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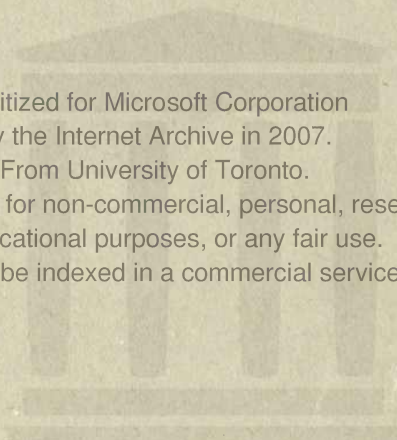
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PHYSICS
D
PRODUCTION AND MEASUREMENT

OF

HIGH VACUUM



By

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PREFACE

The present volume is an expansion and revision of a series of articles published in the *General Electric Review* during 1920-21. The subject of high vacua has become of such technical and scientific importance that it is hardly necessary to apologize for attempting to incorporate the information available on this topic into a convenient form for reference.

Naturally the author has drawn to a large extent upon the results of numerous investigations carried out in this laboratory by Dr. Langmuir and his associates. To Dr. Langmuir, especially, he wishes to express his sincere gratitude for constant encouragement and helpful suggestions.

He also feels greatly indebted to Dr. Whitney for constant interest in the present undertaking, and for placing at his disposal the facilities of the laboratory for pursuing various lines of purely scientific work.

An attempt has been made to give credit whenever possible to all those associated with the author in the field of high vacuum investigation and he can only say in addition that he has appreciated their constant co-operation and efforts in a line of work which is often accompanied by discouragements and negative results.

The individual chapters were originally written as separate discussions, without any attempt at correlation. For the purpose of republication in book form, it was necessary to revise some sections completely and the reader may find errors both of omission and commission. The author will appreciate having his attention drawn to such cases.

Research Laboratory,
General Electric Company.,
Schenectady, N. Y.
Sept. 1, 1922

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INTRODUCTION

"Nature abhors a vacuum." This statement represents the sum total of the knowledge possessed by the ancients of a field of scientific investigation which within the past decade has yielded results of extreme importance. In 1643, Torricelli, a pupil of Galileo, showed that nature abhors a vacuum to a limited extent and the discoverer of the fact that the atmosphere exerts a pressure equivalent to that of a mercury column 30 inches in height, is remembered by the designation "Torricellian vacuum" for the space above the mercury in the barometric tube.

No doubt Torricelli imagined that this space is a "perfect void." We now know, however, that in this space there is mercury vapor at a pressure corresponding to about two or three millionths of an atmosphere and also traces of water vapor and air whose pressure may often amount to one or more millionths of an atmosphere.

In 1654 Otto von Guericke invented the first mechanical air-pump which was subsequently improved by Boyle, Hawksbee, Smeaton and others. During the two hundred years or so that followed, the interest in low pressure phenomena was more or less academic and often that of the dilettante. The paths of glory laid out by Newton, Laplace and Maxwell in mathematical physics, and by Priestly, Lavoisier and Faraday in experimental science, were so enticing that little or no enthusiasm could be aroused in investigations of "empty space." However, with the development of the carbon filament lamp on the one hand, and the discovery by Geissler and others of curious electrical phenomena in gases at low pressures, there began a series of investigations in this field which have not only increased enormously our knowledge of the technique for the production of lower and lower pressures, but have also led to results which have profoundly affected our views of the nature of matter and energy.

When Crookes first observed the phenomena of cathode rays, he thought that he had discovered a fourth, or radiant state of matter. A further investigation of this subject by J. J. Thomson led him, as is well known, to the conclusion that in the con-

duction of electricity through gases at low pressures, the negative current, or so-called cathode rays, is carried by extremely small corpuscles or *electrons*, whose mass is about one two-thousandths of that of a hydrogen atom while the charge is exactly the same as that carried by a hydrogen ion in electrolysis, but opposite, of course, in sign. These electrons are the principal carriers of the current in all cases of conduction in gases at low pressures. It was also observed that electrons are emitted from metals under the influence of light, and Richardson showed that electrons are emitted from incandescent metals. The conclusion was therefore drawn that electrons are present in the atoms of all elements—a conclusion which was very soon corroborated by observations on the radio-active elements.

With the discovery by Roentgen of X-rays, the study of so-called vacuum tube phenomena entered upon a new phase which has led not only to increased knowledge of the structure of matter and the nature of X-rays, but also to vast improvements in both the devices for the production of these rays and their application to medical diagnosis and therapy.

The mutual effects of purely scientific discovery and technical achievement have at no other time been better illustrated than in the history of the development of the hot cathode high vacuum devices which play such an important role at the present time in both the application of X-rays and of wireless telephony. The history of this development has been so interwoven with the progress achieved during the past decade in the field of high vacua that a few remarks on this subject may not be out of place in this connection.

It has already been mentioned that electrons are emitted from the surface of incandescent metals. A careful study of the variation in the number of electrons emitted per unit area with change in temperature led Richardson to the theory that the electrons are emitted from the metal by a process quite similar to that of ordinary evaporation. The mathematical relations are the same in both cases and, as in the case of ordinary molecular evaporation, it is also possible to calculate the heat of evaporation of the electrons for different kinds of surfaces.

This view of the existence of an electron emission *per ipse* was opposed by a large number of investigators who maintained that the observed emission of electrons is a secondary effect due to chemical reactions at the surface, between the metal and the residual amount of gas present in the vessel. There was some excuse for this view, as Richardson's experiments were not carried out at very low pressures. The conclusion was therefore

quite prevalent that in a "perfect vacuum" the electron emission would disappear.

A similar view was held with regard to the photo-electric effect, in which case electrons are emitted by the action of ultra-violet and ordinary visible radiation.

In order to throw some light on these problems, Dr. Langmuir carried out a series of experiments on electron emission in which special care was taken to obtain extremely low pressures. The results of this investigation showed that not only does the electron emission persist even in the best obtainable vacuum, but that the rate of emission at any given temperature is a specific property of the metal. It was found that the power of emitting electrons is also greatly decreased by slight traces of different gases, even at very low pressures. However, if the vacuum is sufficiently good this electron emission is quite reproducible and constant, so that further improvement in degree of vacuum causes no increase in emission. It was also observed that at these low pressures the electron current exhibits space charge effects, that is, the mutual repulsion between the electrons emitted from the hot surface limits the further emission of electrons, and the electron current to the anode is then dependent upon the anode voltage. Such an effect could arise only under such conditions that the number of positive ions formed by collisions between electrons and gas molecules is extremely small, in other words, at very low gas pressures. This accounts for the fact that this phenomenon was not observed by previous investigators.

These discoveries immediately paved the way for development of the hot cathode X-ray tube by Dr. Coolidge and also led to the development of other hot cathode devices, such as the kenotron, pliotron and dynatron, whose application in wireless telephony and telegraphy has been of immense importance. At the same time the necessity for producing and maintaining high vacua in these devices has led to a vast amount of improvement in methods of exhaust.

While the phenomena of electrical conduction in gases at very low pressures have thus served to arouse a great deal of interest in the subject of high vacua, a number of investigations in other fields of physics and chemistry have also led to greater interest in the same field. The work of Knudsen, Smoluchowsky, Gaede and others on the application of the kinetic theory of gases to low pressures, and the striking results obtained by Langmuir on the mechanism of chemical reactions at low pressures have led to new views upon the nature of chemical and physical forces

between atoms and we can look forward, as a result of these investigations, to solving some of the most vexing problems in both physics and chemistry by a study of the phenomena in gases at very low pressures.

Of necessity, as the technique of high vacuum production has improved, methods have been developed for measuring these extremely low gas pressures. A great deal of literature has been published during recent years on this whole subject, and a great deal of information has been gradually acquired in different laboratories about the actual technique of producing and measuring these pressures. In view of the important results to be expected from further investigations of low pressure phenomena it has been thought worth while to describe in the following chapters not only the methods available at present for the production and measurement of high vacua, but also to a lesser extent the more important results which have been obtained by the different investigators who have studied the physical and chemical phenomena exhibited in gases at very low pressures.

$$\text{Megabar} = .750 \text{ mm.}$$

$$1 \text{ mm} = .00133 \text{ megabar} = 1330 \text{ bars.}$$

$$1 \text{ Bar} = .000750 \text{ mm.}$$

$$1 \text{ mm} = .001 \text{ mm} = 1.33 \text{ bars.}$$

$$.075 \text{ mm}$$

CHAPTER I

KINETIC THEORY OF GASES

Laws of Boyle and Gay-Lussac

The state of a gas is ordinarily defined by means of the volume which is occupied by a given mass under definite conditions of temperature and pressure. The three laws of Boyle, Gay-Lussac and Avogadro may be combined in the form of the well-known relation:

$$P V = \nu R T \quad (1a)$$

where P and V denote the pressure and volume respectively, T denotes the absolute temperature (degrees Centigrade + 273.1), ν is the number of mols (mass in grams divided by the molecular weight) and R is a constant for all gases.

The value of this constant is derived from the experimentally determined value of the volume of one mol of an ideal gas at given values of P and T . As standard pressure we shall consider that of 1 *megabar*. By definition, this is equal to 10^6 dynes per cm^2 , and corresponds very closely to a pressure of 750 mm. of mercury at 0 deg. C., lat. 45 deg., and sea level.

For $T = 273.1$ and $P = 1$ megabar, $V = 22,708 \text{ cm}^3$ per mol.

Hence, $R = 83.15 \times 10^6$ ergs per degree abs. Denoting the weight of gas by ω , and its molecular weight by M , equation (1a) may therefore be written in the form,

$$P V = 83.15 \times 10^6 \omega \frac{T}{M} \quad (1b)$$

where P is measured in bars (dynes per cm^2) and V in cm^3 .

Now the pressures which we ordinarily deal with in high vacuum phenomena range from 1 to 10^{-3} bar and even less. It is evident that at these pressures the volume of even a very small amount of any gas may be quite considerable. Thus, by applying the above equation to the case of hydrogen ($M = 2.016$), we find that the volume occupied by 1 milligram of this gas at a pressure of 1 bar and 20 deg. C. (room temperature), is $1.209 \times 10^7 \text{ cm}^3$, while at standard pressure the volume is only 12.09 cm^3 .

Fundamental Postulates of the Kinetic Theory of Gases¹

For a proper understanding of phenomena in gases, more especially at low pressures, it is essential to consider these

¹ The reader will find more complete discussion of the kinetic theory of gases in the following books and articles:

J. H. Jeans, *The Dynamical Theory of Gases* (1916).

K. Jellinek, *Lehrbuch der physikal. Chem. I.* 1 (1914).

W. C. McC. Lewis, *Kinetic Theory of Gases* (1915).

O. E. Meyer, *Kinetic Theory of Gases*.

S. Dushman, *The Kinetic Theory of Gases*, *General Electric Review*, 16, 952, 1042, 1159 (1915).

phenomena from the point of view of the kinetic theory of gases. At the present time we can, as a matter of fact, regard this theory as much more than a mere hypothesis. The evidence of the actual existence of atoms and molecules is so conclusive that very few would care to believe to the contrary. On the other hand, the theory has enabled us to interpret and prophesy so many facts about gases that one naturally uses this point of view in discussing any phenomena in gases.

The kinetic theory of matter, and more especially that of gases, rests essentially upon two fundamental assumptions. The first of these postulates is that matter is made up of extremely small particles or molecules, and that the molecules of the same chemical substance are exactly alike as regards size, shape, mass, and so forth. The second postulate is that the molecules of a gas are in constant motion, and this motion is intimately related to the temperature. In fact, the temperature of a gas is a manifestation of the amount of molecular motion. In the case of solids, at least those that are crystalline, it has been shown by the investigations of Bragg and others that the atoms which constitute the molecules (when the substance is in the gaseous state) are arranged in definite space-arrangements, and in this case the effect of temperature increase consists in increasing the kinetic energy of vibration of the atoms about their mean positions of equilibrium.

But in the case of gases the effect of increased temperature is evidenced by increased translational (kinetic) energy of the molecules, and in fact, a relatively simple calculation based on these assumptions enables us to calculate the velocities of the molecules at any temperature.

Velocity of Molecules

According to the kinetic theory a gas exerts pressure on the enclosing walls because of the impact of molecules on these walls. Since the gas suffers no loss of energy through exerting pressure on the solid wall of its enclosure, it follows that each molecule is thrown back from the wall with the same speed as that with which it impinges, but in the reverse direction, that is, the impacts are perfectly elastic.

Suppose a molecule of mass, m , to approach the wall with velocity G . Since the molecule rebounds with the same speed, the change of momentum per impact is $2 mG$. If n_0 molecules strike unit area in unit time with an average velocity G , the total impulse exerted on the unit area per unit time is $2 m n_0 G$.

But the pressure is defined as the rate at which momentum is imparted to a unit area of surface.

Hence,

$$2 m n_0 G = P \quad (2a)$$

It now remains to calculate n_0 . Let n denote the number of molecules per unit volume. It is evident that at any instant we can consider the molecules as moving in six directions corresponding to the six faces of a cube. Since the velocity of the molecules is G , it follows that, on the average, $\frac{n}{6} G$ molecules will cross unit area in unit time.

Equation (2a) therefore becomes

$$P = \frac{1}{3} m n G^2 \quad (2b)$$

From equation (2b) it is possible to deduce the three fundamental laws of gases that have been mentioned.

Since the product mn corresponds to the density, it follows that at constant temperature the pressure varies directly as the density, or inversely as the volume. This is known as Boyle's law.

Again, from equation (2b) it will be seen that the kinetic energy of the molecules in a volume V is:

$$\frac{1}{2} mn G^2 V = \frac{3}{2} PV \quad (3a)$$

Now we know that if we mix two different gases that were previously at the same temperature there will be no change in temperature; this holds for all temperatures. Consequently, the average kinetic energy of the molecules ($\frac{1}{2} mG^2$) must be the same for all gases at the same temperature and must increase at the same rate for all gases. We can therefore define temperature in terms of the kinetic energy of a gas. If we write

$$\frac{1}{2} mn G^2 V = \frac{3}{2} RT \quad (3b)$$

where R is a constant, it immediately follows that

$$PV = RT$$

which is the law of Gay-Lussac.

Lastly, let us consider equal volumes of any two different gases at the same pressure and temperature. Since P and V are the same for each, and $\frac{1}{2} mG^2$ is constant at constant temperature, it follows that n must be the same for both gases.

That is, equal volumes of all gases at the same temperature and pressure contain an equal number of molecules. This was stated as a fundamental principle by Avogadro in 1811, but it took chemists about fifty years to understand its full import.

If we let V denote the volume corresponding to the molecular weight, the value of the constant R is that defined by equation (1a). Instead of mnV we can write M , the molecular weight, and (3b) becomes

$$\frac{1}{2}MG^2 = \frac{3}{2}RT \quad (3c)$$

Equation (3c) enables us to calculate the so-called *mean velocity* of the molecules. Substituting for R the value 83.15×10^6 ergs per degree abs., we can write equation (3c) in the form:

$$G = \sqrt{\frac{3RT}{M}} = 15,800 \sqrt{\frac{T}{M}} \text{ cm. sec.}^{-1} \quad (3d)$$

Table I gives the values of the mean velocity at 0 deg. C., and 20 deg. C., for some of the more common gases.

It follows directly from this equation that at constant temperature the rates of flow of different gases through a narrow opening must vary inversely as the square roots of the molecular weights. This conclusion is of importance in connection with exhaust problems since it indicates that heavier gases must be more difficult to pump out than lighter ones.

Maxwell's Law of Distribution of Velocities

It is evident that even if all the molecules in a given volume actually possessed the same velocity at any initial instant, the

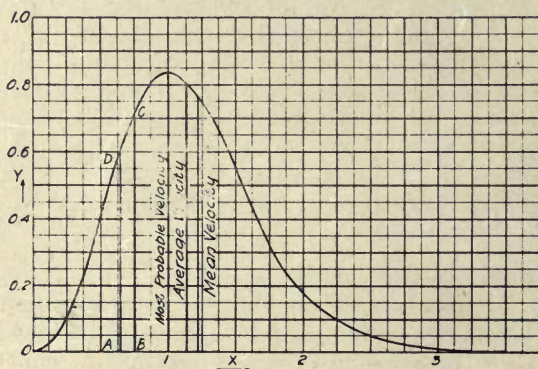


Fig. 1. Maxwell's Law of Distribution of Velocities

collisions constantly occurring would disturb this equal distribution of velocities and a non-uniform distribution would soon be established. By applying the laws of probability, Maxwell showed that it is possible to calculate the law according to which the velocities of the molecules would be distributed at any tem-

TABLE I
MOLECULAR VELOCITIES

Gas	M	MEAN VELOCITY $\times 10^{-3}$ CM. SEC. ⁻¹		Average Velocity at 20° C.
		At 0° C.	At 20° C.	
H ₂	2.016	1.838	1.904	1.755×10^6 cm sec. ⁻¹
O ₂	32.00	0.4613	0.4778	0.440
N ₂	28.02	.4928	.5106	.471
Air	28.96	.4849	.5023	.463
Hg	200.6	.1842	.1908	.176
CO ₂	44.0	.3933	.4076	.376
H ₂ O	18.016	.6148	.6368	.587
A	39.88	.4133	.4282	.395
NH ₃	17.02	.6328	.6554	.604
CO	28.00	.4933	.5109	.471

perature. The curve shown in Fig. 1 represents graphically the distribution of velocities at any temperature, in terms of the most probable velocity, whose value is taken as unity.

The equation of this curve is:

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2}$$

where y denotes the probability of a velocity whose magnitude is x times that of the most probable value. The significance of this curve can be understood better by means of the results tabulated in Table II. Under Δx is given the range of velocities and under Δy the fraction of the total number of molecules which have velocities corresponding to this range. Thus 16.1 per cent of all the molecules have velocities which range between 0.9 and 1.1 times the most probable velocity at any temperature. Similarly it follows that 68.4 per cent of the molecules have velocities ranging between 0.5 and 1.5 times the most probable velocity, while only 3.1 per cent have velocities that exceed 2.5 times the most probable velocity.

TABLE II
RELATIVE DISTRIBUTION OF MOLECULAR VELOCITIES
 (Maxwell's Law)

Δx	Δy	Δx	Δy
0 -0.1	0.001	1.3-1.5	0.112
0.1-0.3	.021	1.5-1.7	.078
0.3-0.5	.063	1.7-1.9	.058
0.5-0.7	.112	1.9-2.1	.034
0.7-0.9	.149	2.1-2.5	.030
0.9-1.1	.161	2.5-3.0	.008
1.1-1.3	.150		
0.5-1.5	.684	0 -2.5	.969

As shown in Fig. 1, the most probable velocity (which may be denoted by W) is different from the mean velocity, G , and the relation between these two values of the velocity is given by the following equation, which can be readily deduced from the equation to the curve for Maxwell's distribution law:

$$W = \sqrt{\frac{2}{3}} G = \sqrt{\frac{2 RT}{M}} = 12,900 \sqrt{\frac{T}{M}} \quad (4)$$

In addition to these values of the velocity, it is important, in connection with a large class of applications of the kinetic theory of gases, to know the arithmetical or average velocity of the molecules at any temperature. This is usually denoted by Ω and may be calculated by means of the relation,

$$\Omega = \sqrt{\frac{8}{3\pi}} G = \sqrt{\frac{8 RT}{M\pi}} = 14,500 \sqrt{\frac{T}{M}} \quad (5)$$

The values of the average velocity at room temperature for some of the more common gases are given in the last column of Table I.

Number of Molecules Per Unit Volume

According to Avogadro's law the number of molecules per gram-molecular weight of any gas ought to be the same. The problem of accurately determining the value of this constant, which we shall denote by N , has naturally been the object of a large number of investigations, and a number of different

methods have been used in order to determine it.² The phenomena of Brownian movement, the accurate determination of the charge on an electron, counting the number of alpha particles expelled from a gram of radium, and finally the study of the laws of black body radiation—all these methods have led to approximately the same value for N . According to Millikan, whose determination is undoubtedly the most accurate we have, this constant has the value of 6.062×10^{23} . From this value it is readily calculated that the number of molecules per cubic centimeter of an ideal gas at a pressure of 10^6 bars and 0 deg. C., is 2.67×10^{19} .

Let us now attempt to interpret this magnitude. The highest vacua attainable at present range around 10^{-4} bar. Even at this extremely low pressure, which would ordinarily be regarded as a "perfect vacuum," the number of molecules per cm^3 , at 0 deg. C., is still 2,670,000,000, a number which is, roughly speaking, of the same order of magnitude as the total population of the earth.

From the above considerations it follows that at any temperature T and pressure P , the number of molecules per cm^3 is given by the relations:

$$\begin{aligned} n &= \frac{NP}{RT} = 7.29 \times 10^{15} \frac{P}{T} \quad (\text{press. in bars}) \\ &= 9.71 \times 10^{13} \frac{P}{T} \quad (\text{press. in mm. of mercury}). \end{aligned} \quad (6)$$

This is the significance attached to n in the following chapters.

Rate at Which Molecules Strike a Surface

It was shown by Meyer that the number of molecules of a gas at rest as a whole that strike unit area per unit time is equal to $\frac{1}{4} n \Omega$.

Substituting for n and Ω the values previously given, we obtain the relation,

$$\frac{1}{4} n \Omega = 2.653 \times 10^{19} \frac{P}{\sqrt{MT}} \quad (\text{press. in bars}) \quad (7a)$$

For air at 20 deg. C., and 10^6 bars, the number of molecules striking 1 cm^2 per second, is 2.88×10^{23} .

Equation (7a) may also be expressed in terms of the mass (w) of gas that strikes 1 cm^2 per second.

² For a detailed discussion of the different methods which have been used for the determination of Avogadro's number, N , the reader is referred to the following:

J. Perrin, *Les Atomes*.

S. Dushman, *General Electric Review*, 18, 1159 (1915).

Let ρ denote the density of the gas, and m the mass per molecule.

$$\text{Then, } \rho = \frac{MP}{RT}$$

$$\text{and } w = 1/4 n m \Omega = 1/4 \rho \Omega = 43.74 \times 10^{-6} P \sqrt{\frac{M}{T}} \text{ gm. cm.}^{-2} \text{ sec.}^{-1} \quad (7b)$$

For air at 20 deg. C., and 10^6 bars,

$$w = 13.8 \text{ gm./cm.}^2 \text{ sec.}$$

Application of Kinetic Theory to Determination of Vapor Pressures

An interesting application of equation (7) has been made by Langmuir to the calculation of vapor pressures from rates of evaporation of metals in high vacua. As this subject is discussed at further length in a subsequent chapter it will be sufficient in the present connection to quote from Langmuir's paper on "The Vapor Pressure of Metallic Tungsten."³

"Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory we look upon the equilibrium as a balance between the rate of evaporation and rate of condensation. That is, we conceive of these two processes going on simultaneously at equal rates.

"At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it. That is, the rate of evaporation in a high vacuum is the same as the rate of evaporation in presence of saturated vapor. Similarly we may consider that the rate of condensation is determined only by the pressure of the vapor."

It is therefore possible, according to Langmuir, to apply equation (7) to calculate the vapor pressure of a metal like tungsten from the observed rate of evaporation (loss of weight at constant temperature) in vacuum.

Thus, at a temperature of 2800 deg. K., the observed value of ω , the loss in weight of a tungsten filament is 0.43×10^{-6} gms. per square cm. per second. Substituting in equation (7b) we find for P , the value 28.6×10^{-6} mms. of mercury, or 38.1×10^{-8} bar.

In the same manner Langmuir and Mackay⁴ have obtained the vapor pressure curves of the metals tungsten, molybdenum and platinum over a large range of temperatures.

³ Phys. Rev. 2, 329 (1913).

⁴ Phys. Rev. 4, 377 (1914).

Mean Free Path of Molecules

While the individual molecules in a gas at rest possess very high velocities, as previously shown, it is a matter of ordinary observation that gases diffuse into each other very slowly. This is explained on the kinetic point of view by assuming that the molecules do not travel continuously in straight lines, but undergo frequent collisions. The use of the term "collision" naturally leads to the notion of *free path*. This may be defined as the distance traversed by a molecule between successive collisions. Since, manifestly, the magnitude of this distance is a function of the velocities of the molecules, we are further led to use the expression "mean free path" (denoted by L), which is defined as the average distance traversed by all the molecules between successive collisions.

However, this definition assumes that the molecules actually collide like billiard balls; that is, the molecules are assumed to be rigid elastic spheres possessing definite dimensions and exerting no attractive or repulsive forces on each other. This, however, can certainly not be in accord with the facts. We have every reason to believe that the structure of atoms and molecules is exceedingly complex. It is probably impossible to state definitely what is the diameter of a hydrogen atom or molecule. Also there is no doubt that the molecules exert attractive forces on each other for certain distances and repulsive forces when they approach exceptionally close. Otherwise how could we explain surface-tension, discrepancies from Boyle's law, and a host of related phenomena? To speak of collisions among molecules such as these is impossible. What meaning, therefore, shall we assign to the free path under these conditions?

It is readily seen that the most essential idea at the back of the term "free path" is this: We imagine it possible to take a cinematograph picture of the molecules in a given portion of space; we then consider their velocity components in a given direction and find that at the end of a certain distance L the average value of the velocity components of all these molecules taken in the same direction has decreased by a certain amount; in other words, the average number of molecules traveling in the given direction is less after they have traversed the distance L . On this basis, the term free path has a physical meaning which is independent of all ideas that we may form of the actual structure of the molecules or of the nature of the inter-molecular forces.

Another method of overcoming the same difficulty is to investigate the relations between the free path and the other

properties of a gas, assuming rigid spherical molecules with or without attractive forces, and then consider the case of any actual gas in terms of this hypothetical gas.

Evidently the mean free path must depend upon the molecular diameter, and simple considerations indicate that the length of the mean free path must vary inversely as the total cross-sectional area of the molecules per unit volume. Again, the magnitude of the coefficients of viscosity, heat conductivity and diffusivity of gases are intimately bound up with the length of the free path; whether it be transference of momentum from one layer to another as in viscosity, or transference of increased kinetic energy of the molecules as in heat conductivity, the rate of this transference must depend upon the number of collisions which each molecule experiences as it passes from point to point. We thus obtain relations between the mean free path, the coefficients of viscosity and heat conductivity on the one hand, and on the other hand, equations that connect the mean free path with the molecular diameter.

Relation Between Coefficient of Viscosity and Mean Free Path

A gas streaming through a narrow bore tube experiences a resistance to flow, so that the velocity of this flow decreases uniformly from the center outwards until it reaches zero at the walls. Each layer of gas parallel to the direction of flow exerts a tangential force on the adjacent layer tending to decrease the

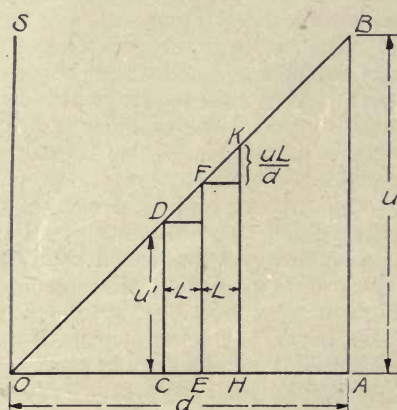


Fig. 2

velocity of the faster-moving and to increase that of the slower-moving layers. The property of a gas (or liquid), in virtue of which it exhibits this phenomenon, is known as *internal viscosity*.

As a simple working hypothesis we may assume, as Newton did, that the internal viscosity is directly proportional to the rate of decrease of velocity in the different gas layers. Furthermore, the viscosity must depend upon the nature of the fluid, so that in a more viscous fluid the tangential force between adjacent layers, for constant rate of decrease of velocity, will be greater than in the case of a less viscous fluid. We thus arrive at the following definition of the *coefficient of viscosity*:

The coefficient of viscosity is defined as the tangential force per unit area for unit rate of decrease of velocity.

With this definition we are in a position to deduce the approximate form of the relation between the coefficient of viscosity and the free path.

Let u denote the velocity of flow of the gas at a distance d from a stationary surface. In the case of uniform flow along a surface, the velocity will decrease uniformly to zero as the surface is approached. We can therefore represent, as in Fig. 2, the velocity at distance $OA=d$ by the ordinate $AB=u$ and velocities at intermediate distances by the corresponding ordinates below the line OB .

We shall imagine the gas divided into layers parallel to the surface, each having a depth equal to the free path, L .

Let us denote the tangential force per unit area between adjacent layers by B . By definition:

$$\begin{aligned} B &= \eta \times \text{velocity-gradient} \\ &= \eta \times \frac{u}{d} \end{aligned} \quad (8)$$

where η denotes the coefficient of internal viscosity.

But according to the kinetic theory, the tangential force per unit area is measured by the rate at which momentum is transferred per unit area between adjacent layers.

Owing to the relative motion of the layers, the molecules moving from a faster into a slower moving layer possess more momentum in the direction of flow than those moving in the opposite direction.

Let us consider any layer, CE or EH of thickness equal to L . We have chosen this particular value of the thickness so that we may be justified as a first approximation in assuming that the molecules starting at either of the planes CD or EF reach the opposite plane without suffering collision, that is, without change of momentum.

The momentum, parallel to the surface, of any molecule reaching the plane EF from the plane CD is $m(u'+G)$, where u' denotes the velocity of flow at the plane CD and G is the mean velocity of the molecules.

The momentum, parallel to the surface, of a molecule reaching the plane EF from the plane HK is $m\left(u'+G+2\frac{uL}{d}\right)$.

The number of molecules that cross unit area per unit time in any direction in a gas at rest is equal to $\frac{1}{6}nG$, and this must be the same for the molecules traveling in a direction perpendicular to the plane EF , for the velocity of flow is assumed to be so small that the density remains constant throughout the different layers.

Hence the net rate of transference of momentum across unit area of the plane EF is equal to

$$B = \frac{1}{3}m n G \frac{uL}{d} \quad (9)$$

From equations (8) and (9) it follows that

$$\eta = \frac{1}{3}m n G L = \frac{1}{3}\rho G L \quad (10)$$

In deducing this equation it has been assumed that the molecules all possess the same velocity G and the same free path L . It is evident therefore that the equation thus derived cannot be accurate. Introducing Maxwell's law of distribution of velocities, Boltzmann deduced the equation

$$\eta = 0.3502 \rho \Omega L \quad (11)$$

where Ω = average velocity

$$= 14551\sqrt{T/M} \text{ cm. sec.}^{-1}$$

and L is defined as the *average free path*.

Meyer in his "Kinetic Theory of Gases" used a different method of calculation and derived a relation of the form,

$$\eta = 0.3097 \rho \Omega L' \quad (12)$$

This is the relation usually adopted in text books on physics. On the other hand, the more recent publications, such as those of Jaeger,⁵ Millikan and Fletcher,⁶ and others, prefer Boltzmann's formula. Following the latter authorities we have made use

⁵ Fort. der Kinetische Gastheorie.

⁶ Phys. Rev. 4, 440 (1914).

in the following calculations of equation (11) to determine the so-called mean or average free path.*

From the preceding equations an interesting conclusion may be deduced regarding the dependence of viscosity on pressure. As has been mentioned, it is evident from very simple considerations that L varies inversely as the number of molecules present per unit volume. Consequently the product ρL is constant and independent of the pressure. The velocity, Ω , depends only upon the temperature and molecular weight. It therefore follows that, for any gas at constant temperature, the *viscosity is independent of the pressure, and must increase with the temperature.* The confirmation of these two deductions has been justly regarded as one of the most signal triumphs of the kinetic theory of gases. As is well known, the viscosity of all ordinary liquids *decreases* with increase in temperature. That the viscosity of gases must increase with temperature was therefore regarded as a remarkable conclusion.

At both extremely low pressures and very high pressures, the conclusion that the viscosity is independent of the pressure is not in accord with the observations, but this is due to the fact that the same derivation as has been used above is not valid under those conditions where either attractive forces between the molecules come into play or the pressure is so low that a molecule can travel over the whole distance between the walls of the enclosure without suffering collision.†

According to the preceding equations, it is therefore possible to calculate L for a gas under given conditions from data on the viscosity. In Table III are given the values of $L = \eta / (0.3502 \rho \Omega)$ calculated for different gases at 0 deg. C. and 20 deg. C. and 10^6 bars. The values of ρ have been calculated from molecular weights, while the values of Ω have been taken from Table I.

In choosing values of η_0 (the viscosity at 0 deg. C.) from the large amount of data available in the literature, an attempt has been made to choose the most recent and most accurate values in each case. The authorities for the different data are given in the footnote to Table III. For η_{20} (the viscosity at 20

* In German text-books, L is referred to as "mittlere freie Weglänge." The term "mean free path" is used by English writers, most of whom adopt Meyer's formula. In view of the fact that we may have several different "means," we prefer the unambiguous designation "average free path."

$$L' \text{ (Meyer)} = \frac{0.3502}{0.3097} L \text{ (Boltzmann)}$$

$$= 1.131 L \text{ (B)}$$

† The observations on viscosity effects at low pressures are discussed in the latter part of this chapter and also in Chapter VI.

TABLE III
 COEFFICIENT OF VISCOSITY⁷ AND AVERAGE FREE PATH AT NORMAL PRESSURE (10⁶ bars)

$$L_t = \frac{\eta}{0.3502\rho_t\Omega_t} \quad (\text{Boltzmann's equation})$$

$$L' (\text{according to Meyer's equation}) = 1.131 L \quad (\text{according to Boltzmann's equation})$$

Gas	$\eta_0 \times 10^{17}$	C	$\eta_{30} \times 10^{17}$	$\rho_0 \times 10^6$	$L \times 10^6$ (0°C.)	$L \times 10^6$ (20°C.)	$\Omega/L \times 10^{-7}$ (20°C.)
Air	1711	(a)	1809	1277	8.560	9.376	4940
H ₂	843	(b)	886	88.72	16.00	17.44	10060
He	1870	(d)	1964	175.7	25.25	27.45	4545
NH ₃	919	(e)	999	760.8	5.916	6.600	9152
H ₂ O	904	(h)	[1320 (m)]	[606.0]		[9.40]	
CO	1660	(n)	1752	1234	8.459	9.232	5101
N ₂	1670	(q)	1764	1234	8.500	9.287	5072
O ₂	1905	(s)	2018	1414	9.046	9.931	4432
A	2107	(t)	2239	1758	8.982	9.879	3998
CO ₂	1375	(v)	1472	1951	5.560	6.148	6115
H _g	1620	(y)	[5320 (z)]	[4200]		[14.67]	

deg. C.) the experimentally observed value has been used in the case of air, while in all other cases use has been made of Sutherland's equation.*

$$\eta_{20} = \eta_0 \left(\frac{273.1+C}{293.1+C} \right) \left(\frac{293.1}{273.1} \right)^{\frac{3}{2}} \quad (13a)$$

where C is a constant for each gas.

Collision-Frequency

From the values of L and Ω we obtain the collision-frequency, Ω/L , that is, the average number of collisions per second. These are given in the last column of Table III for room temperature. Thus, a molecule of nitrogen under ordinary conditions suffers over 5000 million collisions per second. It is not surprising, therefore, that gases diffuse relatively slowly.

Direct Determination of Average Free Path

The magnitude of the average free path under normal conditions is extremely small. As seen from Table III it is about 10^{-5} cm. or $\frac{1}{250}$ mil. But as the pressure decreases the free path increases. At 1 bar, which is about the degree of vacuum attained in exhausting ordinary incandescent lamps, the average free path for most gases is between 5 and 10 cms. A molecule of tungsten evaporated from the filament suffers very few collisions, if any, in traveling to the walls of the bulb, as is evident from the sharp boundaries of the blackened portions.

References to Literature on Determination of η

The literature on this subject is very extensive. Fortunately most of the data have been summarized by Fisher [Phys. Rev. *24*, 385 (1904); Chapman, Phil. Trans. A. *211*, 433 (1911), and Gilchrist, Phys. Rev. *1*, 124 (1913)]. The latter's determination of the coefficient of viscosity for air is probably the most accurate value available of this constant, and has been used by Millikan in his precision measurement of the charge on an ion. According to Millikan [Ann. Phys. *41*, 759 (1913)], the most accurate value for the coefficient of viscosity of air is

$$\eta_t = 0.00018240 - 0.000000493 (23 - t) \\ (23 > t > 12)$$

According to this relation,

$$\eta_{20} = 0.0001809$$

For η_0 , Prof. Millikan quotes three values, see (a), whose average 0.0001711 we have used as probably the most accurate value.

*The derivation of this equation is discussed on pages 24 and 25.

So far as the writer is aware the only investigators who have made any direct determination of the free path are Lenard,⁸ Robinson,⁹ and Franck and Hertz.¹⁰

The method used by all of these was the same—that of determining the average distance traversed by a gaseous ion between collisions. A charged molecule (ion) if endowed with a sufficiently high velocity, is capable of producing other ions by collision. It is therefore possible to measure the minimum distance at which two plates must be placed in a gas in order that it may be possible for the ions passing from one plate to the other to produce fresh ions by collision. Franck and Hertz obtained the following results:

Gas	Pressure (Bars)	L (Cm.)	L CALC. (t = 20 DEG. C.)	
			(Meyer)	(Boltzmann)
H ₂	45	0.436	0.438	0.388
H ₂	81	0.256	0.243	0.215
H ₂	152	0.146	0.130	0.115
H ₂	1670	0.014	0.012	0.011
He	124	0.256	0.250	0.221

*References to Literature on Determination of η (Cont'd)

Vogel [Ann. 43, 1235 (1914)] has carried out similar measurements in the case of other gases. As he referred his results to η_0 for air = 1724×10^7 , we have re-calculated them to correspond with the above value. These are referred to as Vogel's corrected values.

The other authorities to whom reference has been made are:

Kaye and Laby's Tables of Constants (K. & L.).

Jellinek's Physikal. Chem. I, 1, p. 305-7.

Markowski, Ann. Phys. 14, 742.

In the following references, C, F and V denote Chapman, Fisher and Vogel respectively.

(a) Breitenbach, 1708.7; Fisher, 1709.2; Holman, 1715.7.

(b) V, 844; C, 854; Markowski, 841.

(c) F. (d) V, 1862; C, 1885. (e) F, 76.2; C, 75.3.

(f) V. (g) V. (h) Jellinek. (k) V. (m) K. & L. The values in square brackets are for 100 deg. C. (n) V.

(p) F. (q) V, 1666; C, 1672; Markowski, 1674.

(r) F, 110.4; C, 111.7; V, 110.6.

(s) V, 1905; C, 1900.

(t) C, 1303; F, 131.1; V, 133.

(u) C, 2107; V, 2100. (v) C. (w) V, 1370; F, 1387.

(x) C, 249; V, 277; K. & L. 240. (y) K. & L.

(z) K. & L. The values in square brackets are for 300 deg. C.

⁸ Lenard, Ann. Phys. 12, 714 (1903).

⁹ Robinson, Phys. Zeit. 11, 11 (1910).

¹⁰ Franck u. Hertz, Deutsch. Phys. Ges. 14, 596 (1912); 15, 373 (1913).

The observed values of L appear to agree better with the values calculated according to Meyer's equation (12). The experimental evidence is, however, insufficient to be able to form from it a definite conclusion as to which equation is really more satisfactory.

It ought to be observed in this connection that for an infinitesimally small particle in a gas the mean free path according to Maxwell is $4\sqrt{2}L$, where L is the free path for the gas molecules themselves. This relation has been applied to calculate the free path for electrons in gases. However, there is at present little or no experimental evidence in justification of this procedure. In fact, in some recent experiments by Mr. C. G. Found and the writer with the ionization gauge, the results obtained led to the conclusion that the mean free paths are much greater than those expected from the above relation. Partzsch¹¹ has also found that in the case of photo-electrons colliding with gas molecules the actually observed values of the mean free paths are about twice as great as those calculated from Maxwell's formula.

Relation Between Coefficient of Viscosity, Heat Conductivity and Diffusivity

The kinetic theory of gases achieved a great triumph when it led to the conclusion that the viscosity is independent of the pressure. It led to still further important results when it prophesied the existence of simple relations between the coefficients of viscosity, heat conductivity and diffusivity.

From the kinetic point of view it is the same whether the molecules transfer momentum from one layer to another or translational energy. The equations are quite analogous.

As in the case of viscosity, we consider any two layers CE , EH (Fig. 2), each of thickness L , between two plates whose temperatures are T_1 and T_2 and distance apart d . Let c_v denote the heat capacity per unit mass. The relative temperature drop between the planes CD and HK is equal to

$$2(T_1 - T_2) \frac{L}{d}$$

Hence the heat transferred per unit area is

$$\begin{aligned} Q &= \frac{1}{6} n G \cdot 2 m c_v \frac{(T_1 - T_2)L}{d} \\ &= \frac{1}{3} \rho G c_v \cdot L \frac{(T_1 - T_2)}{d}. \end{aligned}$$

¹¹ Ann. d. Phys. 44, 556 (1914).

Therefore the coefficient of heat conductivity,

$$k = \frac{1}{3} \rho G c_v L. \quad (14)$$

From equations (10) and (14) it follows that

$$k = \eta c_v \quad (15a)$$

A more accurate calculation of the heat conductivity shows that this equation is not quite correct, and should be written

$$k = B \eta c_v \quad (15b)$$

where B is a constant (greater than unity), whose value depends upon the nature of the forces that are assumed to exist between the molecules and upon the structure of the molecules themselves.

Similarly it can be shown that the diffusion constant of one gas into any other is proportional to the coefficient of viscosity. The relations are, however, quite complicated.

Chapman¹² has shown that the value of the constant B must be very closely equal to 2.5 for monatomic gases, 1.90 for diatomic gases, and less than this for polyatomic gases. These conclusions have been confirmed experimentally by Eucken.¹³

Table IV taken from Eucken's paper gives the values of k (experimentally determined by Eucken), η (Vogel's data)* and c_v together with the observed values of B at $T=273$.

TABLE IV
COEFFICIENT OF HEAT CONDUCTIVITY AND RELATION
TO COEFFICIENT OF VISCOSITY

Gas	$k \times 10^7$	$\eta \times 10^7$	c_v	B Obs.	B Calc.
He	3360	1876	0.746	2.40	2.50
A	390	2102	0.0745	2.49	
H ₂	3970	850	2.38	1.965	1.90
N ₂	566	1676	0.177	1.905	
O ₂	570	1922	0.155	1.913	
CO	542.5	1672	0.177	1.835	
NO	555	1794	0.1655	1.870	
CO ₂	337	1380	0.1500	1.628	
H ₂ O	(429)	1006	0.342	1.25	
NH ₃	513.5	926	0.388	1.43	

¹² S. Chapman, the Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules, Phil. Trans. A, 211, 433 (1911).

¹³ Eucken, Phys. Zeit. 14, 324 (1914). See also Jeans, Dynamical Theory of Gases, p. 317.

* No correction has been applied to any of the data given in Table IV, as the intention was merely to illustrate the variations in the value of B .

Relation Between Molecular Diameter and Mean Free Path

As mentioned previously, recent speculations on the structure of the atom lead to the conclusion that atoms and molecules are far from being the rigid elastic spheres postulated by the founders of the kinetic theory. According to the present theory of atomic structure we must conceive of the atom as consisting of a positively charged nucleus surrounded by one or more rings of electrons. The diameter of the nucleus is extremely small (less than 1/100,000) compared to the diameters of the electronic orbits, so that it is possible for the alpha particles, which have the same mass as helium atoms, to pass *right through* an atom of a heavy metal like gold. It is therefore certain that in the case of chemical combinations the atoms have inter-penetrated to form the molecule. The evidence deduced by T. W. Richards on the compressibility of atoms is also in accord with these views. On the other hand, it may be reasonable to speak of the diameter of a molecule if we think of it as the smallest distance apart to which the centers of two molecules can approach. Even this definition may not be accurate, but we can make use of it as a physical basis for mathematical relationships.

Denoting the molecular diameter by d_m , it was shown by Clausius¹⁴ that in the case of spherical molecules all possessing the same velocity G , the length of the *free path* is

$$L = \frac{3}{4 \pi n d_m^2} \quad (16)$$

If we take into account the fact that the molecular velocities vary according to Maxwell's distribution law, it can be shown that the *average free path*

$$L = \frac{1}{\sqrt{2} \pi n d_m^2} \quad (17)$$

Jeans has, however, pointed out that this equation cannot be accurate, since it takes no account of the persistence of velocities after collision.¹⁵ "On the average, a collision does not reverse the velocity in the original direction of motion, or even reduce it to rest, but there is a tendency for the original velocity to persist after collision." Jeans shows that in the case of two similar molecules colliding with relative velocities that may vary all the way from 0 to ∞ , the average value of the persistence is very nearly equal to $\frac{2}{5}$ of the value when the molecules col-

¹⁴ See Jellinek, pp. 287-292.

Meyer's Kinetic Theory, pp. 161-3.

¹⁵ Jeans, Dynamical Theory of Gases, p. 276, etc.

lide with equal velocities. That is, on the average, the molecules traveling in a given direction will after collision have lost sixty per cent $\left(\frac{3}{5}\right)$ of their velocity component in that direction.

Hence, according to Jeans, the equation should be written

$$L = \frac{1.319}{\sqrt{2} \pi n d_m^2} \quad (18)$$

According to Chapman, Jeans' formula is not quite correct. He has shown that for the case of rigid elastic spheres with no attractive forces,

$$\eta = \frac{0.4909}{\sqrt{2} \pi n d_m^2} \rho \Omega \quad (19)$$

Comparing equation (19) with equation (11) it is seen that, according to Chapman,

$$\begin{aligned} L &= \frac{0.4909}{0.3502 \sqrt{2} \pi n d_m^2} \\ &= \frac{1.402}{\sqrt{2} \pi n d_m^2} \end{aligned} \quad (20)$$

This formula is true only for rigid elastic spheres with no attractive forces. Assuming the existence of such forces, the effect obviously must be to shorten the free path, and in accordance with Sutherland's¹⁶ conclusion we must write for equation (20) the relation

$$L = \frac{1.402}{\sqrt{2} \pi n d_m^2 \left(1 + \frac{C}{T}\right)} \quad (21)$$

where C is a constant for each gas whose value may be determined from the temperature coefficient of the viscosity.

*This manner of defining the free path could obviously be extended to the case of molecules obeying any other law of force, where no collisions (according to the literal meaning of the word) occur. It has already been observed in a previous paragraph (p. 13) that we might define L in terms of the ratio of the molecules traveling in a given direction at one point to the number traveling in the same direction at a point further along in the same direction. Jeans' concept of persistence of velocities leads us therefore to the following definition of average free path which would hold in all cases except that of unlike molecules. We can define the average free path as being *twice the distance* which the molecules traveling at any instant in a given direction will pass over before losing sixty per cent of their velocity component in that direction. The factor 2 is required because at any instant the molecules have, on the average, covered one-half the distance between collisions.

This definition has been suggested to the writer by Dr. I. Langmuir and although it may not be the usual definition, the latter is so vague that a scientifically correct definition would certainly help to clear the prevailing misunderstanding about the whole subject of *free paths*.

¹⁶ Phil. Mag. 36, 507 (1893).

This equation, combined with equations (19) and (11), leads to the following expression for the variation with temperature of the coefficient of viscosity:

$$\eta_T = \eta_{273} \left(\frac{273+C}{T+C} \right) \left(\frac{T}{273} \right)^{\frac{1}{2}} \quad (13b)$$

Sutherland's equation has been found to be in excellent agreement with the experimental data. The assumption therefore appears to be justified that the molecules approximate fairly closely to rigid elastic spheres surrounded by attractive fields of force.

Equation (21) combined with equation (11) and a knowledge of n enables us to calculate the *molecular diameter from the coefficient of viscosity*.

Relation Between Molecular Diameter and Van der Waals' Constant, b

At very high pressures or temperatures so low that the gases can condense, it is observed that Boyle-Gay-Lussac's equation

$$PV = RT$$

is no longer applicable.

Van der Waals found that the behavior of gases near their critical temperature and pressure¹⁷ could be expressed quantitatively by a modified form of the above equation as follows:

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (22)$$

In this equation, a/V^2 is a correction term added to P , which takes into account the attractive forces exerted by the molecules upon each other. The constant b denotes a small volume whose magnitude compared (to) the molecular volume, V , becomes of importance when we are dealing with gases near their critical state. According to Van der Waals, $\frac{b}{4}$ is equal to the total volume of the molecules.

That is,

$$\frac{b}{4} = N \cdot \frac{\pi}{6} d_m^3$$

or

$$d_m^3 = \frac{3 \cdot b}{2 N \pi} \quad (23)$$

where $N = 6.062 \times 10^{23}$.

¹⁷ S. Dushman, "The Absolute Zero," General Electric Review, February and April, 1915.

The value of the constant b may be determined for each gas from the critical temperature (T_c) and pressure (P_c) by means of the relation:

$$b = R T_c / 8 P_c \quad (24)$$

In this equation b denotes the volume in cm^3 per molecular weight. Ordinarily this constant is given in tables in terms of the volume of the gas at 0°C . and 1 atmosphere pressure as unity. Denoting the latter by b_t it is evident that b in the above equations corresponds to $b_t \times 22,412$.

Jeans has pointed out¹⁸ that since b and a in Van der Waals' equation are not constant down to the critical temperature and pressure, values of b calculated by means of equation (24) are probably far from accurate. He therefore recommends calculating b from the observed deviations from Boyle's law as expressed by equation (22).

There is still a third method by which the molecular diameter may be calculated. According to Clausius and Mossotti, the volume actually occupied by the molecules may be calculated from either the dielectric constant D or the refractive index i by means of the equations:

$$n \frac{\pi}{6} d_m^3 = \left(\frac{D-1}{D+2} \right) \quad (25)$$

$$= \left(\frac{i^2-1}{i^2+2} \right) \quad (26)$$

Table V gives the values of the molecular diameter calculated for different gases by each of these methods. The first column gives the values of d_m calculated from the average free path, L , according to equation (21).

The values of C and L have been taken from Table III.

The second column gives the values calculated recently by S. Chapman¹⁹ and A. O. Rankine²⁰ by a slightly modified form of the same equation.

Column III gives the values, calculated by Chapman by means of equation (23), using the values of b obtained from the observed deviation from Boyle's law. Column IV gives values calculated from the data on critical temperature and pressure by means of equation (24). The critical data used were those given by Jellinek.²¹ Column V gives the values of d_m calculated by

¹⁸ Dynamical Theory of Gases, p. 174, etc.

¹⁹ Phil. Trans. Roy. Soc. A, 216, 279 (1916).

²⁰ Proc. Roy. Soc. 98, 360 (1920).

²¹ Physikal. Chem. I, 1, pp. 444-5.

O. Sackur²² from the refractive index for the *D*-line. These data have been corrected for the difference between the values of *N* used by Sackur and by the writer. Calculations on the magnitude of the molecular diameters are also given by J. L. Jeans,²³ R. Eucken²⁴ and A. Heydweiller.²⁵

The general agreement between the results given in the first three columns is very satisfactory. In view of Jeans' criticism just mentioned, the values in Column IV cannot be considered as having nearly the same degree of accuracy as those in Column III, while the values in Column V indicate that this method gives only approximate results.

As has been pointed out by Rankine²⁰ the above arguments are all based on the assumption that the molecules are spherical. "When we come," he writes, "to consider the case of diatomic molecules—as, for example, in chlorine gas—we are met with the difficulty that we are no longer entitled to regard the molecule

TABLE V
MOLECULAR DIAMETERS
Unit 10^{-8} cm.

Gas	I	II	III	IV	V
H_2	2.403	2.38	2.52	2.341	1.91
N_2	3.146	3.13	3.08	3.146	2.41
O_2	2.975	2.96	2.89	2.919	2.32
<i>He</i>	1.905	1.91	1.96	2.646	1.18
<i>Ne</i>		2.35			
<i>A</i>	2.876	2.87	2.85	2.939	2.36
<i>Kr</i>		3.19	3.14		
<i>Xe</i>		3.51	3.42		
Cl_2					3.33
Br_2					3.88
I_2					4.56
Hg				3.013	
H_2O				2.887	2.28
<i>CO</i>	3.190			3.121	2.52
CO_2	3.335	3.30	3.40	3.231	2.78
NH_3	2.967			3.080	

as a sphere. Hitherto, it has been necessary to regard it as such, and obtain, by the formula which is strictly applicable to single atoms only, an average atomic diameter. All viscosity formulæ merely enable us to calculate an average value of $\pi d m^2$ which is the area presented as a target by the molecule to other

²² Ann. Phys. 40, 87 (1913)

²³ Dynamical Theory of Gases, p. 341.

²⁴ Phys. Zeits. 14, 324 (1913).

²⁵ Ann. Phys. 42, 1273 (1913).

molecules approaching it from all possible directions." Rankine has therefore attempted to calculate the actual arrangement of the atoms in a molecule such as O_2 on the basis of the Lewis-Langmuir theory of atomic structure, utilizing the values derived by W. L. Bragg for the radii of the atoms in crystalline compounds.²⁶ The conclusion arrived at is that the best model for such diatomic molecules is an ellipsoid of revolution whose longer diameter lies along the line joining the centers of the two atoms.

General Considerations Regarding Gases at Low Pressure

As has already been stated, the pressures which interest us in the study of high vacuum phenomena usually range below 1 bar. At these pressures the mean free paths of the molecules are at least of the same order of magnitude as the dimensions of the vessels used in experimental work. Thus, at 1 bar the mean free paths for most gases are about 10 cm. (Table III). It therefore follows that the majority of the molecules travel in straight lines as far as the dimensions of the vessels will allow, and the number of inter-molecular collisions per second becomes relatively small as compared with the rate at which the molecules strike the walls. The following considerations will probably serve to explain the significance of this statement more fully.

Consider a cube, whose volume is D^3 cubic cm., and let n denote the number of molecules per cm.³. The number of collisions between gas molecules per second is

$$C = n D^3 \frac{\Omega}{L}$$

The total number of molecules striking the walls of the cube in each second is

$$A = 6D^2 n \frac{\Omega}{4}$$

Hence, $\frac{A}{C} \propto \frac{L}{D}$. That is, the ratio between the rate at which the molecules strike the walls and the rate at which they collide with each other is given by the ratio between the lengths of the mean free path and of the side of the cube. It can be readily shown that no matter what the shape of the vessel, the ratio $\frac{A}{C}$ is proportional to that of $\frac{L}{D}$, where D is the distance between the walls. Thus, if D is of the order of magnitude of 10 cm., A is greater than C when L is greater than 10 cm., that is, when the

²⁶ Phil. Mag. 40, 169 (1920).

pressure is lower than 1 bar (approximately). Consequently we should expect to find that at pressures of 1 bar and lower, the molecules travel in straight lines toward the walls of the containing vessel.

A very common illustration of this fact is the production of sharp shadows in vacuum type incandescent lamps. As has been shown by the investigations of Langmuir and Mackay,²⁷ the blackening of ordinary tungsten lamps is due to the evaporation of metal from the filament. The pressure in this type of lamp under operating conditions is less than 0.01 bar,²⁸ so that the mean free path of the tungsten atoms is of the order of several hundred centimeters. Consequently, collisions between these atoms and molecules of residual gas are very rare, and the tungsten atoms travel directly to the sides of the bulb, where they are immediately condensed. By interposing some object between the filament and the walls, very sharp shadows can be produced, if the vacuum is good. On the other hand, the shadows are very much blurred if there is present in the bulb a pressure of even several bars of some inert gas like argon. Similar phenomena are observed in the evaporation of other metals, like mercury and sodium.²⁹

This observation that at very low pressures it is possible to obtain very well defined shadows by the evaporation of metals has been applied recently by O. Stern³⁰ to measure directly the translational velocity of molecules. The principle of the method used is as follows:

The vapor produced by evaporation from a metallic filament in a very good vacuum is allowed to pass through a hole L , and a screen with a circular aperture is placed in front of the hole. The beam of molecules passing through the hole L and the opening in the screen forms a sharply defined circular spot on a plate P at a distance from the screen. If now the whole apparatus, including screen and plate P , is rotated about an axis perpendicular to the path of the molecules and passing through the hole L , the spot formed on P is displaced in a direction opposite to that of rotation by an amount s which may be calculated from the following considerations:

If l denotes the distance between the hole L and the plate P , and ν the frequency of rotation of the latter about the

²⁷ I. Langmuir, *Am. Inst. Electr. Eng. Trans.* 32, 1921 (1913), also references given above.

²⁸ S. Dushman, *Phys. Rev.*, 5, 223 (1915).

²⁹ L. Dunoÿer, *Les Idées Modernes sur la Constitution de la Matière*, p. 215 (1913). This article contains a very interesting discussion of low pressure phenomena, especially of Knudsen's work (see p. 31).

³⁰ *Zeits. f. Physik*, 2, 49; 3, 417 (1920).
Sc. Abst. 24, 12, 544 (1921).

axis passing through L , it is evident that during the time τ in which the molecules pass from L to P , the latter will have moved forward a distance s , where

$$s = 2 \pi l \nu \tau$$

But if v = velocity of molecules,

$$\tau = l/v$$

Hence, $s = 2 \pi \nu l^2/v$

Thus, the measurement of s gives a direct determination of v , the velocity of the molecules.

Experiments with a silver-coated platinum wire gave results on the velocity of silver atoms which corresponded very closely with the values calculated by means of equation (5). It will be observed that in the latter equation, the velocity depends upon the molecular weight. Stern has therefore pointed out that the above method may be applied to determine molecular weights in the vapor state.

