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HYDROGEN REMOVAL BY CRYODEPOSITS

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16. Abstract

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SUMMARY

Cryotrapping (or cryosorption) of hydrogen by other gases which readily condense on surfaces of less than 20 to 25 K is a cryopumping process not well understood. The most likely mechanism is shown to be physical adsorption on the interior surfaces of a microporous frost of condensables (pore diameters in the range 10 to 100 Å or 10^{-9} to 10^{-8} m), followed by at least partial filling of the pores with liquid or solid hydrogen depending on surface temperature. Supporting observations are drawn from previous cryotrapping experiments and diffraction studies of condensates. Based on the adsorption model, some qualitative guidelines for the practical use of the effect are stated. Most of them are simply based on creating as porous a frost as possible.

INTRODUCTION

The removal of gases such as helium, neon, and hydrogen from ultrahigh vacuum systems by cryogenic pumping is often a problem because their vapor pressures at temperatures below approximately 20 K are well above 10^{-9} to 10^{-12} torr. This pressure range is generally desirable in many such systems, often because of cleanliness requirements for various surfaces. Thus, these gases are commonly referred to as noncondensables at low temperatures. Their high vapor pressures indicate that they cannot be permanently condensed by the ordinary cryopumping action of nonporous cryogenically cooled surfaces to the extent that most other gases, like H_2O, CO_2, and N_2, are pumped.

Probably the most important such noncondensable is hydrogen, which has a vapor pressure of about 10^{-5} torr at 5 K (ref. 1). Hydrogen is a common residual gas not only because it is a common outgassing product, but also because it is often introduced into systems during an experiment. For example, H_2 is a constituent in the propellent of some small thrusters tested in space simulation chambers.

One way of removing hydrogen is by ion pumps. Also the cryopumping of hydrogen can be considerably enhanced by using molecular sieve materials as the cryopumping surface. However, there is another enhancing cryopumping effect called cryotrapping or cryosorption, which is simple, efficient, and inexpensive. Haygood, Trayer, and Brown presented a review of the vacuum pumping of hydrogen (ref. 2). They conclude from various experimental works that cryotrapping (or cryosorption) of hydrogen by other condensed or condensing gases at liquid helium temperatures is the most promising method for rocket testing at pressures $\lesssim 1$ micron (10^{-3} torr).

In the period 1958 to 1960, several investigators (refs. 3 and 4) observed that some noncondensables were often pumped to pressures decades below the vapor pressure corresponding to the wall temperature, when in the presence of other gases condensed on or condensing on ordinary metal surfaces at cryogenic temperatures. Koga, working with Chuan, referred to the process as trapping. Soon afterward, the terms cryotrapping and cryosorption evolved.

Unfortunately, these terms are only specific enough to convey a general intuitive notion of what is occurring at the surface. As will be shown later, a variety of mechanisms could be responsible. At this time there is no generally accepted quantitative theory for the process. Although several investigators (e.g., refs. 5 to 7) believe it is some sort of physical adsorption process, the exact sense in which the noncondensables are pumped is not known for certain. However, enough accumulated experimental data exists now so that one can deduce a quite plausible mechanism and then propose qualitative guidelines for the practical use of the effect. This is the main purpose of this report. It is not intended to present an exhaustive review of cryotrapping, or even to present an extensive compilation of hydrogen cryotrapping results. Hobson has offered a brief cryotrapping review, covering most of the work up to about 1963, involving various noncondensable-condensable combinations and surface temperatures in the range 4 to 90 K (ref. 8). Haygood, Trayer, and Brown have presented a summary of hydrogen cryotrapping results up to about 1968, particularly in comparison with other H_2 pumping methods (ref. 2).

In very recent studies (Feb., 1970) Tempelmeyer examined hydrogen sorption by condensed layers of CO_2, SO_2, and CH_3Cl, and analyzed previous work on H_2 cryosorption (refs. 9 and 10). He arrived at essentially the same mechanism as is proposed in the present report, and also demonstrated that H_2 cryosorption over condensed CO_2 layers followed the semiempirical Dubinin-Radushkevich isotherm equation. His work is the most complete to date, but does not discuss in detail several considerations in the present report, such as diffraction studies and binding energies, which are suggestive of a certain cryotrapping mechanism. It should be noted that Tempelmeyer uses cryosorption to refer to any adsorption or absorption process at cryogenic temperatures, and the term cryotrapping to specifically refer to the burying pumping process described later. Other workers have used the terms interchangeably, and this will also be done in the present report.

In this report, five of the possible microscopic models for H_2 cryotrapping are described. The discussion is restricted to the surface temperature range 4.2 to 25 K, since no H_2 cryotrapping has been observed at higher temperatures (refs. 11 and 12). Then a physical adsorption process on a microporous array of condensables is suggested as the most likely mechanism. Using data from various previous cryotrapping experiments as well as some X-ray and electron diffraction studies of cryogenic condensates, this mechanism is shown to be both reasonable and consistent. Finally, some qualitative guidelines for the practical use of the effect are discussed.

Models

Some possible mechanisms that have been proposed (e.g., ref. 13) for hydrogen cryotrapping include the following:

(1) Physical adsorption - In an adsorption model, the layer of condensables on the cryosurface is regarded as being porous to some extent. As a result, actual surface area is larger than apparent surface area. It is assumed that the H_2 molecules still have a fairly low sticking probability at each collision with the walls of the pores within the frost, consistent with the high vapor pressure of H_2 in the temperature range 4.2 to 20 K. However, because the porous structure vastly increases the total surface area, they are able to make more collisions with the frost, or diffuse along the pore surfaces (as Tempelmeyer suggests), and hence have more chances to permanently adsorb on the walls of the pores or to condense onto local regions of hydrogen. Such a mechanism could conceivably operate in experiments in which the noncondensables and condensables are deposited onto the cryosurface simultaneously (herein referred to as simultaneous deposition experiments, or SDC experiments (simultaneously deposited condensable)) as well as in experiments in which the noncondensables are pumped by previously deposited layers of condensables (herein referred to as predeposited condensable experiments, or PDC experiments). The terms cryotrapping or cryosorption have been used to describe the pumping action observed in both types of experiments.

According to an adsorption model, in PDC experiments, the H_2 pumping by the frost would saturate in time and the H_2 pressure would return to precryotrapping levels determined by H_2 input rates and auxiliary pumps in the system. This might correspond to the H_2 monolayer completion on inferior frost surfaces, or to filling of the pores with liquid or solid hydrogen. In SDC experiments, the frost pore surface and volume are continually regenerated, and there can be equilibrium constant pressure H_2 pumping, with no saturation and subsequent increase in H_2 pressure.

(2) Physical burying or caging - In such a model, the hydrogen molecules, in temporary residence on a cold surface of condensables, are buried by incoming molecules

of the condensable species. Unless physically struck and buried, the noncondensables would quickly desorb. The H_2 molecules, after their first collision with the surface, are either trapped or escape. Critical parameters in such a model would include residence times, molecular incidence rates, and molecular areas or effective collisional areas. Such a model is probably applicable only in SDC experiments. The stacking procedure in a simple burying model with no surface diffusion implies a resultant mixed, amorphous structure, the H_2 molecules and condensables being more or less randomly intermingled.

(3) Chemical bonding - Here, the pumping mechanism involves a chemical alteration of the hydrogen; perhaps a breaking up of the hydrogen molecule into its constituent atoms followed by formation of H-condensable bonds, or perhaps the formation of a H_2-condensable bond.

(4) Solubility or diffusion - The H_2 molecules could dissolve into the microscopic array of condensables on the cryogenic surface, forming a resultant heterogeneous mixture. The array could be amorphous or crystalline. Actually, this mechanism is related to item (1), except that here, the noncondensable motion is on a more microscopic scale - the "pores" are of the order of lattice constants (~3 to 6 Å or 3×10^{-10} to 6×10^{-10} m).

(5) Combinations of the aforementioned models - Various sequences of the previous models are also possible explanations. For example, one such combination would be physical adsorption of hydrogen within a porous frost (the pores being considerably greater than molecular dimensions), followed by diffusion of the H_2 into the microscopic condensable array that comprises the walls of the pores.

