REVIEW ON THE VACUUM PUMPING OF HYDROGEN

J. D. Haygood, D. M. Trayer, and R. F. Brown

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NOTICES

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FOREWORD

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ABSTRACT

This report summarizes the findings of an investigation into various possible methods of pumping hydrogen (H_2). The objective was primarily to find methods which might prove useful for pumping rocket plumes. A secondary objective was to select H_2 pumping methods for other types of tests. The methods reported include mechanical pumping, diffusion pumping, gettering, cryosorption, chemisorption, and cryopumping. Cryosorption pumping is judged to show the most promise as a pumping method for rocket plume testing, although most of the other methods will be found useful where the pumping speed requirements are less demanding.

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SECTION I

INTRODUCTION

The purpose of this report is to review available and proposed pumping methods which have application to the pumping of hydrogen (H_2) at pressures below 1 micron (μ) (10^{-3} torr). This will furnish the background for further work aimed at developing a method for pumping H_2 in space simulation test facilities (see "Air Force Research Objectives", (AD671000), OAR-68004, 1968). The test capability of proposed rocket plume test facilities will be limited by the balance between the H_2 pumping speed and the H_2 input for a given rocket size and fuel mixture. An increase in H_2 pumping speed will increase both the useful test time and the flexibility of the facility. In addition, a better H_2 pumping capability will improve the simulation of the effects of incident particulate radiation through reduction of the background pressure.

The review starts with a description of commercial pumps with their capabilities and limitations. Next there is a review of gettering by various metals. This includes a discussion of abrasion methods which have been proposed to avoid the large heat loads inherent in the evaporation of metals. In Section IV, cryosorption pumping is reviewed. This is followed by a discussion of the recent work on cryopumping of H_2 on liquid-helium (LHe)-cooled surfaces. Section VI covers the small amount of work which has been done on chemisorption pumping of H_2, including the work done on catalytic oxidation and proposed work on direct chemical oxidation of H_2. A summary and evaluation of the various schemes for pumping H_2 will be found in Section VII of this report. The pertinent properties of H_2 are listed in the Appendix.

SECTION II

COMMERCIALLY AVAILABLE PUMPING DEVICES

Commercially available H_2 pumping devices include mechanical, vapor diffusion, cryogenic, titanium (Ti) sublimation, sputter-ion, and sorption pumps. The cost, size, and pumping speeds of these devices are summarized in Ref. II-1. However, this list does not include the products of all the major manufacturers.

2.1 MECHANICAL PUMPS

Mechanical roughing pumps are widely used for obtaining pressures down to $1\,\mu$. Pumping speeds for H_2 range from less than 1 liter/sec to

over 500 liters/sec. A similar type of mechanical pump is the positive displacement booster pump which operates in the pressure range from 10 to 10^{-3} torr and requires backing by a roughing pump (Refs. II-2 and 3).

Other unique mechanical pumping devices include the molecular drag and turbomolecular pumps. They have pumping speeds from 10 to 10,000 liters/sec for H_2 and operate in the pressure range from 10^{-1} to 10^{-8} torr. They are precision mechanical momentum-transfer devices and operate with rotational rates up to 16,000 rpm and peripheral speeds up to 1150 ft/sec. Pumping is achieved by momentum transfer from the high-speed rotor to the gas molecules. A complete discussion of the theory of these pumps is given in most books dealing with basic vacuum technology (Refs. II-2 and 3).

In summary, mechanical pumping devices are widely used and readily available (Ref. II-1). They can be used to pump H_2, but at pressures above $\sim 10^{-3}$ torr the appropriate safety procedures must be used. Also, the possibility·of system contamination by backstreaming of the mechanical pump oil should be considered. Complete descriptions of the common types are included in basic texts on vacuum technology (Refs. II-2 and 3).

2.2 VAPOR DIFFUSION PUMPS

Vapor diffusion pumps are the most widely used devices to obtain vacuums from 10^{-2} to 10^{-10} torr, and oil is the most common pumping fluid. The basic operation of a diffusion pump is as follows (Refs. II-2 and 3):

1. The pumping fluid is heated and vaporized in a boiler located at the bottom of the pump.

2. The vapor moves to the top of the pump and expands through small orifices and forms high velocity jets in a downward direction.

3. Momentum from the supersonic expansion of the hot vapor imparts momentum to molecules entering the pump, and the result is a higher gas density at the bottom of the pump.

4. The vapor from the jet condenses on the cold walls of the pumps and flows back to the boiler.

The pumping speeds of oil diffusion pumps vary from 10 to 15 liters/sec/cm^2 of pump opening, and commercially available pumps

vary from 2 to 48 in. in diameter. A typical 48-in.-diam oil diffusion pump provides a pumping speed of 140,000 liters/sec for H_2 (Fig. II-1). Factors such as contamination caused by oil backstreaming must be considered when oil diffusion pumps are used.

A special type of oil diffusion pump is the oil vapor booster pump which operates in the 10^{-4}- to 1-torr pressure range. Its pumping speed for H_2 is nearly twice its pumping speed for air. The operation is very similar to that of the standard oil diffusion pump except for the higher pressure (tenfold) of the oil in the boiler (Ref. II-3).

2.3 VAPOR EJECTOR PUMPS

Another pumping device similar to the oil diffusion pump is the vapor ejector pump. Gas aspirator roughing pumps are commercially available, and steam ejectors have been used as pumping devices for several years. Yetman (Ref. II-4) recently investigated the use of steam ejectors to remove the rocket exhaust from an altitude test facility for testing small chemical rockets, and typical operating characteristics and cost estimates are given in Ref. II-4.

2.4 SUBLIMATION PUMPS

In a typical commercially available sublimation pump, Ti is evaporated from a tungsten filament overwound with Ti wire and deposited onto a substrate. Active gases such as nitrogen (N_2), oxygen (O_2), water (H_2O), carbon dioxide (CO_2), carbon monoxide (CO), and H_2 are pumped by the Ti deposit and remain on the substrate. This action is called gettering. The pumping speed is dependent on the sublimation rate, and the maximum utilization, for Ti, has been reported as a H_2-to-Ti ratio of one (Ref. III-6). A typical large pump may have an evaporation rate from 1 to 8 gm of Ti per hour.

In many instances, Ti can be deposited directly on the chamber walls or on cryopanels located within the chamber. However, one factor to consider in using this technique is that at 300°K, only about 20 percent of Ti is used effectively, and the capture coefficient is less than 0.12. A general description of sublimation pumps is given in Ref. II-3, and some of the commercially available pumps are listed in Ref. II-1. Also, Ref. III-3 provides additional information related to sublimation pumping of H_2.

3

2.5 SPUTTER-ION PUMPS

This group of commercially available pumping devices operates in the range from 10^{-2} to below 10^{-11} torr. There are several different configurations on the market (Ref. II-1). Basically they are designed to pump N_2, O_2, H_2, H_2O, CO, CO_2, ammonia (NH_3), and other gases (i. e., He and argon (Ar)) by ion burial and covering (Ref. II-3).

The basic operation of the pumps is as follows (1) positive ions are produced by a Penning discharge, (2) they strike a cathode which is usually made of Ti, and (3) Ti is sputtered from the cathode; Ti compounds are formed with some of the molecules to be pumped, and others are buried by sputtered Ti (Refs. II-5 and 6).

2.6 CRYOPUMPS AND SORPTION PUMPS

Both cryopumps and sorption pumps for pumping H_2 are available from commercial manufacturers (Ref. II-3). However, pumps of this type are designed for special applications. Sections IV and V of this report include discussions of these pumping methods.

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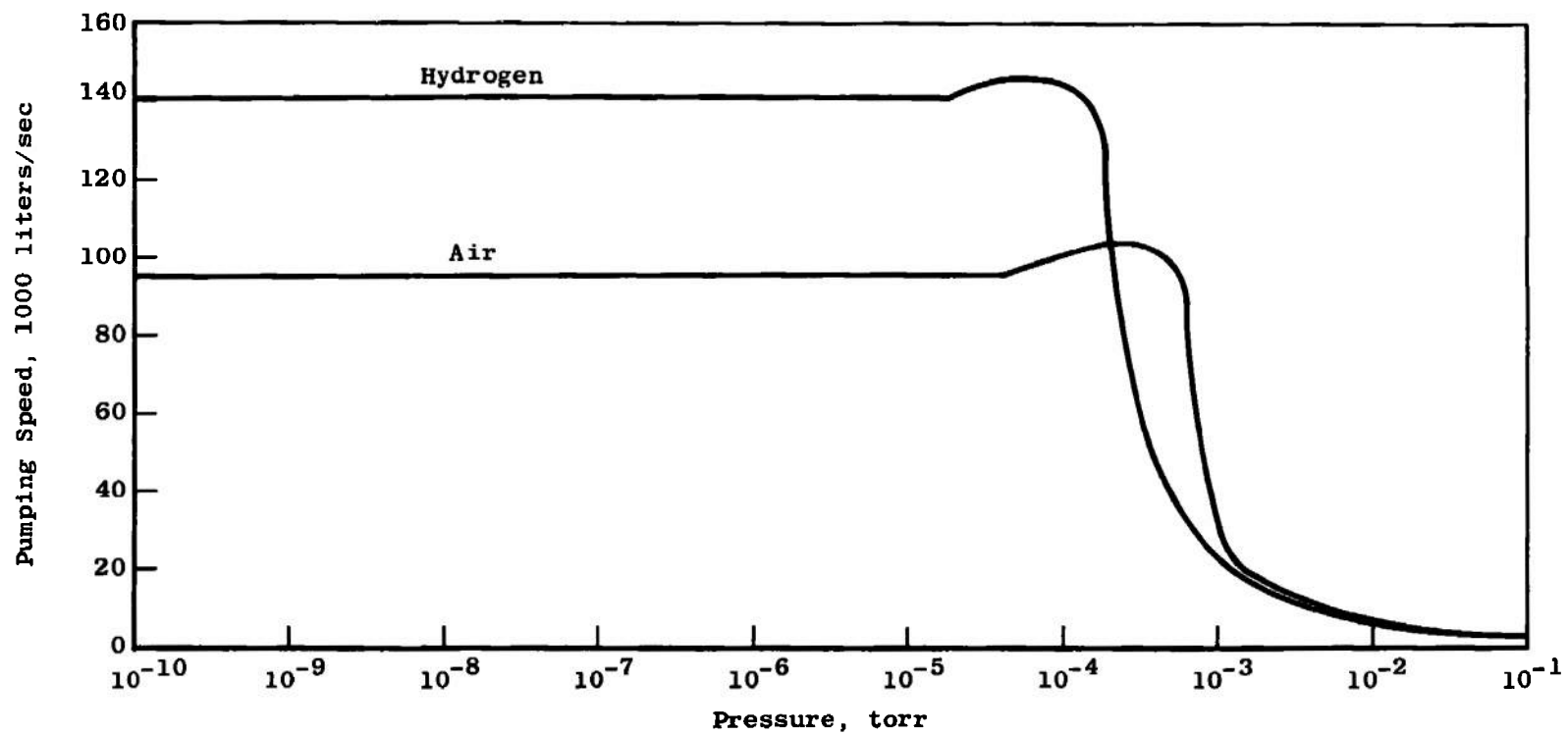
Fig. II-1 Typical Pumping Speed versus Pressure Curves for a 48-in. Diffusion Pump

SECTION III
GETTERING

Gettering may be defined as the sorption of gases by metals. In vacuum pumping the metal is usually evaporated from a bulk source and deposited on the walls of the pump. A substantial amount of research has been conducted on the gettering ability of various metals for gases. Among the metals investigated as getters are titanium (Ti), tungsten (W), molybdenum (Mo), zirconium (Zr), barium (Ba), uranium (U), thorium (Th), niobium (Nb), yttrium (Y), and misch metal.

To describe the gas pumping ability of a particular getter, several parameters should be defined. These include the initial sorption rate, the getter capacity, the capture coefficient, the deposition temperature, and the run temperature. The initial sorption rate is the volume rate of removal of a gas by a fresh getter deposit of known pumping area and is usually expressed in liters per second per square centimeter. The pumping area is taken to be the area of surface covered by the getter deposit and does not necessarily reflect the total (microscopic) surface area of the deposit. The getter capacity expresses the amount of gas sorbed per unit mass of deposited getter, usually with the units of micorn-liters per milligram. The capture coefficient, sometimes called the sticking fraction, is the ratio of the number of gas particles sorbed on the getter to the number of particles incident thereon per unit time. The deposition temperature is the temperature of the pump walls during deposition of the getter. The run temperature, and by inference the gas temperature, is the temperature of the pump walls during sorption of the gas on the getter deposit. In the data presented here, the run temperature, unless otherwise stated, is assumed to be room temperature (300°K).

3.1 TITANIUM

The most widely studied getter for vacuum pumping is Ti, and it is generally used in commercial getter pumps. Titanium pumps may be used in conjunction with other types of pumps. R. A. Outlaw (Ref. III-1) used Ti sublimation to enhance the ultimate pressure of a turbomolecular pump and obtained an ultimate pressure of 10^{-12} torr. The ability of Ti to pump H_2 was shown in the performance of sputter-ion pumps such as the one used by S. L. Rutherford (Ref. III-2).

The gettering action of Ti for H_2 has inspired several studies of the ability of such a system to pump H_2 gas. Clausing et al, at the Oak Ridge

National Laboratory (ORNL), have studied Ti getter pumping of various gases in vacuum systems (Refs. III-3, 4, and 5). They determined the capture coefficients for H_2 in the presence of a resistance-heated Ti filament with deposition temperatures of 78°K (LN_2 cooled) and 283°K (water cooled). In addition, the influence of the presence of an inert gas (He) during the Ti evaporation was determined. The results of these experiments are shown in Fig. III-1 and listed in Table III-1. The capture coefficients were improved by reducing the deposition temperature at the lower values of H_2 surface coverage, but, as the coverage increased above 10^{15} atom/cm^2, the capture coefficient dropped sharply on the lower temperature surfaces. This was believed to be caused by lowered diffusion rates into the deposit at the lower temperatures. A further improvement in sorption was effected by evaporating the Ti getter in the presence of 2.5 x 10^{-3} torr of He. The combination of low deposition temperature and the presence of the inert gas during evaporation produced capture coefficients near unity for surface coverages below 10^{15} atoms/cm^2, corresponding to a specific pumping speed of 38 liters/sec-cm^2 calculated at 300°K.

Other work has dealt with the influence of sublimation conditions on pumping speed. Elsworth, et al, investigated the influence of deposition temperature and run temperature on sorption (Ref. III-6). A greater getter capacity and a greater initial sorption rate were obtained for 83°K deposit and run temperatures than for room temperatures.

Some later experimental work was conducted at AEDC by S. M. Kindall (Ref. III-7), who found capture coefficients as high as 0.45. Kindall verified the favorable effect of having a low pressure of inert gas present in the chamber during deposition of the getter (Ti). Moody, also at AEDC, extended this work with a new experimental technique for determining capture coefficients (Ref. III-8). He measured the capture coefficient as a function of Ti evaporation rate and gas flux and concluded that Ti adsorbed a maximum of one molecule of H_2 per molecule of evaporated Ti.

A Russian paper by Biryukova, et al, (Ref. III-9) gives an initial sorption rate of 6 liters/sec-cm^2 for Ti deposited on a 77°K surface. Other papers reporting H_2 pumping investigations may be found in Refs. III-10 through 14. A summary of the H_2 pumping data using Ti getters by several investigators is presented in Table III-1.

3.2 BARIUM

Barium has been widely used as a getter in the electronics industry, but its H_2 pumping capabilities are not very well defined. Most of the

information comes from surveys of various getter materials (Refs. III-15, 16, and 17). Also, della Porta has produced several publications dealing with H_2 pumping by Ba (Refs. III-18, 19, 20, and 21). He reports data on the influence of the temperature of the film during sorption. The Ba film, unlike the Ti films, had a greater pumping speed at higher temperatures.