Laws of Molecular Flow

It is evident from the preceding considerations that at very low pressures the rate of flow of gases through tubes or narrow apertures must be limited solely by the frequency with which the molecules strike the walls of the tube or aperture and may thus be thrown back in the direction of incidence. At higher pressures the rate of flow of gases through narrow tubes is governed by Poiseuille's law. If Q_1 denotes the amount of gas (measured in terms of $P \cdot V$) which flows per second through a tube of diameter D and length l , and η denotes the coefficient of viscosity, Poiseuille's law may be expressed by means of the equation,

$$Q_1 = \frac{D^4(P_2 - P_1)P\pi}{128 \eta l} \quad (27)$$

where P is the pressure at which Q is measured and $P_2 - P_1$ denotes the difference in pressure at the two ends of the tube. At very low pressures this relation is no longer valid, and for a reason which is self-evident. At ordinary pressures the rate of flow of gases must be limited by the frequency of collisions between molecules, hence the necessity for introducing the coefficient of viscosity in the formula for the rate of flow. At very low pressures, however, where the length of L , the mean free path, is much greater than that of D , it is meaningless to speak of a coefficient of viscosity and it is therefore necessary to discard the hydrodynamical equations upon which Poiseuille's relation is based, in order to arrive at a more accurate relation

for the rate of flow of gases through tubes. A similar difference has been observed for the laws of heat flow in gases at low and high pressures. For pointing out the manner of attacking both these problems and deducing a number of relations which are applicable to gases at low pressures, we are indebted to the theoretical and experimental investigations of M. Smoluchowsky, M. Knudsen, and W. Gaede, who, since 1908, have published a large number of papers dealing with this subject.*

The term "molecular flow" was suggested by Knudsen³¹ to designate the condition of gases flowing through tubes at such low pressures that collisions between the molecules are infrequent as compared with collisions at the walls. As has been shown, at these pressures L is much greater than D and

the ratio $\frac{L}{D}$ increases with decrease in pressure, so that any mole-

cule striking the inner surface of the tube at any point is repelled all the way across the tube until it strikes the opposite wall. Knudsen now assumes that any plane surface, no matter how smooth it may appear, consists in reality of toothlike projections which are probably due to one or more atoms being irregularly piled up above the surrounding atoms; that is, these projections are of molecular dimensions, and they are irregularly distributed over the surface. Consequently, "a gas molecule on striking the surface is repelled in a direction which is totally independent of the direction of incidence, and the distribution of directions of an infinitely large number of molecules after reflection from a surface follows Lambert's cosine law for the reflection of light from a glowing body."

Introducing Maxwell's distribution law and Meyer's equation for the number of molecules in a gas at rest that strike unit area, Knudsen arrives at the following relations for the case in which the diameter of the tube or aperture is infinitesimally small as compared with the length of the mean free path.

In the case of a circular tube of diameter D , and length l , the quantity of gas, Q_2 , which flows through per second, with a difference of pressure $P_2 - P_1$, is given by the equation,

$$Q_2 = \frac{P_2 - P_1}{W_1 \sqrt{\rho_1}} \quad (28)$$

* This subject is discussed at greater length in Chap. VI, and also in connection with the theory of the molecular gauge (p. 101).

³¹ Ann. Phys. 28, 75, and 28, 999 (1908). Abh. Bunsenges. 3, 109 (1914). Also M. L. Dunoyer, loc. cit.

where

$$W_1 = \frac{6l}{\sqrt{2\pi} D^3} = \frac{2.394l}{D^3} \quad (29)$$

and ρ_1 denotes the density at 1 bar pressure and the temperature of the tube.

From the gas laws it follows that,

$$\rho_1 = \frac{M}{83.15 \times 10^6 T}$$

It will be observed that equation (28) is analogous to Ohm's law, so that we may speak of the term $W_1\sqrt{\rho_1}$ as the resistance to flow of the tube at the temperature T for a given gas. For different gases, the value of the resistance varies as the square root of M .

For the case of a circular opening in a thin plate, equation (28) is still valid, but the value of W is given by the equation,

$$W_2 = \frac{\sqrt{2\pi}}{A} = \frac{3.184}{D^2} \quad (30)$$

where A is the area of the opening, and D its diameter.

Hence where we have a tube of diameter D and length l connecting two vessels at low pressures, the total resistance to flow, of this tubing, is

$$W\sqrt{\rho_1} = \left(\frac{2.394l}{D^3} + \frac{3.184}{D^2} \right) \sqrt{\rho_1} \quad (31)$$

By means of these equations it is possible to calculate the quantity of gas that can flow through any given tube or opening at low pressures. The value of Q is obtained in terms of $\bar{P} V$, that is, the volume in cm^3 at a given pressure P , in bars.

TABLE VI
RATE OF FLOW OF AIR AND HYDROGEN AT LOW PRESSURES AND 20 DEG. C.

l	D	W	$\frac{Q_2}{P_2 - P_1}$ (Air)	$\frac{Q_2}{P_2 - P_1}$ (Hyd.)
1 cm.	1 cm.	5.578	5204.	19710.
10	1	27.124	1070.	4053.
1	0.1	2712.4	10.70	40.53
10	0.1	24258.4	1.196	3.60

As an illustration of the application of the above equation, Table VI gives the volume (in cubic cm.) of air or hydrogen (at 1 bar pressure) that would flow through different sizes of tubing for a difference of pressure of 1 bar, and room temperature. For

air at 293 deg. abs, and 1 bar pressure, $\rho_1 = 1.189 \times 10^{-9}$ and for hydrogen, under the same conditions, $\rho_1 = 8.271 \times 10^{-11}$.

From equation (31) and the data in Table VI it is evident that for long tubes of very small diameter (capillaries) the end correction is negligible. The values of Q_2 for air and hydrogen may then be derived from the data in the table for $l = 10$ and $D = 0.1$ by applying equation (29).

These examples illustrate the effect of narrow tubes on the rate of exhaust at low pressures, and it is therefore absolutely essential that in experiments at low pressures where maximum speed of exhaust is desired, the connecting tubing should be as large in diameter as practicable, and also as short as possible.

Laws of Flow at Higher Pressures

The equations given above are strictly accurate only at such low pressures that $\frac{D}{L}$ is infinitesimally small. Actually it has been found by Knudsen that the equations are accurate to within 5 per cent even at pressures where $\frac{D}{L} = 0.4$. For air at room temperature and 1 megabar, the value of L is 9.4×10^{-6} cm., and at a pressure P (bars) $L = \frac{9.4}{P}$. So that in case of a tube 1 cm. in diameter, the equation for molecular flow would be accurate to within 5 per cent for all pressures below about 3.76 bars.

It is of interest in this connection to discuss briefly the manner in which the rate of flow of gas through a tube varies at higher pressures. If we denote the ratio, $\frac{Q_2}{(P_2 - P_1)}$ by F , it is evident from the above discussion that for very low pressures this ratio is constant for any given gas and independent of the pressure. As, however, the pressure is increased the value of F is observed to decrease at first until it reaches a minimum value which is about 0.95 of its value at very low pressures. As the pressure is increased still further, F increases and the rate of increase with pressure is given by Poiseuille's law. From experiments over a large range of pressures with different gases, Knudsen has derived the following semi-empirical relation which is found to hold at all pressures:

$$F = cP + b \frac{(1 + c_1P)}{(1 + c_2P)} \quad (32)$$

where,

$$a = \frac{\pi D^4}{128 \eta l} \text{ (Poiseuille's constant)}$$

$$b = \frac{l}{W \sqrt{\rho_1}} \text{ (Coefficient of molecular flow)}$$

$$c_1 = \frac{\sqrt{\rho_1} D}{\eta} \text{ and } c_2 = \frac{1.24 \sqrt{\rho_1} D}{\eta}$$

For ordinary pressures this equation assumes the form already given for Poiseuille's law, equation (27), while at very low pressures it becomes identical with equation (28). In order to illustrate the application of equation (32) and also show the effect of pressure on the rate of flow of gases it is of interest to calculate by means of this equation the value of F at different pressures for air flowing through a tube 10 cm. long and 1 cm. in diameter, at room temperature. In Table VII, F expresses the volume in cubic cm., measured at 1 bar pressure and room temperature that flows through the tube for a difference of pressure of 1 bar at the ends and an average pressure of P bars.

TABLE VII
RATE OF FLOW OF AIR AT DIFFERENT PRESSURES

P (bars)	F (equation 32)	$F - 1070$
10^6	13.56×10^6	13.56×10^6
100	2227	1157
50	1555	485
20	1160	90
10	1058.1	-11.9
5	1025.7	-44.3
4	1023.6	-46.4
3	1025.2	-44.8
1	1043.6	-26.4
0.1	1065.4	-4.6
0.01	1069.6	-0.4

$a = 135.6$ $b = 1070$ $c_1 = 0.19033$ $c_2 = 0.2360$

These results have been plotted in Fig. 3. It is seen that the minimum value in F occurs at about 4.5 bars. Even at this pressure the difference between the value calculated by means of equation (32) and that calculated by applying the simple equation (28) combined with equation (31) is less than 5 per cent of the value, $F = 1070$, calculated by the last mentioned method. Table VII also shows that the resistance of tubes is very much greater at extremely low pressures than at ordinary pressures.

Thermal Molecular Flow³²

If two vessels at different temperatures are connected by a capillary tube, it is observed that at low pressures (where L is greater than D), there is a flow of gas from the *colder* to the *hotter* chamber until a pressure is established sufficient to check

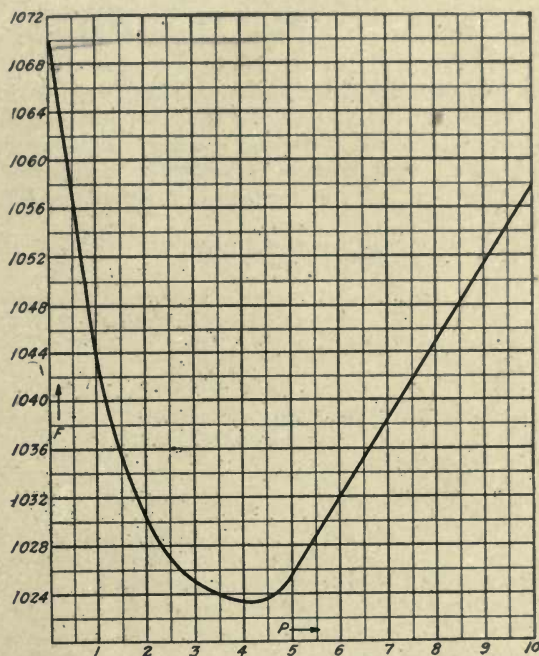


Fig. 3

it. For small differences in temperature, the pressure difference varies directly as the pressure and inversely as the temperature. It is also independent of the nature of the gas. The condition of equilibrium of pressures in the two parts of the system is then given by the relation:

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \quad \text{or} \quad \frac{\rho_1}{\rho_2} = \sqrt{\frac{T_2}{T_1}} \quad (33)$$

As the pressure is increased, the pressure difference rises less rapidly and finally reaches a maximum value. It then decreases and at higher pressures varies inversely as the pressure and also inversely as the density of the gas. Under these conditions there

³² M. Knudsen, *Ann. Phys.* 31, 205 and 33, 1435 (1910); G. D. West, *Proc. Phys. Soc.* 31, 278 (1919). The latter gives a critical discussion of the laws of thermal transpiration at both low and medium pressures.

is a flow of gas from the cold to the hot vessel along the surface of the tube and in the reverse direction along the axis. The condition for equilibrium at ordinary pressures is

$$P_1 = P_2 \text{ or } \frac{\rho_1}{\rho_2} = \frac{T_2}{T_1} \quad (34)$$

Equation (33) is applicable to experiments at low pressures where different parts of a system are maintained at different temperatures. A usual case is where an appendix or trap connected with the vessel to be exhausted is kept immersed in liquid air ($T=80$ approx.), while the pressure in the system is determined by some form of sensitive gauge. Assuming that the latter is at room temperature ($T=298$), it follows that the pressure in the part of the system immersed in liquid air is

$$\sqrt{\frac{80}{298}} = 0.52 \text{ of that read by the gauge.}$$

CHAPTER II

HIGH VACUUM PUMPS

Classification of Methods for the Production of Low Pressures

The methods for the production of low pressures may be classified conveniently under the following headings:

I. Mechanical Pumps

1. Piston pumps
2. Toepler and Sprengel mercury pumps
3. Rotary mercury pumps
4. Rotary oil pumps
5. Gaede "Molecular" pump

II. Mercury Vapor Pumps

1. Gaede "diffusion" pump
2. Langmuir condensation pump

III. Physical-Chemical Methods

1. Charcoal or other absorbing agent at low temperature
2. Clean-up of residual gases by chemical reactions
3. Clean-up of gases by ionization methods

General Theoretical Considerations Regarding Vacuum Pumps¹

In comparing vacuum pumps it is necessary to consider the following factors, which are the main characteristics of a pump:

1. *Exhaust Pressure.* This is the pressure against which the pump may be operated. In general, the higher the degree of vacuum desired on the "fine" or intake side of the pump, the smaller the exhaust pressure should be. The low exhaust pressure is then obtained by means of another (so-called "rough") pump in series with the high vacuum pump. Two or more rough pumps may be used in series in order to obtain a sufficiently low exhaust pressure for the fine pump.

2. *Degree of Vacuum Attainable.* "This is the lower limit of pressure which may be attained in a closed vessel connected to the pump. With most types of pump the degree of vacuum attainable depends to a large extent on the exhaust pressure used. This is usually due to leakage through the pump." In the case of the mercury vapor pumps, there is theoretically no lower limit to the pressure which may be attained, while in that of the Gaede molecular pump the limiting pressure bears a constant ratio to the exhaust pressure.

¹ In writing this section, the author has made extensive use of the article by Dr. Langmuir on "The Condensation Pump," in the *General Electric Review*, Dec., 1916, p. 1060.

3. *Speed of the Pump.* The law for the rate of decrease in pressure in a closed vessel connected to a pump is quite similar to that of chemical and physical reactions of the first order.

It may be stated as follows: If p_0 denotes the lower limit of pressure attainable with the pump, then the rate of decrease in

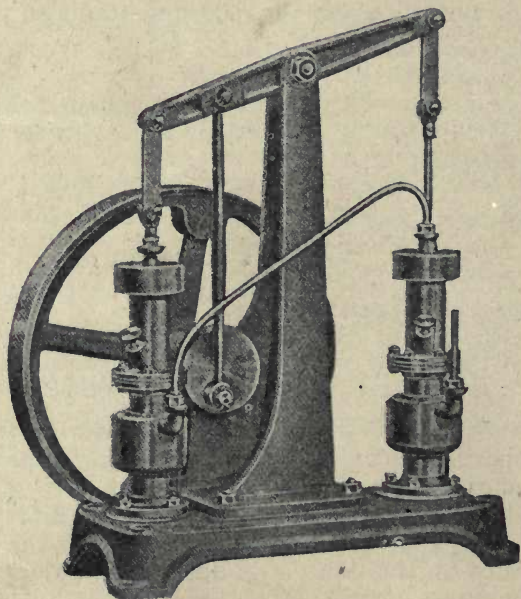


Fig. 4. Geryk Vacuum Pump, Power Drive

pressure at any instant is proportional to $p - p_0$, where p denotes the pressure at that instant. That is,

$$-\frac{dp}{dt} = k(p - p_0) \quad (35a)$$

where k is a constant. Further consideration shows that with a given pump the rate of exhaust must vary inversely as the volume (V) of the vessel to be exhausted. Thus we can write

$$-\frac{dp}{dt} = \frac{S}{V}(p - p_0) \quad (35b)$$

where S is a constant for the given pumping system, that is, pump and connecting tubing. Integrating the last equation we obtain the relation,

$$S = \frac{V}{t} \ln \left(\frac{p_1 - p_0}{p_2 - p_0} \right) \quad (36)$$

where t is the interval of time required to reduce the pressure in the volume V , from p_1 to p_2 .

Gaede² has defined S as the *speed of the pump*, and it is ordinarily measured in cubic cm. per second. It is readily seen that from the above equation S may also be defined as follows:

With a pump of speed S , it is possible to reduce, in each second, the pressure in a volume S cm.³ by 63.2 per cent of the maximum possible decrease in pressure. It is necessary to distinguish between the speed as defined in this manner and the actual speed of exhaustion, which we may denote by E . The latter is defined thus:

$$-\frac{dp}{dt} = \frac{E}{V} p$$

or

$$E = \frac{V}{t} \ln \frac{p_1}{p_2} \quad (37)$$

It is only when $p_0 = 0$, that S and E are identical, and remain constant during the whole period of exhaust. In all other cases the speed of exhaust gradually decreases and as the pressure in the vessel approaches the limiting pressure, p_0 , E decreases rapidly until it becomes zero when the pressure has decreased to p_0 .

The actual speed of exhaust depends not only upon the design of the pump but also upon the diameter and length of the connecting tubing between pump and vessel to be exhausted. The pump and tubing together really constitute a system which is the equivalent of a pump of lower speed. Mention has been made in Chapter I of the results of Knudsen's investigations on the resistance to flow in tubes. According to these results, the quantity of gas, Q , flowing through a narrow tube is given by the relation

$$Q = \frac{p_2 - p_1}{W \sqrt{\rho_1}} \quad (28)$$

where $W \sqrt{\rho_1}$ is the "resistance," and $p_2 - p_1$ is the difference in pressure at the ends. As in the previous chapter we shall write

$$Q = F \quad F = \frac{Q}{p_2 - p_1} = \frac{1}{W \sqrt{\rho_1}} \quad (38)$$

Let us now assume that the volume of the tube is negligible compared to the volume of the vessel to be exhausted, and that the limiting pressure for the pump, $p_0 = 0$. Let p_2 denote the pressure in the vessel and p_1 the pressure at the pump intake (end of the tube). Also let S_1 denote the speed of the pump itself,

²Ann. Phys. 41, 337 (1913).

and S_2 the speed of pump and connecting tubing. Then since the quantity of gas taken out each second by the pump is the same as that flowing through the tube, we have the following relations:

$$Q = F(p_2 - p_1) = S_1 p_1 = S_2 p_2$$

Eliminating p_1 and p_2 from these equations, we obtain the equation,

$$\frac{1}{S_2} = \frac{1}{S_1} + \frac{1}{F} \quad (39)$$

which shows the effect of the added resistance of the tube on the speed of the pumping system. It will be observed that $\frac{1}{S}$ has the same dimensions as $W\sqrt{\rho_1}$ (or $1/F$), that is, the speed of a pump may also be looked upon as the *reciprocal of a resistance* to flow of gases through it, and by analogy with electrical usage we may define $\frac{1}{S_1}$ as the "impedance" of the pump itself and $\frac{1}{S_2}$ as the impedance of pump and tubing. Similarly we may regard S_1 , S_2 and F , as "admittances."

It follows logically from these considerations that "in operating vacuum pumps of high speed it is essential to use tubing of large diameter (and short length) between the pump and the vessel to be exhausted if full advantage is to be taken of the speed of the pump." As an illustration of the effect of narrow tubes in diminishing the effective speed of a pump, let us consider the case of a tube 10 cm. long and 1 cm. diameter connected with a pump of speed $S_1 = 1400$ cm.³ per second (which is the value for a molecular pump under ordinary operating conditions).

The "resistance" of such a tube has been calculated in the previous chapter. For air at room temperature $1/W\sqrt{\rho_1} = F = 1070$. Applying equation (39) it follows that $S_2 = 606$, that is, the speed of the pumping system is about 43 per cent of that of the pump alone.

With a pump which has a speed of 4000 cm.³ per second (such speeds are easily attainable with mercury vapor pumps) the same piece of tubing would diminish the actual speed of exhaust to 844 cm.³ per second. In order to make effective use of the speed of this pump, it would be necessary to use very much larger tubing. Thus, let us assume that the connecting tube has a diameter of 3 cm. and a length of 30 cm. (To use tubing larger than this is usually impracticable, while the length given is about as short as would be practical.)

$$W\sqrt{\rho_1} = 10^{-4} \times 1.04 \text{ (for air at } 20^\circ\text{C.)}$$

$$1/S_1 = 10^{-4} \times 2.5$$

$$\text{Hence, } S_2 = 2825 \text{ cm.}^3 \text{ per second.}$$

These results indicate how seriously the speed of a mercury vapor pump may be limited by the resistance of the tubing unless this is of very large size. It also follows from these considerations that in the case of a low speed pump such as the

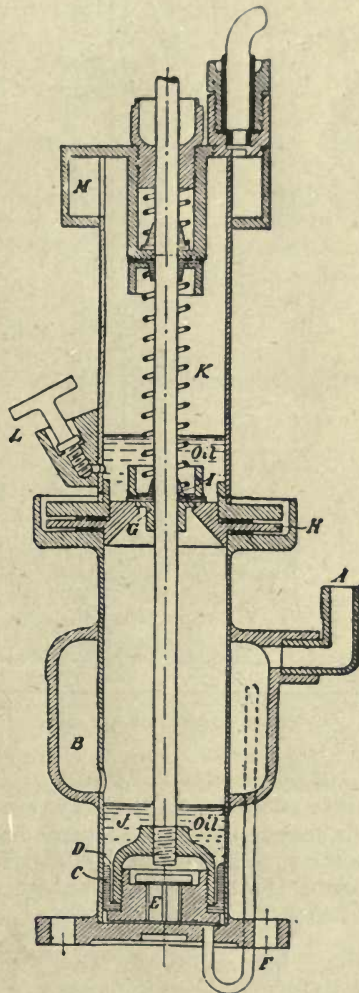


Fig. 5. Details of Construction of Geryk Vacuum Pump

Gaede diffusion pump ($S=80$) or a rotary oil pump ($S=100$), the resistance of the tubing, as long as it is not too large, is not nearly as important a factor as in the case of high speed pumps.

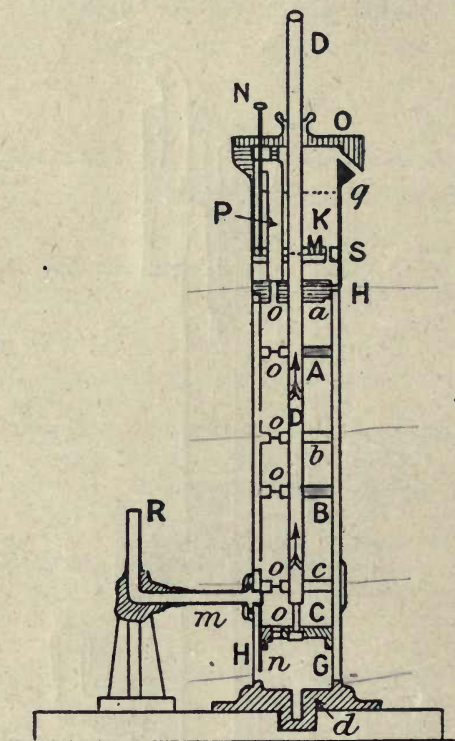


Fig. 6. Gaede Piston Pump

MECHANICAL PUMPS

The early forms of exhaust pumps were of the piston type. As they have been largely superseded in modern practice, especially for high vacuum work, no detailed mention of them need be made in this connection. Moreover, they are described in most elementary text-books on physics.

Geryk Vacuum Pump

This is a modern form of the piston type of pump (see Figs. 4 and 5), made by the Pulsometer Engineering Co. The illustrations

and the following description are given by E. H. Barton:³

"Referring to Fig. 5, A is the suction pipe, B the air port into the cylinder above the piston, C is the piston whose bucket leather is kept up to the cylinder wall by oil pressing in the annular space D, E is the piston valve, F an air pipe to relieve the piston on the first few strokes, G, H and I collars and cover forming a good joint and delivery valve combined.

"When the piston is at the bottom of its stroke as shown, there is a perfectly free opening from A to B. As the piston rises the port B is cut off and the cylinder full of air irresistibly carried up to outlet valve G. No air can get back past the piston as it is covered with oil. When the piston approaches the top of its stroke, it lifts the valve G off its face and gives a free outlet for the air. The oil on the piston then mingles with that shown above G, but the right quantity returns with the piston on the closing of G. L is the plug for filling up with oil, which is very non-volatile, moistureless and non-solvent of air and fills all clearance spaces and seals the valves."

With a single-cylinder pump of this type it is claimed that a pressure of about a quarter of a millimeter of mercury can readily be obtained.

Gaede's Piston Pump⁴

This form, shown in Fig. 6, consists really of three piston pumps in series. The vessel to be exhausted is connected at R. As the piston rod D moves upwards, it carries with it the three pistons A, B, and C. The air is thus forced from N (which communicates with the tube M) through the valves O in the stationary partitions *c*, *b*, and *a* into the chamber K from which it is ejected into the air by the vent *q*. The top chamber K also contains a small amount of oil which forms an emulsion with the water and other vapors condensed above the piston A. "This emulsion is forced, together with the air, through the valve *o* in the cover *a*, through the tube P above the valve, and thence into the chamber K. This chamber is filled with a fibrous mass by which the oil and water emulsion is separated into its components. In consequence of its greater density, the water collects on the bottom M of the chamber, and may be pumped off as often as necessary by means of a glass syringe and rubber tube connected to the tube N extending upwards out of the pump.

³ An Introduction to the Mechanics of Fluids, p. 197 (Longmans, Green & Co., 1915). See also Encycl. Britannica, 11th Edition, Vol. 22, p. 646.

⁴ W. Gaede, Phys. Zeits. 14, 1238, 1913.

See also E. H. Barton, loc. cit. pp. 198-9, from whose book the description given in the text is quoted.

The oil overflows through the tube S into the space between *a* and *M*, whence it re-enters the pump barrel to combine with fresh quantities of water vapor."

According to Gaede's published account it is possible with this pump to obtain a pressure as low as *0.00005 mm. mercury*; i.e. *0.067 bar.*, when exhausting into atmospheric pressure.

Sprengel Pump

The use of a water-jet as a suction pump is quite familiar. With this pump, the minimum pressure obtainable is that corresponding to the vapor pressure of water at the temperature which it has in the supply line; i.e., from 5 to 10 mm. mercury. As the vapor pressure of mercury at ordinary temperatures is only about 1 to 2 bars it is possible by means of a stream of mercury to obtain fairly low pressures, and by interposing a refrigerating chamber between the vessel to be exhausted and the nozzle which communicates with the mercury stream it is possible to obtain still lower pressures. The *Sprengel* mercury pump operates on this principle, and some of the simpler forms are described in most elementary text-books.⁵

G. W. A. Kahlbaum⁶ has described a form of Sprengel pump which he states to be capable of exhausting a 400 cubic cm. bulb in 30 minutes to 0.004 bar. In a subsequent paper⁷ he gives the following data with regard to the speed of exhaust of a 500 cubic cm. bulb:

3 minutes to 0.5 mm. mercury
15 minutes to 0.000165 mm.
30 minutes to 0.000069 mm. = .092 bar

He states that with special care he was able to get a pressure as low as .0024 bar. This pressure is evidently that of residual gas and does not include the pressure of the mercury vapor itself, which, as stated above, would be between 1 and 2 bars.

Geissler-Toepler Pump⁸

The principle of this pump is fundamentally the same as that used by Torricelli in his famous experiment. In this type (Fig. 7) mercury forces the piston and also opens and closes certain ports, so that no valves are needed except one rough glass valve (*g*) to

⁵ See *Encycl. Brit.* loc. cit., also Winkelmann, *Handbuch der Physik*, I, 2, pp. 1314-1332, contains a very detailed description of the different forms of Sprengel and Toepler mercury pumps.

⁶ *Wied. Ann.* 53, 199 (1894).

⁷ See also L. Zehnder, *Ann. d. Phys.* 10, 623 (1903), for a description of an improved form of Kahlbaum's pump.

⁸ See *Encycl. Britannica* and Winkelmann, loc. cit., also Barton loc. cit., from whose book Fig. 7 is taken.

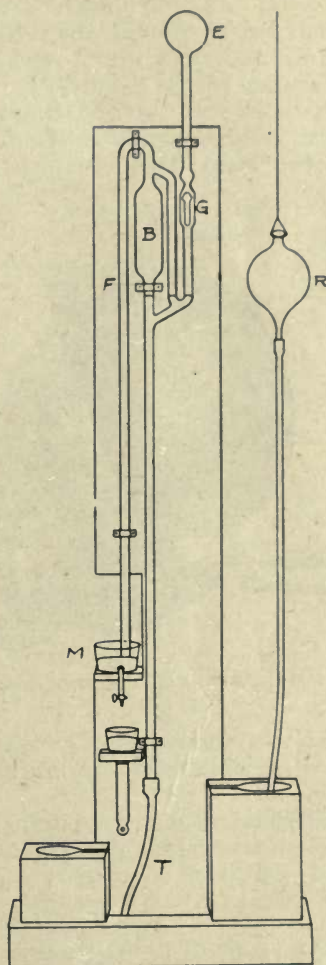


Fig. 7. Toepler Pump

prevent the mercury from entering the vessel, E, which is being exhausted. The essential parts of the pump are made of glass and the air from E is exhausted by alternately raising and lowering the mercury reservoir R which is connected to the tube of baro-

metric length below B. At each upward "stroke," the gas in B is closed from E and forced through the tube F, into the atmosphere at M. Then on the downward stroke, the pressure in E is lowered by expansion of the gas into B. E. Bessel-Hagen⁹ has described a modified form of Toepler pump with which he claims to have obtained pressures of residual gas as low as 0.016 bar.¹⁰ Both the Sprengel and Toepler pumps have rendered very

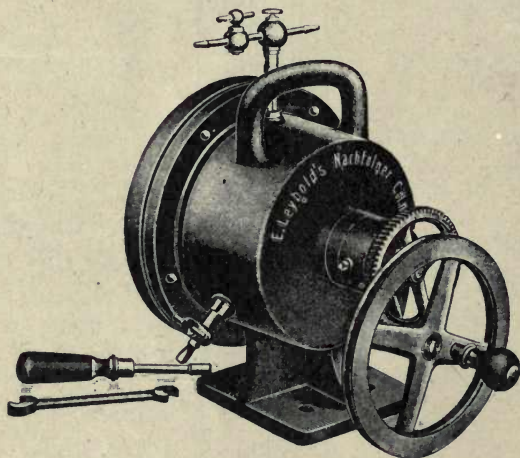


Fig. 8. Gaede Rotary Mercury Pump

useful service in high vacuum investigations, and there is no doubt that with care it is possible to obtain pressures as low as .02 to .01 bar by their use.

The great disadvantages of these pumps are, however, twofold. First, they require constant personal attention during the exhaust and second, the speed of exhaust is extremely slow, as it depends upon the rate at which the mercury can be raised and lowered alternately. It is of interest to note in this connection the results obtained by Scheele and Heuse¹¹ in their investigation of the degree of vacuum attainable with different types of pump. They used a 6 liter bulb and measured the speed of exhaust by means of a very sensitive McLeod gauge.* In the experiments

⁹Wied. Ann. 12, 425, 1881.

¹⁰ Other forms of Toepler pump are described by a A. Stock Ber. deutsch. chem. Ges. 38, 2182, 1905, and E. Grimsehl, Phys. Zeits. 8, 762, 1907.

¹¹ Zeits. f. Instrumentenkunde, 29, 47, 1909.

* See Chapter III for description of this gauge.

with a Toepler pump, each stroke actually required two minutes, and two more minutes were allowed between each stroke for equalization of pressure. Table VIII gives the pressures at the end of different intervals of time.

The last column gives the "speed of exhaust" as calculated by equation (37). Compared with the speed of even 100 cm^3/sec . obtained by a Gaede rotary mercury or an ordinary oil pump (described later) the speeds given in Table VIII are manifestly very low. Considering, furthermore, that in the case where gas is continually evolved from the walls, the minimum attainable pressure is given by the ratio S/q where q denotes the rate of gas evolution, it is seen that in actual practice it would be very difficult to obtain pressures below .01 bar by means of a Toepler pump.

Similar results were obtained by Scheele and Heuse in investigating the rate of exhaust of a 6 liter bulb by means of a Sprengel pump (Zehnder's form).¹²

TABLE VIII
SPEED OF EXHAUST WITH TOEPLER PUMP

t (minutes)	press (mm. Hg.)	$E = \frac{2.3 V}{60 t} \log \frac{p_1}{p_2}$
0	0.0645	0.40
2	0.0399	
24	0.0254	0.38
48	0.0107	
60	0.00709	0.35
108	0.00141	
120	0.00093	0.35
180	0.00024	
192	0.00015	0.39
240	0.000053	
252	0.000038	0.28
264	0.000032	
300	0.000025	0.06

Gaede Rotary Mercury Pump

An automatic form of Toepler pump has been described by U. von Reden,¹³ with which he claims to have exhausted a 500 cm^3 bulb in 13 minutes to a pressure of .00001 mm. From his data, the speed of exhaust is found to be about 20 cm^3/sec . In 1905, W. Gaede designed a rotary mercury pump which has been used to a very large extent in the commercial exhaust of incandescent

¹² Ann. d. Phys. 10, 623 (1903).

¹³ Phys. Zeits. 10, 316, 1909.

lamps and Roentgen tubes until quite recently. The pump as described in the first publication¹⁴ and illustrated in Fig. 8, consists of an iron casing (with glass front) partially filled with mercury, in which a porcelain drum is made to rotate. A rough pump producing a vacuum of 10 to 20 mm. is used as fore-pump. Fig. 9 shows a vertical section of the pump, and Fig. 10 a front view. The iron case is shown at *g*, and *G* is a heavy glass plate through which pass the tubes *R* and *r* which connect to the vessel to be

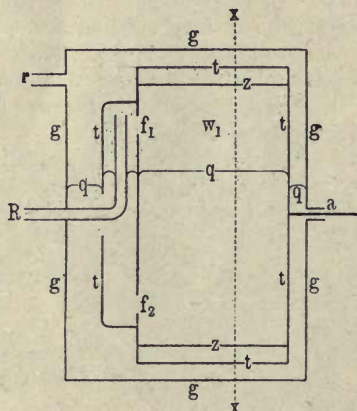


Fig. 9. Gaede Rotary Mercury Pump, Vertical Section

exhausted and the fore-pump respectively. The porcelain drum *t* is built up of two (or more) sections as shown in Fig. 9 and rotates on the axis *a*. As the drum rotates in the direction of the arrow the compartment *W* is at first increased in volume and thus sucks in the gas at the opening *f*, from the vessel to be exhausted. During the second part of the revolution, the opening *f* becomes covered with mercury, as shown at *f*₂, and the gas is then forced out under pressure from the compartment *w*₂ into the space between the walls *Z*₁ and *t*₁ and into the rough pump connection at *P*.

Fig. 11 shows an improved form of the pump in which the opening to the rough pump *r* is brought in through the iron casing. The vessel to be exhausted is connected at *E*, and a side tube *t* is provided with *P*₂ *O*₅ to take up water vapor. The tube *MOF* acts as manometer and also makes it possible to exhaust with

¹⁴ Verh. d. deutsch. Physik. Ges. 7, 287, (1905). Phys. Zeits. 6, 758-760 (1905).

the rough pump alone at the beginning. As the vacuum improves, the mercury in *o* rises and seals off the connection to the rough pump through *a s*₁. The system is then ready for exhausting to lower pressure by means of the mercury pump.

Table IX gives data for the speed of exhaust of a volume of 6250 cm.³ with a Gaede rotary pump operating at 20 r.p.m.

TABLE IX
SPEED OF EXHAUST WITH ROTARY MERCURY PUMP

t (min.)	P (mm.)	$E = \frac{2.3 V}{60 t} \log \frac{P_1}{P_2}$
0	9	
5	0.03	94.5
10	0.0018	46.5
15	0.00023	34.0
20	0.0001	13.8
25	0.00007	6.9
30	0.00007	0.0

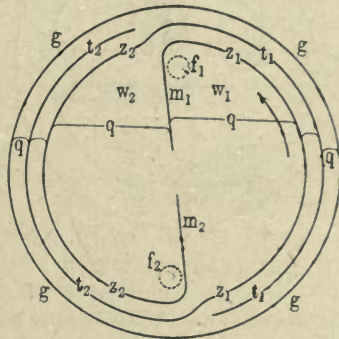


Fig. 10. Gaede Rotary Mercury Pump,
Diagrammatic View

The speed of this pump is therefore approximately 100 cm.³/sec. at the maximum, while the degree of vacuum attainable is about .00007 mm. or 0.1 bar.¹⁵

Rotary Oil Pump¹⁶

Figs. 12 and 13 show the construction of a pump of this type designed by Gaede primarily for the purpose of acting as a fore-

¹⁵ Later improvements in this pump have been described in *Verh. d. deutsch. Physik. Ges.* 9, 639 (1907), and *Phys. Zeits* 8, 852 (1907).

¹⁶ G. Meyer, *Verh. d. deutsch. Phys. Ges.* 10, 753 (1907).

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 pump to the rotary mercury pump just described. It is also shown in Fig. 16 at the right hand side. The pump consists of a steel cylinder A which rotates eccentrically inside a steel casing. The projections at S are held tightly against the inner wall by means of springs, so that as the cylinder rotates the air is sucked in at C and forced out through the valve D into the oil chamber O and from there into the atmosphere at J. The oil serves as

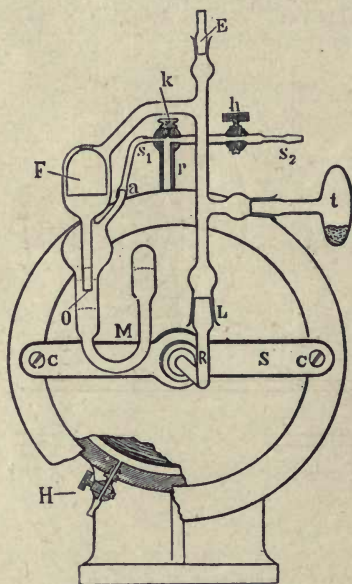


Fig. 11. Improved Form Gaede Mercury Pump

automatic lubricant and also helps to prevent air from leaking back into the fine pump side, by forming a film between the rotating and stationary members.

Fig. 14 illustrates a standard form of rotary oil pump used in incandescent lamp factories and which can also be used as a fore-pump to higher vacuum pumps such as Gaede's Molecular or Langmuir's Condensation pump. With a fore-pump pressure of about 1 cm. mercury, such a pump is capable of exhausting to a pressure of approximately 1 bar, and with two pumps in series the fine side pressure may be lowered to 0.1 bar.¹⁷

¹⁷K. T. Fischer, Verh. deutsch. Physik. Ges., 7, 383 (1905), has described a form of rotary oil pump for use in commercial exhaust operations. With two pumps in series exhausting into atmospheric pressure he states that a pressure of about 2 bars may be obtained.

With a pump of this type operating at about 400 r.p.m., the speed of exhaust is 100–150 cm.³ per second.

Gaede Molecular Pump

The Gaede molecular pump undoubtedly marks a distinct advance in the design of pumps for the production of high vacua. The difference between this pump and the types previously constructed has been well described by Gaede himself in the paper which he published in 1913.¹⁸

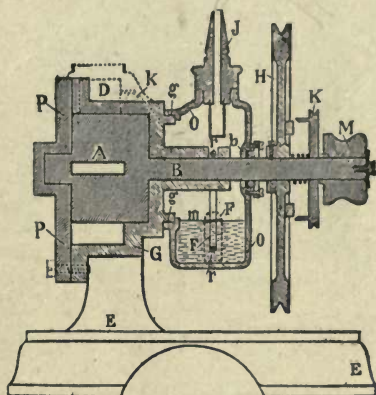


Fig. 12. Gaede Rotary Oil Pump, Side View

“All high vacuum pumps known up to the present consist of an exhaust arrangement which, according to the original idea of Otto von Guericke, separates a definite volume of gas from the vessel to be exhausted, and then gives it up to a fore-vacuum or the atmosphere. It is absolutely essential in these pumps to separate the rough side from the higher vacuum side as much as possible. This is accomplished in the mechanical pumps by tight-fitting pistons and valves, and in the case of mercury and oil pumps by means of the liquids themselves. On the other

¹⁸ W. Gaede, *The Molecular Air Pump*. *Ann. d. Phys.* 41, 337-380 (1913). This paper contains a complete discussion of the theory and construction of the pump. Briefer descriptions may also be found in the following:

W. Gaede, *Physikal. Zeits.* 13, 864-870 (1912), and *Verh. d. deuts. Phys. Ges.* 14, 775-787 (1912).

K. Goes, *Physikal. Zeits.* 13, 1105, and 14, 170-2 (1913). Description of some experiments with the pump and precautions in using it.

Electrician (London), 70, 48-50 (1912).

K. Jellinek, *Lehrbuch d. Physikal. Chemie*, I, 1, pp. 330-333 (1914).

M. L. Dunoyer, *Les Idées Modernes sur la Constitution de la Matière*, pp. 215-271 (1913).

hand, in the case of the molecular pump there is no separation, whether piston or fluid, between the high-vacuum and fore-vacuum." The gas is dragged along from the vessel to be exhausted into the fore-vacuum by means of a cylinder rotating with high velocity inside a hermetically sealed casing. The pump thus represents a logical development and application of the laws of flow of gases at very low pressures as investigated by Knudsen, Smoluchowski, and Gaede himself.

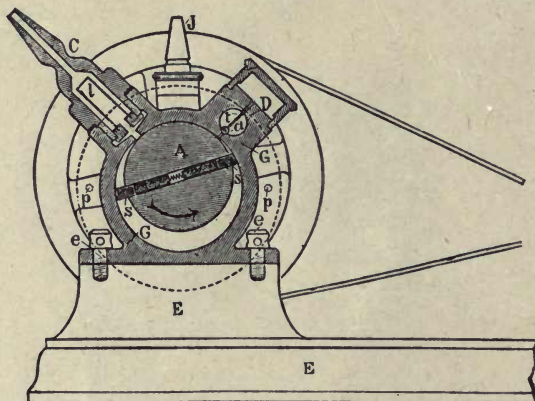


Fig. 13. Gaede Rotary Oil Pump, Front View

The fundamental principle of the pump may be illustrated by means of Fig. 15. The cylinder A rotates on an axis a (in the direction of the arrow) inside the air-tight shell B and drags the gas from the opening n towards the opening m , so that a pressure-difference is built up in the manometer M, as shown by the mercury-levels at o and p . Between m and n there is a slot in the case B as shown in the diagram, while at every other point A and B are very close together. Now, at ordinary pressures the viscosity is independent of the pressure. Under these conditions, as Gaede shows, the difference in pressure at o and p depends only on the speed of rotation u , of the cylinder, the coefficient of viscosity of the gas, η , the length of the slot, L and h the depth measured radially, according to the following relation:

$$p_1 - p_2 = 6 \eta u n / h^2$$

At low pressures, however, the number of collisions between gas molecules becomes relatively small as compared with the

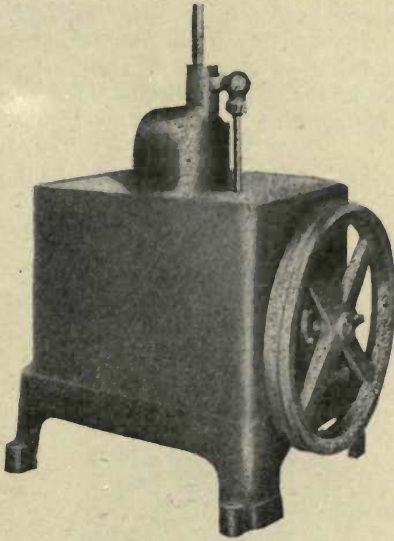


Fig. 14. Standard Form of Rotary Oil Pump

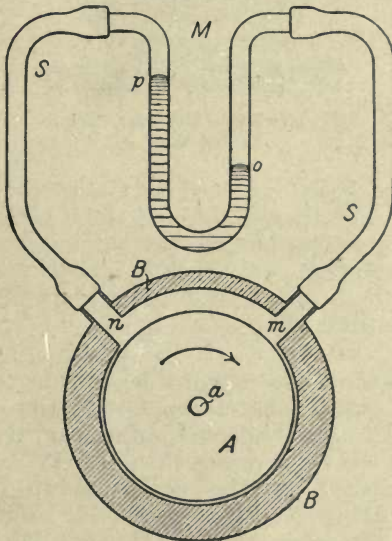


Fig. 15. Diagram Explaining Operation of Molecular Pump

number of collisions between the gas molecules and the walls. Under these conditions the molecules therefore tend to take up the same direction of motion as the surface against which they strike, if the latter is in motion. This conclusion is based upon the investigations of Knudsen on the laws of molecular

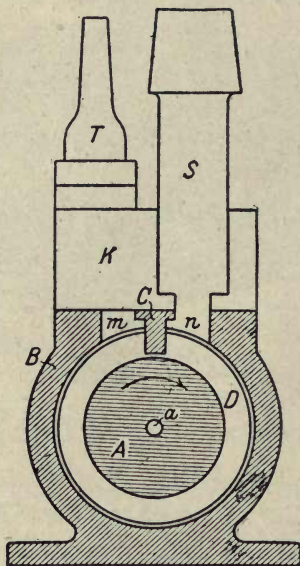


Fig. 16. Gaede Molecular Pump,
Front View

flow, which have been discussed in Chapter I. The relation previously deduced is therefore found to be no longer true and instead of the pressure-difference remaining constant at constant speed of rotation, the *pressure-ratio* is now constant and independent of the pressure in the fore-vacuum. Gaede shows that at very low pressures,

$$P_1/P_2 = Ku$$

where K is a constant whose value depends upon the nature of the gas and the dimensions of the slot in the casing B of the pump, so that at constant speed of rotation u , the ratio between the pressures on the two sides of the pump is constant.

The construction of the actual pump based on these principles is illustrated in Figs. 16 and 17, while Fig. 18 shows the pump connected in series with a Gaede rotary oil pump.

The rotating cylinder A (Figs. 16 and 17) has 12 parallel slots around the circumference, into which project the extensions C from the outer casing. If A rotates clockwise, the pressure at *m* is greater than that at *n*, and in order to increase this pressure different sections are connected in series. The distance between

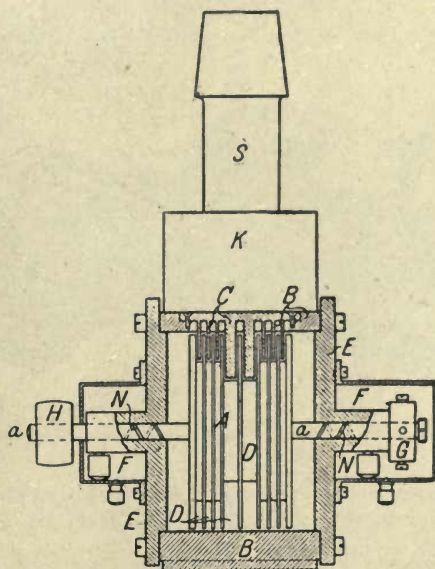


Fig. 17. Gaede Molecular Pump,
Side View

the outer edge of the cylinder A and the inside of the shell B is about 0.01 cm. The over-all radius of A is 5 cm., and the depth of the slots varies from 0.15 cm. in the outer section to 0.6 cm. in the inner ones. With the cylinder rotating clockwise as indicated, the vessel to be exhausted is connected at S, while the opening T is connected to an ordinary mercury or oil pump capable of exhausting to a pressure of less than 0.05 mm. Hg. As the speed of rotation of the cylinder is very high (about 8000 r.p.m.) oil cups are provided at F, and the shaft N is so designed that the oil in the spiral slot is driven outwards by the centrifugal action. The slots in the rotor are so arranged that the lowest pressure is in the center, and the pressure increases uniformly outwards until the ends, where it is equal to that produced by the rough pump.

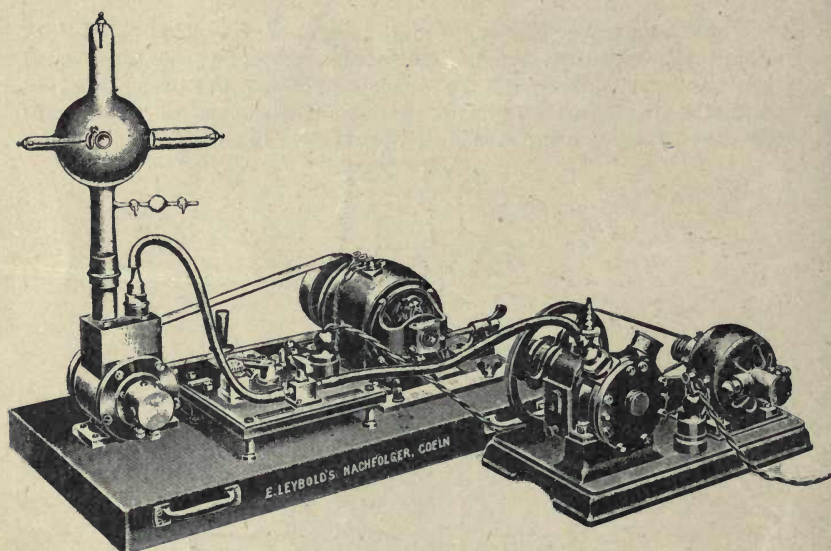


Fig. 18. Assembly of Gaede Molecular and Gaede Rotary Oil Pumps

The effect of varying the speed of rotation or the rough pump pressure on the degree of vacuum produced by the molecular pump, is shown in Table X.

TABLE X
EFFECT OF SPEED OF ROTATION ON DEGREE OF VACUUM
OBTAINED WITH GAEDE MOLECULAR PUMP

Speed of Rotation R.P.M.	Rough-pump Press. mm. Hg.	Press. on Fine Side mm. Hg.
12000	0.05	0.0000003
12000	1	0.000005
12000	10	0.00003
12000	20	0.0003
6000	0.05	0.00002
2500	0.05	0.0003
8200	0.1	Not measurable
8200	1.	0.00002
8200	10	0.0005
6200	0.1	0.00001
6200	1.0	0.00005
4000	1.1	0.00003
4000	1	0.0003

The pressures on the fine side were measured with an extremely sensitive type of McLeod gauge except in the case of the first result given in the table which was estimated. The writer's own experiments¹⁹ with the Gaede molecular pump at 8000 r.p.m. have shown that with a rough pump pressure of 20 mm. the fine side pressure was 0.0004 mm., so that the ratio of the pressures was 50,000—a result which is in accord with figures given by Gaede.

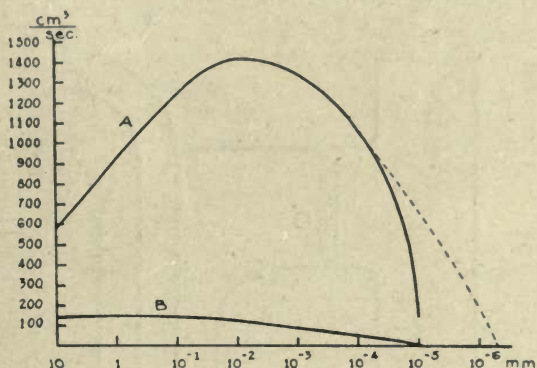


Fig. 19. Effect of Rough-pump Pressure on Speed of Gaede Molecular Pump

The speed of the pump as defined by equation (37) has been found by Gaede to vary with the magnitude of the rough-pump pressure. The curve A in Fig. 19 shows that the maximum speed is about 1400 cm.³ per second with a fore-vacuum of 0.01 mm. For comparison Gaede also shows the curve B for his rotary mercury pump, which has a speed of about 130 cm.³ per sec., at the maximum.

MERCURY VAPOR PUMPS²⁰

The fact that a reduction in pressure can be obtained by a blast of steam or air has been known and applied in the industry for a long time. In steam aspirators or ejectors such as are used for producing the low pressure required in the condenser of a

¹⁹ S. Dushman, *Phys. Rev.* 5, 224 (1915).

²⁰ The introductory remarks are based largely upon the discussion of this subject by I. Langmuir in his paper on, "The Condensation Pump, an Improved Form of High Vacuum Pump," *General Electric Review*, 1916, p. 1060, also *Journ. Franklin Inst.*, 182, 719 (1916), *Phys. Rev.* 8, 48 (1916). An excellent discussion of the mercury vapor pumps described in this section has also been written by A. Gehrts, *Naturwissenschaften*, 7, 983 (1919).

steam turbine, "the high velocity of the jet of steam causes, according to hydrodynamical principles, a lowering of pressure, so that the air to be exhausted is sucked directly into the jet." An analysis of the action of the aspirator shows, according to Langmuir, that in its action two separate processes are involved.

"1. The process by which the air is drawn into the jet.

"2. The action of the jet in carrying the admixed air along into the condensing chamber.

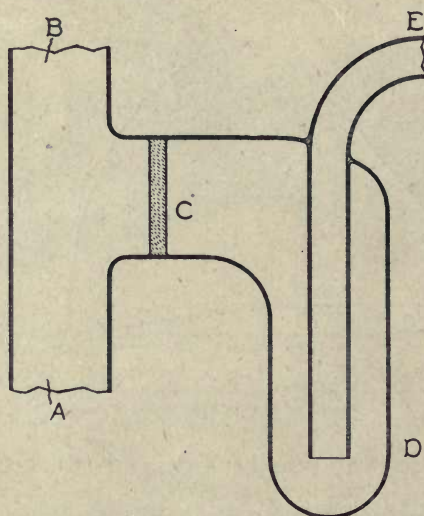


Fig. 20. Diagram Illustrating Principle of Diffusion Pump

"The aspirators cease operating at low pressures because of the failure of the first of these processes. If air at low pressure could be made to enter the jet, and if gas escaping from the jet could be prevented from passing back into the vessel to be exhausted, then it should be possible to construct a jet pump which would operate even at the lowest pressures."

This problem has been solved in two different ways by Gaede and Langmuir. In the pumps devised by each of these, a blast of mercury carries along the gas to be exhausted into the condenser (process 2). In order to introduce gas into the blast of mercury, Gaede has used diffusion through a narrow opening. On the other hand, Langmuir has made use of the fact that the mercury atoms on colliding with the gas

molecules must impart to the latter a portion of the momentum which they possess in virtue of their high average kinetic energy, while the mercury atoms themselves are removed rapidly from the stream of mixed gases by condensation on the cooled walls.

Gaede's Diffusion Pump²¹

The action of Gaede's "diffusion" pump can best be illustrated by referring to Fig. 20. A blast of steam is blown through the tube A B, in which is fixed a porous diaphragm C. The vessel to be exhausted is attached at E. Water vapor diffuses through the capillaries in the diaphragm into the trap D where it is condensed by some refrigerating agent, while air diffuses through the diaphragm in the opposite direction into the tube A B, from where it is drawn away rapidly by the blast of steam. The result is that the pressure in E decreases and finally reaches a very low value.

A study of the phenomena of diffusion of gases through mercury vapor in narrow tubes led Gaede to the conclusion that at sufficiently low pressures, where the mean free path L of the air molecules in mercury vapor is comparable with the diameter d of the tube, the volume of air, V , diffusing through a tube of length l , per unit time, is given by relation of the form:

$$V = k\pi d^3/l \quad (40)$$

where k is a constant for any given gas A. In other words, the speed of exhaust is independent of the actual pressure of the gas in the vessel to be exhausted, and the relative decrease in the pressure per unit time therefore remains constant as the pressure in the system is decreased. This result obtained empirically by Gaede is evidently in agreement with Knudsen's deductions as stated in equations (28) and (29), Chapter I.

The actual construction of the diffusion pump is shown in Fig. 21. The porous diaphragm is replaced by a steel cylinder C with a narrow slit S whose width can be altered by means of the set screws H. The cylinder is set in the mercury trough G, which forms a seal between the low and high pressure parts. The mercury at A is heated and the stream of vapor passes over the slit in the steel cylinder in the directions indicated by the arrows. The air or other gas from the system to be exhausted (connected at F) diffuses into this mercury stream at S, and then passes out through E into the fore-pump which is connected at V. Any mercury vapor passing out through S is condensed on the

²¹ Ann. Phys. 46, 357-392 (1915).

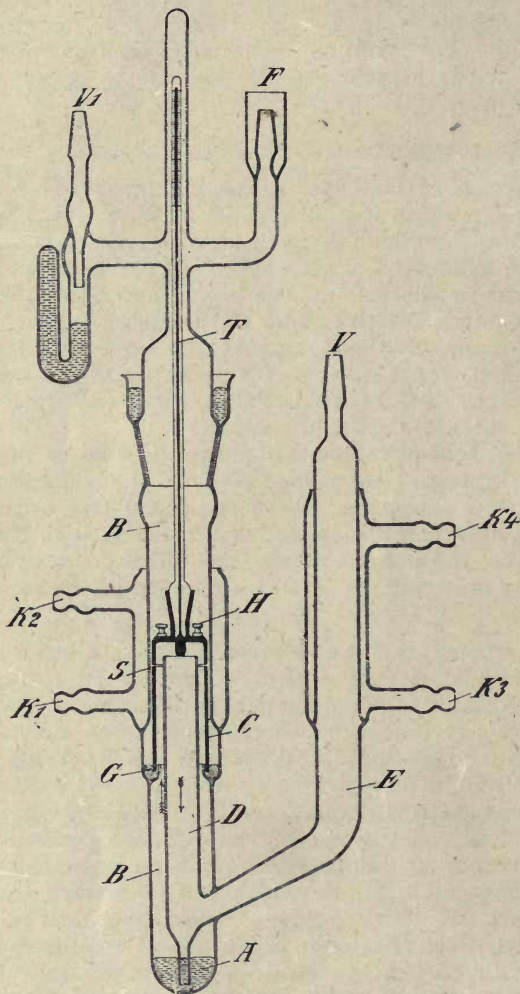


Fig. 21. Gaede Diffusion Pump

glass in the immediate neighborhood, by means of the water cooling jacket K_1 K_2 . The opening V connects with the fore-pump or other source of rough vacuum and is used for exhausting the system until the pressure gets low enough for the operation

of the diffusion pump to become effective. As soon as this stage is reached the mercury in the trap automatically closes this opening and the exhaust then continues by means of the diffusion pump.

