Cryogenic adsorption of noncondensibles in the high-vacuum regime

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Cryogenic vacuum pumps must use cryogenic adsorption means to remove helium, hydrogen, and neon from vacuum systems in order to achieve high vacuum. The capacity of one such cryosorbent, charcoal, is presented in the form of isosteres of hydrogen and helium in the pressure range $10^{-7}$–$10^{-4}$ Torr and temperature range 10–25 K. Certain important dynamic loading effects related to surface mobility and pore clogging are discussed which can, in high-flow environments, appreciably affect the apparent capacity of the adsorbent. The implications of the static and dynamic results are discussed in relation to practical aspects of cryopumping, i.e., partial or selective regeneration and optimal cryopumping temperatures.

I. INTRODUCTION

Cryogenic vacuum pumps create vacuum by removing gases from a closed volume. Most gases are frozen, but certain gases, called type III, must be cryogenically adsorbed (cryoadsorbed) on a suitable adsorbent material at very low temperatures. The capacity of a pump for the noncondensibles (hydrogen, helium, and neon) is orders of magnitude lower than for other gases; also, cryoadsorption is an inherently more complicated phenomenon than freezing. Therefore, proper understanding of the cryoadsorption process is crucial to cryogenic vacuum pump design and system operation.

Hydrogen is nearly always present in significant quantities in the high-vacuum ($10^{-7}$–$10^{-5}$ Torr) regime because of dissociation of residual water vapor from vacuum system surfaces. In addition, many vacuum processes produce $\text{H}_2$ because of water vapor introduced with the product (e.g., coating of plastic films). Hydrogen is also produced during high-temperature processing of certain metals, notably aluminum. The water vapor readily dissociates due to the high energy used in normal processing.

Helium and neon, although generally less of a problem, are present in small quantities in the atmosphere and helium is often used as a leak check medium. Heavy-cycle load lock usage can result in significant buildup of helium or neon in the load lock pump if sufficient capacity is not provided.

Cryogenic adsorption occurs when a very compact porous adsorbent is tightly bonded to a cryopanel maintained at a temperature <20 K by a cryogenic refrigerator (e.g., Fig. 1). The adsorbent material of choice is usually charcoal. Some molecular sieves have higher adsorption capacity than charcoal, but regeneration of the charcoal surface can be accomplished at ambient temperature as opposed to the rather high temperatures needed to clean molecular sieves.

The testing reported here was designed to characterize the adsorption process in the temperature and pressure regimes particular to cryopumps ($10^{-4}$ Torr $> P > 10^{-7}$ Torr, $10 < T < 25$ K). Other investigators have examined a small section or different section of the regime, but these results are only applicable to cryopumps through questionable extrapolations. In the testing reported here, both steady-state and dynamic loading effects are presented.

The testing yielded two important practical conclusions: partial or selective regeneration of a cryopump (i.e., heating the cryoadsorbent panels to devolve adsorbed species at a temperature well below ambient) is possible, but not practical in a production environment. Second, there is an optimal temperature for cryoadsorption of hydrogen and neon that is above the normally achievable minimum temperature found in commercially available cryopumps.

II. TEST DOME, INSTRUMENTATION, AND METHOD

The vacuum apparatus is shown schematically in Fig. 2. The measurement of total flow and pressure above the pump yields pump speed. The upper dome arrangement is used to calibrate ionization gauges by the steady flow method; after calibration, the gauge is moved to the lower position for test runs. The system uses all-metal seals and consistently achieves base pressure in the $10^{-10}$ Torr range.

The flow meter is an MKS molecular flow element. The meter was calibrated over several orders of magnitude of pressure differential using precision bore glass tubes in the flow displacement method. The ionization gauge was calibrated for each gas using the steady flow method. Thermometry was Lakeshore Cryotronics "D" series diodes with appropriate calibration.

Although care was taken to maximize instrument precision, it is important to realize that measurement in the high-vacuum and low-temperature regimes is difficult at best. The largest degree of error is associated with the ionization gauge. It is well known that even under the best of conditions, the sensitivity of hot filament ionization gauges can shift suddenly and unpredictably. The accuracy of the flow measurement is approximately ±5%, the pressure measurement better than ±15%, and the temperature measurement on the order of ±0.25 K.

