

MOLECULAR SURFACE PUMPING: CRYOPUMPING

C. Benvenuti

CERN, Geneva, Switzerland

Abstract

Weak van der Waals attractive forces may provide molecular gas pumping on surfaces cooled at sufficiently low temperatures. Cryopumps make use of a cold surface to adsorb gas molecules. They are usually classed into two families, depending whether they rely on the binding forces between gas molecules and solid surfaces (cryosorption pumps) or on the even weaker forces which bind condensed gas molecules together (condensation pumps). The design features and the possible applications of both types of cryopumps are presented. The peculiar behaviour of condensed hydrogen, i.e. its desorption induced by infrared thermal radiation, is described and discussed.

1. GENERALITIES

1.1 Gas density and pressure at $T \neq 300$ K

A gas pressure is defined only if gas molecules present an *isotropic distribution of directions* and a *maxwellian distribution of speeds*. Under UHV conditions, pressure gauges do not measure pressure but *gas density*.

If two communicating vessels V_1 and V_2 are kept at different temperatures (T_1 and T_2) the gas densities (d_1 and d_2) and pressures (p_1 and p_2) are given by

$$p_1 = \sqrt{T_1/T_2} p_2$$

$$d_1 = \sqrt{T_2/T_1} d_2$$

In other words, in the colder vessel the gas density is higher but the pressure is lower. $\sqrt{T_1/T_2}$ is the *thermomolecular transpiration factor*.