According to Gaede's theory the maximum speed of the pump is attained when the width of the slit S is of the same order of magnitude as the mean free path of the gas molecules in the slit

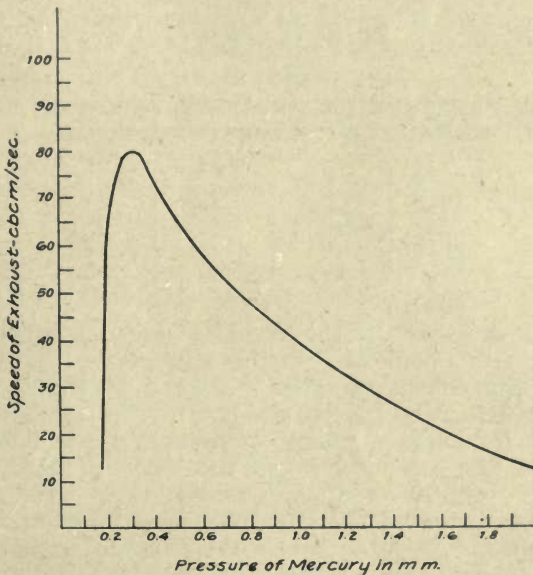


Fig. 22. Effect of Mercury Vapor Pressure on Speed of Diffusion Pump

and when the vapor pressure of the mercury is only slightly in excess of the pressure in the fore-vacuum (at V). Consequently the temperature of the mercury vapor has to be maintained at a fairly constant value. For this purpose a thermometer, T , is placed inside the tube B .

The effect of varying the temperature of the vapor (and consequently its pressure) on the speed of exhaust is shown by the data (given by Gaede) in Table XI and the plot of these in Fig. 22. These results were obtained with a slit width of 0.012 cm. The maximum speed of 80 cm^3 per sec. was attained at a temperature of the mercury vapor of 99°C . At this tem-

perature the pressure of the mercury vapor is 0.27 mm., while the mean free path for air in mercury at this pressure according to Gaede's calculation is about 0.023 cm.

Table XII shows the effect of varying the width of the slit. The noteworthy fact is that the speed of the pump remains constant as the pressure in the exhausted system is decreased, a result which Gaede previously deduced from theoretical consideration, as mentioned already.

The great advantage of the diffusion pump over all the previous types of pump consists therefore in the fact that there is

TABLE XI
EFFECT OF PRESSURE OF MERCURY VAPOR ON SPEED OF EXHAUST WITH DIFFUSION PUMP

T	P (mm.)	S	T	P	S
90°C.	0.165	13.4	118.5	0.72	51
94	0.20	60	127.5	1.10	38
97	0.24	70	134	1.51	23
99	0.27	80	139	1.84	15
113	0.55	62	143.5	2.2	11

theoretically no limit to the degree of vacuum which can be attained by its operation. In the case of the Gaede rotary pump and all mechanical pumps the speed of exhaust decreases with decrease in pressure. In the case of the Gaede molecular pump the minimum pressure attainable depends upon the pressure in the fore-vacuum as the ratio of the pressures is constant for the pump. There is thus with all these pumps a fixed lower limit to the lowest pressure attainable in the exhaust system. While there is no such limitation with the diffusion pump, it does have the double disadvantage of low exhaust speed and the necessity of carefully regulating the temperature of the mercury vapor.

TABLE XII
EFFECT OF WIDTH OF SLIT ON SPEED OF EXHAUST WITH DIFFUSION PUMP

WIDTH OF SLIT = 0.025 CM.		WIDTH OF SLIT = 0.004 CM.	
p	S	p	S
0.025 mm.	77	0.07 mm.	52
0.009	72	0.028	48
0.0025	67	0.006	40
0.0003	72	0.0015	38
0.0002	73	0.0004	41
0.00006	70	0.00007	40

Langmuir's Condensation Pump

Both these disadvantages are removed in the type of mercury vapor pump designed by Langmuir, while the advantages of the diffusion pump are retained. In constructing and operating a pump of this type it occurred to Langmuir that "the limitation of speed could be removed if some other way could be found to bring the gas to be exhausted into the stream of mercury vapor."²⁰ As stated previously, Langmuir comes to the conclusion that the ejector pump must become inoperative at low pressure, since at these pressures, "according to the kinetic theory of gases, the molecules in a jet of gas, passing out into a high vacuum must spread laterally, so that there would be no tendency for a gas at low pressures to be *drawn* into such a blast."

Furthermore, under these conditions, the mercury atoms condense on the walls of the inner tube near the inlet and owing to the latent heat of evaporation raise the temperature of the walls so that condensation ceases, and the mercury atoms are merely reflected from the walls in *all* directions. Consequently there is just as much tendency for the mercury to diffuse back towards the exhaust system as away from it, and the air molecules are thus prevented from entering into the mercury blast at the nozzle.

These considerations and the results of his previous investigations on the mechanism of condensation of gas molecules on solid surfaces* led Langmuir to the conclusion that the mercury atoms could readily be prevented from diffusing back in the direction from which the gas molecules are diffusing by simply cooling the walls of the tube near the mercury vapor outlet. Under these conditions the mercury atoms ought to be rapidly condensed as they strike the walls. At the same time the gas molecules diffusing in from the system to be exhausted would collide with the high speed mercury atoms at the jet and thus acquire a velocity component from the latter which would remove them rapidly from the space around the jet opening. The whole action of the pump constructed on the basis of this reasoning thus rests on the fundamental principle that the mercury vapor is rapidly condensed as it leaves the jet and the temperature is maintained so low that the mercury does not re-evaporate to any measurable extent. Langmuir has therefore suggested that pumps based on this principle should be designated as "*Condensation*" pumps.

* These investigations are discussed in Chapter VI.

A convenient type of glass condensation pump constructed on this principle is shown in Fig. 23.

"In order that the pump may function properly it is essential that the end of the nozzle L shall be located below the level at which the water stands in the condenser J. In other words,

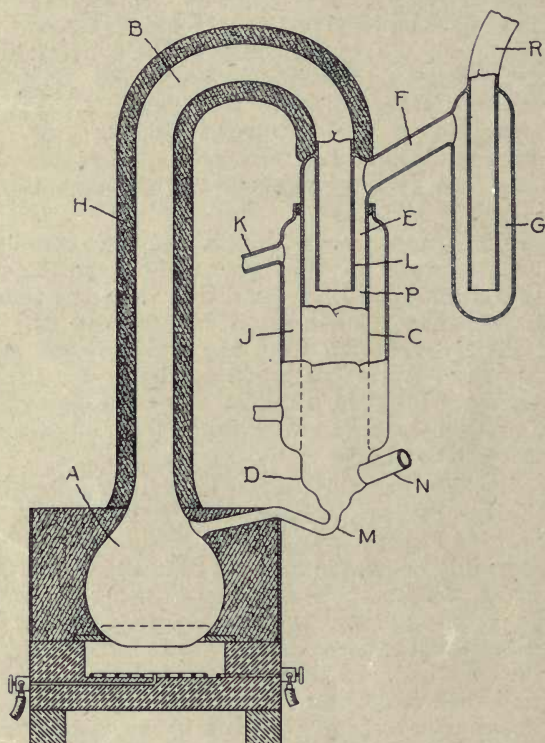


Fig. 23. Langmuir Condensation Pump, Glass Form

the overflow tube K must be placed at a somewhat higher level than the lower end of the nozzle as is indicated in the figure. The other dimensions of the pump are of relative unimportance. The distance between L and D must be sufficiently great so that no perceptible quantity of gas can diffuse back against the blast of mercury vapor, and so that a large enough condensing area is furnished.

"The pump may be made in any suitable size. Some have been constructed in which the tube B and the nozzle L were one and a quarter inches in diameter while in the other pumps this tube was only one quarter of an inch in diameter and the length of the whole pump was only about four inches. The larger the pump the greater is the speed of exhaustion that may be obtained.

"In the operation of the pump the mercury boiler A is heated by either gas or electric heating so that the mercury evaporates at a moderate rate. A thermometer placed in contact with the tube B, under the heat insulation, usually reads between 100 and 120 deg. C. when the pump is operating satisfactorily. Under these conditions the mercury in the boiler A evaporates quietly from its surface. No bubbles are formed, so there is never any tendency to bumping.

"Unlike Gaede's diffusion pump, there is nothing critical about the adjustment of the temperature. With an electrically heated pump in which the nozzle L was $\frac{7}{8}$ in. in diameter, the pump began to operate satisfactorily when the heating unit delivered 220 watts. The speed of exhaustion remains practically unchanged when the heating current is increased even to a point where about 550 watts is applied.

"The back pressure against which the pump will operate depends, however, upon the amount and velocity of the mercury vapor escaping from the nozzle. Thus in the case above cited, with 220 watts, the pump would not operate with a back pressure exceeding about 50 bars, whereas with 550 watts back pressures as high as 800 bars did not affect the operation of the pump."

Condensation Pumps Built of Metal

For most practical purposes a glass pump has many disadvantages. Langmuir has therefore applied the same principles to the construction of a metal pump.

One such type of pump which has proved relatively simple in construction and efficient in operation is shown diagrammatically in Fig. 24. "A metal cylinder A is provided with two openings, B and C, of which B is connected to the backing pump and C is connected to the vessel to be exhausted. Inside of the cylinder is a funnel-shaped tube F which rests on the bottom of the cylinder A. Suspended from the top of the cylinder is a cup E inverted over the upper end of F. A water jacket, J, surrounds the walls of the cylinder A from the level of B to a point somewhat above the lower edge of the cup E.

“Mercury is placed in the cylinder as indicated at D. By applying heat to the bottom of the cylinder the mercury is caused to evaporate. The vapor passes up through F and is deflected by E and is thus directed downward and outward against the water-cooled walls of A. The gas entering at C passes down between A and E and at P meets the mercury vapor

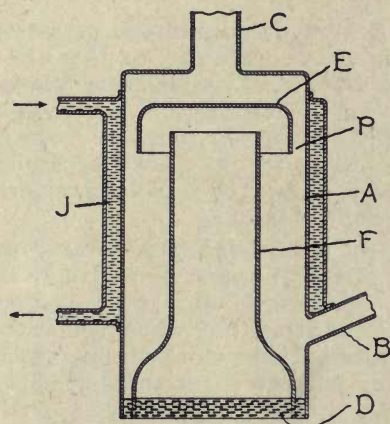


Fig. 24. Diagram of Construction of Condensation Pump, Metal Form

blast and is thus forced down along the walls of A and out of the tube B. The mercury which condenses on the walls of A falls down along the lower part of the funnel F and returns again to D through small openings provided where the funnel rests upon the bottom of the cylinder. A more detailed drawing of the pump as actually constructed is shown in Fig. 25.”

A pump in which the funnel F is 3 cm. in diameter and the cylinder A is 7 cm. in diameter gives a speed of exhaustion for air of about 3000–4000 cm.³ per second. It operates best against an exhaust pressure of 10 bars or less and requires about 300 watts energy consumption in the heater circuit.

Degree of Vacuum Obtainable

“The condensation pump resembles Gaede’s diffusion pump in that there is no definite lower limit (other than zero) below which the pressure cannot be reduced. This is readily seen from its method of operation. A lower limit could only be caused by diffusion of gas from the exhaust side (N in Fig. 23)

back against the blast of mercury vapor passing down from L. The mean free path of the atoms in this blast is of the order of magnitude of a millimeter or less and the blast is moving downward with a velocity at least as great as the average molecular velocity (100 meters per second for mercury).*

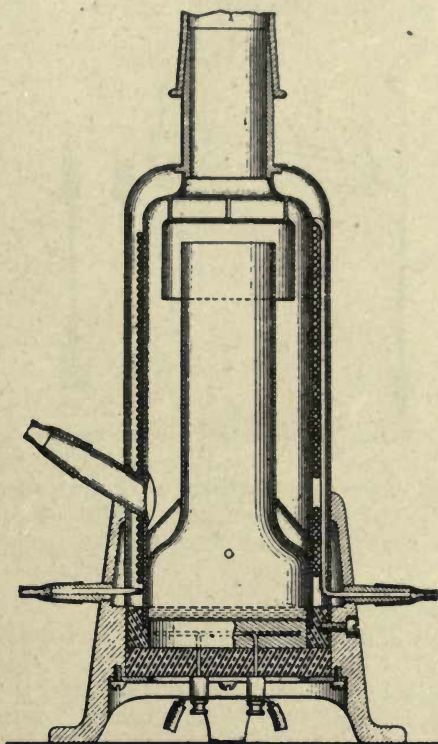


Fig. 25. Langmuir Condensation Pump, Metal Form

“The chance of a molecule of gas moving a distance about 4.6 times the mean free path without collision is only one in a hundred. To move twice this distance the chance is only 1 in 100^2 , etc. If the mean free path were one millimeter the chance of a molecule moving a distance of 4.6 cm. against the blast without collision would be 1 in 10^{20} . In other words, an entirely negligible chance.”

* This is apparent when we consider that no appreciable number of atoms pass up into the space E.

Actual observations with the ionization gauge* in this laboratory have shown that it is possible with the Langmuir condensation pump to obtain pressures which are of the order of 10^{-4} bar or less. The limiting factor which ordinarily makes it impossible to obtain pressures as low as this, is the continuous liberation of gas from the glass walls or metal parts, so

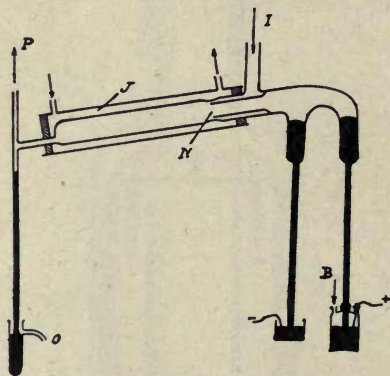


Fig. 26. Condensation Pump, Arc Type

that it becomes extremely difficult to obtain vacua in excess of the above order of magnitude. The necessary precautions in using the pump are discussed at greater length in Appendix I.

Other Forms of Mercury Vapor Pumps

Other forms of mercury vapor pumps have been described by H. B. Williams,²² Chas. T. Knipp,²³ and L. T. Jones and N. O. Russell.²⁴ The construction used by the latter is shown in Fig. 26. The advantage of this form is that it "permits using the pump as a mercury still at the same time that it is being used for exhaustion purposes. Two barometer columns introduce the mercury into the arc, the arc being started by blowing in one neck of the Wouff bottle. As shown at B the mercury vapor is driven through the nozzle N, and condenses in the chamber surrounded by the water jacket, J. The condensed clean mercury is then drawn off at O." With a current of 10-15 amps., a speed of exhaust of 400 cm.³ per sec. was obtained.

* See Chapter III for description of this gauge.

²² Phys. Rev. 7, 583 (1916).

²³ Phys. Rev. 9, 311 (1917), and 12, 492 (1918).

²⁴ Phys. Rev. 10, 301 (1916).

A simple construction for a condensation pump has also been described by W. C. Baker.²⁵ In this form as well as Knipp's the main object of the design is to simplify the glass blowing.

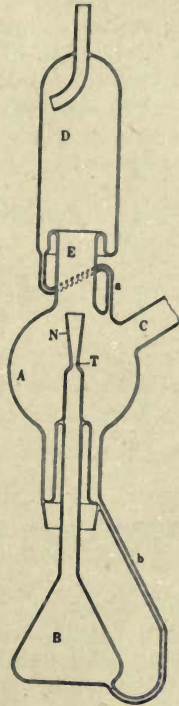


Fig. 27. Crawford's Form
of Condensation Pump.
Vertical Type

J. E. Shrader and R. G. Sherwood²⁶ have used a modified form of Langmuir condensation pump made of pyrex. Full details with all necessary dimensions are given in the original paper. The speed of the pump was measured for different amounts of energy input into the mercury heater and was found to be a maximum at about 400–500 watts input. With

²⁵ Phys. Rev. 10, 642 (1916).

²⁶ Phys. Rev. 12, 70 (1918).

the speed of exhaustion purposely cut down by a special constriction, the maximum speed observed was around 225 cm.^3 per sec. and pressures as low as $2 \times 10^{-8} \text{ mm. Hg}$ were obtained after care had been taken to heat up all the glass parts to a temperature of 500° C. for a long time.

An interesting form of mercury vapor pump is that devised by W. W. Crawford²⁷ and shown in Figs. 27 and 28. "The mercury vapor generated in the boiler B at a pressure of 10 mm. of mercury or more, escapes through the narrow throat T

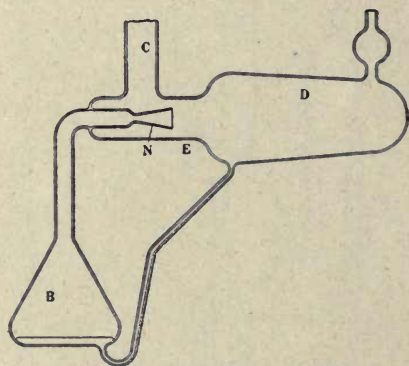


Fig. 28. Crawford's Form of Condensation Pump,
Horizontal Type

(Fig. 27), ahead of the point of entrainment. The vapor expands in the diverging nozzle N, and the issuing jet passes through the tube E, which it fills, and condenses in D, mostly, where it is found at the upper end. A slight amount of vapor escapes into the chamber A and condenses there. The condensed vapor drains back through the tubes *a* and *b*, to the boiler." The vessel to be exhausted is connected at *c*, while D connects with the rough pump. The speed of the pump in series with 10 cm. of tubing, 1.9 cm. in diameter was observed to be around 1300 cm.^3 per sec. at a boiler pressure of 10 mm. of Hg.

A two-stage mercury vapor pump to work against a primary vacuum of 2 cm. given by a water aspirator, has been described by C. A. Kraus.²⁸ It consists essentially of two Langmuir condensation pumps in series. The pump is very rapid and is capable of exhausting 1500 cm.^3 to less than 10^{-4} mm. in 10 min.

²⁷ Phys. Rev. 10, 557 (1917).

²⁸ J. Am. Chem. Sec. 39, 2183 (1917).

H. F. Stimson has also constructed a two-stage pump along the same principles,²⁹ which is illustrated in Fig. 29. "The operation of the pump is as follows: Cooling water entering at tube A flows up through the water jacket B above the lower end of nozzle F, up through the water jacket C above nozzle G, and out tube D. Mercury vapor from the boiler entering through tubes E flows through the nozzles F and G, is liquefied in the condensation chambers H and I, falls into the tubes K, and returns to the boiler through tube L. Gas from the vessel to be exhausted enters at M, flows past nozzle F, is compressed by the jet of mercury vapor in the condensation chamber H, and flows up through N to the intermediate pump. From here it flows past the nozzle G and is compressed through O into the chamber I to a pressure measured by the attached manometer, then out by tube P to the water aspirator."

The speed of the pump as defined by Gaede's equation was observed to be about 250 ccm. per sec.³⁰

General Remarks Regarding Exhaust Procedure

As has been pointed out in a previous section, the vacuum actually attained by the use of any pump is dependent, first, on the type of pump used, and second, on the rate at which gases are given off from the walls of the vessel to be exhausted and metal parts inside it. In the case of the Gaede molecular pump, as stated previously, the degree of vacuum attainable (P_1) is dependent upon the exhaust pressure (P_2) produced by the rough pump. As the value of the ratio P_2/P_1 is about 50,000, it is evident that even with a rough pump pressure of one bar, the pressure attainable with this pump is less than 10^{-4} bar. In the case of the mercury vapor pumps there is theoretically no lower limit pressure, and the only limitation is therefore that due to the second cause mentioned above.

The gases occluded on the walls of the glass vessels consist for the most part of water vapor and carbon dioxide gas along with slight amounts of carbon monoxide and other gases which are not condensable at the temperature of liquid air. Metal parts usually contain carbon monoxide and hydrogen gases.* In order to eliminate these gases it is essential to heat the glass walls and metal parts to as high a temperature as practicable.

²⁹ J. Washington Acad. Sciences 7, 477 (1917).

³⁰ M. Volmer, Ber. 52 (b), 804 (1919), has also constructed a similar form of two-stage condensation pump, which is described briefly in an abstract in J. Chem. Soc. 118, ii, 225 (1919).

* See Chapter IV for discussion of the absorption of gases by glass and metals.

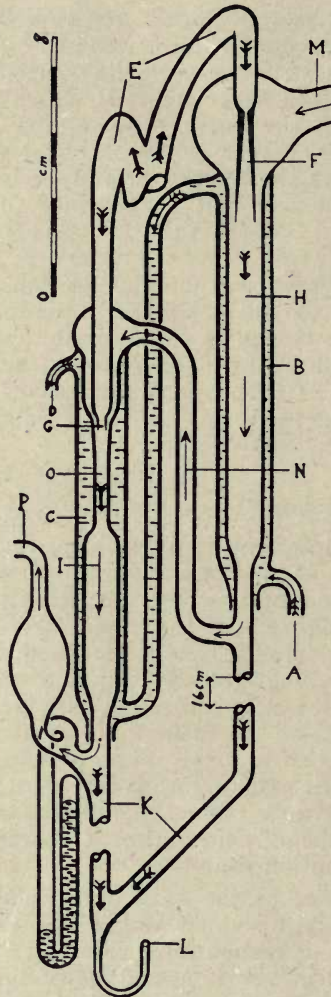


Fig. 29. Stimson's Form of Condensation Pump

The longer the duration of the heating and the higher the temperature, the lower the pressure of residual gases.

A usual procedure is to heat the glass vessels in an oven, during exhaust, for an hour or longer. For lead glass, the temperature in the oven should not exceed 360° C.; in the case of

lime glass, the temperature may be raised to 400°C ., and for vessels made of pyrex, the oven temperature may be increased to 500°C . The oven may be heated either by gas flames, or more conveniently by electrically heated grids, as the latter method permits of a more uniform distribution of temperature inside the oven and also is more convenient for regulation.

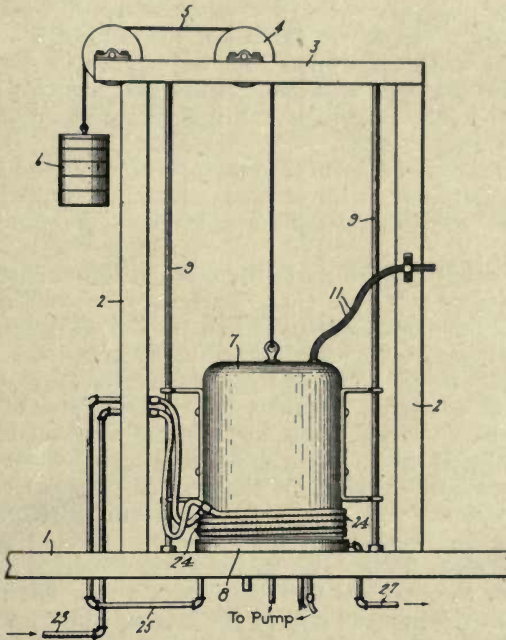


Fig. 30. Vacuum Furnace for High Temperature Exhaust

Where a very high degree of vacuum is desirable it is possible to heat the glass to temperatures higher than those mentioned above, by reducing the pressure of air in the oven itself, so that the glass walls will not collapse because of external pressure. For this purpose Langmuir devised the form of oven shown in Fig. 30.³¹

It consists of a metal chamber 7, which is open at the bottom but rests upon a base plate 8, with which it makes an air-tight joint. The chamber is provided with a heating coil wound on

³¹ I. Langmuir, U. S. Pat. ,994,010, Ma: 30, 1911.

the inside and separated from the walls by heat-insulating lining. The leads for this heating coil are shown at 11. Uprights 9 are provided for the purpose of allowing the oven to be raised or lowered. As the chamber 7 is to be exhausted it is necessary to make the joint between it and the base plate 8 air-tight. This may be accomplished by means of a rubber gasket, and in order to prevent injury to this by the heat, the chamber and the base plate are cooled by water, which flows as indicated by the arrows through the tubes 23, 24, 25 and 27. Openings are provided in the base plate for the connection between the vessel to be exhausted and the pump, and also for exhausting the chamber itself. A rough pump is, of course, all that is necessary in the latter case.

With this type of oven it is possible to heat the glass about 100° C. higher than in an ordinary oven, so that the residual water vapor and other condensible gases are removed more completely.

In the case of metal parts the elimination of gases is a more difficult matter. Where these parts are so constructed that current can be passed through them (wires or filaments) they ought to be heated to as high a temperature as the metal will stand without injury. In the case of hot cathode devices the anodes can be heated to incandescent temperatures by electronic bombardment.³² Heating the metal parts in a vacuum furnace before putting them in the glass vessel also assists materially in the subsequent exhaust on the pump. Special care should be taken to remove all traces of grease and oil from machine-made parts, by washing in acetone and alcohol and drying thoroughly before assembling in the glass vessel.

In order to eliminate mercury vapor and condensible gases emitted from the grease used on the ground glass joint between the pump and the vessel to be exhausted, it is necessary to interpose some form of refrigerating chamber in which these vapors are condensed, as shown at *G* in Fig. 23. (See also Appendix I.)

The most efficient refrigerating agent is, of course, liquid air, which is now available in a large number of laboratories. Failing this, a suspension of solid carbon dioxide in acetone or ether may be used. In the latter case it is well to insert a tube containing P_2O_5 between the oil pump and the fine pump to take care of water vapor. Observations in this laboratory have shown that in using a condensation pump it is possible to

³² For illustrations of this the reader may refer to the following publications:
I. Langmuir, *Phys. Rev.* 2, 450 (1913).
S. Dushman, *Phys. Rev.* 4, 121 (1914).

obtain practically as low pressures with solid CO_2 and P_2O_5 as with liquid air, but the interval of time required to attain this low pressure is ordinarily much longer with the former.

The temperature produced by fresh liquid air evaporating freely into the atmosphere is about -190°C . (83°K .), but rises to a higher value as the nitrogen boils away and leaves the oxygen behind.³³ With solid carbon dioxide a temperature of -78°C . is obtained. Table XIII shows the vapor pressures of a number of different gases at these low temperatures. In the case of methane, ethane and ethylene the pressures given have been extrapolated from the data given in the standard tables for higher temperatures, by plotting the value of $\log P$ against $1/T$, where T is the absolute temperature. The values plotted in this manner are found to lie on a straight line, thus making the extrapolation an easy matter.

Table XIV gives the vapor pressures of carbon dioxide, ice and mercury. In all cases the data for the lower temperatures have been extrapolated in the same manner as for those given in the previous table.

As is evident from these data, ice and mercury have no appreciable vapor pressure at -190°C ., while carbon dioxide has a vapor pressure between 0.001 and 0.0001 bar at this temperature. Under these conditions any of the latter gas if condensed in the liquid air trap would produce a constant pressure of residual gas of at least 10^{-4} bar. Under the same conditions ethylene and ethane would produce pressures that might exceed 10 bars. However, these gases are not met with in ordinary exhaust operations. The other gases are non-condensable at the temperature of liquid air, and are therefore removed by the pump.

It is also evident that at the temperature of evaporating solid CO_2 (-78°C .) the vapor pressure of mercury is negligibly small, but that of ice is quite high, hence the necessity for using P_2O_5 in order to take care of this. It is also advisable in all cases of exhaust operations not to use the refrigerating agent during the initial stages of heating, so that the bulk of condensable gases will be removed by the pump. Otherwise the vapors may be condensed in the trap and maintain a constant pressure of residual gases in the system for a very long time.

Temperatures below -190°C . may be obtained by working with liquid air under reduced pressure. As is evident from Table XIII, it is possible in this manner to obtain a temperature

³³ E. C. C. Baly, Phil. Mag. 49, 517 (1900). This paper gives complete data regarding the relation between composition and boiling point in the distillation of liquid air.

TABLE XIII
 VAPOR PRESSURE OF "NON-CONDENSIBLE" GASES,
 AT LOW TEMPERATURES

Temperature Degrées Centigrade	Absolute Temperature	Pressure in mm. Hg.
Oxygen (O₂)		
-183.0	90.1	760
-211.2	61.9	7.75
Nitrogen (N₂)		
-195.8	77.3	760
-210.6	62.5	86
Carbon Monoxide (CO)		
-190	83	863
-200	73	249
Methane (CH₄)		
-185.8	87.3	79.8
-201.5	71.6	50.2
Argon (A)		
-186.2	78.9	300
-194.2	86.9	760
Ethylene (C₂H₄)		
-175.7	97	0.76
-188	85	.076
-197	76	.0076
-205	68	.00076
Ethane (C₂H₆)		
-150	123	7.6
-180	93	.076
-190	83	.0076
-198	75	.00076

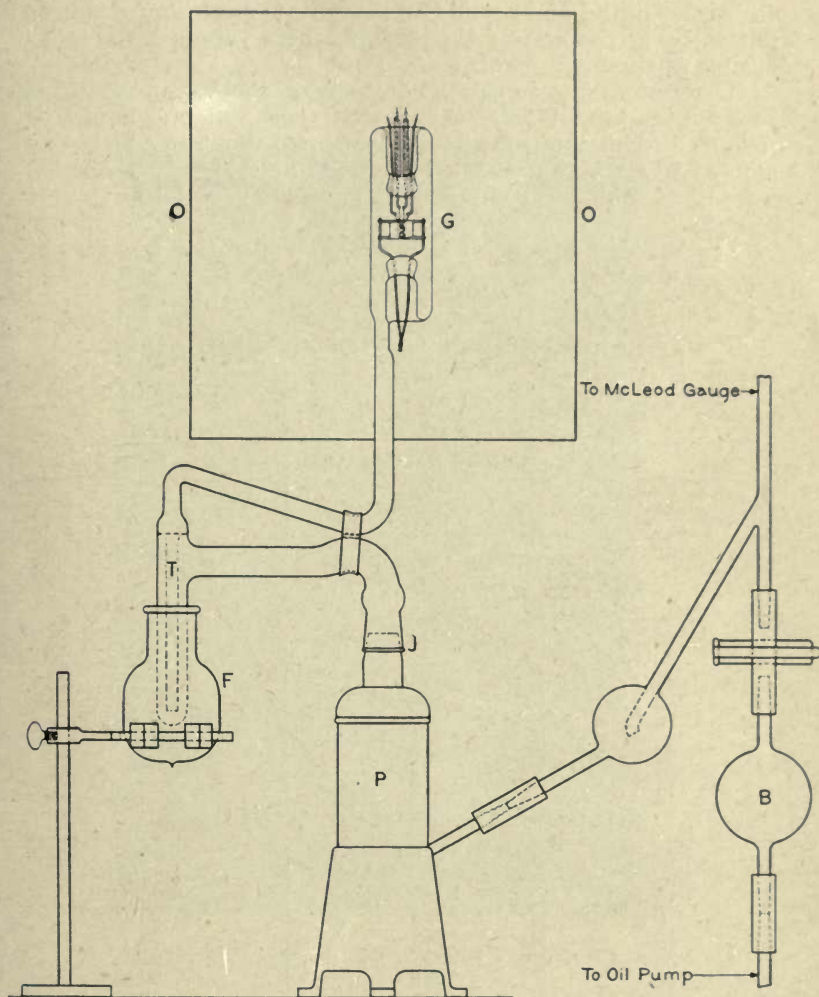


Fig. 31. Arrangement of Exhaust System

as low as -200°C . At this temperature the vapor pressure of solid CO_2 is less than 10^{-5} bar, and it is therefore possible under these conditions to obtain extremely low pressures of residual gases.

Either liquid air or solid CO_2 prevents the diffusion of vapors emitted by grease around the joint, as these vapors are all condensible at these temperatures.

Determinations in this laboratory of the vapor pressures of vacuum pump oils have shown that these range around 1 to 0.1 bar at room temperature, decrease to about one-fifth this value at 0°C ., and are negligibly small at -78°C . Stopcock grease and similar compounds possess even lower vapor pressures.

Further details regarding the actual operation and care of typical exhaust systems are given in Appendix I.

TABLE XIV
VAPOR PRESSURE OF "CONDENSIBLE" GASES

Temperature Degrees Centigrade	Absolute Temperature	Pressure in Bars
Carbon Dioxide (CO_2)		
-148	125	100
-168	105	1
-182	91	0.01
-193	80	0.0001
Ice (H_2O)³⁴		
-20	253	1045
-30	243	384
-40	233	128
-50	223	39
-60	213	9.6
-76	197	1.0
-89	184	0.1
-101	172	.01
-111	162	.001
Mercury (Hg)³⁵		
+30	303	3.7
+20	293	1.6 (2.43)
+10	283	0.65 (1.03)
0	273	.25 (0.47)
-10	263	.087
-20	253	.029
-40	233	.0023
-78	195	4.3 × 10 ⁻⁴
-180	93	2.3 × 10 ⁻²⁴

³⁴ Extrapolated from K. Scheele and W. Heuse's data, *Ann. d. Phys.* 29, 723 (1909).

³⁵ Extrapolated from Knudsen's data, *Ann. d. Phys.* 29, 179 (1909). However, C. F. Hill (*Phys. Rev.* 18, 113) has recently obtained values which are considerably higher. These are given in brackets.

APPENDIX I

Fig. 31 shows diagrammatically an arrangement of the Langmuir condensation pump and accessory connections which is convenient for high vacuum exhaust operation.

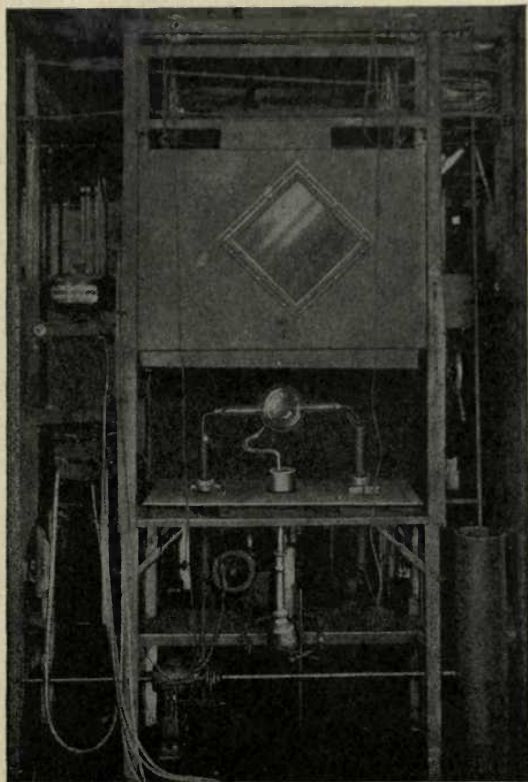


Fig. 32. Photograph of Set-up for Exhausting Coolidge X-ray Tubes

An ionization gauge, G, or other tube to be exhausted, is connected through the liquid air trap T to the pump P. The rough side of the latter is connected to a McLeod gauge and also the oil pump. As mentioned, the tubing between the condensation pump and the vessel to be exhausted should be as wide as possible. The oven for baking out during exhaust is indicated

diagrammatically as OO. Fig. 32 is a photograph of a set-up such as is used in the exhausting of Coolidge X-ray tubes in the factory.

Care of the Condensation Pump: According to the instructions, 626 grams of absolutely clean mercury should be poured into the pump. Under normal conditions, with 300 watts input into the heater and a flow of 1000 cm.³ per minute through the cooling coils, only the lower portion of the pumps should run warm. If for any reason the flow of water ceases and the grease around the joint is melted, the pump should be removed, the mercury emptied out, and the pump cleaned with gasolene as directed in the instructions. Very little mercury should condense in the glass grinding above the pump. If, however, the grinding rapidly becomes covered inside with mercury and feels warm, it is an indication that the pump is not exhausting and a cleaning is required.

Some observations carried out in this laboratory on the variation in exhaust pressure with energy input into the heater are of interest in this connection. The following table gives the watts used and the corresponding minimum pressure obtained as measured by an ionization type of gauge. The oil pump pressure was 0.0146 mm. of Hg.

Watts in Heater	Minimum Pressure in Bars
130	0.27
150	0.07
170	0.04
180	0.023
200	0.013
220	0.007
240	0.0025
280	0.002
300	0.002

Care of Rubber Tubing: All rubber tubing for use in vacuum systems should be cleaned well inside before use. This is best accomplished by washing with a warm 10 per cent solution of caustic soda, then with water and alcohol, and finally drying thoroughly by blowing air through it, or exhausting with a rough pump. The rubber tubing between the condensation pump and glass tube leading to the mercury trap should be as short as possible. Heavy vaseline or grinding grease* should be

* A good stopcock grease may be made by heating approximately equal parts of pure rubber and vaseline. The rubber should be cut into very fine pieces and the heating continued until the mixture has about the consistency of heavy molasses.

used to make the junctions air-tight, and after the tubing is in place a little castor oil should be dripped over the joints, and over the rubber tube itself.

Mercury Trap: This is inserted next to the rough side of the condensation pump and is essential in order to prevent mercury from getting into the oil pumps, where it would gradually disintegrate the bearings. A very good scheme which has been used successfully in this laboratory is to make this trap quite large (about 1 liter volume) and fill it with broken pieces of glass tubing, thus increasing the surface for the condensation of any mercury vapor that diffuses out through the rough side opening of the condensation pump.

Detection of Leaks: A small Tesla coil, one end of which is grounded, is a useful accessory device in all exhaust operations. The high tension terminal of the coil is encased in rubber tubing and provided with a wooden handle so that it can be touched to any part of the glass system. A pin-hole leak will show up by the direct passage of a spark to this point, while at all points there will be a uniform glow if the pressure is over a few bars and there will be no glow at all when the pressure is one bar or less.

Seal-Off Procedure: Constrictions in glass vessels at points where they are to be sealed off after exhaust should not be too thick walled, otherwise a large body of glass will have to be heated during the seal-off, causing the liberation of a great deal of gas. Furthermore, the constriction should be torched till it is almost melting and the pump allowed to exhaust the gas thus liberated for about two minutes, after which the sealing off should be performed as rapidly as possible without heating the glass any more than absolutely necessary.

The importance of these precautions may be judged from the following observations: An ionization gauge, having a volume of about 100 cm.³, was exhausted till the residual gas pressure was less than 0.001 bar. On sealing this off without observing the precautions mentioned, the pressure in the sealed off tube was 0.25 bar, whereas by torching the constriction first and sealing off afterwards, it was possible to obtain a residual gas pressure in the sealed off gauge of less than 0.01 bar.

CHAPTER III

MANOMETERS FOR LOW GAS PRESSURES

For the measurement of pressures that lie between one atmosphere and one cm. mercury, a standard form of mercury barometer is generally used. Such a method is obviously very insensitive when it is necessary to measure pressures below this range, and consequently a number of types of manometers have been developed by different investigators for this purpose.

In the simplest type of low-pressure gauge, the difference between the actual pressure and that in an extremely good vacuum is measured by some very sensitive optical method. This is the principle of Rayleigh's manometer. On the other hand, the McLeod gauge represents an interesting application of Boyle's law to very low pressures. By compressing a given volume of the gas whose pressure is to be measured to a very small known volume, the pressure is amplified several thousand-fold and may be read directly.

Again, instead of attempting to measure the pressure directly, use may be made of the fact that the amount of heat conducted from a surface varies with the gas pressure. Similarly, the damping effect of gas on a body set in vibration or rotation varies with the pressure. In each case, however, it is necessary to know the law of variation between the observed effect and the pressure.

In the following chapter are described some of the different types of low-pressure gauges that have been used by different investigators. Only those forms are described in detail which have proved to be most generally useful in the present state of high-vacuum technique; while other forms, which are of more or less historical interest, are mentioned rather briefly.

MERCURY MANOMETERS

Rayleigh's Gauge¹

The essential parts of this gauge (Fig. 33) are two glass bulbs, one of which communicates with a good vacuum by a tube *C*, and the other with the system in which the pressure is to be measured. Two glass pointers are sealed into the bulbs, and the latter are connected to a T-connection which forms the upper end of a barometric column *A*. Mercury can be raised

¹ Phil. Trans. 196, A. 205 (1901) Zeits. physikal. Chem. 37, 713 (1901).

and lowered in the bulbs by means of the reservoir *D* and the level thus brought up so as to be flush with the ends of the pointers. Any difference in pressure on the mercury in the two bulbs is then measured by gradually tilting the framework *AK* and observing the deflection on a mirror which is fastened vertically on top of the bulbs at *I*. According to Rayleigh this gauge can be used to read pressures between 1.5 mm. and 1×10^{-3} mm. of mercury.

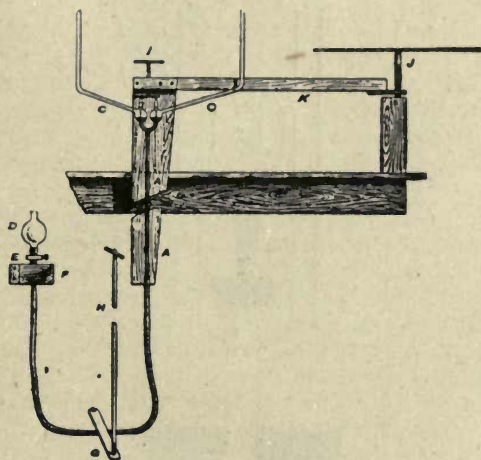


Fig. 33. Rayleigh's Gauge

A modified form of this gauge was used by K. Scheele and W. Heuse² for measuring the vapor pressure of water at temperatures below 0 deg. C., and similar manometers have been constructed by M. Thiesen,³ and E. Hering.⁴

More recently, an ingenious modification of Rayleigh's method has been used by C. F. Mündel⁵ for measuring vapor pressures at very low temperatures. A very sensitive optical method for measuring slight differences in level of two mercury surfaces, developed by K. Prytz,⁶ has been used extensively by different investigators in connection with Rayleigh's method.⁷

¹ Zeits. f. Instrk. 29, 344-349 (1909). K. Jellinek, Lehrbuch d. physikal. chem. I, 1, p. 321. Ann. d. Phys. 29, 723 (1909).

² Zeits. f. Instrk. 6, 89 (1886) and 24, 276 (1904).

³ Ann. d. Phys. (4), 21, 320 (1906).

⁴ Zeits. f. Physikal. Chem. 85, 435 (1913).

⁵ Ann. d. Phys. (4), 16, 735 (1905).

⁷ C. F. Mündel loc. cit., and M. Knudsen, Ann. d. Phys. (4) 53, 1435 (1910).

In the *optical lever manometer*, described recently by J. E. Shrader and H. M. Ryder,⁸ the same object is attained by a very simple construction. The following description is quoted from the original paper:

"A mercury U-tube manometer (Fig. 34) is formed in the usual manner, except that the surfaces of the mercury are so arranged as to be of relatively large area. Above one of the surfaces, within the tube, is arranged an optical lever as shown

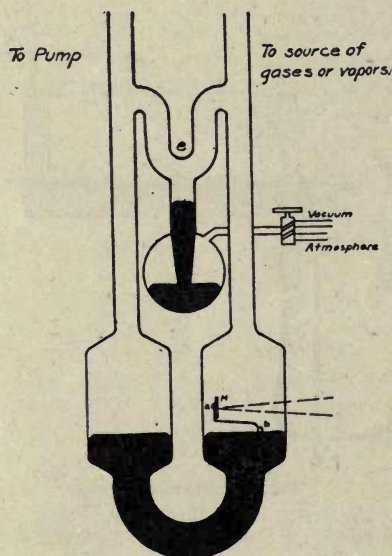


Fig. 34. Optical Lever Manometer

in the illustration. This lever is supported by two knife edges, *a-a*, which rest on loops of wire, which in turn are sealed into the glass walls of the tube; a glass bead *b*, fused to the end of the lever arm, acts as a float on the mercury surface, and in this way transmits the motion of the mercury surface to the lever arm. A mirror *M* attached at the position shown acts in the usual manner to reflect a beam of light from a lamp to a scale, if the gauge is to be arranged as an indicating instrument. If the gauge is to be used for recording variations in pressure, the scale may be replaced by a photographic device such as is used in oscillographic work.

⁸ Phys. Rev. 18, 321 (1919).

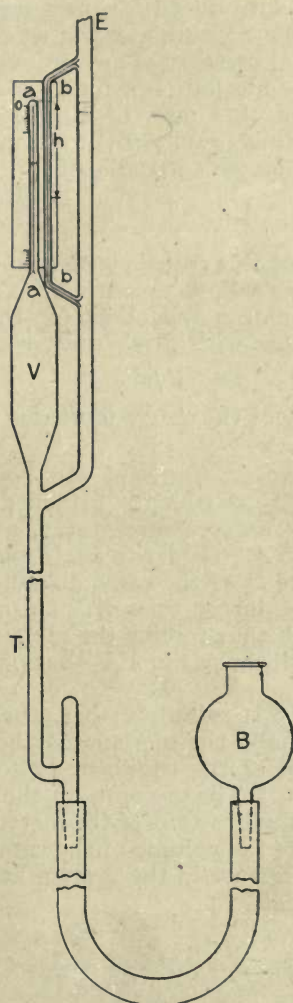


Fig. 35. McLeod Gauge

“The cross connection e provides an easy means of evacuating the whole system with one pump located as shown. With this stopcock or mercury cutoff open, a zero reading can be easily obtained, after which this connection may be closed and

the gases or vapors introduced for measurement. This system provides also for the measurement of small variations in pressure, with an original pressure of any desired value, this value in no way affecting the absolute sensibility of the gauge."

A sensitivity of 10^{-3} mm. of mercury is claimed for the gauge, and it certainly ought to prove useful in those cases where the McLeod gauge is inapplicable.

McLeod Gauge

The principle of this gauge consists in compressing a given volume V of the gas whose pressure P is to be measured, to a much smaller volume v and observing the resultant pressure p which in accordance with Boyle's law is given by the relation

$$p = PV/v.$$

Thus the sensitivity of the gauge increases with increase in the ratio V/v .

One of the simplest forms of McLeod gauge is shown in Fig. 35. The bulb V , to which is attached a capillary tube aa , is connected to the low-pressure system at E and also to the barometric column T . In order to avoid errors due to the effect of capillarity, a tube bb of the same diameter as aa is sealed on as a by-path to the larger tube E . To operate the gauge the reservoir B is raised, thus forcing the mercury in the barometric column upward until the gas in V is shut off from the remainder of the system.

As the mercury is raised further, the volume of gas V is compressed until finally the mercury in the capillary bb is level with the upper end of the capillary aa (corresponding to the point O on the scale). The pressure on the gas in the capillary is then evidently equal to that of the mercury column of height h . Now let a denote the volume of the capillary per unit length, and P denote the pressure in the system at E . Then it follows from Boyle's law that

$$P = \frac{a}{V}h^2 \quad (41)$$

Since a and V are constant for any particular gauge, it follows that the pressure is proportional to the square of the observed value of h . It also follows from this equation that the smaller the ratio a/V the greater the sensitivity of the gauge. Practical considerations, however, make it impossible to use either extremely fine capillaries or very large volumes for V .

The following data for a gauge used by the writer are of interest in this connection as an indication of the range of pressures that can ordinarily be measured with a McLeod gauge:

Gauge No. 1

$V = 171 \text{ cm.}^3$, $a = 0.00407 \text{ cm.}^3$ per cm. length (diameter of capillary = 0.72 mm.).

Hence, measuring h in cm.,

$$P = \frac{0.0407 h^2}{171} = 2.38 \times 10^{-4} h^2 \text{ (mm. of mercury)}$$

$$= \frac{10^6}{750} \times 2.38 \times 10^{-4} h^2 = 0.317 h^2 \text{ (bar)}$$

That is, for $h = 1 \text{ cm.}$, $P = 0.317 \text{ bar}$; and for $h = 1 \text{ mm.}$, $P = 0.0032 \text{ bar}$, so that for a 10-cm. length of capillary aa , the range of pressures that could be measured with this gauge is from 0.003 to 32 bar.

Actually, it is impracticable to make V larger than 500 cm.^3 and with capillaries smaller than 0.5 mm. the mercury tends to stick badly and the gauge is very sluggish in operation. With $V = 500$, and $a = 2 \times 10^{-3}$ ($d = 0.5 \text{ mm.}$), 1 cm. on the capillary would correspond to $4 \times 10^{-5} \text{ mm.}$ of mercury, or approximately 0.053 bar , and 1 mm., to 0.00053 bar. In general, the lower limit of pressure that can be measured with a McLeod gauge is about 0.01 bar.

It is evident that the McLeod gauge does not indicate the pressure of mercury vapor and condensible vapors such as those of oil, water, and ammonia. Even in the case of carbon dioxide the gauge is very inaccurate. In using it to measure very low pressures, such as those produced by a Gaede molecular or Langmuir condensation pump, a liquid air trap should be inserted between the gauge and the remainder of the system in order to prevent diffusion of mercury vapor into the vessel to be exhausted.

Regarding the accuracy of the gauge for indicating the pressure of the so-called permanent gases (H_2 , He , Ne , Ar , O_2 , N_2 and CO) a careful investigation carried out by Scheele and Heuse⁹ has shown that if the bulb and tubing are carefully dried (to eliminate the presence of a film of water) the results obtained in the case of air are certainly reliable down to pressures of 0.01 mm. of mercury and are probably just as exact at lower pressures.

⁹ Ber. d. deutsch. Physikal. Ges. 10, 785 (1908).

Lord Rayleigh¹⁰ found by means of his differential manometer that in the range of pressures 0.001 mm. to 1.5 mm. Boyle's law holds accurately for N_2 , H_2 , and O_2 ; and Scheele and Heuse¹¹ observed the same result with their membrane manometer. A very careful investigation on this point was carried out by W. Gaede¹² in connection with his work on the laws of flow of gases at low pressures. He found that in the case of nitrogen and hydrogen, when care is taken to dry the walls thoroughly, the McLeod gauge is quite accurate down to very low pressures (below 0.0001 mm.), while in the case of oxygen, errors are liable to arise because of the formation of an oxide scum on the surface of the mercury which causes the surface to wet the glass in the capillary. However, this scum may be removed by heating the capillary carefully and the mercury then becomes quite clean again.

There are certain features about the McLeod gauge that must be carefully observed both in its construction and operation. In sealing off the upper end of the capillary *aa* (Fig. 35), care should be taken to have the capillary bore terminate in as blunt a surface as possible, so as to ensure a fair degree of accuracy in reading the very lowest pressures.

The rubber tubing connecting the reservoir *B* and the tube *T* should be thoroughly cleaned and dried before use to get rid of any loose particles and also to eliminate as much as possible the injurious action of the sulphur present in the rubber. Only the cleanest mercury should be used and all glass parts of the gauge should be dried thoroughly before filling with mercury. A new McLeod gauge will be found to give very erratic results at the beginning until all the condensible vapors adhering to the walls have been removed by gentle heating with simultaneous exhaustion.

For extremely sensitive gauges, where the volume *V* is large, the mass of mercury to be raised and lowered is so great that the design shown in Fig. 35 becomes impracticable. In these cases, the reservoir *T* may be replaced by a wide bore glass tube with snugly fitting glass plunger. Where a rough vacuum line is available, the top of the reservoir can be closed by a rubber stopper through which passes a two-way stopcock; one way being connected to the rough vacuum, and the other to the atmosphere. The mercury in *T* can then be raised or low-

¹⁰ Phil. Trans. (A) 196, 205 (1901).

¹¹ Ber. d. deutsch. Physikal. Ges. 11, 10 (1909).

¹² Ann. d. Phys. 41, 289 (1913).

ered by opening the stopcock to the atmosphere or to the rough vacuum respectively.¹³

In order to avoid the error which arises when reading the very small volume of the capillary at the upper end, it is often preferable to compress the gas in the capillary *aa* to a *definite volume* and then observe the height *h* of the mercury in the capillary *bb* above this level. Under these conditions, since

$$P = \frac{v}{V}h$$

it is evident that *h* is directly proportional to the pressure to be measured. The value of *h* may then be observed very accurately by means of a cathetometer. This method of using the McLeod gauge is, however, not as sensitive at low pressures as is the preceding method. Again, in some cases, where the range of pressures to be measured is fairly large, the single capillary *aa* may be replaced by two or more capillaries of gradually increasing bore, the coarser bore being sealed onto the bulb *V* and the finer one on top of this. The serious objection to this construction, however, is the inaccuracy of the measurements at the junction between the two capillaries.

While the construction shown in Fig. 35 is the usual form of McLeod gauge used in exhaust work, a number of modifications have been suggested which are more convenient in special cases. An interesting construction is that designed by H. J. Reiff¹⁴ and shown in Figs. 36 and 37. The advantages of this form are its compactness and avoidance of the use of rubber tubing which, as Reiff points out, sooner or later causes the mercury to get dirty. The gauge is mounted on a board which can be turned 90 deg. about the axis at *C* (Fig. 37). The system in which the pressure is to be measured is connected at *R* by rubber tubing. In the position shown in Fig. 36, the reservoir *G* and tube *V*¹ are filled with mercury up to the stopcock *H*. To measure the pressure, the board is turned into a vertical position and *H* opened until the mercury rises in *M* to the desired level. The bulb *G*¹ prevents any mercury from overflowing into the tube *V*². After the measurement is completed the board is again turned into the position shown in Fig. 36 and the mercury returned into the reservoir *G*.

¹³ An excellent description of the construction of such a McLeod gauge, sensitive to pressures as low as 10^{-6} mm., is given by Gaede in the article referred to in footnote (12). He used a capillary tube 0.35 mm. in diameter, while the volume of the bulb was about 1 liter.

¹⁴ Zeits. f. Instkunde, 34, 97 (1914).

In the same paper Reiff has also described a further modification of this construction in which the readings are directly proportional to the pressure. Other forms of the McLeod gauge have been described by A. Wohl and M. S. Losantisch,¹⁵ and L. Ubbelohde.¹⁶

MECHANICAL MANOMETERS

A number of attempts have been made to construct low-pressure manometers indicating the mechanical deformation suffered by a surface under pressure. At ordinary pressures

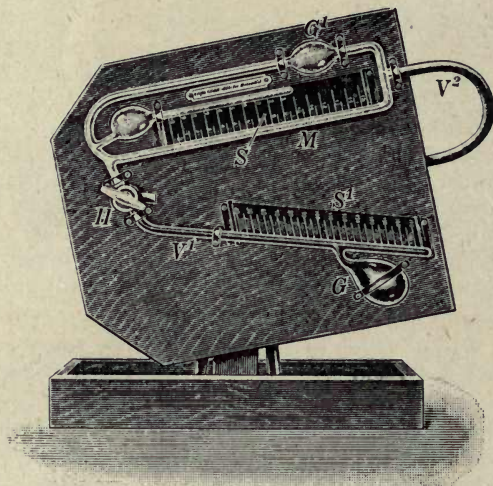


Fig. 36. Short Form of McLeod Gauge, Front View

this principle has been utilized in the construction of the Bourdon Spiral. Ladenburg and Lehmann,¹⁷ and subsequently M. G. Johnson and D. McIntosh,¹⁸ have described a low-pressure gauge consisting of a flat tapered glass tube bent in the form of a spiral. The walls are usually very thin, so that the device may be sensitive to small pressure differences. A glass mirror is attached to the end of the spiral and the latter is sealed into another chamber in which the pressure may be varied. The system whose pressure is to be measured is connected to the

¹⁵ Ber. d. deutsch. chem. Ges. 38, 4149 (1905).

¹⁶ Zeits. f. angew. Chem. 19, 755 (1906).

¹⁷ Verh. d. deutsch. Phys. Ges. 8, 20 (1906).

¹⁸ J. Am. Chem. Soc. 31, 1138 (1909); Zeits. f. Physikal. Chem. 61, 457 (1908).

spiral. In using the instrument, the pressure outside the spiral is varied until it is equal to that in the spiral, as indicated by the mirror, and the pressure outside is then measured by an ordinary mercury manometer. The device has been used for measuring the pressure of corrosive gases like chlorine and ammonium chloride vapor. A similar type of manometer has

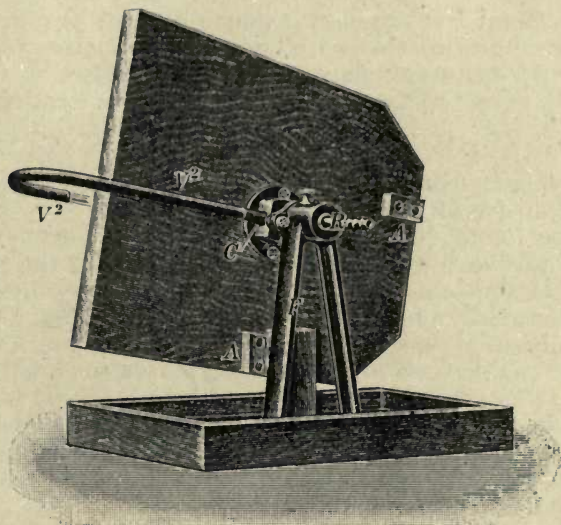


Fig. 37 Short Form of McLeod Gauge, Rear View

also been used very recently by C. G. Jackson for measuring the dissociation pressure of cupric bromide.¹⁹ These gauges are, however, not sensitive to pressures below about 100 bars.

Scheele and Heuse's membrane manometer²⁰ consists of a very shallow cylindrical glass box separated into two compartments (parallel to the flat sides) by a thin copper membrane. One compartment is connected to the system, while the other is connected directly to a high-vacuum pump. The deformation of the membrane, due to the slight difference in pressure on the two sides, is then measured by noting the number of interference rings produced by the pressure of the membrane against a glass plate.

¹⁹ For further details regarding this type of manometer, refer to K. Jellinek, *Lehrb. d. Physikal. Chem.* I, 1, p. 638, also to the references given in footnotes (17) and (18).

²⁰ *Zeits. f. Instrk.* 29, 14 (1909).
Ber. d. deutsch. Phys. Ges. 1909, p. 1.