R. W. Cloud of M. I. T. (Ref. III-22) used Ba in an absorption pump to get an initial sorption rate of 0.125 liter/sec-cm^2. A summary of the work on Ba by several investigators is given in Table III-2.

3.3 OTHER METALS

Several other metals have been used as getters (Refs. III-22 through 31). The H_2 pumping properties of the more important materials are given in Table III-3. None of these surpasses the perform-. ance of Ti. Dushman (Ref. III-32) shows a comparison of the solubility of H_2 at 1-atm pressure in Ti, Th, and Zr as functions of temperature (Fig. III-2). Several sources (Refs. III-28 through 33) state that Ti is superior to the other getters tested. This does not mean that other metals or alloys might not be better suited for some gettering applications. Such factors as high melting points, cost, and high vapor pressure at operating temperatures must be considered when choosing a getter for specific applications.

3.4 ADVANTAGES AND DISADVANTAGES

One of the major advantages of getter pumping is the fact that large pumping surfaces are available. In some instances the entire inner chamber wall may be used as a pumping surface.

Chamber contamination is less from getter pumps than from other types where vapor backstreaming becomes a problem. However, care must be taken to prevent deposition of metal on sensors and gages through line-of-sight shielding.

One of the major problems encountered in using getters is the total heat load placed on the system during evaporation (Table III-4). Although the amount of heat used for evaporation is negligible compared to that which is radiated, the total could cause a thermal overload on cryogenic systems in the chamber. The possibility of mechanically dispersing the getter at lower temperatures would greatly reduce this heat load (see Section 3.5).

Another major disadvantage is poisoning or reduction in H_2 pumping capability because of sorption of other gases (Ref. III-34). As an example, previous adsorption of gases such as N_2 or O_2 will greatly reduce the pumping speed for H_2. Experience in large simulation chambers at AEDC indicates that rocket engine exhaust gases poison the getter in terms of H_2 pumping.

3.5 OTHER METHODS OF UTILIZING GETTERS

There are several possible ways to approach the problem of high heat loads during sublimation of getters. One is the use of a non-evaporable getter (bulk getter). One such pump (Ref. III-35) using a Zr-aluminum (Al) alloy is activated by prior heating to 750°C for 5 min. The getter will then pump H_2 at 500 liters/sec at 400°C. The capture coefficient cannot be determined from available literature data, so the application to large-scale pumping is difficult to evaluate.

Another possible method is the mechanical abrasion of the surface of a getter, thereby continuously exposing a fresh pumping surface. In one of the first of such attempts, M. E. Haine and others (Ref. III-36) simply put a few lumps of abrasive material in a Ti trough. Shaking the trough provided enough fresh surface by abrasion to reduce the pressure from 10^{-4} to 10^{-6} torr. Robert Hirsch (Ref. III-37) of ITT Industrial Laboratories made an abrasion pump in which a tungsten wire brush rotates against the inside of a Ti cylinder. This system pumped a 1-liter test section from 10^{-3} to 10^{-5} torr in 10 sec with the brush rotating at 90 rpm. These examples indicate that methods of getter pumping other than by direct sublimation may be of value.

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$\triangle$ 78°K Surface, 0.11-mole Titanium, 2.5 x 10^{-3}-mm Helium
● 78°K Surface, 0.11-mole Titanium
○ 283°K Surface, 0.15-mole Titanium, 2.5 x 10^{-3}-mm Helium
□ 283°K Surface, 0.13-mole Titanium

Data from Refs. III-3 and 4
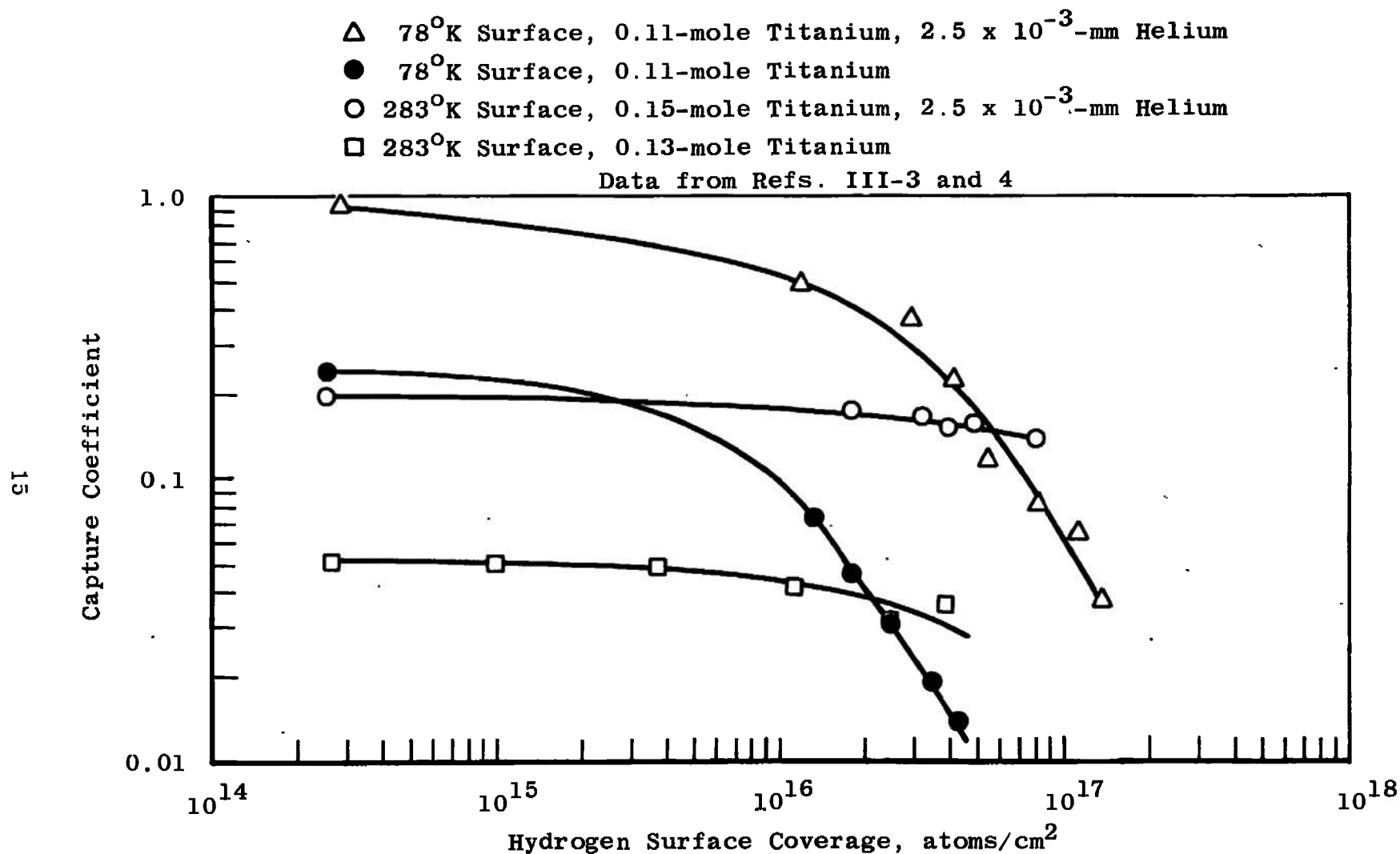
Fig. III-1 Capture Coefficients of Titanium for Various Surface Conditions, Room Temperature Gas
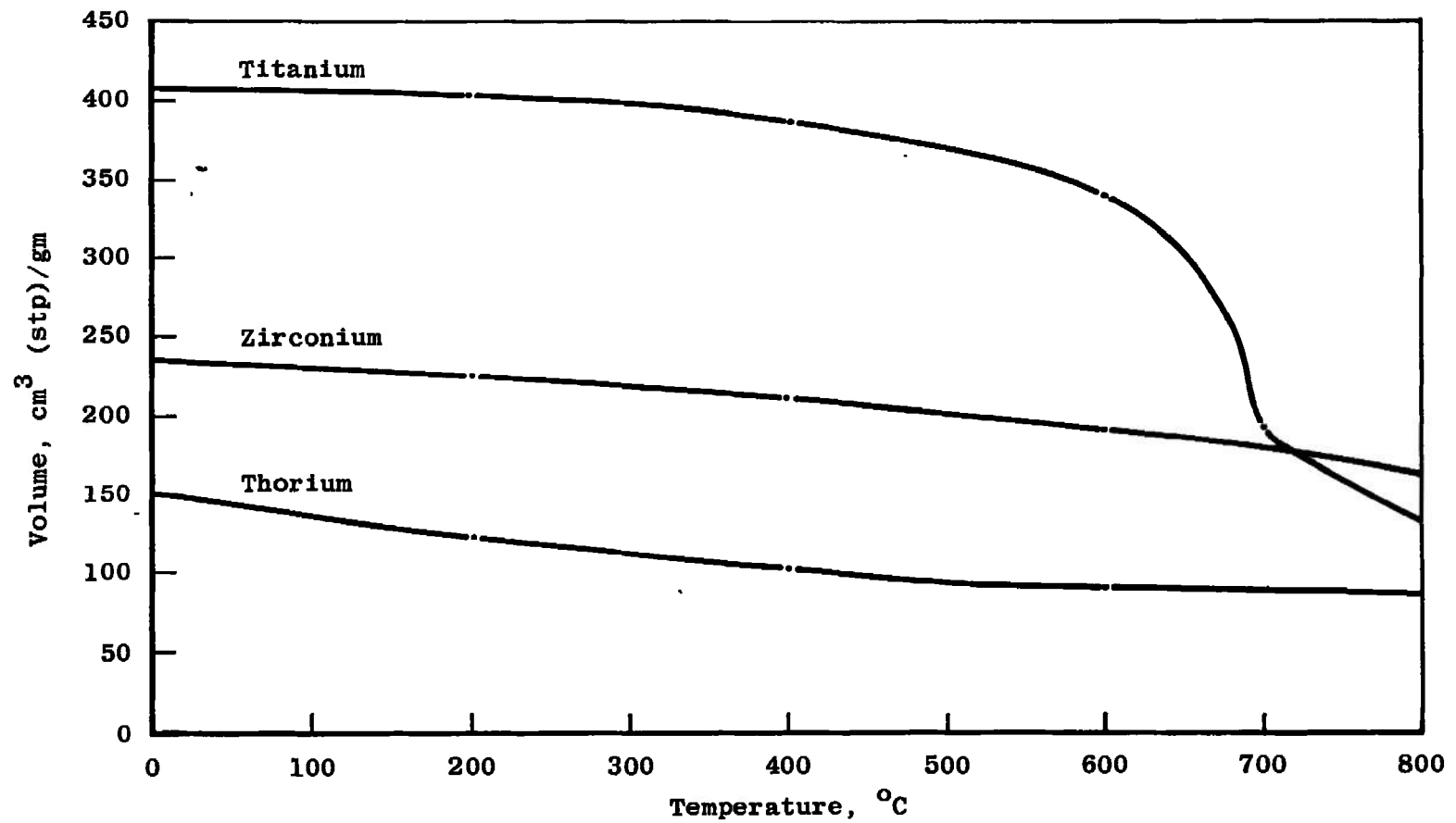
Fig. III-2 Solubility of Hydrogen at 1 atm in Titanium, Zirconium, and Thorium

TABLE III-1

TITANIUM GETTERING OF HYDROGEN

Source	Initial Sorption* Rate, ℓ/sec-cm^2	Initial Capture Coefficient	Capacity, μ-ℓ/mg	Deposit Temperature, °K	Run Temperature, °K
Clausing (Ref. III-3)	2.2	0.05		283	Room
	8.4 (2.5 x 10^{-3} torr He)**	0.19		283	Room
	10.6	0.24		78	Room
	37.6 (2.5 x 10^{-3} torr He)**	0.85		78	Room
Elsworth (Ref. III-6)	0.47	0.01***	15.5***	293	293
	10	0.23***	114 ***	83	83
Kindall (Ref. III-7)	3.59	0.16		273	77
	6.3	0.28		195	77
	10.1	0.45		77	77
Moody (Ref. III-8)	6.7	0.15	46.5	300	300
	4.5	0.20		77	77

*Calculated by assuming that the gas temperature is the same as the run temperature

**Ti evaporation carried out with this pressure of He in the chamber

***Calculated from author's data by assuming a density of 4.5 gm/cm^3 for the substrate

TABLE III-2
BARIUM AS A HYDROGEN GETTER

Source	Initial Sorption Rate, $\ell/sec\text{-}cm^2$	Initial Capture Coefficient	Capacity, $\mu\text{-}\ell/mg$
Ehrke (Ref. III-15)			87.5 (293°K)
Espe (Ref. III-16)			87.2 (293°K)
Holland (Ref. III-17)	0.5		100 (673°K)
della Porta (Ref. III-19)	6.0×10^{-3} (373°K)		135 (373°K)
della Porta (Refs. III-18 and 21)	1.9×10^{-3} (298°K)	4.17×10^{-5} (298°K)	30 to 45 (298°K)
Cloud (Ref. III-22)	0.125		

TABLE III-3

OTHER GETTERS FOR HYDROGEN

Metal	Source	Initial Sorption Rate, ℓ/sec-cm^2	Capture Coefficient	Capacity, μ-ℓ/mg
Misch Metal	Ehrke (Ref. III-15)			46.1 (300°K)
Mo	Hunt (Ref. III-27)	12.5	0.3 (283°K)	
Nb	della Porta (Ref. III-28)		0.02	0.43
Th	Ehrke (Ref. III-15)			19.4 (300°K)
W	Singleton (Ref. III-34)		0.18 (300°K) (5 x 10^{-9} torr)	
U	Ehrke (Ref. III-15)			8.9 (300°K)
Y	Moody (Ref. III-8)		< 0.01	Very low

TABLE III-4
GETTER SUBLIMATION HEAT LOADS

Getter	Heat of Vaporization, kcal/mole	Radiation Loss, watts/cm^2	Minimum Heat Load* per gram H$_2$ Pumped, kw/hr
Ti	112.5	66.4	94
Ba	41.7	3.44	5.55
Zr	145.4	112	234
U	117	176	475
Th	137	140	446
Mo	159	349	860
W	202	850	3240

*Assuming 1 molecule of H$_2$ per metal atom

SECTION IV
PHYSICAL SORPTION PUMPING

One of the more promising methods of pumping H_2 is by physical sorption. Physical sorption is a term used to include both adsorption and absorption in which there is no chemical reaction. Adsorption indicates surface condensation with no diffusion into or solution in the substrate. Adsorption at low pressures is thus limited to about 10^{16} molecules/cm^2 of surface area. This forms the basis of the Brunauer, Emmett, and Teller (BET) method of surface area determination (Ref. IV-1). Absorption is limited only by the volume of substrate available. Because there is no way of distinguishing between these two in the case of cryofrosts, the more inclusive term, sorption, has been chosen for this report. The sorption isotherm shows the relationship between the equilibrium pressure and the amount of sorbed gas at constant temperature.

Although a large amount of work has been done on H_2 sorption (Ref. IV-1), only a fraction of this is applicable to vacuum pumping. The remainder is of interest in the study of sorption theory and serves only a correlative purpose in vacuum work (Refs. IV-1, 2, and 3). The principal work connected with vacuum pumping concerns sorption by three materials. These are charcoal, synthetic zeolites (molecular sieves), and condensed gases.

