CRYOPUMPING

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THOSE of us who have been interested in vacuum technique have witnessed a veritable revolution in vacuum technology during the past decade. In 1954 the Vacuum Society of America held its first symposium. That same year the first Cryogenic Engineering Conference was held. The seemingly divergent interests of these two groups were brought together by the application of cryogenics to vacuum technology in the form of cryopumping.

In 1954 one could be justly proud of experiments carried out below 10^{-6} torr. Since that time the working pressures of vacuum chambers have steadily fallen and today 10^{-8} torr is commonplace, chambers capable of attaining 10^{-10} torr are available commercially, and there are reports in the literature of work at pressures below 10^{-12} torr.

The development of pressure gauges capable of reading these low pressures was important and necessary but the revolutionary development was the introduction of cryopumping as a method of attaining ultra-low pressures. This is not to say that cryopumping is a new technique. James Watt used a form of cryopumping to improve the efficiency of the steam engine.

A by-product of the rapidly developing space programme was a plentiful supply of liquid nitrogen. This relatively inexpensive low boiling liquid was used to cool surfaces for cryopumping and cryosorption of atmospheric gases. These were used in conjunction with diffusion pumps to increase the overall efficiency.

While the effectiveness of this combination was being demonstrated, large capacity helium refrigerators became available and cryopumping replaced the less efficient cryosorption for all gases except helium, hydrogen, and neon.

Although diffusion pumps have been enormously improved in the past ten years, it was soon apparent that they could never play more than an adjunct role in high vacuum systems where cryopumping was possible. The best commercial diffusion pumps can pump only about one-half of the incident gas whereas the efficiency of cryopumping techniques ranges from 60 per cent for carbon dioxide to 92 per cent for water vapour on a 77° K (liquid nitrogen) surface, and the atmospheric gases show pumping efficiencies in this range on a 20° K surface. In addition, cryopumps can cover a much greater fraction of the wall area than diffusion pumps. That there is still a place for sorption pumping and diffusion pumping is due to the limitations of cryopumping. Obviously, the capacity of a cryosurface is not unlimited. At some time the surface must be warmed to remove the condensed gases. To reduce the frequency of this operation the chamber is generally diffusion pumped to a low pressure level before the start of cryopumping. This also effectively eliminates helium and neon from the system. Cryosorption is used to pump hydrogen since cryopumping of this gas would require a temperature below the boiling point of helium and the expense would be prohibitive for large scale application.

Before 1950 a high vacuum chamber of more than 10 l. capacity was considered large, although there were larger chambers in the micron range for vacuum casting of metals. Today chambers up to 100 l. are considered small, medium size chambers range from 100 to 10,000 l. and the large space simulation chambers from 10^4 to 10^6 l. capacity. The large chambers,

which must handle high gas loads, such as exhausts from test firing of vehicle control rockets, and maintain base pressures of 10^{-8} torr, require the added pumping speed per unit area provided by cryopumping.

The foregoing outlines the great improvement in vacuum capability made possible by a large scale application of cryopumping. Although widely used, the techniques of cryopumping have run far ahead of theoretical understanding of just how it works. As a consequence, one cannot predict the area of pumping surface required for a gas not previously tested with any precision. The purpose of this article is to summarize the theoretical and experimental work to date and to indicate areas where more experimental work is needed. The information presented here, both theoretical and experimental, is drawn from the experience of the research group of the Aerospace Environmental Facility.

Definitions

In order to discuss cryopumping it is advantageous to explain some of the terms used in its study. The most important of these are the pressure and pressure ranges, the temperature, thermal transpiration, the pumping speed, and the capture coefficient.

Pressure and pressure ranges

At high pressures collisions between gas molecules are much more frequent than collisions of molecules with the chamber walls. This condition defines the continuum region or viscous flow region of pressure. On the other hand, in high vacuum we find collisions with the walls more frequent than intermolecular collisions. This is called the free molecule region. At intermediate pressures the two collision frequencies are comparable and the system is in the transition region. The Knudsen number is the ratio of the mean free path to a characteristic dimension of the system, usually its diameter. The transition region, by convention, extends from $K_n = 10$ to $K_n = 0.01$. The free molecule region is designated by Knudsen numbers greater than 10 and the continuum region by numbers less than 0.01.

In the continuum region the pressure may be designated by the perfect gas law

$$P = \frac{\rho}{M} RT \qquad \ldots (1)$$

where P is the pressure, ρ is the gas density, M is the molecular weight, R is the universal gas constant, and T is the temperature (all in compatible units).

In the free molecule region it is preferable to use the kinetic theory definition which defines pressure in terms of the rate of incidence of molecules on a surface

$$P = \sqrt{(2\pi mkT)}\frac{dn}{dt} \qquad \ldots (2)$$

where m is the molecular mass, k is the Boltzmann constant, and dn/dt is the incidence rate of molecules per unit area.

Both Equations (1) and (2) require a Boltzmann distribution to define the temperature. If the gas does not have a defined temperature one must use the mechanical definition of the pressure. This pressure is given by the change in momentum of the gas impinging on a unit surface per unit time

$$P = \frac{1}{A}\frac{dmv}{dt} \qquad \ldots (3)$$

where A is the surface area and dmv/dt is the rate of momentum change perpendicular to the surface per unit area per unit time per molecule. Thus we see that, in a vacuum, pressure may be either a scalar or a vector quantity, depending on the conditions.