THE MOST LIKELY MODEL

As will be shown later, the data from cryotrapping experiments, which involve the H_2 pumping process itself, and diffraction studies, which deal with the resultant structure of frosts, indicates that the aforementioned adsorption model is probably closest to the true nature of the process. Hydrogen cryotrapping or cryosorption in the surface temperature range 4.2 to 25 K appears to be physical adsorption on the interior surfaces of a microporous frost of condensables, followed by at least partial filling of the pores by liquid or solid hydrogen, the state depending mainly on surface temperature. For our purposes, microporous means having pores with diameters in the range 10 to 100 Å (10^{-9} to 10^{-8} m).

The phenomenon of H_2 cryotrapping seems closely related to the more familiar gas pumping by molecular sieves. The ability of these materials to adsorb large quantities of gas (their specific areas are of the order 10^3 m^2/g) arises from their porous aluminosilicate framework structure. Adsorption takes place in large roughly spherical cavities (approximately 12 Å or 1.2×10^{-9} m diameter for Linde type 5A sieve) providing that the gas molecules are small enough to pass through the network of pores interconnecting the cavities (ref. 14). Unlike sieve pumping, cryotrapping requires no bakeout or activation. Also, larger H_2 quantities can be pumped than with sieves, by simply using redeposition or simultaneous deposition of the condensables. Unfortunately, microscopic frost structure (specifically, porosity) is much less understood than sieve structure, and is much more sensitive to surface temperature, among other parameters, as will be shown later.

To perhaps a lesser extent, H_2 cryotrapping is also related to the titanium sublimation pump entrainment process, in which adsorbed (mainly chemisorbed) gases are buried by incoming sublimated titanium atoms, which then present a fresh surface for further adsorption. Stopping the titanium flow stops the pumping process. However, in cryotrapping, simultaneous deposition of condensable and noncondensable H_2 is not required to observe the pumping effect. But, simultaneous deposition is often required to observe H_2 pumping which maintains constant H_2 partial pressure for long periods. In SDC H_2 cryotrapping, it appears that the porosity of the newly deposited layers, not merely the fresh, nominally flat surface on top, is mainly responsible for the H_2 pumping.

PREVIOUS FROST STUDIES AND THE ADSORPTION MODEL

We next discuss the primary evidence for the adsorption model. Although a detailed discussion of the experiments in light of the other models is not presented, we will point out where particularly warranted, why some of the other models are less plausible. It is important to note that while some of the other models may be compatible with various experimental findings, only the adsorption model seems consistent with all frost studies involving hydrogen cryotrapping or cryosorption. Thus, the following discussion, in totality, is intended to strongly point toward the adsorption mechanism. Evidence pointing toward the adsorption model includes the following:

(1) Dependence of H_2 cryotrapping on condensable melting temperature and surface temperature - A point in favor of the physical adsorption model is its ability to explain the pronounced dependence of H_2 cryotrapping on the melting temperature of the condensable and the surface temperature: the higher the condensable melting point T_M is above the surface temperature T_S, the higher the H_2 pumping speed and the greater the H_2 capacity of the frost. This result is common to experiments of both types mentioned previously, PDC and SDC.

This melting point dependence supports the adsorption model in the following way:

One might expect that gas molecules condensing on and thermally accommodating to a surface at a temperature far below the melting temperature of the gaseous species would exist in a fairly solid, immobile state. However, field emission studies of Gomer (ref. 15) and Ehrlich and Hudda (ref. 16) have shown that rare gas multilayers (5 to 10 molecules thick) on tungsten at 4.2 to 80 K are surprisingly mobile. Gomer states: "The melting point of bulk argon is 84 K. It is remarkable that the ad-layers behave almost like two-dimensional liquids below 30 K," (ref. 15, p. 471). As will be discussed later, thicker frosts of substances far below their melting points have yielded X-ray and electron diffraction patterns usually closely resembling the known bulk patterns. This implies that enough mobility existed to form at least small crystallites. According to the adsorption model, it is the size and shape of these crystallites and the pores between them that are important in hydrogen cryotrapping. The closer the melting point is to the surface temperature, the more mobile and liquid like one would expect the condensed gas molecules to be. With this increased mobility, thermodynamic considerations indicate the condensate would tend to form or rearrange into a configuration of lower total energy; specifically, surface energy. The simplest way of achieving this is to decrease total surface area. Hence, larger crystallites might form, offering less total surface area for a given mass of condensate. (As will be discussed later, the qualitative dependence of crystallite size on T_S has been observed from the varying sharpness of diffraction rings. Symbols are defined in the appendix.) Theories directly relating recrystallization and crystallite size to surface energies and surface temperature are very difficult to construct mainly because little is known about surface structure, mobilities, and interatomic forces. The reader is referred to reference 17 for a general discussion of surface energies.

Thus, lower values of $T_M - T_S$ probably lead to larger condensable crystallites, with less total surface area and pore volume available for the adsorption of hydrogen. The works to be discussed now, conducted mainly for fixed values of T_S and varying values of T_M, illustrate the correlation.

The effect was noticed by Yuferov and Busol (ref. 7) in PDC experiments on a 20 K cryosurface, for the condensables CO_2 (T_M = 217 K), acetone (T_M = 178 K), gasoline (typically, T_M = 182 K), alcohol (typically, T_M = 175 K), N_2 (T_M = 63 K), and argon (T_M = 84 K). They comment that "substances with complex and polyatomic molecules sorb hydrogen well and have great sorption capacity," but "substances with simple molecules (N_2) or atoms (Ar) have much poorer sorption capacity" (ref. 7, p. 1522).

However, as indicated by other studies with various condensable species, the significant correlation is probably with melting temperature. It so happens that generally, the more complex a molecule, the higher its melting point. But, there are many species, like CO_2 and H_2O, which, in spite of their simple molecular structure, have high melting temperatures. And their condensates at liquid helium temperatures sorb hydrogen quite well.

The relation between pumping efficiency and T_M is also seen in the work of Schimpke and Schügerl (ref. 18), who conducted PDC experiments at $T_S = 4.2$ K for the condensables Ar and CO ($T_M = 68$ K).

The results of PDC experiments at $T_S = 11$ K by Hunt, Taylor, and Omohundro (ref. 12) show that for a given H_2 concentration in the frost, the condensables CO_2, N_2O ($T_M = 182$ K), and H_2O ($T_M = 273$ K) have generally higher H_2 pumping speeds and greater H_2 capacities than the condensables O_2 ($T_M = 55$ K), Ar, or N_2. The greater capacity is indicated by the H_2 pumping speed, or sticking probability (the pumping speed divided by the theoretical incidence rate from kinetic theory), remaining fairly constant and higher over a wider range of H_2 concentrations in the frost for the higher melting point condensables than for the lower melting point condensables, like N_2. (See fig. 1.) The results of Hunt, Taylor, and Omohundro should be considered with care because of lack of reproducibility, which was possibly due to contamination of the frost by unknown species.

The melting point dependence was studied most completely by Hemstreet, Webster, Ruttenbur, Wirth, and Hamilton (ref. 6). They directed binary mixtures of various condensables and hydrogen onto a 20 K cryosurface at various constant total rates in the range 10^{14} to 10^{18} molecules per square centimeter per second, and relative rates in the range 0.37 parts per million H_2 to 5.39 percent H_2. Hydrogen cryotrapping was indicated by the fact that slopes of H_2 pressure against time curves, during addition of the

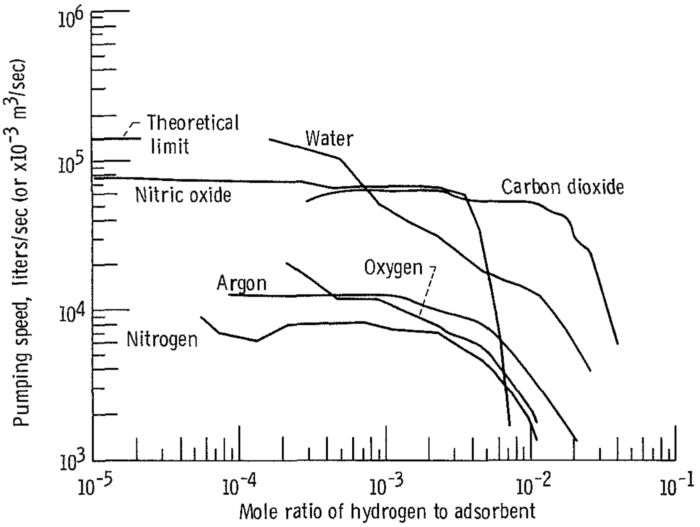

Figure 1. - Hydrogen pumping speed as function of mole ratio within condensate for various adsorbents at 11 K. (Data from ref. 12, as quoted by refs. 2 and 9.)