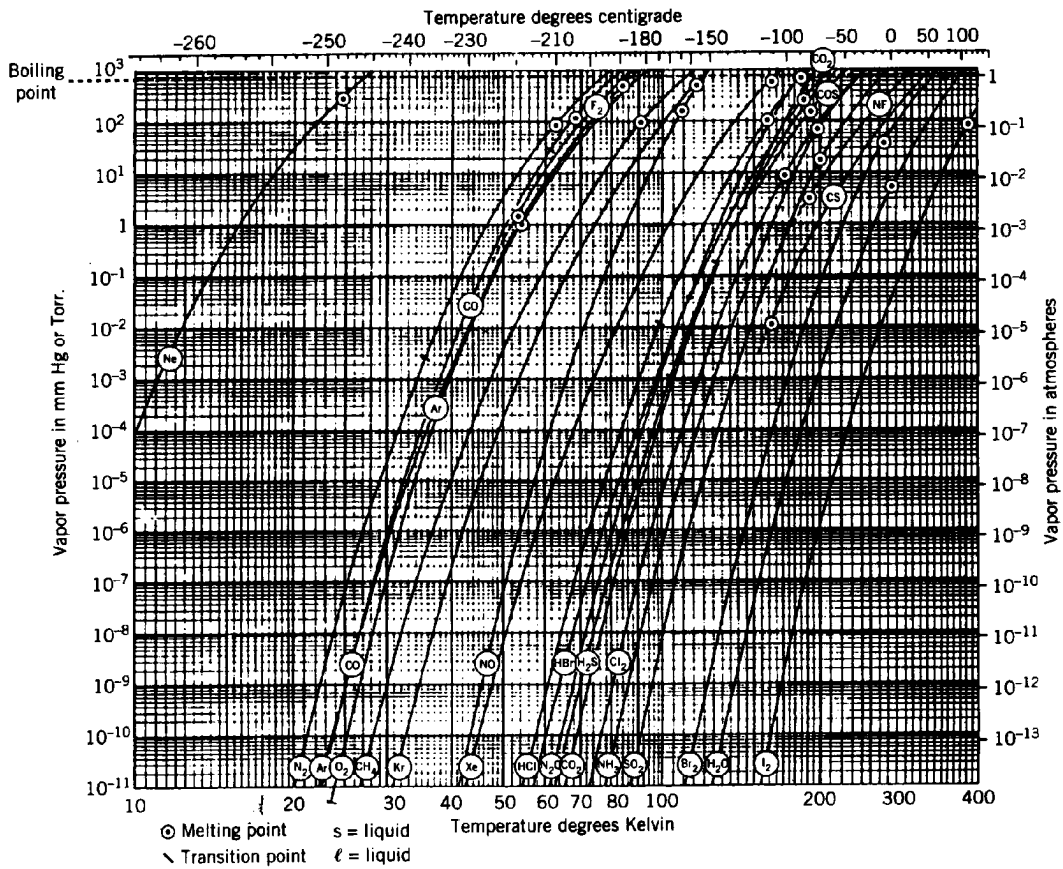
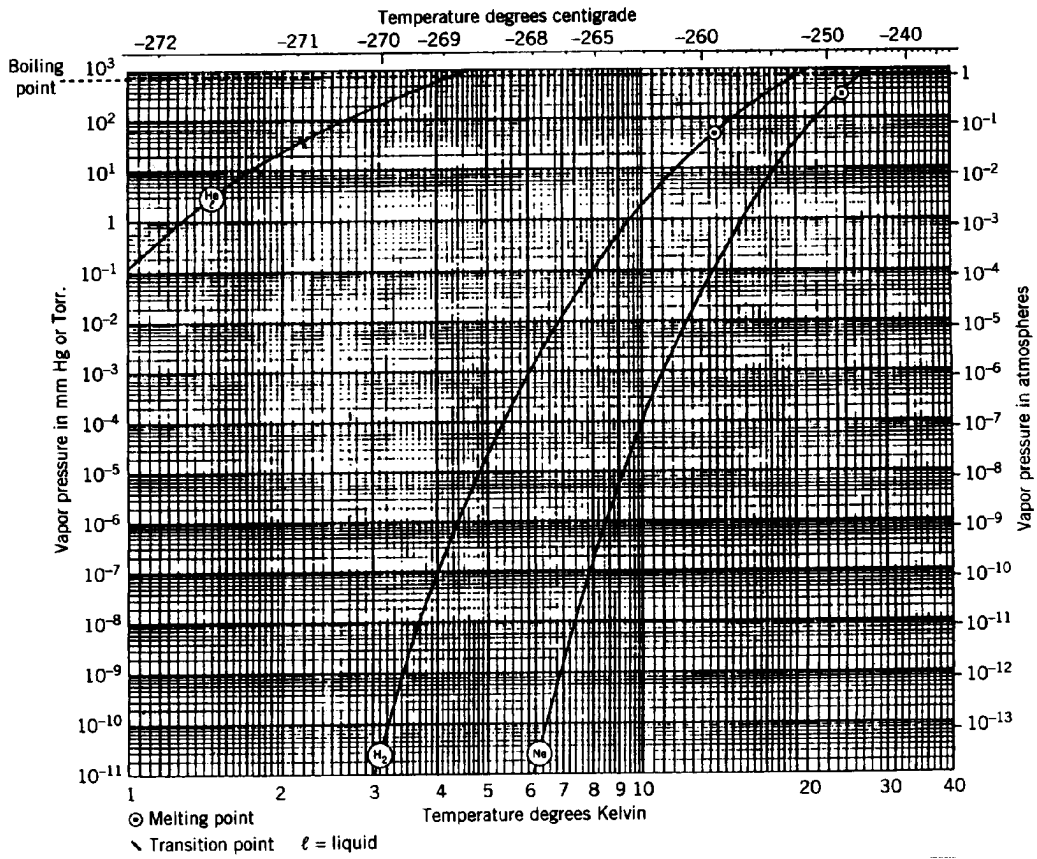
1.2 Gas condensation

When a surface is "cold enough", the sojourn time of the molecules adsorbed on the surface, as defined by the Frenkel equation

$$\tau = \tau_0 e^{\frac{E}{RT}}$$

where E is the energy of vaporisation (kcal mole^{-1}), R the 1.98×10^{-3} ($\text{kcal mole}^{-1} \text{K}^{-1}$) and T the temperature (K), may become appreciably long. The values of the *energy of vaporisation* E for the most common gases are given in Table 1 [1].