The foregoing may seem elementary but in carrying out cryopumping measurements the measured pressure is not always equal to the effective pressure at the cryosurface. The pressure gauge is generally on a wall of the chamber and if there are gradients due to flow or to gas temperature differences, appropriate corrections must be made to obtain the molecular incidence rate at the cryosurface. These corrections are generally simple in the free molecule region but in the transition and continuum regions they become difficult or impossible to calculate.

Temperature

The gas temperature, like the pressure, is fundamental to the calculation of the maximum theoretical pumping speed of a cryosurface. In free molecule flow, with a large ratio of wall area to cryosurface area, the gas temperature is equal to the wall temperature. Therefore the wall temperature should be uniform.

With directed flow or with non-uniform wall temperatures the gas may no longer have a Boltzmann distribution and thus there will be no defined temperature.

Thermal transpiration

If the temperature of the chamber walls is different from the temperature for which the pressure gauge is calibrated and the pressure is in the free molecule flow range, there is a particular interaction of pressure and temperature called thermal transpiration. This effect is simply a consequence of the conservation of mass and the kinetic theory equations for the number of gas molecules incident on a unit area.
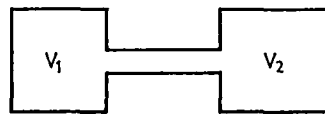

Figure 1. Two-volume system for thermal transpiration

Consider a vessel V_1 at a temperature T_1 connected by a tube to another vessel V_2 at T_2 (Figure 1). For the sake of simplicity, assume that the system, consisting of V_1, V_2, and the tube, contains only a single species of gas. The number of molecules entering the connecting tube from V_1 will be given by equation (2)

$$\dot{n}_1 = \frac{P_1}{\sqrt{(2\pi m k T_1)}} \qquad \ldots (4)$$

and likewise those entering from V_2

$$\dot{n}_2 = \frac{P_2}{\sqrt{(2\pi m k T_2)}} \qquad \ldots (5)$$

After a sufficient time has elapsed, a steady state is reached so that these rates are equal and

$$\frac{P_1}{\sqrt{(2\pi m k T_1)}} = \frac{P_2}{\sqrt{(2\pi m k T_2)}} \qquad \cdot \cdot (6)$$

or

$$\frac{P_1}{\sqrt{T_1}} = \frac{P_2}{\sqrt{T_2}} \qquad \ldots (7)$$

This is the essence of the thermal transpiration effect. In the free molecule region with no net flow the ratio of the pressure to the square root of the temperature is a constant for different parts of the system. Two points are immediately evident; the effect only applies in the free molecule region and the pressures must be constant with time.

Consider what happens when V_2 is an external pressure gauge at an average temperature of 400° K, and V_1 is a vacuum system at 300° K. The gauge is calibrated on the basis of the pressure in V_1 so that the reference temperature for this gauge is 300° K, not 400° K. If the gauge should be cooled by a draught or heated by inadvertent insulation, the gauge calibration will change just as if the temperature of the vacuum system had changed. Because this effect is proportional to the square root of the gauge temperature, it is usually negligible compared to random variations in gauge calibration. Increasing the gauge temperature to 500° K only increases the pressure reading 10 per cent. However, for precision work a constant gauge temperature is desirable.

Pumping speeds

There are two definitions of pumping speed in current use. If one is primarily concerned with mass flows as in the pumping of rocket exhausts and of outgassing then one prefers the mass pumping speed. If, on the other hand, one is concerned with the theoretical aspects of cryopumping, such as capture or condensation probability, then the volumetric pumping speed is preferred. These two pumping speeds are related through the pressure, as shown in equation (8)

$$\frac{P\dot{V}}{RT} = \frac{\dot{g}}{M} \qquad \ldots (8)$$

where $\dot{V}$ is the volumetric pumping speed, P is the pressure, R is the gas constant, T is the absolute temperature, M is the molecular weight, and $\dot{g}$ is the throughput or mass flow (all in compatible units).

In this report, we shall use the volumetric pumping speed because, in the free molecule region, the maximum volumetric pumping speed $\dot{V}_{max}$ is independent of the pressure. It is given by the product of the maximum specific pumping speed and the cryo-surface area

$$\dot{V}_{max} = S_{max}A \qquad \ldots (9)$$

The maximum specific pumping speed may be calculated from kinetic theory and is given by

$$S_{max} = \sqrt{(RT_g/2\pi M)} \qquad \ldots (10)$$

where S_{max} is the maximum specific pumping speed in cm^3/cm^2 sec, A is the cryosurface area, and T_g is the gas temperature.

Thus the criterion for the maximum pumping speed is that every molecule striking the surface will condense (see equations (1) and (4)). A definition of the experimental pumping speed may be developed as follows. By the conservation of mass and the continuity condition, we may state

$$\frac{P_0\dot{V}_0}{RT_0} = \frac{P\dot{V}}{RT_g} + \frac{\dot{P}V}{RT_g} \qquad \ldots (11)$$

where the left-hand side represents the rate of flow of gas into the chamber, denoted by the '0' subscripts, and the right-hand side is the sum of the moles condensed per second. If the rate of change in the number of moles in the gas phase of the chamber volume is zero, $\dot{P}$ is zero, so that

$$\frac{P_0\dot{V}_0}{RT_0} = \frac{P\dot{V}}{RT_g} \qquad \ldots (12)$$

or, rearranging,

$$\dot{V} = (P_0\dot{V}_0/P) \cdot T_g/T_0 \qquad \ldots (13)$$

Equation (13) defines the experimental pumping speed.

