

CRYOPUMPING

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I. INTRODUCTION

Cryopumping¹ is the removal of gas from a system by condensation onto a cold plate. The phenomenon of cryopumping is not new, but it has received much emphasis in the last few years because of the need for very great pumping speeds in space simulation work.² As cryogenic liquids and low temperature refrigerators become more readily available, cryopumps are used in more and more facilities not related to space simulation. The use of liquid helium and liquid hydrogen in particle accelerator programs makes the use of cryopumping quite natural in these facilities.

II. THE CONCEPT OF CRYOPUMPING

The requirement for effectively cryopumping a gas is that the vapor pressure of the condensate shall be quite low, and that gas molecules shall stick to the cold surface upon impact (at least for the majority of impacts).

The change of vapor pressure with temperature follows the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{L}{T (V'_f - V'_i)}$$

where L = latent heat of the phase change,
V'_f = final specific volume,
V'_i = initial specific volume,
T = absolute temperature.

If L is approximately constant, if the specific volume of the gas is much greater than that of the solid, and if the gas approximately follows the ideal gas law, then $\ln p = A - (B/T)$, or $p = C e^{-B/T}$. It is clear that a substantial reduction in temperature can produce a drastic reduction in vapor pressure. For example, hydrogen vapor pressure varies approximately as:

T °K	5	4.2	3.5	3
p (H ₂) torr	1.5×10^{-5}	3×10^{-7}	1×10^{-9}	1×10^{-11}

1. B.M. Bailey and R.L. Chuan, Trans. Fifth National Symposium on Vacuum Technology (Pergamon Press, 1959), p. 262.

2. D.J. Santeler et al., National Aeronautics and Space Administration Report NASA SP-105 (1966).

and nitrogen vapor pressure varies approximately as:

T °K	50	40	30	20
p (N ₂) torr	4	5 × 10 ⁻²	3 × 10 ⁻⁵	1 × 10 ⁻¹¹

The dependence of vapor pressure on temperature³ for a wider range, and for other gases, is shown in Fig. 1.

The effectiveness of cryopumping, assuming a sufficiently low vapor pressure for the condensate, is determined by the fraction of those molecules incident on a cold "pumping" surface which stick to the surface. Only a limited number of sticking fraction experiments have been done,^{4,7-9} and the results are not particularly clear. However, the sticking fraction will, in general, increase with surface roughness and with decreasing temperature. This is expected, because the accommodation coefficient (Fig. 2) is influenced in the same ways,^{5,6} and a high sticking fraction implies a high accommodation coefficient. As a good general rule, nitrogen and oxygen have a high coefficient of sticking (in excess of 0.9) for impact on 20°K or lower temperature surfaces. Water vapor and carbon dioxide have a high coefficient of sticking when contacting 80°K or lower temperature surfaces. Hydrogen has a high coefficient on contacting 4.2°K surfaces. All cryopumping surfaces which have been in operation long enough to build up a film of condensate will be "rough" from a molecular standpoint, and will have relatively high values for accommodation coefficient and for sticking fraction, provided the temperature is low enough.

III. PUMPING SPEEDS AND ULTIMATE PRESSURE

The condensation pumping speed of cold surfaces depends on a number of factors such as (1) sticking fraction at the surface, (2) temperature of the gas being pumped, (3) molecular weight of the gas being pumped, and (4) system geometry, including the presence or absence of thermal (and mechanical) shielding. Also, the ultimate pressure attainable in a cryopumped chamber depends on (1) the magnitude of the introduced gas load, as well as the outgassing load, (2) the temperature of the gas being pumped, (3) the system geometry, (4) the vapor pressure of the condensate, and (5) the amount of "noncondensable" gas present, which must be removed by other pumping methods.

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3. R.E. Honig and H.O. Hook, RCA Review 21, 360 (1960).
 4. J.P. Dawson, J.D. Haygood, and J.A. Collins, Jr., in Advances in Cryogenic Engineering (Plenum Press, 1964), Vol. 9, p. 443.
 5. W.H. Keesom and G. Schmidt, Physica 3, 590 (1936); 3, 1085 (1936); 4, 828 (1937).
 6. H.Y. Wachman, Am. Rocket Soc. J. 32, 2 (1962).
 7. B.A. Buffham, P.B. Henault, and R.A. Flynn, Trans. Ninth National Vacuum Symposium (MacMillan Co., 1962), p. 205.
 8. R.F. Brown and E.S.J. Wang, in Advances in Cryogenic Engineering (Plenum Press, 1965), Vol. 10, p. 283.
 9. J.A. Collins and J.P. Dawson, Arnold Engineering Development Center Report AEDC-TDR-63-51 (1963).

The calculation of pumping speeds and ultimate pressures is in general quite complicated, but there are several very simple geometries for which the analysis is direct and exact. The results for these give indications of what to expect for other, more realistic, systems.

1. Spot Cryopumping

First consider a small condensation spot of area A at some low temperature T_c in a chamber of otherwise uniform conditions. Because the spot is very small, nearly all of the gas is at the wall temperature T_w , and has a corresponding average molecular speed \bar{v}_w . However, if the entire wall were at a temperature T_c , then the gas would all be at temperature T_c in equilibrium with the evaporation from the "condensing spot." If, therefore, we imagine the spot to be replaced by an opening with a chamber at temperature T_c on the other side of the opening, Fig. 3, the resulting imaginary system may be treated by the same analysis as the real system. In particular, the molecules in the imaginary system travel through the opening at different speeds (\bar{v}_w or \bar{v}_c) depending on their origin, so the ultimate pressure in the actual chamber (with no gas addition) is given by the classic thermal transpiration analysis, $p_u = p_v (T_w/T_c)^{1/2}$, where p_v is the vapor pressure of the condensate and also the pressure in the imaginary chamber at temperature T_c , and where molecular speed is proportional to the square root of the absolute temperature. If the condensing spot is at 20°K , the vapor pressure of nitrogen is 10^{-11} torr and the ultimate pressure in the chamber for nitrogen gas alone (no outgassing from the walls and no inleakage) is $10^{-11} (300/20)^{1/2} = 3.87 \times 10^{-11}$ or almost four times the condensate vapor pressure.

The pumping speed is determined by the difference between condensing rate and evaporation rate. However, at pressures significantly higher than ultimate, the amount of evaporation is insignificant as compared to the amount of condensation, so the volumetric pumping speed is (assuming unity sticking fraction) $S = (\bar{v}_w/4)A$, which is the "orifice speed" for gas at temperature T_w . For 300°K nitrogen gas, the orifice speed per unit area is approximately 75 liter/sec for each square inch.