The adsorbent panel used was a standard CTI-Cryogenics Cryo–Torr 8 array attached to the second stage of a refrigerator. The temperature of the array varies perceptibly as the refrigerator cycles at 72 rpm since there is very little "thermal mass," or total heat capacity at temperatures between 10 and 25 K. This variation can be as much as ±0.2 K at these low temperatures and introduces an observational variance in determining the average temperature.

For static capacity tests, the following methodology was used:
(i) Add the test gas at a rate sufficient to keep the pump in the mid-10⁻³ Torr range.

(ii) Stop flow, add heat slowly to raise the temperature of the array to the maximum required to keep the pressure just below 10⁻⁴ Torr. Stabilize.

(iii) Note pressure and temperature.

(iv) Reduce temperature in ~1 K increments for H₂ and 0.5 K increments for He.

(v) Stabilize, note P and T, and repeat until base temperature achieved.

III. CRYOADSORPTION OF NONCONDENSIBLES

Figure 3 presents the steady-state cryogenic adsorption characteristics of hydrogen on charcoal in the form of isosteres, or constant amount lines. With the indicated amount adsorbed, the pressure will rise as the temperature rises. With a greater amount adsorbed, the pressure rise is steeper for a unit temperature change. By suitable recasting, isotherms and isobars can be plotted readily.

Figure 4 presents the results for cryoadsorption of helium in the same form.

Investigation of these test results yields several important conclusions. The specification of cryoadsorption capacity is ambiguous without the specification of pressure, temperature, and slope \(dP/dT\). Normal industry practice for H₂ capacity is to state a capacity at 5 × 10⁻⁶ and 5 × 10⁻⁸ Torr. A generally recognized, but uncodified, standard for specific H₂ capacity is 200 std. cm³/g which specifies slope, but the temperature is not specified. Thus the ambiguity remains.

Cryopumps have a significant capacity for helium. Whether that capacity is useful is dependent on the specific application and equipment, i.e., second-stage temperature,
process pressure, and allowable pressure variation. Adsorption of helium may cause unacceptable pressure fluctuations in synch with the cyclical temperature variations of the cryogenic refrigerator.

Many users of cryopumps try to use the decay in achievable base system pressure as a measure of "fullness" or remaining cryoadsorption capacity. As shown in Fig. 3, even at a H₂ capacity of 200 std. cm³/g, a well-designed cryopump with perhaps a 12 K second stage will achieve base pressures in the 10⁻⁹ Torr range if the system has minimal leakage and outgassing. For a less tight system, the fullness of the charcoal will be masked by leakage, outgassing, and permeation until the pump is indeed full and regeneration required. That is, the decay in base pressure as a function of capacity is so rapid as the charcoal capacity limit is approached that this method gives very little warning margin.

It was not possible to generate accurate cryoadsorption characteristic curves for neon; the helium present in commercially available neon, although small in amount, invariably was the dominant species at higher temperatures. That is, while the neon was tightly bound, the helium was not and it confused the interpretation of the ionization gauge reading since the sensitivity for the two gases is quite different.

**IV. DYNAMIC LOADING EFFECTS**

As shown in Ref. 6, when a gas molecule impinges upon an absorber, it has a residence time proportional to temperature:

\[ t_R = t_0 e^{K/T} \]

where \( t_R \) = residence time, \( t_0 \) = constant, \( K = Q/R \), \( Q \) = energy barrier height, \( R \) = gas constant, and \( T \) = absolute temperature. Also, the molecule "hops" about on the surface, with a mobility related to the residence time:

\[ t_S = k t_R \]

At low temperatures, the functional relation between \( t_R \) (\( t_s \)) and absolute temperature is extremely strong. Figure 5 illustrates this important relationship. After cryoadsorbing a small amount—< 1 std. 1 of neon at 9 K—the pump appeared "full." The pressure was swinging -1 decade in the high-10⁻⁶ Torr range in synch with the refrigerator and was showing little sign of improvement after 1 ½ h.