Capture coefficient

The capture or condensation coefficient may be defined as the ratio of the measured pumping speed to the calculated maximum pumping speed. This definition is incomplete since it leaves the capture coefficient undefined where one is unable to calculate maximum pumping speed. Another definition is to define the capture coefficient as the condensation probability per collision for molecules of an average
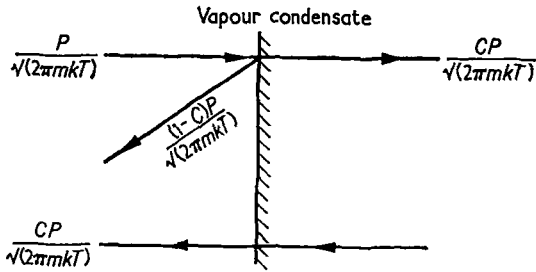
Figure 2. Isothermal capture coefficient

energy equivalent to the gas temperature. This definition of the capture coefficient assumes it to be independent of the rate of incidence on the surface.

In the free molecule region, the maximum pumping speed may be calculated from kinetic theory and is found by combining equations (9) and (10),

$$\dot{V}_{max} = A \sqrt{\left(\frac{RT_g}{2\pi M}\right)} \qquad \ldots (14)$$

where A is the cryosurface area.

The definition of the capture coefficient gives, in the free molecule region,

$$C = \dot{V}/\dot{V}_{max} \qquad \ldots (15)$$

Combining equations (13), (14), and (15), we find

$$C = \frac{P_0 \dot{V}_0}{P T_0 A} \sqrt{\left(\frac{2\pi M T_g}{R}\right)} \qquad \ldots (16)$$

To elucidate further the nature of the capture coefficient, consider a pure condensed gas in an isothermal enclosure. The vapour in equilibrium with the solid will have a pressure equal to the vapour pressure. Assume this pressure to be very small so that the mean free path in the vapour is very large compared to any dimension of the enclosure. The number of vapour molecules incident on the solid per unit area per unit time may be calculated from kinetic theory and was given by equation (2)

$$\frac{dn}{dt} = \frac{P}{\sqrt{(2\pi mkT)}} \qquad \ldots (17)$$

Of these incident molecules, a certain fraction C will condense and a fraction $(1 - C)$ will be reflected. In addition, a certain number of molecules will evaporate. In addition, a certain number of molecules will evaporate. At equilibrium, the number of molecules that evaporate must equal the number condensing. The fraction C is then the isothermal equilibrium condensation coefficient. Figure 2 illustrates the process. Since there is no net transfer of mass or energy the number of evaporating molecules must equal the number of condensing molecules. Thus, from Figure 2,

we obtain

$$\left(\frac{CP_{vap}}{\sqrt{T}}\right)_{condensation} = \left(\frac{CP_{vap}}{\sqrt{T}}\right)_{evaporation} \qquad \ldots (18)$$

Having explored the isothermal case in order to establish our definitions, let us proceed to the case where a temperature difference is maintained between the gas and the solid condensate, as shown in Figure 3. In this case at equilibrium there will be a net energy flow but no net mass flow. The relation is therefore given by

$$\frac{C_g P_g}{\sqrt{(T_g)}} = \frac{C_s P_s}{\sqrt{(T_s)}} \qquad \ldots (19)$$

where the subscripts 'g' and 's' refer to gas and surface conditions, respectively, so that C_s is the evaporation coefficient and C_g is the condensation coefficient. A comparison of the two equations indicates that under isothermal conditions the evaporation coefficient is equal to the condensation coefficient. Note that equation (19) is obtained by the application of the thermal transpiration correction to equation (18).

Conductance

It has been pointed out that the pressure reading at the chamber wall may not accurately reflect the incidence rate of molecules on a cryosurface. That this will be a source of error in the continuum region is obvious. It is less obvious that errors can arise from this source in the free molecule region. This may occur in a variety of ways. A simple case will be shown to illustrate how this problem can be treated. Consider a vacuum chamber in two sections, as in Figure 4.

The gas inlet and pressure measurement are in V_1, the cryosurface (area A) is in V_2, and the equivalent conductance area between volumes is L. Both P_1 and P_2 are low enough so that free molecule conditions exist in both volumes. Steady state conditions are assumed. The continuity condition in the steady state gives

$$\frac{P_0 \dot{V}_0}{RT_0} = \frac{P_1 L}{\sqrt{(2\pi MRT_1)}} - \frac{P_2 L}{\sqrt{(2\pi MRT_2)}} = \frac{P_2 AC}{\sqrt{(2\pi MRT_2)}} \qquad \ldots (20)$$
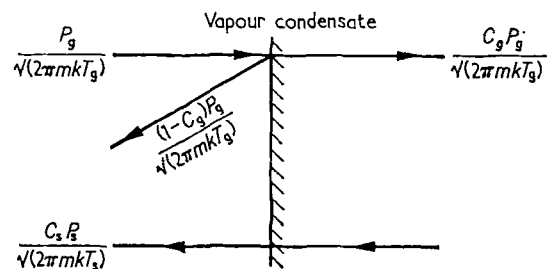