2. Parallel Wall Cryopumping

Next consider the case of two parallel walls,¹⁰ Fig. 4. One is at temperature T_c and condenses a fraction f of all the gas which strikes it. The other wall is at a warmer temperature T_w and reflects all incident gas. For simplicity of calculations, we assume unity accommodation coefficient at both walls. The gas molecules leaving a wall in random directions are different from a normal random gas in that there is no component of velocity back toward the wall. The volumetric flow of such a gas is therefore given by $\bar{v}/2$ rather than the usual $\bar{v}/4$, where \bar{v} is the average speed of the molecules. Consider the mass flow of evaporated vapor from the cold wall to be \dot{w}_c and the mass flow of outgassing from the warm wall to be \dot{w}_w . Define \dot{m}_c as the total flow of gas from the cold wall, and \dot{m}_w as the total flow of gas from the warm wall. Then the total gas flow leaving the warm wall is the outgassing plus the reflected gas from the cold wall, i.e., $\dot{m}_w = \dot{w}_w + \dot{m}_c$. Similarly, the total gas leaving the cold wall is the fraction from the warm wall which is reflected at the cold wall, plus the rate of condensate vaporization. That is, $\dot{m}_c = (1 - f) \dot{m}_w + \dot{w}_c$. Solving these two equations gives:

10. R.W. Moore, Jr., Trans. Eighth National Vacuum Symposium and Second International Congress on Vacuum Science and Technology (Pergamon Press, 1962), Vol. 1, p. 426.

$$\dot{m}_c = \frac{\dot{w}_w (1 - f) + \dot{w}_c}{f} ,$$

$$\dot{m}_w = \frac{(\dot{w}_w + \dot{w}_c)}{f} .$$

The mass flow rate is simply the density multiplied by the volumetric flow rate:

$$\dot{m} = [\rho(\bar{v}/2)A] ,$$

thus

$$\rho_{tot} = \rho_w + \rho_c = \frac{2\dot{m}_w}{\bar{v}_w A} + \frac{2\dot{m}_c}{\bar{v}_c A} .$$

Substituting the expressions for \dot{m}_w and \dot{m}_c , we get an expression for total density in terms of the rates of evaporation and outgassing (or other gas introduction). The net gas load being pumped is that introduced at the warm wall, i.e., \dot{w}_w , and if this is divided by the density, we get a volumetric "speed" S. When we carry out the substitutions, we get

$$\frac{S}{A} = \frac{\dot{w}_w}{\rho A} = \frac{f (\bar{v}_w/2)}{[1 + (1 - f)(T_w/T_c)^{1/2}] + (\dot{w}_c/\dot{w}_w) [1 + (T_w/T_c)^{1/2}]}$$

For $f = 1$, i.e., complete capture, the expression reduces to

$$\left(\frac{S}{A} \right) = \frac{(\bar{v}_w/2)}{1 + (\dot{w}_c/\dot{w}_w) [1 + (T_w/T_c)^{1/2}]}$$

and, if the introduced gas load is much greater than the rate of evaporation (which is true in most practical applications), then

$$(S/A) = (\bar{v}_w/2)$$

which is twice the so-called "orifice speed."

Although the basic expression derived for speed in terms of \dot{w}_w and \dot{w}_c is satisfactory, it is interesting to develop an alternate expression for speed in terms of chamber pressure and condensate vapor pressure.^{10,11} First, we note that when a gas leaves a wall in random directions, the averaged component of molecular velocity normal to the wall is $\bar{v}/2$, where \bar{v} is the average speed of the molecules. Then the mass flow rate away from a wall section of area A is $\dot{m} = A\rho(\bar{v}/2)$, where ρ is the density of that part of the gas which is leaving the wall. The same sort of expression exists for that part of the gas which is incident on the wall. Dividing the difference in mass flow (between incident and evaporated gas) by the total density, $\rho_{tot} = \rho_w + \rho_c$, gives the volumetric pumping speed. That is,

$$\frac{S}{A} = \frac{\rho_w(\bar{v}_w/2) - \rho_c(\bar{v}_c/2)}{\rho_w + \rho_c} .$$

11. E.L. Garwin, in Advances in Cryogenic Engineering (Plenum Press, 1963), Vol. 8, p. 37.

In order to convert the "partial densities" in this expression to pressures, we define $Mp = \rho RT$, where

- M = molecular weight of the gas
- p = "pressure"
- ρ = density
- R = universal gas constant
- T = absolute temperature.

This definition agrees with the "pressure" as measured by a nude ion gauge, where the gauge actually measures gas density. Then

$$\rho_w = Mp_w / RT_w ,$$

and

$$\rho_c = Mp_c / RT_c ,$$

and using

$$\bar{v}_c / \bar{v}_w = (T_c / T_w)^{1/2} ,$$

$$\frac{S}{A} = \frac{\bar{v}_w}{2} \left[\frac{p_w - p_c (T_w / T_c)^{1/2}}{p_w + p_c (T_w / T_c)^{1/2}} \right] .$$

By using the concept of total pressure, $p = p_w + p_c$, and vapor pressure, $p_v = 2p_c$ (that is, the true vapor pressure includes equal flows toward and away from the wall), we get

$$\frac{S}{A} = \left[\frac{p - (p_v/2) (1 + (T_w/T_c)^{1/2})}{p - (p_v/2) (1 - T_w/T_c)^{1/2}} \right] \left(\frac{\bar{v}_w}{2} \right) .$$

Clearly, when $p \gg p_v$, we have a constant speed (twice the orifice speed) independent of pressure. However, we know that at some ultimate pressure the net speed must be zero. Setting $(S/A) = 0$ gives the ultimate pressure

$$p_u = (p_v/2) [1 + (T_w/T_c)^{1/2}] .$$

If we consider the initial fall-off in low pressure speed to occur when $(S/A) = 0.9 (\bar{v}_w/2)$, i.e., when 10% decrease in speed has occurred, then the "fall-off pressure" p^* is given by

$$0.9 = \frac{p^* - (p_v/2) [1 + (T_w/T_c)^{1/2}]}{p^* - (p_v/2) [1 - T_w/T_c]} .$$

The following values are obtained:

T_w °K	T_c °K	p^*
300	100	22.65 p_v
300	20	87.4 p_v

Therefore, in order to maintain full pumping speed the cryoplate temperature must be cold enough that the condensate vapor pressure is well below the operating pressure.