For a given gas and surface temperature, by progressively increasing the surface coverage a *saturation* equilibrium between gas adsorption and desorption is established. The corresponding gas pressure is the *saturated vapour pressure*. The saturated vapour pressure curves for the most common are given in Figs. 1 and 2 [2]. These figures indicate that most gases present a vapour pressure not higher than 10^{-11} Torr at 20 K, while the H_2 vapour pressure is in the 10^{-7} Torr range even at 4.2 K, the boiling temperature of He. Therefore indefinite heavy gas quantities may be effectively condensed on a surface kept at 20 K, while a temperature lower than 3 K for H_2 and still much lower for He would be required.



Figs. 1 and 2 Saturated vapour pressure curves for the most common gases.

Table 1
Energies of vaporisation of the common gases and energies of sublimation of common metals (kcal/mole)

Gas	He	H ₂	Ne	N ₂	CO	Ar	O ₂	CH ₄	Kr	Xe	CO ₂
Energy of vaporisation	0.020	0.215	0.431	1.333	1.444	1.558	1.630	1.995	2.158	3.021	4.041
Metal	Ba	Ag	Cu	Ni	Ti	Pt	Mo	C	Ta	W	
Energy of sublimation	42	68	81	101	113	122	155	171	180	202	

Surface pumps relying on condensation are called *condensation cryopumps*. In a vacuum system pumped by a saturated cryopump the pressure is given by $p = Q/S + p_{sat}$ where Q is the gas load, S the pumping speed and p_{sat} the saturated vapour pressure of the gas to be pumped.

1.3 Gas physisorption

For submonolayer surface coverages the gas molecules experience the attractive van der Waals forces exerted by the cold surface (*cryosorption*). These forces are larger than those existing between the gas molecules themselves (condensation). According to the Frenkel equation, cryosorption provides consequently *much lower equilibrium pressures*.

The energies of cryosorption for the most common gases on various solid substrates are given in Table 2 [3]. By comparing Tables 1 and 2, it may be seen that these energies are larger than those of vaporisation by a factor 2 to 3 for heavy gases, but 10 for H₂ and 30 for He. As a consequence, H₂ may be effectively cryosorbed at 20 K and He at 4.2 K. More generally, submonolayer quantities of *all gases may be effectively cryosorbed at their own boiling temperature* (1 bar). These temperatures are given in Table 3. It may be concluded that all gases except He, H₂, D₂ and Ne may be cryosorbed at liquid N₂ temperature. Furthermore, water vapour is adsorbed at room temperature; to remove it, heating up to above 100°C is required (*bakeout*).

Table 2
Binding energies for physical adsorption of common gases on heterogeneous surfaces at high temperatures and low coverages (kcal/mole)

Solid	Gas							
	He	H ₂	Ne	N ₂	Ar	O ₂	CH ₄	Kr
Porous glass	0.68	1.97	1.54	4.26	3.78	4.09		
Saran Charcoal	0.63	1.87	1.28	3.70	3.66		4.64	
Carbon black	0.60		1.36		4.34			
Alumina					2.80			3.46

Table 3
Boiling temperature (K) of gases at 1 bar

He ₃	3.2	O ₂	90.1
He ₄	4.2	CH ₄	111.6
H ₂	20.3	Kr	119.7
D ₂	23.6	Xe	165.0
Ne	27.1	C ₂ H ₄	169.4
N ₂	77.3	C ₂ H ₆	184.5
A	87.2		

The curve describing the equilibrium pressure evolution obtained by progressively increasing the gas coverage on a given surface maintained at a given temperature is called the *adsorption isotherm*. The pressure described by the adsorption isotherms reaches the value of the saturated vapour pressure for gas coverages of one to three monolayers. A complete review of the different types of adsorption isotherms is given in Ref. [4].

Pumps relying on physisorption are called *cryosorption pumps*. An essential feature of these pumps is the need of a large adsorbing area. Porous materials, such as activated charcoal and zeolites are commonly used. Charcoal may provide adsorbing areas of the order of 1000 m^2 per gram, and may adsorb $3 \times 10^{-6} \text{ Torr } \ell \text{ cm}^{-2}$ of He at 4.2 K before the pressure rises above 10^{-10} Torr [5].