The instrument was found capable of measuring pressures down to about 0.0001 mm. of mercury, but difficulties were encountered in using it because of the continual gas evolution from the walls of the device.

VISCOSITY MANOMETERS

Theory

In Chapter I it was shown that if a plane is moving in a given direction with velocity u relative to another plane situated parallel to it at a distance d , there is exerted on the latter a dragging action whose magnitude is given by the equation

$$B = \frac{\eta u}{d} \quad (8)$$

where η denotes the coefficient of viscosity, and B denotes the rate of transfer of momentum, per unit area.

It was found, however, by Kundt and Warburg²¹ that at very low pressures, where the mean free path of the molecules becomes of the same order of magnitude as the distance between a moving and a stationary surface placed in the gas, there is distinct evidence of a slipping of gas molecules over the planes, so that the apparent viscosity is decreased. As the pressure is lowered the amount of this slip is found to increase and at very low pressures it varies inversely as the pressure.²²

Denoting the coefficient of slip by δ , it can be shown that the amount of momentum transferred per unit area from the moving surface to that at rest is

$$B = \frac{\eta u}{d + 2\delta} \quad (42)$$

Thus, owing to slip, there is an apparent increase in the thickness of the gas layer between the two surfaces, which amounts to δ for each surface.

As has already been stated, Kundt and Warburg found that at very low pressures δ is inversely proportional to the pressure, and approximately of the same order of magnitude as the mean free path L , of the gas molecules at the corresponding pressures.

More generally, we can write

$$\delta = aL$$

where a is a constant. It is evident that at very low pressures,

²¹ Pogg. Ann. 155, 340 (1875).

²² "The diminution of the viscosity at very low pressures is well shown by an incandescent lamp with a broken filament. If this be shaken while the lamp is exhausted it will be a long time before the oscillations die away; if, however, air is admitted into the lamp, through a crack made with a file, the oscillations when started die away almost immediately." Poynting and Thomson. Properties of Matter, pp. 218-220.

where d is small compared to L , equation (42) reduces to

$$B = \frac{\eta u}{2 a L} \quad (43a)$$

Since* $\frac{\eta}{L} = 0.35 p \sqrt{\frac{8 M}{\pi R T}}$

$$B = \frac{2 \times 0.35}{a} p \cdot u \sqrt{\frac{M}{2 \pi R T}} \quad (43b)$$

That is, with a given gas at constant temperature, the rate of transference of momentum is directly proportional to the velocity of the moving surface and also to the pressure. It follows from this that given the value of a , it would be possible from measurements on the mutual effect of a moving surface and one at rest, to measure the pressure of the gas.

The exact interpretation of a from the kinetic theory point of view has, however, proved to be rather a difficult matter. While the further discussion of this subject must be deferred for a subsequent chapter, it may be observed that a relation of the same form as (43b) may also be deduced by considerations similar to those used by Knudsen in connection with his investigations on the laws of molecular flow.†

The relation deduced from this point of view is found to be slightly different from (43b), but both methods of reasoning lead to an equation of the form

$$B = k u p \sqrt{\frac{M}{R T}} \quad (43c)$$

where k is a constant, which may be slightly different for different gases and probably varies also with the nature of the surface.

In applying the above considerations to the construction of a gauge, two different methods have been used. In the first of these, which we may designate for reference as the "decrement" type of gauges, a surface is set in oscillation and the rate of decrease of the amplitude of oscillation is taken as a measure of the pressure. Physically, the damping may be explained as due to the gradual equalization of energy between the moving surface and the molecules of gas striking it.

In the second type of construction, a surface is set in *continuous* rotation and the amount of twist imparted to an adjacent surface is used to measure the pressure. The molecules striking the moving surface acquire a momentum

* See Chapter I, equations (5), (7b) and (11).

† See Chapter I, page 31.

in the direction of motion which they tend in turn to impart to the other surface. If the latter is suspended and free to turn about an axis which is perpendicular to the direction of motion of the rotating surface, it will be twisted around until the force due to the incident molecules is just balanced by the torsion of the suspension. We may, therefore, designate this as the "static" type of viscosity gauge, to emphasize the fact that observations with this method are taken under stationary conditions.

Decrement Type of Viscosity Gauge

A gauge based on this principle was first suggested by W. Sutherland²³ and subsequently a very careful investigation on the same subject was carried out by J. L. Hogg.²⁴ The construction used by the latter, which was essentially the same as that used by Maxwell and Kundt and Warburg in their determinations of the coefficient of viscosity is shown in Fig. 38. A thin glass disc is suspended by means of a wire between two fixed horizontal plates N . The wire carries a mirror which may be viewed through a plate glass window D by means of a telescope and scale. At the top, the wire is supported by clamps and is connected to a soft iron armature J which is supported by the swivel head K . By turning this armature by means of an external magnet, the center disc can be set in oscillation and the rate of decrease of the amplitude of these oscillations is then observed by means of the telescope pointed at the window D .

Now let T denote the period of oscillation, and S_1 and S_2 two successive amplitudes of oscillation. Solving the differential equation for the rate of damping of the central disc, it can be shown that

$$\frac{S_1}{S_2} = e^{\frac{aT}{2}} = e^{\lambda} \quad (44)$$

where λ is defined as the *logarithmic decrement*. That is, the amplitude of oscillation decreases in geometrical progression for successive equal intervals of time. The constant a depends upon the moment of inertia of the vibrating disc and its dimensions.

Thus λ is a measure of the rate of transference of momentum from the vibrating plate to the stationary plates.

²³ Phil. Mag. 43, 83 (1897).

²⁴ Proc. Am. Acad. 42, 115 (1906), and 45, 3 (1909). Contributions from the Jefferson Physical Lab., 1906, No. 4, and 1909, No. 4.

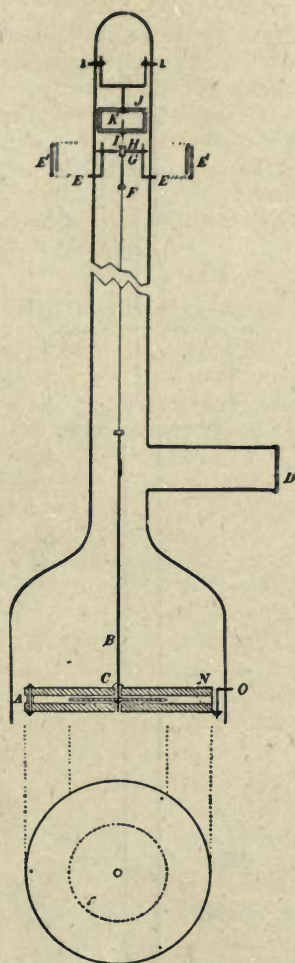


Fig. 38. Decrement Type of Gauge

At higher pressures, since the viscosity is independent of pressure, the logarithmic decrement has a constant value which may be denoted by l . Denoting by μ the decrement due to the suspension itself, it was shown by Sutherland that the following relation ought to hold true:

$$\left(\frac{\lambda - \mu}{l - \mu} - 1 \right) p = C \tag{45a}$$

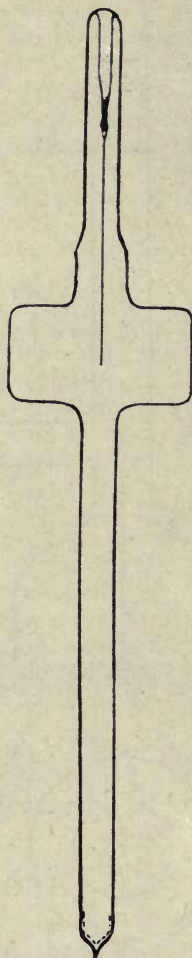


Fig. 39. Quartz Fibre Gauge

where p is the pressure and C is a constant for the particular arrangement used.

The results obtained by Hogg were found to be in satisfactory accord with this equation down to pressures of the order of 0.0004 mm. of mercury in the case of hydrogen.

It is evident from the form of equation (45a) that the gauge is unsuitable for measuring very low pressures (say below 0.0001 mm.) as the value of λ then becomes comparable with that of μ , thus involving large experimental errors. Furthermore, as mentioned by Hogg, the construction of the gauge and its actual manipulation require extremely great care.

A very recent contribution to the theory of this type of viscosity meter has also been published by P. E. Shaw.²⁵ He derives an equation of the form

$$p = C\lambda \quad (45b)$$

and records measurements of pressures down to 0.35×10^{-3} mm. of mercury.

Quartz Fibre Gauge

This method was originally suggested by I. Langmuir²⁶ for measuring the residual gas pressure in a sealed off incandescent lamp, and has been used in this laboratory in a number

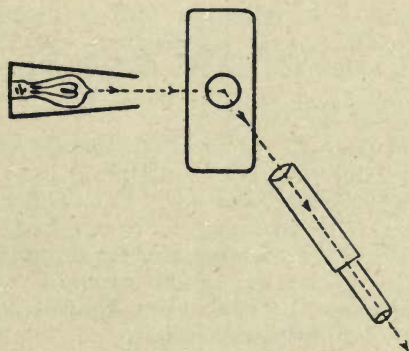


Fig. 40. Optical Arrangement for Quartz Fibre Gauge

of investigations. It is specially useful in measuring low pressures of chemically active vapors such as those of chlorine, iodine, and mercury which are liable to attack metal parts. A discussion of the theory of the gauge and actual details as to its manipulation have been published by F. Haber and F. Kerschbaum.²⁷

The construction of the gauge is shown in Fig. 39. It consists of a thin quartz fibre sealed into the top of a glass

²⁵ Proc. Phys. Soc. London, 29, 171 (1917).

²⁶ J. Am. Chem. Soc. 35, 107 (1913).

²⁷ Zeits. f. Elektrochem, 20, 296 (1914).

tube. The fibre is set in oscillation by gently tapping the glass bulb and the rate of decrease of the amplitude of vibration is then observed by means of a telescope and lamp as shown in Fig. 40.

Let t denote the interval of time required for the amplitude to decrease to half value. Then it has been shown by Haber that

$$p\sqrt{M} = \frac{b}{t} - a \quad (46)$$

where p denotes the pressure, M is the molecular weight of the gas, and a and b are constants for the particular quartz fibre. That is, for any gas, the pressure varies linearly with the reciprocal of t .

In the case where the gas to be measured is a mixture of different vapors, the sum of a number of terms $p\sqrt{M}$ must be taken corresponding to the partial pressure of each constituent.

The constant b in equation (46) is proportional to the diameter of the fibre, that is, the finer the fibre the smaller the pressure at which the amplitude will decay to half value in a given time. On the other hand, a is a function of the elastic properties of the fibre.

It is evident from the form of equation (46) that b/a corresponds to the value t_0 at which the amplitude would decrease to half-value in a perfect vacuum. For calibration, it is necessary to obtain only two points, corresponding to the two constants a and b . One of these may be determined by observing the value t_0 in a very good vacuum, while the other point may be obtained by calibrating against a McLeod gauge with some gas of definite composition.

The following data are given by Haber for a quartz fibre 7.0 cm. long and 0.013 cm. in diameter. Air was used for calibration.

Pressure in mm. H_g	$p\sqrt{M}$	t (seconds)	b
0.00302	0.01625	74	1.22
0.00494	0.02654	46	1.23
0.00775	0.0417	31	1.30
0.0117	0.0630	22	1.39
0.01880	0.101	12	1.23
0.0260	0.140	10	1.40
$a = 0.0003 \dots$	Avg. 1.28

Some measurements with air taken by Mr. Huthsteiner in this laboratory, using a fibre 3.8 cm. long and 0.0045 cm. diameter, are given for comparison.

Pressure in mm. Hg	t (seconds)
0.00058	105
0.00342	31
0.0080	16
0.0190	6.5

Plotting p against $\frac{1}{t}$ gave a straight line whose equation is

103 $p = \frac{131}{t} - 0.655$. For air, $M = 28.96$. Hence, for this particular fibre,

$$p\sqrt{M} = \frac{0.705}{t} - 0.00353$$

Since $t_0 = 200$ in this case, it is evident that this fibre could not be used for measuring pressures below 0.0001 mm. of air. It also follows from the form of the above relation that the heavier the gas the lower the range of pressures over which the gauge may be used.

The optical arrangement suggested by Haber (Fig. 40) may be varied in practice by fastening a scale to the back of the gauge and placing the lamp in such a position that the light beam passes practically parallel to this scale. The scale and tip of the quartz fibre are then sighted by means of a cathetometer.

While Haber used tubes which were more or less flattened on two sides, ordinary cylindrically walled tubes are more convenient and almost as satisfactory. As observed by Haber, care should be taken to tap the glass in such a manner that the fibre vibrates in the plane at right angles to the line of sight from the cathetometer. With a little experience, this can readily be accomplished. In view of the simplicity of construction and relative ease of manipulation, the quartz fibre gauge ought to find a useful field of application in low pressure technique, where the pressures to be measured are not below about 0.05 bar.

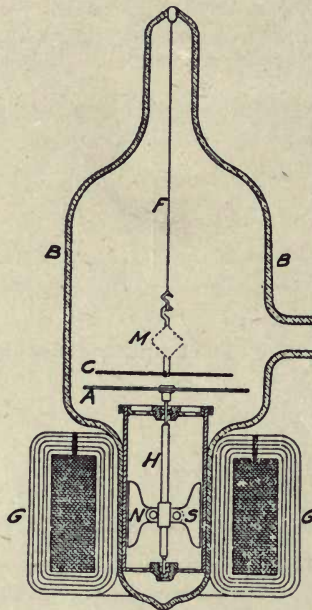
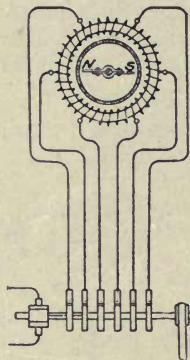


Fig. 41. Molecular Gauge

Fig. 42. Rotating Commutator Connection
for Molecular Gauge

Static Types of Viscosity Gauge

The molecular gauge suggested by I. Langmuir²⁸ represents a direct application of equation (43c). The construction and results obtained with a gauge built on this principle have been described by S. Dushman:²⁹

"It consists of a glass bulb *B* (Fig. 41) in which are contained a rotating disc *A* and, suspended above it, another disc *C*. The disc *A* is made of thin aluminum and is attached to a steel or tungsten shaft *H* mounted on jewel bearings and carrying a magnetic needle *NS*. Where the gauge is to be used for measuring the pressure of corrosive gases like chlorine, the shaft and disc may be made of platinum. The disc *C* is of very thin mica, about 0.0025 cm. thick and 3 cm. in diameter. A small mirror *M*, about 0.5 cm. square, is attached to the mica disc by a framework of thin aluminum. This framework carries a hook with square notch which fits into another hook similarly shaped, so that there is no tendency for one hook to turn on the other. The upper hook is attached to a quartz fibre about 2×10^{-3} cm. diameter and 15 cm. long.

"The lower disc can be rotated by means of a rotating magnetic field produced outside the bulb. This field is most conveniently obtained by a Gramme ring, *GG*, supplied at six points with current from a commutating device rotated by a motor (Fig. 42). In this way the speed of the motor determines absolutely the speed of the disc, and the speed of the latter may thus be varied from a few revolutions per minute up to 10,000 or more."

By applying equation (43c) it can be shown that the angle of torque (α) on the upper disc is given by the equation

$$\alpha = \left(\frac{kt^2 r^4}{2\pi k} \right) p \omega \sqrt{\frac{M}{RT}} \quad (47)$$

where t = natural period of oscillation of mica disc,

k = moment of inertia of disc,

r = radius of rotating disc,

and ω = angular velocity of rotating disc.

Hence, for any one gauge, the torque on the upper disc is proportional to the product of the speed of rotation of the aluminum disc and the quantity $p\sqrt{M/(RT)}$. The sensitivity of the gauge can thus be increased by increasing the speed of rotation; also by illuminating the mirror and using a similar

²⁸ Phys. Rev. 1, 337 (1913).

²⁹ Phys. Rev. 5, 212 (1915).

arrangement to that used for galvanometers, it is possible to use the gauge to measure pressures of the order 10^{-3} to 10^{-4} bar.

The gauge actually used for measuring very low pressures showed a deflection of 1100 mm. per bar of air, at 1000 r.p.m., with the scale 50 cm. from the mirror. Up to a pressure at which the mean free path of the gas molecules becomes comparable with the distance between the two discs, the deflections, at constant speed of rotation, were found to be proportional to the pressure as observed by a McLeod gauge.

At extremely low pressures (below 5×10^{-4} bar) the indications of the gauge were found to be inaccurate because of two sources of error. Firstly, the rotation of the magnetic field produced by the Gramme ring tends to induce eddy currents in the metal frame work used to hold the mirror; and secondly, there is a tendency for the upper disc to start swinging especially at very high speeds of rotation of the aluminum disc. As the damping at low pressures is very feeble, it is very difficult to stop this oscillation when once started.

Working independently of Langmuir, and about the same time, A. Timiriazeff³⁰ also suggested the application of equation (43c) to the construction of a low-pressure gauge. As he was primarily interested in determining the laws of slip for different gases his actual design is not suitable for a very sensitive gauge. Instead of using a rotating disc with a stationary disc situated symmetrically above it, Timiriazeff used a rotating cylinder with a stationary cylinder placed symmetrically inside it and suspended by a phosphor bronze wire.

RADIOMETER GAUGES

Crookes' Radiometer

One of the first instruments to be used for detecting low gas pressures was the radiometer devised by Sir William Crookes in 1873. The instrument, which is described in all text-books, consists of a glass bulb in which a small vane or fly is mounted on a vertical axis. The vane has four arms of aluminum wire on which are attached four small plates of thin mica, coated on one side with lamp black. These plates are set so that their planes are parallel to the axis. If a source of light or heat is brought near the bulb, and the rarefaction is just right, the fly rotates, but at very low pressures the rotation practically ceases.

³⁰ Ann. d. Physik. 40, 971 (1913).

The theory of the device was apparently not very well understood for a long time, and attempts to use it as a gauge for low pressures yielded very unsatisfactory results. Dewar has stated the case for this instrument as follows:

"The radiometer may be used as an efficient instrument of research for the detection of small gas pressures. For quantitative measurements the torsion balance or bifilar suspension must be employed."³¹

Some years ago Mr. W. E. Ruder, of this laboratory, developed a method of using the radiometer for the measurement of the residual gas pressure in incandescent lamps. The following account was prepared by him at the request of the writer:

"It was found that when exhausted to the degree required in an incandescent lamp the radiometer could not be made to revolve, even in the brightest sunlight. In order to get a measure of the vacuum, the radiometer vanes were revolved rapidly by shaking the lamp and the time required to come to a complete stop was therefore a measure of the resistance offered to the vanes by the gas, together with the frictional resistance of the bearings. The latter quantity was found to be so small in most cases that a direct comparison of the rates of decay of speed of the vanes gave a satisfactory measure of the degree of evacuation. In this manner a complete set of curves was obtained which showed the change in vacuum in an incandescent lamp during its whole life and under a variety of conditions of exhaust. The chief objections to this method of measuring vacua were the difficulty in calibrating the radiometer and the difference in frictional resistance offered by different radiometers. For *comparative* results, however, the method was entirely satisfactory."

As a result of his investigations of the laws of heat transfer in gases at low pressures, Knudsen arrived at a clear explanation of the radiometer action and furthermore developed, along the same lines, an accurate gauge for the measurement of extremely low pressures.

According to Knudsen, there is a mechanical force exerted between two surfaces maintained at different temperatures in a gas at low pressure. This is due to the fact that the molecules striking the hotter surface rebound with a higher average kinetic energy than those that strike the colder surface. In the case of the radiometer the blackened surfaces absorb heat from

³¹ Proc. Royal Soc., A, 79, 529 (1907).

the source of light and the molecules rebounding from the vanes are therefore at a higher temperature than those striking the walls of the bulb. Consequently a momentum is imparted to the vanes which tends to make them rotate.³²

Knudsen Gauge

The principle of the gauge constructed by Knudsen³³ may be explained by referring to Fig. 43. Let us consider two parallel strips *A* and *B* placed at a distance apart which is less

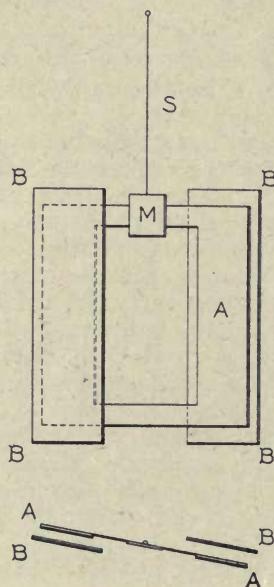


Fig. 43. Elementary Diagram of Knudsen Gauge

than the mean free path of the molecules. Let *A* be at the same temperature *T* as the residual gas, while *B* is maintained at a higher temperature *T*₁. On the side away from *B*, *A* will be bombarded by molecules having a mean velocity *G*, corresponding to the temperature *T*, as given by the equation

$$G = \sqrt{\frac{3RT}{M}} \quad (3d)$$

³² Two recent papers by G. D. West (Phys. Soc. London, 32, 166 and 222, 1920) deal rather fully with the theory of the radiometer, especially at medium pressures, and also with the forces acting on heated metal foil surfaces at low pressures.

³³ Ann. Phys. 32, 809 (1910).

These molecules will of course rebound from A with the same velocity. However, on the side towards B , A will be bombarded by molecules coming from B , and having a higher velocity G_1 corresponding to the temperature T_1 . Consequently A will receive momentum at a greater rate on the side towards B , than on the opposite side, and will therefore be repelled from B .

From theoretical considerations Knudsen has shown that the force of repulsion K per sq. cm. of the two parallel surfaces, when the distance between them is less than the mean free path, varies with the pressure and the temperatures T and T_1 , according to the equation

$$K = \frac{P}{2} \sqrt{\frac{T_1}{T}} - 1 \quad (48a)$$

For small differences of temperature, and for the purpose of pressure measurements, this equation may be written in the form:³⁴

$$P = 4K \frac{T}{T_1 - T} \text{ dynes per sq. cm.} \quad (48b)$$

In order to measure this force of repulsion, Knudsen uses the arrangement shown diagrammatically in Fig. 43. The strip A is replaced by a rectangular vane, cut out in the center and suspended by means of a fibre S . Two strips BB which can be heated are placed symmetrically on opposite sides of this vane, and the force of repulsion is then balanced by the torsion of the fibre. By means of the mirror M , the deflection can then be measured in the same manner as in the case of galvanometers.

For this arrangement, equation (48b) assumes the form:

$$P = \frac{4\pi^2 ID}{rA t^2 d} \cdot \frac{T}{T_1 - T} \text{ dynes per sq. cm.} \quad (48c)$$

where

- I = moment of inertia of the moving vane,
- r = mean radius of the moving vane,
- $2A$ = area of the vane A opposite each strip B ,
- t = period of vibration of the vane,
- D = scale deflection, and
- d = scale distance.

Since all these quantities can be measured directly, it follows that the device can be used as an *absolute manometer*, without the necessity of calibrating against any other gauge. It is also evident that the indications of this gauge must be independent of the gas to be measured.

³⁴ A simple derivation of this and the following equation has been given by G. W. Todd, *Phil. Mag.* 38, 381 (1919).

In his first paper on this subject, Knudsen mentioned several different forms of construction which may be used in making a gauge on the foregoing principle, but gives very few constructional details. One form which appears to be very simple in construction is that shown in Fig. 44.

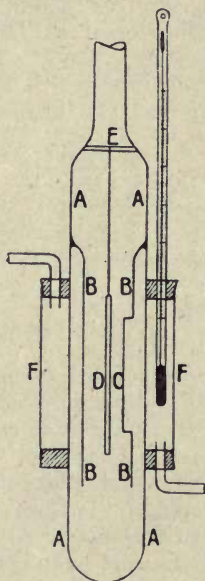


Fig. 44. Simple Construction of the Knudsen Gauge

AA is a glass tube about 1.4 cm. diameter in which is sealed a narrow tube BB. The latter has a rectangular piece cut out at C, 0.41 cm. wide by 2.95 cm. in length. A piece of mica D is suspended in front of this opening by means of a fibre which is fastened at E. The tube AA can be heated by means of an external water-jacket FF. As the temperature of the water in the latter is raised, the mica plate is repelled by the "hot" molecules traveling through the opening C, and the amount of deflection can be observed by means of a microscope.

Variations of this construction are described by Knudsen in a later paper,³⁵ but very few details are given. E. V. Angerer³⁶ has described a Knudsen manometer which consists of a silvered mica vane between two electrically heated platinum strips,

³⁵ Ann. Phys. 44, 525 (1914).

³⁶ Ann. Phys. 41, 1 (1913).

arranged as shown in Fig. 43. He states that pressures as low as 8×10^{-7} mm. of mercury can be measured with it.

The same type of design has also been used by J. W. Woodrow³⁷ on the one hand, and by J. E. Shrader and R. G. Sherwood³⁸ on the other.

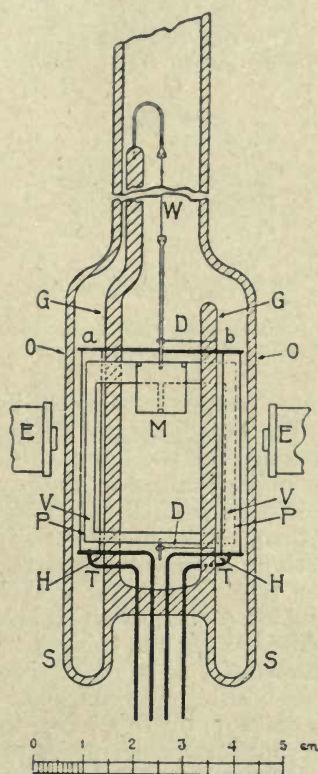


Fig. 45. Woodrow's Modification of the Knudsen Gauge

Woodrow's Modification of Knudsen Gauge

The following description of Woodrow's form of Knudsen gauge is quoted from the original publication:

"Several different gauges were constructed varying in sensitivity so as to be used at different pressures. A typical gauge is shown in Figs. 45 and 46 and the electrical circuits are given

³⁷ Phys. Rev. 4, 491 (1914).

³⁸ Phys. Rev. 12, 70 (1918).

in Fig. 47. The glass rods GG served as supports for the metallic parts of the gauge. All the internal electrical connections and adjustments, with the exception of the final leveling, were made before the outer glass walls OO were sealed on at SS . The suspension W was a phosphor-bronze ribbon 50 mm. in length which had been obtained from W. G. Pye & Co. and was listed by them as No. 0000. The movable vane VV consisted of a rectangular frame of aluminum 0.076 mm. in thickness, the

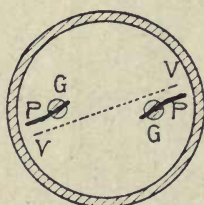


Fig. 46. Cross-sectional View Through the Middle of the Gauge Shown in Fig. 45

dimensions of the outer rectangle being 30 by 36 mm. and the inner 26 by 30 mm. The heating plates PP were platinum strips 4 mm. wide, 40 mm. long and 0.025 mm. thick. The deflections of the movable vane were obtained in the usual way by the reflection of a beam of light from the mirror M . Fig. 46 is a cross-sectional view through the middle of Fig. 45.

"All of the platinum connections were made by electric welding, as that was found much more satisfactory than the use of any kind of solder, especially when heated. After a little practice, it was possible to weld the thin platinum heating vanes to the heavy platinum wire so as to make a perfectly continuous contact throughout its width. The phosphor-bronze suspension was connected at both ends by threading through three small holes drilled into the flattened extremities of the platinum and aluminum wires respectively. The small loops DD were so placed that they supported the movable vane V except when the gauge was leveled for taking readings. This made the gauge readily portable and, by placing in the inverted position when connected to the molecular pump, the danger of the breaking of the suspension by vibration was eliminated. One gauge of medium sensitivity was constructed so as to be sufficiently steady to be used when connected directly to the molecular pump. Large glass tubing was employed in all the connecting portions of the apparatus.

"A small electromagnet, shown at *E* in Fig. 45, was employed in bringing the moving vane to rest. This was found to be quite necessary in working with the most sensitive gauges, since in a very good vacuum the damping is so small that the vane will not settle down sufficiently for the taking of readings for some time after an accidental disturbance has set it vibrating. It should be noted that the electromagnet must have either an air core or one of good, soft Norway iron, for

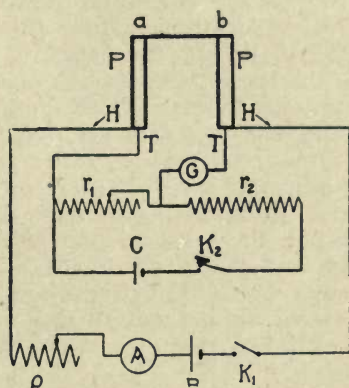


Fig. 47. Electrical Connections of the Gauge Shown in Fig. 45

otherwise the residual magnetism will produce a false zero if the aluminum vane is at all magnetic, as was the case with the samples of metal investigated in this laboratory. Under these conditions it is obvious that the electromagnet should be used only for damping and that the exciting current should be shut off while making observations.

"Several methods were tried for determining the temperature of the heating strips and that shown in diagram in Fig. 47 was finally settled upon as giving the most satisfactory results. The potentiometer leads *TT* were connected by electric welding to the very extremities of the platinum heating vanes *PP*. The heating current was regulated by the variable resistance ρ and its value was read on the ammeter *A*. The resistance r_2 was kept constant at 10,000 ohms and r_1 varied to obtain a balance of the sensitive galvanometer *G*. The potentiometer battery *C* consisted of a carefully calibrated Weston Standard Cell. This arrangement gave an accurate method of measuring the resistance of the platinum strips *PP*, plus the heavy platinum

wire *ab*, the total cold resistance being 0.17 ohm. This cold resistance was determined by plotting the curve connecting resistance and heating current under a constant low pressure and extrapolating backward to the intersection with the axis of resistance. If the resistance is measured for small currents, the value at zero current, that is the cold resistance, can be determined very accurately. The temperature coefficient of resistance of the platinum, which contained a small amount of iridium, was carefully determined and was found to give a linear relation within the range of temperatures employed. The value of the coefficient was 2.35×10^{-3} ohms per deg. C. With this system one can determine the mean temperature of the heating strips with sufficient accuracy, the error for temperature difference of about 50 deg. C. being less than four per cent."

Woodrow also observes that in order to avoid electrical effects it was necessary to silver-coat the outside of the glass walls which were then grounded. Similarly the moving system was connected through the suspension to that terminal of the heating strips which was grounded.

"With the gauge whose dimensions are given above, the period of a complete oscillation was 10 sec., and the calculated moment of inertia of the moving vane was 0.074 gm. cm.² This gives for the pressure,

$$P = 2.9 \times 10^{-5} \frac{T}{T_1 - T} d \text{ (bars)}$$

$$= 2.2 \times 10^{-3} \frac{T}{T_1 - T} d \text{ (mm. of mercury)}$$

where *d* is the deflection in mm. on a scale at a distance of one meter from the mirror." Thus with a temperature difference of 100 deg. C., the gauge could be used to read pressures as low as 3×10^{-3} mm. of mercury.

Shrader and Sherwood's Modification of Knudsen Gauge

The construction used by Shrader and Sherwood differs in a few details from that used by Woodrow. In view of the importance of the Knudsen gauge for low pressure measurements, the description of this modification is worth quoting:

"The gauge is shown in Fig. 48. It is enclosed in a hard glass tube two inches in diameter and nine inches long. The heating strip *aa* is of platinum, 0.018 mm. thick and 7.5 mm. wide with a total length of 18 cm. It is folded at the top forming a cross piece and two parallel sides. The ends are brazed to 20 mil tungsten leading-in wires at the bottom. Fifteen

mil tungsten wires *b* sealed into the glass-rod support serve as a spring support for the platinum strip. This allows accurate adjustment of the strip and sufficient tension is secured to keep the strip taut during heating. One of these wires is carried up the glass-rod support, sealed into it at *c*, leaving a free end *d*

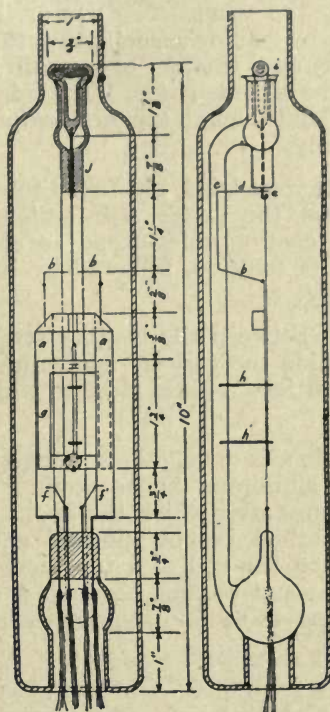


Fig. 48. Shrader and Sherwood's Modification of the Knudsen Gauge

to serve for electrical connection of the moving vane to the heating strip. Connection is made by the wire pressing under tension against the tungsten wire *e* to which the suspension of the vane is fastened. Potential leads of fine platinum wires *f* are welded to the strip about one centimeter from the ends and are brazed to tungsten sealing-in wires.

"The movable rectangular vane *g* is made of aluminum 0.0076 cm. thick. A standard size adopted is 3.2 cm. by 4 cm. outside dimensions, the width of the vane being 0.5 cm. Because

of liability of warping during heat treatment the vane is stiffened by an aluminum wire passing through slits at the top and a hole at the bottom into which the wire is hooked and fastened firmly. For portability, two copper wires h are sealed into the glass-rod support while the free end formed loops around the rod, these forming guides for the vane. The mirror is fastened at the bottom of the vane by leaving a small projection of the aluminum at the lower edge and cutting out small tongues from the material of the vane on either side. The mirror is laid in place and the projection and the two tongues are pressed closely over it, holding it securely.

"Silver mirrors were tried, but failed to withstand the heat treatment to which the gauge and system were subjected. Mirrors made by coating microscope cover glass with china decorators' platinum solution, followed by baking at 500 deg., solved this difficulty.

"The distance between the heating strip and the vane is adjusted from outside the case by magnetic control on a piece of soft iron i sealed into a glass stem to which the suspension is fastened.

"The suspension is 0.0005-inch tungsten wire. This is fastened to small aluminum hooks around which the wire is wrapped several times after which the hooks are pressed firmly together. This method is not difficult and holds the wire securely. A hook on the end of a tungsten wire sealed into a glass stem, the free end passing through a capillary rod j on the glass support, serves to hold the suspension. * * *

"A gauge such as has been described, using a 0.0005-inch tungsten suspension from 6 to 7 cm. long, has such a sensibility that a scale deflection of 1 mm. at a meter's distance with a temperature difference of 150 deg. C. between the heating strip and the movable vane indicates pressures of 1×10^{-8} to 5×10^{-8} mm. Hg. One gauge of other dimensions than those given above would indicate a pressure of 5×10^{-9} mm. Hg. under the same conditions."

The temperature of the heated strips is measured by substantially the same electrical method as that used by Woodrow.³⁹

³⁹ L. F. Richardson (Phys. Soc. London, *31*, 270, 1919) has described a form of Knudsen gauge in which he balances the force of repulsion by means of a magnetic field. The instrument seems, however, quite complicated in construction.

A commercial form of Knudsen gauge brought out recently in Germany by H. Rieger is described briefly in *Engineering*, July 30, 1920.

RESISTANCE MANOMETERS

At ordinary pressures the heat conductivity of gases, like the coefficient of viscosity, is independent of the pressure. However, as the pressure is decreased, a point is reached at which the heat conductivity begins to decrease with the pressure in a manner which is quite analogous to the phenomena observed in the case of viscosity measurements. Kundt and Warburg pointed out, as a result of their experiments on the

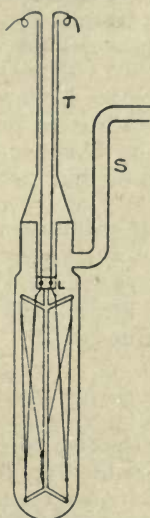


Fig. 49. Hale's Improved Form of Pirani Gauge

coefficient of slip, that a similar phenomenon was to be expected in the case of heat conductance at low pressures. Subsequent experiments by Sutherland, Smoluchowski and Knudsen have shown that such is actually the case.

These experiments have led to interesting speculations upon the mechanism of the heat transfer in gases between surfaces which are separated by a distance which is comparable with or less than the mean free path of the molecules, and the more detailed discussion of this subject will be taken up in a subsequent chapter.

The important experimental fact from the present point of view is that at very low pressures the observed coefficient of

heat conductivity of gases varies with the pressure. E. Warburg, G. Leithauser, and E. Johansen⁴⁰ applied this fact to the construction of a gauge by measuring the change in resistance of a small bolometer strip; while W. Voegé⁴¹ used a small thermocouple attached to a wire heated by a constant alternating current. The temperature of the wire as observed by means of the thermocouple was found to be a function of the pressure.

The fact that the heat conductivity of gases at low pressures varies with the pressure has also been utilized by W. Rohn in the design of a vacuum thermo-element⁴² which is exposed to a source radiating energy at a constant rate (an incandescent lamp maintained at constant voltage). In this case the thermo-element is enclosed in a glass bulb which is connected to the system in which the pressure is to be measured. At pressures above about 0.1 mm., the electromotive force is practically independent of the pressure, but as the pressure is decreased below this value, the heat loss by conduction decreases, and the temperature of the thermo-element rises. Consequently the e.m.f. also increases. Between 0.1 mm. and 0.001 mm., the increase in e.m.f. varies approximately linearly with the *logarithm of the pressure*, but at still lower pressures the e.m.f. reaches a maximum value which remains constant as the vacuum is improved.

Pirani-Hale Gauge

M. Pirani pointed out that in order to construct a gauge based on the relation between the heat conducted from a wire and the pressure, three different schemes could be used.

1. The voltage on the wire is maintained constant, and the change in current is observed as a function of the pressure.

2. The resistance (and consequently the temperature) of the wire is maintained constant, and the energy input required for this is observed as a function of the pressure.

3. The current is maintained constant, and the change in resistance observed as a function of the pressure.

The first scheme was tried using an ordinary 110-volt tantalum-lamp. Better results were, however, obtained when the tantalum wire was clamped tightly to the anchor wires in order to keep constant the heat loss through the supports. With the improved instrument the two other methods were tried, using a Wheatstone bridge arrangement to measure the resist-

⁴⁰ Ann. d. Phys. *24*, 25 (1907).

⁴¹ Phys. Zeits. *7*, 498 (1908).

⁴² Zeits. f. Elektrochem. *20*, 539 (1914).

ance of the wire, and the third one finally recommended as the most sensitive for use in pressure measurements.

While the principle of Pirani's gauge is thus extremely simple, the sensitiveness actually obtained by him was not very great, the lower limit of accuracy being around 0.1 bar.

An improved form of this gauge was constructed by C. F. Hale,⁴³ which is shown diagrammatically in Fig. 49. The following description is quoted from Hale's paper:

"A piece of pure platinum wire, 0.028 mm. in diameter and 450 mm. long, is mounted upon a glass stem carrying two radial glass supports near the top and three at the bottom. The wire

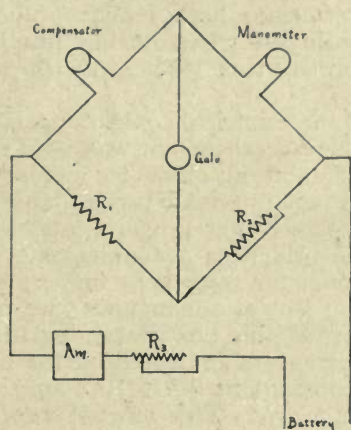


Fig. 50. A Diagram of the Electrical Connections of the Gauge Shown in Fig. 49

is anchored to these radial supports by means of short pieces of platinum wire 0.052 mm. in diameter. The anchor is fused into the radial supports at one end, and the other end is made fast to the manometer wire either by an arc weld or by a tiny glass bead. The leading-in wires at *L*, to which the ends of the manometer wire are welded, are of platinum, 0.31 mm. in diameter. All of the platinum wire employed in making the manometer was drawn from the same lot of larger wire and was assumed to be of uniform purity. The temperature coefficient of the manometer wire was found to be 0.00376 per cent per degree. The platinum leading-in wires are joined to heavy copper leads (1.1 mm. diameter) by welded joints, and these joints are fused into the stem as in electric lamps. The stem is sealed

⁴³ Trans. Am. Electrochem. Soc. 20, 243 (1911).

into a tubular bulb 3.2 cm. in diameter and 11.4 cm. long. This size of bulb is easily obtained, since it is the size regularly used for 50-watt tubular lamps, such as are commonly employed for galvanometer illumination. At *S* is a tube by which the manometer is connected with the system whose pressure is being studied. The upper end of the stem *T* is considerably elongated to permit the complete immersion of the manometer in a constant temperature bath, whose temperature was approximately zero deg. C. This stem tube is made of sufficient length to leave 15 cm. of it above the level of the bath, a provision which we found to be necessary in order to avoid the condensation of atmospheric moisture upon the top of the tube and the leading-in wires during humid weather. For electrical insulation this tube is packed with purified dry asbestos wool."

A diagram of the electrical connections is shown in Fig. 50. A Wheatstone bridge arrangement was used for measuring the resistance changes; and in order to increase the sensitivity of the gauge, an exact duplicate was exhausted as carefully as possible to an extremely low pressure, sealed off, and inserted in one arm of the bridge as a compensator. Both the compensator and manometer were kept immersed in the constant temperature bath. R_1 was a manganin wire resistance of 925.6 ohms, and R_2 a decade plug box containing 10,000 ohms. The strength of the current, as indicated by the milliammeter *Am*, was maintained constant at 9.25×10^{-3} amp. by means of the battery and resistance R_3 . This current was sufficient to raise the temperature of the wire in the manometer and compensator to about 125 deg. at the lowest pressures.

In calibrating the gauge against a McLeod gauge care had to be taken to keep mercury vapor out by means of a liquid-air trap inserted between the manometer and the remainder of the system. Fig. 51 shows calibration curves obtained with air and hydrogen at different pressures.

The difference is due to the higher conductivity of hydrogen, so that the indications of the manometer are dependent to a certain extent upon the nature of the gas used. Hale's measurements show that the lower limit of sensitivity for a gauge of this construction is about 0.00001 mm. (i.e., 0.0133 bar).

More recently some further measurements with a Hale gauge have been carried out by Misamichi So,⁴⁴ and N. R. Campbell.⁴⁵

⁴⁴ Proc. Physico-Mathem. Soc. Japan, 3rd. Ser., 1, 152 (1919).

⁴⁵ Proc. Phys. Soc. 33, 287 (1921).

The construction of gauge used by the former differs in a few slight details from that of Hale. It was found that the sensitivity of the gauge is higher the lower the temperature of the surrounding bath. At zero deg. C., and using a heating

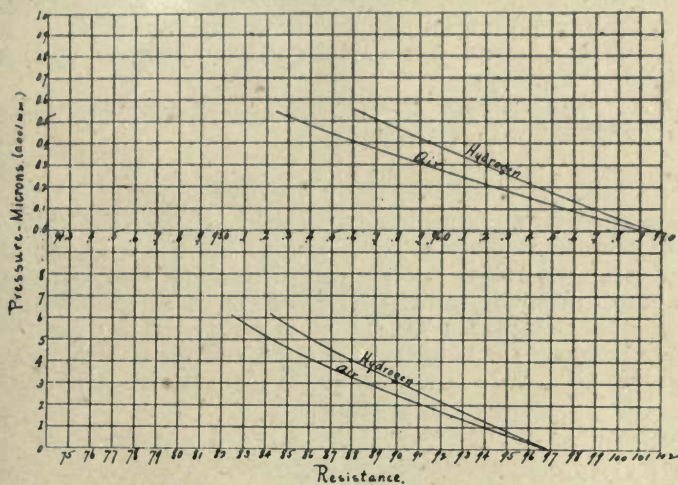


Fig. 51. Calibration Curves of the Gauge Shown in Fig. 49

current of 0.03 amp. for a platinum wire 0.076 mm. in diameter, the sensitivity as measured by $\frac{dR}{dp} \cdot \frac{1}{R}$ was observed to be 1.38×10^{-3} per 1×10^{-4} mm. of mercury. Furthermore, varying the heating current from 0.03 to 0.05 amp. was found to produce no change in sensitivity.

Instead of measuring the change in resistance, Campbell measures the potential which must be supplied to the Wheatstone bridge to keep the resistance (and therefore the temperature) of the wire constant. Three manganin resistances are chosen so that the bridge is balanced when the manometric wire is at a convenient temperature, say 100 deg. C. A voltmeter is connected to the terminals of the bridge, and the potential across the whole bridge varied by means of a rheostat in the battery circuit, until a balance is obtained.

If V_0 is the potential required for a balance when $p = 0$, and V is the potential at any pressure, p , it is found that

$$\frac{V^2 - V_0^2}{V_0^2} = k \cdot f(p) \tag{49}$$

where k is a constant for any given gauge and $f(p)$ is a function of the pressure. The function is actually found to be approximately proportional to p . For pressures ranging as high as 0.15 mm., as pointed out by Campbell, this method of using the Pirani gauge is specially adapted where it is desirable to measure pressures greater than 1 bar. For such pressures the method used by Hale does not give a linear relation between change in resistance and pressure.

A hot-wire manometer based on the same principle has also been described by T. Tschudy.⁴⁶

IONIZATION GAUGES

An electron stream passing through a gas will ionize the latter when the velocity of the electrons exceeds a certain minimum value. In this process, an electron is knocked out of the neutral atom by the incident electron, with the result that the residual portion of the atom is positively charged. The relation between the velocity u of the electrons and the voltage V required to produce this velocity is given by the equation:

$$\frac{1}{2} mu^2 = Ve \quad (50)$$

where

e = charge on electron

m = mass of electron.

During recent years the ionizing potentials of a large number of gases and vapors have been determined with a high degree of accuracy and have been found to vary from 4 to 5 volts for the alkali metals to 25 volts for helium.

The amount of ionization produced by a given electron current increases with the pressure and while this fact has been used as a qualitative guide for the detection of low gas pressures, it is only recently that attempts have been made to apply this principle to the construction of an actual measuring device.

O. E. Buckley⁴⁷ has published a short paper on the results obtained with a manometer of this type in which no details are given as to the actual construction. The gauge consists of three electrodes which are used as cathode (source of electrons), anode, and collector of positive ions respectively. As source of electrons a Wehnelt cathode or incandescent tungsten filament is used. The collector electrode is placed between the anode and cathode, and connected through a galvanometer to the negative terminal of a battery whose positive terminal is con-

⁴⁶ *Elekt. Zeits.* 39, 235 (1918); *Electrical World*, 73, 137 (1919).

⁴⁷ *Proc. Nat. Acad. Sciences*, 2, 683 (1916).

nected to the most negative end of the cathode. The anode potentials used range from 100 to 250 volts, while the magnitude of the electron current is varied from 0.2 to 2.0 milliamperes. At a pressure of 10^{-3} mm. the ionization current was observed to be about one-thousandth that of the electron current and proportionately less at lower pressures; so that with

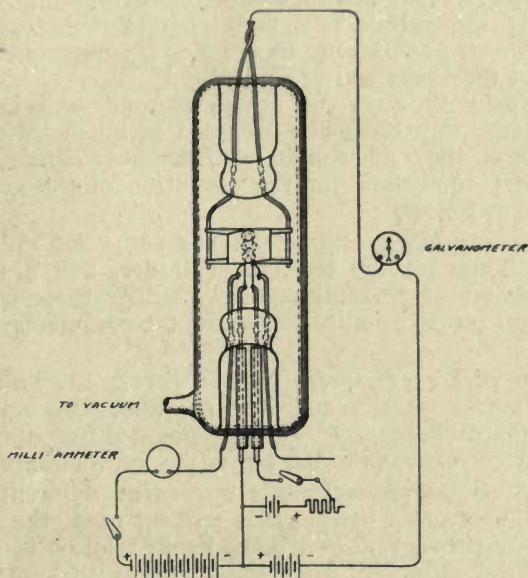


Fig. 52. Ionization Gauge and Connections

an electron current of 2.0 milliamperes, pressure below 10^{-6} mm. could be measured quite easily.

According to Buckley "the exact forms of the electrode are not of great importance." However, subsequent experiments by C. G. Found and S. Dushman⁴⁸ showed that certain designs are much better than others. A gauge consisting of three hair-pin filaments placed in parallel planes shows erratic effects at low pressures because of charges on the walls. Of the many types of construction tested, that shown in Fig. 52 was found to have the best characteristics for measuring low pressures. This illustration also shows the method of connecting up the electrodes.

⁴⁸ Phys. Rev. 17, 7 (1921)

The gauge consists of two tungsten filaments, each wound in the form of a double spiral and mounted co-axially on a four-lead stem which is sealed into the upper end of a glass tube about 4 cm. in diameter and 12 cm. long. The inner spiral is made of 5 turns of 0.125-mm. tungsten wire wound on a 2.25-mm. mandrel. The outer spiral is made of three turns of 0.125-mm. tungsten wire wound on a 3.65-mm. mandrel. Surrounding the spirals is a molybdenum cylinder about 12 mm. in diameter and 12 mm. long which is supported on a two-lead stem at the lower end of the tube.

Before using the gauge for any measurements, it is of course absolutely essential that gases occluded in all metal parts and water vapor on the walls should be thoroughly eliminated.*

The best conditions for the operation of the gauge were found to be as follows:

(a) *For very low pressures (below 1 bar):* 250 volts on the anode, -20 volts on the collector cylinder, and a maximum electron current of 20 milliamperes. Under these conditions, 1×10^{-6} amp. positive ionization current corresponds to 0.0132 bar argon.

(b) *For higher pressures (1 to 50 bars):* 125 volts on the anode, -20 volts on the collector cylinder, and an electron current of 0.5 milliampere. In this case, 1×10^{-6} amp. ionization current corresponds to 0.5 bar argon approximately.

Fig. 53 shows characteristic curves at different electron currents. The greater the electron current used, the lower the upper limit of pressure at which the linear relation is still valid.

It will be observed from these curves that at constant pressure the ionization current is not quite proportional to the electron current. For measuring a considerable range of pressures it is desirable to have this proportionality, since it is then possible to increase the electron current as the pressure is lowered and thus increase the sensitivity of the gauge. The following method of connection has been found to give a linear relationship between ionization and electron current and may therefore be used instead of the arrangement just described. The inner filament is used as collector, the outer filament as cathode and the cylinder as anode. With this connection the ionization current is practically independent of the anode voltage between 125 and 250 volts. The sensitivity is not quite as good as with the first method of connection, 1×10^{-6} amp. positive ionization corresponding to about 0.032 bar argon.

* See Chapter II, pp. 71-75.

An interesting result which was found on studying the behavior of the gauge with different gases is that at constant pressure and with the same conditions as to anode voltage and electron current, the ionization current increases with the number of electrons in the molecule. Thus the number of electrons in an argon molecule (or atom) is 18, while in a mercury molecule (which is also monatomic) the number of electrons is 80. The ionization currents at constant pressure are

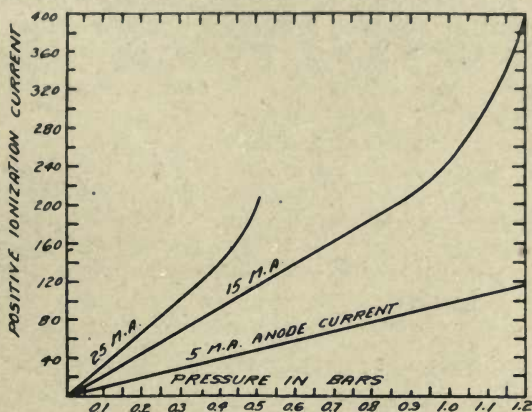


Fig. 53. Characteristic Curves of the Ionization Gauge

found to be in approximately this ratio. Experiments with iodine and water vapor showed that the ionization currents in these cases, as compared with that for argon at the same pressure (and same electron current) correspond to electronic numbers of 106 and 10 respectively, if that for argon is taken at 18. This generalization is apparently not quite true for hydrogen and helium. The ionization currents in these cases correspond to much larger atomic numbers. For all ordinary cases, however, the calibration for nitrogen (14 electrons per molecule) may be used as a general guide to the value of the pressure.

The ionization gauge, as just described, has been found to be very useful in investigating the pressure changes in incandescent lamps and hot-cathode devices after sealing off from the pump. The ease of construction and simplicity of manipulation ought to make it a very useful device in high-vacuum technique. Instead of a tungsten filament as emitter of electrons, a Wehnelt cathode may be used. This consists of a platinum

wire coated with oxides of the alkaline earth metals and its construction and characteristics have been described by H. D. Arnold.⁴⁹ This type of cathode has the advantage over one of tungsten for factory use because it is not apt to be destroyed by accidental leakage of air into the gauge while the filament is lighted.

Some results with a three-filament ionization gauge have also been published by Misamichi So.⁵⁰ The ionization currents were, however, measured at constant cathode temperature, and since the electron emission is affected by gas pressure no linear relation was observed between pressure and ionization current.

⁴⁹ *Phys. Rev.* 16, 70 (1920).

⁵⁰ *Phys. Math. Sc. Jap. Proc. I*, p. 76 (1919).

CHAPTER IV

SORPTION* OF GASES AT LOW PRESSURES

While the use of vacuum pumps is undoubtedly the most generally applicable method of obtaining very low pressures, there are other methods of a physical chemical nature which are of great utility and importance in high vacuum technique. Charcoal, palladium black, and similar substances have been found to absorb large volumes of gas when exposed to very low temperatures. The high reactivity of alkali and alkaline earth metals with all gases except argon, helium (and the other elements of the inert group) has been utilized by different investigators for "cleaning up" residual gases. The fact that the electrical discharge in a low pressure tube causes a gradual disappearance of the gas has been known for a long time and explains the progressive "hardening" of the gas-filled X-ray tubes. In the incandescent lamp industry various chemicals or "getters" are also used for the purpose of improving the vacuum in the lamp after it is sealed off from the pump. All these are illustrations of physical chemical methods of producing high vacua, which we shall discuss in this and the following chapter.

(I) ADSORPTION OF GASES ON CHARCOAL¹

Dewar's Investigations on the Use of Charcoal in the Production of High Vacua

That charcoal and other substances in a finely divided state have the power of taking up large volumes of different gases was observed even in the 18th century. Sir James Dewar² was the first investigator to make use of this phenomenon for the production of high vacua. He observed that charcoal made from coconuts has very much higher adsorptive power than that from other sources. He also found that by heating the charcoal in vacuo for a long time, to expel gases already adsorbed, and then cooling it to a low temperature, large volumes of the ordinary gases could be readily "cleaned-up," so that the pressure in a sealed-off bulb was diminished to a very low value. Thus, in the case of a 2000 cm.³ bulb containing air at 2.19 mm.

* See page 125 for definition of this term.

¹ The literature on this subject is so immense that it is impossible to do more than refer briefly to the most important results. For further references the reader may consult the following:

W. Ostwald, *Lehrb. d. allgem. Chem.*, I, Aufl. 1, p. 778 (Reference to literature previous to 1890).

H. Freundlich, *Kapillarchemie* (1909) pp. 91-125.

² *Proc. Roy. Soc.* 74, 122 and 127 (1904); *Encycl. Britan.* Vol. 16, p. 751 (1912); *Engineering* (London), June 15, 1906; *ib.*, June 14, 1917. His first investigations were reported in *Nature*, July 15, 1875.

pressure, 20 grammes of charcoal cooled in liquid air (-185 deg. C.) effected a reduction in the pressure to 0.00025 mm. The adsorptive power for different gases was observed, in general, to increase with the boiling point of the gas. Some of the earlier observations are shown in Table XV, although it must be noted that much larger adsorptions have since been obtained owing to improved technique in the preparation of the charcoal. The volumes adsorbed are given in cm^3 at 0 deg. C. and 760 mm. pressures.

TABLE XV
GAS ADSORPTION ON CHARCOAL (per cm^3)

	Boiling Point Deg. Cent.	Volume Absorbed at 0° C.	Volume Absorbed at -185° C.
Helium	-268.6	2 cm^3	15 cm^3
Hydrogen	-252.9	4	135
Argon	-186.2	12	175
Nitrogen	-195.8	15	155
Oxygen	-183.0	18	230

The effect of temperature on the relative adsorption of helium and hydrogen is shown in Table XVI. "It will be observed that the adsorption of helium, small in comparison to that of other gases, even hydrogen, increases therefore enormously at the lowest temperature," which is below the boiling point of liquid hydrogen.

Further experiments on the use of charcoal for the production of high vacua were carried out by Blythwood and Allen.³ Their results are extremely interesting. They observed that by using charcoal at the temperature of liquid air, very large volumes of air could be adsorbed. The rate of adsorption was found to be given accurately by the first order reaction equation.

$$\frac{dx}{dt} = k(A - x)$$

where

x = amount adsorbed at time t

A = total amount adsorbed when equilibrium is attained,

and

k = constant.

³ Phil. Mag. 10, 497 (1905).

In one experiment, using 216 gms. charcoal, a volume of about 925 cm.³ was exhausted from an initial pressure of 40 mm. to 0.0009 mm. of mercury in about 3 hours.