It is interesting to use the ultimate pressure in this same expression for the "fall-off" pressure, to get

$$0.9 = \frac{p^* - p_u}{p^* - \left[\frac{p_u}{1 - (T_w/T_c)^{1/2}} \right]}$$

$$\frac{p^*}{p_u} = 10 \left[1 + \frac{0.9}{(T_w/T_c)^{1/2} - 1} \right]$$

This shows that speed falls off for pressures at least one order of magnitude greater than ultimate.

3. Concentric Sphere Cryopumping

There are few true "spot cryopumps" and even fewer parallel wall (two-dimensional) pumping systems. The simplest model for a "three-dimensional" cryopumping situation is that of two concentric spheres, and such pumping situations do exist. The most extensively studied of these (because of its direct application to space simulation work) is that of a warm outgassing sphere concentrically surrounded by a cold cryopumping sphere.^{12,13} The method of determining pumping speed for this situation has the same basis as the methods used for spot cryopumping and for parallel wall cryopumping. That is, the speed is defined as the ratio of mass capture to total gas density ρ at the point of pumping. In a closed system, the mass capture rate (at equilibrium) is simply the rate at which gas is introduced, or in our example, the warm outgassing rate, \dot{w}_w . Therefore, $S = \dot{w}_w/\rho$. The density is obtained as follows. We note, from Fig. 5, that gas which leaves the warm inner sphere at temperature T_w (assuming an accommodation coefficient of unity at all surfaces) will definitely strike the outer surface. The gas leaving the cold wall at temperature T_c may go to the warm inner sphere, or it may bypass the inner sphere and go to another part of the cold wall. Therefore, the gas at any point adjacent to the cryopumping sphere comes from three different sources. These are: (1) gas leaving the cold surface in random directions at average speed \bar{v}_c , (2) gas approaching the cold surface from the warm sphere, moving at an average speed \bar{v}_w within an angle φ to the normal, and (3) gas approaching the cold surface from other parts of the cold wall, moving at an average speed \bar{v}_c and at an angle to the normal greater than φ . The normal component of velocity for any molecule moving toward a surface at a speed v and at an angle θ to that surface is $v \cos \theta$. Averaging over all permitted directions (within some total solid angle Ω), the average normal molecular component of speed toward the surface is given by

$$\frac{1}{\Omega} \int \bar{v} \cos \theta \, d\Omega \quad .$$

12. C.B. Hood and C.B. Barnes, J. Vacuum Sci. Tech. 2, 302 (1965).

13. J.D. Pinson and A.W. Peck, Trans. Ninth National Vacuum Symposium (MacMillan Co., 1962), p. 406.

The mass flow per unit area toward the surface is the product of gas density and average normal component of velocity, so

$$\frac{\dot{m}}{A} = \rho \left[\frac{1}{\Omega} \int \bar{v} \cos \theta \, d\Omega \right] .$$

Consider the molecules moving away from the cold surface in all directions within an angle $\pi/2$ to the normal. Then

$$\begin{aligned} \frac{\dot{m}_c}{A_c} &= \rho_c \left[\frac{1}{2\pi} \int_0^{\pi/2} \bar{v}_c \cos \theta \, 2\pi \sin \theta \, d\theta \right] \\ &= (\rho_c \bar{v}_c / 2) , \end{aligned}$$

where ρ_c is that part of the total density attributed to the molecules under discussion, i.e., those leaving the cold surface. Next consider the molecules moving toward the cold surface from the warm inner surface at all angles $0 < \theta < \varphi$ measured from the normal:

$$\begin{aligned} \frac{\dot{m}_{wc}}{A_c} &= \rho_{wc} \left[\frac{\int_0^{\pi/\varphi} \bar{v}_w \, 2\pi \sin \theta \cos \theta \, d\theta}{\int_0^{\varphi} 2\pi \sin \theta \, d\theta} \right] \\ &= \frac{\rho_{wc} \bar{v}_w}{2} \cdot \left[\frac{\sin^2 \varphi}{1 - \cos \varphi} \right] . \end{aligned}$$

Finally, consider the molecules moving toward the cold surface from other parts of the cold surface (at all angles $\varphi < \theta < \pi/2$):

$$\frac{\dot{m}_{cc}}{A_c} = \rho_{cc} \bar{v}_c \left[\frac{\cos \varphi}{2} \right] .$$

The total density is then

$$\begin{aligned} \rho &= \rho_c + \rho_{wc} + \rho_{cc} \\ &= \frac{2}{\bar{v}_w A_c} \left[\dot{m}_c \left(\frac{T_w}{T_c} \right)^{\frac{1}{2}} + \dot{m}_{wc} \left(\frac{1 - \cos \varphi}{\sin^2 \varphi} \right) + \frac{\dot{m}_{cc}}{\cos \varphi} \left(\frac{T_w}{T_c} \right)^{\frac{1}{2}} \right] . \end{aligned}$$

There remains to express the mass flow in terms of the total outgassing rate \dot{w}_w , and the total evaporation rate \dot{w}_c . This is done by noting that the amount of gas leaving any surface is the sum of gas emitted by that surface and the gas reflected from it. Mass balance gives:

$$\begin{aligned} \dot{m}_c &= \dot{w}_c + (\dot{m}_{wc} + \dot{m}_{cc}) (1 - f) \\ \dot{m}_{wc} &= \dot{w}_w + F \dot{m}_c \\ \dot{m}_{cc} &= \dot{w}_c (1 - F) + (\dot{m}_{wc} + \dot{m}_{cc}) (1 - f) (1 - F) \\ &= \dot{m}_c (1 - F) , \end{aligned}$$

where f is the capture fraction at the cold surface, and F is the view factor from the outer surface to the inner surface, i.e., F is the fraction of molecules which will strike the inner surface A_w after diffusely leaving the outer surface A_c . Solving the equations and substituting into the expression for total density gives