Since vacuum pumping is dynamic, the application of adsorption isotherms and other static properties is somewhat limited. There are usually two distinct regions of sorption pumping. For low gas fluxes, the pumping speed is controlled by the probability that an impinging molecule will be sorbed, whereas at higher flux rates the rate of diffusion of a molecule from the surface into the interior of the sorbent becomes important. The first is characterized by a constant pumping speed and the second by a rather precipitate decrease of pumping speed with the total amount of sorbed gas. The division between these two is related to the capacity of the sorbent.

Another characteristic of sorption pumping is the interaction of sorbed gases. The sorption of a gas other than H_2 can have a measurable effect on the pumping speed of the substrate for H_2. This can result in either an increase or a decrease in the pumping speed, depending on the temperature and on the foreign gas.

4.1 CHARCOAL

Some of the earliest H_2 sorption pumping speed work was carried out by Woodrow (Refs. IV-1 and 4) using charcoal as the sorbent at 83°K. Additional work by Barrer and Rideal (Ref. IV-5) at 78°K gave comparable results. Figure IV-1 compares the two sets of results. Both show indications of the three characteristics of sorption pumping.

1.   An initial high rate of sorption on the clean surface.

2.   A region of constant pumping speed (straight line on semilog plot), probably controlled by diffusion into the interior of the charcoal.

3.   A decreasing pumping speed as the internal sorption sites become saturated.

Work on the sorption isotherms of charcoal was carried out by Rowe (Ref. IV-6) at 90°K, Claude (Ref. IV-7) at 78°K, Huthsteiner (Ref. IV-1) at 77°K, and Winkler (Ref. IV-8) at 90°K. These data are represented in the log-log plot of Fig. IV-2. Note that the slopes of the actual data plots are less than one, indicating a Freundlich isotherm ($P = AV^n$) with an exponent less than one (n = 0.935 at 90°K) (where A and n are experimental constants). Thus, the relative increase in pressure with amount absorbed is greater at low pressures than at high pressure. This effect changes when the pressure is greater than 0.10 torr where the exponent increases with pressure (Ref. IV-7).

In addition to the above work, in a study sponsored by AEDC and carried out by Linde (Ref. IV-9) the sorption isotherms of coconut charcoal at 20.4, 30, and 40.4°K for H_2 were measured. Isotherms of the Freundlich type were again found (Fig. IV-3), but at this low temperature the exponent was greater than one, although it decreases as the temperature increases (20.4°K, n = 12.8; 30°K, n = 6.22; and 40.4°K, n = 3.0). Also, the pressure at which the value of the exponent starts to increase increases with temperature (20.4°K, P = 5×10^{-4}; 30°K, P = 4×10^{-3}; and 40.4°K, P = 10^{-2} torr). Combining these results (Fig. IV-2) with the previous work by Rowe (Ref. IV-6) and Claude (Ref. IV-7), we find n ~ $800\,T^{-3/2}$, and the pressure in torr at which the value of n starts to increase is given approximately by P = $10^{-7}\,T^3$. Additional data on the sorption isotherms of H_2 on charcoal will be found in Refs. IV-10, 11, and 12.

Work carried out at AEDC by Kindall (Ref. IV-13) showed only a small amount of pumping of H_2 by charcoal at 77°K.

4.2 SILICATES

A considerable amount of study has been devoted to solid sorbents other than charcoal, principally the natural and synthetic zeolites. The latter are widely known as molecular sieves. Hydrogen sorption isotherm data are given for chabazite by Lamb and Woodhouse (Ref. IV-14) at high pressures (to 2000 torr). They compared the sorption capacity with the moisture content of the chabazite at 0°C and found that a slight maximum in the capacity for H_2 occurred when a small amount of water (~0.7 percent) was left in the mineral. Similar effects were found for the sorption of O_2 and CO_2.

As a part of work previously noted, Stern et al (Ref. IV-9) have determined the capacities and pumping speeds, for H_2, of silica gel and several synthetic zeolites at 20.4°K. Isotherms for H_2 are shown in Fig. IV-4, and the BET surface areas and other pertinent data are listed in Table IV-1. Pumpdown curves are shown for silica gel (Fig. IV-5) at several initial H_2 pressures. Similar tests were carried out using molecular sieves. Reference IV-9 also includes measurements of the H_2 pumping speeds of various sorbents (Fig. IV-6).

Southerlan (Ref. IV-15) has also reported on the pumping performance of a large (8.35-ft^2) sorption pump coated with molecular sieve 5A at various temperatures from 13.6 to 18.5°K. Although the initial pumping speeds were close to the theoretical maximum, there was a continuous decrease in pumping speed with the amount of H_2 sorbed (Fig. IV-7). Similar results were reported by Gareis and Pitlor (Ref. IV-16). Both reported a progressive loss in pumping speed on reactivation of the molecular sieve in vacuum. Southerlan (Ref. IV-15) attributes this to removal of the last traces of water from the sieve material.

4.3 CRYODEPOSITS

The effectiveness of condensed gases in sorption pumping is suggested by the effect of traces of water on zeolite pumping previously mentioned (Refs. IV-9, 14, and 15). In addition, the work on gas trapping has shown sorption pumping by cryodeposits to be an effective pumping method (Refs. IV-17, 18, and 19). Hemstreet et al (Ref. IV-20) reported H_2 trapping by O_2 and N_2 condensate at 20°K to be ineffective as a means of pumping H_2. Southerlan (Ref. IV-21), however, reported that CO_2 frost is fairly effective up to 20°K, and H_2O frost is excellent up to about 21°K. In a more extensive study of H_2 pumping by CO_2 frost, Dawbarn (Ref. IV-22) examined the temperature range from 1.2 to 20°K

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and obtained promising results (Fig. IV-8). Note that the pumping speed is doubled by the reduction in gas temperature and radiation load on the cryosurfaces when the surrounding shroud is cooled from 300 to 77°K. Similar results were found by Busol (Ref. IV-23).

Dawbarn (Ref. IV-22) has also reported on the deterioration of the H_2 pumping speed of CO_2 frost (at 12°K) caused by N_2 condensation. Hunt, et al (Ref. IV-24) report pumping of H_2 on N_2, NO, H_2O, and CO_2 cryofrosts at 11°K (Fig. IV-9). Table IV-2 compares the results of these various studies. Other studies by Dawbarn (Ref. IV-25) indicate that cryosorption pumping of H_2 has an advantage over cryopumping even at 4.2°K. Although the capture coefficients were about the same (near unity), the base pressure when the H_2 flow was shut off was 4×10^{-9} torr for sorption pumping (Ar substrate) compared to 9×10^{-7} torr for cryopumping.

4.4 ADVANTAGES AND DISADVANTAGES

Between the various sorbent materials, solidified gases seem to offer the most promise, principally because of the ease of cooling the sorbent and the simple renewal of the sorbent layer. As with gettering, poisoning of the sorbent with gases such as O_2 and N_2 presents a problem which can be remedied by lowering the temperature to about 10°K. The sorption characteristics of molecular sieves and charcoal are apparently not as sensitive to temperature changes as are the solidified gases. For example, H_2O frost will not absorb much H_2 above about 22°K, whereas at 30°K, molecular sieve still absorbs appreciably, as does charcoal. The pertinent properties of charcoal, molecular sieve, and CO_2 cryodeposit pumping are summarized in Table IV-3.

