

Hydrogen in Vacuum Systems; an Overview

P.A.Redhead

National Research Council, Ottawa, ON K1A 0R6, Canada

Abstract. Hydrogen is the predominant residual gas in metal vacuum systems at very low pressures (i.e. in the ultrahigh [uhv] and extreme high vacuum [xhv] ranges) and the reduction in the hydrogen outgassing rate is the most challenging problem in achieving xhv. Our understanding of the diffusion and adsorption/desorption processes involved in the outgassing of hydrogen from metals has much improved in recent years and has led to better methods for reducing the outgassing rates of hydrogen from metals such as stainless steel and aluminum alloys. This overview examines some recent advances in our understanding of the effects of hydrogen in vacuum systems; these include a) the adsorption/desorption/diffusion equilibrium at the vacuum-metal interface, b) the effects of multiple energy states of H atoms in the bulk metal, c) the physical adsorption of hydrogen on surfaces at cryogenic temperatures and d) the anomalous effects in pressure measurements of hydrogen with ionization gauges and residual gas analyzers.

INTRODUCTION

When a vacuum system with metal walls has been pumped to its ultimate vacuum the predominant residual gas is hydrogen outgassing from the vacuum envelope and the internal parts of the system (particularly if the parts are heated, such as thermionic emitters and neighboring electrodes). The reduction of the hydrogen outgassing rate is the most challenging problem in achieving ultimate pressures in the extreme high vacuum (xhv) range (pressures below 10^{-10} Pa), particularly in large systems such as accelerators and storage rings. At higher pressures the predominant gas is usually water resulting from the exposure of the system to humid air

Reduction in hydrogen outgassing can be achieved in metal systems by a) minimizing the hydrogen content of the vacuum envelope and the internal components by heat treatment in vacuum, or b) modifying the surface of the vacuum envelope by oxidation or the deposition of thin films (e.g. TiN) to act as a barrier to hydrogen diffusion. The choice of the most appropriate method requires a detailed

understanding of the kinetics of hydrogen diffusion and adsorption/desorption in the metal chosen for the vacuum envelope.

A decade or more ago our understanding of the behaviour of hydrogen in or on the metals used for vacuum envelopes (stainless steel, aluminum, aluminum alloys, and copper) was limited. In the last decade there have been considerable efforts to improve our understanding of the behaviour of hydrogen in metal vacuum systems as lower ultimate pressures have been required in several applications; this paper reviews some of the most important of these improvements in our understanding.

DIFFUSION, ADSORPTION, AND DESORPTION

In 1967 Calder and Lewin published a seminal paper on the reduction of outgassing of hydrogen from metals¹ which assumed that a) there was only one energy state of the diffusing hydrogen atoms and b) the rate-limiting step in the release of hydrogen molecules from the surface was the diffusion step. The assumptions of this paper was the basis of many subsequent papers on outgassing. This model (the diffusion limited model DLM) assumed that the atomic hydrogen concentration at the surface is zero and the hydrogen atoms recombine and desorb as molecules as soon as the hydrogen atoms reach the surface. The DLM predicted higher outgassing rates reasonably well but it failed at lower rates by orders of magnitude. Malev² published a widely cited paper on the theory of outgassing in 1973 which included both diffusion and adsorption/desorption but also assumed only one energy state of the diffusing hydrogen atoms.

More than 60 years ago Barrer³ indicated that the diffusing hydrogen atoms must recombine at the surface in order to desorb as a molecule, and the recombination rate must depend on the square of the surface coverage of H atoms. This requirement is not contained in the DLM. In 1989 Shipilevsky and Glebovsky⁴ used the model shown in figure 1 to calculate the effects of bulk and surface processes on hydrogen evolution from metals into vacuum; here K^0 is the rate constant of hydrogen desorption and v^s and v^0 are the rate constants for the transition of H atoms from the subsurface layer to the surface and vice versa. They showed theoretically that for each metal there exists a characteristic critical number of dissolved monolayers (i.e. the quantity of dissolved hydrogen in the bulk metal) above which the kinetics of desorption are controlled preferentially by the diffusion rate and below which by the recombination rate. Thus the recombination limited model (RLM) is to be preferred for the calculation of outgassing from metal vacuum systems with low dissolved hydrogen concentrations. The RLM was used in a paper by Moore in 1995⁵ to calculate the reduction of hydrogen outgassing by different baking schedules.

The kinetics of hydrogen on metal surfaces has been reviewed by several authors^{6,7}. Figure 2 shows a one-dimensional potential energy diagram of hydrogen atoms and molecules near a metal surface. The coverage of atomic hydrogen is controlled by the four hydrogen fluxes; 1) the flux of H molecules from the gas

phase that dissociate and adsorb as atoms is $f_1 = 2pvs(\theta)$ where p is the gas pressure, v is the rate of arrival of hydrogen molecules per unit area and per unit pressure, $s(\theta)$ is the sticking probability (a function of θ), if the adsorption is Langmuirian then $f_1 = 2pvs_0(1-\theta)^2$ where s_0 is the sticking probability at zero coverage, 2) the desorbed flux of hydrogen molecules is $f_2 = -K\theta^2$, 3) the flux of H atoms into the bulk is $f_3 = -\alpha\theta(1-x)$ where α is the jump frequency and x the atomic fraction of H atoms in the bulk, 4) the flux of H atoms from the bulk to the adsorbed state is $f_4 = \beta(1-\theta)x$, where β is the jump frequency. Some general solutions of these coupled non-linear equations have been found⁸.