Absorption, Adsorption, Occlusion, and Sorption

The clean-up of gases by charcoal and similar substances is apparently a complex phenomenon. It is certainly not a case of chemical reaction in the same sense as the clean-up of oxygen by a heated tungsten filament (where WO_3 is formed as a result of the reaction), although there is some question as to whether in the case of oxygen taken up by charcoal there is a chemical action. Also we are familiar with the occlusion of gases by metals. Here we are apparently dealing with true cases of

TABLE XVI
RELATIVE ADSORPTION OF HYDROGEN AND HELIUM AT
LOW TEMPERATURES

Temp. Deg. Cent.	Helium	Hydrogen
-185	2.5	137
-210	5.	180
-252	160	250
-258	195	

solution, obeying laws similar to the solutions of nitrogen or oxygen in water. While there is some evidence of similar phenomena in the specific case of charcoal and hydrogen (see later) a theory of solution will not account for the general phenomena of clean-up of gases by charcoal. On the other hand, we find that all clean surfaces, after evacuation, absorb definite amounts of different gases. This seems to be a case of condensation on the surface, of a layer of gas about one atom in thickness. The gas molecules are attached to the surface by quasi-chemical forces. Increase in temperature causes rapid evaporation, while decrease in temperature leads to equally rapid condensation of gas on the surface. To distinguish these different kinds of physical chemical reactions, certain terms have been introduced into the literature on the subject.

J. W. McBain⁴ has suggested the term "sorption" as a "generic and non-hypothetical term for phenomena which frequently occur together," to include all cases of clean-up of gases by metals, charcoal, or other substances.

⁴ Phil. Mag. (6), 18, 916 (1909).
Zeits. physikal. Chem. 68, 471 (1909).

The surface condensation of gases is usually referred to as *adsorption*, while the solution of gases in metals or liquids is regarded as an *absorption* phenomenon. The term "occlusion" is also used frequently in referring to the gases present in metals. No doubt, a large number of cases of occlusion of gases by metals ought to be classified as true absorption (solution) phenomena; while other cases must be regarded as illustrations of adsorption reactions. Under these conditions the use of the term occlusion seems superfluous. While the theories of sorption phenomena are discussed in a subsequent section, it has been considered best to introduce these terms in the present connection because of their value in the classification of the different cases of clean-up.

Adsorption of Gases on Charcoal. General Investigations

The clean-up of gases by charcoal is to a great extent an adsorption phenomenon, the condensation of the gas occurring on the large surface presented by the pores in the charcoal. The adsorptive power varies widely with the method of preparation and structure, so that it is impossible to draw any conclusions by comparing the results obtained by different investigators. On the other hand, it has been possible to obtain interesting results by studying the behavior of any given specimen of charcoal, and from these results have been derived certain general conclusions regarding the "laws" of adsorption phenomena.

The relation between the amount of gas adsorbed at constant temperature and the residual pressure is of great importance. The measurements are carried out as follows: The charcoal (or other solid adsorbent) in a tube is heated to a high temperature (400 deg.-600 deg. C.) and simultaneously evacuated from previously adsorbed gases. A measured volume of gas is then brought in contact with this material and the pressure of the residual gas measured after equilibrium is attained. This operation is repeated until, finally, the adsorbent becomes saturated.⁵

Most of the investigators in this field have measured the adsorption at pressures above 1 mm. of mercury, and there are very few published data on the adsorptive power of charcoal at the low pressures which are of interest in vacuum technique.

⁵ Illustrations of the apparatus used and method of measurement are given in the following:

- J. Dewar, *Encycl. Brit.* 16, 751 (1912) Fig. 5.
- M. W. Travers, *Proc. Roy. Soc.* 78, 9 (1907).
- I. F. Homfray, *Zeits. physikal. Chem.* 74, 129 (1910).
- A. Titoff, *Zeits. physikal. Chem.* 74, 641 (1910).
- J. B. Firth, *Zeits. physikal. Chem.* 86, 294 (1913).

H. Baerwald⁶ showed that by heating charcoal to over 500 deg. C., its adsorptive power is increased considerably; also that charcoal from coconut shell is a much better adsorbent than that from the soft part of the nut, or from wood.

The adsorption of nitrogen, oxygen, and air on coconut shell charcoal at about 18 deg. C. has been measured by F. Bergter.⁷

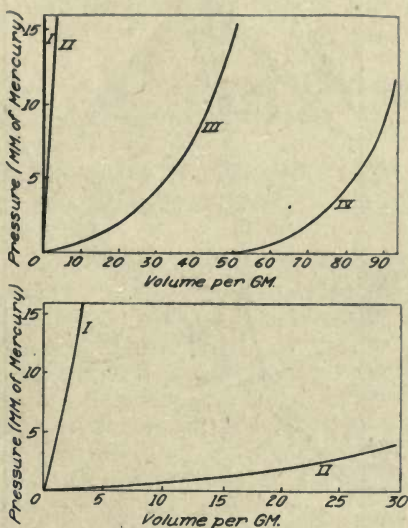


Fig. 54. Adsorption of Gases on Charcoal at Low Pressures (Claude)

The measurements at low pressures (1-10 mm. mercury) show that at the same pressure oxygen is adsorbed in about 30 or 40 times as great an amount as nitrogen, while the adsorbing power of air is about 3 times that of nitrogen. At low pressures the amount adsorbed is proportional to the final pressure. It was also observed that in the case of nitrogen, about 96 per cent of the total amount is adsorbed almost instantaneously, while the rest is adsorbed very slowly.

In the following tables and curves of results obtained by different investigators, the pressure is given in mm. of mercury, the volume adsorbed, in cm^3 (measured at 0 deg. C. and 760

⁶ Ann. Phys. 23, 84 (1907).

⁷ Ann. Phys. 37, 472 (1912). This paper also gives a large number of references to previous work.

mm.) per 1 gm. charcoal (except where otherwise mentioned), and the temperatures are given in degrees on the absolute or Kelvin scale. ($T = \text{deg. C.} + 273$).

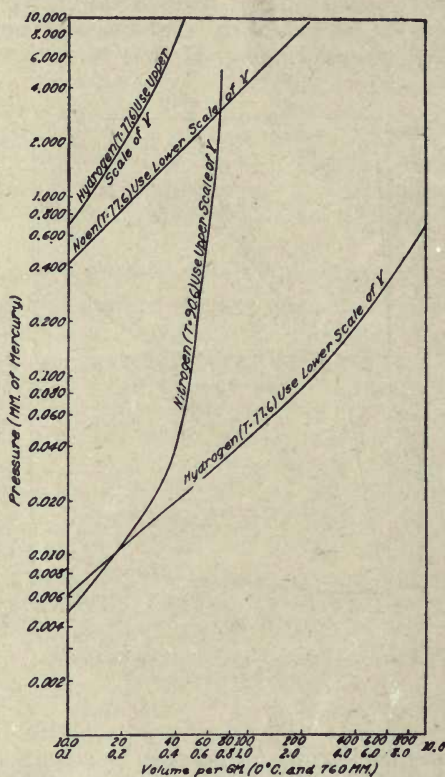


Fig. 55. Adsorption of Gases on Charcoal at Very Low Temperatures (Claude)

G. Claude⁸ has measured the adsorption of H_2 , He, Ne, and N_2 on charcoal at very low temperatures and low pressures. Table XVII gives the results obtained, which are shown graphically in Fig. 54. Curves I, II, and III show the data for He, Ne, and H_2 respectively, at $T = 77.6$, while Curve IV shows the data for N_2 at $T = 90.6$. The lower part of Fig. 54 shows Curves I and II plotted on a different scale.

⁸ Compt. rend. 158, 861 (1914).

The adsorption of helium was observed to be extremely small, 0.21 cm.³ being adsorbed at a pressure of 27 mm.

It will be observed that although hydrogen has a lower boiling point than that of neon, the adsorptive power of charcoal for the latter is much lower than that for hydrogen. At very low pressures the amount adsorbed tends to become proportional to the pressure. For higher pressures, the form of the adsorption relation which has been used, as a general rule, is,

$$v = k \cdot p^{1/n} \quad (51a)$$

where

v = volume of gas (measured under definite conditions)
per unit weight of adsorbent.

p = pressure.

In this equation k and n are constants which depend on the nature of both the adsorbent and gas. Since this relation can be expressed in the form,

$$\log v = 1/n \log p + \log k \quad (51b)$$

it is evident that if p and v are plotted on logarithmic paper, a straight line should be obtained whose slope gives the value of $1/n$. Fig. 55 shows Claude's data plotted in this manner. In this case, the value of $1/n$ is approximately unity, corresponding to a linear relation between p and v . At higher pressures and concentrations, the values of $1/n$ tend to decrease more and more. This is illustrated by Titoff's results⁹ (see Table XVIII and Fig. 56) on the adsorption of various gases on coconut charcoal.

TABLE XVII
ADSORPTION OF GASES ON CHARCOAL (Claude)

NITROGEN (T=90.6)		HYDROGEN (T=77.6)		NEON (T=77.6)	
P	V	P	V	P	V
0.004	9.35	0.006	0.105	0.45	0.105
0.010	18.70	0.0115	0.21	0.88	0.21
0.032	37.4	0.0205	0.42	1.30	0.32
0.088	46.6	0.036	0.84	1.74	0.42
0.385	56.0	0.083	2.05	3.50	0.84
1.107	65.3	0.176	3.71	5.30	1.22
11.50	93.0	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

⁹ Loc. cit.

TABLE XVIII
 ADSORPTION OF GASES ON CHARCOAL (Titoff)

HYDROGEN				NITROGEN				CARBON DIOXIDE			
P	V	1/n	P	V	1/n	P	V	1/n	P	V	1/n
(I) T = 353											
10	0.0064	0.97	11.4	0.0452	1.11	4.3	0.2800	0.93			
35.3	0.0217	0.98	26.6	0.1154	1.07	12.5	0.759	0.94			
73.9	0.0446	0.99	91.8	0.4330	0.95	26.6	1.539	0.93			
183.1	0.1097	0.91	198.9	0.9021	0.94	54.4	2.985	0.84			
310.8	0.1778	0.91	297.2	1.3170	0.92	120.9	5.840	0.76			
454.0	0.2538	1.00	470.9	2.007	0.89	230.4	9.541	0.72			
611.5	0.3413	1.00	622.7	2.572	1.00	356.4	13.07	0.70			
727.3	0.4011	0.93	770.1	3.180	1.00	520.3	17.06	0.70			
(II) T = 273											
17.4	0.0384		4.3	0.111	0.95	0.5	0.849	0.68			
39.3	0.0983	1.16	12.1	0.298	1.02	3.2	3.460	0.73			
66.9	0.1490	0.78	39.3	0.987	0.94	10.9	8.506	0.68			
119.4	0.2704	1.03	129.8	3.043	0.90	25.4	15.15	0.43			
206.9	0.4514	0.93	229.4	5.082	0.83	83.0	27.78	0.49			
427.5	0.9139	0.97	340.1	6.047	0.83	173.5	39.90	0.49			
642.1	1.3430	0.94	562.3	10.310	0.76	315.9	50.24	0.39			
(III) T = 194											
7.9	0.059		1.5	0.145							
19.0	0.148	1.06	4.6	0.894							
67.5	0.531	1.01	12.5	3.47	0.75						
141.9	1.121	1.01	66.4	12.04	0.63						
236.9	1.892	1.02	149.5	20.03	0.56						
347.9	2.787	1.01	271.4	27.94	0.50						
471.8	3.607	0.85	388.4	33.43	0.41						
561.9	4.276	0.97	542.9	38.39	0.41						
721.6	5.414	0.94	740.6	43.51	0.40						

The effect of increased temperature in decreasing the adsorptive power is quite evident. The relative adsorption of different gases at the same pressure and different temperature is shown by the data given in Table XIX.

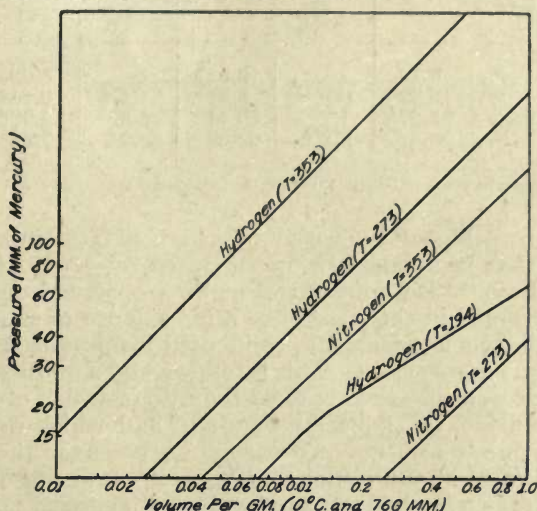


Fig. 56. Adsorption of Hydrogen and Nitrogen on Charcoal at Higher Temperatures (Claude)

Miss Ida F. Homfray published in 1910¹⁰ the results of quite an elaborate series of measurements on the adsorption on coconut shell charcoal of argon, nitrogen, carbon monoxide, carbon dioxide, methane and ethylene.

The observations with the first four gases are shown graphically in the curves given in Figs. 57 to 60. The temperatures are given in degrees absolute, and the volumes absorbed are referred to the constant weight, 2.964 gm., which was used in all experiments.

The results for helium are of interest.¹¹ At the temperature of liquid air, the following absorption data were obtained:

P (mm. of Mercury)	V (Per gm. of Charcoal) in Cm. ³
120.	0.337
171.	0.465
235.	0.81
427.6	1.17
705.0	1.84

¹⁰ Zeits. physikal. Chem., 74, 129 (1910).

¹¹ The adsorption of helium on charcoal has also been measured recently by S. McLean. Trans. Roy. Soc. Can. 12 (III), 79 (1918); Chem. Abst. 13, 1667 (1919). The amounts of helium adsorbed on charcoal at the temperature of liquid air were observed to be very small.

TABLE XIX
COMPARATIVE ADSORPTION OF DIFFERENT GASES (Titoff)
 At $p = 100$ mm.

Temperature (deg. Cent.)	-79	-23.5	0	30	80	151.5
Hydrogen	0.79		0.227		0.0607	
Nitrogen	15.89		2.344	1.178	0.4688	0.1633
Carbon Dioxide	97.27*		30.41	15.89	4.920	1.062
Ammonia		112.2	69.02	29.24	7.96	2.77

*The temperature was -76.5 in this case, as CO_2 solidifies at -79 .

The sorption of hydrogen by charcoal at temperature of liquid air has been specially investigated by J. B. Firth,¹² and J. W. McBain.¹³ Both investigators have observed that equilibrium is attained in this case only after a lapse of many hours. Most of the gas is apparently condensed instantaneously on the surface (true adsorption). This is followed by a gradual diffusion of the hydrogen into the charcoal the rate of which obeys Fick's law of diffusion, as shown by McBain, and which must be regarded as due to solution or occlusion of the gas in the charcoal. Firth finds that at equilibrium the relation between pressure and volume of gas adsorbed per unit weight of charcoal is not given by a linear relation, but by an equation of the form

$$v = kp^{1/4}$$

Table XX gives the equilibrium data observed. The pressures are given in mm. of mercury, and V gives the volume adsorbed (corrected to 0 deg. C., 760 mm.) per gm. charcoal.

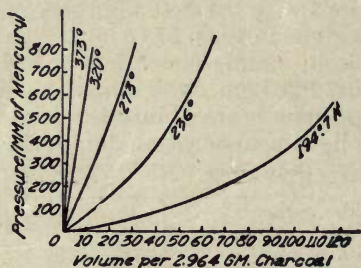


Fig. 57. Adsorption of Argon on Charcoal (Homfray)

¹² Zeits. physikal. Chem. 86, 294 (1913).

¹³ Loc. cit.

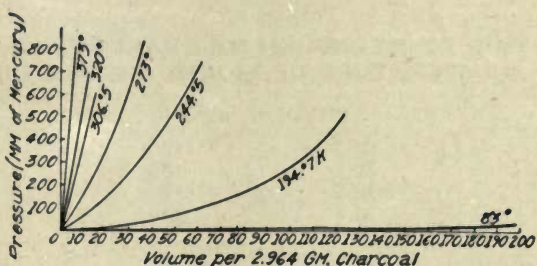


Fig. 58. Adsorption of Nitrogen on Charcoal (Homfray)

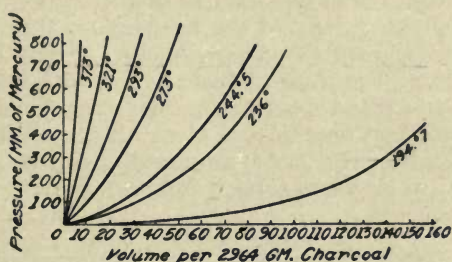


Fig. 59. Adsorption of Carbon Monoxide on Charcoal (Homfray)



Fig. 60. Adsorption of Carbon Dioxide on Charcoal (Homfray)

McBain on the other hand obtains the relation

$$v = k p^{1/2}$$

which would point to the hydrogen being absorbed in the atomic condition. At a pressure of 19 mm. and the temperature of liquid air the amount of hydrogen taken up per gm. of charcoal is 4 cm.³ (at 0 deg. C. and 760 mm.) which is much less than that observed by Firth.

TABLE XX
SORPTION OF HYDROGEN BY CHARCOAL AT THE
TEMPERATURE OF LIQUID AIR (Firth)

P	V	P	V
9	21.5	90	59.3
17	32.1	126	63.1
30	46.5	186	69.2
51	53.3	245	76.0
59	56.0		

Use of Charcoal at Low Temperatures in High Vacuum Investigation

The only comprehensive data in the literature on adsorption at very low temperatures and low pressures is that published by Claude, which was mentioned previously. From his data it is possible, assuming the linear relation to be valid down to very low pressures, to calculate the amounts of nitrogen and hydrogen that can be adsorbed on charcoal at equilibrium pressures below 1 bar. Table XXI gives these amounts in terms of the volume measured at 1 bar pressure (and 0 deg. C.).

TABLE XXI
ADSORPTION ON CHARCOAL AT LOW TEMPERATURES
(Extrapolated from Claude's data)

Hydrogen (T = 77.6)		Nitrogen (T = 90.6)	
P (bars)	V	P (bars)	V
8.	106,000	5.3	9,500,000
1.	13,250	1	1,800,000
0.1	1,325	0.1	180,000
0.01	133	0.01	18,000
0.001	13	0.001	1,800

That is, at a pressure of 0.01 bar (which is a maximum pressure for the efficient operation of hot cathode high vacuum devices), 1 gram of charcoal (such as used by Claude) would clean up about 130 cm.³ of hydrogen or 18,000 cm.³ of nitrogen, from a pressure of 1 bar down to 0.01 bar.

Woodrow¹⁴ measured, with a Knudsen gauge, the amount of clean-up of different gases by charcoal at liquid air temperatures. Neither the volume of the apparatus nor weight of charcoal are given. The latter was heated under simultaneous evacuation till the pressure fell to 1.5×10^{-6} mm. of mercury (2×10^{-3} bar)

¹⁴ Phys. Rev. 4, 491 (1914).

and hydrogen, oxygen, or nitrogen was then introduced at an initial pressure of about 0.65 bar. The rate of clean-up in each case as followed with the gauge is shown in the table:

RATE OF CLEAN-UP BY CHARCOAL

Time	PRESSURE IN BARS		
	Hydrogen	Oxygen	Nitrogen
0	0.647	0.667	0.600
5 sec.		0.387	
10 sec.		0.227	
1 min.	0.613	0.0027	0.020
5 min.	0.547	0.002	
20 min.	0.387		
1 hr.	0.253		0.007
3 hrs.	0.180	0.002	
10 hrs.	0.180	0.002	0.007

Miss M. Daly and the author have carried out some experiments in this laboratory on the adsorption of gases by charcoal at low temperatures. Specially activated products (see below), supplied by Dr. F. M. Dorsey, were used in this work. Pressures were determined by means of the ionization gauge, and the rate of clean-up observed of both hydrogen and residual gases present after sealing off the pump. In the latter case the gauge and tube containing 5 gm. charcoal with a large bulb (total volume = 3000 cm.³) were well exhausted on the condensation pump, heating the charcoal for over an hour to 360 deg. C. After sealing this system off the pump, the pressure was measured, and then liquid air put on the charcoal. The pressures before cooling the latter, and after, were as follows:

V	Initial Pressure (bars)	Final Pressure
3000 cm. ³	0.022	0.0004
3000 cm. ³	0.036	0.0004
3000 cm. ³	0.92	0.0006

It may be noted that the sensitivity of the galvanometer used with the ionization gauge was such that 0.0004 bar was about the lowest pressure that could actually be measured.

In carrying out experiments with hydrogen, the same apparatus was used, except that another side tube was sealed on in which was contained a small thin-walled glass pellet (volume of 3 cm.³) filled with hydrogen at a known pressure. After exhausting the gauge, charcoal tube, and bulb, this system was sealed off, the hydrogen pellet broken by shaking, and the residual

pressure observed after immersing the charcoal tube in liquid air. Five gms. of activated charcoal were used as in the previous experiments. The residual gas pressure was also measured before breaking the pellet. Table XXII shows some of the results obtained.

In general it required about an hour to attain equilibrium. In accord with McBain's observations it was found that the initial condensation was followed by a slow diffusion of gas into the charcoal.

TABLE XXII
CLEAN-UP OF HYDROGEN BY ACTIVATED CHARCOAL
(M. Daly and S. Dushman)

V	Press. After Sealing Off	Initial Press. of Hydrogen	Final Press. at Room Temp.	Press. At Liquid Air Temp.
3025	0.0180 bar	0.31 bar	0.014	0.0004
100	0.104 bar	8.64 bar	0.02	0.0004
3025	0.022 bar	8.33 bar	2.0	0.15
100	0.28 bar	17.7 bar	0.24	0.0016

A certain fraction of this clean-up was no doubt due to the action of the gauge itself. As will be shown in the following chapter there is an electrical clean-up which occurs in all hot-cathode devices. Furthermore, in presence of a heated filament atomic hydrogen is formed which is cleaned up at the temperature of liquid air. A blank experiment carried out without the use of charcoal gave

$V = 340$; pressure after seal off = 1.60 bar.

On breaking the hydrogen pellet, the pressure rose to 7 bars; then fell, owing to clean-up by gauge, to 2 bars. Liquid air was put on the side tube and the pressure fell in the course of 6 hours to 0.16 bar. On removing the liquid air, the pressure came back to 1.2 bar.

In the measurements with charcoal the gauge filaments were lighted only during the time necessary to take a pressure reading, so that any error due to clean-up in the gauge was certainly not very large.

It is evident from these measurements that with a charcoal tube immersed in liquid air it is possible to adsorb appreciable volumes of hydrogen and obtain residual gas pressures of less than 0.0001 bar.

¹⁵ Proc. Roy. Soc. 78 (A) 9 (1907).

¹⁶ Loc. cit.

Preparation of Charcoal. "Activated" Charcoal

The methods of preparing coconut charcoal as used by M. W. Travers,¹⁵ J. W. McBain¹⁶ and others is as follows: The soft part is heated in a muffle furnace for several hours at just below a red heat until no more vapor is evolved; then the temperature is raised to a dull red heat for 30 seconds. After introducing the charcoal into a tube (and before use as an adsorbent) it is heated to 440 deg. C. (bath of boiling sulphur) for several hours, in vacuo.

As mentioned previously, and as is evident from a comparison of the results on adsorption obtained by different experimenters, the sorptive power of charcoal is influenced largely by its structure, that is, mainly the porosity. It was observed that charcoal from the shell of the coconut gave a much greater sorption per unit volume of charcoal than that obtained from less dense forms of wood. But a great stimulus to the investigation of the effect of structure of charcoal on its adsorbing power was provided during the recent war by the necessity of developing a highly efficient absorbent for gas masks. As a result there was evolved a technique for the production of a specially active form of charcoal which will no doubt be of equal utility in the peaceful art of vacuum production.¹⁷

Lemon observed in 1915 that different samples of charcoal made from the same material (coconut shell) showed very wide variations in sorptive power. It was found that this was due to variations in heat treatment and that a considerable increase in sorptive power, "activation," could be produced by repeated evacuations at 650 deg. C., each evacuation being followed by an absorption of air at the temperature of liquid air. On the other hand, by treating the charcoal to between 800 deg. C. and 900 deg. C. during evacuation, a decrease in sorptive power (deactivation) resulted.

The theory was advanced that the successive absorptions of air oxidize non-volatile hydrocarbons present in the charcoal. As a result an air-process of activating charcoal was evolved which consisted essentially of the following operations:¹⁸

¹⁷ The results of the investigations on this subject carried out by the Chemical Warfare Service, U. S. A., have been published mainly in the following papers:

A. B. Lamb, R. E. Wilson, and N. K. Chaney, *Journ. Ind. and Eng. Chem.* 11, 420, 1919, on "Gas Mask Absorbents."

F. M. Dorsey, *ib.* 11, 281, 1919, on the "Development of Activated Charcoal."

H. B. Lemon, *Phys. Rev.* 14, 282, Oct., 1919.

N. K. Chaney, *Trans. Am. Electrochem. Soc.*, 36, 91 (1919).

The writer is indebted to these publications for the information on the properties and preparation of activated charcoal.

¹⁸ F. M. Dorsey, *loc. cit.*

1. Initial distillation of cracked coconut hulls to a temperature of 850 deg. C. to 900 deg. C., and
2. "Air treating" this carbonized material, screened 6 to 14 mesh, at 350 deg. C. to 400 deg. C., for a certain length of time.

The essential characteristics of an active charcoal are:¹⁹

1. High and fine-grained porosity.
2. The presence of amorphous base carbon.
3. Freedom from adsorbed hydrocarbons.

To secure these objects it is necessary to use dense woods, carry out the distillation at relatively low temperatures, and then oxidize the hydrocarbons without injuring the carbon base to any measurable extent. "The permissible range of temperatures for the latter operation is a relatively narrow one, only about 50 to 75 deg." For air oxidation this lies between 350 and 450 deg. C. Subsequently a steam process of activation was adopted, and for this reaction the optimum temperature is between 800 deg. and 1000 deg. C. Other methods of activation have been used in Europe. All these processes yield charcoal which is much more active than that obtained by the simple distillation process used at one time.

"From a study of the slope of the vapor pressure curves of liquids adsorbed upon such charcoal, the indications are that the pores have, if a cylindrical form be assumed, an average diameter of about 5×10^{-7} cm. On this basis, 1 cm.³ of active charcoal would contain about 1000 sq. meters of surface."

The density of activated charcoal from coconut shells is about 0.4. Hence 1 gm. would contain about 2500 sq. meters of surface. Assuming that the clean-up by charcoal is due to a condensation of gas molecules on the surface, and that the diameter of a hydrogen molecule is about 2×10^{-8} cm., it would require approximately 2000 cm.³ (measured at 0 deg. C. and 760 mm.) to cover the surface of 1 gm. of charcoal. Compared with this the adsorptions obtained by Miss Homfray, Titoff and Firth, even at atmospheric pressure, are very low, which may be accounted for partly by the smaller porosity of the charcoal used by them.

It is of interest in this connection to mention a theory regarding the structure of charcoal which has been advanced by N. K. Chaney.¹⁷ According to this theory "elementary carbon (other than diamond and graphite) exists in two modifications, 'active' and 'inactive' or *alpha* and *beta*. All 'primary' amorphous carbon consists essentially of a stabilized complex of hydro-

¹⁹ A. B. Lamb, R. E. Wilson and N. K. Chaney, loc. cit.

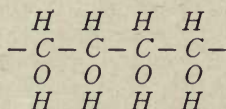
carbons, adsorbed on a base of 'active' or *alpha* carbon. The active modification is formed whenever carbon is deposited at relatively low temperatures by chemical or thermal decomposition of carbon-bearing materials; in general below 500 to 600 deg. C. The inactive modification results from similar decomposition at higher temperatures, in general above 600 to 700 deg. C. The temperature at which molecular carbon is set free is apparently the controlling factor in determining whether it is of the active or inactive variety." The active form is characterized by a very high specific adsorptive capacity for gases. Chaney distinguishes between the true adsorptive capacity characteristic of the active form and a capillary capacity in virtue of which gas is taken up in pores formed by the loosely bound structure which results in carbonization of any carbon-bearing material, and he differentiates these as follows: On saturating an adsorbent and then noting the rate at which the gas is removed, it is observed that the portion absorbed in capillary spaces is given off readily while that adsorbed specifically is given off very slowly. "The weight of gas retained, after rapid weight loss has ceased, called the 'retentivity' of the adsorbent, is a measure, therefore, of the proportion of active carbon present, in a given weight of adsorbent. This test applied to pre-war charcoals shows that their adsorptive capacity is almost wholly capillary and dependent upon the physical structure left by distillation in the primary carbon. In general even this capacity is extremely small compared with present standards." The observation made by McBain that the sorption of hydrogen by ordinary charcoal at low temperatures occurs in two stages finds an explanation from this point of view. The major portion of the gas is taken up very rapidly, while a residual portion requires quite an interval of time to condense.

The problem in preparing active charcoal, according to Chaney, therefore consists in devising some method which will get rid of the hydrocarbons adsorbed specifically by the active carbon at the instant of formation. This adsorbed gas forms quite stable complexes with the carbon base and constitutes the product which he designates as primary carbon, "because it is the original product first occurring in low temperature distillation of carboniferous material." The methods of preparing active charcoal by oxidation with steam and other schemes therefore have for their purpose the removal of these adsorbed hydrocarbons.

In discussing the mechanism of the capillary and specific adsorptions, Chaney remarks: "The simplest theoretical as-

sumption is that capillary adsorption is the filling of actual cells with liquid due to lowered surface tension, and dependent upon the size of capillaries, i.e., the physical structure of the absorbent only. The specific capacity has been assumed to represent a field of force—probably due to unsaturated valences—which is independent of a grosser physical structure of the absorbent, i.e., it represents adsorption on a plane surface.”

While the discussion of the theories of adsorption must be reserved for a subsequent chapter, it is well to point out here that Langmuir has advanced the view, which he supports with a great deal of evidence, that true adsorption consists in a condensation of gas in a layer one atom deep on the surface of the absorbent. As has been shown, the older data on adsorption of gases by charcoal is not in contradiction with this view. Regarding the sorption of gases by activated charcoal, Langmuir has pointed out²⁰ that “truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibers of cellulose from which charcoal is usually formed consist of practically endless groups of atoms



held together by primary valences in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat, the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. *The porosity of the charcoal thus undoubtedly extends down to atomic dimensions.* The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon.”

“Hence,” according to Langmuir, “it is evident that with a structure of this kind, it is meaningless to talk about the surface on which adsorption can take place.” On plane surfaces the maximum adsorption would correspond to a layer one molecule deep; but in the case of charcoal, there is no definite surface which can be covered by a unimolecular layer. The atoms of carbon would be separated by spaces which might hold one or more molecules of the gas, and on the other hand, these spaces might be too small to hold even one molecule.

²⁰ J. Am. Chem. Soc. 38, 2221 (1916).

It will be observed that Chaney agrees with Langmuir in concluding that the specific absorptive capacity of activated charcoal is a measure of the amount of gas condensed as a unimolecular layer.

H. Briggs,²¹ as a result of his investigations on the adsorption of gas on charcoal and silica gel, concludes that while the chemical character of a material affects its properties as a gas-adsorbent, there are, with any given material, two factors which also influence the adsorptive power, viz.: "(a) the degree of canalisation of the substance, i.e., its porosity on the microscopic or ultramicroscopic scale, and (b) the degree of porosity on the molar scale." From the measurements on the size of the pores made by Lamb, Wilson and Chaney,¹⁷ which have already been mentioned. Briggs infers that "the greater part of the internal gaseous space of an efficient adsorbent consists of passages which are not greatly larger than the gas molecules." According to his view, Chaney's assumption of the existence of two allotropic forms in active charcoal is not sufficiently supported by the experimental evidence, and he concludes that the efficiency of activated charcoal is due to the presence of the molar interstices.

H. H. Sheldon²² has shown that while ordinarily nitrogen is more readily adsorbed on charcoal than hydrogen, it is possible by suitable treatment to produce a charcoal in which the relative adsorptive capacities for the two gases are reversed. He has also observed that evacuation of charcoal at 600 degrees C. followed by adsorption of oxygen at low temperatures and this again by re-evacuations at the higher temperature, leads to considerable improvement in the adsorptive capacity of charcoal.

J. C. Philips, S. Dunnill and O. Warkman²³ have made similar observations with wood-charcoal. The greater the facilities for the access of air to the material during heating, the greater the resulting increase that was obtained in the sorptive power. They also observed that the increased activity was accompanied by a decrease in bulk density, indicating, according to Briggs, an increasing degree of "molar" porosity.

These observations are in accord with results obtained in this laboratory. A given sample of charcoal shows marked improvements as a clean-up reagent in high vacuum work, after it has been evacuated and saturated with gas several times in succession.

²¹ Proc. Roy. Soc. (London) 100, 88 (1921).

²² Phys. Rev. 16, 165 (1920).

²³ Trans. Chem. Soc., 117, 362 (1920).

As mentioned previously, the results obtained in this laboratory by the use of activated charcoal in high vacuum investigations have been very encouraging. It is well, however, to point out, as has been done by Briggs, that from data obtained on the adsorptive capacity of an adsorbent at higher pressures, it is not at all safe to predict the behavior at lower pressures. At higher pressures and low temperatures where most gases are near their liquefaction conditions, the attraction between molecules of the gas is much stronger than that between the molecules in the gas and those at the surface of the solid. The contrary is, however, true at very low pressures.²⁴

(II) ABSORPTION OF HYDROGEN BY PALLADIUM BLACK

Absorption Relations

Palladium, on being heated, allows hydrogen to pass through it quite freely. This observation was utilized in early forms of gas-filled X-ray tubes to soften tubes which became hard because of electrical clean-up. Further investigation has shown that the phenomenon is due to the absorption of hydrogen which then diffuses through the metal into the tube.

This absorption of hydrogen by palladium has been studied by a number of investigators. Hoitsema²⁵ found that at temperatures above 100 deg. C., the absorption law is

$$v = k \sqrt{p}$$

where v denotes the volume absorbed per unit weight and p is the pressure. This indicates that the hydrogen is occluded in the atomic condition. The absorption was measured at pressures ranging from 1 to 5000 mm. and at temperatures from 0 deg. to 250 deg. C. The results have therefore no bearing on the utility of palladium as an adsorbent at low pressures and low temperatures. It may be stated that both metal foil and palladium black (described later) were used in this investigation.

A. Sieverts²⁶ has also investigated the behavior of hydrogen and palladium (wire, foil and "black"), with a view to evolving a satisfactory theory of the phenomenon. He considers that the

²⁴ Although not bearing directly on the topic of this discussion, it is of interest to observe that the selective sorption of different gases by charcoal may be used for the purification of gases. Thus, where it is desirable to obtain pure helium, charcoal in liquid air may be used to adsorb impurities such as nitrogen, oxygen and even hydrogen. Similarly the latter gas may be freed of traces of nitrogen and oxygen. In this connection the following recent publications may be consulted:

(1) H. B. Lemon and K. Blodgett. Studies of the Absorption of Gases by Charcoal. *Phys. Rev.* 14, 394 (1920).

(2) R. E. Wilson. Note on the Adsorption of Nitrogen and Oxygen on Charcoal. *Phys. Rev.* 16, 8 (1920).

²⁵ *Zeits. physikal. Chem.* 17 (1895).

²⁶ *Zeits. physikal. Chem.* 88, 103 and 451 (1914). This paper contains numerous references to previous literature.

absorption is a true case of solution. The range of pressures used was from 1 to 760 mm. and the solubility determinations were carried up to temperatures as high as 820 deg. C. The solubility was found to vary with the nature of the sample used. At higher pressures, the relation

$$v = k\sqrt{p} + k_2p$$

was found to be more in accord with the data. This relation was obtained for all the samples.

A. Holt, E. C. Edgar and J. B. Firth²⁷ have concluded that palladium can exist in the form of both active and inactive modifications, as far as absorption is concerned, and the activity of any sample decreases with time. By heating (in hydrogen) the absorbing power can be revived. Furthermore, palladium shows phenomena of diffusion similar to those observed by McBain in the case of hydrogen and charcoal.

S. Valentiner has carried out a series of measurements on the absorption of hydrogen at relatively low pressures.²⁸ The results obtained were not very satisfactory. At the same equilibrium pressure it was found possible to absorb amounts of gas which differed for different samples. Apparently the absorbing power varies not only with the degree of fineness of the palladium black but also with its subsequent heat treatment during evacuation. Some of the data obtained by Valentiner are tabulated in Table XXIII. The remarkable increase in absorptive power at -190 deg. C. is quite evident, although the actual absorptions for the same equilibrium pressure vary widely. In the table, P gives the pressure in mm. of mercury, and V the volume at standard pressure and temperature per gm. of palladium black.

TABLE XXIII
ABSORPTION OF HYDROGEN BY PALLADIUM BLACK
(Valentiner)

TEMP. = 20° C.		TEMP. = 20° C.		TEMP. = 190° C.	
P	V	P	V	P	V
0.001	0.10	0.014	0.27	0.0005	2.05
0.005	0.26	0.031	0.33	0.0015	2.11
0.037	0.40	0.056	0.37	0.001	3.06
0.110	0.52	0.087	0.41	0.001	9.1
0.190	0.59	0.184	0.49	0.002	33.0
0.315	0.70	0.30	0.55	0.005	40.0
0.52	0.82	0.52	0.61	0.012	47.2
0.76	0.92	0.88	0.67	0.025	63.0

²⁷ Zeits. physikal. Chem. 82, 513 (1913).

²⁸ Verh. d. deutsch. physikal. Ges. 3, 1003 (1911).

Compared with the adsorption of hydrogen on charcoal (Claude's data, Table XVII), the absorption by palladium at liquid air temperature is observed to be much greater.

Preparation of Palladium Black

The method of preparation has been described by Hoitsemá. With slight variation this method has been used in this laboratory as follows: The palladium in the form of sheet or wire is dissolved in aqua regia, evaporated on a water bath till acid vapors have disappeared; the solution is then diluted, warmed, and concentrated solution of sodium carbonate added to neutralize free acid. A slight amount 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 breaker. 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 to a U-tube, where it is dried by blowing air over it and then evacuated on a rough pump. The U-tube ought to have side tubes through which gas can be passed and constrictions at which it can be sealed off later. After the rough evacuation (with slight warming of the U-tube), hydrogen is passed over the palladium black for some time, and while the gas is still passing through the tube the latter is sealed off at the constrictions. This leaves the palladium black in equilibrium with hydrogen and it can be kept active for a long time.

For use in exhaust work, the U-tube is opened and a sample transferred to a tube such as is used in the case of charcoal. It is well to cover the top of the palladium black with glass wool in order to prevent it from being drawn into the rest of the apparatus when vacuum is applied.

Experiments on the Use of Palladium Black in the Production of High Vacua

A number of experiments have been carried out in this laboratory by A. G. Huntley, Miss M. Daly and S. Dushman. While the behavior of palladium black was found to be extremely erratic, the results obtained showed that it is possible to obtain samples which possess very high absorbing power.

An ionization gauge with an appendix containing about 1 gm. of palladium black was well exhausted on a condensation pump and sealed off at a residual gas pressure of about 0.2 bar (the gas consisting probably of nitrogen and hydrogen). On

immersing the appendix in liquid air, the pressure decreased to 0.004 bar with the gauge filament lighted. On turning off the filament for some time, and then lighting it for an instant, the pressure was observed to have decreased still further to 0.0005 bar. Apparently, there is a continual slight evolution of gas from the walls of the gauge and filament leads even after the metal parts have been bombarded for a long time. In other experiments pressures as low as 0.0001 bar were obtained in a sealed off gauge with a palladium tube immersed in liquid air.

A number of experiments were carried out using palladium black for absorbing the residual gases in a small kenotron exhausted on an oil pump only. An ordinary lamp exhaust system was used giving an exhaust pressure of about 1 bar. A few *milligrams* of palladium black were placed in a kenotron (about 100 cm.³ volume) which contained a 6-volt 2.5-ampere tungsten filament and a cylindrical molybdenum anode about $\frac{1}{4}$ in. in diameter by $\frac{7}{8}$ in. in length. The tube was exhausted on the oil pump, with simultaneous heating in an oven for 30 minutes at 360 deg. C., and sealed off. The metal cylinder was then bombarded to a white heat by making the filament cathode. The gases evolved were absorbed rapidly by the palladium black, in spite of its being above room temperature, and finally the vacuum became so good that excellent space charge characteristics were obtained. Special experiments showed that in order to obtain this condition the pressure must be at least as low as 0.05 bar. Thus even with a few milligrams of palladium black at room temperature it was possible to clean up appreciable quantities of gas. Similar results were obtained time after time. In fact a large number of small kenotrons and pliotrons were exhausted in this manner with the regular exhaust system used in lamp factories, and without having to use a condensation pump or liquid air.

As subsequent investigation showed that the same results could be obtained with the very much cheaper activated charcoal, and furthermore, as some samples of palladium black absolutely failed for some undetermined reason to act as absorbent, this method was used for only a short time. The results, however, suggest interesting possibilities in the production of high vacua by means of palladium black and further investigation ought to be carried out with a view to determining definitely the conditions under which it can be made active. It has been recently shown by E. B. Maxted²⁹ that hydrogen sulphide inhibits the absorbing efficiency of palladium black. Similar

facts have been known for a long time in the case of various metallic catalysts, and probably the same causes influence the behavior of palladium black.

✓ III. SORPTION OF GASES BY GLASS, METALS AND OTHER SUBSTANCES

Sorption of Gases. General Remarks

From the standpoint of high vacuum technique, the phenomena included under the generic term "sorption" are of importance in indicating what methods may be applied to clean up the residual gases in sealed-off devices. The usual gases present in such cases are hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and water vapor. Inasmuch as the vessels to be exhausted ordinarily consist of glass and also have metal parts, it is furthermore of importance to consider the behavior of different kinds of glass and metals with respect to sorption and evolution of gas.

In the case of charcoal and palladium black, discussed previously, the initially evacuated adsorbent takes up a portion of the gas with which it is in contact and the distribution of gas between the adsorbent and the gas phase depends not only upon the temperature of the former but also upon the initial total amount of gas present. Furthermore, different gases are adsorbed to a widely different extent on the same adsorbent as has already been illustrated in the case of charcoal. A similar statement holds true for the adsorption of the same gas on different adsorbents. Table XXIV taken from Freundlich³⁰ gives a comparison between the behavior of wood charcoal, meerscham, and glass powder as adsorbents.

While the adsorption of gases on charcoal has been studied extensively because this substance is such a powerful adsorbent for most gases, especially at very low temperatures, many other substances have also been found to exhibit the same property. Meerscham, powdered glass, silica, alumina, glass wool, thoria, and other substances in a finely divided state have been used as adsorbents in special cases. The gel of silicic acid has been studied with respect to its adsorbing power for SO_2 ³¹ and also

²⁹ Journ. Chem. Soc. 115, 1050 (1919).

³⁰ Kapillarchemie, 1909, p. 97.

³¹ J. McGavack, Jr., and W. A. Patrick, J. Am. Chem. Soc. 42, 946 (1920). W. A. Patrick, Chem. and Met. Engr. 22, 949 (1920).

for N_2 and H_2 .³² Merton³³ has observed that finely divided copper, obtained by reducing a solution of a copper salt, adsorbs hydrocarbons, nitrogen, and hydrogen with great rapidity. The copper should be heated to a temperature not exceeding 250 deg. C. It gradually loses its adsorbing power with use, but Merton finds that it can be used to clean up the residual gas, after exhausting with an oil pump, to such a low pressure that the space becomes "non-conducting."

TABLE XXIV
ADSORPTION OF GASES ON DIFFERENT ADSORBENTS

Adsorbent	Gas	Vol. Adsorbed at 100 mm. Hg. and 0 deg. C.
Wood charcoal.....	CO_2	24.9 cm ³ /gm.
	NH_3	95.1
	SO_2	73.6
	CH_3Cl	57.7
Meerschaum.....	NH_3	84.5
	SO_2	24.3
	CH_3Cl	27.1
Glass powder.....	CO_2	1
	NH_3	9
	SO_2	6

In general, adsorbed gases are re-evolved on heating the adsorbent; that is, the reaction is reversible or practically so. The sorption of oxygen by charcoal and the metals platinum and palladium is, however, not of a similar nature. The behavior of charcoal in contact with oxygen has been studied by a number of investigators. When charcoal which has adsorbed oxygen is heated, only a portion of the gas is recovered as oxygen, the remainder is re-evolved as carbon monoxide and dioxide. The results of the most recent investigation of this subject, by H. H. Lowry and G. A. Hulett,³⁴ lead to the conclusion that while some of the oxygen is adsorbed on the surface of the charcoal and may be recovered by heating, the rest is held by the charcoal as a surface compound or compounds, which are stable at ordinary temperatures but which break down to CO and CO_2 at 200 deg. C. and above.

³² H. Briggs, loc. cit. He has also shown how the adsorption capacity of silica gel is affected by heat treatment.

³³ J. Chem. Soc., London, 105, 645 (1914).

³⁴ J. Am. Chem. Soc. 42, 1408 (1920). This paper gives a large number of references to previous literature on this subject.

Platinum black (prepared in a manner similar to that used for palladium black) can take up more than 800 times its volume of oxygen. This oxygen is removed with great difficulty, showing that the adsorption is not a reversible phenomenon. Here again, the conclusion has been drawn that PtO is formed on the surface.³⁵ It will be shown in a subsequent connection that in reality these adsorption phenomena are probably not essentially different from the ordinary reversible cases of adsorption.

Sorption of Gases by Metals

A survey of the results obtained by a large number of investigators shows that the sorption phenomena of gases by metals are of quite a complex nature.³⁶ Not only do we have cases of true adsorption, but also cases in which the gases are dissolved in the metals and behave in every way like solutions, and still other cases in which, undoubtedly, stable chemical compounds are formed either on the surface or throughout the body of the metal, and in some cases we do not yet understand the exact mechanism of the reaction. As will be pointed out in the discussion of theories of adsorption, we are dealing in such cases with phenomena which are in the "No-man's" land that exists between so-called physical and chemical reactions. It has therefore been considered best to discuss in this section all those cases in which there is an absorption of gases by solids. The behavior of hydrogen with respect to different metals illustrates all these cases very well and is of special interest from the point of view of vacuum investigations.

The sorption of hydrogen by palladium black has been discussed already. At low temperatures the evidence points to the conclusion that we are dealing with a case of adsorption or surface condensation. On the other hand, there is also very good proof that, at higher temperatures at least, hydrogen dissolves in palladium in the atomic condition. The same conclusions hold for hydrogen and platinum. The latter, in the condition of platinum black, is able to take up about 100 times its volume of gas.³⁷ As a clean-up agent for residual gas in vacuum devices, platinum black is less efficient than palladium black.

An investigation on the behavior of hydrogen towards platinum and iridium has been carried out by A. Gutbier and his associates.³⁸ The results show that the maximum of absorption

³⁵ Engler and Woehler, *Zeits. f. anorg. Chem.* **29**, 1 (1902). Mond, Ramsay, and Shields, *Zeits. f. physikal. Chem.* **25**, 657 (1898).

³⁶ For a general summary of the literature, see *Trans. Faraday Soc.* **14**, 173, 232 (1919).

³⁷ For literature see Bancroft, *Jour. Franklin Inst.*, **185**, 29 (1918).

³⁸ *Ber. d. deutsch. Chem. Ges.* **52B**, 1366-74 (1919).

by platinum black occurs at 0 deg. C., while in the case of iridium black the maximum occurs at 20 deg. C. While the former was observed to absorb as much as 160 volumes hydrogen, platinum sponge only absorbs 1 volume. The sorptive capacity of iridium was also observed to be much less than that of platinum.

The behavior of hydrogen in contact with tantalum is similar in certain respects to the foregoing phenomena. Pirani³⁹ has observed that this metal when heated in hydrogen can occlude about 740 times its volume of the gas. On subsequent heating in a vacuum about 550 volumes are given off, while the rest of the gas is removed only at the melting point of the metal. The occluded hydrogen makes a tantalum filament quite brittle and the electrical resistance is increased considerably.⁴⁰

TABLE XXV
WEIGHT OF H₂ IN mg. DISSOLVED BY 100 g. TANTALUM
AT 760 mm.

deg. C.	mg.	deg. C.	mg.
100	400	630	51.2
183	377	730	33.4
263	327	830	20.3
314	297	980	14.9
474	157	1030	11.9
530	107	1130	9.6
		1230	8.0

A more careful investigation of the sorption of hydrogen by tantalum was carried out by A. Sieverts and E. Bergner.⁴¹ They observed that the amount of gas taken up by the metal decreases with increase in temperature (as in the case of hydrogen and palladium), and that a wire heated to 1200 deg. C. in vacuo absorbs hydrogen slowly at temperatures above 500 deg. However, once the wire is saturated with gas at the higher temperatures, it absorbs very much more easily at lower temperatures. At ordinary pressures, the amount of gas taken up is given by the relation

$$v = k m \sqrt{p}$$

where m = weight of tantalum
 p = pressure of hydrogen.

Thus, as in the case of palladium, we must conclude that the hydrogen in the metal is in the atomic condition. The solubilities

³⁹ Zeits. f. Elektrochem., 11, 555 (1905).

⁴⁰ Similar effects of adsorbed gases on the resistance of carbon filaments have also been observed by K. Sickel, Z. f. Physik, 4, 288 (1921).

⁴¹ Ber. d. deutsch. Chem. Ges. 44, 2394 (1911).

for different temperatures are given in Table XXV. At very low pressures the solubility is less than that calculated by the foregoing relation.

The same investigators also observed that hydrogen is absorbed by tungsten to a very negligible extent.

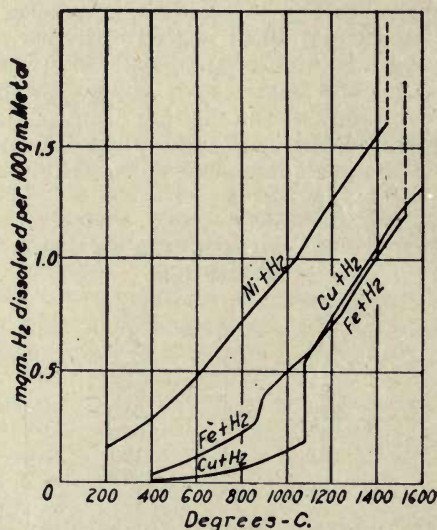


Fig. 61. Solubility of Hydrogen in Copper, Iron and Nickel

In the case of the metals, copper, iron, and nickel, the careful investigations of A. Sieverts and his associates⁴² have shown that the amount of hydrogen dissolved at any given temperature varies with the pressure according to the relation

$$V = k\sqrt{p}$$

which indicates that the hydrogen is present in solution in the atomic condition. Furthermore the amount of gas taken up depends only upon the mass of the metal and not its area (as distinguished from adsorption). Also the solubility *increases* with the temperature, whereas in all cases of adsorption the amount of gas taken up decreases with increase in temperature. Fig. 61 gives for comparison the solubilities of hydrogen in each of the above metals. It will be observed that nickel is capable

⁴² Zeits. f. physikal. Chem. 77, 591 (1911).

of dissolving appreciable amounts of the gas at higher temperatures. At the melting point, the solubility increases abruptly as shown by the vertical dotted lines on the curves for nickel and iron, and under these conditions the former is capable of dissolving twelve times its volume of hydrogen. If the metal saturated with gas at a higher temperature is cooled very rapidly, amounts are retained which are very much larger than those corresponding to equilibrium at the lower temperature. These observations are of great importance as a guide to the composition of the gases which may be evolved from metal parts used in vacuum apparatus.

The equilibrium between metal and gas is attained at a slower rate, the lower the temperature. Hence, it is necessary to heat metals in a vacuum to as high a temperature as they can stand in order to free them thoroughly of dissolved gases.

TABLE XXVI
DISSOCIATION PRESSURES IN mm. Hg OF POTASSIUM
AND SODIUM HYDRIDES

deg. C.	KH	NaH
290		5.01
300	7.3	8.02
320	17.62	18.62
340	39.8	41.98
360	85.9	90.66
380	177.0	181.97
400	592.74	354.8

The metals of the alkali and alkaline earth group combine chemically with hydrogen to form hydrides. Sodium absorbs hydrogen at temperatures above 300 deg. C. and forms the compound NaH. Similarly, metallic calcium combines rapidly with hydrogen at a dull red heat to form CaH₂.

The dissociation pressures of NaH and KH have been measured by F. G. Keyes.⁴³ Table XXVI gives a few of the data obtained at higher pressures. Extrapolating from these we obtain for the dissociation pressure of KH at lower temperatures the following values:

⁴³ J. Am. Chem. Soc. 34, 779 (1913).

deg. C.	press. in mm.
100	7.76×10^{-6}
27	6.84×10^{-10}

That is, potassium ought to clean up hydrogen to a residual equilibrium pressure of less than 10^{-6} bar. The dissociation pressure of CaH_2 and the other hydrides of the alkaline earth group have not been determined.

Similarly some of the rare earth elements, like lanthanum and cerium, absorb hydrogen very rapidly at a temperature of about 250 deg. C. While Moissan and others claim the existence of compounds like LaH_3 , other investigators believe that we have in these cases solid solutions of hydrogen in the metals. Smith⁴⁴ classifies the combinations between hydrogen and metals into three classes:

Compounds Class 1. Hydrogen acts as a base, e.g., H_3Sb , H_3As , etc.

Compounds Class 2. Hydrogen acts as an acid, e.g., CaH_2 , NaH , etc.

Class 3. Sorption compounds, e.g., palladium hydride, solutions of hydrogen in copper, etc.

With regard to a number of metals, the exact nature of the reaction with hydrogen seems very doubtful. Of the metals of the rare earth group, thorium, neodymium, praeosdymium, and samarium appear to absorb measurable quantities of hydrogen, and Smith assigns these to Class 3, while other investigators assume the actual formation of hydrides. Uranium absorbs hydrogen to a slight extent, while tungsten, molybdenum, and iridium absorb little or none at all.

The writer had occasion some time ago to try some experiments on the adsorption of hydrogen by films of tungsten and iron deposited in vacuo on glass. In neither case could any clean up of hydrogen be determined. On the other hand, Heald⁴⁵ has observed that films obtained by cathodic sputtering (with high voltage) of cadmium, silver, and steel showed marked sorption of hydrogen.

⁴⁴ For a general survey of the literature on the subject of hydrogen sorption by metals, reference may be made to the paper by Donald P. Smith, "The Occlusion of Hydrogen by the Metallic Elements and Its Relation to Magnetic Properties," *Journ. Physical Chem.*, 23, 186 (1919); J. H. Andrew (*Trans. Far. Soc.* 14, 232, 1919) has advanced the theory that the occlusion of hydrogen by Pd and Fe is due to the presence of an active, amorphous phase of the metal. A. Gutbier (*Ber.* 52 B, 1366—74, 1919) has investigated the behavior of hydrogen towards iridium and platinum. Iridium absorbs hydrogen only slightly. Platinum black has the maximum absorptive power at 0 deg. C, corresponding to 160 volumes of H_2 .

⁴⁵ *Phys. Rev.* 24, 269 (1907).

On the whole, it can be stated in the light of the present information that while a number of metals take up hydrogen to a larger or smaller extent, palladium and platinum black are the only metals which are known with certainty to clean up sufficient gas to make them of value in vacuum work.

Still less is known of the behavior of other gases with respect to metals. We know that some metals, like those of the alkali and alkaline earth group, also thorium, form nitrides on heating them in contact with nitrogen, but there are very few published data on which to base any conclusion as to whether such reactions can be used in cleaning up nitrogen gas in vacuum work.

An interesting method for removing residual gases based on the reaction between these gases and thorium (or zirconium) at higher temperatures has been suggested by W. D. Coolidge.⁴⁶ "The use of the metals calcium, magnesium, sodium, and potassium," he states, "has been suggested for the chemical removal of (residual) gases. However, the high vapor pressure of these metals offers a serious drawback to their use for all purposes and particularly for certain types of electrical apparatus, having a very high vacuum. On the other hand, the metals of the rare earth group, having a low vapor pressure, particularly thorium and zirconium, are peculiarly well suited for the removal of gases capable of chemical combination, such as oxygen, nitrogen, hydrogen, water vapor, the oxides of carbon, and the like. These metals form by combination with these gases chemically stable compounds of low vapor pressure."

Coolidge uses the metal in the form of a very fine powder. After having first exhausted the tube or bulb in the usual manner (and after all metal parts have been heated to a high temperature) dry air or nitrogen is admitted and powder introduced from a side tube. The bulb is then re-evacuated, sealed off the pump, and the glass heated at the point where the powder is situated. "The metal will be observed to glow as a reaction takes place and the result is a vacuum so high that no gas ionization effects can be observed when an electron current is transmitted" (as in a hot cathode device).

In a similar manner, H. Huthsteiner and the author have observed that a clean copper filament treated in oxygen at low pressure will clean up the gas very rapidly and in large amounts. Apparently the oxygen is able to diffuse into the metal and thus converts it gradually into Cu_2O . On the other hand, some recent experiments by C. A. Kidner and the author have shown that

⁴⁶ Patent No. 1, 323, 386, Dec. 2, 1919.

a freshly formed calcium film obtained by volatilizing the metal in vacuo does not absorb either oxygen or hydrogen, reactions which one would naturally assume ought to occur very rapidly.

The investigations of Langmuir on the clean up of gases by volatilizing tungsten and molybdenum filaments and of Soddy on the clean up of gases by volatilizing calcium (barium, or strontium) have yielded important results. In view, however, of the radically different nature of the reactions studied, the discussion of these must be deferred to the following chapter.

Adsorption of Water Vapor

The problem of completely removing absorbed or dissolved water vapor from the walls of glass vessels is one of the most important in vacuum work. The sorption of water vapor by glass surfaces has therefore been studied by a large number of investigators. Closely allied with this is the problem as to the amounts of water vapor and other gases which are evolved from glass vessels under definite temperature conditions.