Figure 3. Non-isothermal capture coefficient

P_2 may be eliminated by setting up the two equations

$$P_2 = \left[P_1 - \frac{P_0 \dot{V}_0}{LRT_0} \sqrt{(2\pi MRT_1)} \right] \sqrt{\frac{T_2}{T_1}} \quad \ldots (21)$$

$$P_2 = \frac{P_0 \dot{V}_0}{RT_0 AC} \sqrt{(2\pi MRT_2)} \quad \ldots (22)$$

Equating these it is found that not only P_2 but also T_2 has been eliminated. Thus

$$P_1 - \frac{P_0 \dot{V}_0}{LRT_0} \sqrt{(2\pi MRT_1)} = \frac{P_0 \dot{V}_0}{RT_0 AC} \sqrt{(2\pi MRT_1)}$$
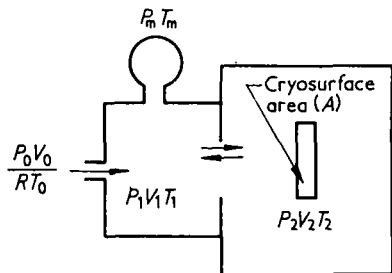$$\ldots (23)$$

Figure 4. Two-volume system for conductance

The wall temperature of the first chamber may be eliminated by invoking thermal transpiration and substituting the measured pressure P_m for P_1, which gives

$$P_1 = P_m \sqrt{\frac{T_1}{T_m}} \quad \ldots (24)$$

If we assume T_m is equal to T_0, then

$$P_1 = P_m \sqrt{\frac{T_1}{T_0}} \quad \ldots (25)$$

Substituting in equation (23) and rearranging, we obtain

$$P_m \sqrt{\frac{RT_0}{2\pi M}} - \frac{P_0 \dot{V}_0}{L} = \frac{P_0 \dot{V}_0}{AC} \quad \ldots (26)$$

but

$$\sqrt{\left(\frac{RT_0}{2\pi M} \right)} = S_{max} \quad \ldots (10)$$

so that, solving for C, we find from equation (26)

$$C = \frac{P_0 \dot{V}_0 L}{S_{max} P_m AL - P_0 \dot{V}_0 A} \quad \ldots (27)$$

If we now define C' as the capture coefficient calculated by assuming no conductance effects, we can show the relationship between the two and get an estimate of the error introduced by ignoring conductance.

Let

$$C' = \frac{P_0 \dot{V}_0}{A S_{max} P_m} \quad \ldots (28)$$

Substituting in equation (27) and rearranging gives

$$\frac{C'}{C} = \frac{L - AC'}{L} \quad \ldots (29)$$

so that unless the product of the capture coefficient C' and the cryosurface area is small compared to the conductance L, the conductance effect cannot be ignored. All this could be avoided by measuring the pressure in the volume V_2 containing the cryosurface, but such a simple solution is not feasible for all cases.

Equipment

The requirements for a cryopumping research test chamber are fairly loose but some reasonable rules of thumb are:

(1) Chamber size from 100 to 500 l.
(2) To minimize outgassing effects the ratio of chamber surface area to volume should be optimized.
(3) Diffusion pump speed, one chamber volume per second.
(4) Ultimate pressure about 10^{-8} torr.
(5) Leak rate (atm cm³/sec) less than 10^{-11} times the pumping speed.
(6) Polished stainless steel walls.
(7) Maximum linear cryosurface dimension less than 1/4 minimum linear chamber dimension, cryosurface preferably spherical.
(8) Cryosurface area less than 10 per cent of wall area.
(9) Cooling lines to cryosurface vacuum-insulated to prevent condensation on lines and to permit accurate knowledge of cryosurface area.
(10) Adequate baffling to reduce directed flow within chamber.
(11) Pressure gauge must read pressure in chamber with cryosurface but line of sight from pressure gauge opening to cryosurface or to gas inlet should not exist.

The chamber shown in Figure 5 fulfills these requirements with a few added features for flexibility and convenience. This chamber is by no means the ultimate in design; however, it is more than adequate for cryopumping measurements. The pressure gauge reads from 1×10^{-4} to 1×10^{-13} torr. The mass spectrometer reads mass numbers 2 to 50 with an average sensitivity of 10^9 divisions/torr. The shroud temperature can be held constant within 5° C over its surface between 77 and 400° K. The cryosurface temperature is variable from 9 to 150° K. The gas flow rates are controlled by a gas addition system consisting of a bank of five standard leaks ranging from 10^{-5} torrs . l./sec to

10^{-1} torrs . l./sec. For gases with vapour pressures less than 760 torrs at room temperature the flow rate was measured by a low range rotameter operating at reduced pressure. Most of the results reported here were obtained in a chamber similar to this.
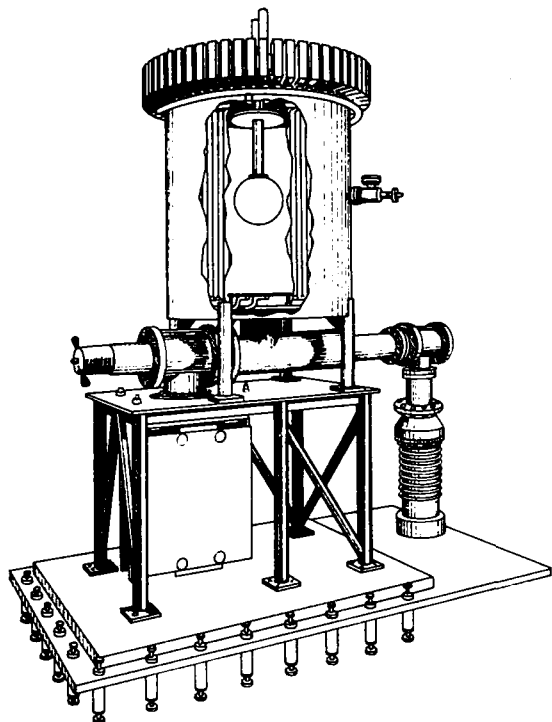