The case of interest to the condition of metal surfaces in vacuum systems at low pressures is when the jump rates from surface to bulk and vice versa (i.e. α and β) are both orders of magnitude greater than the arrival rate from the gas f_1 . Then the bulk and surface come to equilibrium long before the gas comes to equilibrium with the surface, i.e. the surface saturates and slows the equilibration process. The outgassing rate of molecules f_2 , which includes the recombination rate, then becomes the rate limiting step in the desorption process. When two H atoms combine and leave the surface the vacated sites are immediately occupied by H atoms from the bulk before any gas molecules can be adsorbed. In effect the surface behaves as if the sticking probability were zero and the outgassing rate is constant and controlled by the recombination rate.

There is now considerable experimental evidence that the situation outlined above obtains on surfaces of stainless steel, aluminum and its alloys and some copper alloys at low pressures. The gas accumulation method is now widely used to measure low hydrogen outgassing rates. The test system is pumped to its ultimate pressure and the valve to the pump is then closed, the increase in pressure is then measured as a function of time, preferably by a non-pumping gauge (e.g. a spinning rotor gauge). In most cases the hydrogen pressure in stainless steel systems is observed to increase linearly with time for as long as several years^{9, 10, 11, 12}. This indicates that the outgassing rate for hydrogen is constant, independent of pressure, and the effective sticking probability is zero. Fig. 3 shows the linear pressure rise measured by a spinning rotor gauge observed by Jousten with a type 316LN stainless steel chamber. Fig. 4 shows the hydrogen pressure increase in isolated systems of pure copper, type 304 stainless steel, and CrCu alloy measured by Watanabe¹³. In both figures the pressure rise for stainless steel is linear with time as is the case for the CrCu alloy; the curve for pure copper however is non-linear suggesting that the sticking probability is not zero. Some pressure rise measurement by Fremery on stainless steel have continued to be linear over a period of three years, rising from 10^{-5} to 10^{-1} Pa.

As a further test that the effective sticking probability was indeed zero Fremery¹⁴ injected a burst of hydrogen into a stainless steel system while a pressure rise measurement was in progress as shown in fig. 5. The pressure vs. time in two connected chambers (P_1 and P_2) is shown. At 15 minutes a burst of hydrogen was admitted to chamber 1 by opening a valve for 15 seconds to a hydrogen source; at

50 minutes the valve between chamber 1 and 2 was opened for 15 seconds. After both of the two gas expansions the pressures remain constant, showing no signs of pumping action, thus indicating zero sticking probability in both chambers. In effect, the injected bursts of hydrogen behaved as one would expect a rare gas to behave at room temperature.

MULTIPLE DIFFUSION STATES

All the existing models of hydrogen outgassing, both DLM and RLM, have assumed that the H atoms diffusing in the bulk metal exist in only one energy state with a single activation energy. There is considerable experimental evidence, mostly from temperature programmed desorption (TPD), that this is not the case and that there are multiple diffusion states for H atoms in most metals. In hydrogen outgassing under isothermal conditions only the occupied diffusion state with the lowest energy will be significantly involved, so the single state theories are still applicable. However, when calculating the effects of vacuum firing the metal sample at high temperatures in order to reduce the outgassing at room temperature, H atom transfer amongst the multiple diffusion states must be considered.

Several experimenters have studied the evolution of hydrogen from stainless steels by thermal desorption spectroscopy^{15, 16, 17, 18}, in all cases more than one peak was observed in the spectra. The thermal desorption spectra of hydrogen from several samples of type 304 stainless steel observed by Mizuno¹⁶ et al. can be resolved into four peaks at 235, 265, 320 and 390°C. The heating rate β was varied to determine the activation energies for hydrogen release. The activation energies corresponding to the four peaks are 73, 87, 96, and 180 kJ/mol. The state at 73 kJ/mol is identified as hydrogen at grain boundaries and the three other states as associated with CrC precipitates.

Bacher et al.¹⁸ have measured the TDS of H₂ from seven types of stainless steel with differing surface treatments. For example, figure 6 shows the influence of baking in air at 450°C on the hydrogen desorption spectra of 316LN stainless steel. A common peak at 480°C is observed in all spectra with a binding energy of 57 kJ/mol which is identified as diffusible interstitial hydrogen. Other peaks observed were identified as associated with FeO and CrO reduction (350°C), trapping by defects at precipitates (500-600°C), hydrogen blocked by an oxide layer (600-800°C), and the result of recrystallization of the metal (>800°C). Rezaie-Serej and Outlaw used #347 and 304 stainless steel and observed three peaks, the main peak was at 425°C with a binding energy of 59 kJ/mol. The TPD spectra of hydrogen from #316 LS stainless steel have been measured by Hirohata¹⁹ et al., two main desorption peaks were observed at about 650 and 800°C with activation energies of 65 and 97 kJ/mol.

The permeation of hydrogen and its isotopes through stainless steel membranes has been measured by Tison²⁰ who found the activation energy was 53 kJ/mol. Ishikawa et al.²¹ found the activation energy to be 56 kJ/mol for the unoxidized

surface and 47 to 65 kJ/mol for the oxidized surface depending on the degree of oxidation.

Hirohata et al.²² have studied the TDS of H₂ from aluminum and observed two peaks with binding energies of 21 and 50 kJ/mol.