TABLE I. - RELATIVE HYDROGEN TRAPPING

EFFICIENCIES OF VARIOUS SOLIDIFIED

GASES AT 20 K (REF. 6)

Order of hydrogen trapping efficiency (from most effective to least effective trapping medium)	Substance	Melting point, K
1	Carbon dioxide (CO_2)	216 at 5.2 atm
2	Ucon 12 (CCl_2F_2)	115
3	Ucon 22 ($CHClF_2$)	113
4	Ucon 13 ($CClF_3$)	92
5	Carbon tetrafluoride (CF_4)	89
6	Nitrogen (N_2)	63
7	Oxygen (O_2)	54
8	Methane (CH_4)	89

binary mixture, were less than the slopes expected with no cryotrapping occurring. Their results for relative hydrogen trapping efficiencies of various solidified gases at 20 K are shown in table I. The authors note that, with the single exception of methane, the hydrogen cryotrapping ability of these gases was directly related to their melting point (or triple point). Methane has a specific heat anomaly near 20 K which could be due to molecular rotation in the solid. This could cause this particular solid to show little hydrogen adsorptive capacity (ref. 6).

Hemstreet, Webster, Ruttenbur, Wirth, and Hamilton also noticed that after a certain time interval, the H_2 cryotrapping ceased, and p_{H_2} returned to the time dependent behavior expected with no cryotrapping occurring. The interval varied from a few minutes to a few hours, depending on the condensable, total rates, and relative rates. They hypothesized, in accordance with an adsorption model, that as the frost grew in thickness, its surface temperature increased slightly due to thermal radiation from thermal shields, 300 or 77 K. This enabled the condensate to form in a less porous state with less surface area for H_2 pumping. Calculations of the temperature increase are difficult because the frost conductivity obviously depends on the varying, unknown porosity.

Very little controlled work has been done to examine how mixtures of two or more condensable gases cryotrap hydrogen. This would be valuable in predicting how, for example, the other gases in the exhaust plume of a small rocket cryotrap hydrogen when the plume impinges on a nearby cryogenic surface in a space simulation chamber.

Dawburn (ref. 11) has shown that adding nitrogen to predeposited 12 to 20 K CO_2 cryodeposits greatly impedes H_2 pumping. One possible explanation is that if the two constituents of a binary condensable mixture are miscible and the mixture has a melting temperature intermediate to those of the constituents, the crystallite size and, correspondingly, the H_2 pumping ability could be intermediate to those of the constituents. Another explanation is that the N_2 would occupy the same adsorption sites H_2 would have occupied.

Other experimental observations concern what happens to the condensed frost when the surface temperature is changed, and the effect of thermal cycling the frost on H_2 cryotrapping. This also involves the $T_M - T_S$ argument, and will be discussed next.

(2) Dependence of H_2 cryotrapping and condensable crystallite size on surface temperature changes - In this section, we describe an interesting correlation between H_2 cryotrapping and condensable crystallite size. The size, or actually, size change with changing T_S, is directly observed from the sharpness of diffraction patterns, rather than supposed from the value of $T_M - T_S$. As preliminary information, we first discuss more of what is known about frost structure in general, particularly from diffraction studies.

Welby (ref. 19) made visual observations of cross sections of 77 K CO_2 cryodeposits. He states that "at pressures not exceeding 10^{-2} torr the deposit is produced in the form of a compact white substance having a very smooth free surface with crystalline structure visible to the eye (when one proceeds to cut the deposit); it consisted of justaposed needles normal to the cryosurface" (ref. 19, p. 74).

X-ray and electron diffraction studies involve frost structure on a much more microscopic scale than this. Most of this work is primarily concerned with comparing lattice structures and constants to known bulk values (when the frost is not amorphous); in seeing what lattices result for various compositions in condensed binary mixtures; in investigating stability of lattice structures with surface temperature; and so forth. Unfortunately, from the standpoint of cryotrapping, diffraction studies can give practically no direct information on the porosity of condensed layers (private communications from H. Boersch, Technische Universität, Berlin and A. E. Curzon, Simon Fraser University, Burnaby, British Columbia). Apparently, all that can be given is some approximate information about the size of the crystallites formed, and then one must roughly infer the porosity from that. It is generally believed that sharper lines indicate the presence of larger crystallites, because with larger crystallites, there are more atomic planes beneath the surface of each crystallite to reinforce the intensity of the diffraction lines. The ratios of the spacings between the various rings are the indication of the particular crystalline structure. The actual values of the spacings, when compared to known patterns like those from the bare metal substrate on which the frost is grown, yield the lattice constants themselves.

Generally, frosts formed from single species gases at pressures $\lesssim 10^{-2}$ to 10^{-3} torr, to thicknesses of at least 100 Å (10^{-8} m), on either amorphous or crystalline substrates at surface temperatures below the gas species' melting temperature, are usually crystalline with the normal bulk structure. Amorphous films can be formed however; see, for example, reference 20. However, crystallites are usually formed, the size of which seems to increase with increasing surface temperature and increasing deposition pressure. For example, in an X-ray study of 77 K CO_2 cryodeposites, Graft and Paulon noticed that their higher pressures ($\sim 10^{-1}$ torr) gave sharper lines; hence, they believe larger crystallites were present (ref. 21).

Curzon says it is possible to get information about crystal size from electron diffraction but the results must be treated with caution. He estimates the crystals he observed (rare gases, O_2, N_2, H_2, in the T_S range of 5 to 60 K) were a hundred or so angstroms in size because the diffraction rings were reasonably sharp (private communication from A. E. Curzon, Simon Fraser University, Burnaby, British Columbia). Venables states that at low temperature, the crystals of rare gases are extremely faulted with grain size $\lesssim 0.1$ micron = 1000 Å (10^{-7} m) (private communication from J. A. Venables, University of Sussex, Falmer Brighton, G. B.). Boersch comments: "The average size of crystallites in solidified gas films strongly depends on the deposition temperature, deposition rate, and nature of the substrate. Generally, the crystallites are some 100 Å (10^{-8} m) in diameter if the deposition temperature is some 10 K below the sublimation temperature." (Private communication from H. Boersch, Technische Universität, Berlin.) If we assume the crystallites are approximately polygonal and more or less continguous, the pores may be on the order of or less than crystallite dimensions. Hence, we arrive at the estimate of 10 to 100 Å (10^{-9} to 10^{-8} m) given in the previous statement of the adsorption model.

For a direct correlation of H_2 cryotrapping and condensable crystallite size, we consider the electron diffraction work of Curzon, Pawlowicz, and Mascall (refs. 22 and 23). They found that argon, krypton, neon, and xenon deposited onto either carbon (amorphous) or (111) single crystal silver substrates at 7 K would crystallize in their normal face-centered cubic (fcc) lattices. Rare gas mixtures were also fcc, with lattice parameters intermediate to those of the pure components, depending upon molar concentration. They found that the solidified gases completely left the substrate at "evaporation temperatures" considerably below the normal melting points.

Most importantly, they found that heating the deposit considerably sharpened the rings, which they state is consistent with recrystallization into larger crystallites. This was noticed, for example, when argon was heated from 6 K to 20 to 25 K, after which the frost was heated to evaporation at 30 K (T_M = 84 K).