Figure 5. Ultra-high vacuum chamber

Procedure

In order to interpret the results of cryopumping tests it is necessary to calibrate the pressure reading relative to the rate of gas inflow. The most generally used method of calibration is the rate of (pressure) rise. In this method a standard leak is opened to the chamber and when the pressure becomes constant the valve to the vacuum pump is closed. The subsequent rate of pressure rise can be used to calculate the calibration of the pressure reading. By repeating this procedure with various standard leaks a complete relative calibration is obtained. If the chamber leak rate is more than 5 per cent of the smallest standard leak used, it may be necessary to subtract the rate of rise due to the chamber leak alone from that determined with the standard leak. If an absolute calibration is desired, either the pressure gauge or one standard leak must be calibrated independently. As will be shown in the section on data interpretation, absolute calibration is not necessary for pumping speed measurements. The procedure for calibration of the mass spectrometer is identical to that for the pressure gauge.

The procedure for measuring the pumping speed of the cryosurface is similar to that for calibration except

that now the cryosurface is cold and after a transient period one obtains a constant pressure reading instead of a continuous rate of rise when the diffusion pump valve is closed. To complete the pumping speed measurement the standard leak is shut off and the drop in chamber pressure noted. We shall see that this pressure drop is the critical measurement in cryopumping.

Pumping speed measurements cannot be run for most gases much below a pressure of 10^{-7} torr since at lower pressures the sorption of gas by the wall is sensitive to pressure and the capacity is great enough to cause large uncertainties in the measurement of the pumping speed of the cryosurface. The pressure range from 10^{-7} to 10^{-4} torr is quite adequate for measuring the pumping speed, however.

Data interpretation

Data reduction for cryopumping is particularly simple if one has observed proper design of the test chamber and proper test procedure. By using the difference between the chamber pressure with the gas leak on and with it off to calculate the capture coefficient, one not only compensates for the impurity of the gases but also for the vapour pressure of the condensed gas. In addition, by measuring the pressure with a gauge at the same temperature at which it was calibrated, the condensation coefficient is corrected for thermal transpiration, and it is found that the pressure drop for a given leak rate depends only on the condensation coefficient and no additional correction for the gas temperature is required. These two points may be illustrated by putting the value of the condensation coefficient in terms of the measured pressure.

From Figure 3 the number of moles captured per unit area per unit time will be given by the difference between the condensation and evaporation rates

$$\frac{dN}{dt} = \frac{C_g P_c}{\sqrt{(2\pi M R T_g)}} - \frac{C_s P_s}{\sqrt{(2\pi M R T_s)}} \quad \cdots \quad (30)$$

(dN/dt in moles per second) where P_c is the steady state chamber pressure with flow, and P_s is the vapour pressure of gas condensate.

The rate of incidence will be

$$\frac{dN}{dt} = \frac{P_c}{\sqrt{(2\pi M R T_g)}} \quad \cdots \quad (17)$$

The ratio of these two rates will be the effective capture coefficient C^*, which is the quantity of most interest to designers of a pumping system. Dividing equation (30) by equation (17) gives

$$C^* = C_g\left(1 - \frac{C_s P_s}{C_g P_c}\sqrt{\frac{T_g}{T_s}}\right) \quad \cdots \quad (31)$$

From equation (19)

$$C_g = \frac{C_s P_s}{P_g} \sqrt{\frac{T_g}{T_s}} \qquad \ldots (32)$$

so that

$$C^* = C_g \left(1 - \frac{P_g}{P_c}\right) \qquad \ldots (33)$$

Having determined the theoretical relationship between C^* and C_g, the method for experimental determination of these quantities is as follows. The experimental pumping speed is given by

$$\dot{V} = \frac{P_0 \dot{V}_0 T_g}{P_c T_0} \qquad \ldots (34)$$

and from equation (15)

$$\dot{V} = C^* \dot{V}_{max} \qquad \ldots (35)$$

Substituting in equation (34) and solving for C^*, we obtain

$$C^* = \frac{P_0 \dot{V}_0 T_g}{P_c \dot{V}_{max} T_0} \qquad \ldots (36)$$

Combining equations (33) and (36) and solving for C_g gives

$$C_g = \frac{P_0 \dot{V}_0 T_g}{(P_c - P_g) \dot{V}_{max} T_0} \qquad \ldots (37)$$

Thus the use of the difference between the pressure with the leak on (P_c) and the background pressure (P_g), equilibrium chamber pressure with leak off, gives the condensation coefficient corrected for the vapour pressure of the condensed gas. Also, if P_g is much smaller than P_c the effective capture coefficient is equal to the condensation coefficient. To continue this further, substitute

$$\dot{V}_{max} = A \sqrt{\left(\frac{RT_g}{2\pi M}\right)} \qquad \ldots (14)$$

into equation (37) to get

$$C_g = \frac{P_0 \dot{V}_0 \sqrt{2\pi M R T_g}}{(P_c - P_g) A R T_0} \qquad \ldots (38)$$

The thermal transpiration gives the measured pressure denoted by the 'm' subscript in terms of the temperatures and the chamber pressure (see equation (7))

$$\frac{P_c}{\sqrt{T_g}} = \frac{P_{m1}}{\sqrt{T_m}} \quad \text{(flow on)} \quad \ldots (39)$$

and

$$\frac{P_g}{\sqrt{T_g}} = \frac{P_{m2}}{\sqrt{T_m}} \quad \text{(flow off)} \quad \ldots (40)$$