In one of the first investigations on this subject,⁴⁷ Bunsen observed that even at very high temperatures (500 deg. C.) silicates (chemically analogous to glass) retain appreciable amounts of water vapor. The total amount of water liberated from 2.11 sq. meters of glass surface which had previously been dried thoroughly at 20 deg. C. was 22.3 mgm. "Warburg and Ihmori⁴⁸ found that measurable amounts of water vapor were condensed upon the surface of freshly blown glass bulbs and of bulbs which had not been thoroughly washed. After washing or boiling these glass surfaces and then thoroughly drying, no adsorption of water vapor could be detected."⁴⁹ L. J. Briggs measured the sorption of water vapor by quartz powder. Fifty grams were used having a superficial area of 2.0 sq. meters. The amounts taken up at different pressures of water vapor at 30 deg. C., were as follows:

VAPOR		WATER ADSORBED*	
Press. mm. Hg.		mgm.	
26.1		9.0	
19.6		4.6	
0.2		0.5	
10.7		2.9	
31.4		26.7	

* Average of two or more experiments.

⁴⁷ Wied. Ann. 20, 545 (1883); 24, 321 (1885).

⁴⁸ Wied. Ann. 27, 481 (1886); 31, 1006 (1887).

⁴⁹ Quoted from the paper by L. J. Briggs, Journ. Physical Chem. 9, 617 (1905), on the "Adsorption of Water Vapor by Quartz."

The last two values were obtained with samples which had previously been dried to constant weight at 110 deg. C.

The sorption of water vapor by charcoal has also been investigated by H. H. Lowry and G. A. Hulett.⁵⁰ At a pressure of 23.4 mm. and 29.9 deg. C., as much as 783.1 mgm. of water were taken up per gm. of charcoal (estimated area of surface, 300 sq. meters), corresponding to 2.6 mgm. per sq. meter. They conclude that "water vapor is not adsorbed, but is held by capillary action."

The sorption of water vapor by pulverized synthetic quartz and anorthite has been studied by J. R. Katz.⁵¹ "The amount of water taken up reaches a fairly definite limit when the vapor pressure of the water is about 0.7 of the saturated vapor. The quantities of water adsorbed per sq. cm. of surface under these conditions were 1.3×10^{-6} gm. for quartz and 6.2×10^{-6} gm. for anorthite. These correspond to layers of water 13 and 204 molecules deep, respectively."

The result obtained by Briggs for the amount taken up by quartz at 31.4 mm. pressure corresponds to a film 2.66×10^{-6} cm. thick or about 50 molecules deep.

Similar results have been obtained, as will be mentioned below, by Langmuir in studying the gases evolved from glass bulbs. There is no doubt, however, that in all those cases, where apparently the layer of adsorbed gas is more than one or two molecules in thickness, we are not dealing with a true adsorption phenomenon. According to Langmuir, the sorption by glass is to be regarded as a process of solution of the water in the glass, in much the same manner as we know is the case in the absorption of moisture by sodium silicate and gels. It is also quite possible that in the case of powders the moisture may be actually condensed as a liquid in fine capillary spaces between the grains. Bancroft⁵² mentions a number of cases in which very fine powders apparently have appreciable films of air or other gases surrounding each small particle. Thus a liter of carbon black may contain 2.5 liters of air, and it has been observed that "a rock powder which would pass through a 200-mesh sieve surged like a liquid."

The presence of such relatively large amounts of water vapor on glass surfaces and even metal surfaces (as observed by Ihmori) means, however, that in experimenting at very low

⁵⁰ J. Am. Chem. Soc. 42, 1402 (1920).

⁵¹ Proc. Amsterdam Acad. 15, 445 (1912). The abstract is quoted from Langmuir's paper. J. Am. Chem. Soc. 33, 2283 (1916).

⁵² Journ. Franklin Inst. 185, 29 (1918).

pressures special care must be taken to remove the water vapor by heating all parts to high temperatures with simultaneous absorption of the vapor in a liquid air trap or P_2O_5 tube.

Gases and Vapors Evolved from Glass and Metals at Very Low Pressures

While the study of sorption phenomena is of interest from the point of view of clean-up methods, the problem as to the nature and amounts of residual gases evolved in vacuum devices from the glass walls and metal parts is also of extreme importance in vacuum technique.

The evolution of gas from the walls of bulbs such as are used for incandescent lamps has been investigated by I. Langmuir.⁵³ "On heating bulbs of 40-watt lamps for three hours to a temperature of 200 deg. C., after having dried out the bulbs at room temperature for 24 hours by exposure in a good vacuum to a tube immersed in liquid air, the following average quantities of gas were given off:

200 cu. mm. water vapor
5 cu. mm. carbon dioxide
2 cu. mm. nitrogen.

"These are the quantities of gas, liberated by the heating, expressed in cubic millimeters at room temperature and atmospheric pressure.

"By raising the temperature of the bulbs from 200 deg. to 350 deg. C. an additional quantity of water vapor was obtained, so that the total now became

300 cu. mm. water vapor
20 cu. mm. carbon dioxide
4 cu. mm. nitrogen.

"A subsequent heating of the bulbs to 500 deg. C. caused the total amount of gas evolved to increase to

450 cu. mm. water vapor
30 cu. mm. carbon dioxide
5 cu. mm. nitrogen.

"At each temperature the gas stopped coming off the glass after a half hour of heating, only to begin again whenever the temperature was raised to a higher value than that to which the bulb had been previously heated.

"It therefore seems that even by heating the bulb to 500 deg., not all of the water vapor can be removed, but it does seem probable that after this treatment the amount of water vapor that can come off a bulb at ordinary temperatures must be extremely small.

⁵³ Trans. Am. Inst. Elec. Eng. 32, 1921 (1913), and J. Am. Chem. Soc. 38, 2283 (1916).

"The internal surface of this bulb was about 200 sq. cm. The number of molecules of gas given off per sq. cm. was thus 56×10^{15} molecules of H_2O ; 37×10^{15} molecules of CO_2 , and 0.6×10^{15} molecules of N_2 . If we calculate the number of molecules of each of the gases necessary to cover a sq. cm. one molecule deep (taking the molecules to be cubical in shape) we find 1.0×10^{15} for H_2O ; 0.77×10^{15} for CO_2 , and 0.67×10^{15} for N_2 . Thus the quantities of gas obtained from this bulb correspond to: a layer of water 55 molecules deep, a layer of carbon dioxide 4.8 molecules deep and a layer of nitrogen 0.9 molecules deep."

On the other hand, Langmuir has observed⁵⁴ that glass surfaces previously heated to the softening point and then heated in vacuo gave off only 0.18 cu. mm. of water vapor (4.5×10^{15} molecules); 0.032 cu. mm. of carbon dioxide (0.81×10^{15} molecules); and 0.025 cu. mm. of nitrogen (0.63×10^{15} molecules). "These amounts correspond to the following number of layers of molecules: 4.5 for water vapor, 1.05 for carbon dioxide, and 0.9 for nitrogen. It should be noted that the amounts of carbon dioxide and nitrogen correspond to unimolecular layers of these gases."

Some very interesting experiments on determining the optimum conditions for evolution of water vapor from glass were carried out some time ago by Langmuir. It was observed that certain lamps made of sodium magnesium borosilicate glass (G-702-P) and consisting of high wattage filaments in very small bulbs blackened very rapidly if they were baked out at 550-600 deg. C. during exhaust, while lamps baked out at 400-500 deg. C. did not blacken so rapidly. The effect was ascribed to water vapor evolved from the glass during the life of the lamp and experiments were therefore undertaken to try to remedy this condition.

The following description of the experiments is taken from Langmuir's patent specifications.⁵⁵

"Three lots of lamps were made with the same structural details and operating characteristics; the first lot was exhausted at approximately 450 deg. C., the second lot at 550 deg. C., and the third lot at 550 deg. C., at first and then at 400 deg. C. The average life of the first lot was approximately 575 hours, of the second lot 300 hours, and of the third lot over 900 hours, the conditions of operation with all three lots being the same."

The explanation given of this result is as follows: "Apparently the treatment at 400 to 500 deg. C. liberates the water

⁵⁴ J. Am. Chem. Soc. 40, 1387 (1918).

⁵⁵ Patent No. 1, 273, 629, July 23, 1918.

vapor only from a comparatively thin surface layer of the glass. If, however, the exhaust is continued at 400 to 500 deg. C., no more water vapor will be drawn out of the deeper layers, and that which remains in the surface layer will be liberated."

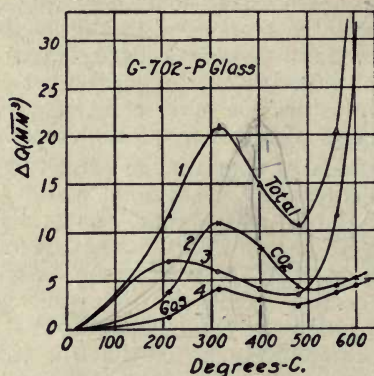


Fig. 62. Evolution of Gas from Corning G-702-P Glass

The main conclusion arrived at by Langmuir is that in order to remove water vapor efficiently from the walls of glass vessels, the heating during exhaust should be carried out in two or more stages of gradually decreasing temperatures. He finds that one half-hour treatment at each of the above temperature ranges is

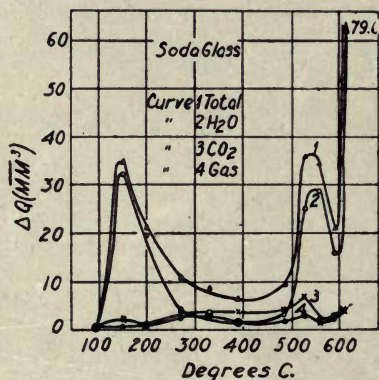


Fig. 63. Evolution of Gas from Soda Glass

sufficient, and makes the interesting observation, which is in accord with that made by Sherwood (see below), that while the gas evolution at temperatures below 500 deg. C. practically ceases at the end of one half hour, the evolution of water vapor at higher temperatures continues indefinitely no matter how long the heating period. Apparently the glass actually suffers a chemical decomposition at higher temperatures.

An extensive series of investigations on the gases and vapors evolved from glass has been carried out at the Westinghouse Research Laboratory by R. G. Sherwood⁵⁶ and J. E. Shrader.⁵⁷

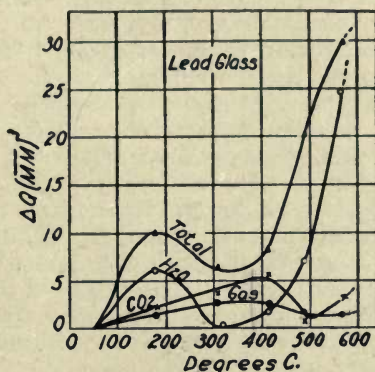


Fig. 64. Evolution of Gas from Ordinary Lead Glass

Sherwood measured the amounts of water vapor, carbon dioxide, and gases non-condensable in liquid air, liberated from different kinds of glass at various temperatures. Fig. 62 shows the results obtained with Corning G-702-P glass. This is a high melting-point glass which is used extensively in the manufacture of the gas-filled type of incandescent lamp. The samples of glass used in these measurements had a total area of about 350 sq. cm., and the curves show the amounts of gas liberated at different temperatures. The period of heating at each temperature was three hours. Figs. 63 and 64 show similar data with samples of soda glass, and lead glass respectively. It will be observed that in all cases the gas evolution first reaches a maximum which is at about 300 deg. C. for G-702-P, 150 deg. C. for soda glass, and

⁵⁶ J. Am. Chem. Soc. 40, 1645 (1918).

Phys. Rev. 12, 448 (1918).

⁵⁷ Phys. Rev. 13, 434 (1919).

See also abstract of a paper by Ulrey, Phys. Rev. 14, 160 (1919), which discusses the same subject.

200 deg. C. for lead glass, then decreases, and again rises rapidly at a temperature which is above the softening point of the glass. Sherwood concludes that the products removed below 300 deg. C. are adsorbed gases, while at higher temperatures there is an actual decomposition of the glass itself. In other experiments, it was observed that at the higher temperatures the gas evolution continued even after the samples were heated for 24 hours and longer. By previously annealing the glass at very high temperatures, the subsequent gas evolution in vacuo was decreased considerably, a result which is in accord with certain observations made by Langmuir and mentioned before. Similar results have been obtained in this laboratory by Mrs. M. Andrews and J. Pangburn in investigating the gases evolved from lamp bulbs. Analysing Sherwood's data, we find that, for instance, in the case of soda glass, the total gas evolved up to 200 deg. C. was about 50 cu. mm., or about 0.15 cu. mm. per cm^2 , most of which was H_2O ; this would correspond to a layer of gas about four molecules deep. Sherwood concludes that the gases which are removed fairly rapidly at lower temperature are genuine adsorption products, as they correspond to quantities which are represented by a layer of gas which does not exceed one or two molecules in thickness. As the temperature of the glass is raised to the softening point, the gas evolved consists practically wholly of H_2O and undoubtedly this arises, as mentioned above, from the chemical decomposition of the glass.

Investigations by C. A. Kidner and H. A. Huthsteiner in this laboratory, on the rate of evolution of water-vapor and non-condensable gases from glass bulbs have shown that at the highest temperatures at which the exhausted bulb can be heated most of the adsorbed gas is evolved in the first two or three minutes. Preheating in dry air is also beneficial in removing most of this adsorbed gas. The pre-heating at ordinary pressure possesses the advantage that the glass can be heated to much higher temperatures, as there is no danger of the bulb's sucking inward.

Some interesting measurements were carried out by Sherwood on the adsorption of water vapor and other gases by dry surfaces of glass. Dry air could be removed very rapidly at ordinary temperature, while in the case of either moist air or air mixed with CO_2 , the rate of leakage at ordinary temperature was very slow. However, on heating to a high temperature practically all this adsorbed gas could be removed in a few minutes. It is interesting to observe that in one experiment, after a pressure of about 10^{-4} mm. H_2O had been reached by exhausting, the bulb (of about 9000 cm^3 capacity) was sealed off and after

standing ten hours the pressure rose to 0.0095 mm. owing to the gas leakage from the walls, but did not materially increase subsequently. This gas could not be condensed in liquid air, thus showing that it was adsorbed air. The writer's experience has shown that invariably there is a slight increase in pressure after sealing off the pump. Part of this increase is due to gases adsorbed on the glass near the constriction which is heated to a high

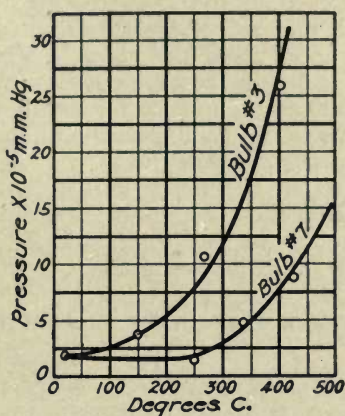


Fig. 65. Increase in Pressure in Sealed Bulb After Re-heating

temperature during sealing off, and a portion is due to gradual leakage from the walls. Even with the utmost precaution in baking out at high temperature and low exhaust pressure, there is always a slight increase in pressure in the sealed-off device.

In an investigation on the minimum pressure attainable with a Gaede rotary pump, S. Dushman observed⁵⁸ that unless care was taken to heat up the tubing connecting the gauge to the pump it was impossible to get below about 0.033 bars, because of the slow evolution of water vapor at ordinary temperature. When, however, the tubing was baked out at 330 deg. C., the pressure could be reduced to 0.0007 bars. Similar results have been reported by Shrader. The volume of the system exhausted in his experiments was about 2 liters. The effect of heat treatment on the vacuum obtainable after pumping until equilibrium

⁵⁸ Phys. Rev. 5, 212 (1915).

was reached at that temperature is shown by the following results:

Temperature	100	200	300	500
20				
Press. in mm.				
1×10^{-5}	1.9×10^{-6}	1.7×10^{-7}	1.2×10^{-7}	2.4×10^{-8}

Shrader also observed that not only does the vacuum in sealed vessels gradually deteriorate with time, at first rapidly and then more slowly, but also that "subsequent heating even at temperatures lower than the heat-treating temperature (on the pump) results in increase of pressure due to further liberation of gases and vapors from the glass." Fig. 65 shows the effect of heating a sealed-off system consisting of a 1500 cm.³ bulb and gauge of 500 cm.³ capacity for one hour at increasing successive temperatures. In each case the bulbs had previously been heated at 500 deg. C. on the pump.

E. W. Washburn, F. F. Footitt and E. N. Bunting⁵⁹ have published some data on the amounts of different gases obtained from glass when molten in vacuo. Table XXVII shows the results obtained with four different glasses:

TABLE XXVII
AMOUNT OF DISSOLVED GASES IN FINISHED GLASS

Glass	WEIGHT PER CENT				VOLUME IN CM ³ PER 100 GM. AT NORMAL TEMP. AND PRESS.			
	O ₂	CO ₂	N ₂	Total	O ₂	CO ₂	N ₂	Total
Barium flint 1	0.035	0.011		0.046	24.5	8.8		33.3
Barium flint 2015	.0045		.020	10.5	3.6		14.1
Light flint0045	.014	0.0025	.21	3.2	11.2	2.0	16.4
Borosilicate0036	.0035	.0031	.010	2.5	2.8	2.5	7.8
Water at 0 deg. Cent.	5.15	179.2	2.24

The last four columns give the volumes in cm.³ at 0 deg. C. and 760 mm. pressure, per 100 gm. glass. The solubilities in water at 0 deg. C. are given for comparison at the bottom of the table. It is evident that the amounts of gases dissolved in molten glass are considerable. Compared with the volumes of gases actually evolved from glass vessels in high vacuum exhaust, even at the highest temperatures practicable, the volumes observed for molten glass are much larger. This probably accounts to some extent for the observed increases in pressure in sealed-off glass vessels.

⁵⁹ Univ. of Illinois Bulletin No. 118. Dissolved Gases in Glass, Dec., 1920.

With regard to gases evolved from metals heated in vacuo, the prevailing opinion has been that very large quantities are evolved. It has been shown, however, by Langmuir⁶⁰ that when care is taken to remove water vapor and carbon dioxide from the glass walls, the amount of gas actually liberated from a tungsten filament is not more than three to ten times the volume of the wire. Most of the gas is eliminated by heating the wire to 1500 deg. C. It consists of about 70 to 80 per cent CO, the remainder being mostly H₂ and CO₂. "The total amount of gas evolved from the filament of a 40-watt lamp, if liberated in the lamp after sealing off, would produce a pressure of from 0.006 to 0.02 mm." Langmuir has also observed that the total volume of hydrogen and carbon monoxide obtained from a platinum wire heated to 350 deg. C. is only about one-tenth of the volume of the platinum.

The following data on the amounts and composition of gases evolved from different metals heated in vacuo were obtained by Mr. S. P. Sweetser of this laboratory. The experimental method used was that developed by Langmuir for the above mentioned measurements on tungsten and platinum. The metal in the form of a filament about 0.05 to 0.06 cm. diameter and 15 cm. long was heated to a bright red heat, and the heating continued until the rate of evolution of gas had decreased to a very low value.

Different samples of "untreated" nickel wire gave off amounts of gas varying from 5 to 15 cu. mm. of gas, consisting of about 75 to 90 per cent CO, and 20 to 10 per cent CO₂, with small amounts of H₂.

Similarly wires of monel metal, copper, and copper coated nickel-iron wire ("dumet" wire used in making lead-in-wires in lime-glass and lead-glass incandescent lamp bulbs) gave amounts of gas varying from 3 to 20 cu. mm. of gas. The composition of the gas was approximately the same as that evolved from the nickel wires.

An investigation of the composition of the gas evolved from the copper anodes used in the radiator-type of Coolidge X-ray tube gave the following average results:

CO ₂	7 per cent
CO.....	92 per cent
N ₂ +H ₂	1 per cent

It will be observed that in the experiments with wires, the total volume of metal used was about 0.03 cm.³ or 30 cu. mm., and only in exceptional cases did the volume of gas evolved on heating the metal exceed the volume of the filament.

⁶⁰ Trans. Am. Inst. Elect. Eng. 32, 1921 (1913). See also Journ. Am. Chem. Soc. 35, 105 (1912) for method of analysis.

Lead-in wires and supports which cannot be heated by passing current through them or by electronic bombardment (in the case of hot cathode devices) gradually evolve gases which cause progressive deterioration of the vacuum in sealed-off vessels, so that it is necessary in such cases either to give all the metal parts that can be heated during the exhaust a much more severe heating than they will be subjected to subsequently, and thus heat the other parts by radiation or else to provide some substance which will clean up residual gases during life.

From the above data it is evident that the gases gradually evolved from imperfectly evacuated metal parts must cause fairly appreciable changes in pressure in sealed-off vessels. Thus, let us consider a 3000 cm.³ (7-inch diameter) bulb exhausted to a pressure of 0.01 bar. If this bulb contains a metal filament of the size used in the above determinations (a not unusual case), which has not been heated on the pump, the amount of gas evolved on subsequent heating, assuming it to be 10 cu. mm., will increase the pressure in the bulb to about 3.4 bars. Such a pressure would absolutely ruin the device for any electron emission phenomena, and in order to keep the pressure below 0.1 bar, the residual gas in the filament would have to be less than 0.3 cu. mm.; that is, over 97 per cent of the total gas contained in the filament would have to be eliminated on the pump.

A modification of Langmuir's method of analysis of small quantities of gas has also been described more recently in detail by H. M. Ryder.⁶¹ The latter has determined by this method the composition of the gases eliminated from untreated commercial copper heated in vacuo.⁶² The gases evolved, in order of decreasing amounts, were CO₂, CO, H₂O and N₂. The total volume from a sample weighing 5 gm. and having a volume of 1.31 cm.³ was over 200 cu. mm. On heating to 750 deg. C. and higher, large amounts of O₂ were evolved, probably due to decomposition of Cu₂O contained in the copper. Here also, the volume of gas evolved was much less than that of the metal.

⁶¹ J. Am. Chem. Soc. 40, 1656 (1918). N. R. Campbell (Proc. Phys. Soc. 33, 287, 1921) has developed a method for the micro-analysis of gases which is based on the differences in condensation temperature of the various gases, and in which use is made of a Pirani-Hale gauge.

⁶² J. Franklin Inst. 187, 508 (1919).

CHAPTER V

CHEMICAL AND ELECTROCHEMICAL CLEAN-UP OF GASES AT LOW PRESSURES

CHEMICAL METHODS FOR THE CLEAN-UP OF RESIDUAL GASES

As has been mentioned in the previous chapter, it is often extremely difficult to draw any distinct line of demarkation between so-called purely physical and purely chemical reactions when dealing with clean-up processes at low pressures. In the general discussion of sorption phenomena it has been necessary to refer to reactions which are undoubtedly chemical inasmuch as definite compounds are formed. Thus, when hydrogen is taken up by the alkali metals, we have every evidence that a chemical compound, a hydride, is formed. On the other hand, it is still a debatable question as to whether a hydride is formed in the reaction between hydrogen and palladium.

In this chapter we shall discuss a type of clean-up reaction in which the gas disappears because of a reaction with a heated solid. The resulting compounds are volatile at the temperature of the reaction and condense on colder parts of the system, thus making it possible for the clean-up to continue as long as residual gas is present. On the other hand, since the rate of clean-up decreases ordinarily with the pressure, a point is reached at which the rate of disappearance of gas is equal to the rate of evolution from walls and other parts of the system.

Clean-up of Gases by Calcium

The use of this method for the production of high vacua was first proposed by F. Soddy.¹ He found that in a gas at reasonably low pressure, the heating of calcium to a temperature at which it begins to volatilize would cause the pressure to decrease rapidly to a point at which the gas is "non-conducting." For heating the calcium, Soddy recommends either a small quartz-tube furnace wound with platinum wire, or an inductive method of heating (analogous to that used in the most recent types of high-frequency furnaces devised by Northrup). No data are given by Soddy as to the degree of vacuum actually attained or to the rate of clean-up. As an indicator of the degree of vacuum, he used a spectrum tube and described his results as follows:

¹ Proc. Roy. Soc. London, 78, 429 (1907).

"If the apparatus (consisting of a large vessel in which is contained the quartz-tube furnace), charged with a small piece of calcium, and furnished with a Plücker spectrum tube, is exhausted by a Fleuss pump and the furnace heated, gases consisting of compounds of hydrogen, carbon, and oxygen are given out by the calcium. If the connection with the pump is then shut off and the heating continued, absorption of the remaining gases accompanied by volatilization of the calcium takes place, and the vacuum rises almost instantly to a point at which no discharge can be passed through the spectrum tube. By a non-conducting vacuum is to be understood one of greater resistance than an alternative spark-gap in air of 2 to 3 cm."

Soddy observes that CO , CO_2 , H_2O , C_2N_2 , SO_2 , NH_3 , and oxides of nitrogen are all readily cleaned up. In the case of hydrogen the absorption is not so great. "There is no doubt," he states, "that a low initial pressure, not exceeding a few millimeters of mercury, is as essential a condition in causing calcium to combine with gases as a high temperature. For rapid and continuous absorption, volatilization is essential. The film of volatilized metal continues, even in the cold, to absorb, although more slowly than the vapor itself."

Argon, helium and the other rare gases are, of course, not cleaned up by calcium, so that this method has proved useful for the purification of the rare gases. J. H. Clough,² of this laboratory, found that for this purpose the best results are obtained by means of a discharge tube containing a solid calcium anode and robust tungsten filament as cathode. The two electrodes are placed fairly close to each other, and on lighting the filament it is possible to start an arc in the rare gases at very low voltages. Under the action of the arc, the calcium at the anode is gradually volatilized and the chemically active gases are absorbed.

Clough also observed that titanium and magnesium are very effective as clean-up metals when used in the above manner. There is some evidence according to G. M. J. Mackay³ that the reaction here is not altogether a straight chemical one. "Apparently the arc activates the gaseous impurities so that they combine more readily with the chemical agents (calcium, etc.), in the bulb."

In order to obtain some data on the practical value of the calcium reaction in cleaning up residual gases, C. A. Kidner and S. Dushman carried out some experiments with hydrogen. This

² Patent Specification No. 1,246,054 (1917).

³ Patent Specification No. 1,208,597 (1917).

gas was chosen because it is the most difficult to clean up, and also because it is the most frequent constituent of residual gases present in high vacuum devices.

Calcium in the form of wire was laid inside a tungsten spiral, so that it could be heated by passing current through the latter. By varying the filament current, the rate of volatilization could be varied and the rate of clean-up measured under different conditions. The pressure was measured by a McLeod gauge, and the volume of the system containing hydrogen was 2500 cm³. In one experiment, the pressure was decreased from 250 to 4 bars (approximately) in almost 30 minutes. At the end of this interval the calcium had been practically all volatilized and covered the sides of the bulb. It was observed that the rate of clean-up increases with the temperature of the calcium and is apparently proportional to the pressure of hydrogen.

Similar experiments were tried with magnesium, but no noticeable clean-up was observed. Soddy found that strontium and barium act similarly to calcium, but as the latter can now be obtained commercially in very pure form it is much more convenient for use. Soddy also observed that the presence of CaH₂ in the calcium makes the metal much more difficult to volatilize.

• Measurements by Kidner at higher pressures (10 to 100 bars) showed that the calcium deposit on the glass does not adsorb either hydrogen or oxygen to any marked extent. Even active hydrogen (formed by heating a tungsten filament to a high temperature in the hydrogen) is only slightly adsorbed by the cold calcium deposit. On the other hand, in some earlier experiments in which an ionization gauge was used, it was observed that with a low initial pressure of hydrogen the calcium deposit does clean-up the gas gradually. Thus, in one case, the pressure in a sealed off system of about 500 cm³ capacity decreased from 2 to 0.7 bars during the volatilization of the calcium (which occurred in a few minutes), and subsequently the deposit continued to adsorb gas until at the end of two hours the pressure had decreased to about 0.0007 bars.

These observations, along with Soddy's results, lead to the conclusion that, in order to clean-up large amounts of gas with calcium, it is necessary to heat the metal to a high enough temperature to cause fairly rapid volatilization. On the other hand, with calcium volatilized in a low pressure of gas so that the deposited metal is presumably not saturated with gas, the cold deposit gradually adsorbs the small amount of residual gas and it is thus possible to obtain a fairly low pressure. In using

calcium to clean-up small traces of residual gas, it is naturally advisable to heat the metal for a short interval of time while the system is still connected to the exhaust pump, to get rid of occluded gases.

Clean-up of Residual Gases by Incandescent Tungsten Filaments

In a series of investigations on the reactions between different gases and heated tungsten filaments, I. Langmuir observed that under certain conditions a chemical clean-up of the gas occurs.⁴ The principal gases studied were oxygen, nitrogen, hydrogen, carbon monoxide and dioxide, chlorine, bromine and iodine, methane, cyanogen, hydrochloric acid, argon, phosphine, and the vapors of many substances, such as mercury, phosphorus pentoxide, sulphur, etc. While the discussion of the theoretical aspects of these investigations must be reserved for a subsequent section, we shall mention briefly, in the present connection, the conditions under which the best clean-up results can be obtained with different gases.

(1) *Clean-up of Oxygen by a Tungsten Filament*⁵

At temperatures above 1200 deg. K., and at pressures below about 100 bars, the oxide WO_3 "distills off as fast as it is formed, leaving the surface clean and bright." The rate of decrease of pressure (at constant filament temperature) is proportional to the pressure at any instant, that is, the reaction is of the first order. If p_0 denotes the original pressure, the pressure p at any interval of time t , after the beginning of the experiment, is given by the relation,

$$-V \frac{dp}{dt} = k \cdot pA$$

or

$$p = p_0 e^{-kt A/V} \quad (52)$$

where k is a *constant* whose value depends on the temperature of the filament, V denotes the volume of the system, and A the area of the filament. Furthermore as k increases exponentially with the temperature, it follows that to obtain a rapid clean-up the temperature of the filament should be made as high as practicable (ordinarily about 2500 to 2700 deg. K.).

In a typical experiment in which the volume of the system used was 1075 cm³, and the initial pressure 9.41 bars (7.06×10^{-3} mm. of mercury), a tungsten filament 5.4 cm. long and 0.0394

⁴ Dr. Langmuir has reviewed the results of these investigations up to 1915 in a paper on "Chemical Reactions at Low Pressures," *J. Am. Chem. Soc.* 37, (1915); also see *J. Industrial and Eng. Chem.*, 1, 348 (1915).

⁵ *J. Am. Chem. Soc.* 35, 105 (1913).

mm. diameter was heated to 1470 deg. K., and it was observed that the pressure decreased to one per cent of its initial value in 23.5 minutes. The initial amount of oxygen, measured at 298 deg. K. and atmospheric pressure was 10 cubic mm. Fig. 66 shows the quantity of oxygen present at any instant plotted

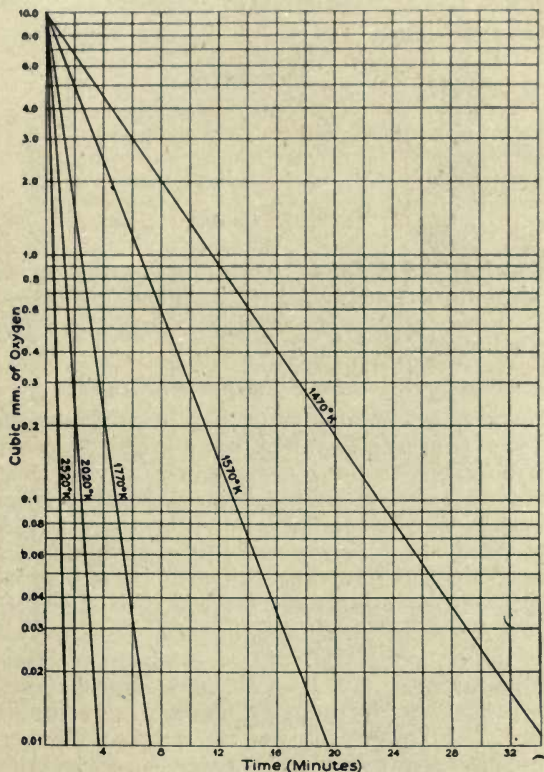


Fig. 66. Rate of Disappearance of Oxygen in Presence of Incandescent Tungsten Filament at Different Temperatures

(on semi-logarithmic paper) as ordinate against the time in minutes. From the form of equation (52) it is evident that, for equal intervals of time, the pressure must decrease in the same ratio, so that plotted on semi-logarithmic paper the resulting graph is a straight line. From this curve and the measurements on the variation in k with temperature, the graphs for a number

of other temperatures have been calculated and drawn in. The table which follows gives the value of the interval of time that would be required to reduce the total quantity of oxygen to 0.1 per cent of its original value if the tungsten filament described were heated to different temperatures.

T (degrees absolute)	t (minutes)
1470	34.5
1570	19.5
1770	7.2
2020	3.7
2290	1.93
2520	1.52
2770	1.22

At pressures below about 0.001 bar there is evidence that oxygen does not perceptibly attack a tungsten filament, so that this would appear to be about the lower limit of pressure attainable with this method.

(2) *Clean-up of Nitrogen by a Tungsten Filament*⁶

At pressures below about 100 bars, the rate of clean-up of nitrogen by a tungsten filament maintained at constant temperature is observed to be *constant* down to pressures as low as about two or three bars. It has been shown by Langmuir that the clean-up is due to combination between tungsten atoms evaporated from the filament and nitrogen molecules to form WN_2 . Hence, in the foregoing range of pressures, the rate of clean-up is governed exclusively by the rate of evaporation of tungsten and increases with the latter. Fig. 67, taken from Langmuir's paper, gives the rate of clean-up in cubic mm. of nitrogen (measured at 298 deg. K. and atmospheric pressure) per minute per sq. cm. of tungsten filament, as a function of the temperature. "At lower pressures the rate is no longer constant because the nitrogen molecules become so scarce that a large fraction of the tungsten atoms strike the bulb without colliding with nitrogen molecules." However, on cooling the bulb containing the filament in liquid air, the tungsten atoms are found to combine with the nitrogen molecules adsorbed on the glass, and the rate of clean-up is materially increased. As will be described more fully in another section this observation has been applied by Langmuir in obtaining extremely high vacua.

⁶ J. Am. Chem. Soc. 35, 931 (1913).
Z. Anorg. Chem. 85, 261 (1914).

(3) *Clean-up of Carbon Monoxide by a Tungsten Filament*⁷

“With the bulb at room temperature, carbon monoxide was observed to behave exactly like nitrogen. In fact, with the filament at a given temperature, the curves obtained first with nitrogen and then with carbon monoxide proved to be identical.

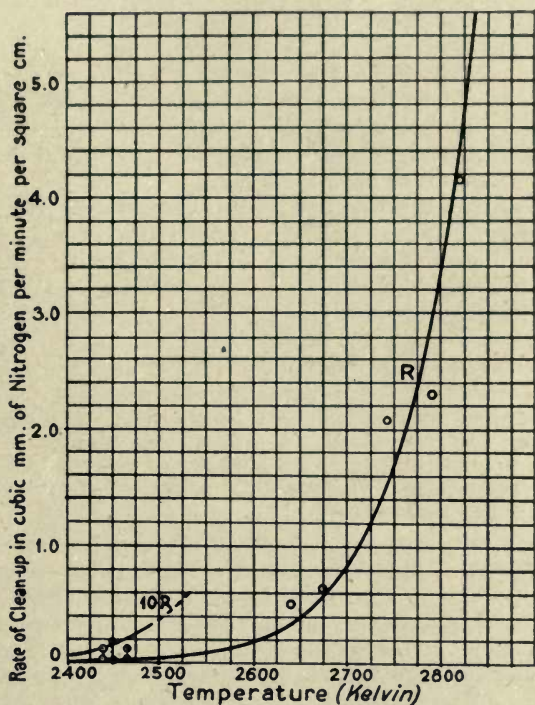


Fig. 67. Rate of Disappearance of Nitrogen in Presence of Incandescent Tungsten Filament

This proved that each atom of tungsten combined with one molecule of CO, presumably to form a compound WCO.” With the bulb immersed in liquid air, the rate of clean-up was observed to be very much greater, but still linear, as in the case of nitrogen and CO at ordinary temperatures of the bulb.

⁷ J. Am. Chem. Soc. 37, 1159 (1915).

(4) *Clean-up of Hydrogen by a Tungsten Filament*⁸

When a tungsten wire is heated to a temperature above 1300 deg. K. in hydrogen at low pressure (1 to 20 bars), a portion of the gas is dissociated into atomic hydrogen and this is readily adsorbed by glass surfaces at room temperatures and much more at liquid air temperatures. It is possible in this manner to clean-up 20 to 50 cubic mm. of hydrogen.⁹ A limit to this clean-up is, however, set by the fact that the "hydrogen atoms react to form molecular hydrogen as soon as they come in contact, even at liquid air temperatures." The amount of hydrogen gas that can be cleaned up in this manner by a heated tungsten filament is very variable and fatigue effects are apt to be observed, so that this method cannot be recommended as very useful in cleaning up residual amounts of hydrogen gas.

Traces of oxides present in a bulb are reduced by the active hydrogen with formation of H₂O. The latter is then dissociated again at the filament forming WO₃ (which distills to the bulb) and active hydrogen, which again reacts with the WO₃ on the bulb to form tungsten and H₂O. The result is that the glass walls become covered very rapidly with a black deposit, due to the disintegration of the filament. This is also the reason that even slight traces of water vapor in the presence of a heated tungsten filament will produce an apparently continuous evolution of gas.¹⁰

(5) *Vacuum Attainable by Heating a Tungsten Filament in Contact with Residual Gases*

The observation that a tungsten filament heated to a very high temperature causes the clean-up of practically every gas to a very low pressure was utilized by Langmuir in the production of the extremely high vacua that are necessary for obtaining accurate data on the electron emission of metals.¹ The method used is as follows: The bulb into which the electrodes are sealed also contains an auxiliary tungsten filament. After evacuating and heating all the metal parts to a high temperature while on the pump, the bulb is sealed off, immersed in liquid air, and the auxiliary filament heated to 2800 to 2900 deg. K.¹² The residual gases are cleaned up to a very low pressure and if the bulb is kept immersed in liquid air while making the electrical measurements, this high vacuum is maintained.

⁸ See references in *J. Am. Chem. Soc.* 37, 1161 (1915).

⁹ *Trans. A.I.E.E.* 32, 1913 (1913).

¹⁰ This effect has been described by Langmuir more fully in the above paper.

¹¹ *Zeits. f. Elektrochem.* 15, 516 (1914).

¹² For method of determining the temperature of tungsten filaments, see I. Langmuir, *General Electric Review*, 19, 208 (1916).

Some experiments made at the writer's suggestion by Messrs. H. Huthsteiner and C. A. Kidner to determine the degree of vacuum attainable by this method yielded interesting results. Using a hairpin filament about 0.0076 cm. diameter and 7.5 cm. long, with heavy nickel leads (0.1 cm. diameter) to prevent excessive heating of the latter, it was possible by heating the filament to 2700 deg. K. to obtain a clean-up from about 0.02 bar to 0.0015 bar, the pressure being measured by an ionization gauge attached to the bulb. An appendix sealed onto the system, consisting of the gauge and bulb, was then immersed in liquid air and on heating the filament to 2700 deg. K. the pressure was observed to decrease to 0.001 bar.

In another experiment in which the bulb containing the tungsten filament was wholly immersed in liquid air during evaporation of the tungsten, the pressure was decreased from about 0.1 bar to 0.005 bar. Taking into account the fact that during these experiments the ionization gauge itself was not immersed in liquid air, there is no doubt that the degree of vacuum attainable in Langmuir's experiments must have been better than 0.0005 bar, and probably nearer 0.0001 bar.

In some more recent experiments, Huthsteiner has observed that a small trace of P_2O_5 , sublimed into the bulb before sealing it off the pump, materially assists, in the presence of the heated filament, in cleaning up residual gases to a very low pressure. This is evidently due to the fact, previously observed by G. M. J. Mackay,¹³ that P_2O_5 is capable of cleaning up very large amounts of atomic hydrogen. Also the well-known hygroscopic properties of P_2O_5 make it a very efficient reagent for absorbing residual water-vapor. The only disadvantage of this substance is its comparatively high vapor pressure even at ordinary temperature. It has, however, been observed in this laboratory that fused P_2O_5 has a lower vapor pressure.

Some experiments carried out a number of years ago by Mackay and Huthsteiner yielded interesting results on the quantities of hydrogen and nitrogen that can be cleaned up by P_2O_5 in the presence of a heated tungsten filament. By heating the filament to 2300 deg. K., the pressure in a volume of 850 cm^3 could be reduced from 150×10^{-3} mm. to 1×10^{-3} mm. of mercury in two minutes. With the filament at 2700 deg. K., the pressure was reduced from 1.005 mm. to 4×10^{-3} mm. in about three minutes. That the clean-up is due to P_2O_5 vapor was shown by cooling the bulb to the temperature of liquid air, when there was observed only a slight disappearance of hydrogen.

¹³ See Patent Specification No. 1,249,978 (1917), and also No. 1,208,597 (1917).

ELECTRICAL CLEAN-UP OF GASES AT HIGHER PRESSURES

The gradual clean-up of gas during the passage of an electrical discharge in a "vacuum" tube was first observed by Plücker in 1858. As the gas disappears, the voltage required to pass current through the tube increases and, finally, the vacuum becomes "non-conducting." In the gas-filled X-ray tube, this phenomenon was known as "hardening," since the higher the voltage required to produce the discharge, the "harder" the resultant X-rays became.¹⁴ In spite of the large number of investigations on this subject, the exact cause of the phenomenon is as yet an open question. "The effect is undoubtedly not a simple one, and there are probably several contributory causes." S. Brodetsky and B. Hodgson¹⁵ have given the following list of the explanations which have been proposed:

- (1) Chemical action between the gas and the glass¹⁶
- (2) Chemical action between the gas and the cathode¹⁷
- (3) Chemical or mechanical action between the gas and the anode^{18 19 20}
- (4) Chemical action due to active nitrogen²¹
- (5) Mechanical occlusion of the gas in the glass²²
- (6) Mechanical occlusion of the gas in the cathode²³
- (7) Mechanical occlusion of the gas in the disintegrated part of the cathode.²⁴

It is well to remember in this connection that, according to our present views, electric conduction in gases occurs by means of electrons and positive ions, the latter being produced either by bombardment of the anode by electrons or by collision of the latter with gas molecules. The positive ions attain, under even moderate voltages, velocities which are much greater than those possessed by ordinary gas molecules in virtue of their kinetic energy of translational velocity. Thus, at ordinary temperature, the mean velocity of a molecule of hydrogen is about 1900 meters per second, and that of a molecule of nitrogen

¹⁴ See, for instance, G. W. C. Kaye, "X-Rays," which gives in Chapter VI, a discussion of this effect as observed in the older type of X-ray tubes.

¹⁵ *Phil. Mag.* 31, 478 (1916).

¹⁶ R. S. Willows, *Phil. Mag.* 6, 503 (1901).

¹⁷ Mey, *Ann. d. Phys.*, 11, 127 (1903).

¹⁸ C. A. Skinner, *Phil. Mag.* 12, 481 (1906).

¹⁹ B. Hodgson, *Phys. Zeits.* 13, 595 (1912).

²⁰ V. L. Chrisler, *Phys. Zeits.* 10, 745 (1909); *Phys. Rev.* 29, 461 (1909).

²¹ S. E. Hill, *Proc. Phys. Soc. London*, 25, 35 (1912).

²² Campbell-Swinton, *Proc. Roy. Soc.* 79, A, 134 (1907).

²³ Riecke, *Ann. d. Phys.* 15, 1003 (1904).

²⁴ F. Soddy and Mackenzie, *Proc. Roy. Soc.* 80, A, 92 (1908).

about 500 meters per second. When these molecules are ionized, the velocity, u , is given by the relation

$$\frac{1}{2} mu^2 = V\epsilon \quad (50)$$

which has been used already in Chapter III in connection with the theory of the ionization gauge.

Converting to ordinary units, this relation becomes

$$u = 1.396 \times 10^6 \sqrt{V/M} \text{ cm. sec}^{-1}. \quad (50a)$$

where V is expressed in volts and M is the molecular weight of the gas. Hence at 100 volts, the velocity of a hydrogen ion

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Page 175, lines 9 and 18

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the reaction is electro-chemical, the nitrogen combining with the tungsten to form the nitride WN_2 . At very low pressures and high anode voltages, the action is apparently purely mechanical (Langmuir designates this the "electrical" clean-up). The nitrogen is driven into the glass in such a form that it can be recovered by heating. The action is thus apparently reversible, and only limited quantities of nitrogen can be cleaned up in this manner. The electric clean-up, as distinguished from the electro-chemical, also exhibits distinct fatigue effects.

It is quite probable that both these two types of clean-up occur simultaneously in practically all the cases where gases disappear during electrical discharge, and we shall find that this point of view enables us to interpret to a large extent the many apparently contradictory results obtained by the different investigators.

Willows¹⁶ observed that the amount of clean-up of gas in a discharge tube varied according to the nature of the glass from

¹⁶ J. Am. Chem. Soc. 35, 931 (1913).

which the tube was made. The absorption was least in Jena glass, more in lead glass, and greatest in soda glass. At constant current, the amount of gas occluded was found to increase with decrease in pressure. The conclusion arrived at was that the clean-up is due to chemical reactions between the gases and the glass walls. In support of this view, S. E. Hills²¹ has shown that absorption is observed with air in an electrodeless discharge. His experiments were carried out in the range of pressures varying from 0.4 mm. to 0.04 mm. of mercury. During these experiments the bulbs became covered with a dark deposit on the walls, presumably due to oxidation reactions. On exhausting these bulbs and filling them with hydrogen at about one mm. pressure, the discharge caused a rapid disappearance of the gas and the deposit became lighter colored, which Hills accounted for by chemical reduction. Willows has repeated Hills' experiments²⁶ with quartz vacuum tubes, and observes that "a new quartz bulb does not absorb air, but if it be fed with repeated doses of hydrogen—which are absorbed when an electrodeless discharge is passed—it then becomes very active. If discharges in hydrogen are alternated with those in air the bulb can be made to absorb large quantities of either gas and the activity with each gradually increases." Willows accounts for these results by assuming, as Hills does, alternate oxidation and reduction.

Mey¹⁷ has shown that when potassium and sodium amalgams are used as electrodes, compounds of these metals with hydrogen and nitrogen are formed during the discharge, and G. Gehlhoff²⁷ has utilized this observation to purify rare gases (Ar, He, Ne, etc.). In the presence of a glow discharge with a heated alkali metal as cathode, all the chemically active gases are removed from a mixture of these with the rare gases. Nitrogen is completely absorbed even with the alkali metal at ordinary temperatures. In the case of hydrogen complete absorption occurs with sodium at 290 deg. C., and with potassium at 175 deg. C., while rubidium and caesium are effective at even lower temperatures. Gehlhoff believes that chemical combination occurs between the vapors of the metals and the residual gases in an active state.

The absorption of hydrogen by sodium-potassium electrodes has also been investigated by R. C. Gowdy.²⁸ Absorption was observed to occur when the alloy was used as cathode, and

²⁶ Proc. Phys. Soc. London, *28*, 124 (1916).

²⁷ Verh. d. deutsch. physikal. Ges. *13*, 271 (1911).

²⁸ Phys. Rev. *4*, 401 (1914).

evolution when used as anode. The hydride is apparently decomposed by the cathode rays.

The most recent work on this subject is that of F. H. Newman.²⁹ He deposited different elements in a pure condition on the cathode of an electric discharge tube and then determined the absorption of different gases on passing an electric discharge. The minimum pressure at which clean-up was observed to occur varied around 0.1 to 1 mm. of mercury. "Measurements were made to compare the amount of nitrogen gas absorbed by the element in the tube with the quantity of electricity passing in the circuit. Potassium, sodium, mercury, cadmium, antimony, magnesium, calcium, zinc, tin, phosphorus, sulphur, and iodine were tested in this way. The rates of absorption were very great with the last three elements. Hydrogen gas was also used in the tube, and absorption occurred with phosphorus, sulphur, and iodine." Newman concludes from his experiments that the clean-up is due to chemical reactions between the elements present on the cathode and the gases which assume active modifications on the passage of an electric discharge.

In this connection it is interesting to refer briefly to the experiments carried out by R. J. Strutt³⁰ on the formation and properties of a chemically active modification of nitrogen. He observed that on passing a condenser discharge through nitrogen at low pressures, a form of nitrogen is obtained which shows an intense yellow glow and is very active chemically. As well known, nitrogen in the ordinary state is very inert chemically. It combines with other elements with difficulty and only under special conditions such as high temperature or high pressure. On the other hand, Strutt finds that the nitrogen passed through the discharge tube under the above conditions is very active chemically. "Drawing it by the pump over a small pellet of phosphorus, a violent reaction occurs, red phosphorus is formed, and the yellow glow is quenched. At the same time the gas is absorbed." Similarly active nitrogen combines readily with iodine, sulphur, and arsenic. There is no doubt, therefore, that the formation of active nitrogen must be taken into account in explaining clean-up effects in electrical discharges.

In a similar manner Newman accounts for the absorption of hydrogen by phosphorus, sulphur and iodine, by assuming the formation of an active modification of the gas. This is probably the same form as that produced by Wendt and Lan-

²⁹ Engineering, Jan. 14, 1921, p. 60.

Proc. Phys. Soc. London, *32*, 190 (1920); *33*, 73 (1921).

³⁰ Proc. Roy. Soc. *85*, A, 219 (1911) and subsequent papers.

dauer³¹ in subjecting hydrogen to α -rays from radium emanation or to high potential corona discharges.

These observations and the results obtained by Langmuir on the electrochemical clean-up of nitrogen by a heated tungsten cathode indicate that the above theory probably accounts for some of the clean-up effects observed in discharge tubes. As pointed out by Kaye: "It may be, also, that the action is stimulated by a species of electrolysis of the glass produced by the high-tension discharge playing over its surface. It is well known that glass may be readily electrolyzed by quite moderate potentials if the temperature of the glass is raised; and it is a matter of experience that the discharge seems to have an ageing effect on the glass, to the detriment of subsequent working on the blow-pipe. Such electrolysis might have a marked effect on the gas film which glass and other solids can condense on their surfaces."

That, however, the clean-up occurs owing to reactions which are not chemical is shown by the fact, observed by Soddy and Mackenzie,²⁴ that both pure helium and neon are also absorbed in electric discharge tubes. With aluminum electrodes, such as were used in their experiments, the electric discharge causes a considerable mechanical disintegration of the cathode, and the portions of glass adjacent to this electrode become covered with a deposit of the metal in a finely divided state. This phenomenon is known as "cathodic sputtering" and occurs to a larger or smaller extent according to the composition of the cathode.

From the fact that the gases could be recovered by heating the tubes, Soddy and Mackenzie concluded that the gases were mechanically adsorbed by the deposits formed around the cathode. The finely divided metal formed by sputtering is thus assumed to behave like palladium or platinum black in the ordinary adsorption phenomena. That cathodically sputtered metals adsorb hydrogen during discharge has been shown by Heald,³² and other investigators.

C. A. Skinner³³ found in his experiments that gas was evolved at the cathode and absorbed at the anode. The gas evolution occurred at a rate given by Faraday's law, that is, 1 gm. of hydrogen for 96,500 coulombs. It is to be noted that with fresh electrodes a number of observers have found that "there is often an initial evolution of gas, especially in hydrogen and nitrogen, or in any gas, with aluminum electrodes. But if the tube is used

³¹ *J. Am. Chem. Soc.* **42** (1920).

³² *Phys. Rev.* **24**, 269 (1907).

³³ *Phil. Mag.* **12**, 481 (1906); *Phys. Rev.* **21**, 1169 (1905); *Phys. Zeits.* **6**, 610 (1905).

and then allowed to stand awhile, on restoring the current, no initial evolution is found in most cases."

L. V. Chrisler²⁰ has also concluded that the absorption in the discharge tube occurs at the anode. On the other hand, the weight of evidence points to the predominating influence of the cathode on the amount and rate of absorption. B. Hodgson¹⁹ and S. Brodetsky and Hodgson¹⁵ have investigated the relation between amount of clean-up and current, and also the effect of varying the chemical composition of the electrodes. The amount of gas absorbed per coulomb was observed to increase with decrease in pressure, as had previously been observed by Willows. The pressures at which these experiments were carried out varied from 2 mm. to 0.03 mm. approximately. A battery giving about 3200 volts was used as source of current, and the actual current strength varied from 0.008 to 0.002 amp. They found that the absorption varied with the rate of disintegration of the cathode, and no absorption was obtained in absence of such disintegration. Furthermore, the absorption was observed to increase with increase in cathode drop. They therefore concluded, in agreement with Soddy and Mackenzie, that the major portion of the clean-up is due to adsorption of the gas by the metal sputtered from the cathode.

These observations have been confirmed to a large extent by L. Vegard.⁴ He finds that absorption is small as long as the cathode drop is below a certain "threshold" value, and he connects the clean-up with cathodic sputtering. The absorption rate follows the cathode drop and runs parallel with the amount of cathodic sputtering. Thus, in oxygen gold electrodes show more sputtering than electrodes of platinum. At the same time, the rate of clean-up is greater with gold than with platinum. Vegard also observed that in the case of helium there is a measurable clean-up which is, however, less than that obtained under similar conditions with either nitrogen or oxygen. In the case of hydrogen both absorption and evolution were found to occur. "When a current of definite value has reduced the pressure to a given value, a larger current causes evolution, and a smaller one, absorption." This probably accounts to a certain extent for Skinner's observations.³³ Vegard concludes from his experiments that absorption occurs at the cathode and is somehow caused by high velocity positive ions impinging on the cathode. In other words, his explanation attempts to compromise between both the chemical and the mechanical theories.

³³ Ann. d. Physik, 50, 769 (1916).

ELECTRICAL CLEAN-UP OF GASES AT LOW PRESSURES

As mentioned previously, an ordinary discharge tube with cold electrodes becomes inoperative when the pressure is reduced to too low a value. In general, this occurs at pressures which range from 1×10^{-3} to 100×10^{-3} mm. of mercury, depending upon the nature of the gas and the maximum voltage of the source of current. The operation of such discharge tubes depends primarily upon the formation of positive ions by the disruptive action of the voltage; and the bombardment of the cathode by these positive ions causes the emission of electrons which in turn ionize more gas molecules, so that the discharge is apt to become quite unstable. In the preceding section we discussed clean-up effects in such discharges at relatively high pressures. Within the past few years, however, a type of vacuum tube has been developed in which conduction occurs by means of electrons emitted from an incandescent cathode. The pressure in these devices must be maintained at a low value, ordinarily below 10^{-2} bar (10^{-5} mm. approximately). Consequently it is of practical importance to consider the changes in gas pressure which are observed in the operation of such tubes. The study of these phenomena is also of theoretical importance because it throws light, as will be shown, on certain clean-up effects in vacuum type incandescent lamps.

Electron Emission Phenomena at Low Pressures³⁵

The electron emission from a heated cathode increases with the temperature according to the equation, first derived by Richardson:

$$i = A \sqrt{T} e^{-b/T} \quad (53)$$

where i = electron emission per unit area, and A and b are constants for any given material. I. Langmuir has shown that the actual magnitude of this emission at any temperature, that is of the values of A and b in this equation, is extremely sensitive to the presence of slight traces of certain gases and the maximum value of the specific emission at any temperature is attained only

³⁵ The literature on this subject has become so extensive in the past few years that only a brief discussion has been considered ample in the present connection. For further references, consult the following books and articles:

- (a) O. W. Richardson, "The Emission of Electricity from Hot Bodies," 1916.
- (b) H. J. Van der Bijl, "Thermionic Vacuum Tube," McGraw-Hill Book Co., 1920.
- (c) I. Langmuir, *General Electric Review*, 18, 327 (May, 1915), 23, 503, 589 (June and July, 1920).
- (d) I. Langmuir, *Phys. Rev.* 2, 402, 450 (1913).
- (e) S. Dushman, *General Electric Review*, 18, 156 (March, 1915).
- (f) S. Dushman, *Phys. Rev.* 4, 121 (1915).

in extremely good vacua. In the case of tungsten, the constants have the values:

$$\begin{aligned} A &= 23 \times 10^9 \\ b &= 52,500 \end{aligned}$$

where i = milliamp. per cm^2 , and T is the absolute temperature. This gives the *maximum electron current* that it is possible to obtain from a unit area of tungsten at any definite temperature.

It was observed by Langmuir that in addition to this limitation due to temperature, there is also present, at very low pressures, a voltage limitation, due to a "space charge" produced by the electrons in the neighborhood of the cathode. The electron current is then limited by the anode voltage V , in accordance with a relation of the form:

$$i = kV^{\frac{3}{2}} \quad (54)$$

where k is a constant whose value depends upon the geometrical arrangement and shape of the electrodes. This relation gives the *minimum voltage* between anode and cathode at which a given electron current can be obtained in the particular tube, under good vacuum conditions.

Ionization Effects

When, however, the gas pressure exceeds a certain value (depending principally upon the nature of the gas and the geometrical dimensions of the device) some of the electrons no longer travel directly from the cathode to the anode. Collisions with gas molecules occur, and if the anode voltage exceeds the so-called ionizing potential³⁶ positive ions are produced, which tend to neutralize a part or the whole of the negative space charge produced by the electrons and consequently the electron current reaches the saturation value corresponding to the temperature of the filament, at much lower voltages than when gas is not present.