Hengevoss did PDC H_2 cryotrapping experiments, the pertinent results of which are shown in figure 2 (ref. 24). When Hengevoss pumped hydrogen using predeposited argon

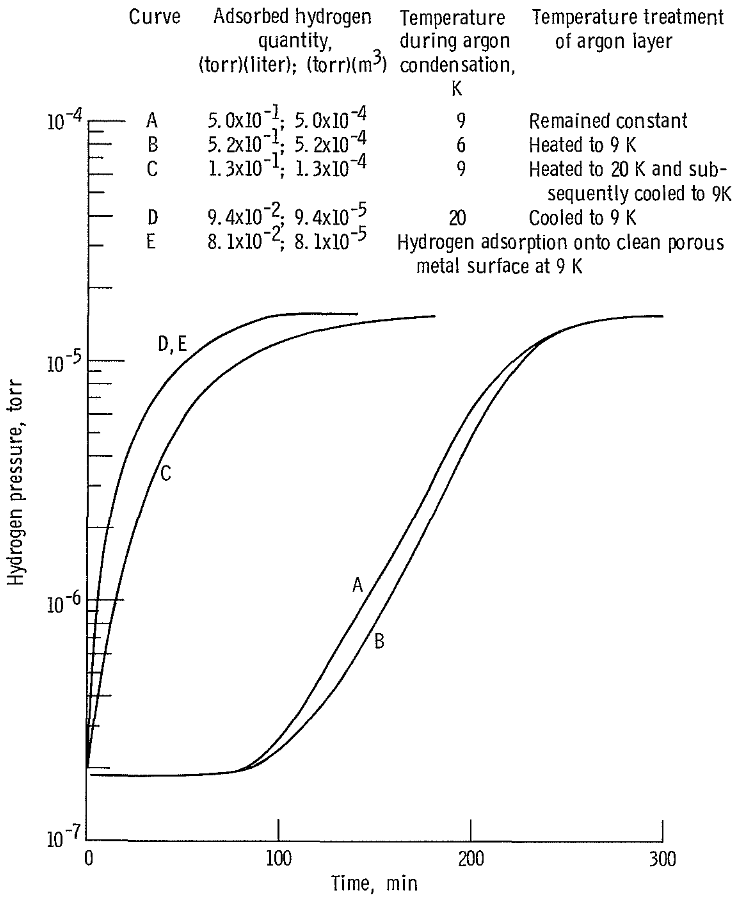

Figure 2. - Pressure-time curves during hydrogen adsorption onto condensed argon layers (0.80 (torr)(liter)(cm^{-2}), (8.0x10^{-4} (torr)(m^3)(cm^{-2})), at 9K (ref. 24).

layers, he noticed that if the layers were deposited at 9 K, heated to 20 K, then cooled to 9 K, they would pump H_2 only slightly better than the bare metal 9 K surface. If the layers deposited at 9 K were not so temperature treated, they could maintain H_2 pressure two orders of magnitude below the value resulting from noncryotrapping pumping alone, for ~100 minutes, with continuing H_2 addition.

So, heating of argon layers leads to both decreased hydrogen pumping ability (Hengevoss) and to the growth of larger crystallites (Curzon). What Hengevoss showed and what Curzon, Pawlowicz, and Mascall apparently did not observe because they heated their frosts to evaporation, was that the recrystallization was irreversible. Had Curzon again cooled the cryodeposit down to 6 K instead of evaporating it, it is quite possible he would have still seen the sharper rings.

(3) Some type I isotherms for hydrogen adsorption on solidified gas films - Yuferov and Busol (ref. 7) found that hydrogen sorption, typically by a CO_2 layer, could be characterized by type I isotherms (see fig. 3). An isotherm is a plot of surface coverage as

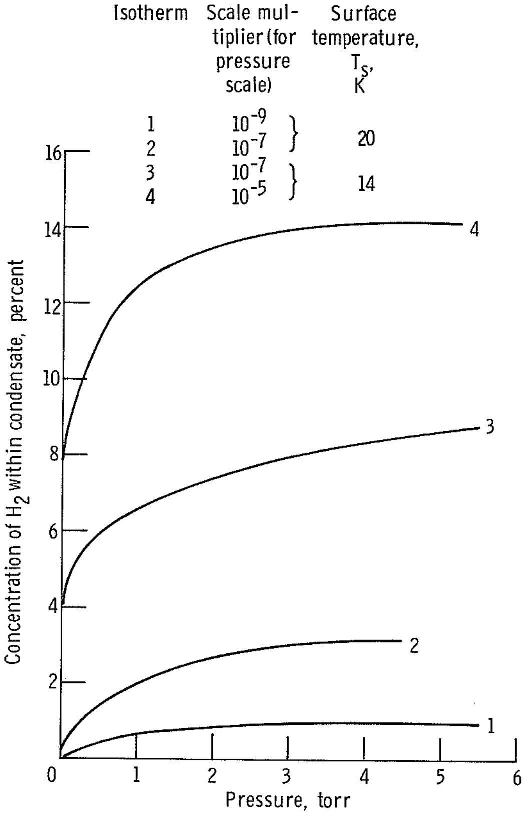

Figure 3. - Isotherms of hydrogen sorption by CO_2 layer (ref. 7).

a function of pressure, or in this case, hydrogen concentration within the condensed layers, for some constant surface temperature. The pressures usually vary from zero to the vapor pressure, although this is not the case in figure 3. A type I isotherm has a plateau, which has classically been interpreted as coinciding with monomolecular layer completion. On the plateau, the coverage remains fairly constant with increasing pressure, until multilayer adsorption begins, driving the coverage up as the pressure approaches the vapor pressure. For known porous adsorbents, monomolecular layer completion is assumed to occur on the interior surfaces of the pores (ref. 25). Yuferov and Busol assumed this was occurring in their experiments, noting the similarity of their results to Langmuir (monomolecular) isotherms. They calculated that if monomolecular layer completion corresponded to the hydrogen vapor pressure, then at 14 K in the case of saturation there would be 2 to 3 CO_2 molecules for one H_2 molecule. This low ratio would indicate a highly porous frost. However, type I isotherms are often observed for known microporous adsorbents like charcoal, having pore diameters typically $\lesssim$20 Å (2×10^{-9} m). Similarly, the isotherms lead to very high porosities, which are inconsistent with the mechanical strength of the adsorbent. So, the assumption is often made that the plateau corresponds not to monomolecular layer completion, but to pore filling, usually in the liquid state (ref. 25). This could explain the large capacity of the adsorbent without requiring unrealistically large porosities.

There is evidence that hydrogen adsorption on condensed gas layers also proceeds beyond monomolecular adsorption, toward pore filling. This will be discussed next.

(4) X-ray diffraction observation of immiscible neon-hydrogen condensed mixtures in the T_S range 2 to 16 K - In what appears to be the only diffraction study of condensed mixtures containing hydrogen, Barrett, Meyer, and Wasserman (ref. 26) found that neon and hydrogen were immiscible in the T_S range 2 to 16 K, for concentrations between 0.25 percent and 99.5 percent neon. Since they observed separate, distinctive hydrogen and neon patterns, there must have been separate H_2 and neon crystalline regions within the frost. A hydrogen monolayer could not have given the well defined hydrogen pattern observed. Such structure argues against microscopic mixing models, such as the chemical bonding model, since these types of models would not be expected to retain the separate, crystalline, chemical identity of the components. Boersch expects for H_2-Ar and H_2-CO_2 mixtures the same behavior as Barrett, Meyer, and Wasserman observed for H_2-Ne mixtures; that is, poor solid solubility and probably no influence on the crystal structure of the components (private communication from H. Boersch, Technische Universität, Berlin). It should be noted that the H_2-Ne solid mixtures of Barrett, Meyer, and Wasserman were grown from the liquid state.