If we now set $T_m = T_0$ and substitute the pressures

from equations (39) and (40) in equation (38), we find that

$$C_g = \frac{P_0 \dot{V}_0}{(P_{m1} - P_{m2}) A} \sqrt{\left(\frac{2\pi M}{R T_0}\right)} \qquad \ldots (41)$$

Thus we see that by using a constant temperature pressure gauge and by using the pressure drop method one obtains the condensation coefficient directly in terms of the calibrated flow and the pressure drop with thermal transpiration and vapour pressure corrections automatically included. However, when $P_{m1} \gg P_{m2}$, the condensation and effective capture coefficient are equal.

Theoretical and experimental results

Pressure effects

The cryopumping speed of a gas shows two major variations with pressure at constant temperature. The first of these occurs at low pressures when the chamber pressure is comparable to vapour pressure of the condensate. At the vapour pressure of the condensate the pumping speed must be zero. At higher pressures the pumping speed increases to the limiting value for free molecular flow according to the relationships developed in the preceding section. As the chamber pressure increases further a region of constant volumetric pumping speed is found. At a pressure for which the mean free path is 5-10 times the cryosurface characteristic dimension, the second variation of pumping speed is found and the pumping speed again starts to increase. In principle, for a pure gas the pumping speed will continue to rise until the mean free path of the molecules is about one-tenth to one-twentieth ($K_n = 0.01$) of the characteristic dimension, at which point it would become constant. This increase in pumping speed may be explained by imagining the cryosurface to act as an orifice. The hypothetical pressure downstream of this orifice will be the upstream pressure times the reflection coefficient (one minus the capture coefficient). If the ratio of these pressures is less than the critical pressure ratio then gas will flow to the cryosurface at the velocity of sound. Pumping at sonic velocities has been experimentally demonstrated. However, in the continuum region, convection and heat conduction effects are appreciable. Even more important, in the continuum region there is appreciable momentum transfer between the condensable gas flowing to the surface and any non-condensable gases in the system. This increases the concentration of the non-condensable gases at the surface and these act as a barrier to the condensable gas, reducing the pumping speed. At very high non-condensable gas pressures the pumping speed will be controlled by the diffusion rate of the condensable gas to the surface.

The effect of non-condensable impurities has not been quantitatively defined but it can be demonstrated
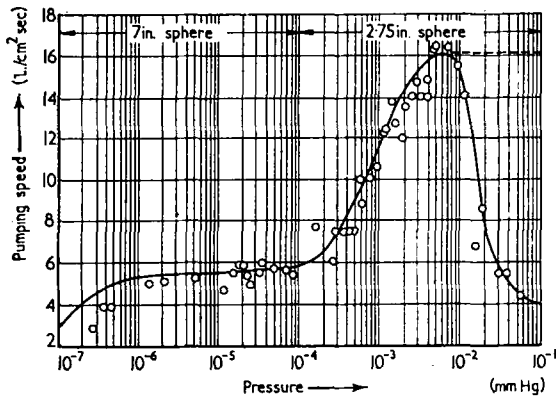
Figure 6. Pumping speed versus pressure for impure carbon dioxide

experimentally. The effects of convection and heat conduction are even less well defined since they are tied up with a change in the cryosurface temperature resulting from the increased heat load. The overall effect is to reduce the pumping speed.

To summarize the effects of increasing pressure on pumping speed one can anticipate that, starting at the vapour pressure of the condensate, the pumping speed will increase from zero to a constant pumping speed in the free molecule flow region. The transition region is then encountered through which the pumping rises to sonic velocity if the gas is reasonably pure. As the continuum region is entered the pumping speed drops sharply. Figure 6 shows the variation of the specific pumping speed of gaseous carbon dioxide on a $77°$ K cryosurface over a wide range of pressures. This is a composite graph of tests on 7 in. and 2·5 in. diameter surfaces. Figure 7 shows the results of cryopumping tests on nitrous oxide for three different purities. The increase in pumping speed with gas purity in the continuum range is obvious.

Temperature effects

The variation of pumping speed with temperature may be divided into the variation of the incidence rate of the molecules on the cryosurface, and the variation
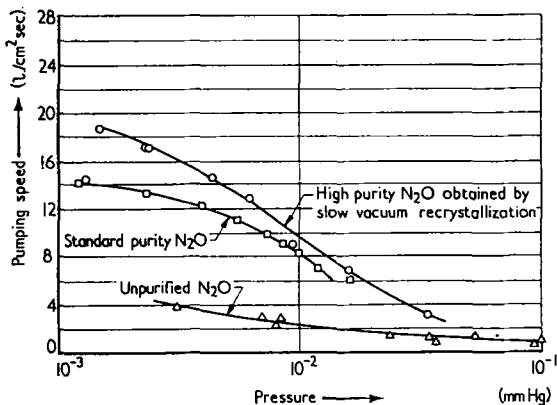

Figure 7. Pumping speed versus pressure for nitrous oxide of three purities

of the capture coefficient. The first of these was given by equation (10).