2. CRYOGENIC CONSIDERATIONS

2.1 Surface cooling

Cryosorption pumps are usually cooled to 10–20 K by means of a closed cycle *refrigerator*. For pumps of small size (up to $5000 \text{ } \ell \text{ s}^{-1}$ pumping speed) the available cooling power is usually of the order of 10 W. For a given refrigerator, the temperature of the cryosurface depends on the thermal load (see Fig. 3). Since low temperatures are desired, the heat load to the cryosurface must be minimised (see next paragraph). To do so, the cold surface must be shielded at $\sim 80 \text{ K}$, a temperature available from the first stage of the refrigerator, which provides a much larger cooling power.

For condensation cryopumping, cooling is achieved by means of *liquid helium*, usually kept at temperatures lower than 4.2 K by reducing the pressure over the He bath. The cold surface is shielded also in this case by means of liquid nitrogen. A heat load of 0.7 W vaporises 1 ℓ of He per hour, while $\sim 45 \text{ W}$ are required to vaporise 1 ℓ of N_2 per hour.

2.2 Thermal load

A cold surface may be thermally loaded via thermal conduction, gas adsorption and thermal radiation absorption.

By properly designing the pump, the thermal conduction may be reduced to negligible values. For UHV applications also the heat of adsorption released by the pumped gas is negligible. On the contrary, the radiative losses may be very large. A surface at temperature T emits thermal (electromagnetic) radiation according to the *Stefan-Boltzmann law*

$$Q = \varepsilon \sigma AT^4$$

where Q is the radiative power (W), ε the surface emissivity ($0 \leq \varepsilon \leq 1$), A the surface area (cm^2), σ the constant $= 5.67 \times 10^{-12} \text{ (W cm}^{-2} \text{ K}^{-4}\text{)}$ and T the surface temperature (K). For $T = 300 \text{ K}$ and $\varepsilon = 1$ (*black body*), $Q = 45 \text{ mW cm}^{-2}$, a heat load which may easily reach a few watts for a surface of medium size.

Due to the fourth power dependence, the radiated power decreases quickly when reducing the temperature. At 77 K for instance the reduction factor is $(300/77)^4 = 220$. Therefore *shields at liquid N_2 temperature* are usually adopted to reduce the thermal load by radiation. The shield design must be optimised in order to minimise the radiation transmission without reducing too much the molecular conductance, i.e. the pumping speed. An example of this optimisation is given in Ref. [6]. By using a "*chevron type shield*", providing a reflectivity of 0.07, the 300 K radiation load has been reduced to below 10^{-3} of the unshielded value, while providing 0.25 of the full molecular conductance to the pumping surface.

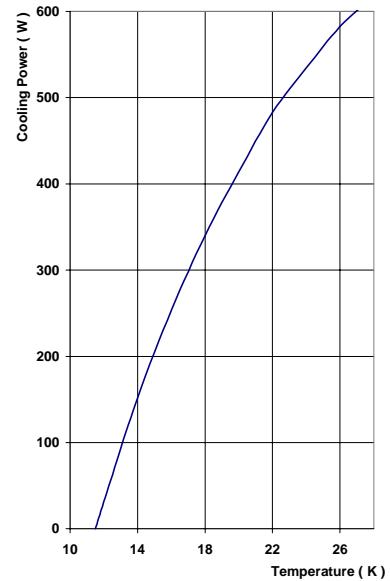


Fig. 3 Variation of the available cooling power as a function of the cold head temperature for a typical refrigerator. Since the required cooling power must be equal to the thermal load, higher values of the latter result in higher cryosurface temperatures.

Another essential precaution consists in *reducing the absorptivity of the pumping surface*. By a careful choice of the surface treatment (*Ag plating*) absorptivities of about 0.01 at 4.2 K have been obtained [7]. Adsorption of water vapour on the pumping surface must be carefully avoided because it may dramatically increase the surface absorption.