The existence of more than one binding state of the diffusing H atoms may explain the observations of an increased outgassing rate after bake-out of the system at higher temperatures. This surprising effect has been observed by at least three experimenters^{23, 24, 13}.

Figure 7 shows Jousten's²³ results where baking of a # 316LN stainless steel chamber at temperatures above 100 °C resulted in an increase in the outgassing rate at room temperature. Similar results were obtained by Fremery²² who found after a 100°C bake an outgassing rate of 1.7×10^{-14} mbar l s⁻¹ cm⁻² which increased to 8×10^{-14} after baking at 250°C.

Watanabe¹³ found the same sort of behaviour with vacuum cast copper, after baking at 100°C the outgassing rate was 8.8×10^{-12} Pa m s⁻¹, after baking at 250°C the rate increased to 1.8×10^{-11} Pa m s⁻¹. Watanabe explains these results on copper by assuming that the CuCO₃Cu(OH)₂ layer, formed after exposure to air, is reduced to CuO by baking at 100°C which tends to block the evolution of H atoms from the bulk. After baking at 250°C the CuO is reduced by H atoms from the bulk and the outgassing rate increases.

Nemanič and his collaborators²⁵ have heated #304 stainless steel samples from 300 to 1000°C and measured the amount of hydrogen evolved after each heating cycle. For temperatures well below 800°C the desorption rate decreased without approaching a limit, typically at about 400°C a desorption rate of 10^{12} molecules H₂ cm⁻² s⁻¹ was achieved in a relatively short time for all samples. For temperatures above 800°C a great amount of hydrogen evolved from the samples for a prolonged time. The amount of hydrogen evolved was as high as 9×10^{19} atoms H cm⁻³, much greater than the published values for solubility. The mechanism proposed for the high temperature behaviour is that strongly bound hydrogen is partially evolved and the rest is redistributed to different binding states of H in the bulk. Thus baking at increased temperatures may result in a redistribution of H atoms from the tightly bound sites into the more weakly bound sites which causes an increase in outgassing rates at room temperature. This proposal is speculative and requires further experimental confirmation but at least it may explain the weakness of existing theoretical models which ignore the existence of more than one binding state of the H atoms in the bulk.

PHYSICAL ADSORPTION OF HYDROGEN

The walls of many vacuum chambers are held at cryogenic temperatures, particularly in accelerators and storage rings with super-conducting magnets. To be able to calculate the behaviour of hydrogen, the main residual gas, in such systems

it is necessary to know the adsorption isotherm for hydrogen at cryogenic temperatures on the material used for the vacuum envelope.

Hobson²⁶ has calculated the hydrogen isotherm from the Dubinin-Radushkevich (DR) equation²⁷

$$\ln \Theta = -B \left[RT \ln \left(\frac{P}{P_0} \right) \right]^2$$

where Θ is the relative coverage, P the equilibrium pressure above the adsorbed layer at temperature T , P_0 the vapor pressure of the adsorbate at temperature T , and B is a constant independent of the adsorbent. Figure 8 shows the calculated isotherms for hydrogen on a heterogeneous surface at 3.0, 4.2, 6.0, and 10 K. The DR isotherm has been shown²⁸ to give a good fit to the adsorption isotherms of Ar, Kr, and Xe on porous silver at 77.4 K over a range of six decades of coverage.

Moulard et al.²⁹ have measured the adsorption isotherms of hydrogen adsorbed at 4.2 K on anodized Al, electroplated copper, and sputtered TiZrV (a non-evaporable getter) coating. Figure 9 shows the adsorption isotherm of hydrogen at 4.2 K on the materials indicated. The increase in capacity with the anodized Al surfaces by a factor of less than 50 compared with the smooth stainless steel surfaces is evident. Pressures were measured with a Bayard-Alpert gauge, the low pressure limit of the gauge (about 10^{-9} torr H_2) is evident in fig. 9. Rao and his colleagues³⁰ have also measured the hydrogen adsorption isotherm at 4.3 K on stainless steel, aluminum, and anodized aluminum, a very large increase in capacity (10^3) was observed for the anodized Al surfaces compared with the smooth stainless steel surface. The large adsorption capacity of the anodized Al surfaces is important for the construction of cryopumps. The reasons for the differences in capacity of the porous Al samples observed by the two experimenters has not been resolved.

Wallén³¹ has also measured the hydrogen adsorption isotherm at 4.2K on Pyrex glass, stainless steel and copper plated stainless steel, all have a similar shape and there is a sharp pressure rise at 1.3 to 1.8×10^{15} H_2 molecules cm^{-2} .

These adsorption isotherm data permit an estimate of the behaviour of hydrogen at very low pressures in cryogenic systems. However, some of the experimental hydrogen isotherms are not a good fit to the DR equation. The measurement of hydrogen pressures in the uhv and xhv ranges is particularly difficult because of errors due to electron stimulated desorption (ESD) in ionization gauges and residual gas analyzers and to the chemical activity of atomic hydrogen produced by hot filaments and ESD³² (these problems are discussed in the next section). The difference between the experimental H_2 isotherms and the DR theory at low pressures may result from an over-estimation of the pressure resulting from hydrogen interactions in the hot-filament ionization gauges. Further work is required to determine the cause of the discrepancy between theory and experiment.