(5) Hydrogen binding energies in solidified gas films - Both Yuferov and Busol (ref. 7) and Hengevoss and Trendelenburg (ref. 27) find that the behavior of hydrogen vapor pressure with varying values of $1/T_S$, for various initial H_2 concentrations (or mixture ratios) in the condensate, conforms well to the simple adsorption isostere (see, e.g., ref. 28, p. 48):

$$\ln p_N = -\frac{Q}{RT_S} + B_a \tag{1}$$

From slopes of graphs of $\ln p_N$ against $1/T_S$, values of Q, the hydrogen binding energy in the condensate, can be derived. Figure 4 shows the results of Yuferov and Busol (ref. 7) for H_2, as well as neon, in a CO_2 cryodeposit. The Q's were determined over a temperature range of about 14 to 20 K. Figure 5 gives the results of Hengevoss and Trendelenburg (ref. 27) for hydrogen in an argon layer. The Q's were determined over a temperature range of about 5 to 20 K. Note in figure 4 the closeness of inert neon energies to hydrogen energies in CO_2 layers. And note from figures 4 and 5 the similarity of hydrogen energies in CO_2 and argon layers; they are the same order of magnitude and definitely in the physical adsorption range (<10 or 20 K/cal/mole (4.184×10^4 or 8.368×10^4 J/mole); see, e.g., ref. 28, p. 32); and both energies decrease

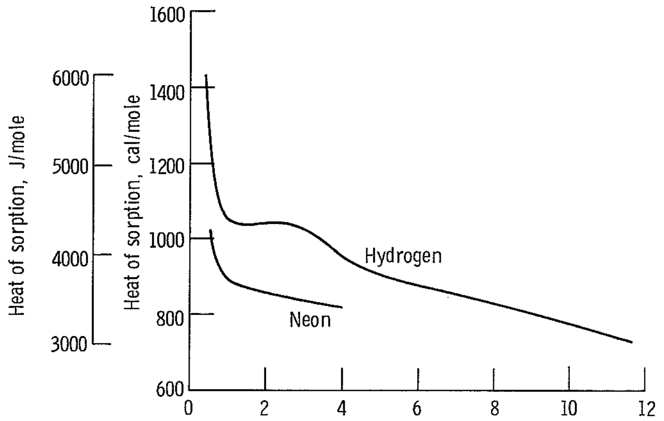

Figure 4. - Heat of sorption as function of concentration of absorbed gas in CO_2 layer (ref. 7).

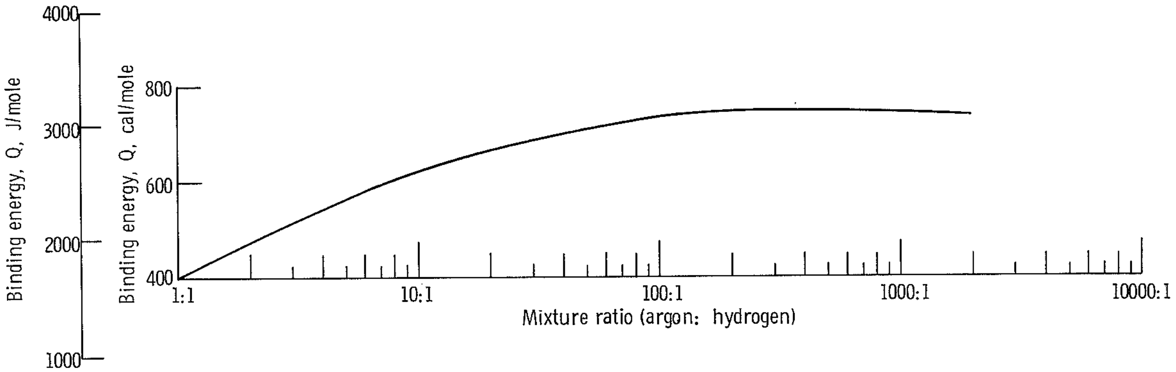

Figure 5. - Binding energy Q of hydrogen within argon condensate as function of mixture ratio or concentration (ref. 27).

slightly with increasing hydrogen concentration in the condensate. All these similarities suggest the sorption is primarily physical.

The hydrogen energies of reference 27 move toward a constant value of 700 to 750 calories per mole (2.9288×10^3 to 3.138×10^3 J/mole) with decreasing H_2 concentration (see fig. 5). The authors comment that this value is lower than the adsorption heat of hydrogen on metal surfaces, which ranges from 1.5 to 45 kilocalories per mole (6.276×10^3 to 1.8828×10^5 J/mole) (ref. 29), but greater than the evaporation heat of pure hydrogen, which is about 220 calories per mole (9.2048×10^2 J/mole). A simplified pictorial representation (fig. 6) of the adsorption model discussed earlier is useful in indicating in a qualitative way how such an intermediate value of Q might arise. Referring to figure 6, the energy required to separate an H_2 molecule from neighboring H_2 molecules at point P_1 may still be 220 calories per mole (9.2048×10^2 J/mole). But, if the condensable frost is microporous, the H_2 molecule may then have to make acti-

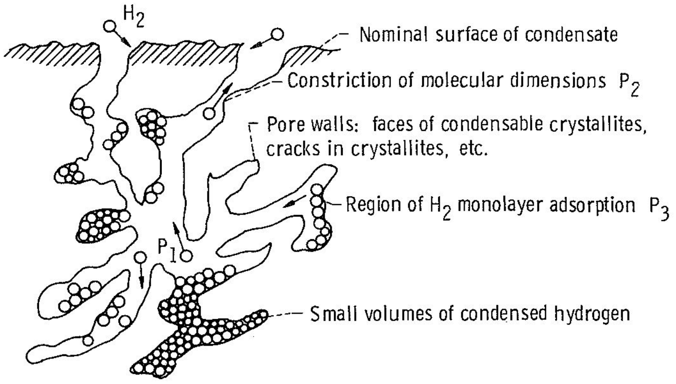

Figure 6. - Simplified picture of pore network containing hydrogen in the adsorption model.

vated entries into and through constrictions of the order of molecular dimensions, as shown at point P_2. These entry rates are often given by $\overline{K} e^{-\epsilon/RT_S}$, where $\overline{K}$ is the "nonexponential" or "frequency" factor of reaction kinetics (ref. 25, p. 215). The total effect of such activation energies ϵ may well increase the overall Q from 220 calories per mole (9.2048×10^2 J/mole) to 700 to 750 calories per mole (2.9288×10^3 to 3.138×10^3 J/mole). One would not expect the Q to be increased to the range of hydrogen adsorption heats on metals, since such adsorption is often chemisorption, involving decomposition of the H_2.

On the basis of this simple picture, one would expect what should be a more porous condensable cryodeposit like CO_2 (T_M = 217 K), with more molecular constrictions, to yield somewhat higher Q's than a less porous frost like argon (T_M = 84 K). Also, one would expect that with increasing H_2 concentration, more pore volume would be filled with hydrogen, and fewer constrictions would have to be traversed by escaping H_2 molecules, so the Q would decrease. Both of these qualitative predictions are verified in figures 4 and 5.

When enough H_2 was desorbed, we would expect to reach the state where the final H_2 monolayer starts desorbing from the interior frost surfaces, as shown in figure 6 at point P_3. From what is known about intermolecular forces between dissimilar molecules, one would expect the Q for this final monolayer to be larger than the Q for the H_2 molecules which originally left a surface of other condensed H_2 molecules before passage through the pores.

