degree of repulsion of the suspendedplate system is measured by the deflection of the mirror as indicated by a reflected beam of light. The force of repulsion $R$ is determined from the area of one side of the cold-plate system, the moment of inertia, the period of oscillation and the angle of deflection of the cold-plate system. Substituting the experimentally determined values of the force of repulsion $R$, the absolute temperature $T_{1}$ of the system of hot plates and absolute temperature $T_{2}$ of the cold-plate system in the Knudsen equation 3-19, the value of the pressure $p$ of the vacuum is obtained.
This gauge is capable of giving readings of pressures of vacua ranging from about $1 \sigma^{-3} \mathrm{~mm}$. down to the highest obtainable vacuum. It can be used with advantage, unlike the McLeod gauge, to measure not only low pressures of gases but also low vapor pressures. Knudsen ${ }^{24}$ measured vapor tension of mercury from $0^{\circ} \mathrm{C}$. up to nearly $25^{\circ} \mathrm{C}$. with his absolute gauge. It is, however, difficult to construct a duplicate of the original absolute gauge of Knudsen, for it is hard to realize a small distance of about 0.1 to 0.12 mm . between a fixed-plate system and an oscillating-
${ }^{24}$ M. Knudsen, Ann. d. phys. 32, 809-842 (1910).
plate system with an arrangement for measuring temperature as in the original model of Knudsen.

3-19. Knudsen Copper-Plate-Cylinder Gauge.-Knudsen constructed an absolute gauge of the design shown in figure 3-19. This instrument consists of a copper cylinder $A_{1} A_{1}$ which is inserted in a hole drilled in a copper block. The diameter of the cylinder is slightly smaller than that of the hole. The cylinder is


Fig. 3-19.
fixed by means of screws through the copper block so that the cylinder remains in a position co-axial with the hole. The points of the screws are made of glass in order to reduce as much as possible the heat conduction between the cylinder and the block. The solid end of the cylinder toward the left is a circular disk, and it is surrounded by the rim of the hole in the copper block which serves as a kind of guard ring. This circular disk forms the fixedplate system of the gauge. It is maintained at a higher temperature by heating the cylinder electrically by means of a resistance coil inside the cylinder. A copper vane $A_{2} A_{2}$, suspended by a fine metal wire with torsional resistance, hangs so that it remains quite parallel to and at a very small distance from the solid end of the cylinder. The vane is furnished with a mirror for reading the deflection of the vane by the lamp-and-scale method and with devices for the determination of the moment of inertia, in order to
use the apparatus for the absolute measurement of forces acting on the vane. The copper block, the vane, and the cylinder are fitted with mercury thermometers $T_{1}, T_{2}, T_{3}$. This measuring device is surrounded by an airtight chamber $C C$, having a tube communicating with the vacuum system whose gaseous pressure is to be measured. In this device the heated surface in the end of the copper cylinder is given a well-defined area.


The copper block and the vane are maintained at the same temperature. In the Knudsen manometer equation, $T_{1}$ is the absolute temperature measured in the cylinder and $T_{2}$ the absolute temperature of the copper block and the vane. The force of repulsion $R$, acting per unit surface of the vane, is determined by the deflection of the vane and the known dimensions of the apparatus. Thus the values of $R, T_{1}$, and $T_{2}$ are experimentally determined in order to compute therefrom the gaseous pressure $p$ of the vacuum system by the relation given in the Knudsen manometer equation 3-19.

The range of pressures measured by this gauge is almost the same as that of the Absolute Gauge.

3-20. Knudsen Glass Plates Mica Strip Gauge.-Knudsen ${ }^{25}$ described the construction of a manometer with torsion fiber in a paper on the determination of the molecular weights of small quantities of gases. It consists of a strip of mica, suspended from a quartz fiber inside a water-jacketed body of the gauge as shown in figure 3-20. Two glass plates of equal dimensions are attached to the walls of the body by thin glass rods so that one remains in front of and one behind the mica strip, each covering half of it and both being parallel to it. The distance between the glass plates and the faces of the mica strip is very small. The edge of the mica strip is viewed through a microscope which is placed at a known distance from the mica strip. The glass plates are maintained at a higher or lower temperature by circulating hot or cold water in the jacket as required by the condition of the experiment.
${ }^{25}$ M. Knudsen, Ann. d. Phys. 44, 525-536 (1914).

The temperature of the fixed glass plates may be taken as invariable because of their large thermal capacity and inappreciable thermal conduction through their small glass supports. The temperature change of the mica strip is much slower than that of the tube walls. After the circulation of cold water for some time, if warm water be sent through the jacket, the mica strip moves toward the fixed glass plates. If this operation is reversed the mica strip moves away from the glass plates and this is obviously the best way for making measurements since the mica strip does not strike the glass plates.

This kind of instrument may be made sensitive to $10^{-6} \mathrm{~mm} . \mathrm{Hg}$. The temperature of the two sides of the mica may be different, and in the absence of suitable arrangements for recording the temperature of the mica strip, the gauge cannot be used for precision and absolute-pressure measurements. It is therefore necessary to calibrate this instrument, as Knudsen did, by the use of the pres-sure-reducing device described in section 3-30 of this chapter.


Fig. 3-21A.
3-21. Dunoyer Radiometer Gauge.-Shortly after Knudsen published his first paper on his gauges, Dunoyer ${ }^{26}$ devised and constructed a manometer whose function is based on the principle of radiometric action. This apparatus is illustrated in figure 3-21A. It consists of the main cylindrical body in a horizontal position,

[^27]with two cylindrical tubes as its limbs, one standing at right angles to the main horizontal body and the other a jar-shaped tube with its solid end thrust and sealed into the horizontal main body. A glass vane is suspended by means of a fiber from the middle of the top of the vertical limb so that it is kept hanging parallel to the flat glass of the horizontal limb, about 1 or 2 mm . from it. The face of the suspended vane which is turned away from the glass plate is concave. The horizontal limb is provided with inlet and outlet tubes to circulate heated air into it. Thus the flat glass of the horizontal limb which forms the fixed vane of the gauge is heated. The difference between the temperature of the heated fixed glass plate and that of the suspended vane, causes the latter to experience a repulsion which is proportional to the pressure. The concave face of the suspended vane can form an image of an incandescent filament on a fixed scale. Thus the position of the plate before and after repulsion may be read from the image on the scale. From the positions of the suspended vane, etc., the force of repulsion $R$ is measured and thence, with the readings of $T_{1}$ and $T_{2}$, the pressure $p$ is determined.


Fig. 3-21B.
3-22. Dunoyer Compact Radiometer Gauge.-This gauge, illustrated in figure 3-21B, in its design and construction, is similar to the Dunoyer Radiometer Gauge. In this compact form the fiber from which the vane is suspended is quite short. Unlike the other form, therefore, the long vertical tube, which forms the support as well as the casing of the fiber, is practically eliminated.

3-23. Woodrow Radiometer Gauge.-Since Knudsen published his papers on his absolute gauge, several workers attempted to construct vacuum gauges, working on the principle of radiometric action, with increased sensitivity and precision. To increase the sensitivity of the gauge, arrangements have been
made to allow larger temperature differences to be set up between the heater and the suspended system. The precision of the gauge, especially at very low pressures may be assured by outgassing the instrument by heat treatment. Angerer ${ }^{27}$ constructed a gauge which, from his description, seems to have attained a fairly satisfactory sensitivity. With his instrument, however, it was not easy to attain precision at low pressures because the gauge was incapable of being freed from surface and occluded gases. It is possible to remove such gases only by thoroughly heating the instrument to a temperature of about $200^{\circ} \mathrm{C}$. while on the pump. Angerer's vacuum gauge could not be heated without danger of cracking. Woodrow ${ }^{28}$ designed and constructed a gauge which had arrangements to allow larger temperature differences for increasing the sensitivity and permit heat treatment for getting rid of the surface gases in order to ensure precision of measurements at and below $10^{-6} \mathrm{~mm}$. pressure.

Woodrow's model of the vacuum gauge is shown in figures $3-22 A$ and $3-22 B$. This gauge is provided with two glass rods $G G$ which serve as supports for the metal parts of the gauge. The suspension $W$ is a phosphor-bronze ribbon 50 mm . in length. The movable vane $V V$ consists of a rectangular frame of aluminum 0.076 mm . thick, the dimensions of the outer rectangle being $30 \times 36 \mathrm{~mm}$. and the inner $26 \times 30 \mathrm{~mm}$. A small mirror $M$ is fixed to the movable vane so that the deflection of the vane may be read by the beam reflected by the mirror. The heaters $P P$, consisting of platinum strips 4 mm . wide, 40 mm . long, and 0.025 mm . thick, are raised to a higher temperature by providing a regulated heating current from the battery $C$ consisting of a carefully calibrated Weston Standard cell, connected by the electrical circuits shown in figure 3-22C. All the platinum connections are made by electric welding to assure perfect contact. The suspension is connected at both ends by threading through three small holes drilled into the flattened extremities as illustrated in figure 3-22A. After the necessary internal electrical connections and adjustments are made, the outer glass 00 is sealed at $S S$. An electromagnet $E E$ is employed to bring the moving vane to rest. The cores of the electromagnet must be such that they do not

[^28]retain residual magnetism which will produce a false zero if the aluminum vane is at all magnetic.

The potentiometer leads $T T$ are connected by electric welding to the very extremities of the heating vanes $P P$. The heating

current is regulated by the variable resistance $\rho$ and is read on the ammeter $A$. The resistance $r_{2}$ is kept constant at 10,000 ohms, and $r_{1}$ is varied to obtain a balance of the sensitive galvanometer $G$. The potentiometer battery $C$ is a precisely calibrated Weston Standard cell. This arrangement gives an accurate method of measuring the resistance of the platinum strips $P P$ together with
the heavy platinum wire $a b$, the cold resistance being 0.17 ohm. With this arrangement the value of the coefficient is $2.35 \times 10^{-3}$ ohms per degree rise of temperature. From the values of the variable resistance read on the ammeter the temperature of the heater is determined.

It is possible to obtain a temperature difference of $100^{\circ} \mathrm{C}$. between the movable vane and the heaters. A deflection of 0.5 mm . on a scale at a distance of one meter from the mirror can be easily read. With a temperature of $100^{\circ} \mathrm{C}$. and a reading of 0.5 mm . deflection, the Woodrow gauge will indicate a pressure as low as $3 \times 10^{-8} \mathrm{~mm}$. Hg.

3-24. Shrader-Sherwood Vacuum Gauge.-Woodrow, with his arrangement of the heating system, etc., increased the sensitivity of the gauge to $10^{-8} \mathrm{~mm} . \mathrm{Hg}$. Shrader and Sherwood ${ }^{29}$ constructed a gauge whose sensitivity is even greater than that of
 Woodrow (figure 3-23).

The arrangement of the Shrader and Sherwood radiometer gauge is carried on a bent glass rod. This rod is fused at its lower end to a small bulb through which wires pass for the conduction of electric current. The upper end of the glass rod is fused onto a cup-shaped support. A small bar rests on the edges of this support. This bar, which carries the suspension, is made from a tube in which a short piece of soft iron is sealed, so that it may be turned by a magnet from the outside. The support of the suspension hook, hanging from the bar, passes through a capillary tube, which guides it without holding it.

The moving vane of the gauge is suspended from the hook by a fine tungsten wire of 0.012 mm . diameter. This moving vane, which is rectangular in shape, is of thin ( 0.076 mm .) aluminum foil. The external dimensions of the rectangle are $3.2 \times 4 \mathrm{~cm}$., the width of the vane being 0.5 cm . To render the vane rigid, an

[^29]aluminum wire is wound through slits at the top to a hole at the bottom of the vane and is hooked and fastened into this bottom hole. A mirror is fastened to the projected hooks at the bottom and holders on the sides of the


Fra. 3-23. Shrader and Sherwood's Modification of the Knudsen gauge. vane. Two copper-wire collars at the ends protect the suspended vane from shocks when the gauge is moved. The fixed system consists of strips of platinum foil, 0.018 mm . thick and 7.5 mm . wide with a total length of 18 cm ., bent as shown in figure 3-23. The two ends of the foil are fused to the tungsten wires for supplying the heating current. These tungsten wires, fused to the glass support, serve as springs to stretch the platinum foil. One of these fused tungsten electric leads is made long enough to touch the suspended hook in order to stop the setting up of an electrostatic field between the suspended vane and the fixed system. Two platinum wires are fused onto the ends of the platinum foil to act as potential terminals for measuring its resistance. This entire arrangement of the gauge is enclosed inside a wide glass tube about 5 cm . wide and 20 cm . long, which serves as its body. All the joints are fused and made perfectly airtight. It can be evacuated and the surface gas molecules in the instrument can be removed by heat treatment.

The fixed system of the gauge is electrically heated. The arrangement of the electrical connections for the gauge's heating
current is similar to that of Woodrow (figure 3-22C). The absolute temperature of the warm plate $T_{1}$ may be determined from the data obtained from the preliminary experiments on the variation of resistance with the temperature for the platinum, and the actual value of the resistance taken at the time of reading with the amount of the deflection of the vane. If the gas is sufficiently rarefied and if the period of reading is short, the absolute temperature of the vane $T_{2}$ may be considered as the initial absolute temperature.

As a result of heating, the temperature of the fixed-plate system is higher than that of the suspended vane. Consequently the velocity of the gas molecules proceeding from the fixed hot-plate system to the vane is greater than that of the gas molecules proceeding from the vane to the hot-plate system. By the impacts of the swiftly moving gas molecules, the suspended vane is repelled. From the degree of repulsion of the vane, which is measured by reading the amount of deflection of the mirror as is indicated by the reflected beam of light on a fixed scale, mounted at a suitable distance, $R$ the repelling force per unit area of the plate is determined. By introducing the values of $R$, the repelling force, $T_{1}$ and $T_{2}$, the absolute temperatures of the fixed-plate system and the suspended vane respectively in Knudsen's equation 3-19, the value of the pressure $p$ is determined. The gauge may also be calibrated experimentally. With Shrader and Sherwood's actual gauge, a deflection of 1 mm . on a scale placed at 1 meter is said to have indicated pressures from $10^{-5}$ to $5 \times 10^{-9}$ for a temperature difference of $150^{\circ} \mathrm{C}$. between the vane and the fixed platinum foil.

3-25. Radiometer Vacuum Gauge (DuMond-Pickels).-The original models of the Knudsen absolute gauge and the subsequent models working on the principle of radiometric action were designed to study the gauge as a research problem rather than as a practical measuring device. In some of the principal models the gauge sensitivity has been successfully extended to $5 \times 10^{-9}$ by careful outgassing in order to verify the theoretical formula developed by Knudsen. To this end elaborate means for measuring the temperature of the heater element have been provided. These gauges, made of glass, presented fairly difficult jobs of glass blowing. Due to the elaborate designs and difficult precautions associated with their use, these gauges, in spite of their manifold
advantages, have been shunned as practical tools. DuMond and Pickels, ${ }^{30}$ however, constructed a gauge simple in design, and suitable for moderately good vacua of the order from $10^{-5}$ to $10^{-6} \mathrm{~mm} . \mathrm{Hg}$. As there is no special advantage in a glass gauge


Fig. 3-24. The Radiometer gauge (DuMond-Pickels).
when the rest of the vacuum system is of metal, their gauge is built of metal, thereby avoiding the glass blowing difficulties.

The vacuum gauge designed and constructed by DuMond and Pickels is illustrated in figure 3-24. The movable vane (1) of the gauge consists of a rectangular frame of $2.5-\mathrm{mil}$ sheet aluminum with the inner and the outer edges folded over for stiffness. An axle (2) of 32 -mil aluminum wire is threaded through slits (3) in
${ }^{30}$ J. W. M. DuMond and W. M. Pickels, Rev. Sci. Inst. 6, No. 11, 364 (1935).
the movable vane at the top and bottom and lightly spot-welded at one point (4) to prevent rotation. A light circular mirror (5) 1 cm . in diameter, with aluminum back support having ears for threading over the axle (2), serves as a reflector for reading the rotation of the vane by the lamp-scale method. The top end of the aluminum axle is bent into a small hook (6) around which the $\frac{1}{2}$-mil tungsten wire ( 7 ), 0.71 mg . per foot in weight, is wound about three times. The hook is then pressed by pliers to shut it tightly for keeping the wire intact without slipping off it. The wire serves as a suspension. The other end of the suspension wire, whose free length is about 5 cm ., is similarly fitted to a hook on a short length of aluminum wire. This aluminum wire is held by means of a screw (8) in a hole in the bottom of the steel taper plug (9) which projects inside the brass taper socket. The taper socket joint is sealed by means of white lead lapping. The ultimate tightness may be insured with a little Apiezon wax pressed in around the top of the plug. The equilibrium position of the vane should be secured after vacuum is established, and the required final gas adjustment should be made so as not to alter or disturb the adjusted equilibrium position of the vane.

Two small loops of 32 -mil aluminum wire are adjusted to the proper alignment and supported in holes with set screws in a vertical post provided for them. It is through these loops that the axle of the vane passes without contact when the gauge is properly leveled. They prevent the vane from swinging or breaking the suspensions when the gauge is being handled.

Two brass disks (11) and (12) form the top and bottom of the gauge. They are held together before fitting the cylindrical brass envelope over the gauge constituents by two copper columns (13) screwed and soldered to the disks for securing vacuum tightness. The use of copper is advantageous because it minimizes the time required for local temperature distributions to reach thermal equilibrium. For the same reason the cylindrical envelope of the gauge is water-jacketed above and below the mirror window.

The system of heaters (14) consists of helices of 60 inches of chromel resistance wire No. 28. The helices are formed by tightly winding this wire on a $\frac{1}{4}$-inch mandrel and then expanding the coil to have satisfactory uniformity of opening between turns. They have a resistance of 25 ohms . It is necessary to adjust the system
of heaters so as to prevent the movable vane from short-circuiting it by the copper post which acts as a stop. The tops of the heater helices are held by set screws on small copper arms (15) projecting from the sides of the copper post. The lower ends of these helices are held by set screws in the electrically insulated vacuum-tight plugs (16) passing through the brass disk which forms the lower end of the gauge. The plugs are assembled and held firmly in position by means of screw nuts (17) on the inside of the vacuum container and shoulders (18) of the plug on the outside. The plugs are insulated from the wall through which they pass with mica washers and sleeves. The cavities in the bottom through which the plugs (insulated with mica washers and sleeves) pass are rendered perfectly vacuum tight by painting the joints with " glyptal" lacquer.
The cylindrical brass envelope (20)-provided with a vacuumtight glass window and water jackets-which is slipped over the entire instrument, forms the body of the gauge. It is permanently soldered to the disk-shaped bottom and top end pieces so as to keep the entire gauge perfectly vacuum tight. The vacuum system whose residual gas pressure is to be measured is joined to the gauge by means of a communicating tube. In this gauge, the arrangement of the vane and the heaters is such that the sides of the vane facing the heaters are repelled from the heaters so that the suspended vane rotates about a vertical axis in the presence of residual gases at low pressure. The amount of rotation is measured by the lamp-and-scale method.

The helical heaters in the gauge are supplied the required heating current by means of a small " mouse power" transformer with its primary directly connected to the 110 volt a.c. mains. The two taps on its secondary supply 44.1 milliamperes and 17.8 milliamperes through the 51.2 ohms resistance to the two heater coils in series, the voltage being 2.25 volts and 0.91 volt and the wattage input 0.0993 and 0.0162 watt respectively. The temperature of the heaters is estimated roughly as $52^{\circ} \mathrm{C}$. and $8.5^{\circ} \mathrm{C}$. at these two connections. With this arrangement and by means of these two different power inputs, two convenient scales of pressure for the gauge are obtained.
This gauge, like every form of the Knudsen gauge, has several advantages. Its construction is much simpler than that of the
original Knudsen absolute gauge or similar gauges subsequently constructed by others for research. It is designed as a practical tool for measuring low pressures. For ready and direct pressure measurement the gauge is calibrated by reading the rotation of the vane at different pressure readings by a suitably sensitive and precise McLeod gauge and drawing a curve of gauge rotation against pressure. On the high-sensitivity scale of this gauge, 1 cm . of rotation corresponds to $10^{-5} \mathrm{~mm} . \mathrm{Hg}$ while on the lowsensitivity scale 1 cm . corresponds to $10^{-4} \mathrm{~mm}$. Hg. The torsional motion can be read to an accuracy of about 1 mm . The gauge can be actually used for measuring low pressures ranging from $10^{-4} \mathrm{~mm}$. to $10^{-6} \mathrm{~mm} . \mathrm{Hg}$.

This gauge has the disadvantage that it must be calibrated against a gauge whose calibration is known. In the absence of the provision for outgassing the instrument by heat treatment, gases liberated from the large metal surfaces, especially in the pressure region of $10^{-6} \mathrm{~mm} . \mathrm{Hg}$, may cause a good deal of trouble in the measurement of pressures.

3-26. Radiometer-Type Vacuum Gauge (Hughes).-Among the radiometer gauges, the vacuum gauge constructed by DumondPickels was the first to be designed as a working tool for measuring pressures. It is simple and rugged, though not very easy to construct. As this gauge is made entirely of metal and is not suitable for heat treatment for getting rid of the surface and occluded gases, low pressure measurements at and below $10^{-6} \mathrm{~mm} . \mathrm{Hg}$ cannot be considered trustworthy. A gauge which is simple in design, easy to construct, and easily lends itself to heat treatment for outgassing, and which is fairly reliable as a working tool for measurement of low pressures, has been designed and constructed by Hughes. ${ }^{31}$

This gauge, shown in figure $3-25$, is made from a pyrex tube, 2.5 cm . in diameter and 15 cm . long. The heater, a thin strip of platinum foil, 10 cm . long, 1.3 cm . wide, and 0.0001 cm . ( 0.4 mil) thick, is mounted between two 50 -mil tungsten leads. The ends of the platinum strip are spot-welded to small pieces of steel which in turn are spot-welded to the tungsten leads sealed through the glass wall of the tube. The amount of metal is kept small in order to minimize the heat capacity, so that the heater quickly comes to temperature equilibrium after a change in the heating current.