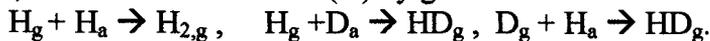
THE MEASUREMENT OF HYDROGEN PRESSURES IN THE UHV AND XHV RANGES

The major problem in measuring hydrogen pressures in the uhv and xhv ranges with ionization gauges and residual gas analyzers (RGA) is caused by electron stimulated desorption (ESD) of hydrogen ions and neutrals from the layer of adsorbed hydrogen on the grid of the ionization gauge or the ion-source of the RGA. The problems caused by ESD ions in pressure measurement have been recognized since the 1960s and special ionization gauge and RGA designs have been developed which permit the separation of the ESD ions from the gas phase ions³³; the separation of ESD from gas phase ions is based on the difference in initial kinetic energy of the two groups of ions. However, it was not until relatively recently that the importance of the very significant errors in pressure measurement resulting from the ESD *neutrals* were appreciated³⁴.

The release of neutral hydrogen by ESD constitutes an outgassing source which is caused by the operation of the gauge or RGA and can cause large errors in pressure measurement in the uhv and xhv ranges where the residual gas is mainly hydrogen. Watanabe³⁵ has made measurements on an ionization gauge of the extractor design where the grid could be resistively heated and has shown that heating the grid to about 500°C resulted in a reduction of the ion-collector current by a factor of about 10 (see figure 10). This reduction in indicated pressure is caused by the reduction of the flux of ESD neutrals from the heated grid. Watanabe has also studied the ESD of neutrals of several adsorbed species³⁶, including hydrogen, on the grid of an RGA and found that, by first cleaning the grid by heating at 900°C and then heating the grid to 500°C, the spurious ESD peak of H decreased by over three orders of magnitude and the mass spectrum becomes mainly H₂ molecules, reflecting the true hydrogen pressure. By these means the relative error in hydrogen pressure measurement decreased from 614% to 8%. The ratio of ESD neutrals to ions was about 2 for hydrogen.

With the use of heated grid ionization gauges or RGAs it is now possible to minimize the errors in uhv/xhv pressure measurements of hydrogen resulting from the ESD of neutrals and ions from the grid. The thermal outgassing from the heated grid must be minimized by using a material of low hydrogen solubility and by intensive heat treatment.

One further set of problems in the measurement of hydrogen pressures results from the use of hot filaments in ionization gauges and RGAs. Atomic H is evolved by the dissociation of H₂ at a hot metal surface, the atomic H can interact with adsorbed species on the cold surfaces of a vacuum system to produce a variety of gaseous contaminants such as CO, H₂O, C_xH_y. The other important reaction of H atoms with adsorbed gas layers³⁷, which is particularly significant in fusion reactors, is the abstraction of H(D) by gaseous H



The abstraction reaction probabilities from metal surfaces have recently been calculated³⁸ as 0.742 (D on D), > 0.64 (H on D), > 0.533 (D on H).

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge valuable discussions with J.P.Hobson.

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Figure Captions

1. Schematic diagram of the elementary processes involved in the desorption of hydrogen from a metal (from ref. 4).
2. Potential energy diagram for atomic and molecular hydrogen near the surface of a metal. The fluxes of hydrogen atoms at the adsorbed layer are explained in the text.
3. Hydrogen pressure vs. time for an isolated stainless steel chamber measured with a spinning rotor gauge.
4. Hydrogen pressure vs. time curves for isolated chambers of pure copper, type 304 stainless steel, and CrCu alloy.
5. Pressure changes in two interconnected chambers after the introduction of a 15 second burst of hydrogen.
6. Thermal desorption spectra of H_2 desorbed from # 316LN stainless steel samples after baking in air at $450^\circ C$.
7. Outgassing rate of #316LN stainless steel, vacuum fired at $1000^\circ C$ for several hours, as a function of the subsequent bakeout temperature. The numbers indicate the order of the measurements.
8. Calculated adsorption isotherm of hydrogen on a heterogeneous surface at 3.0, 4.2, 6.0, and 10 K (adapted from ref. 26)
9. Hydrogen adsorption isotherms at 4.2K on aluminum, stainless steel, TiZrV, and Cu-plated stainless steel and copper-plated stainless steel.
10. The ion-collector current in a hot grid gauge (HGG) vs. the reciprocal of the grid temperature. The crosses indicate the pressure burst intensities after a 20 minute interruption in the electron current.