These phenomena are illustrated by the following observations with a small hot-cathode high-vacuum rectifier (kenotron) in which a tungsten spiral was used as cathode, and a molybdenum cylinder (enclosing the spiral) as anode. To the bulb containing these electrodes was attached an appendix containing a small amount of mercury, and the whole arrangement was exhausted to a very high vacuum. By immersing the appendix

³⁶ For each gas it has been observed that there exists a definite voltage at which the electrons acquire sufficient velocity to produce positive ions by collisions with gas molecules. These voltages have been measured for a number of gases and metallic vapors, and they are found to vary from about 25 volts in the case of helium to approximately 4 volts in the case of the alkali metals. See the report on "Photo-electricity and Ionization Potentials," by A. L. Hughes, Bull. Nat. Res. Council, 2, 83 (1921).

in liquid air the pressure of the mercury vapor could be reduced to such a low value that no ionization effects occurred. Fig. 68 shows the characteristics of the tube under these conditions, at two different filament currents. It will be observed that at 1.35

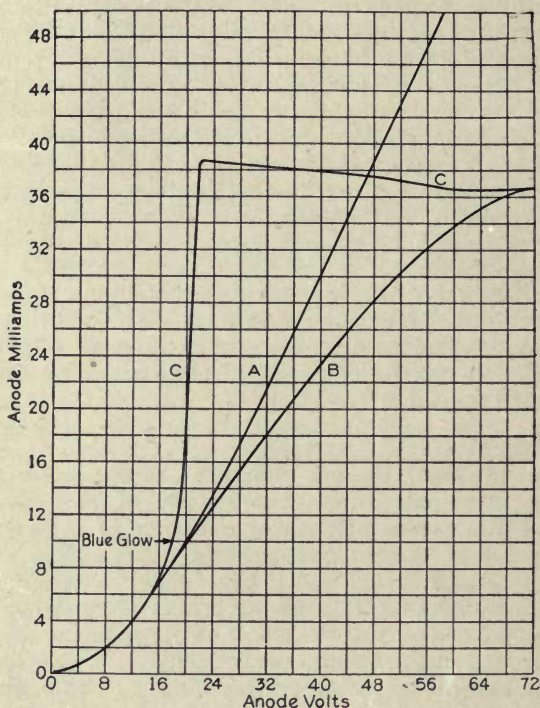


Fig. 68. Illustrating Effect of Mercury Vapor on Characteristics of Hot Cathode Tube

Curve A—Space charge limitation in good vacuum
 Curve B—Space charge and temperature limitation
 Curve C—Same filament temperature as Curve B,
 but in presence of mercury vapor at
 a pressure of two bars

amp. (Curve A), the electron current varied with the anode voltage in accordance with the $3/2$ power relation. At 1.25 amp. the electron current increased at first in accordance with the same voltage law and then tended to reach the value 38 milliamp. corresponding to the emission for that particular temperature (Curve B).

On removing the liquid air from the appendix, so that the mercury attained room temperature and the pressure in the device reached the value of about 2×10^{-3} mm. (corresponding to the vapor pressure of mercury at this temperature), the characteristic obtained with the filament at 1.25 amp. was that shown in Curve C. At 18 volts a distinct blue glow appeared, and at 26 volts this glow extended practically all the way down the appendix. It will be observed that simultaneously with this appearance of blue glow, the electron current increased rapidly until it reached practically the same saturation value as that obtained under good vacuum conditions. That is, even at such a low pressure of mercury vapor, the space charge phenomena practically disappeared and the saturation electron emission corresponding to 1.25 amp. filament current was obtained at relatively low voltages.

Observations on Clean-up in Hot-cathode Devices

Similar phenomena are observed with all other gases in hot-cathode devices. At very low pressures the electron current varies with the voltage according to the $3/2$ power law, but at higher pressures (ordinarily about one to two bars) blue glow appears as the voltage is raised above the ionizing potential and simultaneously with this blue glow the current increases rapidly, as shown in Curve C, Fig. 68, to the saturation emission at the given filament temperature. In the case of most gases this blue glow does not ordinarily persist very long, owing to clean-up effects that accompany the appearance of this glow, and consequently the electron current decreases again gradually until it attains the limiting value corresponding to the space charge.

These clean-up phenomena that are observed in hot-cathode devices are extremely interesting, and they are of great technical importance. The experimental evidence which has been obtained in this laboratory and by other investigators points to the conclusion that these effects are primarily due to the formation of ions by collisions between electrons and gas molecules. There is little or no evidence for any electrical clean-up below ionizing potentials.

Experiments along this line carried out in this laboratory for the past few years have shown that the factors governing this clean-up are quite complex. In general, the rate of clean-up shows a tendency to increase with the anode voltage and with the electron current. In addition to these factors, the condition of the glass walls and the previous history of the bulb exert a profound effect on the rate of clean-up. The disappearance

of gas by electrical clean-up is observed even at the very low pressures where space charge effects are present and blue glow is therefore absent. Numerous observations in connection with hot-cathode devices, such as are made up in this laboratory, have confirmed this conclusion. Thus a kenotron (hot-cathode rectifier) may be sealed off at 0.05 bar and by subsequently operating it with a current of a few milliamperes at 120 to 240 volts, the pressure will be found to decrease to 0.01 bar or less.

At any given electron current the residual gas pressure in the sealed off tube reaches an equilibrium value which increases with the electron current. Part of this increase is probably due to an increased rate of evolution from metal parts and glass walls until equilibrium is attained with the increased rate of clean-up. The pressure may thus be found to vary from 0.01 to as low as 0.0001 bar, depending upon anode voltage and electron current. Similar effects have been observed with the ionization gauge in using it to measure low pressures of chemically active gases, such as nitrogen, hydrogen, and oxygen. That this clean-up is not due in these cases to purely chemical reactions at the surface of the tungsten filament is easily shown by taking off the anode voltage, when the clean-up practically ceases. Moreover this clean-up also occurs with the inert gases argon and helium.

A preliminary account of some recent observations made by Mrs. M. Andrews, H. A. Huthsteiner, and the author, on this subject, may be of interest in this connection. In these experiments a tube containing two adjacent tungsten filaments was used, so that either filament could be made cathode, and the rate of clean-up was investigated in the case of argon and nitrogen. Gas from a large reservoir was allowed to flow continuously through this tube at practically constant pressure, and the rate of clean-up was determined by collecting the gas after it left the tube. The pressures used in most of the experiments were so low that no blue glow effects were observed, and during any one set of observations both the electron current and the anode voltage were maintained constant. The magnitude of the current was varied in different runs from a few microamperes to several milliamperes, and the anode potential was varied from 25 to 250 volts. The rate of clean-up was observed in these experiments to increase almost linearly with increase in pressure. With electron currents below a milliampere, the rate of clean-up also varied linearly with the current, but showed a tendency to increase much less rapidly with electron currents exceeding this value. At anode voltages in excess of 25, the rate of clean-up was observed to be practically constant and inde-

pendent of the voltage. With freshly baked out glass bulbs, the fatigue effects observed were quite pronounced. On covering the glass surface inside with a tungsten deposit (by evaporation of one of the filaments) the rate of clean-up was found to increase considerably, and much more gas could be cleaned up before fatigue effects occurred. The rate of clean-up of argon was found to be about half of that of nitrogen under otherwise similar conditions.

The following observations were made on a system consisting of a five-inch bulb containing two adjacent tungsten filaments to which was attached an ionization gauge. The volume of the arrangement was about 1200 cm³. After a thorough exhaust on the condensation pump, followed by a flashing of the filaments at a high temperature, argon at a pressure of 1.35×10^{-3} mm. of mercury was let into the system and the whole sealed off the pump. One of the tungsten filaments was then made cathode and raised to the temperature necessary to give an electron emission of five milliamperes. With 250 volts on the other filament as anode, the pressures indicated in the following table were obtained at different intervals of time.

Time <i>t</i> (minutes)	Pressure mm. $\times 10^{-3}$	$k = \frac{1}{t} \log (\rho_0/\rho)$
0	1.35	
2	1.2	0.0255
4	1.05	0.0273
15	0.65	0.0212
27	0.36	0.0213
		Avg. = 0.0238

The constancy of k in the last column shows that the rate of clean-up at any instant was proportional to the pressure.

Observations were made in the same manner with nitrogen. In one experiment, using 5 milliamp. and 250 volts, the nitrogen cleaned up from a pressure of 8×10^{-3} mm. to 1×10^{-3} mm. in 36 minutes. In all these cases, if after cleaning up a certain amount of gas, more gas was let into the bulb, the rate of clean-up was observed to be much lower.

Regarding the mechanism of this clean-up, it is difficult to draw any positive conclusions. In the foregoing experiments there was no evidence to show that the gas was cleaned up at the cathode, as for instance by the formation of WN₂. This would certainly not be true in the case of argon; the gas was most

probably driven into the walls. Subsequent heating rarely caused the evolution of as much gas as had been cleaned up, so that the ions must penetrate the glass quite deeply.

Observations similar to those mentioned have been made by other investigators working with hot-cathode devices. Thus W. H. Eccles, in a discussion on thermionic valves,³⁷ makes the following very interesting comments regarding clean-up effects:

“Many interesting phenomena are observed with the traces of residual gases always present even in the hardest of tubes. After running for some time with a given electron current to the positive electrode and a given voltage, a steady value for the pressure of the residual gas may be reached. If now the voltage is increased, but not sufficiently to overheat the positive electrode, the tube will harden, i.e., some of the residual gas will be absorbed. On the other hand, if the voltage is reduced, and particularly if the filament is simply heated without any voltage being applied to the positive electrode, the amount of residual gas will increase.

“These effects are well known to radiologists and various suggestions are put forward in explanation. But from the point of view of the development of the high-power valves, the whole problem requires careful investigation.

“The fact that an increasing voltage at the positive electrode hardens the valve leads to the conclusion that the effects are due to the action of the ionized gas. At these voltages the ions are positive, and their observed disappearance must be due to their being driven into the hot filament, or into the walls of the containing vessel. If they are driven into the filament, how are they retained with the filament at 2000 deg. C.? Is any chemical action involved, or is it the same process as the occlusion in the positive electrode? Or is it only the walls of the containing vessel that absorb the ions?

“A suggestion has been put forward by Dr. G. B. Bryan of the Physics Laboratory, at Royal Naval College, Greenwich, that the occlusion of the gases and the emission of positive ions from metallic surfaces at moderate temperature are closely related. He visualizes the process as follows: Some proportion of the gas to which the electrodes are exposed will probably be ionized hydrogen. A positive hydrogen ion is a very small heavy projectile with considerable powers of penetration. On striking the surface of a solid it will pass through the outer surface and pick up an electron, so becoming neutral. Now, however, it is a

³⁷ *The Radio Review*, 1, 26 (1919).

large body entrapped in among the atoms of the metal and unable to escape under ordinary conditions. But at moderate temperatures the electrons may be shed again, and the positive ion, being no longer encumbered by the outlying electron, can escape, so constituting the positive emission. One peculiar fact has frequently been observed by Dr. Bryan when exhausting a valve, viz., that a small liberation of occluded gas will give rise to a greater tendency to arcing than the introduction of a much greater quantity of ordinary air. If the gas liberated from the electrodes is already ionized, the observation is immediately explained.

“This theory is a very interesting one, and is one on which some light could be thrown by the entire removal of all traces of hydrogen. At present, however, it has never seemed possible to do this, as such extremely small quantities are involved; and possibly other ionized gases may be entrapped in the same way. If it is the outer electron that is lost, this would seem to be quite possible.”

That the positive ions attain, under even moderate voltages, velocities which are much greater than those possessed by the corresponding molecules at ordinary temperatures, has already been pointed out in the discussion of electrical clean-up at higher pressures. It is therefore interesting to observe that Eccles and Bryan also consider that this may be a possible explanation of the observed clean-up effects in hot-cathode devices.

On the other hand, in a very recent paper by A. Ll. Hughes³⁸ another explanation has been made which is to a certain extent equally probable. In these experiments the electrical clean-up of nitrogen and hydrogen was studied in a tube containing as cathode a platinum filament coated with BaO and SrO. In most of the experiments the whole tube was kept immersed in liquid air and the electron current was maintained constant in any one set of measurements. The rate of clean-up was found to decrease gradually during any run, owing to gradual saturation of the walls of the tube (as in the experiments mentioned previously). The initial pressures used in these experiments varied from 50×10^{-3} mm. to 2×10^{-3} mm. of mercury. The conclusions as stated by Hughes are as follows:

“For hydrogen, no disappearance was obtained unless the electrons had energy above 13 volts. The rate of disappearance rose rapidly as the energy of the electron was increased to about 70 volts, after which no rapid change was noted (the rate ap-

³⁸ *Phil. Mag.* 41, 778 (1921).

peared to diminish somewhat when the energy of the electrons was raised from 150 to 300 volts). For nitrogen, the rate of disappearance was at first much less than for hydrogen, but when the energy of the electrons was raised sufficiently (roughly 200 volts) the rate of disappearance of the nitrogen exceeded that for hydrogen."

In explanation of the mechanism of clean-up Hughes concludes that "this disappearance is due to the splitting of the molecules into atoms when electrons collide with the molecules, and these atoms condense on the adjacent surfaces particularly if they are cold." This explanation would account for the

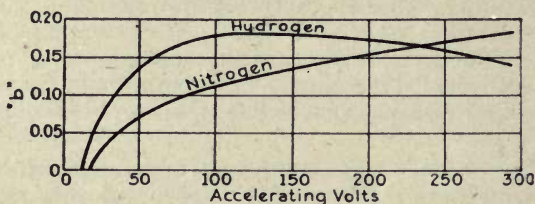


Fig. 69. Hughes' Experiments on Clean-up of Gases. Variation with voltage in the ratio (b) of the number of molecules cleaned-up to the number of collisions between electrons and molecules

observations made in the experiments of Mrs. Andrews and Huthsteiner that a charging up of the tungsten deposit on the walls, with either positive or negative potentials, produced no effect on the rate of clean-up of nitrogen. On the other hand, such an explanation could obviously not account for the clean-up of argon. Hughes has also calculated the ratio between the number of molecules disappearing and the number of collisions between electrons and molecules. Fig. 69 taken from his paper gives the relation between the value of this ratio (designated b) and the anode voltage for both nitrogen and hydrogen. It is seen that with approximately 250 volts on the anode, about one molecule disappeared for every six collisions, and presumably this molecule disappeared in the form of atoms. The theory that collisions between electrons and molecules may not only lead to the formation of ions but also to a dissociation of these molecules is extremely suggestive and may be a satisfactory explanation of the clean-up effects in some cases, but it is hardly possible that it is of general application.

Clean-up and Glow Phenomena

The disappearance of gas in hot-cathode devices has also been discussed at considerable length in three papers by the research staff of the General Electric Company, Ltd., London.³⁹ In the first one of these papers, after discussing the previous work on clean-up phenomena in electrical discharge tubes and

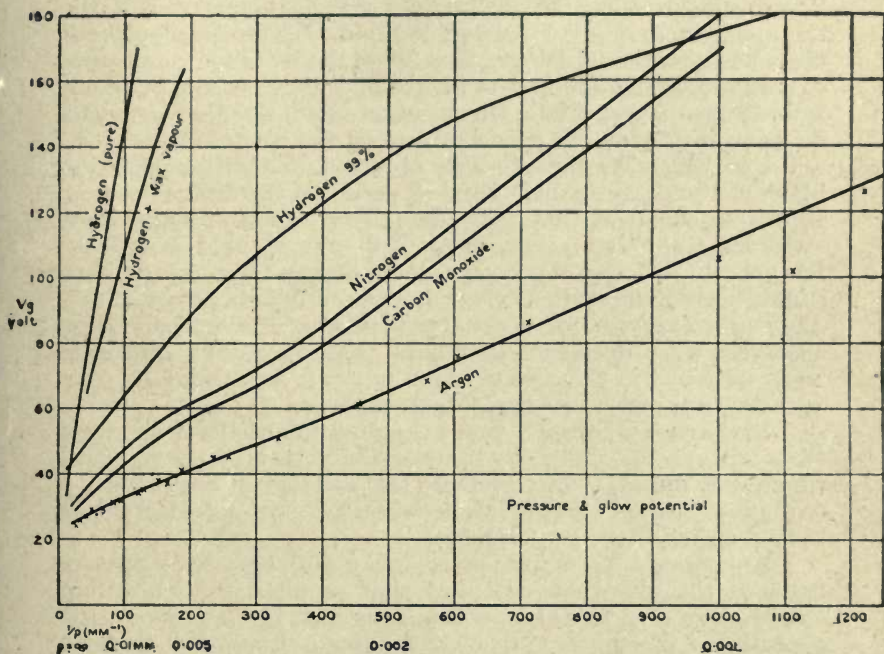


Fig. 70. Relation between Pressure and Glow Potential for Various Gases (Campbell)

Langmuir's work on purely chemical clean-up, the writers point out the effect of gas in eliminating space charge, as has already been described and lay special stress upon the appearance of the glow as an essential factor for the occurrence of clean-up. Accordingly they have made very careful measurements of the potentials at which this glow occurs. "The first observations," it is stated, "proved that the glow potential is independent of the temperature of the filament and of the thermionic emission

³⁹N. R. Campbell, *Phil. Mag.* 41, 685 (1921); N. R. Campbell and J. W. H. Ryde, *ib.* 40, 585 (1920); *ib.* 41, 227 (1921). Observations on the clean-up effect in presence of blue glow are also recorded by C. F. Hagenow, *Phys. Rev.* 13, 415 (1919).

from it in wide limits. If there is no thermionic emission, the glow does not appear of course until the spark potential of the gas is reached, but the change from this condition to that in which the glow occurs at the very much lower potential obtained with a hot-cathode is so rapid that it could not be determined certainly whether the change was continuous or discontinuous. Once the lower value is obtained, no further change occurs even if the thermionic emission is increased 100-fold. There is no evidence that the glow potential depends at all on the thermionic emission, so long as it is great enough to give at all a glow potential distinct from the spark potential. On the other hand, the glow potential depends greatly on the pressure, and on the nature of the gas."

Fig. 70 shows the relation obtained in this investigation between the pressure and the glow potential for different gases. It will be observed that the potentials are plotted against the reciprocal of the pressures. The argon used contained five per cent nitrogen. The curves for hydrogen show the effects of slight traces of impurities. The glow potentials observed with increasing voltages were invariably somewhat higher than those observed with decreasing voltages, the maximum difference being obtained in the case of argon where it was about 10 volts at a pressure of 5×10^{-3} mm. of mercury.

In the case of mercury vapor the glow potential was observed to be always 32.5 volts, "whatever the nature of the gas with which it is mixed." Furthermore the addition of any impurity to a gas was often observed to decrease the glow potential below that of either of the constituents.

An important distinction is drawn by these investigators between the glow potential and that required for ionization. "It is clear that the glow potential is not, like the ionization potential, a direct property of the individual atoms of the gas, it must also be a function of their mode of reaction with each other or with the walls of the vessel; for the glow potential is not, like the ionization potential, independent of the pressure. There is no evidence, therefore, that the glow represents a new form of ionization of the individual atoms."

Some interesting observations are recorded on the rate of disappearance of different gases in the presence of a glow discharge. In the case of CO, it was found that the gas cleaned up in consequence of the reaction, $2\text{CO} = \text{C} + \text{CO}_2$, the carbon dioxide formed being adsorbed on the glass walls. The complete elimination of mercury vapor is essential for the occurrence of this reaction. "If mercury vapor is completely removed, the disappearance continues until the discharge stops, owing to the

rise of the glow potential—at any rate, if a potential greater than 300 volts is not employed. If fresh CO is admitted, it disappears again under the discharge at a rate apparently unchanged; a limit to the absorption has not been found, although a quantity has been adsorbed equal to at least five times that representing a monomolecular layer on the walls.” On baking the vessel to over 330 deg. C., the greater part of the gas was re-evolved, mostly as CO₂.

Nitrogen was observed to disappear in the same manner as does carbon monoxide, “in apparently unlimited quantities.” This is accompanied by some decrease in the filament diameter and a blackening of the bulb. Probably WN₂ is formed as has been shown by Langmuir,⁴⁰ although Campbell seems inclined to believe that the tungsten is cathodically sputtered off the filament and covers the nitrogen which is adsorbed on the glass.

The rate of clean-up of argon was observed to be less than one-fifth that of nitrogen, and at the same time rapid blackening of the bulb occurred. “In both nitrogen and argon there is the intimate connection between cathode sputtering and absorption of gas which Vegard⁴¹ has noted in the discharge without an incandescent cathode.”

The observations with hydrogen in the absence of a discharge were in agreement with Langmuir's observations on the formation of atomic hydrogen.⁴² Campbell finds, however, that in the presence of a discharge the rate of clean-up is much less than that obtained because of purely thermal dissociation.

Very interesting phenomena were observed on passing a discharge in mercury vapor. In an otherwise thoroughly exhausted glass bulb, it was observed that under these conditions *hydrogen is liberated* from the walls. The fact that the discharge may evolve gas from the walls instead of causing it to disappear had already been noticed by Campbell as occurring to some extent in nitrogen, CO, and argon. In the presence of mercury vapor this phenomenon is extremely marked.

“And it should be noted that the gas thus liberated cannot be liberated by mere heating of the walls to their softening point; gas can be attached to the walls in some such way that it can be liberated by the discharge but not by heating. Of course, the attachment may consist of chemical combination; it is possible that glass contains hydrogen chemically combined, probably as water. But it should be observed that the hydrogen liberated, if

⁴⁰ J. Am. Chem. Soc. *35*, 931 (1921).

⁴¹ Ann. d. Phys. *50*, 769 (1916). See also p. 179.

⁴² J. Am. Chem. Soc. *37*, 1161 (1915).

piled up on the glass, would form a layer at least 25 molecules thick; some of it must therefore have come from a layer at least 25 molecules deep. Since the potential driving the discharge in these experiments was often as low as 50 volts, it is hardly to be expected that the electrons or ions could penetrate so far into the glass simply in virtue of the energy which they receive from the discharge. It seems easier to believe that a layer on the surface, subject to the action of these particles, is constantly renewed by diffusion from within."

The conclusions drawn by Campbell from these experiments are as follows:

"(a) All gases can be made to adhere to glass by the discharge in such a way that part, at least, can be restored by heating the glass.

"(b) The amount of gas that can be made so to adhere depends on the nature of the gas and on the state of the glass.

"(c) The adhesion is not due primarily to chemical reaction, although such reaction (as in the conversion of CO to CO₂) may aid adhesion by converting the gas into another which adheres more readily.

"(d) The discharge can also liberate gas from the walls, doubtless by bombardment of the charged particles, and some of the gas so liberated cannot be liberated by heating the glass to the softening point.

"(e) The limit in the disappearance of the gas is reached when the rate at which gas is caused to adhere to the glass by the discharge becomes equal to the rate at which it is liberated by the bombardment."

The second paper referred to above deals with the theory of clean-up in presence of phosphorus vapor, and is discussed in a subsequent section. In the third paper, Campbell again takes up the problem of glow potentials and the relation between primary electron and ionization currents. The most important result obtained in this investigation is the demonstration that, "in a discharge vessel with electrodes, of which the area is small compared with that of the walls, those walls can act as a third electrode, receiving almost all the positive ions, the charge on which is neutralized by electrons from the cathode." By coating the inside wall of the two-electrode tube with a deposit of silver and charging the latter with a small negative potential (with respect to the hot cathode) it was possible to measure the positive ionization current produced by any definite electron current between the hot cathode and anode. Fig. 71 illustrates a typical series of observations at a pressure of 0.156 mm. of CO. The

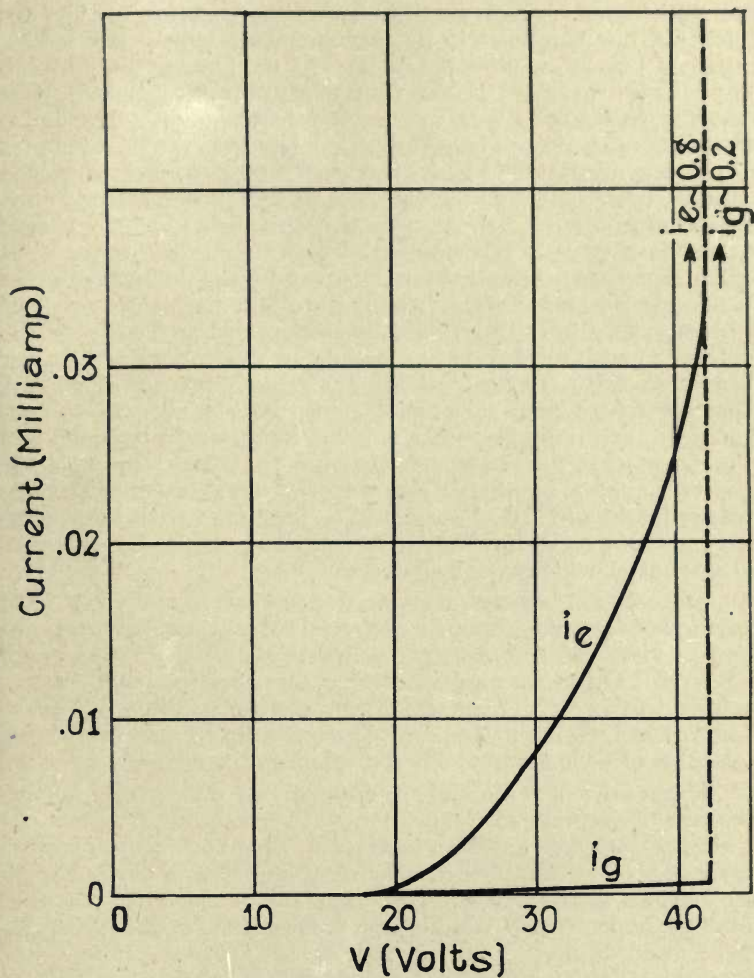


Fig. 71. Typical Series of Observations at a Pressure of 0.156 mm. of CO.

electron current, i_e , rises steadily from the ionization to the glow potential, but the positive ion current, i_p , is barely perceptible until just before the glow potential. At the glow potential, both i_p and i_e rise rapidly. If the third electrode is insulated, it is observed to charge up to approximately the same potential as the cathode, and nearly all the positive ions travel to it, as shown by the magnitude of i_p , when this electrode is connected to the cathode through a galvanometer. That this third electrode must also be receiving electrons in quantity to neutralize the charge of the positive ions is evidenced by the observation that "at higher pressures, though the current and energy carried by the discharge may be sufficient to melt the anode, the latter does not become visibly hot; all the heat is communicated to the walls." In this respect all observations made in this laboratory on the electric discharge in hot cathode devices in presence of gas are in accord with Campbell's conclusion. It is interesting to note that Campbell finds the ratio i_p/i_e to be practically independent of pressure until the pressure falls so low that the applied voltage is below the glow potential. On the other hand, as shown by the measurements of C. G. Found and S. Dushman with the ionization gauge the ratio varies directly with the pressure for pressures below that at which blue glow occurs.*

The relation between the positive ionization and the rate of clean-up of CO gas (previously referred to) was studied from this point of view and the conclusion drawn that the production of CO₂ from CO by the discharge takes place by the collision of a positive CO ion with a neutral CO molecule. Thus, for every positive ion arriving at the grid, there is a disappearance of two molecules of CO, namely, the ion itself and a neutral molecule.

The results of some experiments carried out in this laboratory are of interest in connection with these observations obtained by Campbell and his associates. That the clean-up effects are more pronounced in the presence of blue glow is undoubtedly true but, as already mentioned, the rate of electrical clean-up in hot-cathode devices is quite appreciable even at low pressures where the voltages used are below the corresponding glow potential. Again, the actual values of the glow potentials as given in Fig. 70 are probably dependent upon the form of the electrodes and the vessel, a conclusion which is also expressed by Campbell. Thus, the glow potential for mercury at 2×10^{-3} mm is given by the latter as 32.5 volts, whereas, as before stated, concerning experiments carried out in this laboratory with a

* See Chapter III, pp. 119-120.

different construction of hot-cathode tube from that used by Campbell, blue glow has been observed at as low as 18 volts.

With regard to the relation between blue glow potential and electron emission, Mrs. Andrews* has observed that in the case of both argon and nitrogen the voltage required for the appearance of blue glow shows a tendency to decrease with increase in emission. At higher pressures it is possible to observe two glow potentials; at the lower of these, blue glow appears below the anode, and at the upper voltage the glow occurs both above and below the anode. Furthermore, with 250 volts on the anode, it was observed that the electron emission at which blue glow appeared varied approximately inversely with the pressure. Thus, at 45×10^{-3} mm. of argon, the electron emission required to produce blue glow was about 0.15 milliamp., whereas at 4×10^{-3} mm. the necessary emission was about 1.4 milliamp. In these measurements an ionization gauge was used, with the inner filament as cathode and the other one as anode. At the same time the positive ion current was measured to the cylinder surrounding both filaments, and it was observed that this current was approximately the same in all cases when blue glow appeared. This means that for the appearance of glow in any device it is apparently necessary to have a certain density of positive ions. This conclusion would also be in accord with the observation mentioned previously that the electron current required for blue glow to appear varies inversely as the pressure.

Electrical Clean-up Phenomena in Incandescent Lamps

The observations discussed in the previous section have a fundamental significance from the point of view of the clean-up effects observed in vacuum type incandescent lamps.

In European practice it is customary to exhaust lamps to a very high degree of vacuum, the residual gas pressure being usually less than one bar. Care is taken to eliminate water vapor as much as possible by a thorough baking out of the glass, and the filaments are flashed on the pumps. On the other hand, in this country various economic considerations have led to greater and greater speed of production in all lines, not excluding that of lamp manufacture. Consequently the period of exhaust has been reduced, and at present it is the normal practice to complete the whole exhaust operation in a period which may vary from five minutes to as low as one-half minute. In this short period of time the pressure is reduced from atmospheric to a few bars, the glass is raised to a high temperature to eliminate as much water vapor as possible and the lamp sealed off.

* A complete account of these experiments will be published in the near future.

It is evident that under these conditions there must remain in the lamp a considerable amount of residual gas, to which must be added the gas that is subsequently evolved on lighting the filaments. As a matter of fact, the residual gas pressure in actual practice varies from as low as one bar to over 100 bars, depending upon the nature of the exhaust process used. In view of the fact, which has been known for a long time, that the life of an incandescent lamp is considerably increased by improvement in vacuum and through elimination of water vapor, it has therefore been necessary to devise methods by which the residual gas can be cleaned up.

The most usual method of attaining this result is that suggested by Malignani in 1894. As used in the days of the carbon filament lamp,⁴³ "this process, in its most perfect form, consisted in distilling into the bulb a small amount of some such substance as arsenic, sulphur, iodine, or phosphorus. At the instant when one of these vapors was introduced, a high current was passed through the filament, the lamp being closed from the pump. In case of incandescent lamps where the voltage is above 50 for a fair brilliancy of filament, a blue discharge passes through the bulb and this blue quickly disappears when such vapors are introduced."

Further investigation, notably in this laboratory, showed that during the disappearance of blue glow there occurred a considerable improvement in vacuum. It was furthermore observed that this blue glow and clean-up also occurs if no phosphorus is used. "In improving the vacuum this latter way, however," states Dr. Whitney, "it is known that the filament is injured and apparently a part of its material has been vaporized. The process soon causes blackening of the lamp by carbon." The connection between blue glow and Edison currents in carbon lamps is also mentioned in the same paper. It was observed that if a platinum plate is sealed into a lamp and charged positively, a continuous current can flow to it from the negative half, or end of the filament, but not from the positive end. The current was found to vary with gas pressure and also the relative location of the plate in the lamp. At that time, of course, the phenomena of electron emission from heated filaments had not been studied thoroughly and for this reason no satisfactory explanation of the Edison effect could be given.

The observations on electron emission and clean-up effects in hot-cathode tubes obviously throw considerable light on this phenomenon. The negative end of the filament emits electrons,

⁴³ W. R. Whitney, *Trans. Am. Inst. Electrical Eng.* 31, 921 (1912).

and under the influence of the positive voltage produced by the other end of the filament the residual gas is ionized. Hence the appearance of blue glow. The positive ions are, then, cleaned up rapidly by the action of the voltage, in the same manner as has already been described, and the blue glow disappears.

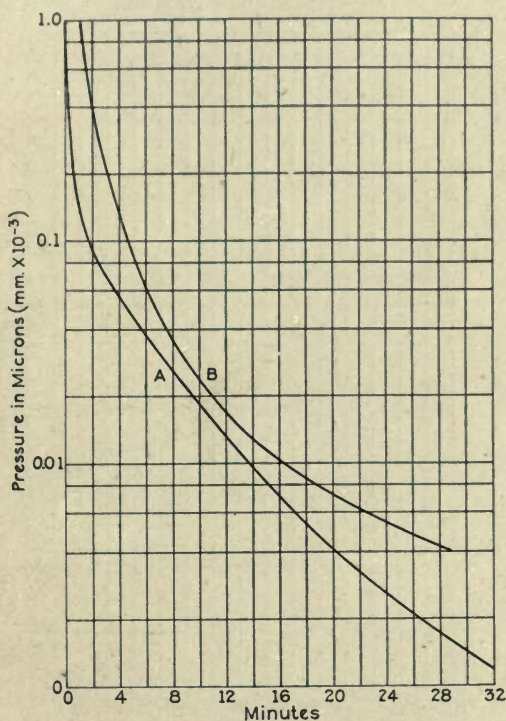


Fig. 72. Clean-up of Residual Air in 100-watt, 120-volt "Ungettered" Lamp

A—Initial pressure, 1.33 bar (1 micron)
 B—Initial pressure, 6.67 bar (5 microns)

The phenomena in tungsten lamps are similar to those observed in carbon lamps. While in the older process the phosphorus was distilled into the lamp from a top tube with simultaneous flashing of the filament, the present process consists in coating the wire with an alcoholic suspension of red phosphorus and some salt (to prevent subsequent blackening by evaporated

tungsten). After the lamp is exhausted and sealed off, it is flashed with gradually increasing voltage, and as the phosphorus is volatilized from the filament, blue glow occurs and the residual gases are cleaned up.⁴⁴

Before discussing the theories that have been suggested in explanation of the function of phosphorus in cleaning up residual

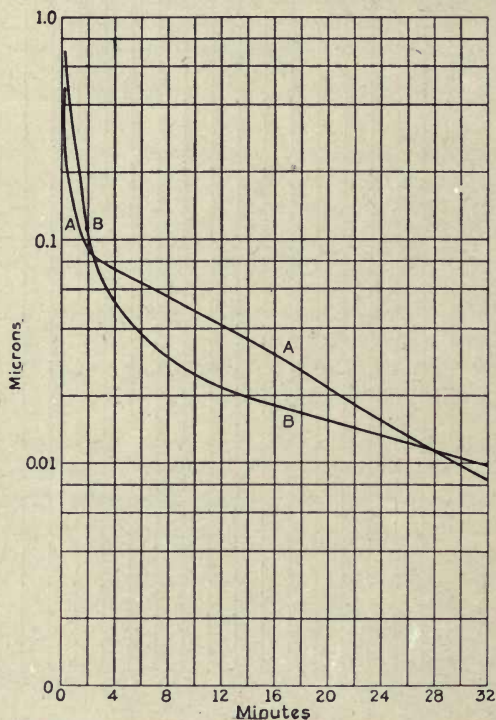


Fig. 73. Clean-up of Residual Air in 100-watt, 120-volt "Gettered" Lamp

A—Initial pressure 10 microns
B—Initial pressure, 5 microns

gases, it is of interest to mention some of the experimental results that have been obtained by H. Huthsteiner and S. Dushman on the rate of clean-up of gases in lamps under various conditions. Fig. 72 shows the clean-up of residual air in a regular type 100-watt, 120-volt lamp in which no phosphorus or other clean-up

⁴⁴ For similar observations see also S. Dushman, *Phys. Rev.* 4, 123 (1914), 5, 212 (1915). C. F. Hagenow, *ib.* 13, 415 (1919).

reagent was used. An ionization gauge attached to the lamp was used to measure the pressure. In lamp practice, any substance put on the wire or in the lamp for the purpose of either improving the vacuum or preventing blackening is known as a "getter." In these experiments therefore, of which the results are given

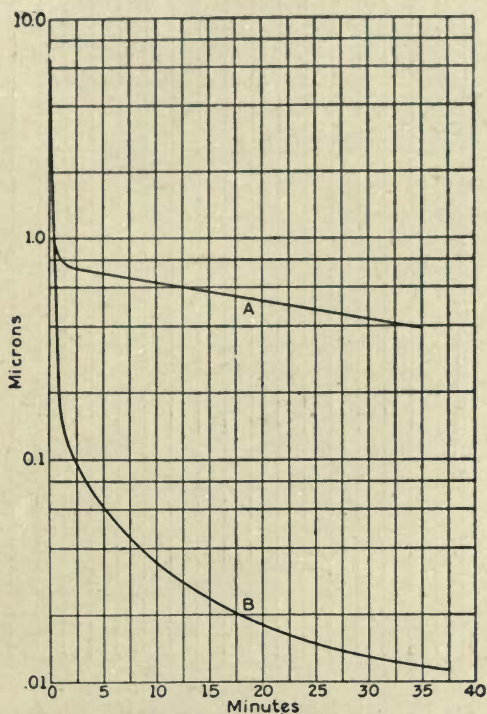


Fig. 74. Clean-up of Argon (Curve A) and Air (Curve B) in 100-watt 120-volt Phosphorus "Gettered" Lamp, Flashed at 144 volts

in Fig. 72, the lamps were ungettered. Before introducing the air at a definite initial pressure, the lamp and ionization gauge were well exhausted by baking out at 360 deg. C. for one hour on the pump and flashing the filaments to a high temperature, thus eliminating gases occluded in the glass walls and filament; the electrodes in the gauge were also well bombarded. Curve A shows the rate of clean-up with an initial pressure of 1.33 bar

(1 "micron,"*) and Curve *B* with an initial pressure of 6.67 bar (5 microns). The initial flash of blue glow disappeared in a fraction of a minute, and as will be observed from the curves most of the gas cleaned up in this period. The subsequent rate of clean-up was not as rapid. The flashing voltage used was 156

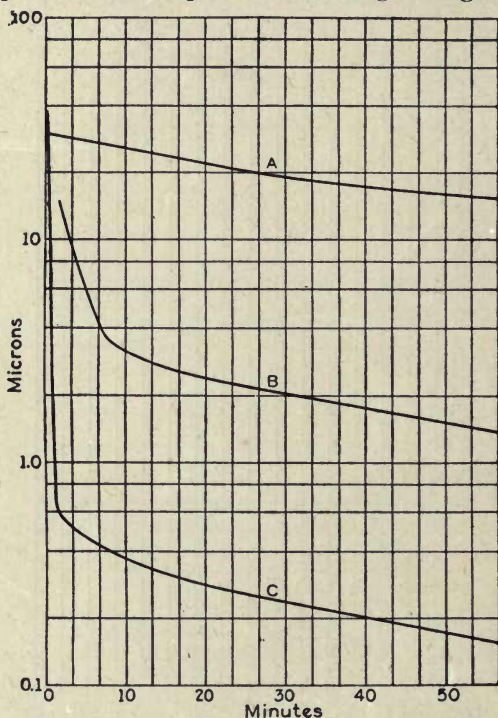


Fig. 75. Rate of Clean-up in Two-filament Kenotron
 Curve *A*—No red phosphorus, no voltage on second filament
 Curve *B*—No red phosphorus, 250 volts on second filament
 Curve *C*—Red phosphorus on leads of cathode filament, 250 volts on anode filament

volts, corresponding to 130 per cent of the normal operating voltage.

Fig. 73 shows the results obtained with a similar lamp in which red phosphorus was used as getter. In this case the lamp and gauge were exhausted as before, then air was let in, the lamp

* The micron, 1×10^{-3} mm. of mercury, is used as a convenient unit of pressure in lamp practice.

removed from the pump, and a suspension of red phosphorus in alcohol painted on the leads just below the filament. The combination was then re-exhausted, given a five-minute bake out at 360 deg. C. and sealed off. On flashing at 156 volts, the leads heated up sufficiently to volatilize the phosphorus and the clean-up curves shown in Fig. 73 were obtained.

In these cases, also, most of the gas cleaned up during the period of blue glow, and as will be seen by comparing these results with those shown in Fig. 72, the initial rate of clean-up is much greater in the presence of phosphorus. In the case of the lamp sealed off with air at 10 microns pressure, about 97 per cent of the gas disappeared in the first minute.

Fig. 74 shows the difference in the rate of clean-up of argon and air. In the case of argon (Curve *A*) the initial pressure was 6.5 microns, and in that of air (Curve *B*) the residual gas pressure was 4.5 microns. These observations also show the effect of phosphorus in accelerating the clean-up.

In general, over 90 per cent of the residual gas is cleaned up in a lamp during the blue glow period, and the rate of clean-up during this time is much more rapid than that obtained subsequently. The final pressure attained on flashing varies from 0.01 to 0.001×10^{-3} mm. of mercury. During life the pressure continues to decrease very slowly, and even after the filament burns out, there is no increase in pressure.

Observations with different types of lamps have shown that there is no appreciable clean-up below 30 volts, but the rate of clean-up increases rapidly as the voltage is increased above this value, and is extremely rapid in case of 220-volt lamps.

Theory Regarding Action of Phosphorus in Improving Vacuum

Any theory regarding the action of the phosphorus in incandescent lamps must primarily take into account the phenomena observed in hot-cathode devices. Fig. 75 shows some results obtained with a two-filament kenotron (similar to that used in studying electrical clean-up effects without phosphorus) on the clean-up of residual air. Curve *A* serves as the blank to take into account any purely chemical clean-up, while Curves *B* and *C* show the effect of the presence of phosphorus. These observations show definitely that the phosphorus is most effective during the blue glow period, as has already been emphasized in describing the clean-up phenomena in lamps. The similarity between Curves *B* and *C* and those obtained in incandescent lamps also leads to the conclusion that the clean-up phenomena in the latter and in hot-cathode devices must be quite similar

in origin, that is, the reactions probably involve the formation of ions as an essential intermediate stage.

The action of phosphorus in a lamp is undoubtedly not very simple. It may be partly chemical, as probably some P_2O_5 is formed in the presence of residual oxygen and this would assist materially in eliminating water vapor and hydrogen. In some experiments carried out by Messrs. Mackay and Huthsteiner, it was observed that very large amounts of hydrogen could be cleaned up by the action of P_2O_5 vapor in a lamp and that a black deposit was formed on the walls. This deposit was assumed to consist of solid compounds of hydrogen and phosphorus, although no conclusive evidence for this was obtained.

Also, as was mentioned in the discussion of clean-up effects at higher pressures, it is probable that under the influence of the discharge active modifications of the gases are produced which react readily with phosphorus. The fact that according to Newman, phosphorus, sulphur, and iodine are most effective in cleaning up hydrogen, while these three substances have also been found to be very efficient "getters" in cleaning up residual gas in lamps, lends much support to this point of view.

Phosphorus itself is a very interesting substance chemically. As is well known, it exists in at least two forms at ordinary temperatures—the white and the red. On heating the white to just below 247 deg. C., it is converted into the red modification. The latter has an extremely low vapor pressure even at 300 deg. C., while the white form is quite volatile. Again, on passing a discharge through the vapor of white phosphorus it is converted into the red modification which deposits as a fine yellow to red coloration on the walls of the glass bulb. This phenomenon has been investigated very fully by V. Kohlschütter and A. Frumkin.⁴⁵

One theory of the action of phosphorus which has some foundation is that the phosphorus vapor at the moment of condensation on the glass removes positive ions from the gas in much the same manner as C. T. R. Wilson observed in the case of supersaturated water vapor. In the latter experiments it was found that on suddenly expanding a gas saturated with water vapor (in order to condense this vapor) there was a removal of ions on the surface of the extremely small drops of water.

The most recent and most interesting contribution to the elucidation of this problem is that published by N. Campbell.⁴⁶ He finds in agreement with other investigators that on passing

⁴⁵ Zeits. f. Elektrochem. 20, 110 (1914).

⁴⁶ Phil. Mag. 14, 693 (1921). A short discussion of this subject has also been published by L. Hamburger, Proc. Amst. Acad. Sciences, 21, 1062 (1919), whose observations are on the whole similar to those recorded above.

a glow discharge through phosphorus vapor, it is converted into the red form, which deposits on the walls. Hydrogen, carbon monoxide, and nitrogen when mixed with phosphorus vapor clean up in the discharge very rapidly and in large amounts. An interesting observation (in accord with those made in this laboratory) is that "a lower final pressure can be reached with a given applied potential in the presence of phosphorus than in its absence." The explanation of this as given by Campbell is as follows:

"The absorption of gas ceases when the glow discharge ceases; and the glow discharge ceases when the falling glow potential becomes equal to the applied potential. The admixture of phosphorus vapor with the gas increases the pressure corresponding to any given partial pressure of the gas, and thus decreases the glow potential corresponding to that partial pressure. It therefore enables the discharge and the absorption of gas to continue when the partial pressure has fallen so low that, if the gas were present alone and its partial pressure were the total pressure, the potential applied could no longer be sufficient to maintain the discharge. When the partial pressure of the gas has fallen sufficiently, the phosphorus vapor, and not the gas, begins to disappear; and the disappearance of this vapor proceeds until the pressure of the phosphorus has fallen so low that the discharge can proceed no longer. And when the discharge ceases because the falling glow potential has become equal to the applied potential, it is not started again except by a very great increase of potential, owing to the wide difference between the falling and rising glow potentials in this vapor."

Furthermore, Campbell concludes that the reaction leading to the conversion of the phosphorus vapor into the red solid is reversible in presence of the discharge. The equilibrium is pushed towards the vapor phase when the red phosphorus on the walls is bombarded by positive ions, so that "as long as there is gas present in considerable quantity the conversion of white into red is never complete; there is always enough white phosphorus re-evaporating to maintain the discharge; and it is only when the gas has been greatly reduced in quantity that the equilibrium moves once more towards the solid phase, and a complete disappearance of all gaseous molecules is obtained."

This theory would account for the observation, often made in lamp practice, that clean-up effects can be made to occur in lamps in which red phosphorus is present on the bulb walls, instead of being on the leads or filament. The action in this case would be due to the bombardment of the red deposit by positive ions, with the resulting formation of a slight amount of vapor.

Regarding the chemical theory of the action of phosphorus, Campbell concludes that there is no evidence for any such theory and gives the following experimental observations to confirm this:

“(a) If the gas that has disappeared is restored, it is found to be in the same chemical state as it would have been if it had disappeared in the absence of phosphorus.

“(b) There is no simple relation between the quantity of gas that can be made to disappear and the quantity of phosphorus necessary for its disappearance. There is nothing approaching to a ‘law of constant proportions.’

“(c) The amount of gas that will disappear depends very greatly on the surface condition of the walls of the discharge vessel.”

As a working theory Campbell suggests that the red phosphorus covers the deposited gas and prevents it from being liberated again by bombardment. At the same time this red deposit provides a new surface on which gas can be absorbed. That the red phosphorus deposit adsorbs gas even in the absence of any discharge has been observed by the writer in a number of experiments.

From the point of view of this theory, it therefore is possible to account for the action of red phosphorus as used in lamp practice as follows: As well known the ordinary red phosphorus undoubtedly contains small traces of the white modification, as shown by the formation of P_2O_5 when it is exposed to air. Furthermore, when the glow discharge starts, some of the red phosphorus deposited on the walls becomes converted, as already stated, into the white form which volatilizes. This assists in maintaining the glow discharges at much lower residual gas pressures than is possible in the absence of phosphorus. The positive ions (or dissociation products according to Hughes) formed in the discharge are driven into the walls and immediately become covered with the red deposit. The gas pressure is therefore reduced very rapidly and finally reaches a value at which no glow discharge can occur with the given applied potential.

As mentioned by Dr. Whitney, arsenic, sulphur and iodine act in a similar manner to phosphorus in cleaning up gas in incandescent lamps. In fact any substance that can be readily sublimed acts in the same manner. It seems therefore that the most plausible theory would be that firstly the vapor formed by volatilization of these substances assists in maintaining a glow discharge at lower residual gas pressures, and secondly that the deposit formed by condensation of these vapors covers the gas driven into the walls (whether as positive ions or neutral dissociation products) and thus prevents it from being re-evolved readily.

CHAPTER VI

THEORY OF ADSORPTION AT LOW PRESSURES

Theory of Unimolecular Layer

In the preceding chapters we have discussed the different methods for the measurement and production of high vacua. This discussion has to some extent involved a certain amount of theoretical consideration of the principles involved, but in the main the object has been to present the matter from an experimental point of view. The theory has been, as it were, a by-product of the experiments.

There has, however, been developed in recent years a point of view of low pressure phenomena which is of extreme importance for a thorough understanding of the significance of observations in this field.

Although Dr. I. Langmuir developed this theory¹⁻² as a result of his numerous investigations on the kinetics of chemical reactions at low pressures and the effect of these pressures on the electron emission from heated solids, he was also inspired in this viewpoint by the results obtained by Laue, the Braggs, and others, on crystal structure.

As was first pointed out by these investigators, an examination of crystalline substances by means of X-rays leads to the conclusion that the atoms in such solids possess regular geometrical arrangements which correspond to the geometrical structure of the crystals themselves. Thus in a crystal of rock salt (*NaCl*), the atoms of sodium and chlorine are arranged at the alternate corners of a cube, each atom of sodium being surrounded by six of chlorine and each atom of chlorine by six sodium atoms. This is in agreement with the observation that sodium chloride crystallizes according to the cubical system.

The method used by the Braggs has been modified and applied by A. W. Hull to the investigation of the crystalline structure of metals, and at present we have definite knowledge regarding the arrangement of the atoms in a large number of metals, whenever these occur in the crystalline state.³

In order to account for this arrangement of atoms in solids Langmuir considers that there exist between these atoms both

¹I. Langmuir, "Chemical Reactions at Low Pressures," *J. Am. Chem. Soc.* **37**, 1139 (1915).

²I. Langmuir, "Constitution of Solids and Fundamental Properties of Solids and Liquids. Part I, Solids," *J. Am. Chem. Soc.* **38**, 2221 (1916).

These papers contain the most comprehensive discussion of Langmuir's theory of adsorption and its bearing on other phenomena at low pressures.

³A. W. Hull, "The Positions of Atoms in Metals," *Trans. Am. Inst. Elect. Eng.*, Oct. 10, 1919.

primary and secondary valence forces,² the latter differing from the former only in degree. It is therefore impossible to speak of a molecule of $NaCl$ in connection with a crystal of salt. The whole crystal constitutes a molecule whose composition is Na_xCl_x , where x is infinitely large. Only when the salt vaporizes do we have molecules corresponding to the formula $NaCl$ in the gas phase.

According to this point of view the layer of atoms constituting the surface of a solid would present unbalanced and unsaturated valences on their outer side. From well known thermodynamical considerations it follows that these atoms must tend to rearrange themselves so that the total energy in the field surrounding them is a minimum. In this manner we perceive that surface energy (surface tension of liquids also) is of the same nature as the energy of cohesion which holds the atoms together in the solid itself, and both cohesion and surface tension are to be regarded from this viewpoint as similar in nature to chemical forces. In fact, the distinction between so-called physical and chemical forces disappears on this basis. It would take us too far beyond the scope of the present discussion to mention the application which Langmuir has made of this suggestion to account for certain surface tension phenomena of liquids, but the subject is extremely interesting.⁴

As shown by Langmuir, "the attractive force between atoms in a solid becomes practically negligible when the distance between the centers of the atoms becomes twice as great as the distance at which the atoms are in equilibrium." This smallness of the range of atomic forces compels us therefore to conclude that "in general the distance through which the surface atoms are shifted from their original positions in the solid is small compared to the average distance between the atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only. The surface of a solid (or liquid) therefore does not contain, as is usually assumed, a transition layer consisting of several layers of atoms or molecules in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. *The surface of a crystal must then consist of an arrangement of atoms as definite as that existing in the interior of the crystals, although slightly different from the latter. The surface must thus be looked upon as a sort of checkerboard containing a definite*

⁴I. Langmuir, "The Constitution and Fundamental Properties of Solids and Liquids. Part II, Liquids," *J. Am. Chem. Soc.* 39, 1848 (1917), also "The Mechanism of the Surface Phenomena of Flotation," *Trans. Farad. Soc.* 15, 1 (1920).

number of atoms, of definite kinds arranged in a plane lattice formation.* The space between and immediately above (away from the interior) these atoms is surrounded by a field of electromagnetic force more intense than that between the atoms inside the crystal."

The existence of this field of force at the surface (which as before shown is due to the fact that the atoms there have only part of their valences satisfied) is according to Langmuir of fundamental importance in accounting for all the various phenomena that occur at the surface of a solid, such as the adsorption of gases, rates of chemical reactions, and the effect of gases on electron emission.

Adsorption is regarded from this point of view as the attachment of outside molecules or atoms to the exposed free valences of the atoms comprising the surface layer. As shown in Chapter I, equations (7a) and (7b), the rate at which gas molecules come in contact with a surface is given by the equation

$$\omega = p \sqrt{\frac{M}{2\pi RT}} \quad (7c)$$

where ω denotes the weight of the gas striking unit area per unit time, M is the molecular weight of the gas, R the gas constant, T the absolute temperature, and p the pressure.

Langmuir arrives at the conclusion that in almost all cases the molecules striking the surface *condense* on it. That is, there is practically little or no reflection.⁵ "This holds true at all temperatures. The surface film so formed tends to be a continuation of the space lattice of the solid. On the other hand, evaporation of such a film is going on as an independent process, being so rapid at high temperatures as to keep the surface practically clean. Adsorption is a direct consequence of the time lag between condensation and evaporation, and is the result of the kinetic equilibrium."⁶

Previous investigators had concluded that at the surface of a solid we usually have present an *adsorbed film of variable thickness*; that, in fact, the adsorbed film may be a large number of molecules (or atoms) thick, and attempts have even been made to calculate the density of this condensed gas on the surface. According to this older theory the speed of a reaction between a gas and a solid would be limited by the rates of diffusion of the reacting gas molecules and reaction products through the film.

*The italics are due to the writer.

⁵I. Langmuir, "The Evaporation, Condensation, and Reflection of Molecules and the Mechanism of Adsorption," *Phys. Rev.* 8, 149 (1916).

⁶J. W. McBain, "Theories of Occlusion, and the Sorption of Iodine by Carbon," *Trans. Faraday. Soc.* 14, 1 (1919).

According to Langmuir, however, *the thickness of the adsorbed film is almost never in excess of one molecule (or atom)*, and the rate of a chemical reaction at the surface of a metal is therefore "limited not by the rate of diffusion through the adsorbed film, but rather by the rate at which the surface becomes exposed by the evaporation of single molecules from an adsorbed layer one molecule deep." Similarly, in the case of electron emission, the adsorbed film covering the surface to a larger or smaller extent tends to lower the emission, and the actual decrease depends upon the equilibrium between the rate of condensation and that of evaporation of the gas. At low temperatures, where the rate of evaporation is lower, the film covers a larger extent of the surface, and the decrease is therefore much greater, while as the temperature is raised, the area covered by gas molecules decreases and at very high temperatures the emission therefore tends to approach that of the metal in a very good vacuum.

In the following sections we shall discuss the application of this theory to the phenomena of evaporation, adsorption, and chemical reactions at low pressures.

Evaporation of Metals in High Vacua

As has been shown, the rate at which molecules from a gas strike a surface is given by equation (7c).

In the case of most of the metals the vapor is monatomic. When such a metal in the solid state is in equilibrium with its own vapor, at a pressure p , this equation must give the rate at which the atoms from the vapor strike the surface. On the other hand, since there is equilibrium there are just as many atoms evaporating per unit area per unit time as condense. Consequently, the preceding equation must give the rate of evaporation of the solid at the temperature T , so that by observing the rate of decrease in weight of a given filament at any temperature T , it is possible to calculate the vapor pressure at this temperature. In this manner, Langmuir has measured the vapor pressure of metallic tungsten over the range of temperature from 2000 deg. K. to 3540 deg. K.⁷ and Langmuir and Mackay⁸ have obtained similar data for the metals platinum and molybdenum. M. Knudsen⁹ has shown that equation (7c) also holds accurately for the case of a clean surface of liquid mercury evaporating into a good vacuum.

Langmuir and Mackay have also applied the same method to the determination of the vapor tension data in the case of the

⁷I. Langmuir, Phys. Rev. 2, 329 (1913).

⁸I. Langmuir and G. M. J. Mackay, Phys. Rev. 4, 377 (1914).

⁹M. Knudsen, Ann. Phys. 47, 697 (1915).

metals iron, nickel, copper and silver, but have not published their results as yet. The method is so extremely simple that it ought to find a large field of application in the solution of certain metallurgical problems.

Adsorption at Low Pressures

The above theory leads to a precise definition of adsorption, as distinguished from absorption, occlusion and similar terms which are used quite loosely in the literature. We can speak of adsorption only as it relates to the gas which is condensed on the surface of any solid as a unimolecular layer. As already stated, adsorption is the direct result of a kinetic equilibrium between the rate of condensation and that of evaporation. "If the surface forces are relatively intense, evaporation will take place only at a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In the case of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer the surface forces are chemically saturated. Where, on the other hand, the surface forces are weak, the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules. In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of 10^{-8} cm. That is, the effective range of the forces is usually much less than the diameter of the molecules. The molecules thus usually orient themselves in definite ways in the surface layer, since they are held to the surface by forces acting between the surface and particular atoms or groups of atoms in the adsorbed molecule."¹⁰

The evidence adduced by Langmuir in favor of this theory is of a three-fold nature. First, there are "the observations of the electron emission from heated filaments in various gases at low pressures and of the velocity of chemical reactions in gases at low pressures." Second, direct experimental evidence was obtained that "thin oil films on the surfaces of liquids, as well as absorbed films of substances dissolved in liquids do not normally exceed one molecule in thickness." Third, Langmuir has actually carried out measurements on the amounts of gas adsorbed on three typical surfaces: those of glass, mica, and platinum, at pressures ranging around 100 bars or less. The results of these latter determinations are in accord with the above theory. It

¹⁰I. Langmuir, "The Adsorption of Gases on Plane Surface of Glass, Mica, and Platinum," *J. Am. Chem. Soc.* 40, 1361 (1918).

must of course be realized that extreme precautions were taken in this investigation to have the surfaces thoroughly freed of previously adsorbed gases before letting them come in contact with the gas whose adsorption was to be measured. "At room temperature the adsorption by mica and glass was negligible, certainly not over one per cent of the surface being covered by a single layer of molecules. At -183 and -118 deg. C., relatively large amounts of gas were adsorbed, except in the case of hydrogen, and at the higher pressures used the surfaces tended to become saturated with gas. The *maximum quantities adsorbed even with saturated surfaces were always somewhat less than the amounts to be expected in a unimolecular layer.* The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the following order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide. The adsorption of these gases was easily and quickly reversible."