Figure 7 shows the results of Hengevoss and Trendelenburg for slow heating of the condensation surface (with the diffusion pump on). Two hydrogen partial pressure maxima are revealed, at 13 and 23 K. Unfortunately, the authors do not give such additional information as the rate of temperature rise (K/sec) which in general is needed to analyze such peaks in detail. But fortunately, it can be shown (see, e.g., ref. 30) that the cor-

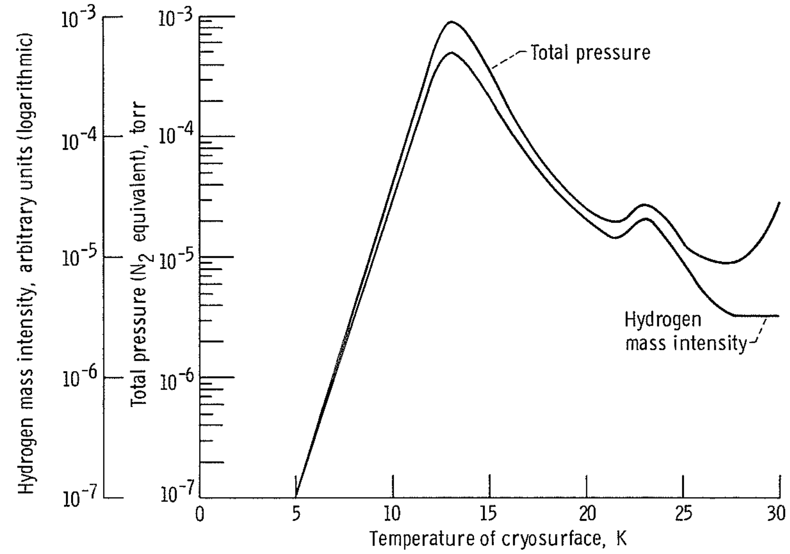

Figure 7. - Total pressure and hydrogen mass intensity as functions of cryosurface temperature during warmup of condensate mixture of H_2 and argon (ref. 27).

relation between desorption energy associated with such pressure maxima and the temperatures at which the maxima occur is fairly insensitive to rates of temperature rise, initial coverages, and even to the order of the desorption reaction (one or two), when the temperatures of the maxima are less than about 50 K. It can be shown that the 13 K peak corresponds to a desorption energy of about 750 calories per mole (3.138×10^3 J/mole), about the same value as the Q derived from the isosteres. This is reasonable because the 13 K peak is about 20 times the magnitude of the 23 K peak, and should contribute most to an overall Q. If we subtract 220 calories per mole (9.2048×10^2 J/mole), the H_2 evaporation heat, from 750 calories per mole (3.138×10^3 J/mole) we get about 530 calories per mole (2.21752×10^3 J/mole) as an estimate of the total energy associated with passage of H_2 molecules through the frost. Similarly, the 23 K peak corresponds to an energy of about 1320 calories per mole (5.52288×10^3 J/mole). On the basis of figure 6, the assumption that this peak results from the removal of the final H_2 monolayer leads to an estimate of $1320 - 530 \simeq 800$ calories per mole (3.3472×10^3 J/mole) for the binding energy of this final monolayer to the inner argon surface. To the author's knowledge, there is no other independent experimental measurement of this particular energy.

The sharp upturn in Q in figure 4 at about 1 percent hydrogen concentration may also be due to the onset of desorption of the last H_2 monolayer.

(6) Comparison of H_2 pumping speeds in PDC and SDC experiments - The quantity of greatest interest to users of the cryotrapping effect is the pumping speed S commonly expressed in liters per second per square centimeter ($m^3/(sec)(cm^2)$). The maximum pumping speed of a surface is the rate obtained assuming every impinging molecule

sticks permanently, and is given by the incidence rate from kinetic theory (see, e.g., ref. 31, p. 15):

$$S_{max} = 3.638\left(\frac{T_G}{M}\right)^{1/2} \frac{\text{liters}}{(\text{sec})(\text{cm}^2)} = 3.638\times10^{-3}\left(\frac{T_G}{M}\right)^{1/2} \text{m}^3/(\text{sec})(\text{cm}^2) \tag{2}$$

The quantity $C = S/S_{max}$ is commonly referred to as the condensation or sticking coefficient. Usually, the temperature of the gas striking the cryosurface of interest T_G is taken as 77 K because the 77 K thermal radiation shields customarily used are generally at least one or two orders of magnitude larger in area than the 4.2 to 25 K surfaces on which the hydrogen cryotrapping process occurs.

A seldom mentioned precautionary note regarding gas temperature is the following. Depending on the gas input-cryosurface geometry, the temperature of the H_2 gas striking the cryosurface of interest can be considerably higher than 77 K and less well defined than is usually assumed. Thermal accommodation coefficients α for room temperature hydrogen (298 K), a light gas, on either gas-covered or clean metal surfaces with $T_S \gtrsim 77$ K are generally small, in the range 0.1 to 0.4 (ref. 32). For $\alpha = 0.25$, a representative literature average, it can be shown that 11 collisions with the 77 K surface are required to bring the original room temperature H_2 molecules to within 10 percent of 77 K. Thus, H_2 condensation coefficients, involving T_G through S_{max} and possibly S also, should be quoted and used with some care. To the author's knowledge, H_2 gas temperature has not been treated as a controlled variable parameter in cryotrapping experiments.

From the standpoint of the possible models, the important point is that H_2 pumping speeds on <u>either</u> predeposited condensable layers <u>or</u> with simultaneous deposition are relatively high (sticking coefficients in the range 0.6 to 1.0); this argues against the previously described burying mechanism, where physical burying by incoming condensables is required to complete the pumping. High speeds have been noticed in PDC experiments by Hunt, Taylor, and Omohundro (ref. 12), Dawburn (ref. 11), Hengevoss (ref. 24), and Yuferov and Burol (ref. 7); and by Hengevoss and Trendelenburg (ref. 27) in SDC experiments.

In PDC experiments, H_2 pumping saturates in time, or equivalently, saturates with increasing H_2 concentration within the condensate, in a manner qualitatively in accord with the adsorption model. For example, the higher the condensable's melting temperature T_M or the lower the surface temperature T_S, the longer it requires, or equivalently, the more H_2 concentration within the condensate is required, for the cryotrapping effect to saturate. (See, e.g., figs. 1 and 8.)

In SDC experiments, there can be constant pressure, steady-state hydrogen pumping

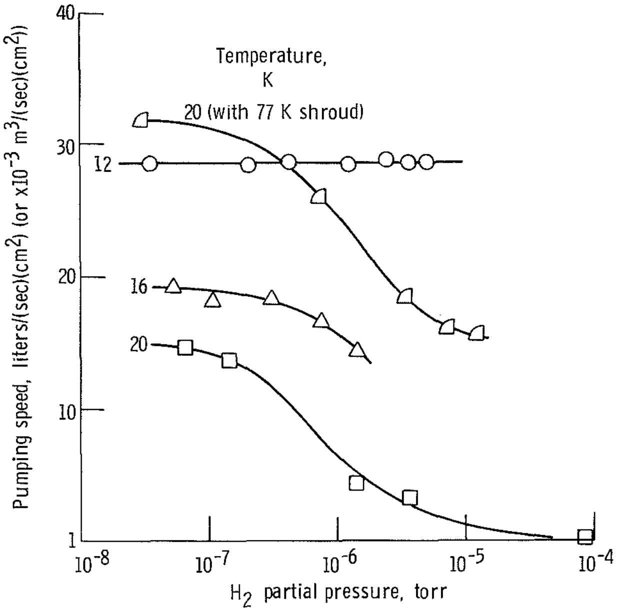

Figure 8. - Pressure dependence of pumping speed of H_2 over CO_2 cryodeposits at temperatures shown (ref. 11).

over long periods. One such experiment was done by Hengevoss and Trendelenburg (ref. 27). First, a hydrogen flow into their cryostat was established so as to maintain a hydrogen partial pressure of 2×10^{-6} to 2.5×10^{-6} torr with the diffusion pumps operating, for each of the chosen cryosurface temperatures. Since this pressure value is below the H_2 vapor pressure at each of the chosen cryosurface temperatures, no ordinary net cryopumping was exerted on the hydrogen by the cryosurface. Then, the argon flow rate was increased in steps, and steady-state partial pressures were reached after each increase. Families of knee-shaped curves relating the two steady-state partial pressures were found, each curve being for a fixed surface temperature, as shown in figure 9.

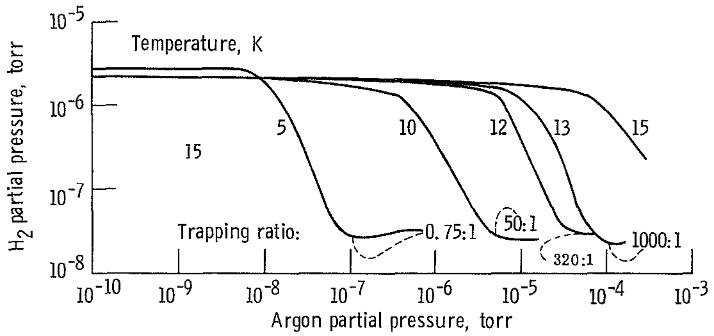

Figure 9. - H_2 partial pressure as a function of argon partial pressure for various surface temperatures in simultaneous deposition experiment of Hengeross and Trendelenburg (ref. 27).