<div align="center">

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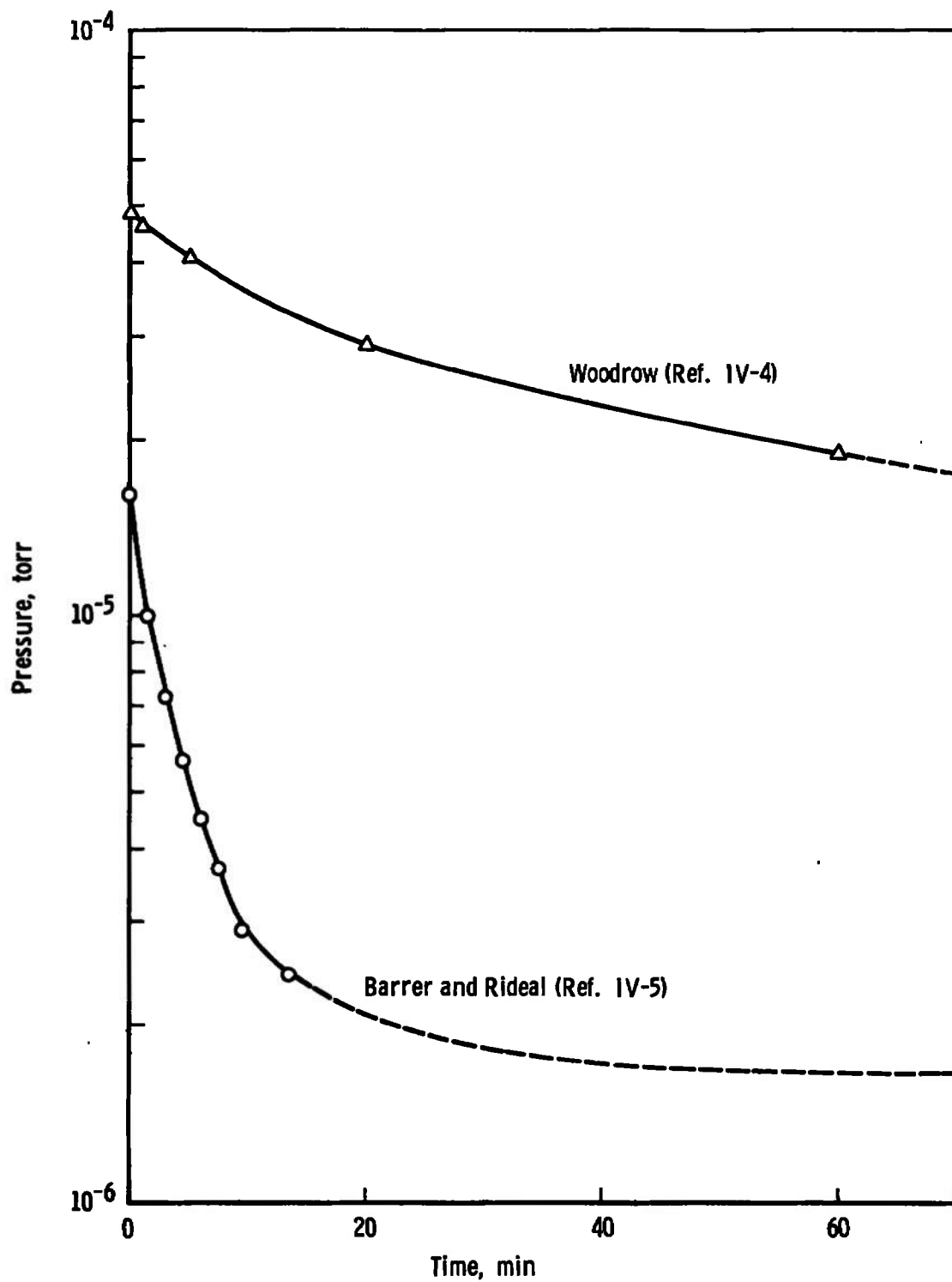
Fig. IV-1 Hydrogen Pumping by Charcoal at 78°K
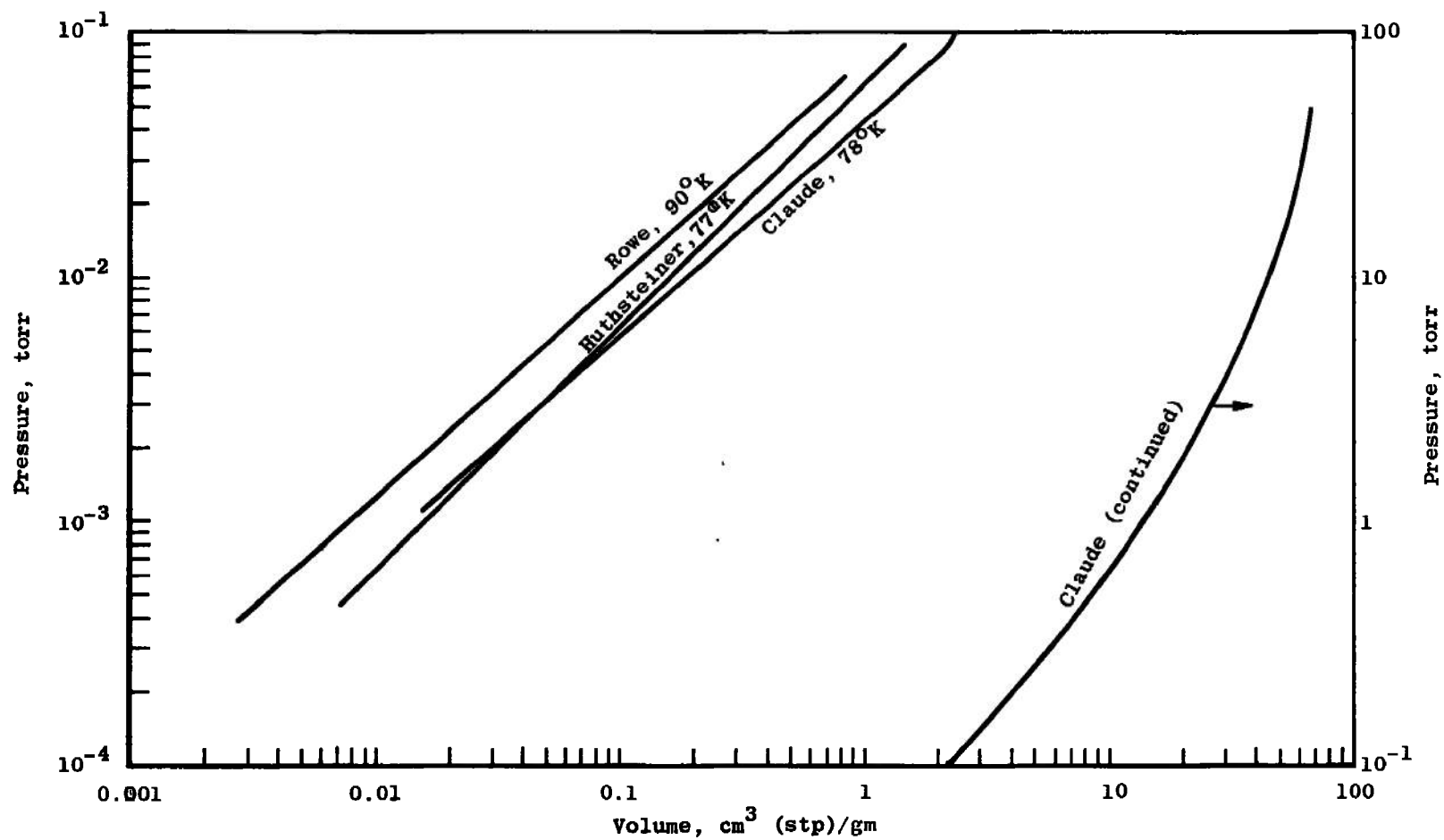
Fig. IV-2 Sorption Isotherms of Hydrogen on Charcoal at Various Temperatures
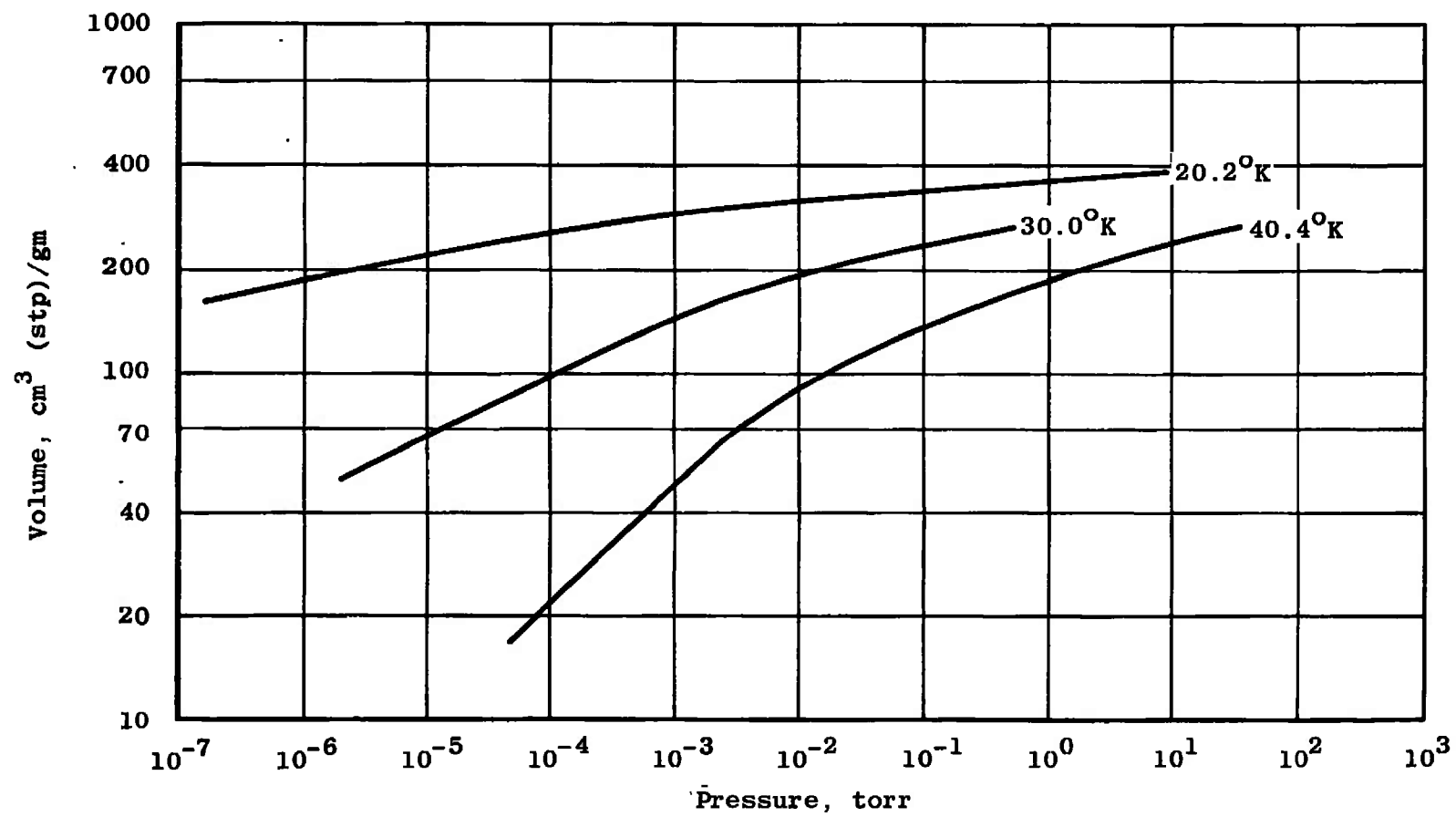
Fig. IV-3 Sorption Isotherms of Hydrogen on Coconut Chorcoal ot Vorious Temperatures
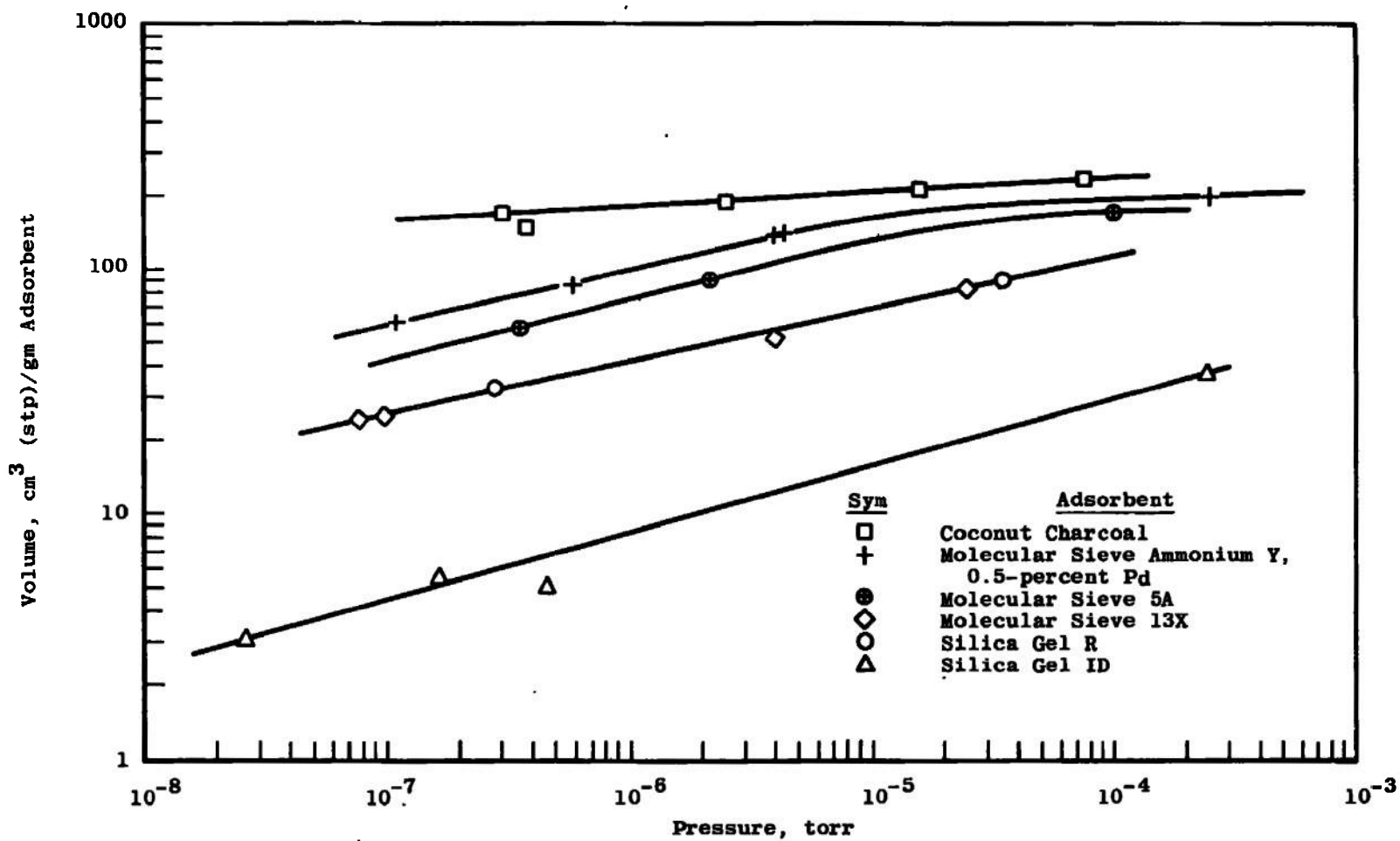
Fig. IV-4 Isotherms for Hydrogen Sorption on Silica Gel and Molecular Sieves (20°K)
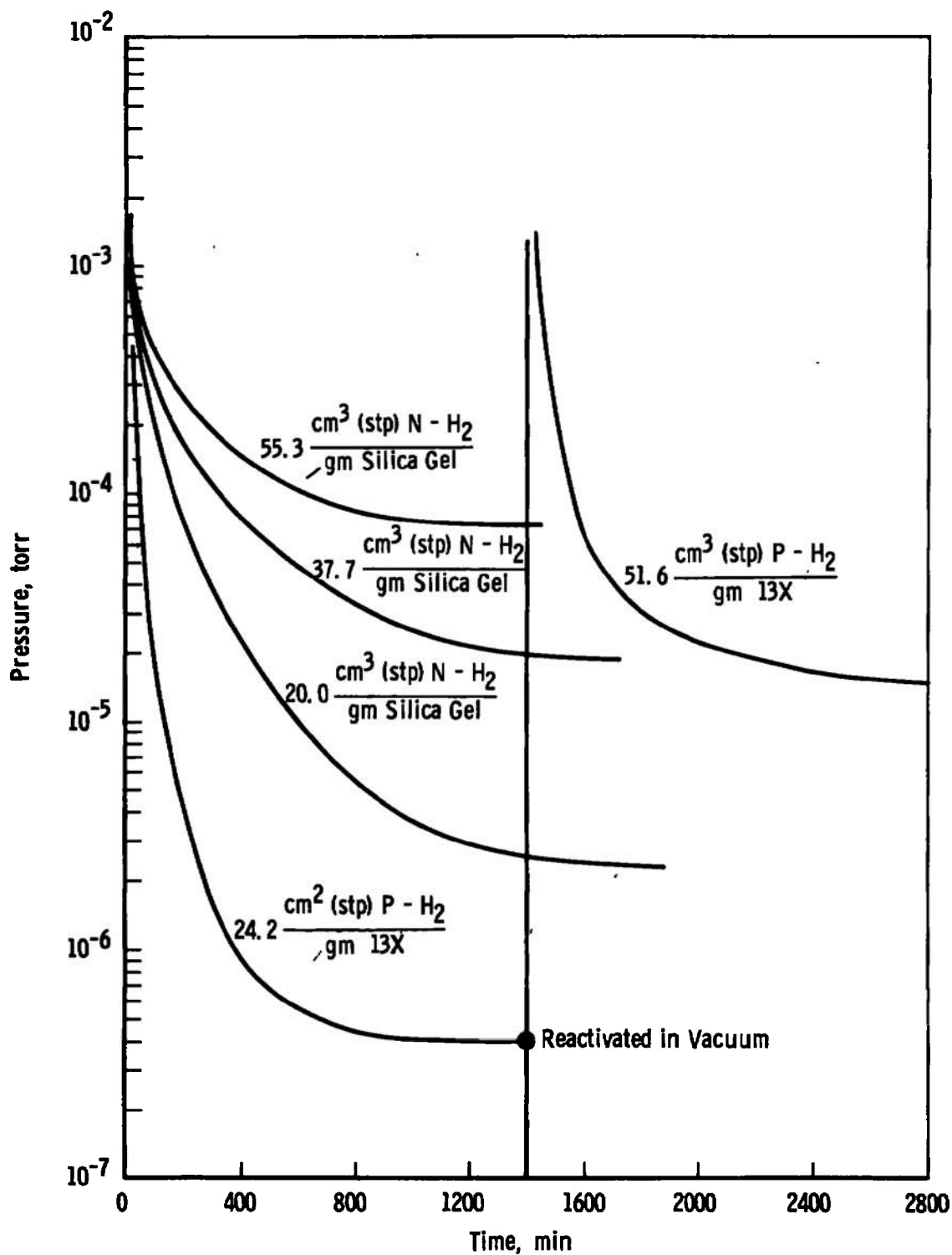
Fig. IV-5 Hydrogen Pumping by Silica Gel and Molecular Sieve (13X) (20°K)
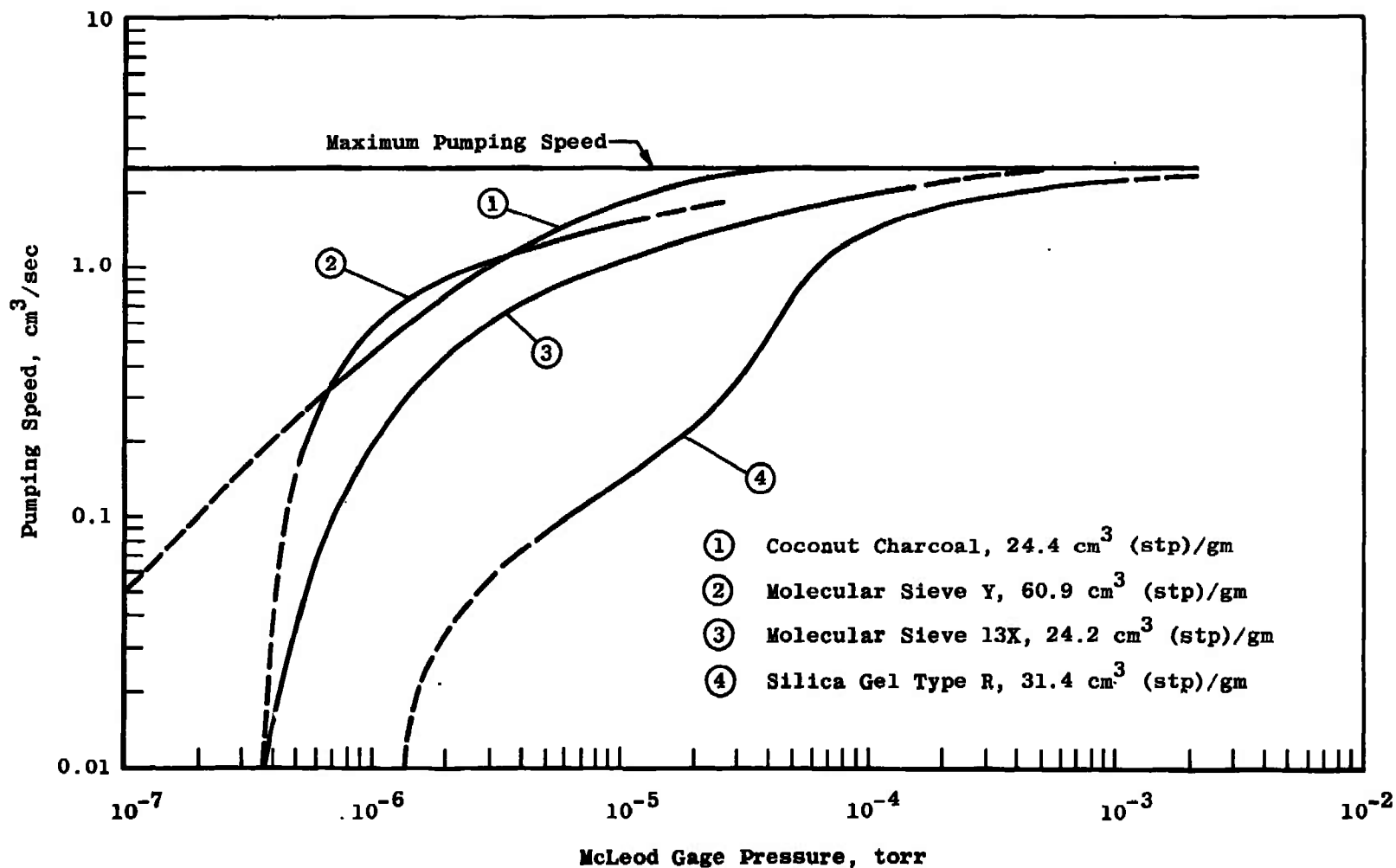
Fig. IV-6 Steady-State Hydrogen Pumping Speed Measurements (20°K)