On the other hand, in the case of platinum no adsorption of gases could be observed at even -183 deg. C. until the platinum had been previously "activated" by heating to 300 deg. C. in a mixture of hydrogen and oxygen. It was then found capable of adsorbing oxygen, carbon monoxide, or hydrogen, and the maximum quantities adsorbed corresponded to unimolecular layers. But the adsorption was not reversible, reactions apparently occurring on the surface "due to chemical forces of the primary valence type."

Before discussing the theoretical derivation of the relation between amount of gas adsorbed and the pressure observed in the above experiments, it may be well to point out the reasons given by Langmuir for the difference between these results and those observed by previous investigators on the adsorption of gases by charcoal and glass. "There appear to be three main reasons," he states, "which have led these investigators to conclude that adsorbed films are relatively thick. In most cases the experiments have been carried out with porous materials, such as charcoal, so that it has not been possible to determine with certainty the effective absorbing surface. Other workers have employed metal foil or other surfaces, of known area, but in order to get sufficiently large surfaces, have packed so much foil, etc., into small vessels that enormous numbers of capillary spaces were formed. They then employed saturated or nearly saturated vapors bringing about actual condensation of liquid in the capillary spaces. The third cause of error has consisted in the use of substances which actually dissolved the vapor thought to be adsorbed. The so-called adsorption of water-vapor by glass is an example of this kind."

In discussing, in Chapter IV, the sorption of gases by charcoal and glass and also the gas evolution from glass and metals at low pressures, a number of observations have been mentioned which are in agreement with this theory. It was mentioned in that connection that estimates have been made by various investigators of the effective surface per gm. of activated varieties of charcoal, and that on this basis, the largest amount of any non-condensable gas adsorbed by the charcoal would correspond to a layer less than one atom in thickness. Where the gas adsorbed is nearly saturated vapor (as is the case in a large number of the experimental observations), there is an actual condensation of liquid in the capillary spaces, so that in general we have, in the case of adsorption by charcoal, both condensation to liquid in the pores and true adsorption, or surface condensation.

On the other hand, as pointed out by Langmuir, it is hardly possible to conceive of charcoal as possessing an "effective surface," since it is very probable, in view of the observations made by Chaney¹¹ and others, that the porosity of charcoal and similar substances extends down to atomic dimensions.

The sorption of gases by glass has been another case where, according to Langmuir, actual solution of gases in the gel-like structure has been confused with true adsorption, and the experiments on the adsorption of gases by mica confirm this view.

Adsorption Relations

In 1909 Freundlich proposed¹² the semi-empirical relation between the quantity of gas adsorbed, q , and the pressure, p , at constant temperature, which has the form,

$$q = k \cdot p^{1/n} \quad (51a)$$

This equation has been mentioned previously in Chapter IV in connection with the adsorption of gases on charcoal. For low pressures or high temperatures, where the quantities adsorbed are small, the value of $\frac{1}{n}$ approaches unity, while at high pressures or low temperatures it often becomes as small as 0.1. These conclusions are well exemplified by the observations made by Claude and Titoff on the adsorption of gases by charcoal at various temperatures. Thus, referring to Table XVIII, Chapter IV, it will be observed that in the case of hydrogen $\frac{1}{n}$ is approx-

¹¹Trans. Am. Electrochem. Soc. 36, 91 (1919). See Chapter IV for discussion of these observations.

¹²Kapillarchemie Leipzig, 1909.

imately equal to unity at all temperatures and pressures. On the other hand, in the case of nitrogen and carbon dioxide, $\frac{1}{n}$ decreases rapidly with increases in pressure and temperature. On the whole, the relation has been found to be in very unsatisfactory agreement with experimental observations over large ranges of pressures.

Quite recently A. M. Williams¹³ has derived relations between the pressure, quantity adsorbed, and temperature by a combination of arguments based on thermodynamics and the kinetic theory of gases.

For the change in adsorption with temperature he obtains the relation

$$\log\left(q \cdot \frac{RT}{p}\right) = B + \frac{A}{T} \quad (55)$$

and for the adsorption isotherm, the relation

$$\log\left(q \frac{RT}{p}\right) = A_0 - A_1 q \quad (56a)$$

The latter may be expressed in the form

$$q/p = K \epsilon^{-A_1 q} \quad (56b)$$

where A_1 , A_0 , and K are constants at any temperature. It will be observed that for small values of q , that is, small amounts of adsorption, the exponential term is practically unity, so that at low pressures and high temperatures, the latter equation reduces to the simple form,

$$q = k \cdot p. \quad (57)$$

These relations are found by Williams to agree well with the observations mentioned previously on the adsorption of gases by charcoal, especially those of Miss Homfray. The kinetic theory considerations used in deriving the above relations led Williams also to interesting conclusions which are in agreement with Langmuir's theory. He finds on this basis that the surface area of the charcoal used by Miss Homfray was about 130 sq. meters per gram of adsorbent, which appears reasonable in view of the fact that activated charcoal has an estimated surface area of about 2500 sq. meters per gram. Furthermore, the theory enables Williams to determine the range of molecular attraction between adsorbent and gas, and he finds this to vary from 3.2 to 4.1×10^{-8} cm., that is, of the same order as the molecular

¹³Proc. Roy. Soc. (Edin.) 39, 48 (1919).
Proc. Roy. Soc. (London) 96, 287 (1919).

diameter. As already stated, Langmuir arrives at the conclusion that these forces must diminish to practically zero at distances which are twice as great as the distance at which the atoms are in equilibrium. The agreement in conclusions arrived at from totally different points of view is certainly striking.

As discussed above, Langmuir's theory regards adsorption as the result of a kinetic equilibrium between the rate of condensation and that of evaporation. On this basis the quantitative form of the adsorption isotherm, that is, the relation between amount adsorbed and pressure, at constant temperatures, depends upon the nature of the mechanism of both the condensation and evaporation.¹⁴ Langmuir points out that "the surface of crystals resembles to some extent a checkerboard, and when molecules of gas are adsorbed by such a surface these molecules take up definite positions with respect to the surface lattice and thus tend to form a new lattice above the old. A unit area of any crystal surface, therefore, has a definite number of 'elementary spaces,' each capable of holding one adsorbed molecule or atom. There will frequently be cases where there are two or three different kinds of spaces. * * * Each kind of elementary space will, in general, have a different tendency to adsorb gases. As the pressure of gas is increased the adsorption will then tend to take place in steps, the different kinds of spaces being successively filled by the adsorbed molecules." The phenomena that may be met in the study of adsorption are thus quite varied and may often be very complex. It is therefore not to be expected that one single equation should cover all cases of adsorption. As an illustration of Langmuir's mode of reasoning we shall discuss his derivation of the adsorption isotherm for the simplest case of adsorption, that in which we have only one kind of elementary space and in which each space can hold only one adsorbed molecule.

The number of gram-molecules striking unit area per second is, in accordance with equation (7c)

$$\mu = \frac{\omega}{M} = \frac{p}{\sqrt{2\pi MRT}} \quad (7d)$$

A certain fraction of these molecules, which we may call α , will condense. Consequently, the rate of condensation on a bare surface is $\alpha\mu$. If θ represents the fraction at any instant of the surface which is bare, the *rate of condensation* of gas on the surface is $\alpha\theta$. Similarly the *rate of evaporation* of molecules from the surface at this instant is $\nu\theta_1$, where $\theta_1 = 1 - \theta$ is the fraction

¹⁴I. Langmuir, J. Am. Chem. Soc. 40, 1361 (1918).

of the surface covered with molecules, and ν is the rate of evaporation from a surface completely covered.

At equilibrium,

$$\alpha\theta\mu = \alpha(1-\theta_1)\mu = \nu\theta_1 \quad (58)$$

Let us place

$$\frac{\alpha}{\nu} = \sigma$$

Then

$$\theta_1 = \frac{\sigma\mu}{1+\sigma\mu} \quad (59)$$

But we can write θ_1 in another form. Let N_0 denote the number of elementary spaces per unit area. Then, if q denotes the number of gram-molecules of gas adsorbed per unit area of surface,

$$q = \frac{N_0\theta_1}{N}$$

where $N = 6.062 \times 10^{23}$, the number of molecules per gram-molecule.

Substituting for θ_1 by means of equations (7d) and (59) it follows that

$$q = \frac{abp}{1+bp} \quad (60a)$$

where

$$b = \frac{\sigma}{\sqrt{2\pi MRT}}$$

and

$$a = \frac{N_0}{N}$$

It will be observed that for small values of b , that is, large values of ν , the above equation tends to approach the form

$$q = abp \quad (61)$$

That is, when the rate of evaporation is very high (at higher temperatures) and at low pressures, we have a linear relation between q and p .

In order to test equation (60a) Langmuir writes it in the form

$$\frac{p}{q} = \frac{1}{ab} + \frac{p}{b} \quad (60b)$$

so that by plotting $\frac{p}{q}$ against p , the slope of the straight line gives $\frac{1}{b}$, that is, $\nu\sqrt{2\pi MRT}$. In nearly all cases, the value of α

is practically unity. Hence it is possible to calculate from the observed values of b at any temperature the rate of evaporation per unit area. In the experiments with mica and glass, Langmuir finds that this relation is in good accord with the observed data for all the gases tested. His conclusions with regard to the thickness of the adsorbed film have already been discussed.

Instead of calculating the rate of evaporation, Langmuir has calculated the values of $\sigma = \frac{\alpha}{\nu}$ for the different cases. The

physical significance of this quantity is that it expresses the "relative life" of the molecules on the surface. Thus for oxygen adsorbed on mica at 90 deg. K., $\sigma = 97,000$ seconds, while at 155 deg. K., $\sigma = 69,000$ seconds. In a similar manner it is possible to calculate from the vapor tension data the relative life of a molecule at the surface of liquid oxygen at any temperature. A comparison of the values of σ thus calculated for the gases in the adsorbed state and the same gases in the liquid state shows that the relative life in the first case is anywhere from 10,000 to over 1,000,000 times as great as in the latter case. "The forces involved in the adsorption of these gases are thus very much more intense than those holding the molecules of the liquids together."

In a similar manner Langmuir derives relations for other cases of adsorption. An interesting case is that in which the gas is adsorbed as atoms (e.g., hydrogen by palladium); it is shown that under these conditions the amount adsorbed must vary as the square root of the pressure even at relatively low pressures.

It is evident from the previous discussion that in the case of porous substances, such as charcoal, no simple adsorption relation can hold valid, since we cannot speak of any definite surface, and furthermore, depending upon the magnitude of each individual space in such a structure, the rate of evaporation of adsorbed gas will vary tremendously.

Evidence for Adsorption Theory from Study of Chemical Reactions at Low Pressures

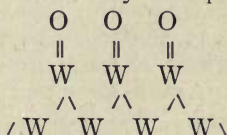
Most interesting evidence for the unimolecular layer theory of adsorption has been obtained by Langmuir in his numerous investigations on chemical reactions at low pressures. Some of these investigations have been mentioned in Chapter V in discussing chemical methods of clean-up. The interest in the present connection lies rather in the conclusions which Langmuir has derived regarding the mechanisms of these reactions.

Let us consider the reaction between *oxygen at low pressures and a heated tungsten filament*. At any temperature of the filament it is observed that the rate of clean-up is proportional to the pressure. From this rate it is possible to calculate the value of ϵ , the ratio between the number of molecules of oxygen disappearing per unit time and the number that strike the filament in that time. Table XXVIII shows how ϵ varies with the temperature.

TABLE XXVIII
RATE OF CLEAN-UP OF OXYGEN

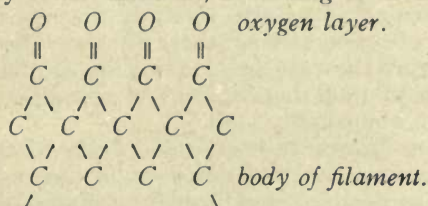
Temperature, Deg. K.	1070	1270	1470	1570	1770
ϵ	0.00033	0.0011	0.0053	0.0094	0.0255
Temperature, Deg. K.	2020	2290	2520	2770	
ϵ	0.049	0.095	0.12	0.15	

It is evident that ϵ is always less than unity, but tends to approach this value with increase in temperature. In order to form the oxide WO_3 , at least two molecules of oxygen must react with each atom of tungsten on the surface, and from considerations based on the kinetic theory of gases, Langmuir concludes that the manner in which this reaction occurs is as follows: The tungsten atoms on the surface adsorb oxygen atoms forming a layer which may be represented thus:

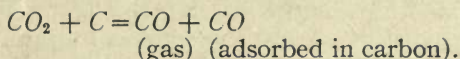


That is, oxygen atoms are held on the surface by means of primary valencies from the tungsten atoms. Oxygen molecules striking this layer combine with the group WO to form WO_3 which immediately distills off as a single molecule. The layer of oxygen combined with tungsten atoms on the surface is extremely stable. It will not react with hydrogen even at 1500 deg. K. This means that the surface of tungsten at this temperature is completely covered with a layer of oxygen one atom deep, and the presence of this oxygen acts as a catalytic poison for the reaction between hydrogen and oxygen. In a similar manner when a tungsten filament is heated in a mixture of carbon monoxide and oxygen, none of the CO reacts with the oxygen even with the filament temperature as high as 2800 deg. K., but the oxygen attacks the tungsten filament at the same rate as if CO were absent.

In view of what has been stated regarding the structure of active charcoal and its high capacity for adsorbing gases, the experiments on the reaction between *oxygen and carbon* are extremely interesting. "Experiments with carbon filaments in oxygen, and in carbon monoxide or dioxide, have shown that oxygen acts as a catalytic poison, on the reaction between oxygen and carbon, and on that between carbon dioxide and carbon. It was also proved that this poisoning effect is due to a remarkably stable film of adsorbed oxygen, so stable in fact that the filament must be heated in a good vacuum for nearly half an hour at 2300 deg. K. in order to distill it off. In this case there is very clear evidence that this film consists of oxygen atoms chemically combined by primary valencies to the carbon atoms forming the body of the filament, according to the formula."



With carbon dioxide evidence was obtained that the reaction occurs as follows:



The reaction between *carbon monoxide and oxygen in contact with platinum*¹⁵ is another illustration of the catalytic effect of an adsorbed film. The rate of clean-up in this case was observed to be directly proportional to the pressure of oxygen, but inversely proportional to the pressure of carbon monoxide. In order to account for this Langmuir assumes that the reaction occurs when *CO* molecules strike oxygen on the surface, but does not occur when *O*₂ molecules strike *CO* on the surface. Thus *CO* acts as a catalytic poison for the reaction at a platinum surface.

It is evident that this theory must exert a profound influence on our views of the phenomena of catalysis, a subject of immense importance in chemical technology, and there is no doubt that an application of Langmuir's theory to this field is going to bring about practical results of great value.

¹⁵I. Langmuir, Trans. Far. Soc. 17, Part 3 (1921). This paper is of special interest as it represents the application of the condensation theory to two historically noteworthy cases of catalysis by platinum: the reactions, $2 CO + O_2 = 2 CO_2$, and $2 H_2 + O_2 = 2 H_2O$.

Evidence for Adsorption Theory from Study of Effect of Gases and Thorium on Electron Emission of Tungsten

The effect of gases in decreasing the electron emission from heated metals has been studied in some detail by Langmuir¹⁶⁻¹⁷ and the observed phenomena are strikingly accounted for by the theory of adsorbed films one molecule in thickness. In fact, there is a remarkable similarity between the effect of these films in poisoning the catalytic activity of a filament and in decreasing the electron emission.

Thus oxygen and water vapor, which react with a tungsten filament forming an adsorbed layer of oxygen atoms, both lower the emission enormously even at very low pressures (0.001 bar). By observing the rate of decrease of emission when gas is let in, and the rate of increase of emission when the filaments are heated in vacuo it is possible to study the rate of formation and also the rate of evaporation of these films at various temperatures. "The fact that the rate of evaporation of these films even at temperatures of 1800 deg. K. is slow enough to measure proves that they are remarkably stable."

Nitrogen lowers the emission only when voltages high enough to cause ionization are used in measuring the electron currents. The positive ions formed by bombarding the nitrogen molecules with electrons form an adsorbed film on the surface of the filament and thus lower the emission. On pumping out the nitrogen and heating the filament to a high temperature this film gradually distills off and the emission returns to its normal value.

Interesting effects are obtained with tungsten filaments containing small amounts of thorium. If such a filament is heated in a very high vacuum to 2900 deg. K. for a short time and the electron emission at 1800 deg. K. is then measured, it is found that the emission is the same as that of pure tungsten. By now heating the filament a few minutes at about 2200 to 2300 deg. K., the electron emission at 1800 deg. K. is found to have increased over 10,000 fold, if the vacuum is very good. This effect is accounted for on the theory that thorium forms an adsorbed layer on the surface of the filament. At 2900 deg. K., the thorium, which is much more volatile than tungsten, distills off and leaves a surface of pure tungsten. At 2300 deg. K., the rate of evaporation of thorium is fairly low, but the rate of diffusion through the tungsten is sufficiently high to allow the

¹⁶"The Effect of Space Charge and Residual Gases on Thermionic Currents in High Vacuum," *Phys. Rev.* **2**, 450 (1913).

¹⁷"The Electron Emission from Tungsten and the Effect of Residual Gases," *Phys. Z.* **15**, 516 (1914).

accumulation of thorium atoms on the surface, while at 1800 deg. K., the rate of diffusion is so low that no more thorium comes to the surface. By studying the rate of increase of the emission at temperatures between 1800 and 2300 deg. K., and the rate of decrease of emission at temperatures above 2300 deg. K., it is possible to obtain data on the rates of diffusion and of evaporation of the thorium.

If a pure tungsten filament is adjacent to the thoriated filament and the latter is heated to a temperature at which the thorium evaporates fairly quickly, it is found that the pure tungsten filament gradually assumes the same electron emitting activity as the thoriated filament and there is very strong evidence that a layer of thorium one atom deep gives just as high an emission as a layer several atoms deep.

The effect of gases in lowering the emission of thorium is even more pronounced than in the case of tungsten. An adsorbed oxygen layer on the surface of thorium is so stable that it does not distill off unless the temperature of the filament is raised to 2900 deg. K.

Similar phenomena have been observed in studying the effect of gases on the photoelectric activity of metals and there is no doubt that in all these cases adsorbed films play an important role in decreasing the electron currents.

Evidence for Adsorption Theory Based on Viscosity Phenomena at Low Pressures

The fundamental postulate of Langmuir's theory that the fraction of the molecule impinging on any surface, which suffers specular reflection, is extremely small (or more usually, zero) is also supported by various observations on viscosity phenomena at low pressures.

In discussing the theory of viscosity manometers* it was pointed out that at these pressures there is distinct evidence of a slipping of gas molecules over planes.

At very low pressures the amount of momentum B , transferred from a plane moving with velocity u parallel to a stationary plane is given by the relation,

$$B = \frac{\eta u}{2\delta} = \frac{\eta u}{2aL} \quad (43a)$$

where δ is known as the "coefficient of slip," L denotes the mean free path, η , the coefficient of viscosity, and a is a constant whose value is given by the relation

$$\delta = aL \quad (62)$$

*Chapter III, p.92.

This relation holds valid only at such low pressures that the mean free path exceeds the distance between the moving and stationary planes.

Physically this relation is accounted for, as has been pointed out in a previous connection,* by the fact that at very low pressures the molecules can travel from one surface to the other without mutual collisions. We have here the condition designated by Knudsen as that of "molecular flow."

Knudsen,¹⁸ Timiriazeff¹⁹ and Baule²⁰ have attempted to derive a relation between δ and the mean free path (L).

According to the kinetic theory of gases

$$\eta = \frac{1}{3} \rho \Omega L \quad (10)$$

where ρ = density, Ω = average (arithmetical) velocity, and the factor $\frac{1}{3}$ has been taken as the average of the values 0.31 used by Meyer and 0.35 used by Boltzmann.†

Substituting for ρ and Ω the relations

$$\rho = \frac{Mp}{RT}$$

$$\Omega = \sqrt{\frac{8RT}{\pi M}} \quad (5)$$

we therefore obtain the relation

$$L = \frac{3}{4} \cdot \frac{\eta}{p} \sqrt{\frac{2\pi RT}{M}} \quad (63)$$

and consequently

$$\delta = \frac{3a}{4} \cdot \frac{\eta}{p} \sqrt{\frac{2\pi RT}{M}} \quad (64)$$

All the investigators mentioned above are agreed in the conclusion that the exact value of a must depend upon the ratio between the number of molecules reflected according to the laws of specular reflection and the number actually striking the surface. Knudsen assumes that in general this ratio is practically zero. In other words, the momentum of all the molecules striking a surface is practically completely transferred to this surface. On this basis he derives the relation

$$a = \frac{32}{9\pi} \cdot \frac{C_1}{C_2} \quad (65)$$

and determines experimentally the value of C_1/C_2 to be 0.81.

*Chapter I, p. 28.

†Chapter I, equations (11) and (12).

¹⁸M. Knudsen, Ann. Phys. 23, 75 (1908); 35, 389 (1911)

¹⁹A. Timiriazeff, Ann. Phys. 40, 971 (1913).

²⁰B. Baule, Ann. Phys. 44, 145 (1914).

Substituting this result in equation (62), we obtain the relation

$$\delta = 0.917 L \quad (66)$$

Timiriageff, on the other hand, assumes that the amount of reflection in viscosity effects is the same as that observed in heat conduction at low pressures (see below), and derives the relation

$$\delta = \frac{2-f}{f} \cdot \frac{2}{3} L \quad (67)$$

where f is the so-called "accommodation coefficient" for heat transfer in gases.

If we assume $f = 1$, as Knudsen does, we obtain the relation

$$\delta = 0.67 L \quad (68)$$

There is evidently here a difference between the deductions obtained by Knudsen and Timiriageff.

Baule, who has discussed the subject in considerable detail, disagrees with the assumption made by Timiriageff that f has the same value for both viscosity and heat conduction. The relation derived by him may be written in the simplified form

$$\delta = \frac{1+s}{1-s} \cdot \frac{2}{3} L \quad (69)$$

where s is a complicated function of the dimensions of the molecules in the gas and those constituting the surface. The value of this constant may vary from 0 to 0.5; consequently the value of δ lies between 0.67 and 2.0.

The actual experimental data on this subject are not sufficiently exact to make it possible to reach any certain conclusions. From his experiments on the flow of gases at low pressures through capillary tubes, Knudsen concluded that in the case of hydrogen there cannot be a specular reflection amounting to more than about one per cent. On the other hand, "Millikan²¹ has calculated the coefficient of slip from his measurements on the fall of small spheres and has calculated that the slip in air is about 10 per cent, and in hydrogen about 8 per cent greater than would be expected according to Knudsen's assumption regarding the absence of specular reflection."

Gaede²² has made the interesting observation that at pressures ranging from 0.001 mm. to 20 mm. the amount of gas

²¹Quoted by Langmuir, *Phys. Rev.* 8, 155 (1916).

²²*Ann. Phys.* 41, 289 (1913).

which flows through a narrow tube is *less* than that calculated by Knudsen on his theory. This would correspond to a *negative* value of the coefficient of slip, and Gaede therefore concludes from his measurements that a certain fraction of the incident molecules tend to return after collision in the direction from which they came.

“Temperature Drop” at a Surface in Gases at Low Pressures

In analogy with the existence of slip in viscosity effects at low pressures there has been observed in the case of heat conduction at low pressures between two surfaces the existence of a temperature drop at each surface corresponding to a fictitious distance γ . This constant is designated as the *coefficient of discontinuity of temperature*. The analogy between this coefficient and that of slip is seen from the relation for the heat transferred per unit area per unit time, which assumes the form

$$\frac{Q}{T_2 - T_1} = \frac{\kappa}{d + 2\gamma} \quad (70)$$

where κ is the heat conductivity. The similarity between this equation and equation (42) is evident.

The existence of this effect, although predicted by Kundt and Warburg as a result of their investigations on the coefficient of slip, was first observed and investigated theoretically by Smoluchowski²³ in 1898.

Assuming, as Maxwell did in his treatment of slip, that the fraction f of the incident molecule is absorbed and evaporated again with a velocity distribution corresponding to that in the still gas at the temperature of the solid, while the fraction $1-f$ is reflected, Smoluchowski derived a relation which may be written in the form

$$\gamma = \frac{2-f}{f} \cdot \frac{5}{4} L^* \quad (71)$$

Assuming that f in heat transfer has the same value as in the case of slip, it follows by comparison with equation (67) that

$$\gamma = \frac{15}{8} \delta \quad (72)$$

It will be observed that for $f=1$, equation (71) becomes

$$\gamma = 1.25L$$

Actually it was observed that between glass surfaces in air, $\gamma = 1.70L$ and in hydrogen, $\gamma = 6.96L$. According to equation (71) this would correspond to the values 0.85 and 0.305 for f in

²³Phil. Mag. 46, 192 (1898); Ann. Phys. 35, 983 (1911).

*Using the factor 0.31 in Meyer's equation for L in terms of η , Smoluchowski derives a relation with the coefficient $15/4\pi$ in place of $5/4$.

air and hydrogen respectively. That is, in the case of hydrogen, 69.5 per cent of the molecules striking a heated glass surface would suffer specular reflection.

Smoluchowski also suggested another method of considering this phenomenon. When molecules with kinetic energy corresponding to a temperature T_1 strike a surface at a higher temperature T_2 , the molecules leaving this surface have this temperature only if there is complete equalization of temperature during the act of impact on the plate. If this is not the case, the molecules leaving the surface have a temperature T intermediate between T_1 and T_2 such that

$$T - T_1 = \alpha(T_2 - T_1) \quad (73)$$

or

$$T = \alpha T_2 + (1 - \alpha)T_1$$

where α is a number less than unity, which has been designated as the "accommodation coefficient" by Knudsen.

At very low pressures, where the mean free path is greater than the distance between the plates, it can be shown that the amount of heat transferred per unit time per unit area and per unit difference of temperature between the plates is

$$Q = \frac{\alpha}{2 - \alpha} \cdot E \cdot p \quad (74)$$

where E denotes the molecular heat conductivity at the temperature T .

Since at these pressures

$$Q = \frac{\kappa}{2\gamma}$$

it follows that

$$\gamma = \frac{\kappa}{p \cdot E} \cdot \frac{2 - \alpha}{\alpha} \quad (75)$$

For a monatomic gas

$$\frac{\kappa}{p \cdot E} = 2.5 L \quad (76a)^*$$

For a diatomic gas

$$\frac{\kappa}{p \cdot E} = 1.83 L \quad (76b)^*$$

Hence for monatomic gases

$$\gamma = \frac{2 - \alpha}{\alpha} (2.5 L)$$

and for diatomic gases

$$\gamma = \frac{2 - \alpha}{\alpha} (1.83 L)$$

*These relations have been calculated from the equations given by Baule for E and the relations derived for κ in the kinetic theory of gases. See Chapter I, equations (15b), and (10).

For $\alpha=1$ we must therefore obtain values of γ which vary from 0.915 L in case of diatomic gases to 1.25 L in that of monatomic gases.

Baule²⁴ who, as previously mentioned, has critically discussed the whole problem of slip and temperature drop, has shown that it does not at all follow that the accommodation coefficient should be the same for both slip and heat conduction. Instead

of the value $\frac{\delta}{\gamma} = \frac{8}{15}$ as deduced by Smoluchowski, he concludes

that $\frac{\delta}{\gamma}$ must vary with the nature of the gas and that of the surface.

For the case of a nickel surface he calculates for air, carbon dioxide and hydrogen, the values 8/13, 8/13, and 8/80, respectively. These values are in substantial agreement with the experimentally observed results.

Langmuir²⁴ has adopted Baule's theory as a starting point but points out that the latter has failed in his arguments to take into account the existence of attractive (and repulsive) forces between the atoms on the surface and the colliding molecules. The existence of these forces would tend to lessen the velocity of molecules after collision and thus modify to a certain extent the values derived by Baule from theoretical considerations, and the conclusion is arrived at that the probability of any considerable amount of specular reflection is extremely small except in such a case as that of hydrogen.

Experimentally it has been found that in the latter case the coefficient of accommodation for heat transfer is only about 0.19. This is lower than that observed in any other case, and Langmuir has suggested various reasons for this exceptionally low value. On the whole the experimental work on temperature drop leads to the conclusion that the amount of specular reflection in heat transfer is ordinarily quite negligible and does not exceed a few per cent.

Recent Experiments of Wood and Knudsen on Condensation

Some more recent experimental observations made by R. W. Wood²⁵ and M. Knudsen²⁶ have been interpreted by these investigators as indicating that under certain conditions there may be considerable reflection of molecules at surfaces upon which they impinge. In Wood's experiments a stream of cadmium vapor in a well exhausted bulb was allowed to strike a glass

²⁴For a summary of Baule's discussion, the reader may consult Langmuir's paper, *Phys. Rev.* 8, 149 (1916).

²⁵*Phil. Mag.* 30, 300 (1915); 32, 364 (1916).

²⁶*Ann. Phys.* 50, 472 (1916).

surface at different temperatures. No visible deposit was observed unless the glass was held at a temperature below about -90 deg. C. On the other hand, once a deposit was started by cooling the glass at that spot with liquid air, the deposition of cadmium continued even after the deposit was warmed to room temperature.

From these and similar observations Wood concluded that while cadmium atoms condense on a cadmium surface at any temperature, they condense on glass only if the temperature is below about -90 deg. C. At higher temperatures all the atoms are reflected.

Similar observations have been made by Knudsen and still more recently by J. Weyssenhoff.²⁷ Knudsen experimented with mercury vapor and observed that at temperatures above -130 deg. C. most of the molecules impinging on a glass surface were apparently reflected. With other vapors a similar "critical temperature" was observed above which no condensation occurred. In the case of NH_4Cl , this critical change occurred at -183 deg. C., in that of copper at temperatures varying between 350 deg. and 575 deg. C., while in the case of zinc, cadmium and magnesium, the critical range extended between -183 deg. and -78 deg. C. All these observations held true only for a glass surface. On the other hand, mercury atoms condensed on a mercury surface at all temperatures. This latter observation had been made by Knudsen in a previous investigation,²⁸ and in fact he had applied equation (7c) to determine the vapor tension of mercury at extremely low temperatures from the rate of evaporation. As has been pointed out in a previous connection, the application of this equation involves the assumption that there is no reflection of atoms of the vapor striking the surface from which evaporation is occurring.

Weyssenhoff carried out some experiments in order to determine the amount of reflection of mercury atoms striking surfaces of gold and iron. While no absolute determinations of the amount of reflection were obtained, he concludes from his experiments that at -100 deg. C., the reflection from gold is 5 to 10 times less than that from iron.

These observations have been interpreted by these investigators as indicating that at some temperature the accommodation coefficient for condensation changes very rapidly from zero to unity. Langmuir has, however, repeated Wood's experiments²⁹ and concludes from his observations that this deduction is not justifiable.

²⁷Ann. Phys. 53, 505 (1919).

²⁸Ann. Phys. 43, 1113 (1915).

²⁹Proc. Nat. Acad. Sciences 3, 141 (1917).

In his experiments, Langmuir used cadmium vapor in a well exhausted bulb and investigated the effect of cooling a portion of the glass surface to different temperatures. He finds that "traces of residual gas may prevent the growth of the deposit, particularly in those places which have been most effectively cooled. This is probably due to the adsorption of the gas by the cooled metal deposit." By using a side tube containing charcoal immersed in liquid air this effect was eliminated.

"If all the cadmium is distilled to the lower half of the bulb and this is then heated to 220 deg. in an oil bath while the upper half is at room temperature, a fog-like deposit is formed on the upper part of the bulb in about fifteen seconds. This deposit is very different from that obtained by cooling the bulb in liquid air. Microscopic examination shows that it consists of myriads of small crystals. According to the condensation-evaporation theory, the formation of this fog is readily understood. Each atom of cadmium, striking the glass at room temperature, remains on the surface for a certain length of time before evaporating off. If the pressure is very low, the chance is small that another atom will be deposited, adjacent to the first, before this has had time to evaporate. But at higher pressures this frequently happens. Now if two atoms are placed side by side on a surface of glass, a larger amount of work must be done to evaporate one of these atoms than if the atoms were not in contact. Not only does the attractive force between the cadmium atom and the glass have to be overcome, but also that between the two cadmium atoms. Therefore, the rate of evaporation of atoms from pairs will be much less than that of single atoms. Groups of three and four atoms will be still more stable. Groups of two, three, four atoms, etc., will thus serve as nuclei on which crystals can grow. The tendency to form groups of two atoms increases with the square of the pressure, while groups of three form at a rate proportional to the cube of the pressure. Therefore the tendency for a foggy deposit to be formed increases rapidly as the pressure is raised or the temperature of the condensing surface is lowered.

"On the other hand, according to the reflection theory, there seems to be no satisfactory way of explaining why the foggy deposit should form under these conditions.

"Experiments show clearly that when a beam of cadmium vapor at very low pressure strikes a given glass surface at room temperature, no foggy deposit is formed, although when the

same quantity of cadmium is made to impinge against the surface in a shorter time (and therefore at higher pressure) a foggy deposit results. This fact constitutes strong proof of the condensation-evaporation theory.

"A deposit of cadmium of extraordinarily small thickness will serve as a nucleus for the condensation of more cadmium at room temperature. Let all the cadmium be distilled to the lower half of the bulb. Now heat the lower half to 60 deg. C. Apply a wad of cotton, wet with liquid air, to a portion of the upper half for one minute, and then allow the bulb to warm up to room temperature. Now heat the lower half of the bulb to 170 deg. C. In about thirty seconds a deposit of cadmium appears which rapidly grows to a silver-like mirror. This deposit only occurs where the bulb was previously cooled by liquid air."

Langmuir calculates from the vapor pressure data for cadmium that "a deposit which forms in one minute with the vapor from cadmium at 60 deg. contains only enough cadmium atoms to cover $3/1000$ of the surface of the glass. Yet this deposit serves as an effective nucleus for the formation of a visible deposit."

At lower temperatures where the vapor pressure is much smaller the probability that the atoms striking the glass will fall into positions adjacent to atoms already on the surface becomes very much smaller and the latter re-evaporate before this occurs, consequently there is no apparent condensation. Langmuir states the difference between his point of view and that of Wood and the others quite clearly:

"When an atom strikes a surface and rebounds elastically from it, we are justified in speaking of this process as a reflection. Even if the collision is only partially elastic, we may still use this term. The idea that should be expressed in the word 'reflection' is that the atom leaves the surface by a process which is the direct result of the collision of the atom against the surface.

"On the other hand, according to the condensation-evaporation theory, there is no direct connection between the condensation and subsequent evaporation. The chance that a given atom on a surface will evaporate in a given time is not dependent on the length of time that has elapsed since the condensation of that atom. Atoms striking a surface have a certain average 'life' on the surface, depending on the temperature of the surface and the intensity of the forces holding the atom. According to the 'reflection' theory, the life of an atom on the surface is simply the duration of a collision, a time practically independent of temperature and of the magnitude of the surface forces.

"The above experiments prove," as stated by Langmuir, "that the range of atomic forces is very small and that they act only between atoms practically in contact with each other. Thus a surface covered by a single layer of cadmium atoms behaves, as far as condensation and evaporation are concerned, like a surface of massive cadmium."

In this manner it is possible therefore to account very well for the apparent reflection of cadmium and mercury from glass surfaces and it is seen that these observations are not all in contradiction with Langmuir's theory.

The most recent experiments on this subject are those of M. Volmer and I. Estermann.³⁰ They conclude that for liquid mercury, the accommodation coefficient (α) for condensation is unity, while for the solid it is slightly smaller. They also state that for other substances, such as sulphur, phosphorus and benzophenone, they have observed values of α varying from 0.2 to 0.5. On the whole, they are in accord with Langmuir in concluding that the first stage in the condensation of molecules on a crystalline surface consists in adsorption. They, however, make the additional assumption that these adsorbed molecules possess a certain degree of mobility, thus accounting for the observation that crystals produced by condensation from a vapor grow more in certain directions.

Concentration Drop at a Surface

As pointed out by Langmuir³¹ "the diffusion of one gas through another is a phenomenon closely related to heat conduction. In the case of the evaporation of a solid surrounded by a gas, where the vapor must diffuse outward through the gas, the partial pressure of the vapor at the surface of the solid will be less than that of the saturated vapor. In other words there will be a 'concentration drop' at the surface, just as there is a 'temperature drop' in the analogous case of heat conduction, and a 'slip' in gases where viscosity effects are involved. Analogy suggests that this concentration drop will be inversely proportional to the pressure."

Thus, in the case of a tungsten filament evaporating in argon it is to be expected that there will be a difference in the concentration of the tungsten vapor at the surface and that existing at a distance from this surface, corresponding to the mean free path of tungsten atoms in the particular pressure of argon.

³⁰M. Volmer and I. Estermann, *Zeits. f. Physik*, 7, 1 and 13 (1921).

³¹*J. Am. Chem. Soc.* 37, 419 (1915).

This drop in concentration is a maximum in vacuo and decreases as the pressure of argon is increased, thus tending to prevent more and more the escape of tungsten atoms from the filament. Consequently the actual rate of evaporation of tungsten is decreased by the presence of the gas, as atoms of tungsten colliding with gas molecules tend to be thrown back towards the surface of the tungsten.³²

When hydrogen molecules strike a heated filament they are partly dissociated into atoms. As a result there is a drop in concentration of both atoms and molecules at the surface of the filament, and Langmuir has shown how the actual magnitude of this drop can be calculated in this particular case.

Significance of ϵ and its Relation to the Accommodation Coefficient

Mention has been made quite frequently of the quantity ϵ introduced by Langmuir in his discussion of chemical reactions at low pressures. By definition, ϵ is the ratio between the number of molecules actually used up in any reaction and the total number of collisions in unit time. Thus, in the case of oxygen reacting with a heated tungsten filament, ϵ is the ratio between the number of molecules of oxygen disappearing per unit time per unit area, and the number of molecules of oxygen striking unit area per unit time. In the case of reaction between two gases, such as tungsten vapor and nitrogen, ϵ is the ratio between the number of atoms of tungsten combining with N_2 molecules to form WN_2 and the number of collisions between W atoms and N_2 molecules in unit time.

In the latter case, Langmuir finds that ϵ is equal to unity, that is, combination occurs at every collision, while in the reaction between oxygen and tungsten ϵ is extremely small at low temperatures and tends towards unity as the temperature is increased to very high values. In order to account for this observation, Langmuir assumes³³ that oxygen atoms striking the filament condense either as O_2 or $O-O$, forming either WO_2 or WO on the surface, and these two forms are in equilibrium at any temperature. An oxygen molecule striking WO forms WO_3 which distills off; on the other hand, an oxygen molecule striking WO_2 does not react with it. Thus the low value of ϵ at lower temperatures is referred to the presence of a very stable layer of WO_2 on the surface, and this view is confirmed by the behavior of hydrogen-oxygen mixtures in presence of a heated tungsten filament.

³²I. Langmuir, Am. Inst. Elect. Eng., Oct. 10, 1913, p. 1895.

G. M. J. Mackay, Trans. Illum. Eng. Soc., Sept., 1914.

³³J. Am. Chem. Soc. 37, 1139 (1915).

In a similar manner, Langmuir accounts for low values of ϵ in other reactions between gases and a metal surface by the theory that some constituent adsorbed on the surface acts as a catalytic poison for the reaction. The point is that the low values of ϵ are not due to any reflection of gas molecules from the metal surface. There is every evidence, as has been repeatedly stated, that the accommodation coefficient is in general approximately equal to unity, and therefore low values of ϵ whenever they are observed in heterogeneous chemical reactions must be accounted for by some condition of the surface.

It has already been stated that the accommodation coefficient for hydrogen in viscosity effects is practically unity. However, in the case of heat transfer there is good evidence that the accommodation coefficient is much lower. Langmuir has observed³⁴ that at temperatures up to about 1500 deg. K., at a tungsten surface, the accommodation coefficient is about 0.19. "In other words, only about 19 per cent of all the hydrogen molecules striking the filament reach *thermal* equilibrium with it before leaving it." This is in good agreement with the value 0.26 obtained by Knudsen with platinum at room temperature. On the other hand, at high temperatures it is observed that 68 per cent of all the hydrogen molecules striking the filament reach *chemical* equilibrium before leaving it. "The explanation of this apparent paradox is that the surface of the tungsten is largely covered by adsorbed hydrogen at lower temperatures, whereas at the higher temperatures it is practically bare. The 19 per cent thus corresponds to the fraction of the molecules which condense when they strike a surface already covered with hydrogen, while the 68 per cent represents the fraction condensing on a bare surface."

In the case of the homogeneous gas reactions so far investigated by Langmuir, ϵ has been observed to be unity. If any cases should be found in which it is less than this, the most plausible assumption would be that the molecules must collide in some particular manner in order that reaction should occur, and this might easily be expected where the molecules are large and complex. In another connection the author recently carried out some calculations on the velocities of decomposition and formation of hydrogen iodide.³⁵ It was found that the observed velocities could be quantitatively accounted for by the theory that *every collision* between hydrogen and iodine molecules is effective in the formation of hydrogen iodide, and simi-

³⁴J. Am. Chem. Soc. 38, 1147 (1916).

³⁵S. Dushman, J. Am. Chem. Soc. 43, 397 (1921).

larly every collision between hydrogen iodide molecules is effective in producing hydrogen and iodine. In a similar manner the conclusion was drawn that in the case of the dissociation of iodine vapor (I_2) into atoms, every collision between the atoms must lead to the formation of a molecule of I_2 . So that there is no evidence that would point to any reflection in collisions between atoms or simply constituted molecules. It is, however, probable that in the dissociation of such a complex molecule as $(CH_3COOH)_2$ not every collision between the dissociation products would result in the formation of a di-acetic acid. Association would then occur only when certain groups in each molecule are adjacent. The possible existence of such a "steric" factor has been pointed out by other investigators, but further investigation is necessary before any definite conclusions regarding this point can be formed.

APPENDIX II

For the convenience of those engaged in high vacuum investigations, the following tables have been added, which give a summary of formulas from the kinetic theory of gases, molecular data and various constants. The formulas given in Table I have all been discussed in different chapters and are gathered together here for convenience of reference. Table II contains formulas and data which are of importance in dealing with electron emission phenomena in high vacua.¹ Tables III and IV represent an amplification and revision of similar data published by the writer in 1915, as an appendix to a series of papers dealing with the kinetic theory of gases.² The reader is therefore referred to this publication for a discussion of the method of deriving these constants and for references to previous literature.

Table III gives molecular data which are of special interest in high vacuum work. The values have been calculated from the equations given in Table I, for a temperature of 25 deg. C., as this is the most usual room temperature. In the calculation of the mean free path, the values of η used were those derived from the coefficients of viscosity at 0 deg. C. as tabulated in the publication referred to, corrected for 25 deg. C. by means of Sutherland's formula. The values given for the molecular diameters were taken from the tables given there. For the case of monoatomic vapors from metals an approximate value of the molecular (or atomic) diameter (d_m) may be obtained from the density, ρ , and the atomic weight, A , by means of the relation

$$\frac{1}{d_m} = \sqrt[3]{\frac{\rho \times N}{A}} = \sqrt[3]{\frac{\rho \times 6.062 \times 10^{23}}{A}}$$

Hence the number of atoms per cm.² required to form a layer 1 atom deep is

$$1/d_m^2 = 10^{15} \times 7.163 \left(\frac{\rho}{A}\right)^{2/3}$$

Comparing the values given in Table IV with those published in 1915, it will be observed that the value of Planck's constant, h , generally accepted at present is 6.55×10^{-27} . This is probably accurate to about 0.15 per cent. The enormous

¹I. Langmuir, *Phys. Rev.* **2**, 450 (1913); *Trans. Am. Electrochem. Soc.* **29**, 125 (1916).

A. W. Hull, *Phys. Rev.* **18**, 31 (1921).

H. D. Arnold, *Phys. Rev.* **16**, 70 (1920).

²General Electric Review, **18**, 952, 1042, 1159 (1915). See also W. C. McC. Lewis, "A System of Physical Chemistry," Vol. III, Quantum Theory (1919). An excellent little volume on the same subject has recently been published by Armand Colin, Paris. It is entitled, "Théorie Cinétique des Gaz" par E. Bloch.

number of investigations carried out in the past few years on the determination of this constant have been summarized by R. T. Birge³ and R. Ladenburg.⁴

The former arrives at the value $h = 6.5543 \pm 0.0025$, while Ladenburg concludes that the most probable value is 6.54×10^{-27} erg. sec. The value given in Table IV is the approximate average of these. This value had been used in calculating the radiation constants in the Planck and Wien equations given in the table. It ought to be noted that in recent publications from the Nela Research Laboratories the value of $c_2 = 1.435$ cm. deg. has been used.⁵ This agrees with the value $h = 6.564$. On the other hand, the value $h = 6.55$ leads to the derived value $c_2 = 1.432$. For this reason both values of c_2 have been given in the table, and for the present it is recommended that in all investigations dealing with optical pyrometry the value $c_2 = 1.435$ be used.

The value $e/m = 1.769 \times 10^7$ is that given by Ladenburg. Sommerfeld in his book on "Atombau und Spektrallinien" (Nov., 1919) calculates the value 1.7686. In a recent paper⁶ Langmuir has drawn attention to a method of deriving h which is independent of Millikan's determination of e (the value given in the table). The chemical "integration constant," C , has attained considerable importance in recent years, in connection with calculations of vapor pressures and equilibrium constants of chemical reactions.⁷ At present the value usually adopted is that based on the equation given in Table IV.

³Phys. Rev. 14, 361 (1919).

⁴Jahrbuch d. Elektronik, 17, 93 (1920).

⁵See especially the "1919 Report of Standards Committee on Pyrometry," by W. E. Forsythe, J. Opt. Soc. Am. 4, 305 (1920).

⁶J. Franklin Inst., May, 1920, p. 603.

⁷R. Ladenburg, Jahrb. d. Rad. u. Elektronik, 17, 273 (1921).

APPENDIX II
TABLE I
FORMULAS FROM KINETIC THEORY OF GASES

(1) *Velocity of molecules*

$$\text{Root-mean-square velocity, } G = \sqrt{\frac{3 RT}{M}} = 15,800 \sqrt{\frac{T}{M}} \text{ cm. sec.}^{-1}$$

$$\text{Average (arithmetical) velocity, } \Omega = \sqrt{\frac{8 RT}{\pi M}} = 14,551 \sqrt{\frac{T}{M}} \text{ cm. sec.}^{-1}$$

$$\text{Most probable velocity, } W = \sqrt{\frac{2 RT}{M}} = 12,900 \sqrt{\frac{T}{M}} \text{ cm. sec.}^{-1}$$

(2) *Amount of gas striking unit area per unit time*

$$m = (1/4) \rho \Omega, \text{ where } \rho = \text{density}$$

$$= 43.74 \times 10^{-6} p \sqrt{\frac{M}{T}} \text{ gm. cm.}^{-2} \text{ sec.}^{-1} \text{ (} p \text{ in bars)}$$

$$= 58.32 \times 10^{-3} p \sqrt{\frac{M}{T}} \text{ gm. cm.}^{-2} \text{ sec.}^{-1} \text{ (} p \text{ in mm. mercury)}$$

$$n = \text{No. of molecules} = 6.062 \times 10^{23} \frac{m}{M} = 2.653 \times 10^{19} \frac{p}{\sqrt{MT}} \text{ cm.}^{-2} \text{ sec.}^{-1} \text{ (} p \text{ in bars)}$$

$$= 3.535 \times 10^{22} \frac{p}{\sqrt{MT}} \text{ cm.}^{-2} \text{ sec.}^{-1} \text{ (} p \text{ in mm. mercury)}$$

(3) *Mean free path*

$$L = \frac{3}{\rho \Omega} \eta = 17.15 \times 10^3 \frac{\eta}{p} \sqrt{\frac{T}{M}} \text{ (} p \text{ in bars; } \eta = \text{viscosity in c.g.s. units)}$$

$$= 12.86 \frac{\eta}{p} \sqrt{\frac{T}{M}} \text{ (} p \text{ in mm., } \eta \text{ in c.g.s. units)}$$

(4) *Speed of exhaust*

$$S = 2.303 \frac{V}{l} \log \frac{p_1}{p_2} \quad (\text{ordinary logs})$$

where V = volume exhausted (in cm.³).

p_1 = initial pressure.

p_2 = pressure at end of period t (in sec.).

(5) *Rate of flow of gases through an opening or tube*

$$F = \frac{Q}{P_2 - P_1} = \frac{9.118 \times 10^3 \sqrt{T}}{W} \sqrt{\frac{T}{M}} \quad (\text{cm.}^3 \text{ at 1 bar})$$

where $P_2 - P_1$ = pressure difference in bars.

and $W = \frac{3.184}{D^2}$ for circular opening of diameter D cm.

$$= \frac{2.394 L}{D^3} + \frac{3.184}{D^2} \quad \text{for tube of length } L, \text{ and diam. } D.$$

RATE OF FLOW OF AIR AND HYDROGEN AT LOW PRESSURES AND 20 DEG. C.

L	D	W	F (Air)	F (Hydrogen)
1 cm.	1 cm.	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

[NOTE. — These relations are valid for pressures so low that the mean free path is equal to or greater than D .]

For pump exhausting through resistance

$$\frac{1}{S_o} = \frac{1}{S_p} + \frac{1}{F}$$

where S_o = observed speed of exhaust.

S_p = speed of pump through negligible resistance.

TABLE II
LAWS OF ELECTRON CURRENTS IN HIGH VACUA

(1) *Richardson's Equation:* $i = A \sqrt{T} e^{-b/T}$
If i = saturation current in amperes per cm.² at temperature T , the values of A and b are as follows:

Substance	A	b	i at 2000° K
W	23.6×10^6	52,500	0.0042
Mo	21.0×10^6	50,000	0.013
C (untreated)	200×10^6	48,000	
Th	16×10^4	39,000	30.0
Oxide coated Pt.		20,000	325

(2) *Space Charge Equations (Langmuir)*

- (a) For filament in axis of cylinder of radius r cm. Current per cm. length, $i = \frac{2\sqrt{2}}{9} \sqrt{\frac{e}{m}} \cdot \frac{V^{3/2}}{r} = \frac{14.69 \times 10^{-6}}{r} V^{3/2}$ amps., where V = anode volts.
- (b) For parallel plane electrodes separated by d cm. Current per cm.², $i = \frac{2.33 \times 10^{-6}}{d^2} V^{3/2}$ amps.

(3) *Effect of Magnetic Field (Hull)*

For filamentary hot cathode in axis of cylindrical anode of radius r

$$H = \sqrt{\frac{8m}{\epsilon}} \cdot \frac{V^{1/2}}{r}$$

where H = magnetic field strength required to decrease electron current to zero with anode potential V .
For H in gauss, V in volts, and r in cm.

$$H = \frac{6.725 \sqrt{V}}{r}$$

TABLE III
MOLECULAR DATA

	H ₂	He	N ₂	O ₂	A	Hg	CO	CO ₂	H ₂ O
Mass of molecule Unit = gm. $\times 10^{-24}$	3.326	6.582	46.23	52.78	65.79	330.9	46.20	72.59	29.73
Mean velocity at 25 deg. C. Unit = cm. $\times 10^5$ sec. ⁻¹	1.922	1.366	0.515	0.482	0.432	0.193	0.515	0.411	0.643
Average velocity at 25 deg. C. Unit = cm. $\times 10^5$ sec. ⁻¹	1.769	1.257	0.475	0.444	0.398	0.177	0.474	0.379	0.592
Mean free path (in cm.) at 25 deg. C. and 1 bar	19.2	29.6	10.0	10.7	10.6	[3.24]*	9.92	6.68	[6.03]*
Molecular diameter (<i>d</i>) Unit = cm. $\times 10^{-8}$	2.4	1.91	3.15	3.0	2.9	3.0	3.2	3.3	2.9
(1/ <i>d</i>) ² $\times 10^{-15}$ Number of molecules per cm. ³	1.74	2.74	1.01	1.11	1.19	1.11	0.98	0.92	1.19
Mass of gas striking 1 cm. ² per sec at 25 deg. C. and 1 bar Unit = gm. $\times 10^{-6}$	3.597	5.062	13.42	14.33	16.01	35.89	13.42	16.81	10.76
Number of molecules striking 1 cm. ² per sec. at 25 deg. C. and 1 bar Unit = 10 ¹⁷	10.82	7.693	2.837	2.717	2.433	0.1085	2.837	2.317	3.620

*Values in square brackets refer to 0 deg. C.
NOTE.—1 bar = 0.75×10^{-3} mm. mercury.

TABLE IV
ATOMIC AND ELECTRONIC CONSTANTS

Volume per gram-molecular weight of ideal gas.	
At 0 deg. C. and 1.01323×10^6 bars (760 mms. Hg)	$V = 22,412 \text{ cm.}^3$
At 0 deg. C. and 1×10^6 bars (750 mms. Hg)	$V = 22,708 \text{ cm.}^3$
Gas constant	$PV/T = R = 83.15 \times 10^6 \text{ erg./deg.}$ $= 1.987 \text{ cal./deg.}$
Faraday constant	$F = 96,500 \text{ coulombs.}$
Unit electric charge	$e = 4.774 \times 10^{-10} \text{ e.s.u.}$ $= 1.591 \times 10^{-20} \text{ e.m.u.}$ $F/e = N = 6.062 \times 10^{23}$
Number of molecules per gram-molecular weight	
Number of molecules per cm^3	$N/V = 2.7048 \times 10^{19}$
At 0 deg. C. and 1.01323×10^6 bars	$= 2.6696 \times 10^{19}$
At 0 deg. C. and 1×10^6 bars	$R/N = k = 1.372 \times 10^{-16} \text{ erg./deg.}$
Boltzmann gas-constant	$= \frac{3}{2} k \times 273.1 = 5.621 \times 10^{-14} \text{ erg.}$
Kinetic energy of a molecule at 0 deg. C.	
Mass of hydrogen atom	$m_H = 1.008/N = 1.663 \times 10^{-24} \text{ gm.}$
Ratio of charge to mass of electron	$e/m_0 = 1.769 \times 10^7 \text{ e.m.u. gm.}^{-1}$
Mass of electron	$m_0 = 8.995 \times 10^{-28} \text{ gm.}$
Velocity of light	$c = 2.9986 \times 10^{10} \text{ cm. sec.}^{-1}$
Constant of quantum theory	$h = 6.55 \times 10^{-27} \text{ erg. sec.}$
Constant of Einstein's photo-electric equation	$\frac{h}{e} = 1.372 \times 10^{-17} \text{ (c.g.s. units)}$
Potential corresponding to frequency ν	$V = h\nu/e = 4.115 \times 10^{-15} \nu \text{ (volts)}$
Potential corresponding to wave length λ (Angstroms)	$V = \frac{hc}{\lambda e} = 12,340/\lambda \text{ (volts)}$
Constant in specific heat equations	$\beta = h/k = 4.774 \times 10^{-11} \text{ sec. deg.}$
Planck's Distribution Law for "Black Body"	$I_\lambda = \frac{c_2}{e^{\lambda T} - 1}$

Radiation Constants

$$c_1 = 2 \pi c^2 h = 3.700 \times 10^{-5} \text{ erg. cm.}^{-2} \text{ sec.}^{-1}$$

$$c_2 = ch/k = 1.432 \text{ (1.4350) cm. deg.}$$

$$\lambda_m T = \frac{ch}{4.9651} = 0.2883 \text{ cm. deg. (Wien's displacement constant)}$$

$$I_m = \frac{2 \pi k^5 (4.9651)^5 T^6}{c^3 h^4 (e^{4.9651/T} - 1)} = 1.305 \times 10^{-4} \text{ erg. cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-5} \text{ (maximum intensity)}$$

Stefan-Boltzmann law: Total energy radiated from surface..... = $\int_0^\infty I_\lambda d\lambda = \sigma(T^4 - T_0^4)$

$$\sigma = \frac{12 \pi \times 1.0823 k^4}{c^2 h^3} = 5.722 \times 10^{-6} \text{ erg. cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}$$

Rydberg's constant (Bohr's theory).

$$\nu_0 = 2 \pi^2 m_0 e^4 h^{-3} = 3.287 \times 10^{15} \text{ sec.}^{-1}$$

Radius of first Bohr ring of hydrogen atom.

$$r_1 = \frac{e}{m_0} \cdot \frac{4 \pi^2 e^3}{h^2} = 0.5294 \times 10^{-8} \text{ cm.}$$

Chemical constant, $C = C_0 + 1.5 \log M$
where M = molecular weight

$$C_0 = \log \frac{N^2}{h^2} \times 1.013 \times 10^6$$

$$= -1.5877 \text{ (press. in atmospheres).}$$

$$= 1.2931 \text{ (press. in mm. of mercury).}$$

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