$$\left(\frac{\bar{v}_w A_c}{2 \dot{w}_w} \right) \rho = \left(\frac{T_w}{T_c} \right)^{\frac{1}{2}} \left\{ \frac{\dot{w}_c}{\dot{w}_w} \cdot \frac{1}{f} + \left(\frac{1-f}{f} \right) + (1-F)^{\frac{1}{2}} \left[\frac{\dot{w}_c}{\dot{w}_w} \cdot \frac{1}{f} + \left(\frac{1-f}{f} \right) \right] \right\} \\ + [1 - (1-F)^{\frac{1}{2}}] \left\{ \frac{\dot{w}_c}{\dot{w}_w} \cdot \frac{1}{f} + \frac{1}{F} + \frac{1}{f} - 1 \right\} ,$$

where the substitution $\cos \varphi = (1-F)^{\frac{1}{2}}$ has been made also. The speed of pumping is therefore

$$S = \frac{\dot{w}_w}{\rho} \\ = \frac{(\bar{v}_w/2) A_c}{[1 - (1-F)^{\frac{1}{2}}] \left[\frac{\dot{w}_c}{\dot{w}_w} \cdot \frac{1}{f} + \frac{1}{F} + \frac{1}{f} - 1 \right] + [1 + (1-F)^{\frac{1}{2}}] \left(\frac{T_w}{T_c} \right)^{\frac{1}{2}} \left[\frac{\dot{w}_c}{\dot{w}_w} \cdot \frac{1}{f} + \left(\frac{1-f}{f} \right) \right]}$$

The additional complications of the three-dimensional analysis are obvious.

The equation just developed for speed may be put into a better form for practical solutions. For spheres,

$$(A_w/A_c) = F$$

and

$$\frac{\dot{w}_c}{\dot{w}_w} = \frac{\dot{w}_c/A_c}{\dot{w}_w/A_w} \cdot \frac{1}{F} .$$

Then, using the symbol R to represent the ratio of evaporation per unit area of the cold wall to outgassing rate per unit area of the warm sphere,

$$\left(\frac{\dot{w}_c}{\dot{w}_w} \right) = R/F ,$$

and

$$\frac{S}{A_c} = \frac{\bar{v}_w}{4} \left\{ \frac{2F}{[1 - (1-F)^{\frac{1}{2}}] \left[\frac{R}{f} + 1 + \frac{F}{f} - F \right] + [1 + (1-F)^{\frac{1}{2}}] \left(\frac{T_w}{T_c} \right)^{\frac{1}{2}} \left[\frac{R}{f} + \left(\frac{1-f}{f} \right) \right]} \right\}$$

which is orifice speed per unit area multiplied by a correcting factor. For $F = 1$ (indicating that the two spheres are nearly equal size) this expression reduces to

$$\frac{S}{A_c} = \frac{f(\bar{v}_w/2)}{(1+R) + (T_w/T_c)^{\frac{1}{2}}(1-f+R)}$$

This is the same expression developed earlier for parallel walls.

4. Arguments in the Definition of Speed and Pressure

The analysis for cryopumping speed, in the system of an infinitesimal warm sphere (or outgassing source) at the center of a perfectly condensing spherical cryopumping surface gives (for $F \rightarrow 0$ and $f = 1$) $S = 4(\bar{v}_w/4)A$, which is a factor of four greater than orifice speed. Most vacuum texts imply that orifice speed is an upper limit to pumping rates, and represents a "perfect system." This apparent contradiction is really only a conflict in initial assumptions. The classical analysis of orifice speed is the determination of the volumetric rate at which gas strikes a perfectly reflecting surface in a closed system in equilibrium. If a pinhole orifice in this surface allows gas to escape to a perfect vacuum, the volumetric rate of escape out of the orifice is given by $(S/A) = (\bar{v}/4)$. The orifice is so small that equilibrium is only slightly disturbed. If the orifice size is increased, equilibrium is disturbed, completely random motion no longer exists, and the definition of volumetric pumping speed becomes ambiguous. However, we can think of at least one completely nonequilibrium case in which volumetric speed seems clearly indicated. In this case, a perfectly collimated beam of molecules is completely captured by a surface perpendicular to the direction of motion. If the average molecular speed is \bar{v} , then the volumetric speed of molecular capture per unit area of capturing surface is \bar{v} . It seems reasonable, therefore, to define pumping speed at a point in terms of the gas conditions at that point.^{14,15} Such a definition always gives a unique speed if we simply divide mass capture rate by gas density, both measured at the point in question. This definition gives the true volumetric speed, and has been used throughout the present discussion.

There have been objections to a definition of pumping speed based on nonequilibrium conditions. However, we note that "beaming" of molecules, i.e., collimated motion, does usually cause an increase in the molecular capture rate. It seems only reasonable to say that increased capture rate indicates increased "speed," and the definition of volumetric speed as mass capture rate divided by density certainly seems better than any alternate proposals.

There is also some confusion concerning the definition of pressure. The basic definition is, of course, the force per unit area on a surface, this definition is satisfactory for an equilibrium gas. When a gas is not in equilibrium, then true pressure becomes directional. However, in most cases we are really interested in "how much" gas is present in a given volume, i.e., in the density. It is for that reason that the foregoing analysis used $p = \rho RT/M$ as the definition of gas pressure, regardless of directions. If a nude, or nontubulated, gauge is used, then it is actually density rather than true pressure that is being measured. Therefore, we must add the qualification, in our analyses, that the theoretical results will correspond to measured results only if a nude gauge is used to measure pressure.

IV. MASS CAPTURE RATES

The mass capture rate of a cryopumping system is sometimes quite difficult to calculate. For the simplest geometries, discussed in Sections III.1, III.2, and III.3, it is sufficient to separate the gas leaving each surface into the gas originating from that surface and the gas reflected from it.¹⁰ Then a set of equations may be set up which are solved for the total gas leaving each surface, expressed in terms of the gas originated at all other surfaces. This method is, in principle, adequate for all

14. C.B. Barnes, Vacuum **14**, 429 (1964).

15. W.W. Stickney and B.B. Dayton, Trans. Tenth National Vacuum Symposium (MacMillan Co., 1963), p. 105.

analysis, but in fact it becomes difficult to use if the systems are very complicated. For that reason, we present three other techniques for determining mass flows (or throughput flows) in general systems.

1. Network Analogy

There is an analogy between free molecular gas transfer and radiant energy transfer which is quite striking. For example, a variation of the Oppenheim network method for radiant transfer may be used to determine the free molecular mass gas flow between arbitrary surfaces.¹⁴ In this technique,

$$Q_{\text{net}} = (J - G)A$$

where G = incident mass rate per unit area on the surface,

J = mass rate per unit area leaving the surface.