3. CRYOSORPTION PUMPS

Cooling is usually achieved by a two stage refrigerator providing about 80 K on the first stage and 10–20 K on the second. These temperatures are transmitted to the thermal shield and pumping surface by mechanical contact. A part of the cold surface is coated with a *porous material* (e.g. charcoal) to provide a large pumping capacity for H_2 (a few Torr ℓ per gram, depending on temperature and required pressure).

Loading of the adsorbent by other gases should be avoided not to spoil the pumping of H_2 . Since all heavier gases condense at 20 K, pump geometry should force the gas molecules to interact with the 20 K uncoated surfaces, where they are trapped before reaching the porous adsorbent material. The thermal contact with the refrigerator and the glue used to bind the adsorbent material usually do not allow baking. After use the gases are released at room temperature (*regeneration*).

Cryosorption pumps may be advantageously used when very *large pumping speeds* are needed (higher than $10^4 \ell s^{-1}$) and the *vacuum requirements* are *not very stringent*. An interesting application of cryosorption consists in the *initial evacuation* of atmospheric air making use of a large amount of a porous material cooled at liquid N_2 temperature.

4. CONDENSATION CRYOPUMPS

A typical condensation cryopump is shown in Fig. 4. This pump, described in Ref. [7], may provide an ultimate pressure lower than 10^{-12} Torr and pumping speeds of 9, 3, $15 \ell s^{-1} cm^{-2}$ for H_2 , $CO(N_2)$ and H_2O , respectively. The thermal losses are almost completely due to thermal radiation from the N_2 cooled shield. The (low pressure) life-time for a He fill depends on the He vessel volume, and equals 70 days for 70 ℓ of helium (heat load ≈ 30 mW).

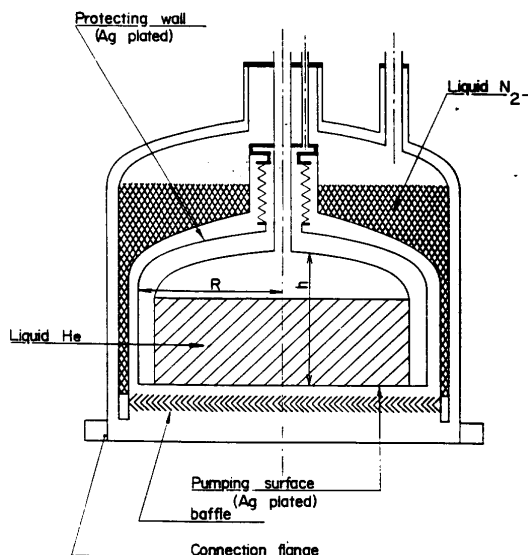


Fig. 4 First version of the CERN condensation cryopump

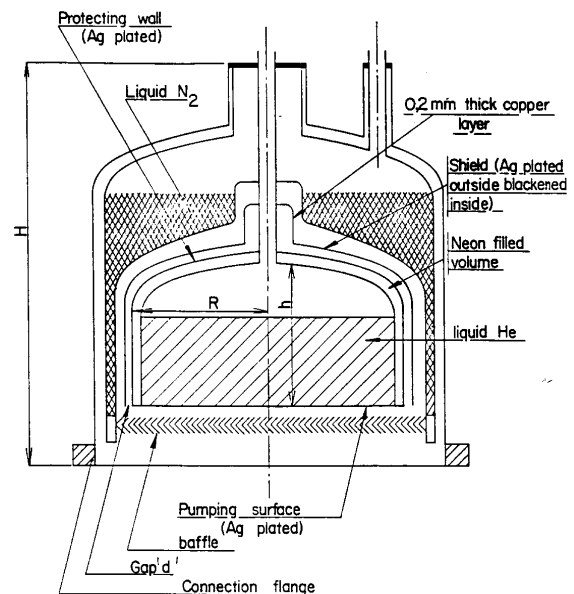


Fig. 5 Improved version of the CERN condensation cryopump

This pump model, developed at CERN for pumping the experimental regions of the ISR, has been later improved by adding a shield between the He and the N_2 vessels [8] (see Fig. 5). This shield absorbs the radiation from 77 K, which is then removed by the cold He gas escaping from the pump

neck, to which the shield is connected. The total heat load resulting in He boil-off is reduced in this way to a few mW, depending on pump size. For instance, a pump providing a speed of 4500 l s^{-1} for H_2 may be operated for 190 days with 12 l of liquid He.