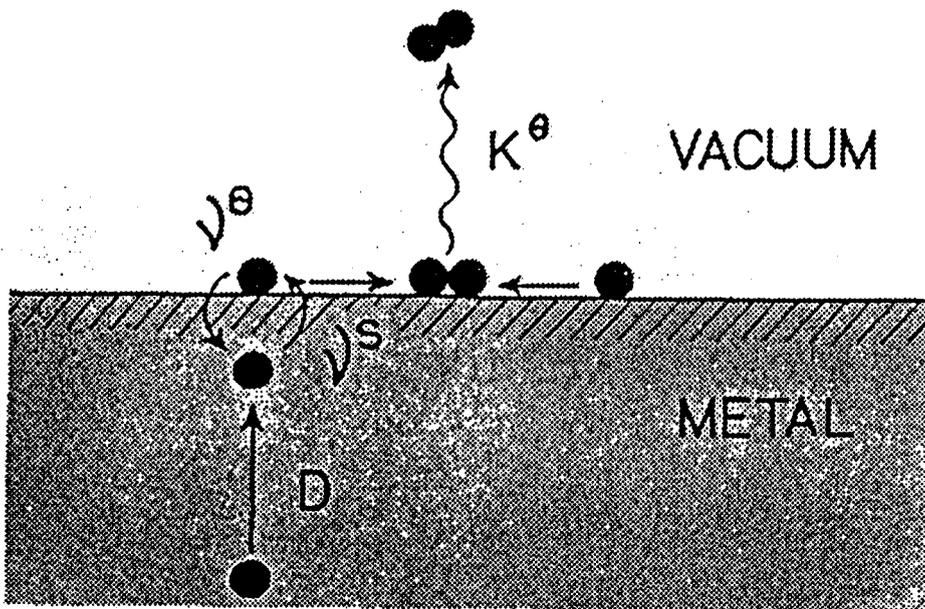
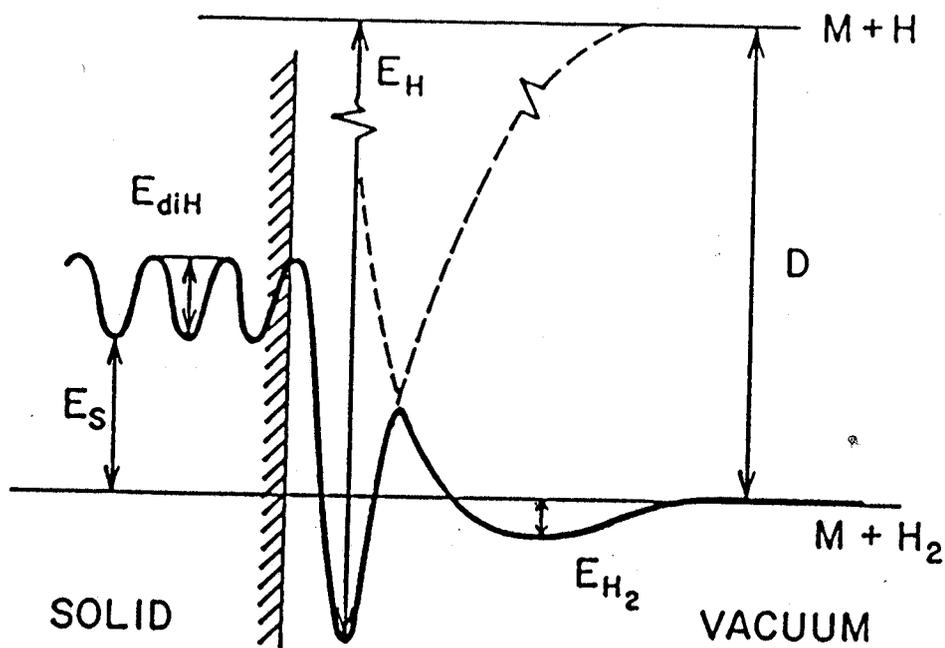