Also, $J = W' + (1 - f)G$,

where W' = outgassing (or evaporation) mass rate per unit area,

f = capture fraction of incident molecules.

The last equation may be written

$$(1 - f)(J - G) = f \left(\frac{W'}{f} - J \right)$$

from which

$$Q_{\text{net}} = \frac{\left(\frac{W'}{f} - J \right)}{\left(\frac{1 - f}{fA} \right)}$$

The "electrical" analogy is that the "potential difference" corresponds to $(W/f) - J$ and the "resistance" corresponds to $(1 - f)/fA$. For any two surfaces A_i and A_j , the net free molecular mass flow between them is

$$(Q_{\text{net}})_{ij} = A_i F_{ij} J_i - A_j F_{ji} J_j = A_i F_{ij} (J_i - J_j),$$

where the view factor F_{ij} is the fraction of diffusely emitted molecules which leave A_i and strike A_j . Here, "potential difference" corresponds to $J_i - J_j$, while the "resistance" corresponds to $(A_i F_{ij})^{-1}$. For example, consider the simple two-surface system of Fig. 6 where the total potential difference is divided by the sum of the resistances to get the net gas transfer:

$$Q_{\text{net}} = \frac{\frac{W'_1}{f_1} - \frac{W'_2}{f_2}}{\frac{1 - f_1}{f_1 A_1} + \frac{1}{A_1} + \frac{1 - f_2}{f_2 A_2}}$$

In our treatment of two infinite planes, the warm surface did not capture, and therefore the net mass flow was simply the outgassing of the warm, noncapturing surface. In the equation above, this is obtained by setting $f_1 = 0$, so that $Q_{\text{net}} = W'_1 A_1$.

The basic technique may be extended to any number of surfaces in a closed system. The network for a four-surface system is shown in Fig. 7, where the net gas flow is determined just as is current in an electrical system.

2. Adopted Gebhart Method

Another, and probably better, technique of determining mass flow to arbitrary surfaces is an adoption of the Gebhart method of matrix solution to radiant heat transfer. In the adopted Gebhart method, we define B_{ij} as the fraction of molecules which diffusely leave a surface A_i and are captured by another surface A_j . The fraction includes not only direct motion from A_i to A_j , but also motion from A_i to other surfaces and then, after reflection(s), capture by A_j . In a closed system, the fraction of molecules which leave A_i and are eventually captured by A_j can be expressed as a sum of terms, of which a typical one is $F_{ik}R_kB_{kj}$. In this term, F_{ik} is the fraction of molecules going directly from A_i to A_k , where a fraction R_k is reflected. Of these reflected molecules (from surface A_k) a fraction B_{kj} will eventually be absorbed by A_j , going there by whatever paths are available. This expression of B_{ij} as a sum of terms is:

$$B_{ij} = F_{i1}R_1B_{1j} + F_{i2}R_2B_{2j} + \dots + (F_{ij}R_jB_{jj} + F_{ij}f_j) + F_{in}R_nB_{nj}$$

The term $F_{ij}f_j$ represents the fraction of molecules captured by A_j after a direct flight from A_i . This basic equation may be rewritten as:

$$-F_{ij}f_j = F_{i1}R_1B_{1j} + F_{i2}R_2B_{2j} + \dots + (F_{ii}R_i - 1)B_{ij} + \dots + F_{in}R_nB_{nj}$$

Fixing j and allowing i to vary from 1 to n gives n equations, which can be solved by Cramer's rule:

$$\Delta = \begin{vmatrix} (F_{11}R_1 - 1) & F_{12}R_2 & F_{13}R_3 \dots & F_{1n}R_n \\ F_{21}R_1 & (F_{22}R_2 - 1) & F_{23}R_3 \dots & F_{2n}R_n \\ F_{31} & & & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ F_{n1}R_1 & F_{n2}R_2 \dots & & (F_{nn}R_n - 1) \end{vmatrix}$$

$$B_{kj} = - \frac{f_j}{\Delta} \begin{vmatrix} (F_{11}R_1 - 1) & F_{12}R_2 \dots & F_{1,k-1}R_{k-1} & F_{1j} & F_{1,k+1}R_{k+1} \dots & F_{1n}R_n \\ F_{22}R_1 & (F_{22}R_2 - 1) \dots & F_{2,k-1}R_{k-1} & F_{2j} & F_{2,k+1}R_{k+1} & F_{2n}R_n \\ \cdot & & & & & \\ \cdot & & & & & \\ \cdot & & & & & \\ F_{n1}R_1 & F_{n2}R_2 \dots & F_{n,k-1}R_{k-1} & F_{nj} & F_{n,k+1}R_{k+1} \dots & (F_{nn}R_n - 1) \end{vmatrix}$$

If we restrict the meaning of B_{ij} (whatever the values of i and j) to the fraction of molecules emitted by A_i (that is, originating at A_i) and captured by A_j , then we have a direct and comparatively simple method of determining capture fractions for systems of many surfaces, including partly shielded cryopumping surfaces. The advantage of the adopted Gebhart method over the network method is the direct solution of the former. In the network method, equations must still be set up and solved even after the network itself has been drawn.

3. Monte Carlo Technique

Finally, the molecular capture fraction of a cryopumping system may be determined by Monte Carlo techniques.¹³ Possible paths of molecules are traced by mathematical expressions in a computer program; many such computed paths determine the approximate capture fraction of the system. The Monte Carlo technique has been used extensively in determining free molecular conductance fractions,^{16,17} i.e., Clausing factors, and may also be used for any closed system where the geometry and sticking fraction are known. One great advantage of the Monte Carlo technique over most others is that nondiffuse reflection may be programmed into the solution. In the adoptions of the Oppenheim and Gebhart methods to free molecular gas flow, it is essential that all reflections be diffuse and therefore that molecules do not have a "memory" after striking a surface.