[^30]A strip of aluminum leaf 12 cm . long, 0.4 cm . wide, and 0.00005 cm . ( 0.2 mil ) thick, is suspended from a small nickel plate which is spot-welded to a $50-\mathrm{mil}$ tungsten lead sealed through the bottom wall of the ground-glass joint fitted to the main tube. The top end of the aluminum leaf is attached to the nickel plate and held in position by means of a spring. The ground-glass joint which


Fig. 3-25. closely fits the tube is sealed on the outside by Shell wax or by Apiezon grease whose vapor pressure at normal temperature is very low. The aluminum leaf is connected electrically to the heater to prevent the occurrence of any electrostatic effects which would cause an undesirable deflection of the leaf.

The temperature of the heater is raised by the heating current, which is provided by a storage battery and measured by an ammeter. The gas molecules at low pressure proceeding from the heater and impinging on the side of the leaf facing the heater impart more momentum to it than those impinging on the side facing the cooler region. Hence the suspended leaf in a gas at low pressure experiences a resultant force which pushes it away from the heater platinum strip. The consequent deflection of the leaf is observed through a suitable microscope focused on the top of the free end of the leaf, and is measured with the eyepiece scale. A sensitivity of the order of one eyepiece-scale division per $10^{-6} \mathrm{~mm}$. pressure is easily obtained, and it can be altered readily by merely altering the temperature of the heater so that the full scale, comprising 100 divisions, corresponds to $10^{-4}, 10^{-3}$, or $10^{-2} \mathrm{~mm}$. The sensitivity for various heating currents is given in Table 3-3.

This gauge, obviously, is not absolute, in the sense that it cannot be calibrated from its own dimensions. It must be calibrated either directly with a sensitive McLeod gauge or, at comparatively
low pressures, by means of a sensitive McLeod gauge in conjunction with the flow-tube method or with the use of a pressurereducing device. If the gauge is not mounted properly, vibrations of the aluminum leaf are easily set up and are apt to persist for an appreciable time at low pressure. This difficulty can be surmounted by firmly mounting the gauge on a stable and rigid stand and taking care not to jolt it.

Table 3-3

| Heating current <br> (amps.) | 1 scale division equals | $10^{-6} \mathrm{~mm}$. pressure |
| :---: | :---: | :--- |
| equals |  |  |$|$| 0.2 | $304 \times 10^{-7} \mathrm{~mm}$. |
| :---: | :---: |
| 0.5 | 46.5 |
| 1.0 | 12.4 |
| 1.5 | 6.5 |
| 2.0 | 137 |
| 2.5 | 3.16 |

3-27. Radiometer-Type Vacuum Gauge (Lockenvitz).-Of the gauges which utilize the principle of radiometric action, the two gauges (the DuMond and Pickels and the Hughes) are constructed for use as practical tools for low-pressure measurement rather than as objects of a research problem as were the original model of Knudsen and other early models. These two gauges, however, have the disadvantage that their pressure readings are not absolute, as they must be calibrated against a gauge whose calibration is known. The Hughes gauge is simpler to construct than that of DuMond and Pickels. The Hughes gauge can be outgassed, which is a distinct advantage in a glass system. A new radiometer-type vacuum gauge, which is simple in construction and which gives absolute pressure measurement because the gauge is calibrated directly from its own dimensions, and for which the temperature of the moving system does not matter, has been designed and constructed by Lockenvitz. ${ }^{32}$

This radiometer-type vacuum gauge is shown in figure 3-26. The body of the gauge is made of duralumin. Two plates which are machined out of copper are sealed to the body of the gauge by means of lead washers. Steam is passed through one plate to keep
${ }^{82}$ A. E. Lockenvitz, Rev. Sci. Inst. 9, No. 12, 417 (1938).
it at a higher temperature and cold running water through the other so as to keep it at a uniformly lower temperature. Consequently they serve as the hot- and the cold-plate systems of the gauge. Thermometers are inserted in the steam and water chambers of these plates to determine their temperatures. Glass


Fig. 3-26
windows for the observation of the deflection of the leaf are inserted and sealed in with Apiezon $W$ wax. An aluminum leaf 0.01 mm . thick is hung from a fine tungsten wire 0.025 mm . in diameter by folding the top edge of the leaf over by about 0.5 mm . so that the distance between the hot plate and the leaf and that between the leaf and the cold plate are small compared with the mean free path. A microscope, fitted to the body of the gauge, is focused on one bottom corner of the aluminum leaf so that a deflection of 0.005 mm . can be easily read on the scale in the micrometer eyepiece.

This gauge is absolute in the sense that it can be calibrated from the dimensions of the gauge itself. As the molecules impinging
the surface of the leaf facing the hot plate impart more momentum to it than the molecules striking it on the side facing the cold plate, the leaf will experience a resultant force of deflection from the hot plate toward the cold plate. If the leaf be thin, swinging freely from its upper edge, the force $R$ necessary to deflect the bottom of the leaf a distance $x$, small compared to the length $l$ of the leaf, is given by the equation:

$$
\begin{equation*}
R=W x / l \quad \text { or } \quad R=\operatorname{lbtdg}(x / l) \tag{3-20}
\end{equation*}
$$

where $W$ is the weight of the leaf and $l, b, t, d$ are the length, breadth, thickness, and density respectively of the leaf and $g$ is the acceleration due to gravity. The pressure $p$ of the residual gas between the two plates is given by

$$
\begin{equation*}
p=2 \frac{x t d g \sqrt{T}}{l \sqrt{T_{2}-T_{1}}} \tag{3-21}
\end{equation*}
$$

where $T, T_{1}, T_{2}$ are the absolute temperatures respectively of the residual gas in the gas chamber, and in the cold and the hot plates.

With the set-up described, the lower limit of this gauge is nearly $7.5 \times 10^{-6} \mathrm{~mm} . \mathrm{Hg}$. It could, however, easily be extended to about $5 \times 10^{-7} \mathrm{~mm} . \mathrm{Hg}$ by using a thinner or a longer leaf or a thinner and longer leaf. When the gauge limit is to be extended to $5 \times 10^{-7} \mathrm{~mm} . \mathrm{Hg}$, it is necessary to construct the gauge of glass, for in this range of pressure the gases given off by the large metal surfaces are troublesome.

3-28. Gold-Leaf Radiometer Gauge.-It is not easy either to construct or to use radiometer gauges with torsion fibers. The torsion control of the deflection of the vane is rather troublesome because of its slow damping, particularly at very low pressures and also because of the relatively large moment of inertia of the suspended vane. Usually a magnetic damping device is used, but this leads to complications and to a drifting zero. These gauges are susceptible to tremor even with suitable damping devices, and for this reason it is difficult to use them with a molecular pump.

To eliminate these disadvantages of the radiometer gauges with torsion fibers, alternative forms of the instrument have been designed. Among these, the Knudsen gold- or aluminum-leaf
radiometer gauge was originally designed for determining the molecular weight of small quantities of gas. This form of gauge, in which the moving system is a thin gold or aluminum leaf, like the leaf of an electroscope, damps down readily without the aid of any external device even at very low pressures, on account of the small inertia of the leaf. This instrument, illustrated in figure 3-27, consists of a water-jacketed glass tube in which a thick copper cylindrical tube is firmly held by hooked springs at itslower and upper parts. The copper tube is split right down the middle as shown. A small bar is soldered to the upper part, nearly at the top of the copper tube, from which hangs a very thin gold or aluminum leaf 10 cm . long. A small window is cut in the lower part of the copper tube, through which the lower end of the gold or aluminum leaf is viewed with a microscope. The jacketed glass tube is silvered on the inner surface, except directly opposite the window through which the leaf is viewed, in order to cut down thermal exchanges. The temperature of the walls of the glass tube can be varied by passing hot and cold water at temperatures equidistant from the normal temperature through the jacket so that the temperature of the copper tube remains unchanged. The repulsion of the leaf from the hot silvered wall is observed through the observation window with a telescope in order to take a series of readings for the determination of pressure. It is essential to insure that the temperature of the copper tube remains constant throughout a reading in order to obtain a precise value of the pressure.

The leaf of this instrument, unlike the suspended vane of the radiometer gauge with torsion fiber, is heavily damped and has
little moment of inertia. It is not sensitive to vibration. This arrangement, however, has not come into extensive use because of the uncertainty of the temperature of the leaf and its incapability of being used as an absolute manometer. But when the instrument is calibrated over the whole of its range by comparison, it can be used with advantage.

3-29. "Absoluteness" of Radiometer Gauges.-It has been pointed out that there are two types of radiometer gauges, one with a torsion arrangement and the other with a gold or aluminum leaf. The manometers of the latter type are not absolute because the temperature of the deflecting system, which is somewhere between that of the enclosure and the heated plate, cannot be known and therefore will remain uncertain. In the gauges of the torsion-arrangement type, the thermal capacity of the vanes being sufficiently large, the temperature of the suspended system remains practically unchanged and is therefore equal to that of the enclosure even when the fixed system is heated for a few seconds in order to maintain small temperature differences between the fixed and the suspended systems. Inasmuch as conduction and convection at the pressures of high vacua are almost negligible for small temperature differences, the radiated heat is likewise inappreciable. The temperature of the gold leaf, however, cannot be taken as unchanged and equal to that of the enclosure because of its small thermal capacity.
In the torsion-arrangement apparatus, the temperature of the surfaces of both the fixed and the oscillating systems can be measured as in Knudsen's original model. Manometers of this type, wherein the temperature of the vanes can be actually measured, are looked upon as "absolute," provided the distance between the fixed and the moving systems is small compared with the mean free path of gas molecules (not greater than $\frac{1}{260}$ of the mean free path). It is difficult to realize this very small distance between the fixed and the moving systems. In consideration of this difficulty, if the essential condition be not satisfied, as in the latter models wherein the distance between the fixed and the moving systems is about a millimeter or more, the gauges cannot be deemed to be absolute even with knowledge of the temperature of the vanes, because in such cases the nature of the gas as well as the distance between the fixed and the moving systems-as was
found by West ${ }^{33}$ and is obvious from the graph of his results (figure 3-28)-considerably influence the radiometric forces. They must, therefore, be calibrated empirically, and the calibration will do only for the gas for which it is made except for very low pressures.


Fig. 3-28.
3-30. Limits of Working Range and Calibration.-The radiometer gauges may be conveniently used for measuring even the lowest attainable pressures. At the range of high pressures, the mean free path of gas molecules is comparatively much smaller than that of the gas molecules at lower pressures. Usually the distance between the surfaces of the fixed and the moving systems of these gauges is small compared with the mean free path of the gas molecules at the pressures of high vacua. When the mean free path is no longer large compared with the distance between the surfaces of the fixed and the moving systems of any particular gauge, the upper limit of its working range is naturally reached. Hence the upper limit of any particular gauge depends on the distance between the opposite surfaces and is always lower than $10^{-8}$

[^31]$\mathrm{mm} . \mathrm{Hg}$. These gauges are satisfactory for the measurement of pressures lower than this limit. Pressures above this limit, especially of the permanent gases, may be measured with the McLeod gauge. Lower vapor tensions such as that of mercury, which cannot be measured with a McLeod gauge, can be measured with the radiometer gauges.
It is difficult to construct a truly absolute radiometer gauge such as Knudsen's original model. To avoid this difficulty, present models of radiometer gauges are constructed without realizing the


Fig. 3-29.
conditions necessary for the construction of an absolute gauge. Such gauges, in spite of certain restrictions, are, as indicated, useful. They must, however, be calibrated before they are used for pressure measurements. The calibration of these gauges can be effected by using the pressure-reducing device, originally designed by Knudsen. ${ }^{34}$ This consists of a number of bulbs placed in series and joined together by a flow tube provided with suitable taps as shown in figure 3-29. Before the adjustment, the volume of each section of the apparatus is actually determined by calibrating the small bulbs, the connecting tube, and the tap passages with mercury and the large bulbs with water. One end of the device is joined to a high-vacuum pump and the McLeod gauge; the other end is joined to the radiometer gauge, which is to be calibrated, through a liquid air trap. The entire system is evacuated as completely as possible. Then some permanent gas under known pressure is introduced only into the small bulb which is adjacent to the McLeod gauge and the pump and is remote from the radiometer gauge. The tap that separates this bulb

86 M. Knudsen, Ann. d. Phys. 444, 581 (1914).
from the pump is closed and the contents of this bulb are shared with its adjacent large bulb and the middle small bulb. This middle one is then isolated and its acquired pressure is then shared with the second large bulb and the third small bulb. Finally the latter one is isolated and the gas in it is allowed to expand into the radiometer gauge. Now the gas pressure is calculated from Boyle's law.

This calibration of the radiometer gauge can be applied to the gas used in calibration only for the higher pressures of its working range. These gauges must have a separate calibration for almost every individual gas.

## Section IV. High-Vacuum Gauges Depending on Gaseous Thermal Conductivity

3-31. Introduction.-It has been shown already in chapter I, section IV, 1-21, that when a gas is under normal pressure, the coefficient of gaseous thermal conductivity $K$ is a function of the product of $\eta$, the coefficient of viscosity, and $C_{v}$, the specific heat of the gas at constant volume, which may be expressed:

$$
K=\epsilon \eta C_{v}
$$

where $\epsilon$ is the value of the transport of translational energy in terms of the value of the transport of other forms of energy as a unit. As the coefficient of viscosity is independent of pressure and $C_{v}$ is a constant, the coefficient of thermal conductivity is independent of pressure. To consider this in concrete form, let there be a bulb, containing a gas, with a hot filament in the middle. If the containing gas be under normal atmospheric pressure, the thermal conductivity of the gas from the hot filament to the walls of the bulb will be, as indicated, independent of pressure. But the condition is quite different if the pressure is in the range of high vacua.

When the pressure of the gas is reduced, the number of gas molecules and that of the collisions between them per second become correspondingly small but their mean free paths become proportionately large. If the gas pressure is reduced to such an extent that the mean free path of the gas molecules becomes large compared with the size of the bulb and the actual free path of each
molecule is limited only by the dimensions of the bulb, then the influence of viscous forces is naturally altered. Hence many of the gas molecules pass diectly from the hot filament to the walls of the bulb without intermolecular collisions. In this case the heat from the filament is conducted by the gas molecules directly to the walls of the bulb and now the thermal conductivity of the gas is a function of pressure. In other words, in the range of the pressures of high vacua, when the influence of viscous forces is altered, the gaseous thermal conductivity varies with the variation of pressure, inasmuch as the nun.ber of gas molecules that directly transport heat from the hot filarent to the walls of the bulb is proportional to the pressure.
The phenomenon of the variation of thermal conductivity of gases at low pressures with the variation of pressures may be utilized as a means for the measurement of the pressures of high vacua. Now in the example given, to maintain the filament at a constant temperature higher than that of the walls of the bulb, a certain amount of energy equal to that conducted by the gas must be supplied to the filament. So a variation of the gaseous thermal conductivity can be measured by reading the variation of this quantity of energy put into the filament required to keep its temperature constant. Since the thermal conductivity of a gas is a function of the pressure, a change in the pressure can be determined from the measurement of the amount of energy put into the filament. These, therefore, lead to the construction of another class of manometers.
3-32A. Pirani-Hale Gauge.-Pirani ${ }^{35}$ realized this principle in his design of a pressure gauge. His gauge, using the rate at which heat energy is transported from a hot filament by the surrounding gas molecules as a measure of gas pressure, was the first of its kind. $\mathrm{Hale}^{36}$ subsequently perfected the original design of Pirani. His form of the gauge is very similar to an incandescent lamp in design and construction. In his actual instrument (figure 3-30), the filament was of pure platinum wire 0.028 mm . in diameter and 45 cm . long, having a temperature coefficient of 0.00376 per degree, which is large enough to have the filament sensitive to temperature. The wire was wound on a framework in such a way that the fila-

[^32]ment would remain tight so that the distance between it and the walls of the glass bulb would be constant. To secure constant thermal contact between the filament and its several supports, the filament was arc-welded to short pieces of platinum wire 0.52 mm . in diameter which were fused into small glass rods, branched


Fig. 3-30. at the lower and upper ends of the central main glass rod. The arrangement was such that there was minimum heat loss through the filament supports.

This entire framework was kept in a glass bulb 11.4 cm . long and 3.2 cm . in diameter, and the topmost end of the central rod of the framework was fused to the sealed upper end of the bulb, so that the axis of the central main rod would coincide with the axial line of the bulb. A tube, containing two insulated electric wires, was fused outside to the sealed top of the bulb, and the wires of platinum, 0.31 mm . in diameter, passing through the sealed top wall of the bulb, were connected to the terminals of the filament by spot-welding. This tube, containing these electric wires, was packed with cotton wool to keep water from condensing there. Another tube of suitable diameter, which was joined to the upper part of the bulb, connected the vacuum to be measured with the gauge. This instrument was mounted in an enclosure, which was kept at a constant temperature of $0^{\circ} \mathrm{C}$., so as to keep the bulb from being exposed to variations of temperature from outside. The filament was maintained at temperatures between $100^{\circ} \mathrm{C}$. and $125^{\circ} \mathrm{C}$.

3-32B. Necessity for Calibration.-In this gauge, as well as in every one of the forms of this type, even at low pressures, the thermal energy transfer, besides being the function of the number of the gas molecules, as pointed out already, depends also on the nature of impact and rebound which vary with the nature of the gas
and that of the surface of the filament. Knudsen's accommodation coefficient $\alpha$-the ratio of the heat which is actually transferred to the gas from the filament to the amount which would pass if the molecules coming into contact with the filament came into temperature equilibrium with it-has been found to vary not only with the nature of the gas and that of the surface of the filament but also with the temperature. Langmuir considers that a layer of gas molecules always sticks to the surface of the filament according to the nature of the surface, and that the molecules rebound from this layer. Because of the dependence of the thermal energy transfer on the nature of impact and rebound, the PiraniHale gauge, or any other form whose function is based on gaseous thermal conductivity, can never be used as an absolute manometer. It may be used only when it is calibrated; and the calibration of this gauge is effected by direct comparison or by indirect comparison through the Knudsen pressure-reducing device with an absolute gauge. After calibration this instrument is very useful for measuring pressures of condensable gases and vapors for which a McLeod gauge cannot be used.

3-32C. Methods of Manipulation.-To prepare the Pirani-Hale gauge for measurements, it is necessary to connect it to a Wheatstone bridge and to determine the thermal energy loss of the filament either by keeping the temperature of the filament-and, therefore, the difference of potential between the terminals of the filament-constant and measuring the change in the heating current as the pressure varies, or by keeping the heating energy constant and measuring the variation of the resistance of the filament and so the change in its temperature as the pressure alters. Hale applied the latter method to the measurement of pressures of high vacua. These gauges must be calibrated and the calibration, in fact, is strictly applicable only under the same conditions as those under which the calibration has been effected. Therefore the procedure of measuring the potential which must be applied to the Wheatstone bridge to keep the resistance of the filament-and thus its temperature-constant as the pressure alters, should be preferable, as shown by Campbell. ${ }^{37}$ In this case, the calibration curves for different gases can be very simply correlated.
${ }^{27}$ N. R. Campbell, Proc. Phys. Soc, 33, 287-298 (1921).

3-32D. Arrangements for Manipulation of Pirani-Hale Gauge. - In Hale's procedure, the gauge is placed in one arm of the Wheatstone bridge, one of the adjacent arms being a compensator and the rest of the arms being composed of resistances with very low temperature coefficients, as illustrated in figure 3-31. $R_{1}$


Fia. 3-31.
which is adjacent to the manometer is a variable Dekadenstöpfel (decade plug containing) resistance of 10,000 ohms and $R_{2}$ is an invariable manganin wire resistance of 925.6 ohms. In this arrangement a milli-ammeter is used, connected in series with the battery and the rehostat $R_{3}$. While this rheostat $R_{3}$, which is in series with the ammeter, is varied so as to keep constant the current applied to the bridge circuit, readings are taken from the variable bridge resistance $R_{1}$ which is changed according to the variation of pressure in order to keep the bridge balanced. In the course of its manipulation the gauge and the compensator are
mounted in a constant-temperature enclosure so as to maintain them at a constant outside temperature.

In Campbell's method the arrangement shown in figure 3-32 is such that the filament of the gauge forms one of the arms of the Wheatstone bridge, while the three other arms constitute resistances of manganin with very low temperature coefficients. One of the arms, adjacent to the manometer, is composed of a variable resistance $R_{1}$, the other two being invariable. This variable bridge resistance $R_{1}$ is adjusted so that the galvanometer in the center of the Wheatstone circuit will have no deflection when the resistance of the filament corresponds to any definite chosen filament temperature (of say $100^{\circ} \mathrm{C}$.). A sensitive and precise voltmeter $V$ is connected to the terminals of the Wheatstone bridge in conjunction with the battery circuit. While the required current is applied to the bridge circuit, the bridge voltage which corresponds to the gas


Fig. 3-32. pressure is read from the voltmeter $V$. The bridge potential which is being measured by the voltmeter varies with the variation of pressure.

During the manipulation of the gauge, there are thermal energy losses by the filament which are due to radiation, to conduction along the supports, and to convection or conduction in the gas which may be taken to be nearly proportional to the difference of temperature between the filament and the surrounding walls of the bulb, with its other contents. Let the loss due to radiation and conduction along the supports, which is independent of the pressure of the gas, be $r d$, and that due to the gas $c f(p) d$, where $p$ is the pressure. Since the resistance of the bridge is always the same, the thermal energy supplied to the filament must be proportional to the square of the potential $V$ applied to the bridge. Let this be $\alpha V^{2}$. Then we have

$$
\begin{equation*}
d r \cdot d c f(p)=\alpha V^{2} \tag{3-22}
\end{equation*}
$$

and if $V_{0}$ is the potential required for the balance when $p=0$

$$
\begin{equation*}
d r=\alpha V_{0}^{2} \quad \text { or } \quad d=\frac{\alpha V_{0}^{2}}{r}, \tag{3-23}
\end{equation*}
$$

giving

$$
\begin{equation*}
\left(\frac{\alpha V_{0}^{2}}{r} \cdot r\right)+\left(\frac{\alpha V_{0}^{2}}{r} \cdot c f(p)\right)=\alpha V^{2}, \tag{3-24}
\end{equation*}
$$

which may be rewritten

$$
\begin{equation*}
\alpha V_{0}^{2}+\frac{\alpha V_{0}^{2}}{r} \cdot c f(p)=\alpha V^{2} \tag{3-25}
\end{equation*}
$$

and, on simplifying, finally giving,

$$
\begin{equation*}
\frac{V^{2}-V_{0}^{2}}{V_{0}^{2}}=\frac{c}{r} \cdot f(p) \tag{3-26}
\end{equation*}
$$

From his investigations, Campbell found that $c / r$ is almost constant for considerable variations in the gauge. This coefficient does not change rapidly with the length of the filament if the loss of heat due to conduction along the supports is small. It is nearly independent of the diameter and the material (platinum or tungsten) of the filament. If the changes of the temperature of the filament and its surroundings are so small that all heat losses may be taken to be proportional to $d, c / r$ does not change with those small changes of the temperature. Within the range of all those changes, the function $\left(V^{2}-V_{0}{ }^{2}\right) / V_{0}{ }^{2}$ is independent of everything except the pressure and the nature of the gas. This function changes only with the pressure and the nature of the gas.