According to the adsorption model, the upper plateau, where the argon incidence rates are low, corresponds to almost instant saturation of the regenerated argon layers by H_2, followed by rapid desorption of the temporarily adsorbed hydrogen through the relatively thin added condensable layers. Little or no net H_2 pumping is observed. On the lower plateau, where the argon incidence rates are higher, the incoming H_2 molecules "see" almost a completely new, thick porous argon condensate. The overall H_2 sticking coefficient of the frost is at its maximum, 0.7, on the lower plateau. By previous discussion, the colder the surface is, the more porous the argon layers are and the less incoming argon is required to pump the H_2. This could explain the variation of the curves with T_S.

(7) Success of Kraus' theory in predicting some partial pressure relations of Henegevoss - Kraus has presented an H_2 cryotrapping theory with some quantitative success (ref. 33). He assumes that the combined adsorbate, noncondensable plus condensable (e.g., hydrogen and argon, respectively) behaves like a mixture of two miscible liquids. From the standpoint of relevance to the adsorption model for cryotrapping, the simplified adsorption model in figure 6, while not a true binary liquid mixture, can be regarded as a quasimixture, a mixture on a near molecular scale, since the condensate is assumed to be microporous. It is reasonable to assume Kraus' equations could to some degree be applicable to the quasimixture, as well as to a true liquid mixture.

It can be shown (from, e.g., ref. 34, pp. 178 to 180) that the vapor pressure of the noncondensable over the true liquid mixture, p_N, is given by the following simple equation (ref. 33)

$$p_N = p_{O,N} \exp\left(-\frac{n_C}{n_N}\right) \tag{3}$$

where

$p_{O,N}$ vapor pressure of noncondensable (H_2) in its pure, bulk state

n_C mole fraction of condensable (Ar) within the condensate

n_N mole fraction of noncondensable (H_2) within the condensate

This equation results from equating the evaporation-condensation work $n_N R T_S \ln (p_{O,N}/p_N)$ to a term $n_C R T_S$, approximating the osmotic work needed to remove noncondensable from the condensate to a reservoir of pure noncondensable.

Kraus further assumes that

$$\frac{n_C}{n_N} \simeq \frac{n'_C}{n'_N} \tag{4}$$

where the primed quantities are the net condensation rates at equilibrium and are given by the phenomonological equations

$$n'_N = \left(p_{H_2} - p_N\right)\beta_{H_2} \frac{A}{RT_G} \tag{5}$$

$$n'_C \simeq p_{Ar}\beta_{Ar} \frac{A}{RT_G} \tag{6}$$

neglecting the small argon vapor pressure, at low temperature, and where $\beta_{H_2} = \mu_{H_2} (\bar{v}_{H_2}/4)$, μ_{H_2} is the H_2 sticking coefficient, A is the surface area, $\bar{v}_{H_2}$ is the mean H_2 velocity, and $\beta_{Ar} = \mu_{Ar} (\bar{v}_{Ar}/4)$. Another equation for n'_N, involving hydrogen flow rates and pumping speeds, is

$$n'_N = q - \frac{p_{H_2} S}{RT_G} \tag{7}$$

where q is the H_2 inflow rate and S is the pumping speed of the auxiliary (diffusion) pump. Combining equations (3) to (7) yields p_{Ar} as the following function of p_{H_2} and the four parameters, qRT_G/S, $\beta_{H_2}A/S$, $\beta_{Ar}A/S$, and $p_{O,N}$:

$$p_{Ar} = \left[\left(\frac{qRT_G}{S} - p_{H_2}\right)\frac{S}{\beta_{Ar}A}\right] \ln \left[\frac{p_{O,N}\frac{\beta_{H_2}A}{S}}{p_{H_2}\left(1 + \frac{\beta_{H_2}A}{S}\right) - \frac{qRT_G}{S}}\right] \tag{8}$$

Values of these four parameters are deduced from each of three of Hengevoss' knee-shaped curves of p_{H_2} against p_{Ar}, for three different values of q, all at $T_S = 4.2$ K. With these values, equation (8) yields the predictions shown with the data in figure 10.

However, Kraus' theory as it stands now fails to deal correctly with several impor-

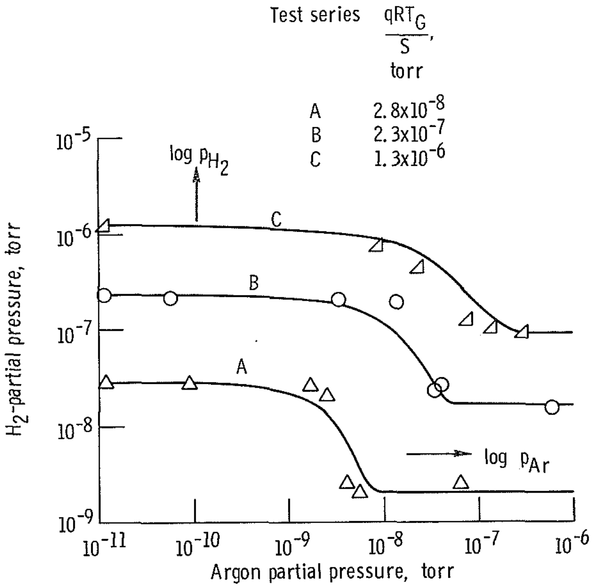

Figure 10. - Hydrogen partial pressure p_{H_2} as a function of argon partial pressure p_{Ar} for three different hydrogen admission rates, according to measurements of Hengevoss and Trendelenburg. The curves were calculated from equation (8). The surface temperature is 4.2 K for all data (ref. 33).

tant results involving surface temperature. Hengevoss and Trendelenburg measured p_N, the hydrogen vapor pressure over the mixed condensate, and found it was described well by equation (1). In other types of experiments, the SDC cryotrapping experiments of figure 9, p_{H_2} was measured, not p_N. Hydrogen and argon inflows were present then, and one would not expect to measure equilibrium hydrogen vapor pressures. But in his explanation of these experiments, Kraus assumes p_N is given by equation (3). If we combine these two expressions for p_N, equation (1), experimentally observed, and equation (3), theoretically assumed, Kraus' theory predicts that

$$\frac{n'_C}{n'_N} \simeq \frac{n_C}{n_N} \propto \frac{1}{T_S} \tag{9}$$

But Hengevoss and Trendelenburg observed an exponential dependence on surface temperature for this condensation rate ratio, or trapping ratio, as shown in figure 11, not linear with $1/T_S$. It should be noted that even the trend in equation (9) is incorrect: the trapping ratio in figure 11 decreases, not increases, with decreasing temperature.

Also, in another experiment discussed previously (ref. 23 and fig. 2), Hengevoss found that temperature cycling of predeposited argon layers could drastically alter their

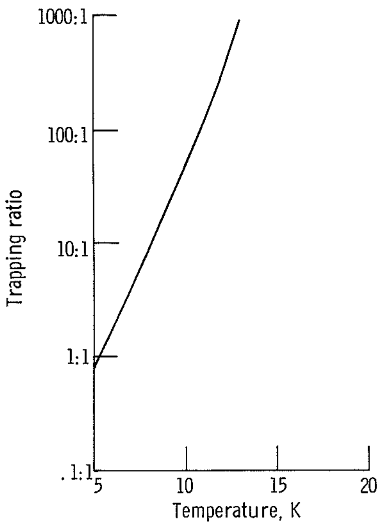

Figure 11. - Trapping ratio, or condensation rate ratio (argon: H_2) as function of cryosurface temperature in the simultaneous deposition experiment of Hengeross and Trendelenburg. See figure 9 for points where ratios are taken (ref. 27).

hydrogen adsorptivity. This dependence on surface temperature hysteresis, as well as the dependence on T_S itself indicated in figure 9, may be concealed in Kraus' theory in such data fitted parameters as β_{H_2}. The theoretical agreement in figure 10 is for a single surface temperature.