The scaling laws defining how pumping speed, He boil-off rate, intermediate shield temperature and operating life-time vary when changing pump dimensions are given in Ref. [8].

5. THE HYDROGEN "ANOMALY"

Extrapolation from higher temperature data indicates that a saturated vapour pressure of the order of 10^{-13} Torr could be obtained for H_2 at 2.5 K. Therefore condensation cryopumping seems a reasonable choice to pump very large quantities of H_2 at low pressure.

However, measurements carried out in different laboratories [9] [10] revealed the existence of an unforeseen desorption mechanism resulting in a *temperature independent H_2 equilibrium pressure* in the $10^{-10} - 10^{-11}$ Torr range, depending on the experimental conditions. This "anomalous" pressure was found to be caused by thermal radiation from higher temperature surfaces (particularly those at 300 K). In a first attempt to justify this effect, it has been suggested [9] that thermal radiation absorbed by the condensed H_2 could produce a localised heating ("thermal spikes") resulting in enhanced H_2 desorption. However, more refined measurements [11] provided strong evidence against this hypothesis by showing that the H_2 desorption

- decreases when increasing the thickness of the condensed layer (Fig. 6)
- is proportional to the radiating power absorbed on the substrate, and not to that impinging on it (Fig. 7).

The emerging picture favours a rather indirect desorption mechanism, according to which photons absorbed on the H_2 condensing substrate produce phonons energetic enough to cause desorption when reaching the surface of the H_2 film. Further evidence in favour of this mechanism has been obtained by condensing a few monolayers of a heavier gas (N_2 , Ne, Ar...) prior to H_2 . Having a lower Debye temperature, these gases do not transmit the energetic phonons responsible of first order H_2 desorption, which is consequently strongly reduced. This model was later confirmed by other laboratories [12] [13], although a more direct desorption process seems to take place in some specific cases [14].

The main practical conclusion to be derived from these considerations is that a very careful 77 K shielding is necessary to reduce the condensed H_2 equilibrium pressure to below 10^{-12} Torr.

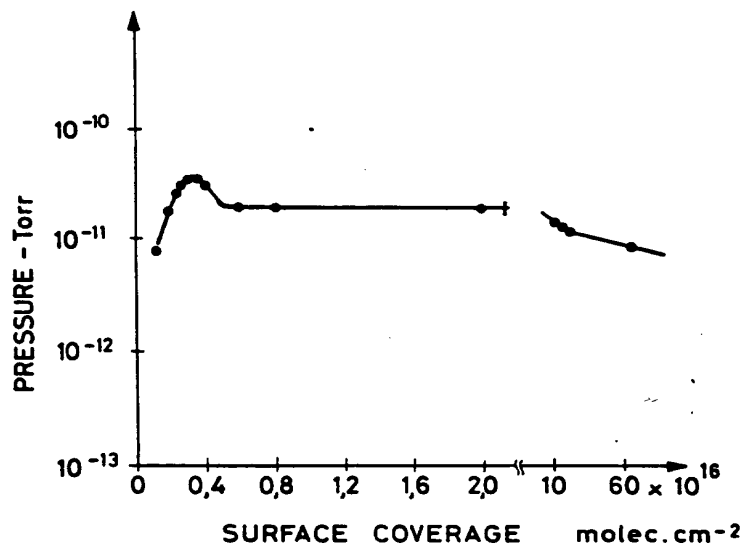


Fig. 6 Typical H_2 adsorption isotherm at 2.3 K showing a radiation induced desorption maximum corresponding to a coverage of one monolayer.