With Campbell's method, the calibration curve plotted is $p$, the pressure of the gas against $\left(V^{2}-V_{0}^{2}\right) / V_{0}^{2}$, where $V_{0}$ is the potential required for a balance when $p$ is the lowest attainable pressure. The chief advantage of this method of using the gauge is that $f(p)$ is approximately proportional to $p$ and the calibration curve is approximately straight. From figure $3-32 A$, which represents Campbell's calibration curves for different gases and water vapor, the initial curvature appears with CO and is more pronounced with $\mathrm{CO}_{2}$, for the McLeod gauge, as is well known, is not accurate for $\mathrm{CO}_{2}$. It is possible that some of the curvature in $\mathrm{CO}_{2}$ stems from errors in measuring the pressure. There is
also a slight deviation of the curve for water from a straight line, and the condensation of water accounts for such a deviation from a straight line at low pressure. It is obvious that for gases other than hydrogen, the calibration curves lie close together and may be taken as nearly coincident for approximate measurements.


Fig. 3-32A.

3-32E. Subsequent Models.-The influence of various construction factors upon the sensitivity of a gauge of this type was investigated by Stanley. ${ }^{38}$ In his construction he used a single wire loop of very fine platinum wire operated at temperatures below $100^{\circ} \mathrm{C}$. With this arrangement, pressures between $2 \times$ $10^{-5}$ to $4 \times 10^{-6} \mathrm{~mm} . \mathrm{Hg}$ could be measured quite satisfactorily.

A simple form of this type of the instrument whose function is based on gaseous thermal conductivity and which could give
${ }^{28}$ L. F. Stanley, Proc. Phys. Soc. 41, 194 (1929).
direct pressure readings has been developed by Thompson and Hennelly. ${ }^{39}$ The gauge and the compensator each consist of a glass tube 1 inch in diameter and approximately 3 inches long, in which four or more standard 25 -watt, 115 -volt tungsten filament coils are welded to supports, the total resistance being about 15 ohms at room temperature. The pressure-measuring device $I$ and the compensator $C$ are inserted, as shown in figure $3-33 A$, in


E
Fig. 3-33A. Wheatstone bridge connections for resistance gauge.
the two arms of a Wheatstone bridge, while the other two arms consist of two resistances $R_{1}$ and $R_{2}$, each about 14 ohms, and a resistance $R_{3}$, of about 2 ohms. The resistance $R_{3}$ can be adjusted so as to obtain zero current in the ammeter $A$. A battery supplies the constant source of potential.

Pressure measurements obtained with this arrangement are represented in figure $3-33 B$, in which the current, measured in milliamperes, is plotted against pressure read in microns $\left(10^{-3}\right.$ $\mathrm{mm} . \mathrm{Hg}$ ). Curves $A, B$, and $C$ refer to dry air at three different voltages, while $D$ and $E$ refer to hydrogen and argon respectively. It can be seen that for pressures below 40 microns the currentpressure relations are linear.
${ }^{39}$ See S. Dushman, J. Franklin Inst. 211, No. 6, 745 (1931).

In calibrating any one of the models of this type of gauge by comparing with a McLeod gauge, it is necessary to use a mercuryvapor trap cooled by liquid air. The trap is inserted in the vacuum


Cursent pressure relations for realstance gaugen
Fig. 3-33B.
line between these two gauges. The insertion of such a trap, however, would be useless if a mercury pump were used, and in this case there would be no need of eliminating the mercury vapor from the McLeod gauge. It is advisable to calibrate the gauge with Knudsen's pressure-reducing device, shown in figure 3-29.

3-32F. Working Range and Advantages.-The working range of the models of this type varies from about $10^{-1} \mathrm{~mm} . \mathrm{Hg}$ to a pressure of about $10^{-6} \mathrm{~mm} . \mathrm{Hg}$. The Pirani-Hale gauge has certain advantages. It is capable of indicating pressures not only of gases but also of vapors. It does not, however, have the advantage of greater working speed. There is practically no difference in the time of one reading between a gauge of this type and a McLeod gauge, for in the former it takes about one minute for the establishment of thermal equilibrium. This gauge, if suitably arranged and manipulated, is capable of following variations of pressure, provided that the variations are not very rapid. It lends itself to self recording and automatic devices.

3-33. Pfund Pirani-Hale and McLeod Combination Gauge.The measurement of very low pressures with an ordinary McLeod gauge is impracticable, inasmuch as the difference between the mercury levels in the open and the closed capillaries becomes so small that it admits no possibility of accurate measurement. Pfund ${ }^{40}$ extended the lower limit of a McLeod gauge. He incorporated a Pirani-Hale gauge which, in the form of a small loop of a fine tungsten wire, is sealed into the top of the closed capillary. This small filament forms one of the arms of a Wheatstone bridge. The thermal conductivity of the compressed gas in the closed capillary as a function of pressure naturally forms the means of low-pressure measurement. The cooling effect of the compressed gas on the electrical resistance of the heated filament is measured by reading the deflection of the galvanometer in the Wheatstone circuit. The instrument is calibrated for each gas separately through the use of the McLeod gauge over its normal working range. The change of pressure is proportional to the galvanometer deflection and the proportionality varies with different gases. Therefore the instrument must be calibrated for each gas separately.

With this instrument the pressure of common air was measured and the lower limit of the working range was extended to a pressure of $1.7 \times 10^{-7} \mathrm{~mm} . \mathrm{Hg}$ with the use of an ordinary galvanometer. This limit of the working range can further be extended by using a sensitive wall galvanometer.

[^33]
## Section V. High-Vacuum Gauges Babed on the Principle of Electrical Conductivity at Low Pressures

3-34. Preliminary Remarks.-When an electron current is produced at low pressures between hot filament and anode, the electrons will ionize the residual gas molecules provided $\frac{1}{2} m u^{2}>V e$, where $m$ is the mass, $u$ the velocity, $e$ the charge associated with the electron, and $V$ the ionization potential of the gas. This current of electrons from the filament ionizes the gas to an extent depending on the number of gas molecules. The positive ions produced in this way can be collected by an electrode, arranged as a collecting device, and the magnitude of the ionization current, which can be measured with sufficient precision, may therefore be used as a measure of pressure.

3-35. Ionization Gauges of Buckley and Misamichi So.Gauges depending on this principle were first studied by Buckley ${ }^{41}$ and subsequently by Misamichi So. ${ }^{42}$ Buckley's instrument had a bulb enclosing three V-shaped filaments of platinum foil, mounted side by side about 5 mm . apart and parallel to one another. One of the outer filaments was used as anode, while the other outer filament, which was oxide coated, when raised to incandescence, served as cathode, emitting thermo-electrons. The potential difference between the cathode and anode was kept well above the ionization potential of the gas. The positive ions produced were collected by the third filament and the intensity of the ionization was used as an indication of pressure. Misamichi So's gauge consisted of a bulb enclosing three V-shaped tungsten filaments mounted in parallel planes. One was raised to red heat to serve as a hot cathode, one was used as the anode for the electron current, while the third acted as a collector-electrode for the positive ions. The ion-collector electrode was maintained at a potential lower than that of the lower-potential terminal of the hot filament.

3-36A. Dushman-Found Ionization Gauge.-Dushman and Found ${ }^{43}$ have shown that the position of the collector is of importance in its affect on the sensitiveness and on the constancy of the relation between ionization current and pressure. They considered that the arrangement of the three electrodes is important

[^34]in eliminating the uncertainty in the readings which is apt to be introduced by the charging up of the walls of the bulb. They have designed a gauge of a construction for which there is a linear relation between the ionization current and the pressure. In their design, unlike in those of Buckley and Misamichi So, the electrodes are mounted concentrically to eliminate the charging


Frg. 3-34. up of the glass walls. Their gauge is, in many respects, very similar to a triode radio tube. It consists of two filament electrodes and one hollow cylindrical electrode, enclosed in a bulb 12 cm . long and about 4 cm . in diameter (see figure 3-34). The two filament electrodes are supported from the same end, and each of these has two current leads. The other electrode, supported on a two-lead stem at the upper end of the tube, has only one current lead. The bulb is provided with a suitable inlet tube for joining the gauge to a vacuum system. Of the two electrodes from the same side, one, which is the inner, is a tungsten filament of diameter 0.125 mm . wound in a double spiral of 5 turns on a $2.25-\mathrm{mm}$. mandrel, while the outer one, made of the same wire, is in the form of three turns of double spiral on a $3.65-\mathrm{mm}$. mandrel. The hollow cylindrical electrode of molybdenum fixed from the other end is about 12 mm . long and 12 mm . in diameter, and it surrounds the other two electrodes.

## 3-36B. External Collector and Internal Collector Arrangements.

 -The electrical circuits of the gauge may be set up in two different ways. In the first arrangement (figure 3-35A) the inner tungsten filament, which is heated by the current from a battery $B_{1}$ flowing through a regulating resistance $R$, serves as the hot cathode. The electron current is of the order of 0.5 to 20 milliamperes. The second filament surrounding the inner filament is the anode, and the field for the electron current, measured by the milliammeter, is produced by a second battery $B_{2}$. The potential on this filament is of the order of 125 to 250 volts. The molybdenum cylinder which functions as the collector electrode is brought to a potential below that of the negative terminus of the hot filament by the third battery $B_{3}$, which in this case is -22 volts. The positive-ion current is measured by means of a highly sensitivegalvanometer. This set-up is called the external collector arrangement.

In the second, known as the internal collector arrangement (figure $3-35 B$ ), while the outer filament and the molybdenum


Fig. 3-35A.
cylinder function as the hot cathode and the anode respectively, the inner filament serves as the collector electrode. In this case the outer filament is heated by a current from a battery $E_{1}$ flowing through a regulating resistance $R$. The anode current is produced by the battery $B_{2}$. The inner filament, which is the collector electrode, is brought to a potential below that of the negative end of the hot cathode and the ionization current is measured by a galvanometer of high sensitivity. In this arrangement, as well as in the external collector arrangement, the electron emission is controlled by the temperature of the filament.

With the external collector arrangement for moderate electron emissions, ranging from 0 to 10 milliamperes, the relation between the electron and the positive-ion currents is well-nigh linear when the anode potential is 250 volts. At high emissions, however, this relation no longer holds, and the ionization current increases at a slower rate than before. This is because the electrons that pass


Fig. 3-35B. through the anode filament and traverse the space beyond, being repelled by the collector, are drawn back to it. The emission increases with the increase of the space charge and the path of the electrons repelled by the collector electrode outside this space correspondingly decreases. In this case the gauge constant $C$ is no longer independent of the pressure and the electron emission.

In the internal collector arrangement, the relation between the electron and the ion currents is constant for electron currents up to 20 milliamperes, as the path of the electrons, being surrounded by the outer plate, is not dependent upon the current density and the anode voltage. It is not so much affected by the lack of constancy in the applied potentials. The sensitivity, which is readily controlled by the filament temperature, is inferior to that of the external collector arrangement, being as low as one-third; on the other hand, it is easier to adjust the electron current to suit the pressure to be measured.

3-36C. Method of Measurement and Calibration.-The actual determination of pressure of the gas in the tube is based on the ratio of the positive-ion current $i_{c}$ between the collector and the cathode to the electron current $e_{c}$ flowing from cathode to anode. It has been empirically found that for pressures of the range of high vacua, the positive-ion current is directly proportional to the
gaseous pressure and to the magnitude of the electron current $e_{c}$ at any given value of the anode potential. Then an expression for the pressure $p$ of the gas may be written in the form,

$$
\begin{equation*}
p=C \frac{i_{c}}{e_{\epsilon}} \tag{3-27}
\end{equation*}
$$

where $C$ is a constant, depending upon the geometrical form of the gauge, the potential of the anode, and the nature of the gas. Even for one and the same arrangement of the gauge, because $C$ varies


Fig. 3-36. Calibration of ionization gage by method of flow.
with the variation of anode potential and the nature of the gas, the ionization gauge requires different calibrations for different values of anode potential and for different gases.

Preliminary to calibration and before using the gauge for pressure measurement, it is necessary to remove the water vapor absorbed on the glass walls and the gases occluded in the metal constituents of the gauge. The water vapor is removed by heating the gauge in an oven to a temperature of $360^{\circ} \mathrm{C}$. for at least one hour. The molybdenum cylinder, the spirals, and the leads supporting them are thoroughly outgassed by electric bombardment. In each case a suitable anode potential is employed and the amount of heat developed depends on the emission from the filament.

The calibration of an ionization gauge at ordinary low pressures may be done by comparing it with a sensitive McLeod gauge. To obtain a calibration of the gauge at pressures lower than those measurable on a McLeod gauge, Dushman and Found devised the flow-tube method based on Knudsen's law of molecular streaming, already dealt with in chapter 1, section VI, par. 1-27A. This device, shown in figure 3-36, consists of two large bulbs $A$ and $B$,
each of approximately the same volume, connected by a fine capillary tube $C, 127.3 \mathrm{~cm}$. long with a diameter of 0.068 cm . A McLeod gauge is connected to the bulb $A$ at $M$ and an ionization gauge $G$ to the bulb $B$.
These bulbs, $A$ and $B$, are directly connected at $P_{1}$ and $P_{2}$ through mercury traps $S_{1}$ and $S_{3}$ to a high-vacuum pump. A mercury trap $S_{2}$ followed by a liquid-air trap $L_{1}$ are inserted between the bulb $A$ and the capillary tube. The liquid-air trap $L_{1}$ condenses the mercury vapor and prevents its flow through the capillary tube. The other end of the capillary is joined to the bulb $B$ through a liquid-air trap $L_{2}$, which prevents the mercury vapor and other volatile gases from entering the gauge. The whole system is exhausted to a high degree and the bulb $B$ and the ionization gauge are thoroughly outgassed until the ionization current decreases to a very small value, and remains stationary when the gauge and the bulb $B$ are closed off by mercury traps $S_{2}$ and $S_{3}$ from the rest of the system. After the bulb $A$ is closed off from the rest of the system, it is washed out with argon which is let in through $I$. When $A$ is at a pressure of from 10 to 20 dynes/ $\mathrm{cm} .^{2}$ of argon, the trap $S_{1}$ is closed. If the trap $S_{2}$ between $A$ and the capillary tube be opened, the argon flows into the bulb $B$ and ionization gauge $G$. The rate of increase of pressure can be calculated from Knudsen's equation 1-120 which may be rewritten in the form:

$$
Q=V \frac{d p}{d t}=\frac{P_{A}-P_{B}}{W \sqrt{\rho_{1}}},
$$

where $Q$ is the quantity of gas flowing through the capillary per second, $V$ the volume of the bulb, $d p / d t$ the rate of increase of pressure in $B, P_{A}$ the pressure in the bulb $A$ read on a McLeod gauge, $P_{B}$ the pressure in bulb $B$ and the ionization gauge, $\rho_{1}$ the density of the gas at unit pressure and the temperature of the capillary, and $W$ the "resistance" of the capillary which is given by equation 1-123 which may be rewritten,

$$
W=\frac{2.394 L}{D^{3}}+\frac{3.192}{D^{\prime 2}} .
$$

In this way Dushman and Found have calibrated the gauge at low pressures.

The voltages depend on the form and construction of the gauge as well as on the set-up. In the Dushman and Found gauge with external collector arrangement the anode potential was 250 volts and the collector potential -22 volts. With these potentials the Dushman and Found ionization manometer, after preliminary treatment for outgassing, was calibrated for argon at three different electron emissions, as shown in figure 3-37, where the ionization current is plotted against the gaseous pressure in dynes


Fig. 3-37.
per square centimeter. The need of this sort of calibration is, in fact, its disadvantage. If the gauge, however, be once calibrated for different anode potentials with different gases, it can be used with advantage to measure low pressures. For measuring the lowest attainable pressures with precision, the sensitivity of this kind of gauge can be increased by increasing the yield of positive ions.

3-37A. Jaycox-Weinhart Ionization Manometer.-For convenience of measuring any given pressure by means of an ionization gauge, it is desirable that the positive-ion current be as large as possible. The positive-ion yield may be increased by increasing the magnitude of the electron current. The increase of the electron current, however, is limited by the fact that high electron current may, if suitable arrangement is not made, be dissipated and heat up the part enough to cause the evolution of gas from the heated part and thus disturb the pressure measurements.

The positive-ion yield may also be increased by increasing the path that an electron must traverse before it can reach the anode. By this procedure the number of collisions between gas molecules and electrons is increased, creating a greater yield of positive ions. The increase in length of the path may be accomplished by increasing the distance between the cathode and the anode or, preferably, by reducing the size of the anode to such an extent that most of the electrons reach the anode only after gyrating many times around it. This procedure also has its limitation, inasmuch as the swinging of electrons back and forth between the tube elements gives rise to a condition favorable to the production of Barkhausen oscillations-oscillations in the potential of the tube elements. The presence of these causes spurious pressure indications.

Another means of increasing the positive-ion yield for increasing the sensitivity of the gauge for a given electron current at a given pressure is that of increasing the potential of the anode. This procedure also, with due care, is advantageous. Of course for the use of higher potential it is necessary that the positive-ion collector insulation must be correspondingly better.

In order to obtain greater sensitivity by increasing the positiveion yield in the different methods outlined, Jaycox and Weinhart ${ }^{44}$ constructed a gauge different from that of Dushman and Found. In the construction of this gauge particular attention is paid to the positive-ion collector insulation. Two thoriated filaments are used, one for bombarding the (grid) anode and the other for operating the gauge. Barkhausen oscillations are eliminated by enlarging the size and the number of wires constituting the anode.

This gauge, illustrated in figure $3-38 B, C, D$, and $E$, is similar to a three-element thermionic bulb. It consists of a filament, grid, plate, supporting stem, and bulb. The filament of thoriated tungsten wire which serves as a cathode is mounted in the form of an " $M$ " with three connections to it, one at each end and one at the center. The anode collects the electrons emitted from the cathode, and the arrangement is such that the emitted electrons gyrate about the thin wires of the anode before being collected upon it. The positive-ion collector consists of two electrically connected parallel nickel plates, one on either side of the

[^35]filament-grid structure. With this arrangement the positive-ion collector is maintained at a potential of from 6 to 9 volts negative to the cathode. Good insulation of the positive-ion collector is insured by fixing glass collars on the supporting arbor. The leadin wire is brought out through a separate ear of the glass bulb.


Fig. 3-38B, C, D, and E. Working drawing of manometer.
3-37B. Measurement and Calibration.-The electrical circuit in which this manometer is used, shown in figure 3-39A, is to some extent similar to the circuit used in the operation of the DushmanFound gauge with the external collector arrangement. In this circuit the negative end of the cathode is the common point from which all potentials are measured. Another interesting circuit in which this gauge will operate directly from a $110-125$-volt d.c. outlet is shown in figure $3-39 B$. The gauge operates continuously and automatically, once the value of the electron current has been adjusted by means of the relay Bu . With the use of 120 volts the anode potential is set at about $105-110$ volts and that of the positive-ion collector at -10 to -6 volts with respect to the negative end of the cathode. If the electron current is maintained
at 20 milliamperes, the pressure in millimeters of mercury is equal to five times the positive-ion current $\left(p=5 i_{c}\right.$, where $i_{c}$ is in amperes).


Fra. 3-39A. General circuit for the operation of the manometer.


Fig. 3-39B.
The relation between pressure and positive-ion current, when the anode potential is 120 volts and the collector potential -6 volts with an electron emission of 20 milliamperes, is shown in figure

3-40. The curves $A$ and $B$ were taken using the entire filament and half of the filament respectively as cathode. In either case a linear relation exists which is convenient for making measurements.

This gauge can be used with advantage to measure pressures of the order of $10^{-9} \mathrm{~mm} . \mathrm{Hg}$. The zero of this kind of manometer is


Fig. 3-40.
well defined in that it indicates the presence of any gas, and this is its advantage over the Pirani-Hale gauge. Gases other than those of the inert group may possibly interact with the hot filament and thus vitiate pressure measurements.

## Section VI. High-Vacuum Gauges Depending on the Viscosity of Gases

3-38. Theoretical Introduction.-At normal pressure, temperature remaining constant, the viscosity of a gas is, as expected from the viscosity expression 1-72b (see chapter 1, section IV, par. 1-20), independent of density and therefore of pressure. If, however, the gaseous pressure is so low that the collision frequency becomes vanishingly small and the mean free path, $\lambda$, large compared with the dimensions of the containing system under consideration, the effects of the individual molecules being additive, the viscosity is proportional to the density and therefore to the pressure. A meas-
ure of the variation of viscosity of a gas at low pressures can, therefore, be used as a measure of pressure. A device which utilizes the measure of the variation of the viscosity of a gas at low pressure as the measure of pressure is known as a viscosity gauge.

A measurement of viscous forces is carried out by measuring the damping between an oscillating disk on a torsion fiber and a fixed parallel disk. The dragging action can also be measured by rotating the disk which was initially stationary and measuring the angle of twist of the fiber support of the other disk. While Kundt and Warburg ${ }^{45}$ utilized the former for the measurement of viscous forces, Langmuir ${ }^{46}$ proposed the use of the latter for low-pressure measurement, and Dushman ${ }^{47}$ designed and constructed a gauge based on this principle. The operation of this gauge, the principle of measurement, and the method of calculation of pressures by means of this gauge may be deduced from the following consideration of the kinetic theory of gases.

If there be two parallel plane surfaces at a distance $d$ apart and one of them moves in its plane in a given direction with velocity $u$ relative to the other, the rate of transference of momentum across unit area to the latter at comparatively higher pressures, where the mean free path is considerably smaller than the distance $d$, is given by the equation,

$$
\begin{equation*}
B=\frac{\eta u}{d} \tag{3-28}
\end{equation*}
$$

where $\eta$ denotes the coefficient of viscosity. In this case $B$, the tangential force per unit area of the stationary surface, is independent of pressure.