Fig. IV-7 Pumping Speed versus Hydrogen Pressure for Molecular Sieves

Fig. IV-8 Pumping Speed versus Hydrogen Pressure for Carbon Dioxide Frost at Various Temperatures
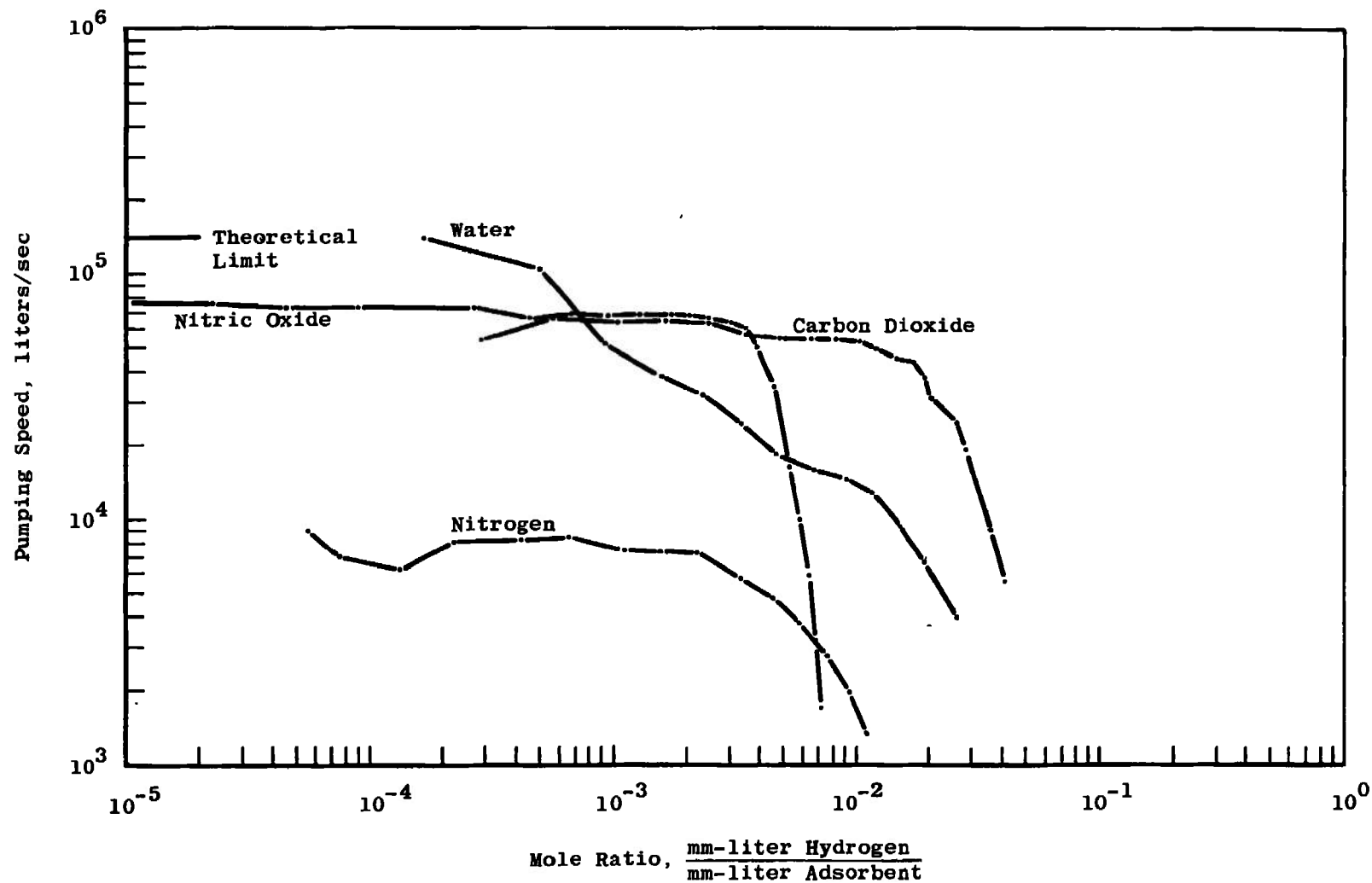
Fig. IV-9 Hydrogen Pumping Speed versus Mole Ratio for Various Adsorbents at 11°K

TABLE IV-1
CHARACTERISTICS OF VARIOUS HYDROGEN SORBENT MATERIALS

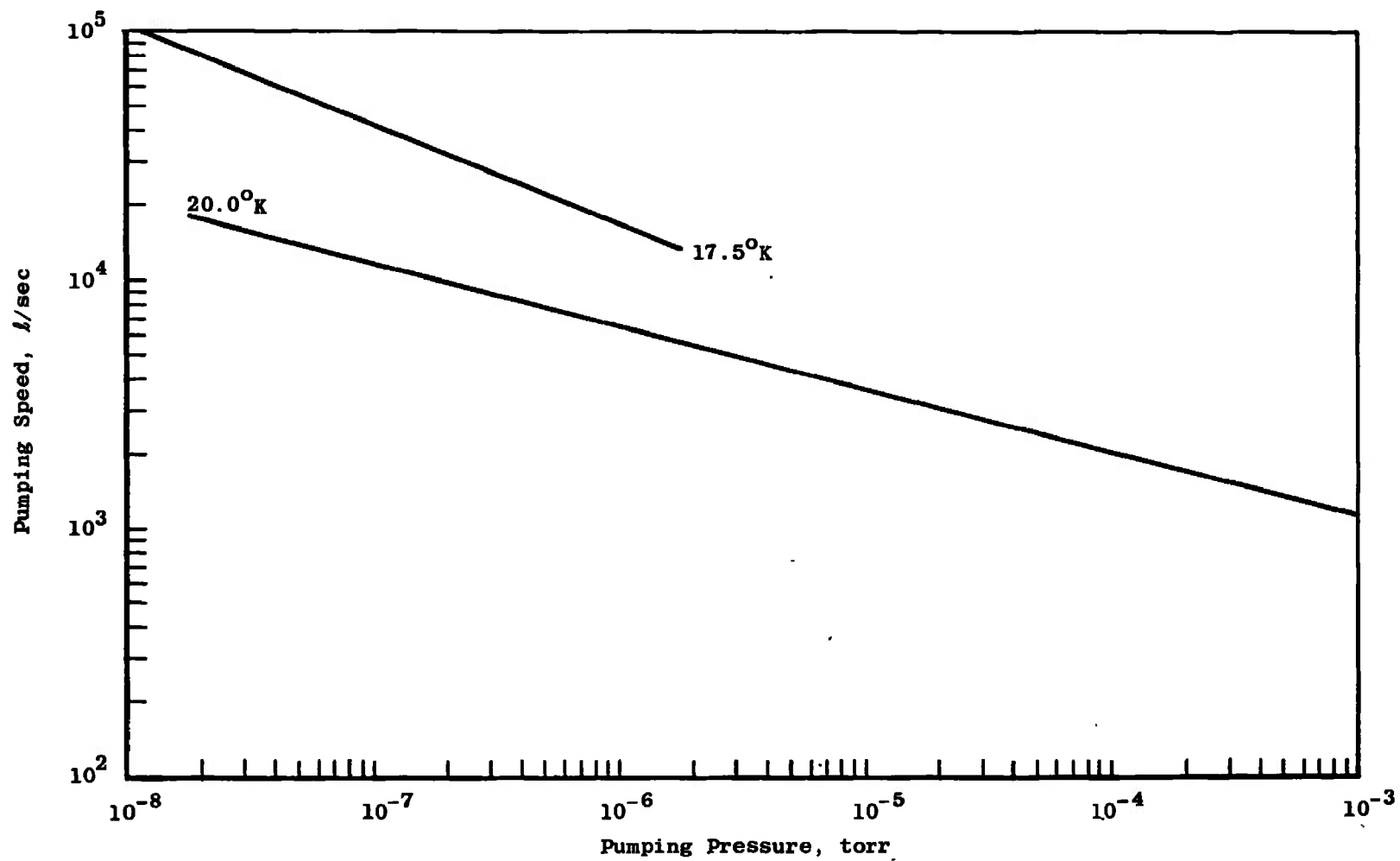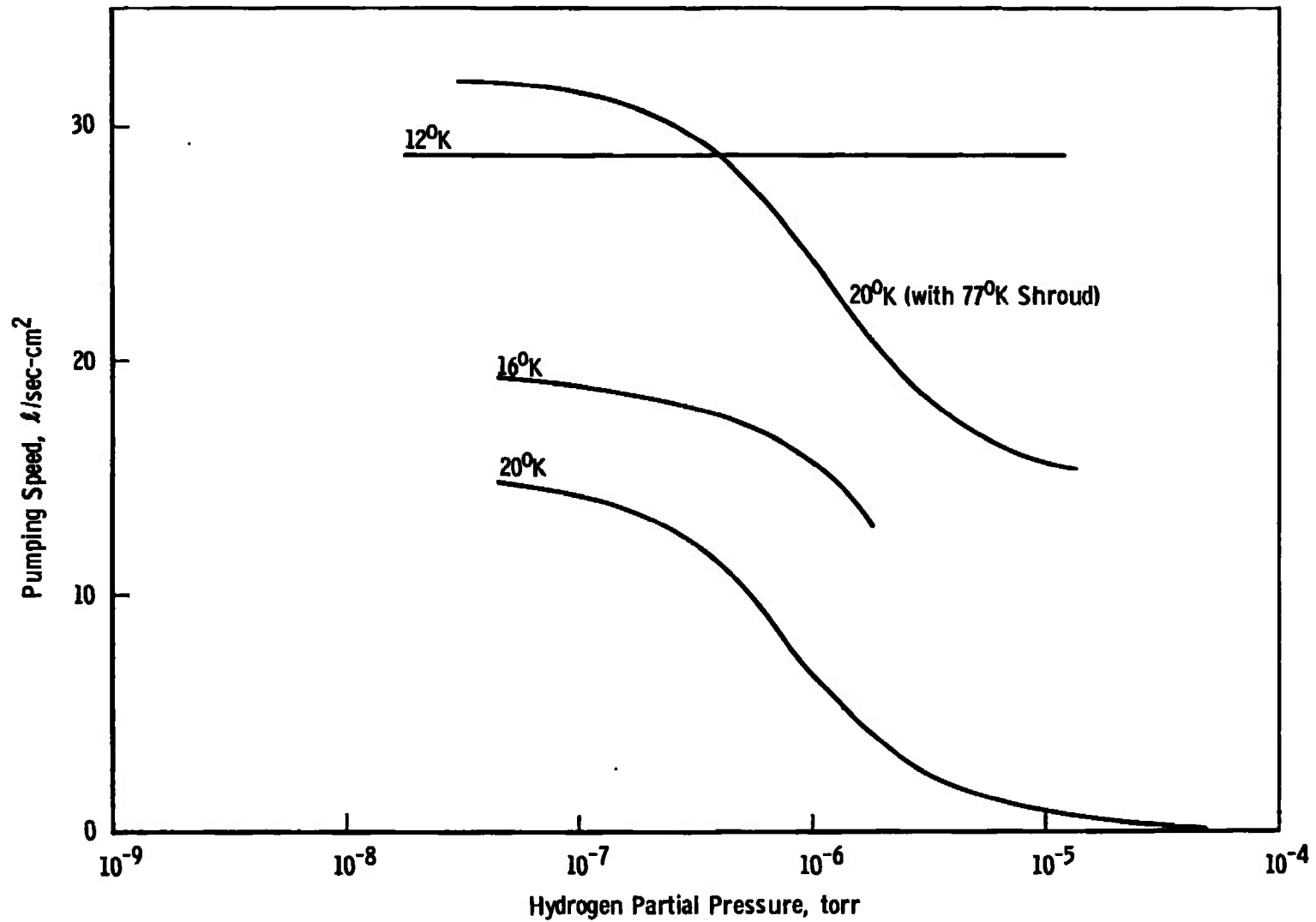| Adsorbent	Form	Size	Surface Area, m^2/gm**	Pore Volume, cm^3/gm***	Bulk Density, gm/cm^3	Average Pore Diameter, $Å$†	Activation	Pressure at End of Activation, torr
Silica Gel, Type R	Granule	14 to 20 mesh	784	0.45	0.72	22	17 hr 175°C	2×10^{-4}
Silica Gel, Type ID	Granule	10 mesh	311	1.16	0.50	140	19 hr 175°C	1×10^{-7}
Coconut Charcoal	Granule	6 to 14 mesh	889	0.54	0.49	10-30	41 hr 200°C	1×10^{-5}
Linde Molecular Sieve, Type 13X	Powder	1 to 5μ	514	1.32	0.53	9-10	23 hr 380°C	1.5×10^{-5}
Linde Molecular Sieve, Ammonium Y Decationized, Loaded with 0.5-percent Palladium by Weight	Pellet No Binder	3/16-in. diameter	586	0.74	0.45	8-9	19.5 hr 405°C	2×10^{-6}
Linde Molecular Sieve, Type 5A	Pellet 20-percent Binder by Weight	1/16-in. diameter	600*	0.75	0.69	5	67 hr 420°C	2×10^{-7}

*Based on weight of 5A-in. pellet
**B.E.T. method, N_2 at 77°K
***Determined by measuring density in H_2O and Hg
† Taken from manufacturer's data and literature

TABLE IV-2
CRYOSORPTION PUMPING OF HYDROGEN BY CONDENSED GASES

Investigator	Substrate Gas	Substrate, gm/cm^2	Pumping Speed, $liters/cm^2-sec*$	Surface Temperature, °K	Gas Temperature, °K
Hunt (Ref. IV-24)	H_2O	2.2×10^{-6}	9.5	11	300
	CO_2	4.9×10^{-6}	12.3	11	300
	N_2O	4.5×10^{-4}	15.1	11	300
	N_2	5.1×10^{-6}	1.5	11	300
	O_2	3.9×10^{-6}	2.3	11	300
	A	2.2×10^{-6}	2.3	11	300
Southerlan (Ref. IV-21)	H_2O	6.1×10^{-3}	39.1	21.3	300
	CO_2	8.8×10^{-3}	1.6	16.3	77
	CO_2	8.8×10^{-3}	23.4	15.3	77
Dawbarn (Ref. IV-22)	CO_2	$~12 \times 10^{-3}$	28	12	300
	CO_2	$~12 \times 10^{-3}$	19	16	300
	CO_2	$~12 \times 10^{-3}$	14	20	300
	CO_2	$~12 \times 10^{-3}$	30	20	77
Hemstreet (Ref. IV-20)	O_2	Continuous Deposition	20	20	20
	N_2	Continuous	5.2	20	20
Busol (Ref. IV-23)	H_2O	---	24.4	20	78
	CO_2	---	20	20	78
	CO_2	---	20	14	78

*Calculated at 300°K

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TABLE IV-3
COMPARISON OF HYDROGEN PUMPING AT 20°K BY CHARCOAL, MOLECULAR SIEVE, AND CRYOFROST

	Coconut Charcoal	Synthetic Zeolite	CO_2 Cryofrost
Capture Coefficient at $P = 10^{-4}$ torr	1.0	0.9	- - -
$= 10^{-6}$	0.65	0.4	0.57
$= 10^{-8}$	0.025	~ 0	0.72
Capacity (NTP), cm^3/gm, at $P = 10^{-4}$ torr	230	185	18.3
$= 10^{-6}$	180	100	5.6
$= 10^{-8}$	110	35	1.5

SECTION V
CRYOPUMPING OF HYDROGEN

Cryopumping is defined as the removal of a gas from an environment by condensation on a surface at cryogenic temperatures. This technique is widely used to produce and maintain the vacuum environment, especially in large space simulation chambers. However, the use of cryopumping to pump H_2 is difficult and expensive. This is the result of the high vapor pressure of H_2 at temperatures greater than 6°K (Ref. V-1).

The most common method used to cryopump H_2 is to fill a cavity within a cryopump with LHe and to use the resultant 4.2°K surface as the cryopump. This technique has been used successfully to pump a 0.05-gm/sec flow rate of H_2 and has been proposed for use in pumping a flow rate of 2 gm/sec in a plume testing chamber (Ref. V-2).

Several groups have experimentally investigated the cryopumping phenomenon in general (Refs. V-3 through 6). Chubb et al, at the Culham Laboratory in England, have investigated the cryopumping of H_2, deuterium (D_2), and hydrogen deuteride (HD) in detail (Refs. V-7 and 8). They have reported the following trends for H_2:

1. The capture coefficient increases with surface coverage until a coverage of 10^{16} condensed H_2 molecules per cm^2 is obtained on the surface (Fig. V-1).