But the fundamental difficulty is probably in equation (3). It is obvious from the failure of equation (9) and from the predeposited argon experiments that hydrogen vapor pressure over the mixture depends on more than simply the ratio of condensables to noncondensables within the condensate, as indicated in equation (3). That is, the frost is not strictly behaving like a mixture of miscible liquids. This is not too surprising, considering how far below its melting point the condensed argon is.

However, even if the condensate did behave as a liquid mixture, there is some doubt whether equation (3), specifically, the osmotic work term n_CRT_S used in its derivation, holds for the concentration ratios of the 4.2 K condensates of Hengevoss used as data by Kraus. These ratios were approximately 0.5 or 1.0 to 1.0, for H_2 to Ar, from reference 27. The osmotic work term is only well approximated by n_CRT_S for ideal solutions or solutions dilute in argon. (This can be shown from, e.g., ref. 34, pp. 178 to 180.)

To summarize Kraus' work, a simple, phenomenological theory based on equation (3) has had some success in predicting H_2 cryotrapping partial pressure relations. Recognizing its limitations regarding surface temperature effects, this equation is probably a fair first approximation for the quasimixture in figure 6, as well as the miscible mixture of two liquids, as we stated earlier. This follows since the equality of the two work terms previously mentioned could still hold. A microporous array of condensables, which enables the noncondensables to have many opportunities to condense into local regions of liquid or solid hydrogen, seems to have the effect of reducing what we call vapor pressure, which is usually associated with equilibrium between gaseous H_2 and pure liquid or solid H_2. However, the reduction is probably not as simple as that given in equation (3).

GUIDELINES FOR THE USE OF HYDROGEN CRYOTRAPPING

The adsorption model for hydrogen cryotrapping is at least qualitatively consistent with all relevant experiments. Unfortunately, a definitive quantitative theory for the process does not exist. The main reason is a lack of experimental and theoretical knowledge about porosity in frosts. One possible approach would be a Monte Carlo treatment, in which individual noncondensable trajectories are traced within some model of a porous frost of condensables. The frost thickness in the model could be allowed to increase with time to explain SDC experiments. One assumes knowledge of the individual H_2-pore wall collisions, such as re-emission or scattering patterns, energy accommodation coefficients and sticking coefficients, as well as the porosity (pore sizes, shapes, distributions, etc.). By suitable averaging over many trajectories, some of which are terminated within the frost, H_2 pumping speeds could be derived. However, not only is the frost structure virtually unknown, but so are the gas-pore wall collisional properties needed. Indeed, conventional gas-wall characteristics, like cosine emission, could well be meaningless in small micropores, especially those partially filled with hydrogen.

Despite lacking a complete quantitative theory for the process, a brief list of qualitative guidelines for the practical use of the cryotrapping effect can now be offered. Most of the following comments are simply based on creating as porous a frost as possible:

(1) Use a condensable of high melting temperature, like CO_2, H_2O, or SF_6 (T_M = 223 K). For H_2 cryotrapping, the chemical nature of the condensable is probably most important as it affects the melting temperature.

(2) If a mixture of condensables is used, try to make the "average" melting temperature high. Low melting point constituents tend to poison H_2 pumping ability. For example, as mentioned previously, N_2 can poison CO_2 cryodeposits.

(3) Apply the condensables to the cryosurface at the lowest possible surface temperature (e.g., not during a cooldown phase), and at the highest possible deposition rate.

Higher temperatures seem to fix low porosity into the condensate. Little or no H_2 cryotrapping has been observed for surface temperatures above 20 or 25 K.

(4) Simultaneous deposition of hydrogen and condensable is needed if larger quantities of H_2 are to be pumped. The safest procedure is to monitor the H_2 partial pressure, and make provisions for adding condensable layers on the cryosurface in situ.

(5) Apply the condensable to the largest possible area.

(6) Avoid sources of temperature gradients in the condensable frost, such as thermal radiation (even room temperature radiation). Desorption of cryotrapped H_2, as compared with desorption of the condensables, is sensitive to temperature changes at the surface of the frost. Minimize thermal radiation loads to the cryotrapping surface. Because of this temperature effect, large areas are generally preferable to large thicknesses.

SUMMARY OF RESULTS

Hydrogen, in the presence of other gases condensed on or condensing on ordinary metal surfaces at temperatures less than 20 to 25 K, can often be pumped to pressures well below its equilibrium vapor pressure at these temperatures. These other gases are commonly called condensables. This cryopumping process, referred to as cryotrapping or cryosorption, is not well understood.

Five possible types of cryotrapping models are described: (1) physical adsorption, (2) burying or caging, (3) chemical bonding, (4) solubility or diffusion, and (5) combinations of the previous types. The most likely mechanism for hydrogen cryotrapping is shown to be physical adsorption on the interior surfaces of a microporous frost or condensables (pore diameters in the range 10 to 100 Å or 10^{-9} to 10^{-8} m), followed by at least partial filling of the pores with liquid or solid hydrogen depending on surface temperature. The observations supporting this model, drawn from previous cryotrapping experiments and diffraction studies of condensates, include the following:

1. The higher the condensable melting temperature or the lower the surface temperature, the better the H_2 cryotrapping. This probably results from formation of smaller crystallites of the condensables, hence, the creation of more surface area.
2. A correlation between cryotrapping ability and condensable crystallite size, with temperature cycling of frosts, has been observed: heating and cooling frosts lessens cryotrapping ability and enlarges crystallite size.
3. Some type I isotherms for hydrogen sorption on solidified gas films, similar to those observed for known microporous adsorbents, have been observed.
4. X-ray diffraction studies reveal that neon-hydrogen condensed mixtures are immiscible.

5. Hydrogen binding energies in solidified gas films behave in accordance with a physical adsorption process.

6. The behavior of H_2 pumping speeds by predeposited condensable layers or by condensables cryodeposited simultaneously with the hydrogen suggests an adsorption mechanism.

7. Kraus' theory has had partial success in predicting the behavior of H_2 partial pressure with condensable partial pressure, when both species are cryodeposited simultaneously. The theory is based on a reduction of H_2 vapor pressure over the mixed condensate, which could resemble the H_2-condensable mixture previously described.

Based on the adsorption model, some qualitative guidelines for the practical use of the effect are stated. Most of them are simply based on creating as porous a frost as possible.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 13, 1970,
124-09.

APPENDIX - SYMBOLS

A	surface area
B_a	constant in adsorption isotere, eq. (1)
C	sticking or condensation coefficient, S/S_{max}
$\underline{\overline{K}}$	nonexponential or frequency factor
M	molecular weight
n_C	mole fraction of the condensable within condensate
n'_C	net condensation rate of condensable
n_N	mole fraction of the noncondensable within condensate
n'_N	net condensation rate of noncondensable
p_{Ar}	argon pressure, torr
p_{H_2}	hydrogen pressure, torr
p_N	vapor pressure of noncondensable over condensate mixture, torr
$p_{O,N}$	vapor pressure of noncondensable over pure, bulk noncondensable, torr
Q	binding energy, cal/mole; (J/mole)
q	H_2 inflow rate
R	universal gas constant, cal/(mole)(K); (J/(mole)(K))
S	pumping speed, liter/(sec)(cm^2); (m^3/(sec)(cm^2))
S_{max}	maximum pumping speed at surface, 3.638 $(T_G/M)^{1/2}$, liters/(sec)(cm^2); ($\times 10^{-3}$ m^3/(sec)(cm^2))
T_G	gas temperature, K
T_M	melting temperature, K
T_S	surface temperature, K
$\bar{v}_{Ar}$	mean argon velocity
$\bar{v}_{H_2}$	mean hydrogen velocity
α	thermal accommodation coefficient
β_{Ar}, β_{H_2}	constants in eqs. (5) and (6)
ϵ	activation energy needed for passage through constrictions in microporous adsorbents
μ_{Ar}	argon sticking coefficient
μ_{H_2}	hydrogen sticking coefficient

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