At very low pressures where the mean free path is comparable with or even larger than the distance $d$, the gas molecules slip over the planes and the amount of slip is inversely proportional to pressure. With these observations and from hydrodynamical considerations, Kundt and Warburg showed that the tangential force $B$ is given by

$$
\begin{equation*}
B=\frac{\eta u}{\alpha+2 \delta} \tag{3-29}
\end{equation*}
$$

[^36]where $\delta$ is the coefficient of slip. Since $\delta$ may be expressed in terms of the mean free path $\lambda$ by the relation $\delta=\alpha \lambda, \alpha$ being the coefficient depending on the nature of gas and that of the planes of contact, and since at low pressures $\delta$ is large compared with d, expression 3-29 may be reduced to
\[

$$
\begin{equation*}
B=\frac{\eta u}{2 \alpha \lambda} \tag{3-30}
\end{equation*}
$$

\]

By the viscosity expression $1-72 a$, the term, $\eta / \lambda$, of equation 3-30 can be given in terms of the density $\rho$ and the mean molecular velocity $v_{m}$, and hence we have

$$
\begin{equation*}
\frac{\eta}{\lambda}=\frac{0.499 \rho \lambda v_{m}}{\lambda}=0.499 \rho v_{m} \tag{3-31a}
\end{equation*}
$$

which, when expressed in terms of the molecular weight $M, p$ the pressure, and $T$ the absolute temperature of the gas, will be

$$
\begin{equation*}
0.499 \frac{M p}{\breve{R} T} \sqrt{\frac{8 \breve{R} T}{\pi M}} \text { or } c \frac{M p}{\widetilde{R} T} \sqrt{\frac{8 \breve{R} T}{\pi M}}, \tag{3-31b}
\end{equation*}
$$

$c$ being the numerical coefficient 0.499 .
Therefore equation 3-30 reduces to

$$
\begin{equation*}
B=\frac{c}{\alpha} \sqrt{\frac{2}{\pi}} p u \sqrt{\frac{M}{\bar{R} T}} \tag{3-32}
\end{equation*}
$$

From equation $3-32$ it is obvious that at very low pressures $B$, the rate of transference of momentum across unit area, is proportional to the pressure $p$.

An expression for $B$ almost of the same form is also derived from other considerations of the kinetic theory of gases. The mass of gas molecules which strike unit area of the surface in one second, by ( $1-48 b$ ) is

$$
\frac{1}{4} m n v_{m}=\frac{1}{4} \rho v_{m}=\frac{1}{4} \frac{M p}{\breve{R} T} \sqrt{\frac{8}{3 \pi}} \sqrt{\frac{3 \breve{R} T}{M}}=\sqrt{\frac{M}{2 \pi \breve{R} T}} \cdot p
$$

If we assume that Knudsen's accommodation coefficient is unity, which for gases at very low pressures is justifiable, ${ }^{48}$ then the rate of transference of momentum per unit area of surface

[^37]moving with the velocity $u$ is given by
\[

$$
\begin{equation*}
B=u p \sqrt{\frac{M}{2 \pi \breve{R} T}} \tag{3-33}
\end{equation*}
$$

\]

Another expression for $B$, derived from certain theoretical assumptions by Baule, ${ }^{49}$ is

$$
\begin{equation*}
B=\left(\frac{1-\alpha^{\prime} \nu}{1+\alpha^{\prime} \nu}\right) u p \sqrt{\frac{M}{2 \pi \breve{R} T}}, \tag{3-34}
\end{equation*}
$$

where $\alpha^{\prime} \nu$ is a function of the masses and diameters of the molecules and solid and the distances between the molecules in the plane surface.

Whatever may be the difference in the manner in which the coefficient is calculated, it may be concluded with justification that at pressures of high vacua there is a relation between $B$ and $p \sqrt{M / \breve{R} T}$ of the general form,

$$
\begin{equation*}
B=k u p \sqrt{M / R T}, \tag{3-35}
\end{equation*}
$$

where $k$ is a constant whose exact value depends on the nature of the gas and that of the suiface of contact. It is on this expression 3-35 that the construction of the Langmuir-Dushman molecular gauge, its operation as a pressure measuring device, and the method of pressure reading are based.

3-39. Langmuir-Dushman Molecular Gauge.-This gauge, illustrated in figure 3-41, consists of a glass bulb $B$, having a rotating disk $A$ of aluminum, attached to a steel shaft mounted on jewel bearings and carrying a magnetic needle $N S$, and another disk $C$ of very thin mica about 0.0025 cm . thick and 3 cm . in diameter, suspended above $A$. The disk $C$, provided with a mirror $M$, is suspended from the top of the glass bulb by means of a quartz fiber $F$, about $2 \times 10^{-3} \mathrm{~cm}$. in diameter and 15 cm . long, in such a way that it hangs centrally over the lower disk in a perfectly horizontal plane at a distance of less than 1 cm . from the upper surface of the disk $A$.

The disk $A$ is set rotating by means of a rotating magnetic field produced outside the bulb in a Graame ring $G G$ supplied with a current at 6 points from a commutating device run by a motor
${ }^{49}$ B. Baule, Ann. d. Phys. 44, 145 (1914).
(figure 3-41A). With this arrangement the speed of the disk may be varied, according to the requirements, from a few up to 10,000 or more revolutions per minute.

The entire construction is such that the gauge can be thoroughly heated up to a temperature of $300^{\circ} \mathrm{C}$. for outgassing the whole gauge.


Fig. 3-41.


Fig. 3-41A.

With the rotation of the disk $A$ the gas between the two disks moves so that the suspended disk experiences a torque in the same direction. The torque which is balanced by the twist in the fiber is proportional to the product of the speed of rotation of the aluminum disk $A$ and the function $p \sqrt{M / R T}$ so that the torque at constant speed and uniform temperature varies as $p \sqrt{M}$. As the gauge readings are influenced by the nature of the gas, the instrument must be calibrated separately for each gas.

The working range of this gauge is from $10^{-3}$ to $10^{-7} \mathrm{~mm} . \mathrm{Hg}$. In the range of very low pressures serious difficulties arise, from deviations due to Foucault currents, which are greater at these low pressures than those due to the gas. It is not possible to
eliminate entirely the Foucault currents. Because of these disadvantages, the gauge is not of practical value for routine pressure measurements.

3-40. Langmuir Quartz Fiber Gauge.-This gauge, devised by Langmuir, ${ }^{50}$ is made with a flattened quartz fiber about 50 microns thick, from 5 to 10 times as wide, and 5 cm . long. It is mounted on one end of a glass bulb about 2.5 cm . in diameter, as shown in figure 3-42. Below the end of the


Fig. 3-42. quartz fiber in the body of the shell an iron armature, fitted to a glass pivot in sockets and put into motion by a magnet, activates the fiber.

When the ribbon is set into vibration in a high vacuum, the amplitude changes very slowly, as the damping by the residual gas is quite insignificant. Since the internal viscosity of the fused quartz is low, the loss of vibrational energy from this source is correspondingly low. From atmospheric pressure down to a few millimeters of mercury damping produced by gas molecules is independent of pressure. Below this range of pressures, the time required for the amplitude of vibration to decrease to half value is an index of pressure. In this range there exists a relation between the pressure $p$, the molecular weight $M$ of the residual gas, and the time $t$ which is given by

$$
\begin{equation*}
t_{i}^{-1}=A+B \sqrt{M} p \tag{3-36}
\end{equation*}
$$

where $A$ and $B$ are constants whose values may be determined by actual measurements. The gauge requires calibration by comparison. It is very useful in measuring pressures between $2 \times$ $10^{-2}$ and $5 \times 10^{-5} \mathrm{~mm} . \mathrm{Hg}$.

This gauge is very compact in form and simple in construction. It is suitable for measuring the pressure of corrosive gases, as there are no metal parts exposed. This instrument in conjunction with

[^38]an absolute gauge may be used for measuring the molecular weight of an unknown gas.

3-41. Haber-Kerschbaum Quartz Fiber Gauge.-Haber and Kerschbaum ${ }^{51}$ also devised a useful form of quartz fiber gauge (figure 3-43). It is simple in construction and is useful. It consists of a single quartz fiber 9 cm . long and 0.2 to 0.4 mm . in diameter mounted on one end of a glass bulb. The fiber is illumi-


Fig. 3-43.
nated by a small lamp with a dark background. The amplitude of the motion is observed by a microscope fitted with an eyepiece scale. A gentle tap is given to set the fiber vibrating in ohe plane.

As the pressure decreases the duration of the oscillations increases. Haber and Kerschbaum gave an empirical expression for the relation between the pressure $p$ and the time interval $t$ in which the vibration decreases to half its initial amplitude, which may be written

$$
\begin{equation*}
\sum(p \sqrt{M})+A=\frac{B}{t} \tag{3-37}
\end{equation*}
$$

where $A$ and $B$ are constants and $\sum$ is the sum of the products of partial pressure and the square root of the molecular weight of each gas present in the gauge.

The authors used their gauge to measure pressures as low as ${ }^{51}$ Zeits. f. Electrochem. 20, 296 (1914).
$1.2 \times 10^{-5} \mathrm{~mm} . \mathrm{Hg}$. Pressures even much smaller than this can be measured by this instrument. In the operation of this gauge and that of Langmuir, however, it is not easy to persuade the fiber to vibrate in one plane, and this causes some trouble in the measurements.


Fig. 3-44.
3-42. Coolidge Bifilar Quartz Fiber Gauge.-The difficulty arising out of the non-planar motion of the fiber of the singlefiber gauges was surmounted by Coolidge, ${ }^{52}$ who adopted a bifilar suspension (figure 3-44).

The bifilar suspension, consisting of two quartz fibers 9 cm . long and 0.004 mm . in diameter, is mounted in a body of Pyrex. The two fibers are joined by a glass tip to decrease the frequency and therefore the rate of damping of the vibration. This permits the measurement of the logarithmic decrement at pressures so high that the ordinary single fiber would be brought to rest in a few seconds. A guard ring is provided to prevent breakage. The projecting points are useful for conveniently determining the time required for the amplitude of vibration to fall to a series of values to be noted. Its lower limit is of the same order as that of the

[^39]others of the same class. Its upper limit is, however, higher than that of the single-fiber gauges.

3-43. King Quartz Fiber Gauge.-King ${ }^{53}$ developed a form of quartz fiber gauge, shown in figure 3-45, in which the oscillations are photographed. A vertical quartz fiber is mounted in a silica framework in such a way that it remains rigid. A second quartz fiber, each end of which is fused into a sphere about 0.05 mm . in


Fig. 3-45.
diameter, is fitted across the middle of the vertical fiber and at right angles to it. A small piece of iron at the cross junction of the fibers serves to start the vibrations of the cross fiber, the damping of which is measured by a photographic record. The fused end of the cross fiber functions as a convex mirror of small radius of curvature in reflecting light from a lamp through a lens and prism onto the photographic plate. The prism is slowly rotated so that a trace of the damped oscillation may be spread along the photographic plate.

This instrument has the advantages of a definite plane of oscillation and a stationary zero. It is not so much influenced by external tremor and is free from metal parts. The method, how-
${ }^{68}$ E. B. King, Proc. Phys. Soc. 38, 80 (1925).
ever, is more tedious in necessitating the direct observation of the decrement. The gauge is capable of measuring pressures between $10^{-2}$ and $10^{-6} \mathrm{~mm}$. Hg.

## Section VII. General Survey of High-Vacuum Gauges

3-44. The McLeod Gauge.-This gauge is one of the oldest and most used of the vacuum-measuring devices. It is simple in construction. It is easy to outgas and its readings are reliable if the residual gas obeys Boyle's law and is free from condensable vapors. It is a standard instrument for the measurement of low pressures, but its readings are not dependable below $10^{-5} \mathrm{~mm} . \mathrm{Hg}$. It does not give continuous reading of pressure, for the act of taking a reading necessitates cutting off the gauge from the rest of the system for a period of one or two minutes. Mercury vapor, whose pressure at normal temperature is fairly high, may easily find access into the vacuum system and destroy the high vacuum. This gauge, therefore, requires a refrigerative trap between the gauge and the high-vacuum system to prevent mercury vapor from entering it. The McLeod gauge does not indicate the pressures of condensable gases and vapors. It is, however, absolute in the sense that it can be calibrated by the direct calibration of its constituents.

3-45. The Backovsky-Slavik Gauge.-Among the non-volatile liquid-filled gauges, the Backovsky-Slavik gauge is a reliable and absolute instrument for measuring vacuum pressures down to $10^{-6} \mathrm{~mm} . \mathrm{Hg}$. It is quite simple in design and construction. The priming and outgassing are equally simple and easy. It gives continuous reading of pressures of both gases and vapors. Vapor of these gauge-filling fluids is not injurious to the brass and copper parts of the vacuum system. If the vacuum system is not required to be of exceptionally low pressure, this gauge does not require a refrigerative trap. The gauge indicates pressures of both condensable gases and vapors. It is, however, not suitable for the measurement of pressures of those gases which act upon the gauge-filling liquid.

3-46. The Knudsen Radiometer Gauge.-This instrument, unlike the McLeod gauge, does not involve the use of the seriously objectionable mercury with an undesirable vapor. The gauge is capable of giving both instantaneous and continuous registration
of pressures. It has no filament sufficiently hot to burn out or to decompose the residual gases or vapors whose pressures are to be measured. It measures the pressures of all vapors and gases alike, independently of the masses of the molecules or condensability. The zero point of the gauge can be readily controlled at any time by turning off the source of heat to the heater and thus bringing down its temperature to the temperature of the rest of the gauge. It is quite stable and is not so sensitive to external tremor. Its use does not involve very expensive electrical instruments. Some of the designs are complicated and their construction is not easy, though there are some among these types whose construction is not very difficult. This gauge needs mounting on a stable and rigid stand close to the vacuum system to be measured. The readings can be taken conveniently and directly only from the gauge scale.

3-47. Pirani-Hale Gauge.-This gauge is simple and compact in form and is readily attached to the vacuum system. It lends itself to self-recording and automatic-control devices. The vacuum-pressure readings may be taken at a distance from the gauge, as it may be connected to the bridge by several feet of twin flex. It is sensitive to tremor and to electrostatic fields so that some uncertainty may be easily introduced in the pressure readings when the gauge is in the neighborhood of an electrostatic field or is in the sphere of influence of external vibration. The PiraniHale gauge does not give an absolute measurement of vacuum pressure and requires calibration by comparison. It is difficult to establish a steady zero. It cannot be used with confidence to measure pressures below $10^{-5} \mathrm{~mm} . \mathrm{Hg}$. It indicates, however, small changes of pressure which take place in short intervals of time.

3-48. The Ionization Gauge.-This instrument has a wide measuring range from $10^{-2}$ down to $10^{-8}$ or $10^{-9} \mathrm{~mm}$. Hg. At very low pressures it requires thorough outgassing for obtaining fairly accurate results. It has high sensitivity and is capable of giving continuous registration of vacuum pressure. It gives a fairly accurate record of low-saturation vapor pressures. It requires expensive auxiliary equipment such as batteries and meters. Since the positive-ion yield per electron collision depends on the nature of the molecule, the readings cannot be converted into pressures unless the nature of the gas is known. The filament emission is altered by exposure to certain gases, and the filament

Table 3-4

| Name of gauge | Measures | Nature of measurement | Working range (mm. Hg ) |
| :---: | :---: | :---: | :---: |
| McLeod gauge | Only gases which obey Boyle's law | Absolute | $10^{-1}$ to $10^{-5}$ |
| Backovsky-Slavik gauge | Gases and vapors | Absolute | $10^{-1}$ to $10^{-6}$ |
| Knudsen absolute gauge | Gases and vapors | Absolu | $10^{-3}$ to $10^{-6}$ |
| Woodrow radiometer gauge | Gases and vapors | Absolute | $5 \times 10^{-4}$ to $3 \times 10^{-8}$ |
| Shrader-Sherwood radiometer gauge | Gases and vapors | Absolute | $5 \times 10^{-4}$ to $5 \times 10^{-9}$ |
| DuMond-Pickels radiometer gauge | Gascs and vapors | Relative | $5 \times 10^{-8}$ to $10^{-6}$ |
| Hughes radiometer gauge | Gases and vapors | Relative | $5 \times 10^{-3}$ to $10^{-6}$ |
| Lockenvitz radiometer gauge | Gases and vapors | Absolute | $5 \times 10^{-3}$ to $10^{-6}$ |
| Gold-leaf radiometer gauge | Gases and vapors | Relative | $10^{-2}$ to $10^{-6}$ |
| Pirani-Hale gauge | Gases and vapors | Relative | $\begin{aligned} & 10^{-1} \text { to } 10^{-5} \\ & \text { or } 10^{-6} \end{aligned}$ |
| Dushman-Found ionization gauge | Gases and vapors | Relative | $10^{-3}$ to $10^{-8}$ |
| Jaycox-Weinhart ionization gauge | Gases and vapors | Relative | $10^{-3}$ to $10^{-9}$ |
| Langmuir-Dushman molecular gauge | Gases and vapors | Relative | $10^{-3}$ to $5 \times 10^{-}$ |
| Quartz fiber bifilar suspension gauge | Gases and vapors | Relative | $10^{-1}$ to $10^{-6}$ |

itself may be destroyed if exposed to certain gases at too high a pressure. The instrument does not give an absolute measurement of vacuum pressure and requires calibration by comparison. Vapor from a diffusion pump having synthetic organic fluid as pumping medium, coming in contact with the hot filament, may easily crack to a more permanent gas, which would disturb pressure readings. The filament is usually short-lived and it is a tedious job to replace it.

3-49. The Langmuir-Dushman Molecular Gauge.-This instrument is complicated and is difficult to construct. It does not give absolute pressure values, and needs calibration by comparison. It involves the use of special high-speed motors. At low pressures

the gauge readings are heavily influenced by Foucault currents. The gauge seems to be useful for studying the properties of gases. It is, however, of little value as a pressure gauge for routine use.

3-50. General Characteristics of High-Vacuum Gauges.-For a ready reference, the characteristics of the different high-vacuum pressure gauges are given in Table 3-4; and in figure 3-46, the different ranges of pressures which can be measured with them are graphically represented.

## CHAPTER 4

## THE TECHNIQUE OF HIGH VACUOM

## Section I. The Equipment of High Vacua

4-1. Vacuum Systems.-The equipment of high vacua usually consists of vacuum generators, pressure-measuring devices, and vacuum systems, including vacuum enclosures, conducting tubes connecting different parts of these systems, and other accessories such as valves, refrigerating traps, and charcoal traps. The valves are used to direct gaseous flow and control pressures in vacuum systems. Refrigerating traps prevent vapors from entering vacuum enclosures.
4-2. Glass as Construction Material of Vacuum Systems.From the earliest days of the development of the technique of high vacua, glass has been used extensively for the construction of vacuum systems. Glass has many advantages. It is transparent and is a good electrical insulator. It is easily cleaned and put into condition for high vacuum. Its vapor pressure is negligibly low. It can be easily baked and sealed off to give a practically permanent vacuum. Glass tubes can be joined onto the vacuum-enclosing apparatus by fused glass joints and metal joints fused onto glass. Such fused joints are highly efficient for highvacuum work. Glass tubes may also be connected by waxed or cemented joints and by greased ground-taper joints.

4-3. Fused Joints.-(A) Glass-to-Glass Joints. - In the construction of glass vacuum systems, it is quite usual to connect the different glass elements by fused glass joints which can be made in the following way: At first all openings are closed by means of corks, except the two at the ends to be heated and one to be applied to the lips for blowing the joints. The glass elements are heated with rotatory motion in a gas flame of approximately the same diameter as that of the tubes. They are held in rotation in the flame so as to face each other in alignment, with the axis of their joint perpendicular to that of the flame. They are heated
in this way until they are thoroughly soft at the ends. They are then taken out of the flame and touched together at right angles. Using this contact as a hinge to steady the heads, the two tubes are brought together so that the edges of both tubes come into exact coincidence. They are then pressed together gently in alignment. The joint is heated with continuous rotation in the flame until it shrinks, and is then blown to a uniform outside diameter.
If a joint must be made directly on apparatus which cannot be rotated, the ends of the elements to be joined are thoroughly squared and are accurately fitted together. Initially the joint is gently heated all round by a hand torch to a uniform temperature and is then locally heated, a small section of the circumference at a time, until it is thoroughly soft. Each time the softened locality of the joint is worked by alternate shrinking and blowing until the wall is smooth. After completing this process all round the joint, it is uniformly heated for final blowing, alignment, and annealing.
(B) Metal-to-Glass Joints.-In the construction of vacuum systems, it is often necessary to connect glass and metal parts by metal joints fused on to glass. Metal-to-glass joints can be successfully made when the coefficient of expansion of the glass and of the metal to be used are in close agreement over the temperature range employed. Platinum has approximately the same coefficient of expansion as that of lead glass or soda glass. Therefore platinum wires which serve as electric leads can be fused through the walls of a vacuum enclosure. Even platinum tubes are joined direct to glass tubes, and since there is practically no inequality in the coefficients of expansion of platinum and glass, there will be no stress to cause fracture of the joint.
Also the expansion coefficient of tungsten is nearly equal to that of Pyrex glass. Hence tungsten-to-Pyrex joints may be effected directly. The tungsten wire or rod is first cleaned and then oxidized in the blowpipe flame. A bead of Pyrex glass is melted onto the tungsten. Then the tungsten-Pyrex joint is made in the oxidizing flame.
Sometimes copper tubes are brought through the glass walls through the intermediary of a flared platinum collar welded to the copper and fused onto glass. Another method of effecting a copper-to-glass joint is through the intermediary of a bright-
platinum deposit. The best procedure of effecting this is to see that the surface at the end of the glass tube which is to be joined to the copper tube is roughened slightly, and evenly painted with a fine emulsion of platinum chloride in an essential oil such as clove oil. Then, when it is gently and uniformly heated to a dull red, a bright uniform layer of platinum is deposited, which is copper plated electrolytically. Then the copper-plated platinized end of the glass tube can be soldered in the usual way to a copper tube. Also, a fairly hot platinized glass tube, when dipped in either molten lead or tin and withdrawn, takes a fine covering of bright lead or tin which can be soldered to any metal tube.