FIG. 1



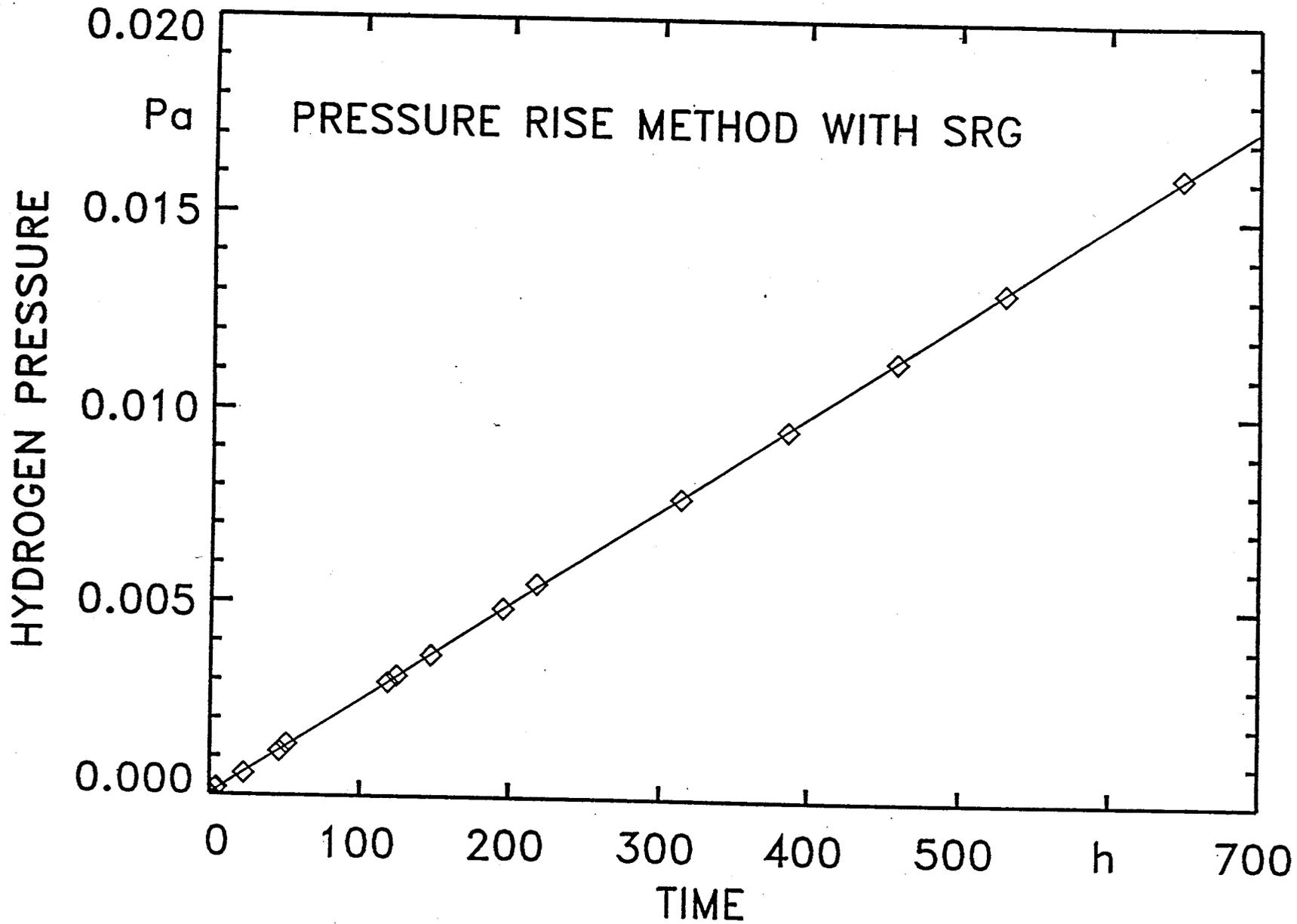
$$f_3 = -\alpha\theta(1-x) \leftarrow$$

$$\leftarrow f_1 = 2pvs(\theta)$$

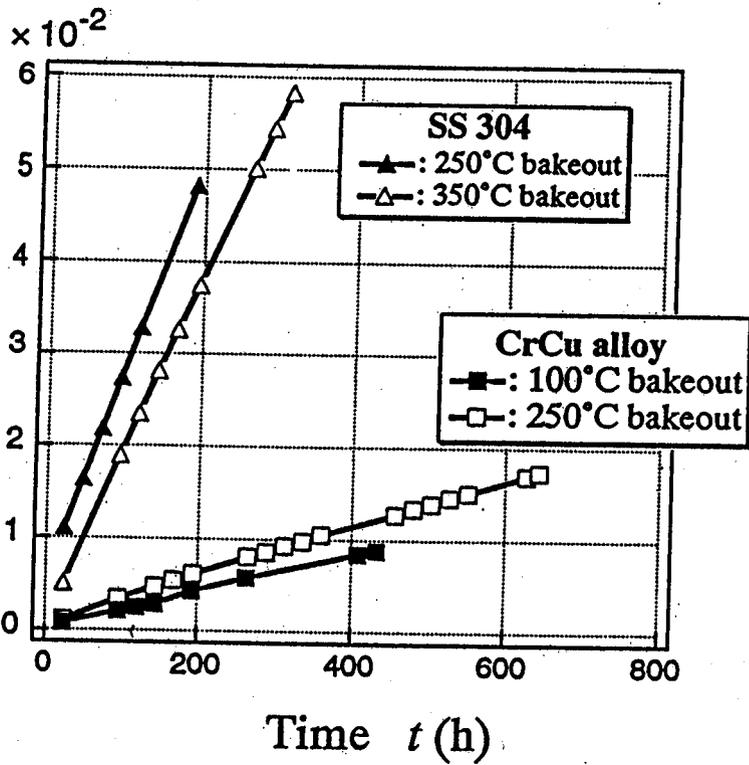
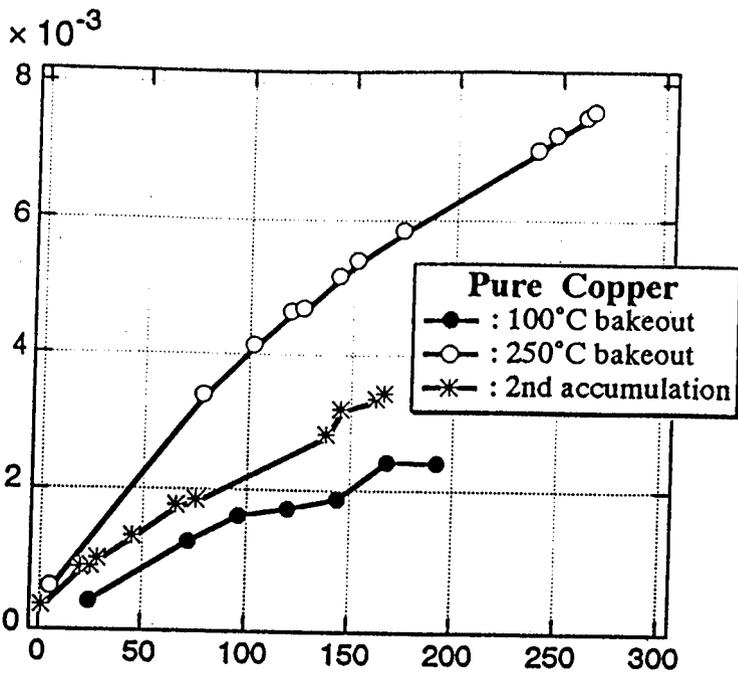
$$f_4 = \beta(1-\theta)x \rightarrow$$