2. The capture coefficient increases as the incident gas strike rate increases.

3. The capture coefficient varies inversely with the square of the incident gas temperature.

4. The desorption rate increases roughly in proportion to the radiation load as the radiation load varies from 9×10^{-3} to 30×10^{-3} watts/cm^2.

The increase in the capture coefficient for H_2, as the surface coverage and gas incident rate increases (Ref. V-7), is in qualitative agreement with the trends reported for CO_2, Ar, and N_2 (Refs. V-3 and 6). Also, a variation of the capture coefficient with the incident gas temperature was observed by previous investigators (Ref. V-9). However, later experiments using molecular beam techniques have revealed that the capture coefficient of a surface for beams of N_2 and Ar does not vary as the incident gas temperature increases from 300 to 1400°K, but with incident gas temperatures greater than 1400°K, the capture

coefficient for Ar beams does decrease with increasing gas temperature. Data are not available at this time for H_2 or N_2 at temperatures greater than 635 and 1400°K, respectively.

The decrease in the capture coefficient of LHe-cooled surfaces for H_2 as the incident gas temperature increases and the increase in the evaporation rate as the radiation load increases (Ref. V-7) may limit the use of cryopumping in plume testing. Any shielding to reduce the radiation load and precool the hot H_2 also shields the cryopump from H_2 and lowers the effective pumping speed.

Other data that should be considered in evaluating the use of cryopumping to remove H_2 from space simulation chambers are summarized in Figs. V-2 and 3. These data clearly indicate that 2500°K Ar is reflected from surfaces with quasi-specular spatial distributions. If this phenomenon is also characteristic of H_2, it may be used to advantage in the pumping of high energy H_2.

Additional data reported by Chubb, et al (Ref. V-7) that should be discussed are shown in Fig. V-4. These data indicate that the vapor pressure of H_2 on from 2.0 to 3.7°K surfaces departs radically from an extrapolation of the normal H_2 vapor pressure curve. Currently this has not been satisfactorily explained. However, the data indicate that the ultimate pressure obtainable by using cryopumping for H_2 may have a limit and that this limit is much higher than expected. This would make it impractical to use LHe-cooled surfaces to pump H_2 in space simulation facilities that require background pressures less than 10^{-9} torr.

In summary, four factors are apparent from a survey of the existing data on the cryopumping of H_2:

1. A very limited amount of experimental data is available, and Chubb at the Culham Laboratory in England appears to have conducted the most extensive investigation to date.

2. An LHe-cooled cryosurface will cryopump 300°K H_2, and the capture coefficient is very high (i. e., greater than 0.8).

3. The capture coefficient of a cryosurface for H_2 is a function of the incident gas temperature, the radiation load on the cryosurface, and the incident gas flux. However, the extent of the influence of these factors on the cryopumping of large flow rates of H_2 is undefined at this time.

4. The current data indicate that the use of cryopumping to pump H_2 at pressure less than 10^{-9} torr is impractical.

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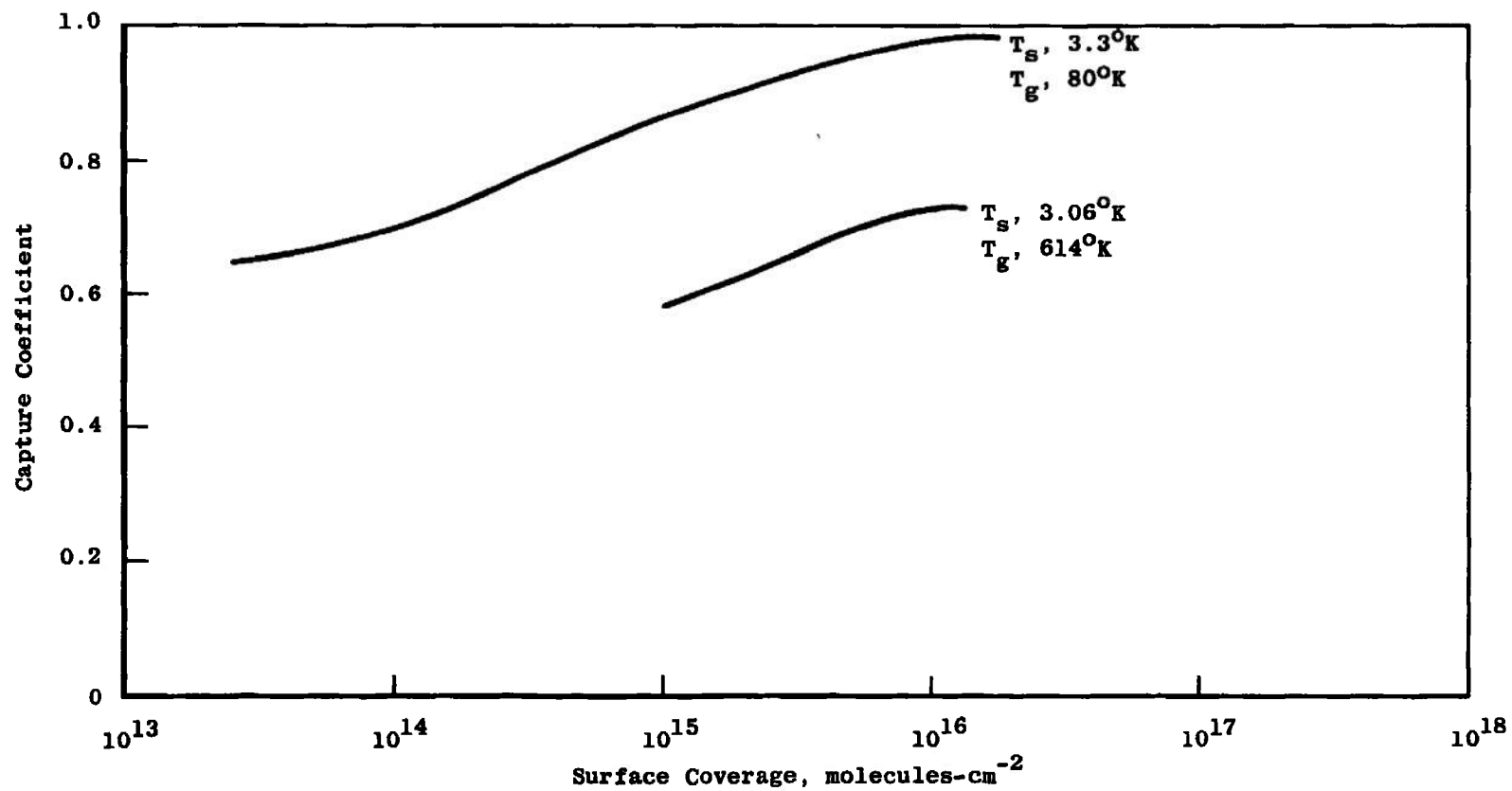   Press, New York, 1967.

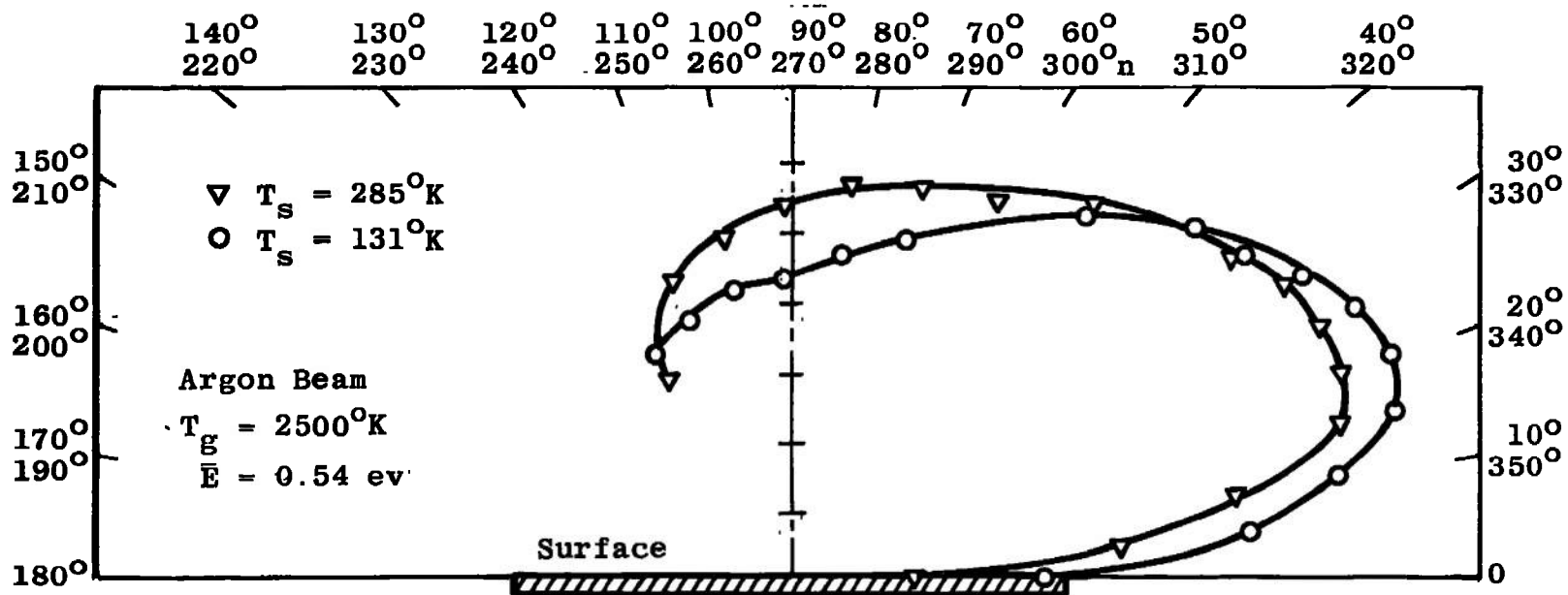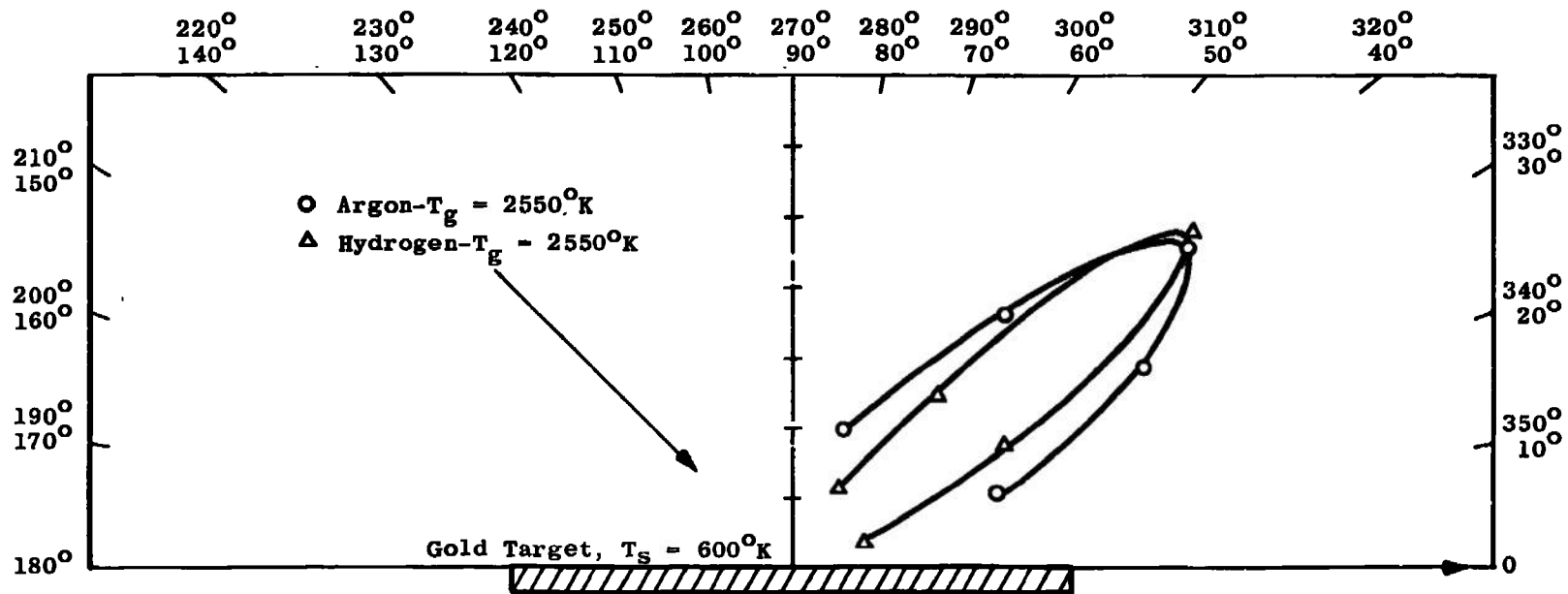Fig. V-1 Examples of the Variation of Capture Coefficient with Gas Temperature (Chubb's Data)

Fig. V-2 Spatial Distribution of 2500°K Argon Reflected from a Dirty Copper Surface at Several Temperatures

Fig. V-3 Similarity between Reflected Spatial Distributions of 2550°K Argon and Hydrogen Reflected from a Clean Gold Surface (Ref. V-1)

Note: Research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, under Contract AF 49(638)-1192 (Ref. V-11).

Quote from the above paper: "At higher beam energies (2550°K), H_2, He, Ne, and Ar are specular....At these higher energies, the specular components for all gases studied show close agreement with one another despite the wide variation in the mass of the incident particle and the magnitude of its interaction with gold." Ref. V-10, p. 491.
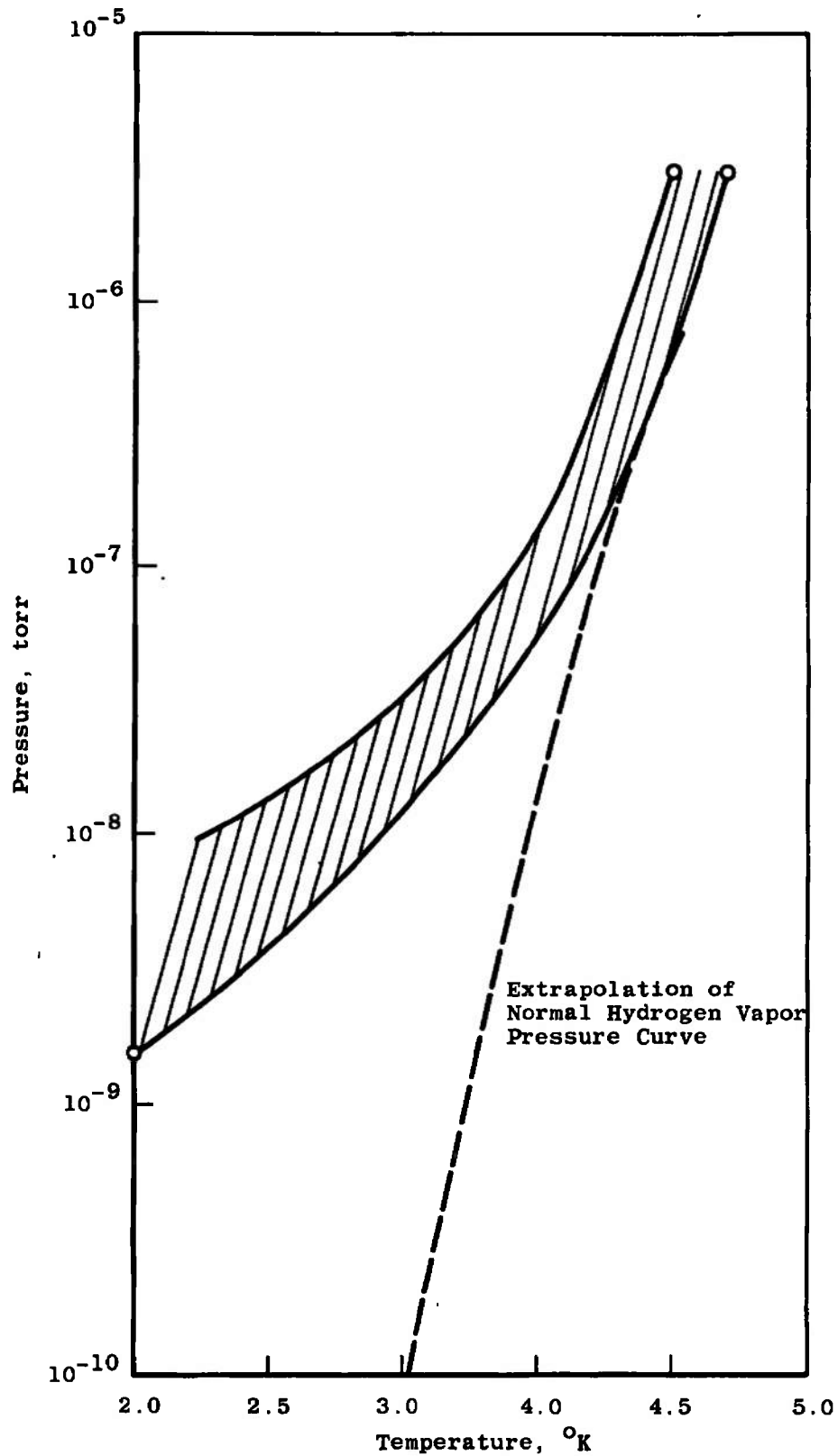
Fig. V-4 Limiting Pressures Obtainable by Using Cryopumping
to Remove Hydrogen (Chubb's Data)