There is an efficient and direct method of effecting metal-toglass joints even when their coefficients of expansion differ widely. In this method the ends of the joints are designed in such a way that either one of them can accommodate itself to the stresses due to inequality of the coefficients of expansion so as to maintain the stresses with the mechanical strength of the joint. This method was developed and extensively used by Housekeeper, ${ }^{1}$ of the Western Electric Co., to make copper-to-glass joints. The end of the copper tube is beveled to a fine feather edge all around so as to form, when attached either inside or outside the glass tube, a well-fitted taper joint whose overlap is not more than a few millimeters. The end of the copper tube is heated in an oxidizing blowpipe flame until a coating of black oxide is formed. It is then dipped into a saturated solution of borax and heated again in the flame. This process is repeated until a fine layer of salt is formed which subsequently, combining with the copper oxide, changes into a thin film of red copper borate. Then on joining this end of the copper tube to the glass tube over not more than a few millimeters and heating them together in the blowpipe flame, the glass will readily adhere to the copper, forming an excellent and durable copper-to-glass joint.

4-4. Ground Taper Joints.-In the application of vacua to some branches of experimental and technical sciences, it is often necessary to join some parts of the vacuum system by waxed or sealed joints so that changes or alterations may be made in various parts of the apparatus. Greased joints are used to permit rotation of some part.

[^40]In preparing the metal ground joints, the metal elements are correctly tapered on a lathe. However, for the glass joints, the male taper is shaped in a blowpipe flame by means of standard graphite mold and the female taper is formed by expanding tubing of a corresponding size in a blowpipe flame using a fluted brass reamer of the corresponding size and taper. These tapers, whether glass-to-glass or glass-to-metal or metal-to-metal, are ground using fine carborundum paste as the abrasive in the initial stages and fine carborundum flour with thin oil in the final stage. For glassground joints glycerine, or turpentine, or, preferably, fine abrasive M $303 \frac{1}{2}$, is used as the finishing medium.

Taper, and ball-socket joints, made of Pyrex glass, and ground with precision in various standard sizes, are manufactured by the Corning Glass Works, Corning, New York. These greased-ground joints, both taper and ball-socket type, are used for the construction of vacuum systems in which the tubes in the vacuum line must be rotated.

4-5. Rubber Tubing.-Rubber is a very important factor in vacuum equipment. Rubber tubing cannot be used for connections in the high-vacuum part of the system, but may be employed for joining the fore-vacuum pump to the high-vacuum generator. The rubber tubing used for this purpose should be thick walled with large diameter and of as short a length as possible. It is frequently used in McLeod gauges, where the gases given off by the rubber tubing are prevented from entering the gauge by an air trap between the mercury reservoir and the gauge-bulb. Rubber tubing used for vacuum work and McLeod gauges should be free from cracks and deterioration and should have a minimum of sulphur content. These tubes should be boiled for a number of hours in caustic soda solution, then washed in distilled water, and finally dried with a blast of dust-free, dry, warm air in order to get rid of free sulphur. This process reduces the emission of gas. After such treatment rubber tubing can be employed with advantage for the fore-vacuum as well as for the McLeod gauge.

4-6. Sylphon Tubing.-Flexibility between parts of a vacuum system may be obtained by the use of sylphon tubing, a seamless corrugated tubing of red brass or tombac alloy. These tubes with plain ends may be readily joined to vacuum systems either by vacuum wax or cement or, preferably, by soldering.

A sylphon tube of 0.6 cm . internal diameter may be bent into a circle of radius 15 cm ., while one of 5 cm . internal diameter may be bent so as to have a radius of curvature of 14 cm .
4-7. Vacuum Waxes, Cements, and Stopcock Greases.-
(A. 1) Apiezon Greases. - "Apiezon $L$ " is a grease used to seal demountable joints of vacuum systems. The surfaces of contact of a joint are coated with a thin film of grease, and then joined gently but firmly, thus filling the space between the surfaces with grease and rendering the joint vacuum-tight. Its vapor pressure is $5 \times 10^{-6} \mathrm{~mm} . \mathrm{Hg}$ at a temperature of $20^{\circ} \mathrm{C}$.
" Apiezon M " and " N " are similar products used for the same purpose. These greases are more viscous and more suitable if the joints are exposed to temperatures above $20^{\circ} \mathrm{C}$. "Apiezon M" grease, in use in a vacuum system, attains a vapor pressure of about $5 \times 10^{-7} \mathrm{~mm}$. Hg after some hours of pumping. ${ }^{2}$ If it is baked in vacuum at $90^{\circ} \mathrm{C}$. for about a couple of h hurs, its vapor pressure can be reduced to $10^{-9} \mathrm{~mm} . \mathrm{Hg}$.
Apiezon greases are suitable for stopcocks. A stopcock, if properly greased, will give continued service satisfactorily for as much as three months.
Care must be taken not to contaminate these greases with moisture and dirt. They must be kept free from contact with the atmosphere when not in use, for occluded air is more detrimental to vacuum than the high vapor pressure.
(A. 2) Apiezon Wax "W."-In the technique of high vacuum, waxes and cements are used to seal tube joints and vacuum systems, and greases are employed to seal ground taper joints and taps. Of all the waxes available, Apiezon wax " W " has the lowest vapor pressure, being $10^{-3} \mathrm{~mm} . \mathrm{Hg}$ at $180^{\circ} \mathrm{C}$. and of the order of $10^{-6}$ $\mathrm{mm} . \mathrm{Hg}$ at room temperature. This quality gives a marked advantage in vacuum technique. Its softening and wetting temperatures are $65^{\circ} \mathrm{C}$. and $100^{\circ} \mathrm{C}$. to $105^{\circ} \mathrm{C}$. respectively. It can best be applied to joints and vacuum systems at about $100^{\circ} \mathrm{C}$. It is pliable at a temperature of above $25^{\circ} \mathrm{C}$. and is more plastic than shellac or some of its derivatives. It is more or less affected by benzene, carbondisulphide, chloroform, ether, turpentine, and Xylene oil.
(A. 3) "Apiezon Q."-"Apiezon Q" is a plasticine-like substance. It consists of graphite mixed with the residual products ${ }^{2}$ G. Seydal, Zeits. f. Phys, 16, 107 (1935).
of paraffin oil distillation, with low vapor pressure. This semisolid substance, being pliable, can be readily pressed and worked with the fingers round a joint in glass or metal for vacuum sealing. Its vapor tension is $10^{-4} \mathrm{~mm} . \mathrm{Hg}$ at a temperature of $20^{\circ} \mathrm{C}$. It cannot be used above $30^{\circ} \mathrm{C}$., which is about its temperature of liquefaction. It is soluble in benzine, ether, and turpentine.
(B) Shellac.-Shellac, in the pure state, has a high tensile and shear strength. It dissolves in alcohol and the concentrated solution is useful in finding leaks in vacuum systems. It is he essential adhesive base of cements such as Dekhotinsky cement. It may be used alone, but when so used develops hair-line cracks, causing leaks injurious to vacuum. This undesirable condition can be remedied by reinforcing it with other materials. It is the principal ingredient of cuperior qualities of sealing wax adapted for vacuum work. Shellac when tempered with butyl phthalate is useful for sealing joints and vacuum systems. Because of its very low vapor pressure, it is particularly suitable for high-vacuum work.
(C) de Khotinsky Cement.-Shellac is tempered to varying degrees with " North Carolina oil of tar" in water bath to obtain de Khotinsky cements, soft, medium, and hard. The vapor pressure of this cement at normal room temperature is of the order of $10^{-3} \mathrm{~mm} . \mathrm{Hg}$. It is therefore useful for vacuum work and is extensively used in America. Before applying this cement, the objects to be cemented together should be perfectly free from grease and dirt. A new type of tempered shellac, available under the trade name Sealstix, has a greater working range of temperature than pure shellac. It has a high strength, and is odorless and inflammable.
(D) Sealing Wax.-Sealing wax of superior grade, used for vacuum work, is composed of pure shellac, Venice turpentine, and the coloring material vermilion or Chinese red. The softening and wetting temperatures are $60^{\circ}$ to $80^{\circ}$ and $100^{\circ}$ to $125^{\circ} \mathrm{C}$. respectively. Its vapor pressure is of the order of $10^{-5} \mathrm{~mm} . \mathrm{Hg}$ at normal room temperatures. The waxed joint, on standing, may develop imperceptible cracks, injurious to vacuum.
(E) Prcmin.-This sealing substance is composed of hydrocarbons from rubber, shellac, and bitumen. Its low vapor pressure makes it useful for high-vacuum work. It is in two grades, one having a liquefying temperature of $80^{\circ} \mathrm{C}$, and the other of
$105^{\circ} \mathrm{C}$. It is useful for sealing tubes together and repairing leaks in vacuum systems. It is not brittle and the sealed joints do not develop cracks. It is practically unaffected by water and alcohol. Surfaces with picein can be cleaned by benzol and turpentine. Its vapor pressure is $3 \times 10^{-4} \mathrm{~mm}$. Hg .
(F) Universal Wax.-This wax, one of the most useful substances for sealing, is made from five parts of purified beeswax and one part of Venice turpentine. It has good adhesive and plastic properties. Its exposed parts oxidize and consequently become hard. It is therefore advisable to prepare this wax in small quantities. It is plastic at temperatures slightly higher than room temperature. It is fairly rigid when cool. The vapor pressure of this wax is $0.9 \times 10^{-3} \mathrm{~mm} . \mathrm{Hg}$. Another composition, similar to Universal wax, is made from four parts of purified beeswax and one part of Venice turpentine. It has almost the same vapor pressure as the Universal wax.
(G) Beeswax-Rosin Compound.-This wax is prepared by melting equal parts of beeswax and rosin. It adheres well to cold metals. It is satisfactory for sealing vacuum systems though not very strong. It is quite plastic at normal temperature. Surfaces, undesirably waxed with this material, can be cleaned with a mixture of equal parts of carbon tetrachloride and ethyl alcohol.
(H) Stopcock Grease.-Stopcock grease is employed for sealing the dead space in stopcocks and in taper joints in vacuum systems. It is made by digesting equal parts of small cut pieces of pale crepe rubber and Apiezon compound " M." This digestion is carried out in a flask with a thorough mechanical stirring at a raised temperature obtained from a gently heated sand bath until the content of the flask becomes uniform without any trace of the kernels of the rubber pieces. The flask is then removed from the sand bath and is fitted to a fractionating still and is heated again in an oil bath under high vacuum to free the grease from light ingredients. After thus removing the volatile and light components, the heavy part will be a very efficient grease for highvacuum work. It can be used with advantage to grease the tapered joints of the electrodes of an experimental x-ray tube of the Coolidge type.
(I) Vapor Pressures of Waxes, Cements, Greases, etc.Many waxes, cements, and greases are available in the market for
vacuum work. For the right selection of a suitable wax or cement or grease for a vacuum system of a given pressure, it is very important to know their vapor pressures. Zabel ${ }^{3}$ measured the rapor pressures of many of these substances by means of an ionization gauge. His measurements of vapor pressures of these materials at $23^{\circ} \mathrm{C} . \pm 2^{\circ} \mathrm{C}$. relative to that of brass are given in Table 4-1.

4-8. Metals as Construction Material of Vacuum Systems.Glass is fragile, and vacuum systems made of glass easily tend to break. Therefore it is being replaced by metals. Brass and copper may also be employed, with the former preferred because it is cheaper. The vapor tension of brass, though higher than that of glass, is considerably lower than that of iron and steel which are also sometimes used. In addition, brass may be easily repaired and altered in a machine shop. A good vacuum-tight system can be made from plates and cylinders of yellow brass, assembled, fitted together, and soft-soldered or silver-soldered, depending on the temperature resistance and strength required. Systems can also be made from plates and cylinders of yellow brass, screwed together and rendered vacuum-tight by a fine coating of beeswax and rosin mixture on the outside to close the intervening cavities and leaks. When flexibility between the parts of a vacuum system is required, they are connected with sylphon tubes, made of tombac alloy or red brass. A sylphon tube joint is easily effected by soldering.

4-9. Soft Soldering and Hard Soldering.-The different parts of a vacuum system, made of metal, are either soft-soldered or hard-soldered, depending on the temperature resistance and strength required in order to effectively join and seal them together and render the joints perfectly tight. Solders are usually composed of an alloy of two or more metals. The solders must have a lower melting point than the metals to be joined by them. The fusing point of the chosen solder should, however, approach as nearly as possible that of the metals to be joined in order to create a more tenacious joint. The hard solders fuse at a red heat, the soft solders at a comparatively low temperature.

Soft solders consist chiefly of lead and tin, as shown in Table 4-2A. Other metals are added to lower the melting point as in the

[^41]Table 4-1

| Substance | Ratio of vapor pressure to that of brass |
| :---: | :---: |
| Pyrex | 0.7 |
| Pyrex after heat treatment | 0.06 |
| Brass | 1.0 |
| Iron | 3.5 |
| Iron heavily coated with rust | 250.0 |
| Wax |  |
| . Picein (melting point $105^{\circ} \mathrm{C}$.) | 3.5 |
| Picein (melting point $80^{\circ} \mathrm{C}$.) | 4.0 |
| Dennison's Royal Scarlet | 4.5 |
| Beeswax 1 part, Rosin 1 part | 5.5 |
| Glycol-Phthaiic Anhydride Resin | 8.5 |
| Extrafein | 10.0 |
| Sealing Express | 10.5 |
| Universal | 12.0 |
| Beeswax 4 parts, Venice turpentine 1 part | 12.0 |
| Dennison's No. 2 | 12.0 |
| de Khotinsky (hard) | 15 |
| de Khotinsky (medium) | 21.5 |
| de Khotinsky (soft) | 25.0 |
| Glyptal |  |
| Lacquer (baked 4 hours at $200^{\circ} \mathrm{C}$.) | 2.0 |
| Lacquer (dried 14 days) | 5.0 |
| Lacquer Green (baked 4 hours at $200^{\circ} \mathrm{C}$.) | 3.5 |
| Lacquer Black (baked 4 hours at $200^{\circ} \mathrm{C}$.) | 5.5 |
| Lacquer Red (baked 4 hours at $200^{\circ} \mathrm{C}$.) | 7.0 |
| Stop-cock greases |  |
| Central Scientific Co. | 7.0 |
| Lubriseal (improved formula) | 7.5 |
| Ramsay Fett | 85.0 |
| Gum Chicle clues | 50.0 |
| $N$-di-butyl phthalate at $25^{\circ} \mathrm{C}$. | 5.4 |

case of wood metal. Hard soldering is usually effected by silver solder, while brazing is done by a copper-zinc alloy known as brazing compound. In using either soft or hard solder, their appropriate flux must be employed for fusing it on the surfaces in order to join them together and seal them airtight. The different

Table 4-2a. Soft and Intermediate Solders

| Solder | Composition, per cent | Melting point, ${ }^{\circ} \mathrm{C}$. |
| :---: | :---: | :---: |
| Wood metal | Bi 50, Cd 12.5, Pb 25, Sn 12.5 | 61 |
| Soft solder of superior strength | Pb 34, Sn 66 | 180 |
| Half and half | Pb 50, Sn 50 | 205 |
| Intermediate solder | Ag 20, Cu 3, $\mathrm{Zn} 2, \mathrm{Sn} 75$ | 400 |

Table 4-2b. Hard Soldrr and Brazing Alloy

| Solder | Cumposition, per cent | Melting point, ${ }^{\circ} \mathrm{C}$. |
| :--- | :---: | :---: |
| Ag 45, $\mathrm{Cu} 30, \mathrm{Zn} \mathrm{25}$ | 720 |  |
| Brasing compound | $\mathrm{Cu} 54, \mathrm{Zn} 46$ | 875 |

Table 4-2c. Fluxes for Soft and Intermediate Solders

| Flux | Composition |
| :--- | :--- |
| Liquid flux | $40 \mathrm{ZnCl}_{2}, 20 \mathrm{NH}_{4} \mathrm{Cl}, 40 \mathrm{H}_{2} \mathrm{O}$ |
| Flux paste | 90 paste of petroleum, $10 \mathrm{NH}_{4} \mathrm{Cl}$ |
| Spirit of rosin | A solution of rosin in alcohol |

Table 4-2d. Fluxes for Hard Soldering

| Flux | Composition |
| :--- | :---: |
| Borax-boracic acid paste | A thin paste of 10 parts of powdered borax, 1 <br> part of boracic acid in water <br> Dry borax |

kinds of solders, their melting points, compositions, and appropriate fluxes with their compositions are given in Tables 4-2A, $4-2 B, 4-2 C$, and 4-2D.

4-10. Detection of Leaks.-Leaks in a vacuum system are the principal source of trouble in maintaining the limiting pressure obtainable by a pumping system. Such leaks, when minute, present a perplexing and annoying problem of detection.

The parts of a vacuum system are, when practicable, immersed in water, preferably in soap solution. Compressed air is then blown into the system. The positions of the leaks are indicated by the emission of bubbles.

A leak in a vacuum system made of glass can be easily detected by means of a Tesla coil. The vacuum system is probed, by moving the Tesla coil slowly over its surface. If the pressure is of the order of a few dynes per square centimeter, the vacuum system glows and a brush discharge, especially visible in darkness, takes place between the probe end of the Tesla coil and the surface of the walls of the vacuum system. If the probe passes over a leak in the glass, the brush discharge changes to a bright spark discharge between probe and the gas inside, through the minute leak.
The detection of leaks by this method in the metal part or in the metal-glass joint of a glass-metal vacuum system is impracticable. In this case a glow discharge is produced in the system by placing the Tesla coil probe on the glass part of the vacuum system or by incorporating a discharge tube. A clean rag soaked in alcohol or, preferably, ether is then slowly moved all along the surface of the vacuum system. When this rag passes over the region of the leak, the vapor of the volatile liquid enters the system and changes the color of the glow discharge, indicating the position of the leak.
A Pirani gauge, incorporated in a vacuum system, may be a very useful accessory device for detecting leaks. After exhausting the vacuum system to the limiting pressure by means of a fore-vacuum pump, the maximum resistance, which remains stationary, is measured by a Wheatstone bridge. Then a narrow jet of hydrogen is directed against the surfaces of the vacuum system and especially of the joints. When hydrogen is blown over the region at the leak, the gas enters the vacuum system and increases the pressure. The increase is instantaneously registered by the fall of resistance, indicating the position of the leak. Then, when the hydrogen jet is removed, the resistance increases again by the fall of pressure to the initial value. In this way the detection of the position of the leak is verified.
The detection of a leak in an all-metal vacuum system by the Pirani-gauge method is preferable in many respects to the others.

## Section II. Requisites of Vacuum Tecinique

4-11. Mercury Cutoffs.-In the application of high vacua either for experimental and applied sciences or for technical uses, it is often required to separate temporarily two parts of a vacuum
system having a pressure difference which is not great. Such a separation is effected usually by means of large greased taps. Grease from such taps may sometimes easily enter the vacuum


Fig. 4-1.
line of the system, and this may be objectionable. If grease is objectionable, stopcocks are replaced by mercury cutoffs shown in figure 4-1.

Of these, those in figures 4-1A and $B$ are of barometric arrange-
ment. The tube connecting the rough-vacuum and high-vacuum parts of the vacuum system is joined by fusion to a barometric tube. The fore-vacuum limb of the cutoff, shown in figure 4-1A, may be isolated from or joined to the high-vacuum limb by raising or lowering the mercury reservoir at the lower end of the barometric tube. In the model of the mercury cutoff shown in figure $4-1 B$, these operations are done either by opening the stopcock at $B$ so that the atmospheric pressure acts on the mercury column
 in the reservoir for raising it above $A$ or by suction through the tap to lower the mercury column below $A$.
The two forms shown in figures 4-1A and $B$ are quite efficient, but in some cases their size is objectionable. This objection is removed in the two forms shown in figures $4-1 C$ and $D$. The former is put into operation by exposing the mercury in the reservoir to rough 3 vacuum or to atmospheric pressure, while the latter is magnetically operated.
4-12. Valves.-Among the equipment for high-vacuum technique, gas valves may be considered highly useful requisites. A valve is a device for regulating the flow of gases and controlling pressure. These valves are of immense value not only for the technique of high vacua, but also for the industry of gas-filled x-ray tubes and gas-filled lamps. For the study of various kinds of physFig. 4-2. ical phenomena which demand vacua with variable gas flow and regulated pressures of gases, these valves are of great practical value. There are various types of valves; some of the simpler and most useful are described here.
(A) Capillary Valve with Porous Material.-A capillary valve ${ }^{4}$ made of glass is shown in figure 4-2. It has a fine capillary tube closed at one end by a porous wall. It permits a flow of gases and a regulation of gas pressure. It consists of a glass tube (1), which is drawn out into a fine capillary (2) and is fused in a glass tube (3). The fine aperture of the capillary ends in a porous wall (4) of any suitable porous material such as clay, graphite, carbon, porous glass filter, etc. Gas from the glass tube (3) enters through the porous wall of the inlet of the capillary into the glass

[^42]tube (1), whence it flows into the apparatus with which it is connected.
(B) Variable Valve with Porous Wall.-A variable valve ${ }^{5}$ with a porous wall, simple in design and easy to construct, is shown in figure 4-3. It consists of a cylindrical main casing, the upper and the lower ends of which are connected to tubes. At the upper end of the lower tube is a conical porous wall. A soft iron anchor, whose lower end is fitted to a glass tube having an inlet aperture in the middle, is inserted in the main casing so as to let its lower end remain plunged in a small column of mercury. The upper end of the main casing is surrounded by a solenoid. By means of the solenoid the anchor and attached gas tube may be raised or lowered, thus varying the height of the mercury column and hence the effective area of the porous wall.

When the surface of the porous wall is freed from mercury, the gas from the upper inlet tube, passing the entrance by the side of the anchor and entering through the inlet aperture into the tube connected with the anchor, reaches the surface of the porous wall. Then, passing through the porous wall, the gas reaches the connected apparatus through the tube at the lower end. If the anchor is released it


Fig. 4-3. goes down to the bottom of the cylindrical body and raises the mercury column so as to cover the entire surface of the porous wall, thus stopping the flow of gas into the apparatus.