The variation of the capture coefficient with temperature is more complex and is still a subject for further research. In general the capture coefficient is a function of both the gas and surface temperatures and many approaches to the definition of this function are possible. The variation of the capture coefficient with gas temperature may be separated from the variation with surface temperature by considering condensation as a process in which the incident molecules lose energy to the surface irreversibly. By analogy to friction losses, the amount of energy loss would be roughly proportional to the velocity of the incident molecules so that the faster molecules would lose more energy than the slower. With the initial energies of the molecules proportional to the velocity squared and the loss proportional to the velocity, there would be a critical velocity in any Boltzmann distribution for which the energy loss was just equal to the initial energy. Thus there would be a minimum energy of the incident molecules for reflection. This minimum ideally would be determined by the properties of the surface alone.

The number of incident gas molecules having an energy greater than the critical value may be determined from kinetic theory and is given by

$$\frac{n}{N_0} = \exp\left(-E/kT_g\right) \qquad \ldots (42)$$

The fraction of incident molecules with sufficient energy to escape is equal to one minus the capture coefficient so that one may immediately write

$$\log\left(1 - C\right) = -E/kT_g \qquad \ldots (43)$$

where C is the capture coefficient at T_g, E is the critical energy determined solely by T_s, and k is the Boltzmann constant.

Carrying this to the next logical step

$$T_{g1} \log\left(1 - C_1\right) = T_{g2} \log\left(1 - C_2\right) = -E/k \qquad \ldots (44)$$

or

$$C_1 = 1 - (1 - C_2)^{T_{g2}/T_{g1}} \qquad \ldots (45)$$

which gives the relationship between the capture coefficient at T_{g1} and the capture coefficient at T_{g2}. Thus the effect of gas temperature is completely defined by this hypothesis.

Table 1 summarizes the results of tests on the effects of gas and surface temperatures on the capture coefficients of five gases. In Figure 8, the critical energy values E calculated from these data using equation (43) are shown plotted against surface temperature. The hypothesis proposed to separate the effects of gas and surface temperatures would require
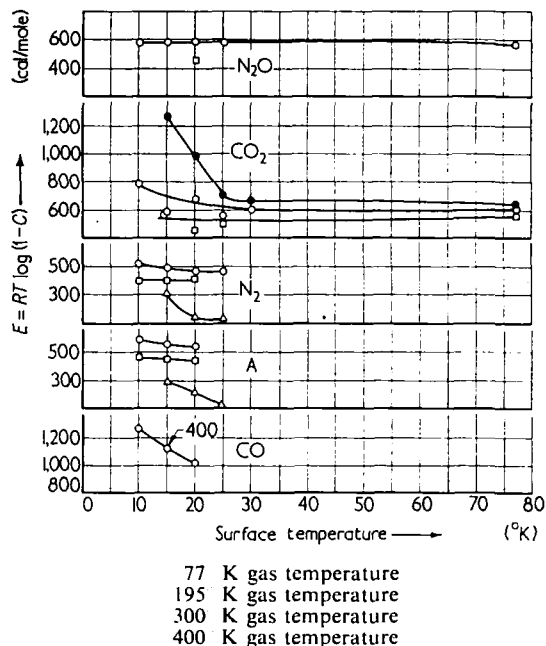
Figure 8. Effects of gas and surface temperatures on the critical energy for five gases

77 K gas temperature
195 K gas temperature
300 K gas temperature
400 K gas temperature

that, at constant surface temperature, the calculated values of E should be the same for all gas temperatures. From Figure 8 it would appear that the hypothesis is not exact. On the other hand, the capture coefficient values given in Table 1 are not considered to have an accuracy of better than 5 per cent so that the hypothesis is not disproved by these results.

The effect of surface temperature on the capture coefficient is not as clear as the gas temperature effect. This is due to our meagre understanding of the nature of the energy exchange between a gas molecule and a surface. It seems likely, however, that such parameters as the vibrational energy spectrum and the Debye temperature of the surface will be the major factors. Thus one would predict that the capture coefficient should be different for amorphous and crystalline condensate at the same temperature. The capture coefficient will change if the nature of the surface changes as in condensing a gas on an initially clean metal surface. A phase change such as the melting or recrystallization of the condensate as the temperature of the surface increases would result in a discontinuous change in the capture coefficient.

Intuitively, one might expect the capture coefficient to approach a value of zero when the surface temperature is equal to the critical temperature of the gas but this idea is based on the fact that the pumping speed must be zero above the critical temperature of the gas. Referring to Figure 2 we see that a zero condensation coefficient would require the evaporation coefficient to be zero at the critical temperature. The high evaporation rates of gases near the critical temperature would indicate that the condensation coefficient does not approach zero but may become constant at higher surface temperatures. This hypothesis is supported experimentally by the constant capture coefficients found for carbon dioxide over a wide range of surface temperatures (Table 1 and Figure 8). There does seem to be an increase in the capture coefficient at the lowest temperatures tested for low gas temperatures. This probably results from a coupling, or resonance exchange, between the less

Table 1. Capture coefficients of common gases

Cryosurface temperature	N₂			A		
	77 K	300 K	400 K	77 K	300 K	400 K
10	1·0	0·65	0·49	1·0	0·68	0·50
12·5	0·99	0·63	0·49	1·0	0·68	0·50
15	0·96	0·62	0·49	0·90	0·67	0·50
17·5	0·90	0·61	0·49	0·81	0·66	0·50
20	0·84	0·60	0·49	0·80	0·66	0·50
22·5	0·80	0·60	0·49	0·79	0·66	0·50
25	0·79	0·60	0·49	0·79	0·66	0·50
77						