Upon heating, the pressure rose and remained cycling until the pump slowly reached 11 K. At this point, the pressure dropped almost two decades in < 1 min and remained low even after heating the second stage to 15 K. Upon cooling (not shown), the pressure remained low and stable and residual gas analysis (RGA) showed little evidence of neon; helium was the major peak. When the temperature was subsequently held at 13 K during a steady capacity test, more than 12 std. 1 of neon were cryoadsorbed with no indication of excessive pressure swing or other untoward events.

Thus, each noncondensible has a critical temperature which is a function of cryoadsorbent system, temperature, and loading rate. In effect, if the noncondensible does not have the surface mobility to clear the outer surface, the pores will clog and appear full. For neon/charcoal at high loading rates, the critical temperature is 11 K. Similar investigations for hydrogen show the critical temperature to be 13.5 K at high hydrogen loadings (> 1/2 std. 1/h). The critical temperature for helium, if present, is below normally attainable cryopump temperatures.

**V. PRACTICAL APPLICATION TO CRYOPUMPS**

Figure 6 illustrates the practical importance of this hydrogen dynamic pumping effect. The plot shows the result of three speed versus capacity tests, at 10, 14, and 16 K. It is clear that an adsorbent temperature slightly in excess of the

**Fig. 4. Cryoadsorption isosteres, helium on charcoal.**

**Fig. 5. Increase in surface mobility, neon on charcoal.**

**Fig. 6. Adsorbent efficiency vs temperature, hydrogen on charcoal.**
critical temperature yields superior pumping characteristics under this high-load condition.

Since the surface mobility which leads to clearing of the outer adsorbent pores is lower at lower temperatures, the time to clear will be longer. Under very low loading, the surface mobility even at minimum temperatures will likely be sufficient to avoid clogging.

Several investigators (e.g., Refs. 7 and 8) have proposed partial regeneration schemes for cryogenic vacuum pumps. Since, in many cases, the pump's capacity for hydrogen is exceeded while the pump is still able to pump other gases, the schemes involve heating only the second stage of the pump to $> 25$ K in order to devolve the hydrogen, then cooling quickly and returning on line. The attractiveness of these schemes is that the partial regeneration should take much less time than a full regeneration, thus increasing uptime.

Examination of the isosteres of Fig. 3 reveals why these schemes will be very difficult to implement in a production environment. If the partial regeneration is attempted when the pump is very full, say at a loading of 250 std. cm$^3$/g, the pressure rise upon heating will be very high indeed, more than one decade for a 2 K warmup. This implies the need for both a well-controlled heater and a very high speed secondary pumping means if thermal overload of the pump from gas conduction is to be avoided. Attempting to regenerate the cryopump at very low loadings ($< 50$ std. cm$^3$/g) will require rather high temperatures that may result in the devolution of other gas species with detrimental effects. A high-speed secondary pump will still be required to perform the removal quickly.

Thus, in order to be successful, partial regeneration requires (i) monitoring of hydrogen loading levels, (ii) accurate temperature control, preferably with pressure feedback, and (iii) a very high speed (i.e., expensive) secondary hydrogen pump. These requirements dictate a system design that must be carefully compared to alternate systems, e.g., multiple cryopumps alternately regenerated or a secondary pump for noncondensibles—for each specific application.

VI. SUMMARY

(i) The capacity of charcoal for noncondensibles in the high-vacuum regime is a complex function of pressure, temperature, and the acceptable $dP/dT$. Specific capacities of charcoal for hydrogen and helium are presented in Figs. 3 and 4.

(ii) There is a critical temperature for cryoadsorbing hydrogen and neon on charcoal below which the adsorbent may clog, i.e., the noncondensible does not have sufficient surface mobility to clear the outer surface of the charcoal under high-loading conditions.

(iii) Partial regeneration of cryopumps is complicated by the need for monitoring $H_2$ levels, accurate temperature control, and a very high speed secondary pump.

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2W. A. Steele, The Interaction of Gases with Solid Surfaces (Pergamon, New York, 1974.)
4Chan, Tward, and Boudaie, Cryogenics 24(9) (1984).