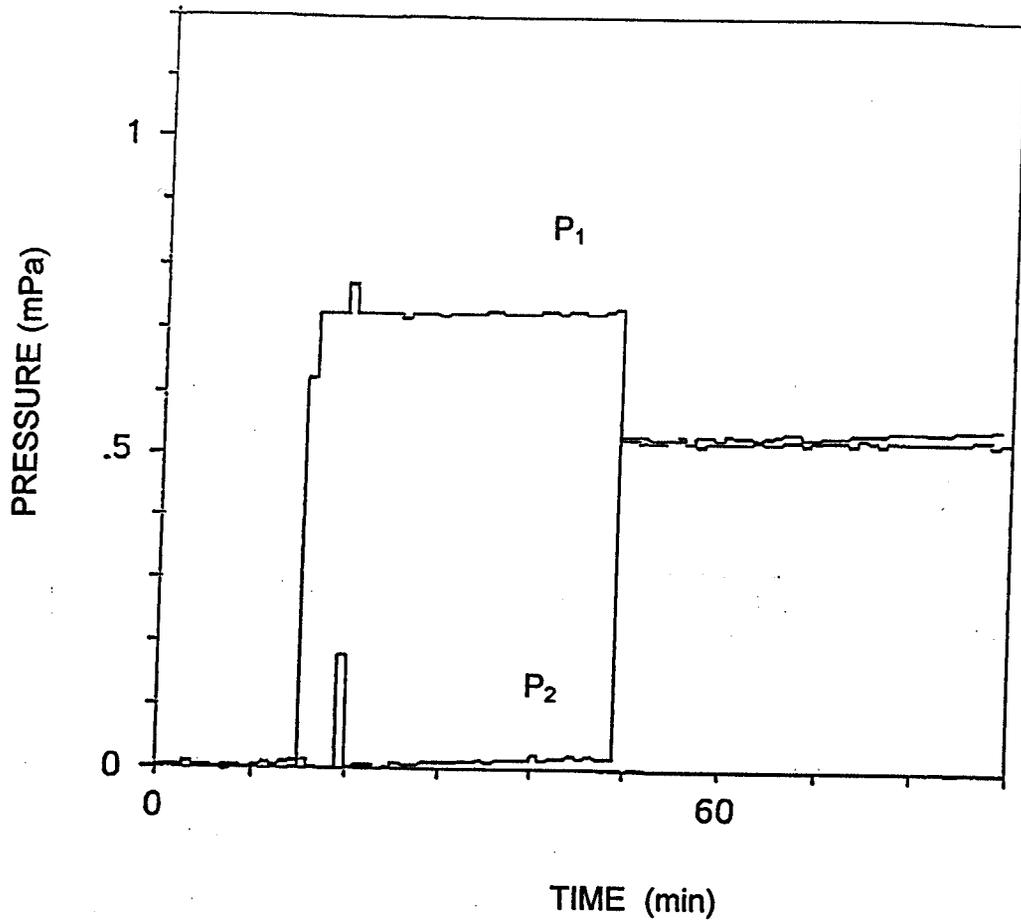
$$\rightarrow f_2 = -K\theta^2$$

FIG. 2



Hydrogen Pressure P (Pa)