In this way the valve regulates the flow of gas and the gas pressure by controlling the effective area of the porous wall.
(C) Variable Valve with Porous Tube.-A valve ${ }^{6}$ with a porous tube for regulating the flow of gases is shown in figure 4-4. The main body of the valve consists of two cylindrical bulbs, the lower ends of which are joined by means of a tube bent twice at right angles and provided with a stopcock. A glass tube, the lower
${ }^{5}$ W. Kohler and R. Rompe: Die Elektriscen Leuchtrohren, Braunschweig (1933); E. Lax and M. Pirany, in Geiger-Schell, Handbuch der Physik 19, 351 (1929) (Lichttechnik); W. Espe and M. Knoll, Werkstoffkunde der Hochvakuumtechnik, Berlin (1936); J. B. Slavik, Ventily Pro Regulaci Tlaku Plynu, Prague (1937).
${ }^{6}$ O. H. Wansbrough-Jones, Proc. Roy. Soc. 127A, 530 (1930).
end of which is joined to the porous tube having a closed bottom, is inserted into and fused at the top of the main cylindrical bulb on the left. The upper end of this inserted tube is joined to a horizontal tube. Another tube which branches out from the side at the upper part of this bulb is joined to the horizontal tube. The horizontal tube is provided with a stop-


Fig. 4-4. cock between the two joints. Mercury is put in the main outer body of the valve. The tube connected to the top of the cylindrical bulb on the right is also provided with a stopcock.

The variation of the effective length of the porous tube is effected by raising or lowering the level of the mercury column. The valve permits regulation of gas flow and minute control of gas pressure.
(D) Valve with Porous Pipe for Regulating Gas Flow.-A variable valve ${ }^{7}$ with porous pipe for controlling gas pressure is shown in figure $4-5$. The main body of this valve consists of two limbs shaped like test tubes and joined by a connecting tube. A porous pipe with closed bottom is inserted in the shorter limb. The mouth of the porous pipe is fixed airtight in a cap, having an outlet tube which can be joined to an apparatus. This cap covers and seals the mouth of the shorter limb at its upper end. An inlet tube is provided to this shorter limb in its side wall, just below the cap. The porous pipe extends from the top down to the level where the shorter limb is joined to the longer one.

A long cylindrical plunger, fitted with a cork at its upper end, is inserted in the longer limb. It is held in any desired position by a screw attached to the cap of the longer limb. Mercury is poured into the casing so as partly to fill the limbs and to keep part of the porous pipe and the plunger immersed in the mercury column. The mercury column may thus be either raised or
${ }^{7}$ J. E. Dorn and G. Glockler, Rev. Sci. Inst. 7, No. 8, 319 (1936); J. B. Slavik, Ventily Pro Regulaci Tlaku Plynu, Prague (1937).
lowered to vary the effective length of the porous pipe and regulate the gas flow. With the aid of the valve, gas pressure can be easily and effectively controlled.

All the valves with porous material are fairly efficient in their operation. They have, however, one disadvantage: It takes too long to exhaust a valve with porous material, when the entire apparatus is to be thoroughly evacuated.


Fic. 4-5.


Fig. 4-6
(E) Invariable Gas Valve.-A form of valve ${ }^{8}$ which admits or cuts off a gas flow but is incapable of varying it, is shown in figure 4-6. The principal part consists of a V-shaped tube. The closed limb, inserted in a solenoid, contains a glass plunger with a soft iron core. The other limb has two tubes, one inserted and
${ }^{8}$ W. Espe and M. Knoll, Werkstofkunde der Hochvakuumtechnik, Berlin (1936).
fused at the top and the other fused in the side wall, which form respectively the inlet and the outlet of the valve. The U-tube contains mercury.

The level of the mercury in the open limb may be raised or lowered by means of the plunger, thus closing or opening the inlet. The small bent capillaries in the inlet and outlet tubes control the rush of gas when the valve is opened. The constriction at the lower part of the open limb prevents a sudden rush of mercury into the open limb.

As the size of the orifice at the end of the inlet tube cannot be regulated, the gas flow cannot be varied. One of the advantages of this valve, however, is that it can be put into operation even from a distance. Practically it serves as a mercury cutoff.
(E.1) Gas Valve with Invariable Leak.-A valve ${ }^{9}$ with invariable leak which permits the regulation of the gas content of a discharge tube is shown in figure 4-7. It consists of a glass chamber (1) of $50 \mathrm{~cm} .^{3}$ volume, containing a gas such as hydrogen or nitrogen, into which a tube with a fine capillary (2) is inserted and fused. A fine tungsten wire (3) of uniform diameter is fitted into the capillary so that the free passage of the capillary has a diameter of 0.01 mm . A compound strip (5) of two metals having different coefficients of thermal expansion with a small rubberlined plate is mounted upright so as to close the aperture of the capillary. A chrome-nickel wire (6) 0.2 mm . in diameter and 110 cm . long is wound over the compound strip (5). With a heating current of 1 amp ., the compound strip is heated so that it turns away from its upright position, thereby opening the aperture of the capillary passage. Thus when the aperture of the capillary is opened, the gas from the valve chamber flows through the capillary into the exhausted discharge tube.
If the valve-chamber of $50 \mathrm{~cm} .^{3}$ containing hydrogen at a pressure of $360 \mathrm{~mm} . \mathrm{Hg}$ be opened to an exhausted discharge tube of $500 \mathrm{~cm} .^{3}$, in one hour 3.5 per cent of the gas flows from the former to the latter, raising its pressure by $0.02 \mathrm{~mm} . \mathrm{Hg}$ per minute. In the chamber of the same volume, if nitrogen at $360 \mathrm{~mm} . \mathrm{Hg}$ be substituted for hydrogen, 1 per cent of the nitrogen enters the exhausted tube of $500 \mathrm{~cm} .^{3}$ in one hour, which corresponds to the rise of pressure of $0.0055 \mathrm{~mm} . \mathrm{Hg}$ per minute.
${ }^{9}$ K. Becker and M. Pirani, Zeits. f. techn. physik 13, 216 (1932).


Fig. 4-7.
(F) Micrometer Needle Valve.-A micrometer needle valve, ${ }^{10}$ shown in figure 4-8, has a main body machined from brass with a side piece screwed and soldered into it. There are two separate parts within this body. Of the two, one is a controlling head or stopper, with a circular knurled head having scale divisions on its upper surface. It is ground to fit in a taper hole in the body. The other part is a steel screw with a tapered needle. These two parts are connected together by means of a tongue on the upper end of the steel screw which fits in a diametral slot in the lower end of the stopper, to enable the two parts to turn together. The screw has a diameter of 6 mm . and a pitch of 0.5 mm . A uniform groove along one side of the screw, whose depth exceeds that of the screw thread, permits the flow of gas.
${ }^{10}$ L. Saggers, J. Sci. Inst. 12, 93 (1935).

The amount of the projection of the taper needle into the lower fine aperture is regulated by turning the head. The clearances between the screw and the stopper and in the slot above the tongue permit the desired motion of the screw upward and downward.


Fig. 4-8


Fig. 4-9.
(G) Needle Valve for Gas X-Ray Tubes.-A needle valve, ${ }^{11}$ shown in figure 4-9, is designed for regulating the flow of a gas into gas x-ray tubes. It consists of a fixed frame in which is arranged a needle $H$, attached to a holder with two screws. A handle (1) is mounted on the holder with screws. Just below the lower end of the needle, a hole is drilled on the seat into which the needle, when brought down, smoothly enters and closes it. At the lower end of the drilled hole, a tube of suitable dimensions is fitted to connect the valve with apparatus or a gas x-ray tube.

The handle (1) turns the screws (2) and (3) in their respective nuts. Screws 2 and 3 have 30 and 31 threads per inch respectively so that when the handle is turned one revolution in a right-hand direction, the screw (2) moves downward $\frac{1}{30}$ inch and the nut ( $F$ ) is raised $\frac{1}{3 T}$ inch, while the consequent net motion of the needle is
${ }^{11}$ H. Kersten, Rev. Sci. Inst. 6, No. 6, 175 (1935).
about one thousandth of an inch downward. The fine motion of the needle into the socket of the drilled hole results in a fine regulation of the flow of gas into the connected apparatus or the gas x-ray tube.

This valve does not require a fore vacuum and is easily adjusted. It has no greased joints and can be modified for use with gases other than air. It is primarily intended to regulate the flow of gas, but does not stop it altogether. If complete stoppage is required, a glass stopcock may be introduced in the tube connecting the valve and the apparatus.
(H) RubberCapillary Gas Valve.A form of variable capillary gas valve, ${ }^{12}$ shown in figure 4-10, is made by squeezing a heavy nitrometer rubber tubing in a broad clamp. Variation of the leak is easily effected by turning the screws of the clamp. The clamp, however, should be opened every few days to prevent sticking of the inner surfaces of the rubber tubing. One undesirable feature of this valve is that a deposit of fine powder


Fig. 4-10. accumulates in the interior of the tubes passing large currents. This dcposit absorbs large amounts of gas which may subsequently be given out into the vacuum under the influence of discharge. The parts where deposits accumulate should be cleaned by thoroughly scraping out the deposit after the tube has run for some time with a large power input.
(I) Variable Capillary Gas Leak.-A variable capillary gas leak ${ }^{13}$ consists of a German-silver tube, 6 mm . in diameter with walls 0.5 mm . thick, somewhat flattened in the middle, as shown in figure 4-11, by pounding until a leak of required magnitude is obtained, and bent into a U-shaped spring. Variation of the gas flow can easily be effected by opening and closing the spring with the attached screw.

Under certain conditions, this leak operates over a pressure range from 0.5 to 300 dynes $/ \mathrm{cm} .^{2}$
${ }^{12}$ R. W. G. Wyckoff and J. B. Lagsdin, Rev. Sci. Inst. 7, No. 1, 37 (1936).
${ }^{18}$ R. D. Fowler, Rev. Sci. Inst. 6, No. 1, 26 (1935).
(J) Glass Needle Valve.-This valve, ${ }^{14}$ shown in figure 4-12, has a cylindrical body with a capillary $C$ inside which a glass needle slides. The body, surrounded


Fig. 4-11. by a solenoid $S$, contains a glass rod with a soft iron core. The end of the glass needle which is away from the capillaryis connected to thisglass rod. The axis of the glass needle and that of the capillary are in perfect alignment so as to permit smooth sliding of the needle into the capillary without any hindrance. When the current is switched on, the field of the solenoid actuates the iron-cored glass rod so that the glass needle moves as desired along the axis. The valve is thus electromagnetically operated.
A properly made instrument may have a fairly satisfactory range of operation, the low limit giving a flow of $0.1 \mathrm{~cm} .^{3}$ per hour.

In dealing with gases which attack metals or which dissolve in the grease used in some kinds of valves, this all-glass valve will be very usful.


Fig. 4-12.
(K) Capillary Valve for Gases.--This instrument ${ }^{15}$ is made of two small pieces of glass tube and a metal pinchcock (figure 4-13). Of the two pieces, one is an outer one into which the second, having a capillary ending, is inserted and fused. The end of the capillary is closed. The capillary contains a lengthwise crack and a transverse crack branching from it. It is advisable to use pyrex for the construction of this valve.

The two arms of the valve are slightly separated and the pinchcock, when operated, reduces the separation, thus producing a
${ }^{14}$ J. J. Hopfield, J. Opt. Soc. Am. 12, 391 (1935).
${ }^{15}$ J. J. Hopfield, J. Opt. Soc. Am. 12, 391 (1935).
slight twist in the tubes which in turn opens the cracks in the capillary. The valve can be made to give a wide variation of gas flow. With a properly made valve of this type, it is possible to reduce the gas flow to $0.1 \mathrm{~cm} .^{3}$ (measured at atmospheric pressure) per hour when the gas passes from atmospheric pressure into a vacuum. By varying the opening of the cracks, effected by springing the arms together, the gas flow can be increased to many times this value.

This valve is simple and compact, and it is particularly useful with gases which attack metals.


Fia. 4-13.
(L) Long Split-Leak Valve for Controlling Gas Flow.A long split-leak valve, constructed by Slavik, ${ }^{16}$ is shown in figure 4-14. This valve, in its essential parts, consists of a glass tube, closed at the bottom end, with a long split-leak, inserted into and fused to another tube at its top. The long leak in the glass tube can be made by first ruling with a sharp diamond cutter and then splitting it by gently passing a red-hot glass needle over the cut line. The upper end of the split tube is joined to an apparatus in which the gas pressure is to be controlled. The glass tube surrounding the split tube forms the upper shell of the valve and is provided with a small branch which serves as an inlet tube. The lower end of the valve shell is joined to another tube by rubber tubing. The shell and the tube are clamped verti-

[^43]cally on a stand and mercury is put in them so that part of the split-leak tube remains submerged in the mercury column. When the tube is raised or lowered by means of the screw connected to


Fig. 4-14.
the clamp, the mercury column in the valve-shell rises or falls, thus varying the effective length of the split-leak. In this way the gas flow is regulated from the inlet branch tube through the split-leak to the apparatus.

This valve is capable of thoroughly regulating gas flow and minutely controlling the pressure. When the gas passes from
atmospheric pressure into a vacuum, the flow may be reduced to as low as $0.01 \mathrm{~cm} .^{3}$ (measured at atmospheric pressure) per hour.

4-13. Traps.-(A) Introduction.-In some branches of experimental, applied, and technical sciences, the use of high vacua is imperative. These required high vacua must be free from mercury vapor and all other condensable vapors, including traces of water vapor and those of oils and greases. Mercury vapor from


Fig. 4-15.
mercury condeusation pumps, mercury-filled gauges, mercury cutoffs and some kinds of valves, oil and other vapors from oil condensation pumps, rotary pumps, and greases diffuse into the vacuum systems and contaminate high vacua. To prevent the vapors from entering the vacuum systems and thus to avoid such contamination, certain devices, known as traps, are used. Of these, the refrigerant traps are very effective. They are, however, quite expensive and are not always available.
(B) Refrigerant Traps.-The devices commonly used for effectively condensing mercury and other vapors and gases are refrigerant traps. They fall into two types as shown in figures $4-15 A$ and $B$. The traps ( $A$ ) are immersed in refrigerants contained in Dewar flasks, while traps ( $B$ ) contain their own refrig-
erants. The ( $B$ ) types of traps, however, are more expensive to keep cold because of inferior heat insulation.

The refrigerants commonly used for this purpose are liquid air and carbon dioxide snow. The temperature of liquid air varies from $-190^{\circ} \mathrm{C}$. to $-183^{\circ} \mathrm{C}$., depending on the extent to which the nitrogen has been boiled out of the liquid air, leaving behind liquid oxygen. At these temperatures, vapors of mercury and water are almost completely trapped since their freezing points are so much higher. The vapor pressure of carbon dioxide being nearly $10^{-7} \mathrm{~mm} . \mathrm{Hg}$ at the temperatures of liquid air, this gas also is removed effectively by a liquid-air trap. But carbon monoxide and the light hydrocarbons, ethylene, ethane, and methane, which have appreciable vapor pressures even at temperatures lower than that of liquid air, are not adequately trapped even by liquid air.

Carbon dioxide snow can be obtained by releasing liquid carbon dioxide into atmospheric pressure and catching it in a linen bag. After it is pressed, acetone or alcohol is added to form a slush. In this form the mixture thoroughly packs the walls of the trap. At $-78^{\circ} \mathrm{C}$., the temperature of this refrigerant mixture, the vapor tension of mercury is $3.2 \times 10^{-9} \mathrm{~mm} . \mathrm{Hg}$, and all the mercury vapor is eliminated after a lapse of a couple of hours. The vapor pressure of water at the tomperature of this refrigerant is about $10^{-3} \mathrm{~mm} . \mathrm{Hg}$, and so water vapor cannot be adequately trapped by this means. Therefore a bulb containing anhydrous phosphorus pentoxide is inserted in the vacuum line in order to remove the water vapor. The vapor pressure of oil used in the rotary pumps and that of grease are quite low at the temperature of carbon dioxide mixture, so that the vapors of oils and greases are effectively removed by this refrigerant.

It is important not to cool the traps by refrigerants too soon after the evacuation is started, to avoid so-called virtual leaks. In using the refrigerants for freezing vapors of mercury and water and carbon dioxide, care must be taken not to cool the trap until the other less easily condensable vapors are exhausted by the pump in order to avoid consequences which degrade the vacuum. It is advisable to keep the trap warm until a pressure of $10^{-2} \mathrm{~mm}$. Hg , at which mercury vapor begins to diffuse into the vacuum system, is obtained. Then only the bottom of the trap is kept in
contact with the refrigerant until the limiting vacuum is reached. Finally the trap is immersed to its full depth in the refrigerant.
(C) Drying Agents.-Many vapors, including that of water, are most effectively removed by refrigerant traps. For the removal of water vapor, a number of drying agents, listed in Appendix I, may be employed with advantage. Of these, phosphorus pentoxide is the most frequently used drying agent. It is usually placed in a porcelain boat which may be inserted in a


Fig. 4-16.
demountable glass bulb shown in figure 4-16. The bulb is joined to the vacuum line and the phosphorus pentoxide is fused in order to reduce its vapor pressure and to prevent it from being blown into the other parts of the apparatus.
(D) Potassium- or Sodium-Lined Traps.-Liquid-air traps are effective in arresting mercury vapor, but often a supply of liquid air is either difficult or impossible to get. If this condition exists, potassium- or sodium-lined traps, as shown by Hughes and Poindexter, ${ }^{17}$ are useful for trapping mercury vapor. A small piece of potassium or sodium is put into a trap which is inserted between the mercury condensation pump and the apparatus to be exhausted and is, after vacuum is obtained, distilled onto the sides of the trap. A mercury condensation pump in conjunction with a potassium trap readily obtains a limiting pressure of the order of $10^{-9} \mathrm{~mm}$. Hg. In arresting mercury vapor, potassium-lined traps are nearly as effective as liquid-air traps.
${ }^{17}$ A. L. Hughes and F. E. Poindexter, Phil. Mag. 50, Series 6, No. 296, 423 (1925).
(E) Traps for Vapors of Oils.-Vapor pressures of oils and paraffins used as pumping media are very low. Oils and to a certain extent paraffins may decompose by the action of heat. Such thermal decomposition may give rise to the evolution of gases with consequent deterioration of vacuum. When an x-ray tube of the Coolidge type is exhausted by mean of an oil condensation pump, it is found that a fine deposit of carbon is formed


Fig. 4-17. Charcoal trap.
on the target of the tube, and the gases, due to thermal decomposition of the oil, cause the rapid destruction of the filament of the x-ray tube. With the paraffin condensation pump, these influences, though remarkably less, are appreciable. They can be practically eliminated by using a trap cooled by solid carbon dioxide mixture. Sometimes electric-refrigerator units are used to trap vapors from pumps in which oils or paraffins are used as pumping media.

In routine experimental work, a charcoal trap of the type shown in figure $4-17$ is satisfactory for use with an oil condensation pump. Such a trap takes in oil and condensable vapors and gases to such an extent that the resulting pressure of the residual gas will be as low as $10^{-8} \mathrm{~mm} . \mathrm{Hg}$. Charcoal traps have the disadvantage of offering very high resistance to the gases passing
through and thus considerably reducing the effective speeds of the pumps.
After some use, a charcoal trap becomes saturated with oil and vapor and hence ineffective. Its effectiveness, however, may be revived by baking it out in vacuum and thus eliminating the oil and vapor.


Fig. 4-17A. The Hickman water-cooled trap.
For ordinary experimental work the Hickman water-cooled trap of the design shown in figure $4-17 A$ is good enough for use with a pump in which Octoil ${ }^{18}$ or paraffin is used as the pumping medium. This trap is slightly less effective than a charcoal trap. But unlike the latter, the resistance $W$ which it offers is so insignificant that the effective speed of exhaust does not differ much from the actual pumping speed.
${ }^{18}$ K C. D. Hickman, J. Franklin Inst. 221, 215 and 383 (1936).

## CHAPTER 5

## PREPARATORY OPERATIONS FOR VACUUM WORK

## Section I. Cleaning Processes

5-1. Cleaning.-A high vacuum cannot be obtained, much less retained, in a system that is not clean. Even a clean vacuum system, after some use, may become contaminated with oil, mercury, and stopoock grease. Then it ceases to be satisfactory for high vacuum. It is therefore necessary to clean the system thoroughly. A vacuum system of glass, when contaminated, can be cleaned by using a saturated solution of potassium bichromate in sulphuric acid, which is much more effective if used hot. Strong nitric acid containing a few drops of methylated spirit and applied directly to the portion to be cleaned is also an effective agent. Either one of these chemical-cleansing processes should be followed first by washing with warm distilled water and then by drying with a blast of dry and dust-free air. Metal vacuum systems contaminated by oils and greases are best cleaned by washing first in solvents such as ether, benzene, etc., and then by warming.
Mercury used in certain types of pumps, gauges, valves, and cutoffs should be perfectly clean. An effective method of cleaning mercury is to filter it and shake thoroughly in a bottle with chromic acid and then in water. It is then allowed to fall in a fine spray, from a leather filter held in a large funnel having a capillary ending, through a very long column of dilute nitric acid in a "drip" tube (figure 5-1) and then similarly through a long column of distilled water. It is then dried by evaporation at about $350^{\circ} \mathrm{C}$. To obtain the cleanest mercury, this filtered and dried mercury is distilled in vacuum with the distilling apparatus shown in figure 5-2. The mercury in the bulb $A$ is heated by an electric heater. Mercury vapor condenses on the air-cooled walls of the bulb $B$, falls into the groove $C$, and thence runs out at $D$.
Even a clean system is not necessarily fully ready for high vacuum. After thorough cleaning, a layer of gas molecules con-
tinues to adhere to the surfaces of the vacuum system. The walls also hold gases in occlusion and in chemical combination. These gases, which can be removed neither by the chemical-cleansing processes nor by continued exhaustion, prevent the attainment of


Fia. 5-1.


Fig. 5-2.
the highest vacuum, and so such gas molecules must be removed. The phenomena of adsorption and occlusion, and the process of elimination of adsorbed and occluded gases, are treated separately in the following section.

## Section II. Adsorbed and Occluded Gases and Their Elimination

5-2. Introduction.-A gas or vapor, brought in contact with an evacuated solid, is partly absorbed by the solid. The part of gas or vapor that disappears from this phase either enters the inside of
the solid or remains outside attached to the surface. The former phenomenon is called occlusion or absorption, the latter adsorption. In adsorption equilibrium, the volume of gas adsorbed is proportional to some power of pressure. An empirical expression of this relation, which is known as Freundlich ${ }^{1}$ adsorption isotherm equation is

$$
\begin{equation*}
v=k p^{1 / n} \tag{5-1a}
\end{equation*}
$$

where $v$ is the volume of the adsorbed gas measured under definite conditions, $\boldsymbol{p}$ the pressure, $k$ and $n$ are constants depending on the adsorbent and gas. The equation, however, cannot describe an isotherm completely from the lowest to the highest pressure region.