4. Shielded Array Capture Fractions

Cryopumping may be used even in the presence of high temperature surfaces which radiate great amounts of thermal energy. In such situations, the cryopumping surfaces are shielded by cool panels, which panels absorb the majority of the thermal radiation load. For example, the array shown in cross section in Fig. 8 has been used in many space simulation systems. The 20°K plates are separated from each other by one plate width, and are separated from the back-up sheet by at least one plate width. The front shields and the back-up sheet are cooled to between 77°K and 100°K. The back-up sheet is painted with a highly absorptive material (for absorbing thermal radiation). Radiant energy incident on the array will be partly reflected (or absorbed) by the front shields and partly transmitted to the back-up sheet. If the spaces and plates are exactly equal in width, then half of the incident radiation will pass between the shields through the back-up plate, where 10% will be reflected. Half of the reflected radiation will strike the 20°K plates, and half will return to the openings. If these plates are "bright" so that about 90% of the incident radiation is reflected, then the total fraction of incident radiation which is eventually absorbed at the 20°K plates is $(\frac{1}{2})(0.1)(\frac{1}{2})(0.1) = 0.0025$, or a quarter of one percent. On the other hand, if the sticking fraction for molecules is unity on the 20°K plate (and zero on the other sheets), the array capture fraction for incident molecules is $(\frac{1}{2})(1)(\frac{1}{2})(1) = 0.25$ or 25%. The 20°K plates in the array, therefore, capture molecules rather well, but are shielded from the thermal radiation. This simple situation was easily analyzed, but most other geometries are more complicated^{18,19} and usually require the use of a network solution, the Gebhart method, or a Monte Carlo analysis as described in the preceding sections.

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16. L.L. Levenson, N. Milleron, and D.H. Davis, Trans. Seventh National Symposium on Vacuum Technology (Pergamon Press, 1961), p. 372.
 17. D.W. Jones and C.A. Tsonis, J. Vacuum Sci. Tech. 1, 19 (1964).
 18. F.C. Hurlbut and P.J. Mansfield, in Advances in Cryogenic Engineering (Plenum Press, 1963), Vol. 8, p. 46.
 19. C.B. Barnes and C.B. Hood, in Advances in Cryogenic Engineering (Plenum Press, 1962), Vol. 7, p. 64.

It is important to note that there is no simple, direct relation between cryoplate area and pumping speed. A small perfectly capturing plate of area A inside a large chamber will pump gas at the rate $(\bar{v}/4)A$, where \bar{v} is the average molecular speed. This is a direct application of the orifice speed concept, and shows that for this simple situation, speed is directly proportional to pumping area. However, for the shielded array which we analyzed, the speed is $\frac{1}{4}[(\bar{v}/4)A]$, where A is the frontal area of the array. Actually, the cryoplate has two sides so that the cryoplate surface area is as much as the frontal area, but shielding has reduced the plate effectiveness to one fourth. If we were to use wider cryoplates, simultaneously reducing the space between the plates, we would have even more cryoplate area for a given frontal area, but the pumping speed would actually be reduced.

Also, it is important to distinguish between cryoplate sticking fraction and cryopumping array capture fraction. The sticking fraction is the fraction of molecules which will stick to a cold plate upon striking it. The cryopumping array capture fraction is the capture fraction of molecules incident on the frontal area (not plate area) of an array of cryoplates and shields.

V. CONDENSATE PROPERTIES

The thermal and physical properties of cryogenic condensates can be important. For example, the amount of radiant heat transfer to a cryopanel from surrounding warmer surfaces is dependent on the surface emissivities. When the condensate is sufficiently thick to obscure the base material, emissivity values are those of the condensate^{20,21} and obviously are not dependent on the base material. Experiments with deposits of water vapor on 77°K surfaces receiving nominal 300°K radiation shows emissivity values of 0.9 or greater²²; this is for thickness of 0.001 in. and more. On the other hand, the emissivity of CO₂ deposits is less than that of water vapor deposits, assuming equal thicknesses. The emissivity of many heavy cryodeposits receiving high temperature thermal radiation (composed of wavelengths in the low micron region) is in the range $e = 0.4$ to $e = 0.6$ although, naturally, there are exceptions. The effect of changing the cryosurface emissivity is to change the heat load to the cryogenic refrigeration system. This is usually of economic importance because the cost of refrigeration increases greatly with decreasing temperatures.

The presence of a thick cryodeposit can also prevent cryopumping at low pressures. Whatever heat load is absorbed at the deposit outer surface must be transferred across the deposit to the cold metal substrata. The temperature change across the deposit thickness is

$$\Delta T = \frac{t}{K} (\dot{Q}/A) ,$$

where (\dot{Q}/A) = heat load per unit area,

t = deposit thickness,

K = thermal conductivity.

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20. T.M. Cunningham and R.L. Young, in Advances in Cryogenic Engineering (Plenum Press, 1963), Vol. 8, pp. 85-92; Discussion, p. 92.
 21. R.P. Caren, A.S. Gilcrest, and C.A. Zierman, in Advances in Cryogenic Engineering (Plenum Press, 1964), Vol. 9, p. 457.
 22. B.C. Moore, Trans. Ninth National Vacuum Symposium (MacMillan Co., 1962), p. 212.

For example, solid nitrogen at 20°K has a thermal conductivity of about 4 mW/cm °K. If the condensate vapor pressure must remain below 10⁻⁷ torr (a typical value), then the condensate outer surface must not be warmer than 25°K. Under such conditions,

$$(\dot{Q}/A)t = K \Delta T = 0.02 \quad \text{W/cm} \quad .$$

The radiant heat load from a "black" 300°K surface is 0.045 W/cm². If a nominal 20°K cryoplate with nitrogen condensate were in a relatively large chamber surrounded with 300°K radiation surfaces, then the maximum allowed condensate thickness (with 25°K surface temperature) would be

$$t = \frac{0.02}{0.045} \text{ cm} \\ = 4.3 \text{ mm} \quad .$$

Therefore, it is not absolutely essential to shield nitrogen pumping cryopanel in a system where none of the surroundings are warmer than 300°K, unless a condensate thickness greater than a few millimeters is present, or unless the total heat load on the refrigeration system is excessive.

The physical properties of cryogenic solids²³ are, in general, not well known. The properties of solid cryodeposits are even less well known. Values given for condensate density, for example, are usually only educated conjectures. For example, cryopumped nitrogen²⁴ may have a specific gravity near unity, but it may also be much less dense, depending on whether it was formed with an ice-like structure or a snow-like structure. Other properties, such as brittleness, tensile or compressive strength, and hardness (as several examples) are known only to within orders of magnitude.