Cryosurface temperature	CO₂			CO		
	195 K	300 K	400 K	77 K	300 K	400 K
10	1·0	0·75		1·0	0·90	0·73
12·5	0·98	0·70		1·0	0·85	0·73
15	0·96	0·67	0·50	1·0	0·85	0·73
17·5	0·92	0·65	0·49	1·0	0·85	0·73
20	0·90	0·63	0·49	1·0	0·85	0·73
22·5	0·87	0·63	0·49	1·0	0·85	0·73
25	0·85	0·63	0·49	1·0	0·85	0·73
77	0·85	0·63	0·49	1·0	0·85	0·73

Cryosurface temperature	N₂O			O₂		
	195 K	300 K	400 K	77 K	300 K	400 K
10	1·0	0·63	0·50			
12·5		0·62	0·50			
15	0·94	0·62	0·50			
17·5		0·61	0·50			
20	0·86	0·61	0·50	1·0	0·86	
22·5		0·61	0·50			
25	0·85	0·61	0·50			
77		0·61	0·50			

Table 2. Capture coefficients;
300° K gas temperature, 77° K cryosurface temperature

H₂O	0·92
NH₃	0·45
CH₃OH	1·0
C₂H₅OH	1·0
CCl₄	1·0
CH₃Cl	0·93
CH₂Cl₂	0·82
CF₂Cl₂	0·76
SO₂	0·74
CO₂	0·63
N₂O	0·61
CH₃Cl	0·56
CH₃COCH₃	0·55

energetic gas molecules and the unoccupied lattice energy levels below the Debye temperature of the surface.

Molecular species effects

Since the capture probability is intimately associated with the properties of the gas and surface, one might hope to elucidate the problem by testing a number of gases with widely different properties. Table 2 shows the capture coefficients found for thirteen different gases. The gas temperatures were all 300° K and the surface temperature was 77° K. No rigorous correlation was found but there does seem to be some effect of molecular weight, as shown by Figure 9.
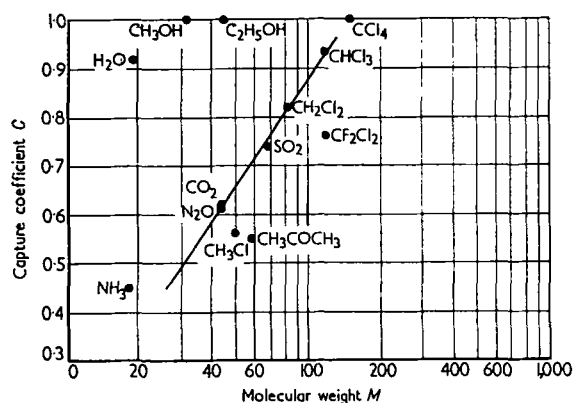
Figure 9. Correlation of capture coefficient using molecular weight as a parameter

It should be pointed out that the properties which intuitively are most closely connected with condensation, the vapour pressure and heat of condensation, apparently bear no direct relationship to the capture coefficient. Thus the capture coefficient of carbon dioxide is higher than that of ammonia at 77° K and lower than that of argon at 20° K as indicated in Tables 2 and 1, respectively.

Cryopumping of gas mixtures

The cryopumping of gas mixtures may in general be predicted by adding the cryopumping speeds of the various components. To be sure, there are interaction effects since the composition of the surface is changed. However, based on published results,† these effects are not greater than about 15 per cent. As might be expected, the effect of a second gas on the cryopumping speed of the first is completely unpredictable. In some cases the capture coefficient is increased, in others it is decreased, and for still others there seems to be no measurable effect.

Because of the absence of large interaction effects the cryopumping of mixtures of condensable gases

†'Prediction of Cryopumping Speeds in Space Simulation Chambers.' Presented at Space Simulation Testing Conference, A.I.A.A., Pasadena, Calif., 16 November 1964.

has not been studied extensively. On the other hand, the cryopumping of condensable gases in the presence of non-condensable gases has been studied because of the possibility of sorption of non-condensable gases by the condensed phase followed by covering with the condensable gas. This is called trapping. If one could effectively pump nitrogen on a 77° K surface by the addition of water vapour the saving in refrigeration costs would be impressive. Experimentally it has been found that although nitrogen (and air) can be pumped by condensing water vapour, the ratio of water to nitrogen is so large at low pressures as to make this impractical. Work is continuing on this rather specialized type of cryopumping, but at lower temperatures. There is some evidence that hydrogen and even helium may be effectively pumped on a 10° K surface by condensing water vapour or carbon dioxide.

Concluding remarks

The principal application of cryopumping has been as a more efficient addition to conventional pumping methods. In space simulation chambers the cold walls also simulate, to a large extent, the cold background of the space environment. For low density wind tunnels, boundary layer removal in the expansion nozzle by cryopumping has resulted in a marked increase in uniform core diameter as well as an increase in the Mach number of the core.

The engineering applications of cryopumping have been most impressive. Cryopumping offers a tool with which one can examine the more subtle aspects of the interactions of gases and surfaces. One can effectively look at the encounter of a single gas molecule with a surface and determine the energy and momentum exchange as a function of velocity and angle of incidence by using well defined molecular beams of incident molecules. This comes under the heading of future research.

The present generation of large space simulation chambers with base pressures of about 10^{-8} torr should more properly be called orbital chambers. True space simulation chambers with base pressures of 10^{-13} torr and below are just now beginning to make their appearance. These will have walls cooled to liquid helium temperatures and will thus be much smaller, at least initially. But with these new chambers the study of the effects of ultra-high vacua will begin.

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