Until 1914 there was no satisfactory interpretation of the adsorption mechanism. Thereafter Langmuir made a great advance in the field of the theoretical treatment of the adsorption of gases, leading to the most important adsorption isotherm equation.

5-3. Langmuir Theory of Adsorption (Unimolecular Theory).With the aid of x-ray diffraction patterns of crystals, including those of metals, von Laue, Bragg, and others have shown that the atoms in solid crystalline substances form into regular geometrical arrangements. Langmuir ${ }^{2}$ postulates that there are primary and secondary valence forces between these atoms and that the difference between these two is one of degree. The layer of atoms constituting the surface of a solid presents unbalanced and unsaturated valencies on their external boundary. The field of force surrounding the space lattice of this layer and the space immediately above it is more intense than that between the atoms of the arrays inside the crystal, inasmuch as the atoms of the surface layer have only a part of their valencies satisfied. The existence of such a field of force at the surface accounts for the phenomenon of adsorption, which may be regarded as the attachment of outside atoms or molecules of a gas to the exposed free valencies of the atoms comprising the surface layer.

Gas molecules are in ceaseless agitation and strike at random any surface with which they come in contact. The rate at which they strike a surface has a definite value, which is given by expression 1-48b. According to Langmuir, in almost all cases and at

[^44]all temperatures the molecules striking the surface do not rebound but are held at the surface by the field of force surrounding it so as to form a film which tends to continue the space lattice of the solid. While this process, which is in a way identical to the condensation of vapors on solid surfaces, continues, evaporation of the condensed layer goes on as an independent process. At highly elevated temperatures, this latter process is rapid, and the surface becomes practically free from the film of gas molecules. If, on the ather hand, the field of forces on the surfaces be relatively intense, the rate of evaporation is negligibly small, and the surface becomes completely covered with a layer. Thus the processes of condensation and evaporation conversely function with the ensuing kinetic equilibrium between the rates of condensation and evaporation. Langmuir regards the direct result of such a kinetic equilibrium between the rates of condensation and evaporation as adsorption. In the case of true adsorption, this layer is usually unimolecular, fcr as soon as the surface becomes covered by a single layer one molecule deep, the surface forces are, so to speak, saturated.
Gas molecules in the unimolecular adsorbed layer fill in definite positions with respect to the surface lattice, tending to form a lattice above that of the surface. In crystals there may be a definite number of either the same kind of elementary spaces or other kinds of spaces, while in amorphous bodies the elementary spaces may vary continuously. In both cases, each elementary space has a definite tendency to receive gas. As the pressure of the gas increases, adsorption takes place in steps, the different kinds of spaces being successively filled by adsorbed molecules or atoms. Though the phenomena connected with adsorption are thus varied, some being simple and others complex, Langmuir studied them individually to determine the amount of gas adsorbed as a function of pressure. He has derived quantitative forms of the adsorption isotherm, that is, the quantitative relation between the volume of gas adsorbed and pressure at constant temperature expressed by
\[

$$
\begin{equation*}
v=\frac{v_{\mu} b p}{1+b p}, \tag{5-2}
\end{equation*}
$$

\]

where $v$ is the volume of gas adsorbed, $v_{\mu}$ the volume adsorbed
when the surface is covered with unimolecular layers, $p$ the pressure, and $b$ a constant. At low pressures on plane surfaces the calculated and experimental values were found to be in agreement. ${ }^{3}$ Also Bawn's data ${ }^{4}$ for the adsorption of carbon monoxide and oxygen at $90^{\circ}$ absolute were adequately represented by the Langmuir equat on. His results for argon could not be expressed by a simple equation. The thickness of the adsorbed film of carbon monoxide, oxygen and argon was not greater than would correspond to a unimolecular layer. But at high pressures, experimental values do not agree with the Langmuir equation.

5-4. Multimolecular Theory.-The phenomenon of adsorption of gases at 'ow pressures obeys the Langmuir relation. But at high pressures, deviation from this relation sets in. For most adsorbents, the adsorption isotherms of gases at the ranges of their condensation temperatures are concave toward the pressure axis at low pressures and convex at high pressures. The highpressure adsorption phenomenon, represented by the convex region of the adsorption isotherms, may be attributed to the formation of multimolecular layers.

Brunauer, Emmett, and Teller ${ }^{5}$ have developed the theory of multilayer adsorption. On the assumption that the forces, active in condensation, also produce the phenomenon of Van der Waals' adsorption, they derived an isotherm equation by the method of generalizing Langmuir's treatment of unimolecular adsorption. It is

$$
\ddot{-}-\begin{gather*}
v_{\mu} c p  \tag{5-3a}\\
\left(p_{0}-p\right)\left\{1+(c-1)\left(p / p_{0}\right)\right\}
\end{gather*}
$$

which may be written in the form:

$$
\begin{equation*}
\frac{p}{v\left(p_{0}-p\right)}=\frac{1}{v_{\mu} c}+\frac{c-1}{v_{\mu} c} \frac{p}{p_{0}} \tag{5-3b}
\end{equation*}
$$

where $v$ is the volume of gas adsorbed, $v_{\mu}$ the volume adsorbed when the surface is covered with a complete unimolecular layer of adsorbed gas, $p$ the pressure, $p_{0}$ the saturation pressure of the gas, and ca constant.

[^45]Equation 5-3b is the isotherm equation of the multimolecular adsorption theory for adsorption on a free surface. It represents the general shape of the actual isotherms and also gives fairly satisfactory values for the mean heat of adsorption in the first layer and for the volume of gas required to form unimolecular layer on the adsorbent.

In expression $5-3 a$ as $p \ll p_{0}$, the equation reduces to

$$
\begin{equation*}
v=\frac{\frac{v_{\mu} c}{p_{0}} p}{1+\frac{c}{p_{0}} p} \tag{5-3c}
\end{equation*}
$$

a form of the Langmuir equation with the constant $b$ having the value $c / p_{0}$. At high pressure $p \rightarrow p_{0}, v$ increases and the curve becomes convex to the pressure axis.

5-5. Occluded Gases.-Besides the adsorbed gases on the surfaces, there are gases occluded throughout the material. As regards occluded (absorbed) gas, the methods of production of glass and many metals with which vacuum system; are made, involve liquefaction, which results in the presence of large quantities of dissolved gases throughout the mass of the solidified material. These gases are slowly released when they are exposed to low pressures, with a consequent deterioration of high vacuum. In order to obtain and maintain the highest degree of vacuum it is necessary to eliminate the adsorbed and occluded gases from the vacuum system. At low pressures, the rate of condensation being low and at elevated temperature, the rate of evaporation being comparatively rapid, the surface of a vacuum system can be freed from adsorbed gases when it is brought to higher temperatures while being exhausted. This process of heat treatment in vacuum is very effective. Sherwood ${ }^{6}$ did detailed work on the effect of such heat treatment in vacuo at different temperatures. His results given in the Table 5-1 and represented in figures 5-3, 5-4, and $5-5$, in which volumes of gas are plotted against temperature, show that prolonged heating of glass at $150^{\circ} \mathrm{C}$. to $350^{\circ} \mathrm{C}$. in vacua, removes the surface gases as well as the unimolecular layer of water and absorbed gases. Other gases are liberated also when the

[^46]

Fig. 5-3.


Fig 5-4.


Fig. 5-5.
heating is carried above this temperature. But they originato from the decomposition of glass.

The elimination of adsorbed and occluded gases from a glas
Table 5-1

|  | Cubic millimeters of total gas given off by glass surface <br> area of $350 \mathrm{~cm} .^{2}$ at temperatures |  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Glass | $100^{\circ} \mathrm{C}$. | $150^{\circ} \mathrm{C}$. | $200^{\circ} \mathrm{C}$. | $300^{\circ} \mathrm{C}$. | $400^{\circ} \mathrm{C}$. | $500^{\circ} \mathrm{C}$. | $600^{\circ} \mathrm{C}$. |
| Soda glass | 0 | 36 | 22 | 8 | 6 | 11 | 50 |
| Lead glass <br> G-702-P glass, a <br> borosilicate of <br> sodium and <br> magnesium | 4 | 10 | 10 | 7 | 8 | 12 | 30 |

vacuum system is effected by baking it in an electric or gas oven up to a temperature just below the lowest softening point of the material, from a quarter of an hour to an hour or more. The most
efficient heat treatment is attained when lead glass is heated to $350^{\circ} \mathrm{C}$., soda glass to $400^{\circ} \mathrm{C}$., G-702-P $450^{\circ} \mathrm{C}$. to $500^{\circ} \mathrm{C}$., and Pyrex glass to $600^{\circ} \mathrm{C}$. to $650^{\circ} \mathrm{C}$. These glasses must not be heated to higher temperatures, for the annealing heat of lead glass is $425^{\circ} \mathrm{C}$., soda glass $550^{\circ} \mathrm{C}$., G-702-P glass $600^{\circ} \mathrm{C}$., and Pyrex glass $650^{\circ} \mathrm{C}$. to $700^{\circ} \mathrm{C}$.

5-6. Sorption of Gases by Metals.-The phenomena of sorption of gases by metals are quite complex in nature. When metals are heated strongly, quite appreciable quantities of gases are evolved. These evolved gases comprise adsorbed as well as occluded gases and gases arising from dissociation of oxides, present at the surface. Oxides at the surface layer of metals, excepting that of chromium, are readily dissociated at elevated temperatures. It is difficult to remove gases under the surface layer of metals; both dissclved gases and those held in chemical combination tend to remain even at higher temperatures. Such gases can, however, be removed by the fusion of metals in vacua or by prolonged heating for a number of hours in vacua to near the melting point. Some metals are cleaned by heating in a hydrogen atmosphere and then outgassing in vacua to eliminate the dissolved hydrogen.

The metal components such as electrodes of x-ray tubes, Kenotrons, and electron tubes must be thoroughly outgassed before inserting them in the glass envelopes. This may be effected best in a vacuum stove, the pressure of which is maintained at $10^{-3} \mathrm{~mm}$. Hg or lower. The outgassing temperatures for some metals are given in Table 5-2.

It is essential to eliminate the absorbed and occluded gases from electrically conducting materials such as metal or carbon filaments and other electrodes inside outgassed electrical insulator envelopes. This may be best effected by heating these materials to red or white heat by means of radio frequency eddy currents while the previously outgassed envelope is being exhausted. In this process the temperature must not be raised above the point where the vapor pressure of the metal reaches $10^{-7} \mathrm{~mm} . \mathrm{Hg}$ or volatilization of the metal will occur.

After outgassing the bulb of an incandescent lamp, if its tungsten filament is heated in vacuum to a temperature of $1500^{\circ} \mathrm{C}$., it gives off gases which, measured at normal temperature and pressure, amount to as much as 3 to 10 times the volume of the tungsten
filament. ${ }^{7}$ These gases, which are given off almost instantaneously, consist of some 70 to 80 per cent of carbon monoxide while the rest is mainly hydrogen and carbon dioxide.

Langmuir observed that a platinum filament, heated in vacuum to a temperature of $350^{\circ} \mathrm{C}$., gave off hydrogen and carbon monoxide which, measured at room temperature and pressure, amounted in all to nearly one-tenth of the volume of the filament.

Table 5-2

| Metal | Maximum outgassing temperatures, <br> ${ }^{\circ} \mathrm{C}$. |
| :--- | :---: |
| Copper and copper alloys | 500 |
| Nickel and nickel alloys | $750-950$ |
| Molybdenum | 950 |
| Iron | 1000 |
| Platinum | 1000 |
| Tantalum | 1400 |
| Graphite | $1500-1800$ |
| Tungsten | 1800 |

The different gases given off by filaments of different metals, heated to bright red heat in vacuo until the rate of evolution has decreased to an insignificant value, were studied by Sweetser. ${ }^{8}$ He found that different samples of nickel wire gave off quantities, varying from 5 to $15 \mathrm{~mm} .^{3}$ of gas, while wires of monel, copper, and copper-coated nickel-iron alloy treated similarly gave off 3 to 20 $\mathrm{mm} .^{3}$. The gases evolved from these different metal wires consist of 75 to 90 per cent carbon monoxide and 10 to 20 per cent carbon dioxide, with small amounts of hydrogen. None of these different metal filaments gives off a volume of gas much exceeding that of the filament itself.

The copper anodes used in Coolidge x-ray tubes have been found to give off gases consisting of:

| carbon monoxide. . . . . . . . . . . . | 92 per cent |
| :--- | ---: |
| carbon dioxide. .............. | 7 per cent |
| hydrogen and nitrogen together | 1 per cent |

[^47]Ryder ${ }^{9}$ investigated the nature and composition of the gas evolved by heating untreated commercial copper in vacuo. He found that this metal gives off (in order of decreasing amounts) carbon dioxide, carbon monoxide, water vapor, and nitrogen. A

Table 5-3. Gases Evolved from Copper Heated to $1250^{\circ} \mathrm{C}$. in Vacuum

| Sample | Volume of gas in cm. ${ }^{3}$ per 100 grams of metal | Volume of gas per cm. ${ }^{8}$ of metal | Composition of gas in volumetric per cent |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{SO}_{2}$ | $\mathrm{H}_{2}$ | CO | $\mathrm{N}_{2}$ |
| Refined copper (1) | 2.72 | 0.24 | 58.20 | 7.90 | 19.5 | 14.40 |
| Refined copper(2) | 1.46 | 0.13 | 85.70 | 7.43 |  | 6.87 |
| Refined copper (3) | 1.79 | 0.16 | 33.90 | 28.55 | 37.55 |  |
| Refined copper (4) | 0.73 | 0.07 | 61.10 | 11.11 | 22.22 | 5.57 |
| Electrolytic copper | 7.98 | 0.71 | 10.88 | 39.52 | 49.70 |  |

sample of copper having a volume of $1.31 \mathrm{~cm} .^{3}$, when heated in vacuum to temperatures below $750^{\circ} \mathrm{C}$. gave off gas amounting to $0.2 \mathrm{~cm} .^{3}$ In other words, the total volume of evolved gas was about one-sixth that of copper.

Table 5-4. Gases Evolved from Nickel Heated to $1470^{\circ} \mathrm{C}$. in Vacuum

| Sample | Volume of gas in cm. ${ }^{3}$ per 100 grams of metal | Volume of gas per $\mathrm{cm} .^{3}$ of metal | Composition of gas in volumetric per cent |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{CO}_{2}$ | CO | $\mathrm{H}_{2}$ | $\mathrm{N}_{2}$ |
| Cube nickel | 482 | 42.9 | 2.30 | 90.00 | 3.50 | 4.20 |
| " Mond " nickel | 113 | 10.1 | 2.92 | 72.38 | 24.70 |  |
| Electrolytic nickel | 7.88 | 0.7 | 0.00 | 21.10 | 78.90 |  |

The nature and composition of gases given off by different samples of copper and nickel, heated to $1250^{\circ} \mathrm{C}$. and $1470^{\circ} \mathrm{C}$. respectively in vacua were studied by Hessenbrucher ${ }^{10}$ and the results of his investigation are given in Tables 5-3 and 5-4.

Gases evolved from steel at different elevated temperatures in
${ }^{9}$ Ryder, J. Amer. Chem. Soc. 40, 1656 (1918).
${ }^{10}$ W. Hessenbrucher, Zeits. f. Metalkunde 21, 46 (1929).
vacuo were investigated by Alleman and Darlington. ${ }^{11}$ They measured the volumes of gas given out by a gram of the metal at different temperatures and found the composition by microanalysis. Some of their data are given in Table 5-5.

Table 5-5. Gabes Evolved from Steel

| Sample | Volume of gas in cm. ${ }^{3}$ per gram of metal | Volume of gas in $\mathrm{cm} .^{3}$ per cm. ${ }^{3}$ of metal | Maximum temperature ${ }^{\circ} \mathrm{C}$. | Analysis of gas collected |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | $\mathrm{CO}_{2}$ | $\mathrm{O}_{2}$ | CO | $\mathrm{H}_{2}$ | $\mathrm{N}_{2}$ |
| Steel (1) | 25.2 | 197 | 1468 | 013 | 2.08 | 59.8 | 18.8 | 19.81 |
| Steel (2) | 18.6 | 146 | 1500 | 120 |  | 79.8 | 11.65 | 7.35 |
| Steel (3) | 8.5 | 67 | 1100 | 0.68 | 1.57 | 26.15 | 43.40 | 28.20 |

Similarly, gas evolved from Bessemer steel ( 0.1 per cent carbon) heated to different temperatures has been analyzed, with the results shown in Table 5-6. The total amount of gas evolved was $28.1 \mathrm{~cm} .^{3}$ per one gram of the metal. From these data, it is obvious that hydrogen and carbon dioxide were given off at $1250^{\circ} \mathrm{C}$.

Table 5-6. Gases Evolved from Bessemer Steel at
Different Temperatures

| Gas | At $1000^{\circ} \mathrm{C}$. | At $1250^{\circ} \mathrm{C}$. | At $1500^{\circ} \mathrm{C}$. | At $1675^{\circ} \mathrm{C}$. |
| :--- | :---: | :---: | :---: | :---: |
|  | 1.08 | 0.62 | 0.00 | 0.00 |
| $\mathrm{CO}_{2}$ | 2.4 | 3.07 | 4.28 | 6.25 |
| $\mathrm{O}_{2}$ | 48.9 | 56.10 | 18.75 | 8.42 |
| CO | 21.16 | 15.08 | 4.20 | 1.10 |
| $\mathrm{H}_{2}$ | 26.46 | 25.13 | 72.77 | 84.23 |
| $\mathrm{~N}_{2}$ |  |  |  |  |

and lower, while the outgassing of nitrogen, oxygen, and carbon monoxide requires much higher temperatures. The volumes of gas given out by different samples of steel are comparatively larger than those given out by tungsten, copper, and nickel.

Tungsten and graphite are outgassed by prolonged heating in vacuo to a temperature of $1800^{\circ} \mathrm{C}$., and molybdenum to $1000^{\circ} \mathrm{C}$. These vacuum-treated samples may be exposed to normal pressure

[^48]and the gases which they then take up can be readily eliminated by subsequent reheating to moderate temperatures in vacuo if they are not touched with the fingers.
Some metals, if slightly oxidized, give up their gases in vacuo only with great difficulty. Many metals of this type may be subjected to heat treatment in a hydrogen atmosphere to remove the surface contamination. Dissolved gases near the surfaces of metals are to some extent replaced by hydrogen. This hydrogen substitute, however, is readily forced off by subsequent heat treatment in vacuo. It is essential to outgas a vacuum system made of either glass or metal by heat treatment in vacuo in order to prepare it properly for the highest vacua.

## CHAPTER 6

## PRODUCTION OF HIGH VACUA BY PHYSICAL CHEMICAL METHODS

6-1. Introduction.-Evacuation of gases from an enclosure by means of vacuum pumps is an effective method. Among the vacuum pumps, condensation pumps exhaust the gases which rough-vacuum pumps are unable to remove. High vacuum attained by condensation pumps may be maintained by continuous pumping. But if the high-vacuum enclosure be sealed off from the pumping system, the pressure of the residual gas rises considerably higher than the limiting pressure attained by the pump, because in the sealing process the heated glass gives off considerable gas into the vacuum enclosure. The abstraction of residual gases from such sealed-off enclosures can be effected by physical-chemical methods and by electrical clean-up. Of these, the former involve the use of "getters" which remove the residual gases from the evacuated sealed-off enclosures and maintain the vacuum against certain deteriorating effects. Among the getters, the operation of those which are of suitable porous nature depends on the adsorption of residual gases on their refrigerated surface. There are others whose abstraction performance is based on the absorption of residual gases. Besides these two trpes, there are getters whose function is based on their chemical combination with the residual gases.

6-2. Refrigerated Outgassed Charcoal as a Getter.-Dewar ${ }^{7}$ found that refrigerated charcoal which had been previously outgassed was an effective getter for the production of high vacua. It is the most outstanding of its kind; this may be due to its enormous surface area, presented by the pores in the charcoal, as great as 2500 square meters per gram. Dewar recommended the use of coconut charcoal. Charcoal may be made from soft coconut kernel and also from its shell. Charcoal from coconut shell is

[^49]denser and as an adsorbent more effective than that from the soft part of the coconut.

The activation of charcoal for use as a getter is effected by heating it in a suitable glass bulb to a temperature range of $400^{\circ} \mathrm{C}$. to $600^{\circ} \mathrm{C}$. in vacuum produced by rough-vacuum pumps until the gas evolved from the charcoal is insignificant. Charcoal, however, should not be heated to higher temperatures (of the order $850^{\circ} \mathrm{C}$. or more), as its adsorptive power will then be impaired by crystallization and the consequent loss of surface area.


Fig. 6-1. After outgassing, the charcoal bulb (figure 6-1) is cut off from the pump and cooled to a low temperature, in which condition it serves as an effective getter for adsorption of residual gases from a vacuum system.