SECTION VI
CHEMISORPTION PUMPING

Although cryopumping at $4.2°K$ on an LHe-cooled surface is a reliable method for high vacuum H_2 pumping, the high cost of LHe makes this a very expensive technique, especially in chambers where the heat load is high. A distinct cost advantage might be attained if H_2 could be reacted with other chemicals to form low vapor-pressure compounds which would pump on $77°K$ surfaces. Some reactions of H_2 would have to be induced by catalysis or by addition of energy in the form of an electric spark or by heat resulting from a more energetic chemical reaction. The reaction of GH_2 and O_2 is initiated by such means. Other reactions, such as those between H_2 and fluorine and other hypergolic oxidizers, will proceed without external initiation, over a wide range of conditions. In many instances the reaction products of H_2 and oxidizing substances can be effectively cryopumped at $77°K$.

6.1 CATALYTIC OXIDATION

Although much work has been done in the area of catalytic hydrogenation reactions, most of it has been concerned with high pressure reactions. Very little has been done in the vacuum range. Vladimir Ponec (Ref. VI-1) of the Czechoslovak Academy of Sciences reports that H_2 in the 10^{-2} to 10^{-3} torr range reacts at $78°K$ with O_2 preadsorbed on a platinum (Pt) surface. The product of this reaction is believed to be water which is frozen to the surface. The reaction rate is slow when compared to the adsorption of H_2 of clean Pt, but the fact that the reaction occurs at $78°K$ and in vacuum is promising. No ultimate chamber pressures or capture coefficients were reported in this paper, so it remains to determine how such a system would perform as a vacuum H_2 pump.

A limited study was made on the possibility of pumping H_2 in rocket exhaust plumes by mixing the gas with injected O_2 and reacting the mixture by passing it through beds of palladium-coated alumina pellets (Ref. VI-2). The reaction products were subsequently cryopumped on LN_2-cooled surfaces. Two catalyst bed configurations were tested. The more efficient of these showed a maximum H_2 pumping speed (without diffusion pump backing) of 0.5 liters/sec-cm^2 at 3×10^{-3} torr and fell to zero at 1.2×10^{-3} torr. Heated H_2 (approximately $3000°K$) did not show an appreciably greater pumping speed.

From these studies, it appears that H_2 pumping systems utilizing catalytic oxidation followed by 77°K cryopumping have little application to very high vacuum pumping without further development. At the present state of development, reaction rates are slow, and catalytic activity would probably be reduced by the presence of other gases.

6.2 DIRECT CHEMICAL OXIDATION

Hydrogen will react in the gas phase with several strongly oxidizing gases such as the halogens, the halogen fluorides, and oxygen difluoride (OF_2).

The concept of using such reactions for vacuum pumping is to interact the H_2 molecules with strongly oxidizing gas molecules on the surface of a 77°K cryosurface where the resulting reaction products would then be cryopumped. The advantage of this method over catalytic reaction is a reduction in the probability of poisoning by other gases and a reduction of the heat load on the internal chamber, since no heat would be required as is the case with heated catalytic beds. The major disadvantage is the potential for chamber component damage by the highly reactive oxidizers.

One test has been made at AEDC to determine if such a reaction could be carried out between room temperature H_2 and a 77°K cryo-deposit of chlorine trifluoride (ClF_3). The ClF_3 was predeposited on an LN_2-cooled surface in considerable excess of the stochiometric amount. Hydrogen gas was then metered into the chamber and equilibrium pressures measured. No significant H_2 pumping was observed even at H_2 pressures as high as $30\,\mu$.

The pure halogen gases and other halogen fluorides might exhibit more reactivity at cryogenic temperatures than does ClF_3. The more reactive of the oxides of N_2 might also react. Chemical reactions at very low temperatures and pressures have been studied very little. No reliable method is available at present for selecting candidates for such reactions, since the chemical properties of substances at cryogenic temperatures are largely unexplored.

6.3 REACTION WITH CARBON ATOMS

Experiments carried out at the U. S. Naval Research Laboratory in 1962 showed that H_2 at equilibrium pressures around 10^{-4} torr reacted with carbon atoms from a d-c carbon arc to form hydrocarbons which pumped on LN_2-cooled cryoliners (Ref. VI-3). No pumping speed

values or ultimate chamber pressures were reported, but test runs in a chamber equipped with diffusion pumping and LN_2 cryopanels indicated that one-half to two-thirds of the flowing H_2 was pumped by the carbon arc. Mass spectral analyses of the gases evolved from the cryopanels as they were warmed revealed the presence of both saturated and unsaturated hydrocarbons up to mass 59. No further development of this technique has been reported.

6.4 CHEMISORPTION ON BORON

Hydrogen adsorbs readily on vacuum-deposited boron films at a pressure of about 10^{-3} torr and at 300°K (Ref. VI-4). Since the adsorption is irreversible, it is interpreted to be a chemisorption. The sorption is initially rapid, and BET surface area measurements using xenon indicate a relatively large H_2 uptake: approximately 0.5 H_2 molecules per BET adsorption site. Film densities were not reported, but an 18-percent reduction in surface area was measured as a result of H_2 sorption. No pumping speed values were reported.

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SECTION VI

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SECTION VII
SUMMARY

In this review the various methods for vacuum pumping H_2 have been examined. Diffusion pumps are the most widely used pumps; however, they cannot be recommended where very clean systems are required because of the possibility of oil contamination of the test environment. Diffusion pumps also are limited in pumping speed by the requirement for a chamber wall penetration and, usually, a chevron baffle for each pump. The number of pumps that can be attached to a given chamber is limited by structural and geometric considerations. In addition, the effective capture coefficient of the diffusion pump opening is of the order of 0.3 for H_2 (0.1 with baffle). For very high vacuum and small gas loads, Ti evaporation combined with ion pumping is to be recommended.

Synthetic zeolites require long periods of time for both cooling and for activation, which limit their usefulness. One ideal application seems to be the use of synthetic zeolites or charcoal to replace mechanical roughing pumps on ultraclean systems.

For pumping a large H_2 flux at low pressure, it appears that cryosorption pumping by condensed gases is to be preferred over the other methods of pumping H_2. The cooling time for the sorbent is negligible, the capture coefficient is high, the area of the pumping surface can be a large fraction of the chamber wall area, and the sorbent can be renewed without warming.

Cryopumping at 4.2°K would be equally useful; however, the higher refrigeration costs will generally limit its use to small installations where base pressures below 10^{-6} torr are not a requirement.

The ranges of the various pumping methods are compared in Fig. VII-1, and the pumping characteristics are listed in Table III-1.

Having selected cryosorption pumping by solidified gases as the most promising method of pumping large quantities of H_2, there remain several unexplored areas which should be investigated in order to obtain design parameters. The primary requirement is the measurement of isotherms and pumping speed curves for representative sorbent gases. These should be measured for various surface and gas temperatures. Variations in the incident H_2 gas temperature up to 3000°K can now be carried out using the newer molecular beam techniques. These should also be used to examine the reflection patterns of H_2

from surfaces at various temperatures in order to determine the optimum geometry for plume testing. For H_2 temperatures of 300 and 77°K, the pumping speed curves and sorption isotherms may be measured by both the molecular beam and by the usual techniques for determining capture coefficients (Ref. V-5). This should give increased confidence to the results.
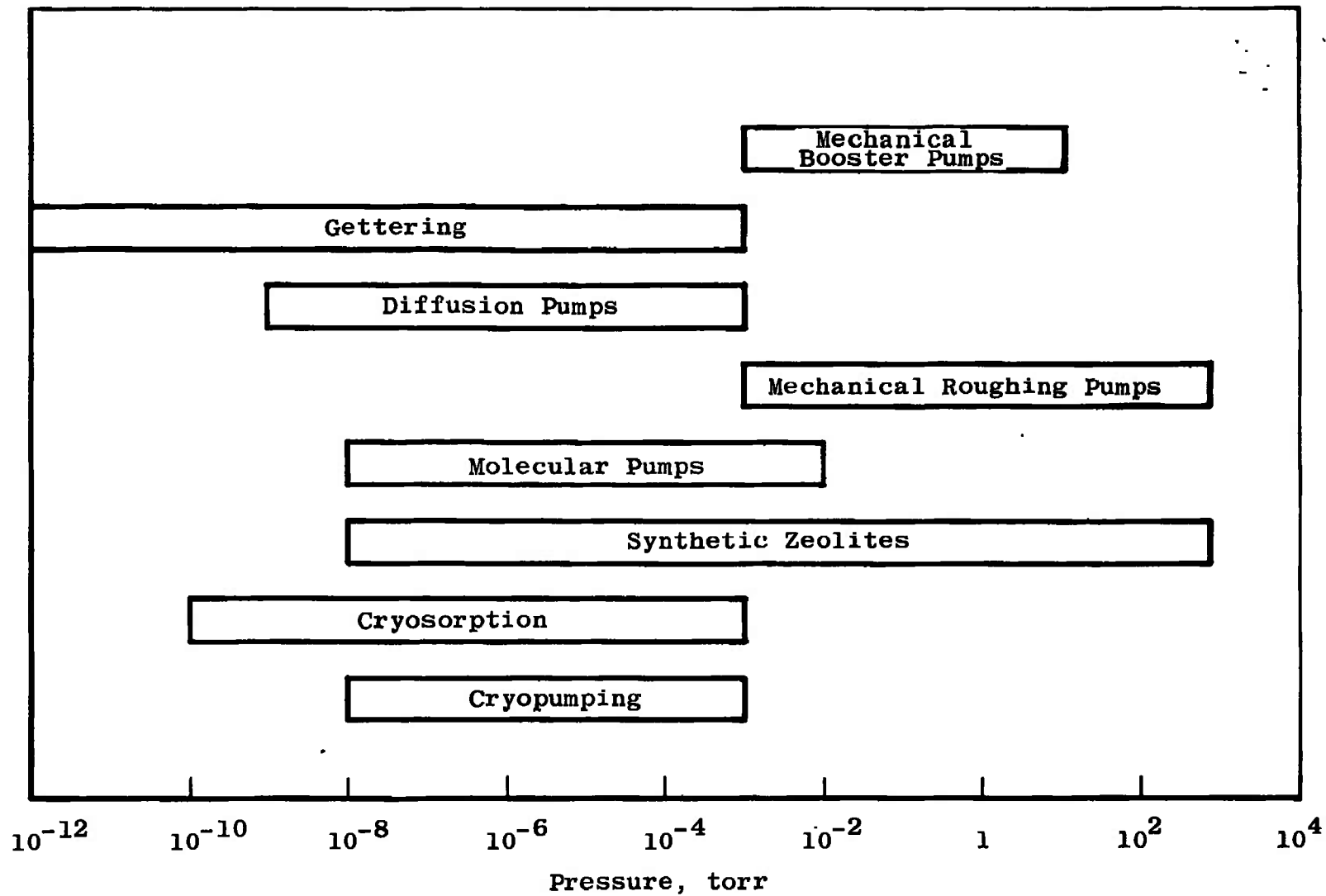
Fig. VII-1 Pressure Range for Various Hydrogen Pumping Methods

TABLE VII-1

COMPARISONS OF METHODS OF PUMPING HYDROGEN

Method	Pressure Range, torr	Initial Capture Coefficient	Surface Temperature	H_2 Pumping Speed, liters/cm^2-sec
Gettering	10^{-3} to 10^{-12}	0.2	77°K	10
Diffusion	10^{-3} to 10^{-9}	0.25 to 0.3	---	12
Cryosorption	10^{-3} to 10^{-10}	>0.9	< 20°K	40
Cryopumping	10^{-3} to 10^{-8}	>0.9	4.2°K	40
Synthetic Zeolites	760 to 10^{-8}	0.3 to 1.0	20°K	40
Turbomolecular	10^{-2} to 10^{-8}	Low	---	Low

APPENDIX
HYDROGEN PROPERTIES

Hydrogen is the lightest gas (MW = 2.016, density 0.089 gm/liter at 760 torr, 273°K). It exists in two forms, ortho and para. The heat of transition from ortho H_2 to para H_2 is 253 cal/mole (Ref. A-1). Figure A-1 shows the variation of equilibrium composition as a function of temperature (Ref. A-1). These two forms of H_2 have slightly different molar volumes in the liquid phase, as shown in Fig. A-2. Normal H_2 refers to the room temperature equilibrium mixture of one part para H_2 and three parts ortho H_2. Normal H_2 also has a slightly higher vapor pressure than does para H_2; however, the difference is less than 1 percent and is not indicated on the vapor pressure curve (Fig. A-3, Ref. A-2). The heat of vaporization of para H_2 is shown in Fig. A-4. The solid range was calculated by the authors from the specific heat of the solid (Ref. A-1). The liquid range is given in Ref. A-1. Several relationships which prove useful in the study of H_2 pumping are given below (Ref. A-3). The temperatures are in degrees Kelvin, and pressures are in torr.

Strike rate	$2.47 \times 10^{22} \, P/\sqrt{T}$, molecules/cm^2-sec
Mean velocity	$1.027 \times 10^4 \sqrt{T}$, cm/sec
Collision frequency	$3.28 \times 10^8 \, P/\sqrt{T}$, collisions/molecule-sec
Collision rate	$1.592 \times 10^{27} \, P^2/T^{3/2}$, collisions/cm^3-sec

In using H_2 one should keep in mind the fact that H_2 is an inflammable gas and constitutes a possible safety hazard. The explosion limits for mixtures of H_2 with air are from 4- to 75-percent H_2 by volume (Refs. A-4 and 5). The ignition temperature is 1076°F (580°C) in air (Ref. A-4). Appropriate safety measures should be employed (Refs. A-4 and 5).