VI. CRYOSORPTION AND CRYOTRAPPING

Condensation pumping is the simplest cryogenic vacuum-pumping technique, but other techniques do exist. Cryosorption pumping, for example, offers advantages in refrigeration requirements. If activated charcoal or a zeolite (whether artificial or natural) is cooled to low temperatures, gases may be absorbed, to low pressures, at their normal boiling temperature.²⁵⁻²⁸ For example, nitrogen gas may be sorbed to sub-micron pressures by Molecular Sieve 5A cooled to 77°K. Ordinary condensation pumping would require a cryoplate temperature of less than 34°K to achieve the same result. Similarly, helium can be pumped to very low pressures (in the range 10⁻⁶ to 10⁻¹⁰ or lower depending on conditions) at temperatures around 3.5°K to 4°K. As is well known,

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23. V.J. Johnson (ed.), National Bureau of Standards Technical Report WADD 60-56 (1960).
 24. R.L. Chuan, University of Southern California Report USCEC 56-201 (1957).
 25. R.A. Hemstreet et al., Arnold Engineering Development Center Report AEDC-TDR-64-100 (1964).
 26. S.A. Stern et al., Arnold Engineering Development Center Report AEDC-TDR-62-200 (1962).
 27. F.T. Turner and M. Feinleib, Trans. Eighth National Vacuum Symposium and Second International Congress on Vacuum Science and Technology (Pergamon Press, 1962), Vol. I, p. 300.
 28. J.E.A. John and W.F. Hardgrove, Am. Inst. Aeron. Astronaut. Publication CP-11 (1964), p. 1.

helium does not solidify under vacuum conditions, and ordinary cryopumping techniques can never be used to pump helium gas. Although cryosorption pumping has much to recommend it, there are numerous disadvantages. Gases which freeze on the sorption surface are obviously not absorbed; and for such gases there is no advantage over ordinary cryopumping. Also, if frozen gas covers the surface, then the blockage will prevent all gases from being absorbed. Examples of troublesome freezing situations are moist air being sorption pumped at 77°K, and nitrogen contaminated hydrogen being sorption pumped at 20°K. Even if the gas being pumped is appropriate for the sorbent and for the sorbent temperature, the rate of pumping is strongly history dependent. If the sorbent pumps long enough, in a closed container, an equilibrium will be established between the "saturated" gas in the cold sorbent and the gas at reduced pressure in the container. Equilibrium exists when the net pumping speed is zero. This equilibrium condition will occur at higher pressures for greater total absorption. It would seem logical that pumping speed should decrease at lower pressures, and should depend in some way on the difference between actual system pressure and the "equilibrium pressure" corresponding to the amount of gas absorbed. Such dependence does indeed occur. However, it is usually masked by another effect, which is: speed is reduced by high rates of absorption. That is, if the mass absorption rate is high, the pumping speed (indicating molecular capture fraction) will continuously decrease; if the throughput is reduced, the molecular capture fraction (and therefore the volumetric speed) will increase as the sorbent material "recovers." The net result of these effects is that pumping speed varies in a complicated way with both the total amount of gas absorbed and rate at which it is being absorbed.

Another technique of cryogenic pumping is cryotrapping. In this technique, rapid cryopumping of one gas results in trapping of a "noncondensable" gas impurity into the condensate. For example, limited amounts of helium can be cryotrapped in the process of cryopumping relatively large amounts of nitrogen at 20°K. The disadvantage of cryotrapping is its gross inefficiency, which prevents pumping of more than trace amounts of gas.

VII. CRYOGENIC PUMPING, PRO AND CON

The disadvantages of a cryogenic pumping system are primarily:

- a) The cryogenic liquids and/or refrigerators are so expensive that usually only high speed systems can be justified economically.
- b) Cryogenic pumping, whether by condensation or sorption, is quite selective in the gases pumped. The same gas can be cryosorbed at a higher temperature than it is cryopumped, for example, but then the sorption material must be protected from higher freezing point gases freezing on the surface.
- c) Cryopumping is not economically justified at pressures high enough that the heat of condensation is a major part of the heat load.
- d) Cryosorption systems do not maintain constant pumping speeds; the speed varies both with the total amount of gas absorbed and with the mass rate of absorption.

On the other hand, cryogenic pumping has three great advantages over other pumping systems. First, the total area which can be cryogenically cooled is large relative to the pumping orifices of most pumps; consequently, speeds of as high as several millions of liters per second are attained in very large chambers, while speeds of as high as a few tens of thousands of liters per second are attained in chambers containing several square feet of cryopumping sheets. Second, cryogenic pumping is "clean" pumping; a failure of the pumping system will raise the chamber pressure but will not cause

contamination such as that from back diffusion by oil diffusion pumps. Third, the cost of cryopumping in terms of dollars per liter/sec is lower than for any other vacuum pumping system, provided that the system is large enough (and the heat load low enough) that the basic fixed costs (engineering, etc.) are not the major costs. At the present time, simple 20°K cryopumping systems compete economically with other vacuum pumping systems for system speeds of around 50 000 liter/sec or more (free molecular region). Special purpose cryosorption systems (particularly those using liquid nitrogen cooling) can compete even at very low speeds if the total amount of the gas to be absorbed is not too great. Finally, various systems which already contain low temperature liquids or other means of cryogenic refrigeration may sometimes be adapted to cryopumping with a minimum of effort. One example is that of vacuum jacketed, cryogenic tankage in which the cold inner tank surface may be used, with proper engineering, for cryopumping and/or cryosorption.