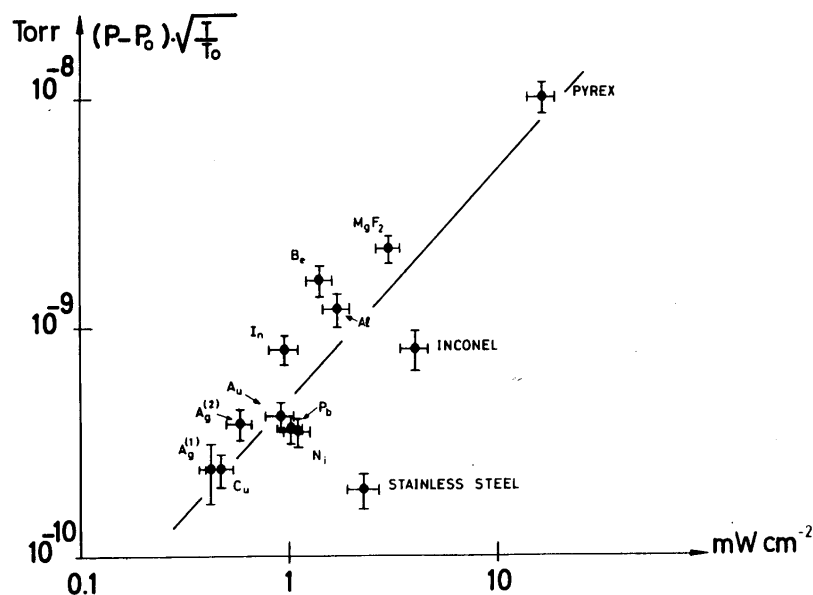


Fig. 7 Variation of the radiation induced H_2 desorption from various substrates at 2.3 K and fully exposed to 300 K radiation as a function of the radiating power absorbed.

REFERENCES

- [1] P.A. Redhead, J.P. Hobson and E.V. Kornelsen, *The Physical Basis of Ultrahigh Vacuum* (American Institute of Physics, New York, 1993), p. 25.
- [2] J.M. Lafferty, *Foundations of Vacuum Science and Technology*, (John Wiley & Sons, Inc, New York, 1998) p. 709-710.
- [3] P.A. Redhead, J.P. Hobson and E.V. Kornelsen, *The Physical Basis of Ultrahigh Vacuum* (American Institute of Physics, New York, 1993), p. 26.
- [4] D.M. Young and A.D. Crowell, *Physical adsorption of Gases*, (Butterworths, London, 1962) p. 3.
- [5] J.P. Hobson, *J. Vac. Sci. Technol.* **10**, 1 (1973) 73.
- [6] C. Benvenuti, D. Bleschschmidt and G. Passardi, *J. Vac. Sci. Technol.* **19**, 1 (1981) 100.
- [7] C. Benvenuti, *J. Vac. Sci. Technol.* **11**, 3 (1974) 591.
- [8] C. Benvenuti and M. Firth, *Vacuum*, **29**, 11-12 (1979) 427.
- [9] J.N. Chubb, L. Gowland and J. Pollard, *Br. J. Appl. Phys. Ser 21* (1968) 361.
- [10] C. Benvenuti and R.S. Calder, *Phys. Lett. A* **35** (1971) 291.
- [11] C. Benvenuti, R.S. Calder and G. Passardi, *J. Vac. Sci. Technol.* **13**, 6 (1976) 1172.
- [12] P.M. Ferm, S.R. Kurtz, K.A. Pearlstine and G.M. McClelland, *Phys. Rev. Lett.*, **58**, 24 (1987) 2602.
- [13] J. Cui, S.C. Fain Jr. and W. Liu, *J. Vac. Sci. Technol. A* **7**, 3 (1989) 1850.
- [14] M. Hassel, K. Svensson, M. Persson and S. Andersson, *Phys. Rev. Lett.* **80**, 11 (1996) 2481.