Many investigators in this field have measured the adsorption of gases by charcoal. Most of the available data, however, comprise the measurements of the adsorption of gases at pressures above 1 mm . Claude ${ }^{2}$ measured the adsorption of $\mathrm{H}_{2}, \mathrm{He}, \mathrm{Ne}$, and $\mathrm{N}_{2}$ by charcoal at very low temperatures and low pressures, and his measurements, being of special interest to the science of high vacua, are given in Table 6-1.
From these results it is obvious that the adsorption of neon by charcoal is much lower than that of hydrogen, although the former has a higher boiling point than the latter, and that the volume of a gas adsorbed at very low pressures tends to be proportional to pressure. At comparatively higher pressures the volume $v$ of the adsorbed gas, measured under definite conditions, may be expressed by Freundlich's equation 5-1 $a .^{3}$ Equation 5-1 $a$ which expresses the adsorbed gas-volume-pressure relation may be written in the form,

$$
\begin{equation*}
\log v=\frac{1}{n} \log p+\log k \tag{5-1b}
\end{equation*}
$$

Therefore, if $v$ be plotted against $p$ on log-log scale, a linear volume-pressure-relation is obtained as expected. The slope of this straight line gives the value of $1 / n$ which at low pressures ap-

[^50]
## 6-2. REFRIGERATED OUTGASSED CHARCOAL

proaches unity. Hence the volume of adsorbed gas at this range of pressure is proportional to pressure as Claude's results suggest. Assuming this adsorption law to be valid down to very low pres-

Table 6-1. Adsorption of Gases by Charcoal

| Nitrogen $90.6^{\circ}$ abs. |  | Hydrogen $77.6^{\circ}$ abs. |  | Neon $77.6^{\circ}$ abs. |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\stackrel{p}{\mathrm{~mm} .} \mathrm{Hg}$ | $v$ c.c. at atm. press. | $\stackrel{p}{\mathrm{~mm} .} \mathrm{Hg}$ | $\begin{gathered} v \\ \text { c.c. at } \\ \mathrm{a}: \mathrm{m} . \text { press. } \end{gathered}$ | $\begin{gathered} p \\ \mathrm{~mm} . \mathrm{Hg} \end{gathered}$ | $v$ c.c. at atm. press. |
| 0.004 | 9.35 | 0.006 | 0.105 | 0.45 | 0.105 |
| . 010 | 18.70 | 0115 | . 21 | . 88 | . 21 |
| . 032 | 37.4 | . 0205 | . 42 | 1.30 | . 32 |
| . 088 | 46.6 | . 036 | . 84 | 1.74 | . 42 |
| . 385 | 56.6 | . 083 | 2.05 | 3.50 | . 84 |
| 1.107 | 65.3 | . 176 | 3.71 | 5.30 | 1.22 |
| 11.50 | 93.0 | . 475 | 8.40 | 7.20 | 1.63 |
| 33.2 | 103. | 1.060 | 14. | 11.30 | 2.44 |
| 90. | 112. | 3.50 | 28. | 15.5 | 3.25 |
| 247. | 121. | 8.7 | 42. | 19.4 | 4.06 |
|  |  | 20.6 | 56. | 30.5 | 6.18 |
|  |  | 43.7 | 63. | 40.5 | 8.01 |

sures, from Claude's data, Dushman ${ }^{4}$ derived the amounts of hydrogen and nitrogen in terms of their volumes, measured at a pressure of 1 dyne $/ \mathrm{cm}^{2}{ }^{2}$, adsorbed by 1 gram of charcoal at equi-

Table 6-1a. Adsorption of Gas by Charcoal at Low Temperatures

| Hydrogen ( $77.6^{\circ}$ abs.) |  | Nitrogen ( $90.6^{\circ} \mathrm{abs}$.) |  |
| :---: | :---: | :---: | :---: |
| $\begin{gathered} p \\ \left(\text { dynes } / \mathrm{cm} .{ }^{2}\right. \text { ) } \end{gathered}$ | $v$ (c.c. measured at 1 dyne $/ \mathrm{cm} .{ }^{2}$ ) | $\begin{gathered} p \\ \text { (dynes/cm. }{ }^{2} \text { ) } \end{gathered}$ | $v$ (c.c. measured at 1 dyne $/ \mathrm{cm} .{ }^{2}$ ) |
| 8. | 106,000 | 5.3 | 9,500,000 |
| 1. | 13,250 | 1 | 1,500,000 |
| 0.1 | 1,325 | 0.1 | 180,000 |
| 0.01 | 133 | 0.01 | 18,000 |
| 0.001 | 13 | 0.001 | 1,800 |

librium pressures below 1 dyne $/ \mathrm{cm} .^{2}$ These extrapolated values are given in Table 6-1A.

- Dushman, Gen. Elec. Rev. 24, No. 1, 63 (1921).

It may be observed that at a pressure of 0.01 dynes/cm. ${ }^{2}$ (which is maximum pressure for the efficient operation of hot cathode high vacuum instruments) 1 gram of charcoal, such as used by Claude, would clean up about $130 \mathrm{~cm} .^{3}$ of hydrogen or $18,000 \mathrm{~cm} .^{3}$ of nitrogen from a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ down to 0.01 dyne/cm. ${ }^{2}$

From Table 6-1A, with the units used we may obtain the following values of $k: k=1.325 \times 10^{4}$; for hydrogen at $77.6^{\circ}$ abs. $k=1.8 \times 10^{6}$; for nitrogen at $90.6^{\circ}$ abs.
(A) Limiting Pressure Attained by "Activated" Char-coal.-To deduce an expression for the limiting pressure $p$ obtained by activated charcoal, consider a vacuum system whose volume is $V$ with an initial pressure $p_{0}$ and whose gaseous content, under the same chosen condition of pressure of 1 dyne $/ \mathrm{cm} .^{2}$ at $0^{\circ} \mathrm{C}$., occupies the volume $v_{0}$. When the charcoal is cooled with liquid air the gaseous content in the vacuum system continues to be adsorbed until the pressure of the residual gas attains the equilibrium pressure at liquid air temperature. If $v$ be the volume of adsorbed gas measured at a pressure of 1 dyne $/ \mathrm{cm} .^{2}$ and $0^{\circ} \mathrm{C}$., the volume of residual gas, left behind in the vacuum system, measured under the same conditions will be $v_{0}-v$, exerting a pressure of $\left(v_{0}-v\right) / V$ in the vacuum system. The limiting pressure attained by the adsorbent, therefore, is given by

$$
\begin{equation*}
p=\frac{v_{0}-v}{V} \tag{6-1a}
\end{equation*}
$$

where
Hence

$$
\begin{align*}
& v=k p^{1 / n} \text { and } v_{0}=V p_{v} \\
& p=\frac{v_{0}-k p^{1 / n}}{V} \text { or } p V=v_{0}-k p^{1 / n} \tag{6-1b}
\end{align*}
$$

so that if $n$ is taken to be unity, which is certainly justifiable at these low pressures, a simple expression for the limiting pressure $p$ can be obtained which may be written

$$
\begin{equation*}
p=\frac{v_{0}}{V+K}=\frac{V p_{0}}{V+K} \tag{6-2}
\end{equation*}
$$

In the limiting pressure equation 6-2, the values of the terms $V$ and $p_{0}$ are known by direct measurement. The value of $k$ for any gas may be derived from the adsorption measurements of the gas.

If the measured values $V$ and $P_{0}$ and the calculated values of $k$ fbr each gas separately be introduced in equation 6-2, we have the limiting pressure for each gas obtained by the adso bent charcoal. Daly and Dushman ${ }^{5}$ measured the adsorption of hydrogen and the limiting pressure obtained by 3 grams of activated charcoal immersed in liquid air. Their results, given in Table 6-2, may serve as a verification of the limiting pressure expression.

In this way it was found that a charcoal getter cooled by liquid air is capable of absorbing appreciable volumes of hydrogen giving limiting pressures of the order of less than 0.0001 dynes $/ \mathrm{cm} .^{2}$

Table 6-2

| Volume <br> (cm. $^{8}$ ) | Pressure <br> (dynes/cm. $^{2}$ ) <br> after seal- <br> ing off | Initial <br> pressure in <br> dynes/cm. <br> of hydrogen | Final pres- <br> sure at room <br> temperature <br> (dynes/cm. $^{2}$ | Pressure at <br> liquid-air <br> temperature <br> (dynes/cm. $^{2}$ ) |
| :---: | :---: | :---: | :---: | :---: |
| 3025 | 0.0180 | 0.31 | 0.014 | 0.0004 |
| 100 | .104 | 8.64 | .02 | .0004 |
| 3025 | .022 | 8.33 | 2.0 | .15 |
| 100 | .28 | 17.7 | 0.24 | .0016 |

6-3. Getters Based on Sorption of or Chemical Combination with Residual Gases.-(A) Palladium Black.-Some metals under certain conditions may serve as getters on account of their appreciable absorption power. Palladium black is known as an absorbent of hydrogen. It exists, however, as far as absorption of hydrogen is concerned, in both active and inactive forms. The activity of any sample which may decrease with time may be revived by heat treatment in hydrogen. The absorbing power of palladium black varies with the degree of fineness of its sample and with the subsequent heat treatment during exhaustion.

To use palladium black as an effective getter for the absorption of hydrogen, it must be carefully prepared. The method of preparation, described by Hoitsema and Dushman, ${ }^{6}$ is as follows: The palladium in the form of sheet or wire is dissolved in aqua regia and evaporated on a water bath until the acid vapors have disappeared; the solution is then diluted, warmed, and a con-

[^51]centrated solution of sodium carbonate is added to neutralize free acid. A small quantity of acetic acid is then added, the solution is warmed, and a warm concentrated solution of sodium formate added. The palladium comes down as a black flocculent precipitate which settles rapidly at the bottom of the beaker. The supernatant liquid is decanted and the precipitate washed with distilled water till the wash water shows no traces of chlorides. The palladium black is then washed with alcohol and transferred, while damp, into a U-tube where it is dried by blowing dry and dust-free air over it. To prevent palladium black from being blown away, plugs of glass wool may be used. This U-tube of palladium with gentle warming is exhausted by a rough-vacuum pump and is kept ready for use as a getter to absorb residual hydrogen from a sealed-off vacuum system.

The absorption of hydrogen by such prepared active samples of palladium black at liquid-air temperature is much greater than that of the same gas by charcoal. Certain specimens of palladium, however, for undetermined reasons are incapable of absorbing hydrogen. Its erratic behavior renders doubtful its value as a getter. But there are active specimens which are quite efficient in this respect (see appendix III). Even at higher temperatures such specimens can be used advantageously as getters. Though the sorption of hydrogen by palladium black, at the temperature of liquid air, is a phenomenon of adsorption, there is reason to believe that at higher temperatures, at least, it is one of absorption.
(B) Platinum as a Clean-up Agent.-Platinum black, prepared much in the manner of palladium black, is a getter. At the temperature of liquid air, hydrogen is also adsorbed, while at higher temperatures, it is absorbed by platinum black. It is able to take up 100 times its volume of hydrogen, and more than 800 times its volume of oxygen. The oxygen is removed with great difficulty. This fact indicates that the adsorption is not a reversible phenomenon. Platinum black, however, is less efficient as a getter, than palladium black.
(C) Other Metals as Getters.-The behavior of hydrogen in contact with tantalum is in certain respects similar to that of the same gas in contact with platinum black. The former, however, absorbs larger volumes of hydrogen than the latter. Tantalum aboorbs as much as 740 times its own volume of the gas at temperar.
tures of the order of $600^{\circ} \mathrm{C}$. On subsequent heating to higher temperatures in a vacuum, about 550 volumes are given off, while even the rest of the gas is removed at the approach of the melting point of the metal. This metal at elevated temperatures takes up the residual gases, oxygen and nitrogen; the sorption in these cases is mainly effected by chemical combination of these gases with the metal. Because of these properties, tantalum is frequently used for radio tube anodes.

Metals having low vapor pressures, such as thorium, zirconium, and columbium, are highly suitable as clean-up agents for the removal of chemically active gases, such as oxygen, nitrogen, hydrogen, water vapor, the oxides of carbon, and the like. These metals in certain respects behave in much the same way as tantalum.

Tungsten and molybdenum are not frequently used as getters. They may, however, under certain conditions be utilized for the removal of residual gases, and they are effective at temperatures above $950^{\circ} \mathrm{C}$. and at pressures below 100 dynes $/ \mathrm{cm} .^{2}$ Residual oxygen is cleaned up by the chemical combination of the gas with the metals, forming oxides which are volatile above $1000^{\circ} \mathrm{C}$. Hydrogen, dissociated by the high temperature, condenses as atomic hydrogen on the walls of the container, cooled by liquid-air refrigeration.
Alkali metals react with nitrogen, oxygen, hydrogen, and mercury vapor. They combine chemically with hydrogen to form hydrides. Sodium takes up hydrogen at temperatures above $300^{\circ} \mathrm{C}$. and forms the compound $\mathrm{Na}_{2} \mathrm{H}$, while potassium absorbs it and forms the compound $\mathrm{K}_{2} \mathrm{H}$. Similarly, metallic calcium rapidly combines with hydrogen at a dull red heat temperature to form $\mathrm{CaH}_{2}$. The sorption of nitrogen, oxygen, and hydrogen is especially strong when the alkali metal is the cathode of a glow discharge. The dissociation pressures in $\mathrm{K}_{2} \mathrm{H}$ and $\mathrm{Na}_{2} \mathrm{H}$ being low, these metals should clean up hydrogen to a very low residual equilibrium.
Magnesium, calcium, and barium are extensively used as cleanup agents, since they combine chemically with all the gases except those of the inert group. After introducing these metals in the vacuum systems, they are vaporized and condensed on the walls of the sealed-off vacuum devices so as to form mirror films. These metallic films are effective getters, but are slower in action than
when in the vapor phase. They will react chemically with the residual gases which may subsequently be liberated from the walls of the apparatus. Their surfaces being clean, the residual gases are removed even by adsorption.

6-4. Clean-up of Gases at Low Pressures by Electrical Dis-charge-" Aging by Voltage."-The gradual lowering of gas pressure during the passage of an electrical discharge in a " vacuum tube " was first observed as long ago as 1858 by Plücker. As the gas pressure decreases, the voltage required to pass current through the tube increases until the vacuum becomes nonconducting. Similarly, gas-filled x-ray tubes harden when a discharge is passed for some time, since the higher the voltage to produce the discharge, the harder the resulting x-rays become. In spite of many investigations on this effect, with the experiments on high potentials and cold cathodes, the mechanism of the clean-up remained more or less obscure. Much of the obscurity has been got over by the fairly precise information obtained from the experimental study of incandescent lamps and thermionic tubes.

From the information, it was concluded ${ }^{7}$ that the following causes contribute to the " aging" by voltage:
(1) Chemical action between the gas and the glass, ${ }^{8}$ and the gas and the cathode. ${ }^{9}$
(2) Chemical or mechanical action between the gas and the anode. ${ }^{10,11,12}$
(3) Chemical action due to active nitrogen. ${ }^{13}$
(4) Mechanical occlusion of the gas in the glass, ${ }^{14}$ the cathode, ${ }^{15}$ and the disintegrated part of the cathode. ${ }^{16}$

The life of a vacuum-type incandescent lamp depends on gas pressure in the lamp and is much longer for lower pressures. To realize the lower pressures, it is usual to exhaust the lamps to a

[^52]high degree of vacuum, the residual gas pressure being less than 1 dyne $/ \mathrm{cm} .^{2}$ The adsorbed and occluded water vapor and gases are eliminated by heat treatment in vacuo for a considerable length of time. In view of the necessity in individual economy for speedy and large-scale production, the long time consumed in this thorough exhaustion is an objectionable feature. This economic difficulty has been surmounted by increasing the speed of the lamp manufacture and production. The time of exhausting a lamp from atmospheric pressure to a pressure of a few dynes per square centimeter has been reduced to an extent very small compared to the earlier time of exhaust and that of subsequent outgassing. In a very short period of time, the lamp is exhausted from atmospheric pressure to a low pressure, the glass is raised to a higher temperature to eliminate as much water vapor as possible, and the lamp is sealed off.

Under these conditions, there remains a considerable amount of residual gas, to which is added the gas subsequently evolved by sealing off the tube and heating the filament. In view of the fact that such rise of pressure will be a serious handicap to the lifetime of a lamp, methods by which residual gases can be cleaned up to obtain the required low pressures have been devised.

One of the methods for cleaning up residual gases from sealed-off incandescent lamps whose pressures usually vary from $10^{-1}$ to $10^{-3} \mathrm{~mm} . \mathrm{Hg}$, involves running of such incandescent lamps at a potential higher than for normal running and exceeding the socalled ionizing potential. In this range of pressures which exceeds a certain critical value, the electrons emitted by the negative end of the filament, under the influence of the positive voltage produced by the other terminal, ionize the residual gas. As a result of this ionization phenomenon, a blue glow fills the bulb of each incandescent lamp, then diminishes in intensity, flickers, and finally disappears with the accompaniment of the clean-up of the gas. In this way Dushman and Huthsteiner, ${ }^{17}$ using a voltage 130 per cent of the normal working range, could reduce the residual gas pressure from $5 \times 10^{-3} \mathrm{~mm}$. to $10^{-5} \mathrm{~mm} . \mathrm{Hg}$ in about sixteen minutes.

6-5. Clean-up of Gases by Electro-Chemical Methods.-In improving the vacuum by an electric discharge without employing ${ }^{17}$ See S. Dushman, Gen. Elec. Rev. 24, No. 7, 677 (1921).
a getter, the filament, according to Whitney, is disintegrated and part of its material is vaporized, with a blackening effect of the lamp. These drawbacks are eliminated in the method of an elec-tric-glow discharge with a getter. With this method, the clean-up of residual gas is much accelerated.

The use of phosphorus as a getter in conjunction with electric discharge was suggested by Malignani in 1884. Formerly this method consisted of distilling a small amount of some such substance as phosphorus, arsenic, sulphur, or iodine into the bulb of an incandescent lamp from a top tube. With the introduction of one of these vapors, a high current was simultaneously passed through the filament, the lamp being closed from the pump and sealed off. This flash gave rise to a blue glow which would quickly disappear with the accompaniment of a considerable drop of pressure.

In the present process, the wire is coated with an alcoholic mixture of red phosphorus and some salt such as sodium silicate to prevent subsequent blackening by tungsten vapor from the filament. After the lamp is exhausted, outgassed by heat treatment, and sealed off, it is flashed with gradually increasing voltage. Consequently, as the phosphorus is vaporized from the filament, the blue glow which fills the bulb disappears soon and the residual gases are cleaned up. In this method, a small quantity of phosphorus cleans up 90 per cent of the residual gas in the lamp during the blue-glow period, which lasts for about a minute. The rate of clean-up during this time is much more rapid than that obtained subsequently. The final pressure attained on flashing varies from $10^{-2} \mathrm{~mm}$. to $10^{-6} \mathrm{~mm}$. of Hg . During life the pressure drops very slowly and even after the filament burns out there is no pressure increase in the bulb.

To study the characteristic effects of the method of glow discharge and the method of an electrical glow discharge with phosphorus getter, Dushman and Huthsteiner ${ }^{18}$ took a lamp containing two independent filaments and joined it to an ionization gauge. The characteristic results of the clean-up by electric discharge without and with phosphorus getter are shown in figure 6-2. Curve $A$ represents the fall of pressure due to only one filament raised to incandescence without the use of phosphorus getter, the
${ }^{18}$ S. Dushman and Huthsteiner, Gen. Elec. Rev. 24, No. 7, 678 (1921).
electric potential being applied between the two ends of the incandescent filament. Curve $B$ shows the pressures obtained without getter by using the second filament as anode and raising it to 250 volts. Curve $C$ represents the clean-up of the residual gas by the phosphorus-gettered electrical discharge with 250 volts


Fig. 6-2.
on the anode filament. The pressure drop due to the latter method obviously is much more rapid than that due to the method of ungettered electric discharge.

In the method of gettered electric discharge, the vapor formed by volatilization of any getter such as phosphorus, arsenic, sulphur, iodine, or any substance that can readily be sublimated, assists in maintaining a glow discharge at lower residual gas pressures; and furthermore the deposit, subsequently formed by condensation of these vapors, seals up the gases driven into the glass walls.
.

## APPENDIX I

Values of Mg of Residual Water Vapor per Liter of Gas Dried at $25^{\circ}$ C.*

| Drying agent |  | $\mathrm{Mg} \quad \mathrm{H}_{2} \mathrm{O}$ |
| :---: | :---: | :---: |
| A filter at $-194^{\circ}$ |  | $1.6 \times 10^{-28}$ |
| Phosphorus pentoxide | $\mathrm{P}_{2} \mathrm{O}_{5}$ | $2 \times 10^{-5}$ |
| Magnesium perchlorate | $\mathrm{Mg}\left(\mathrm{ClO}_{4}\right)_{2}$ | $5 \times 10^{-4}$ |
| Magnesium perchlorate trihydrate | $\mathrm{Mg}\left(\mathrm{ClO}_{4}\right)_{2} 3 \mathrm{H}_{2} \mathrm{O}$ | $2 \times 10^{-3}$ |
| Potassium hydroxide | KOH (fused) | 0.002 |
| Aluminum oxide | $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 0.003 |
| Sulphuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 0.003 |
| Sulphuric acid, $95.1 \%$ | $\mathrm{H}_{2} \mathrm{SO}_{4}, 95.1 \%$ | 0.3 |
| Magnesium oxide | MgO | 0.008 |
| Sodium hydroxide | NaOH (fused) | 0.16 |
| Calcium bromide | $\mathrm{CaBr}_{2}$ | 0.2 |
| Calcium oxide | CaO | 0.2 |
| Calcium chloride (gran) | $\mathrm{CaCl}_{2}$ (gran) | 0.14 to 0.25 |
| Calcium chloride (fused) | $\mathrm{CaCl}_{2}$ (fused) | 0.36 |
| Zinc chloride | $\mathrm{ZnCl}_{2}$ | 0.8 |
| Zinc bromide | $\mathrm{ZnBr}_{2}$ | 1.1 |
| Copper sulphate | $\mathrm{CuSO}_{4}$ | 1.4 |

* International Critical Tables, Vol. III, p. 385. McGraw-Hill Book Co., New York (1928).


## APPENDIX II

## Vapor Prebsures of Liquids Useid in Cleansing Process, etc.

The pressures are in millimeters of mercury at $20^{\circ} \mathrm{C}$.
Liquid
Vapor Pressures mm . of Hg at $20^{\circ} \mathrm{C}$.
Acetone $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}$

184.8

Carbon disulphide $\mathrm{CS}_{2}$
298.0

Chloroform $\mathrm{CHCl}_{3}$
159.6

Ethyl alcohol $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$
43.9

Ethyl bromide $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{Br}$ 387.0
Methyl alcohol $\mathrm{CH}_{4} \mathrm{O}$ ..... 96.0
Turpentine $\mathrm{C}_{10} \mathrm{H}_{6}$. ..... 4.4
Water $\mathrm{H}_{2} \mathrm{O}$. ..... 17.535
Mercury Hg ..... 0.001201

## APPENDIX III

Adsorption of Hydrogen by Palladiom Blaci*
$P$ is the pressure in millimeters of Hg , and $V$ the volume at stendard pressure and temperature per gram of palladium black.

| $-190^{\circ} \mathrm{C} .:$ | $P=$ | 0.0005 | 0.001 | 0.002 | 0.005 | 0.012 | 0.025 |
| ---: | :--- | :--- | :--- | :---: | :---: | :---: | :---: |
| $V=$ | 2.05 | 3.06 | 33.0 | 40.0 | 47.2 | 63.0 |  |
| $+20^{\circ} \mathrm{C} .: P=$ | 0.001 | 0.005 | 0.037 | 0.110 | 0.315 | 0.76 |  |
| $V=$ | 0.10 | $0: 26$ | 0.40 | 0.52 | 0.70 | 0.92 |  |

[^53]
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