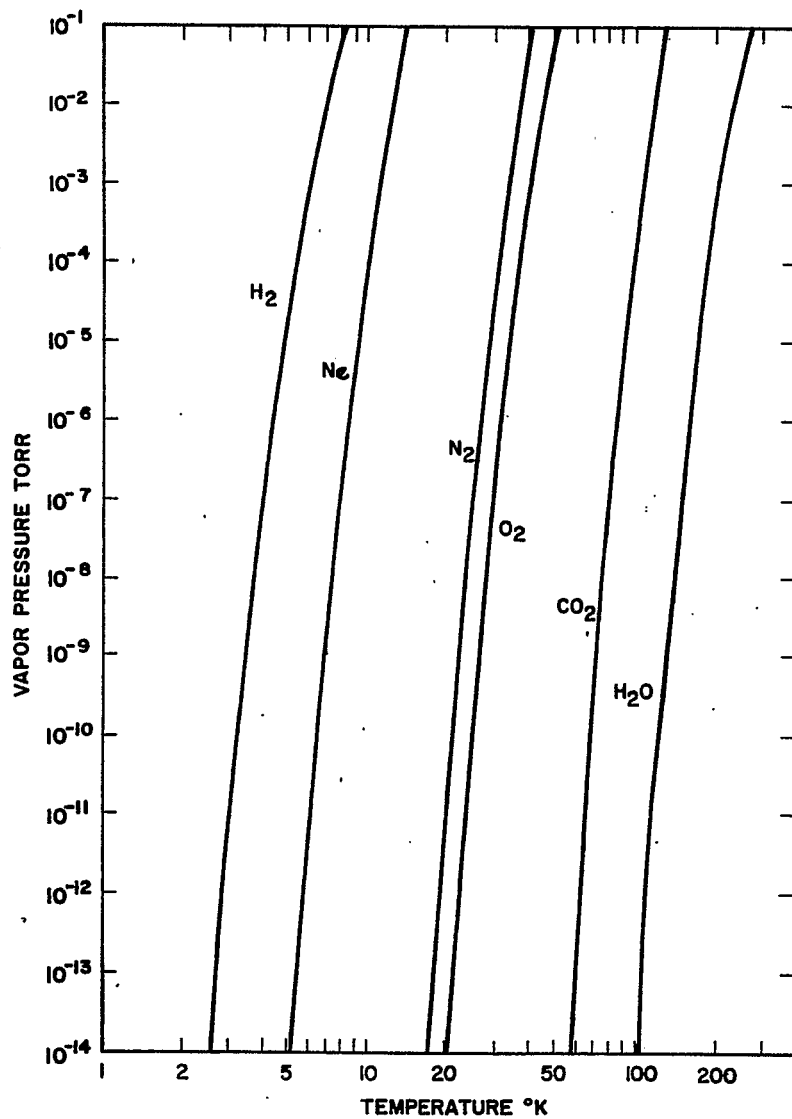


Fig. 1. Vapor pressure vs temperature of condensate.

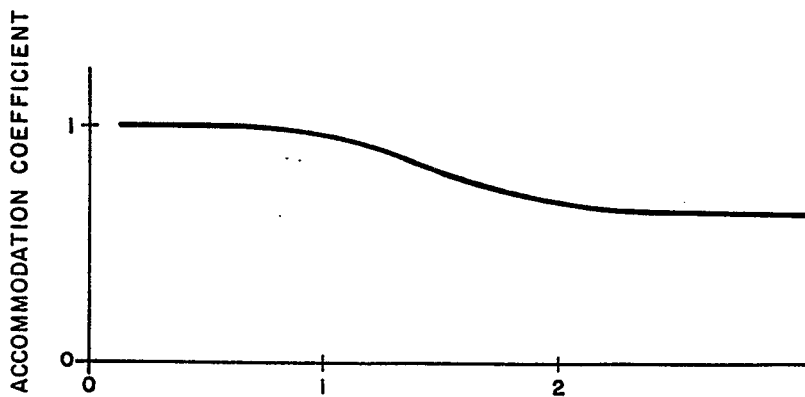


Fig. 2. Reduced temperature T/T_c

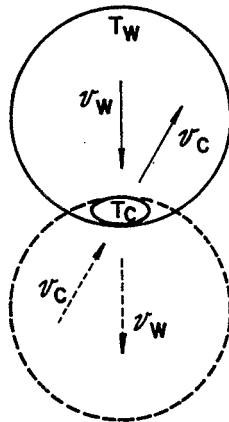


Fig. 3. Schematic of spot cryopumping

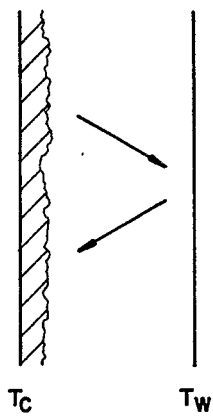


Fig. 4. Parallel plate.

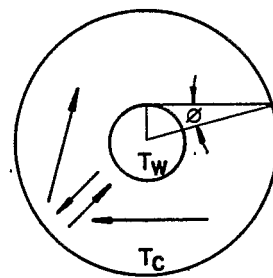


Fig. 5. Spherical cryopumping systems.

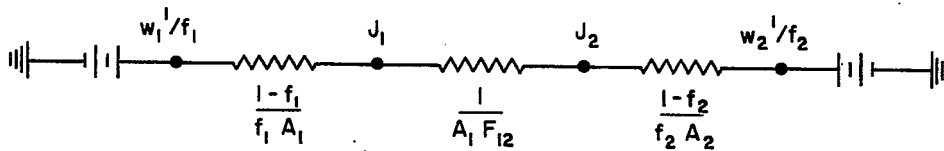


Fig. 6. Two-surface network.

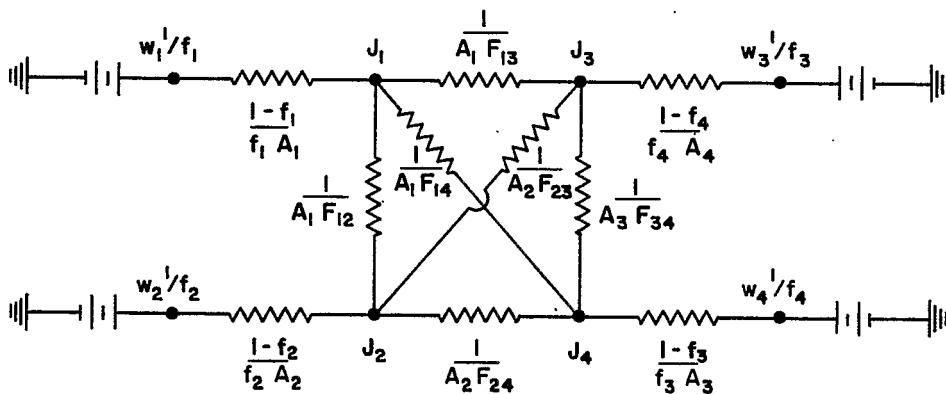


Fig. 7. Four-surface network.

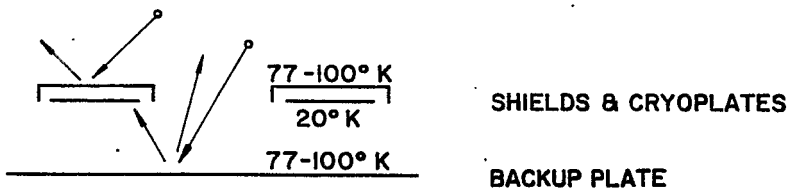


Fig. 8. Shielded cryopumping array.