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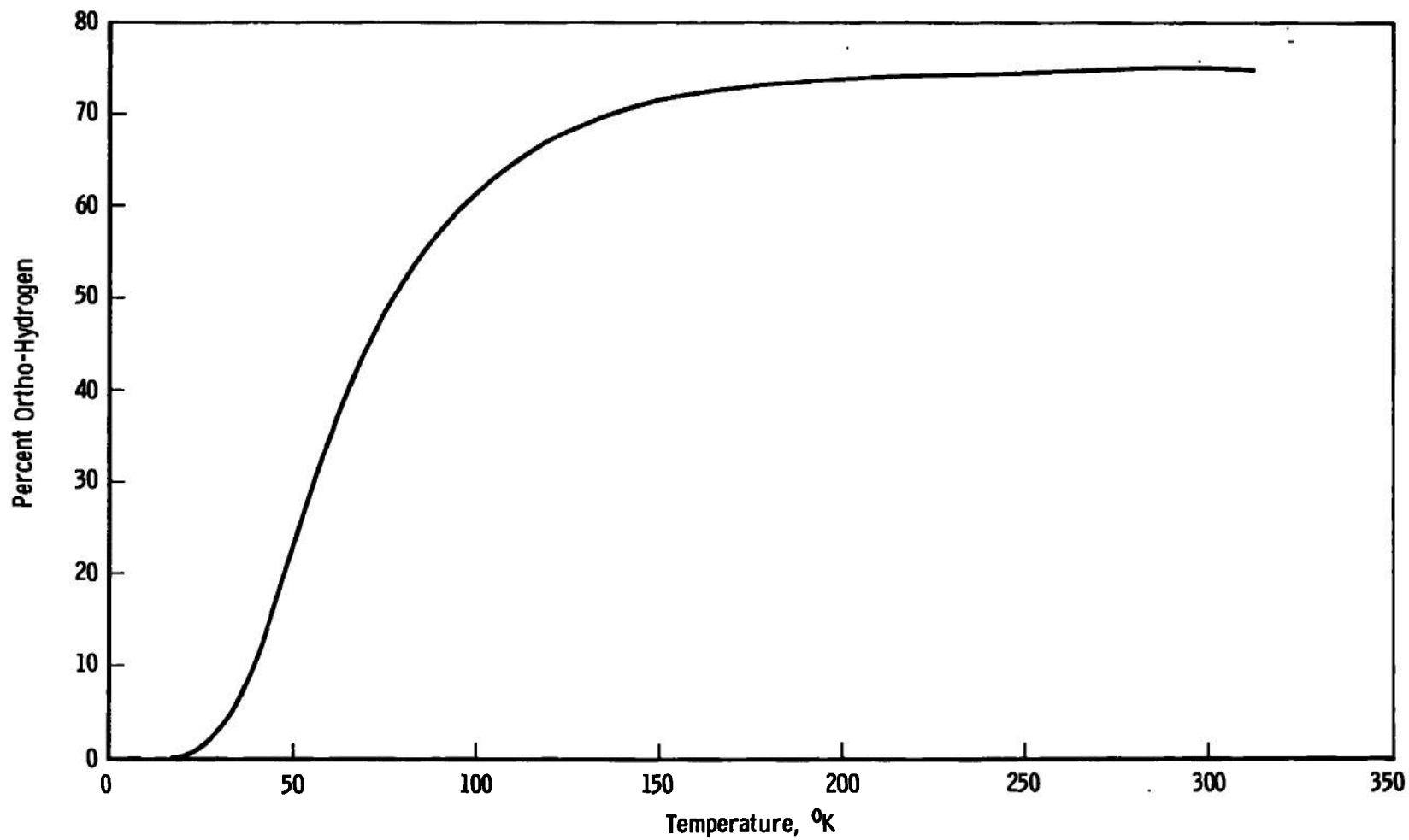   1968.

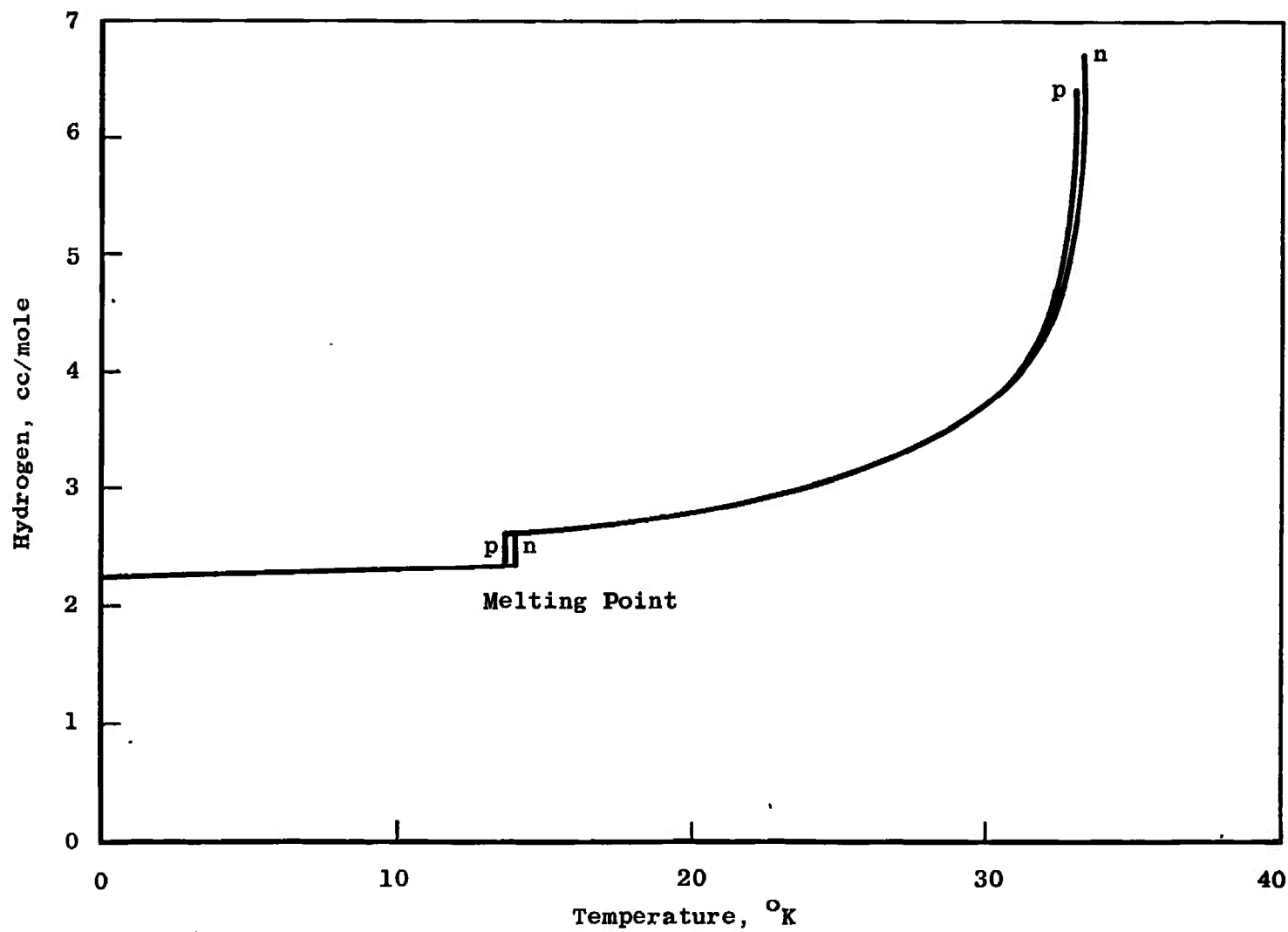Fig. A-1 Equilibrium Percent Ortho-Hydrogen versus Temperature

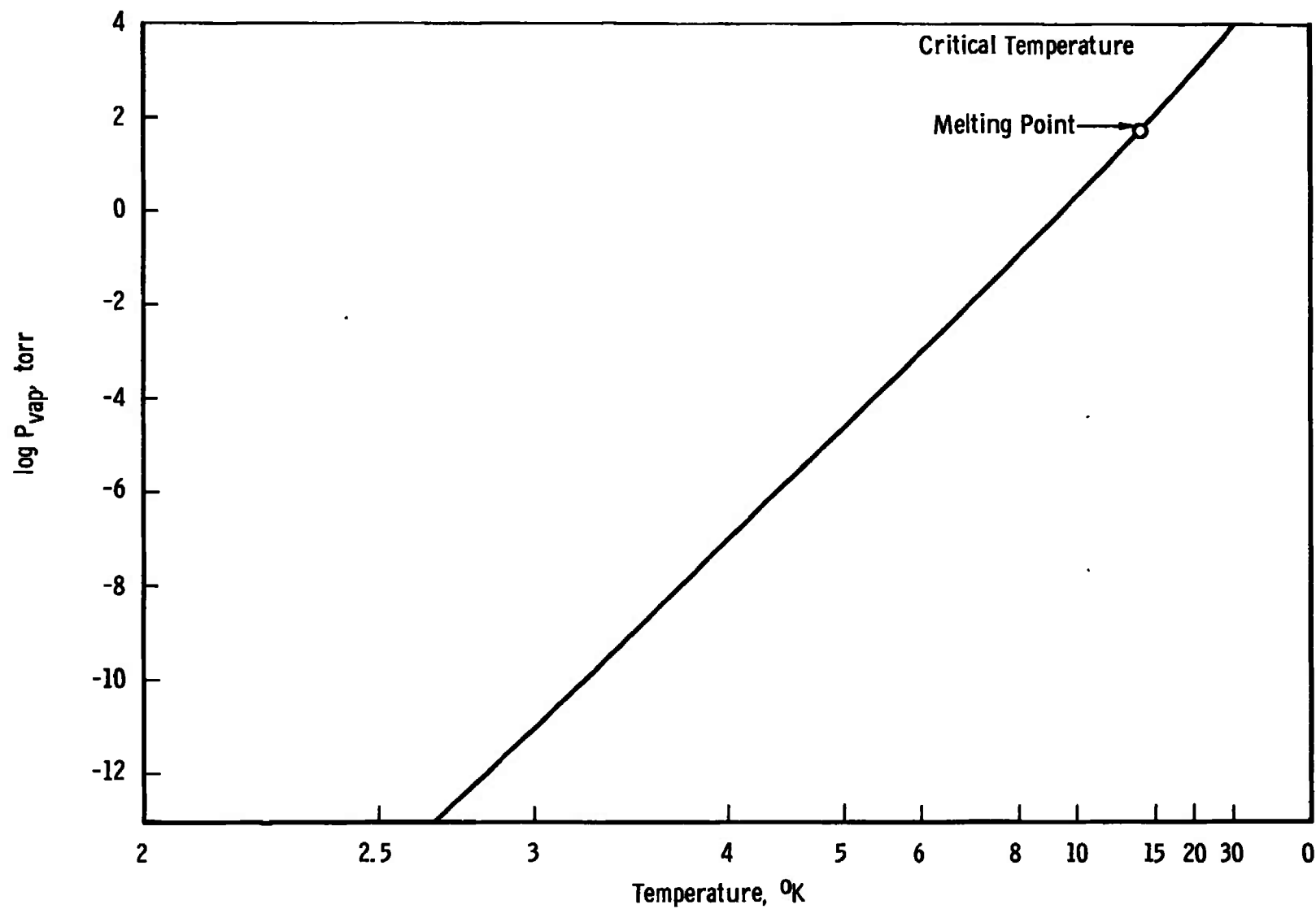Fig. A-2 Volume/Mole of Hydrogen, Normal (n) and Para (p)
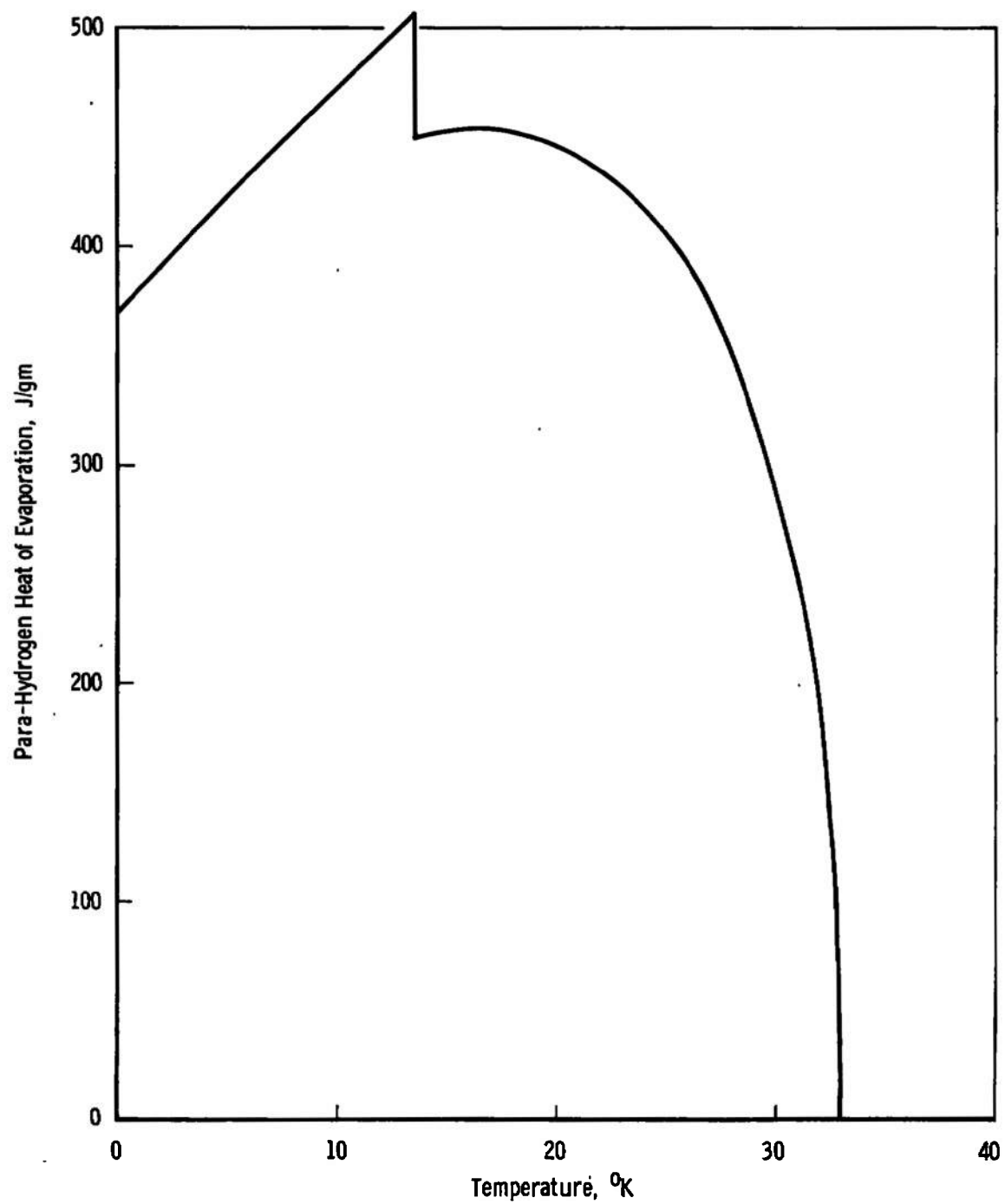
Fig. A-3 Vapor Pressure of Hydrogen (Ref. A-2)

Fig. A-4 Heat of Evaporation of Para-Hydrogen versus Absolute Temperature

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13 ABSTRACT

This report summarizes the findings of an investigation into various possible methods of pumping hydrogen (H_2). The objective was primarily to find methods which might prove useful for pumping rocket plumes. A secondary objective was to select H_2 pumping methods for other types of tests. The methods reported include mechanical pumping, diffusion pumping, gettering, cryosorption, chemisorption, and cryopumping. Cryosorption pumping is judged to show the most promise as a pumping method for rocket plume testing, although most of the other methods will be found useful where the pumping speed requirements are less demanding.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
vacuum pumps						
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chemisorption						
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