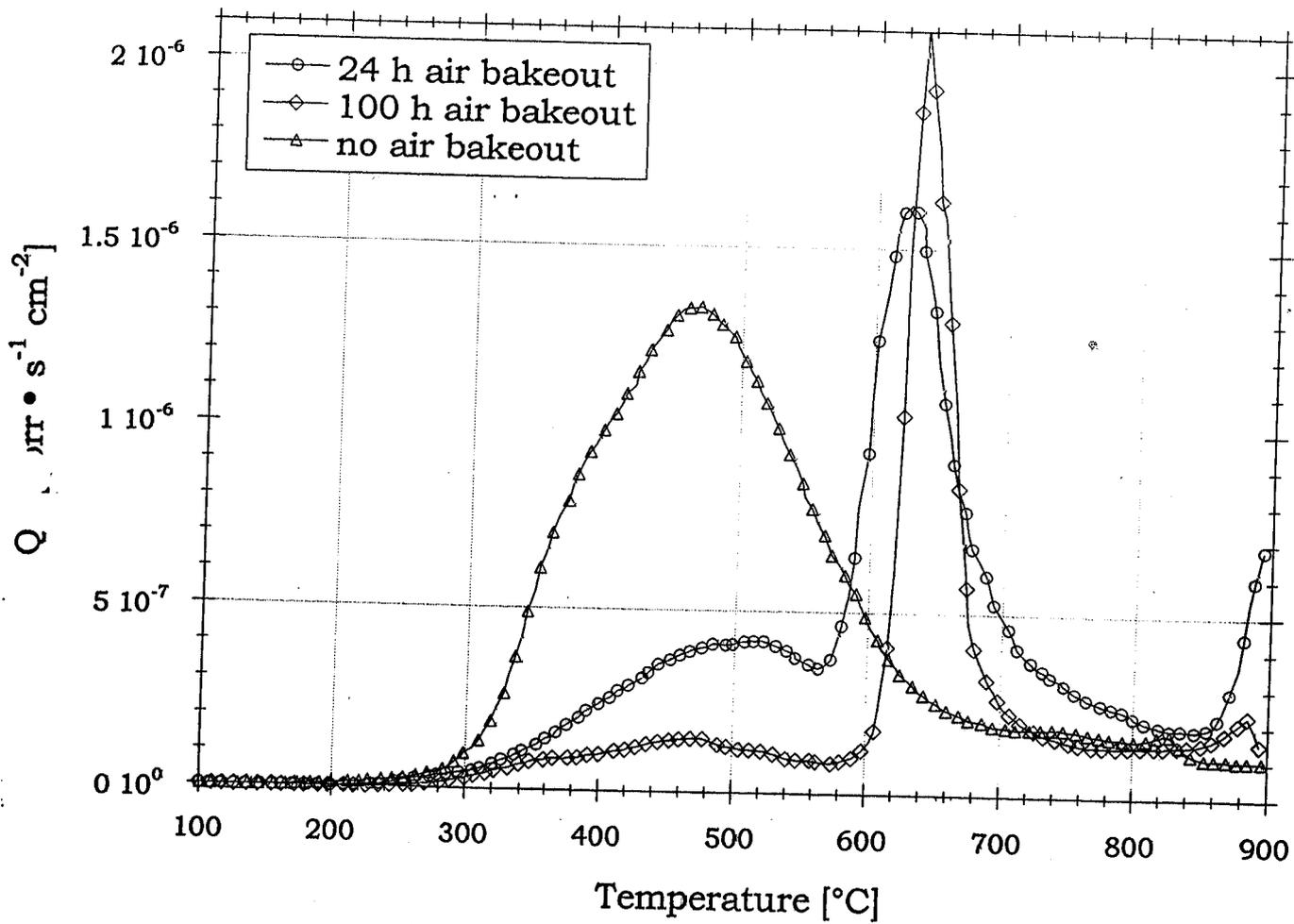


Fig. 6

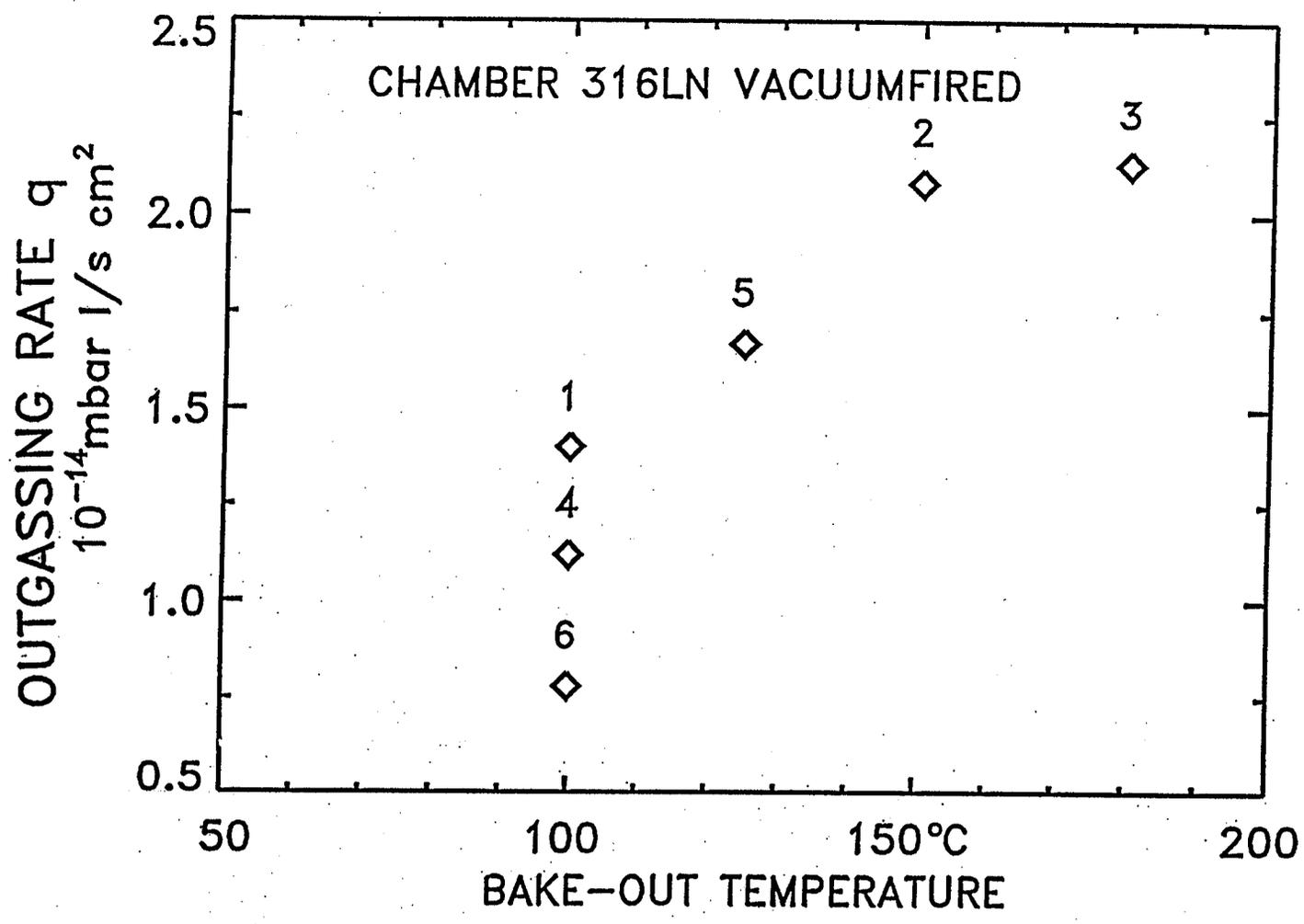


FIG. 7

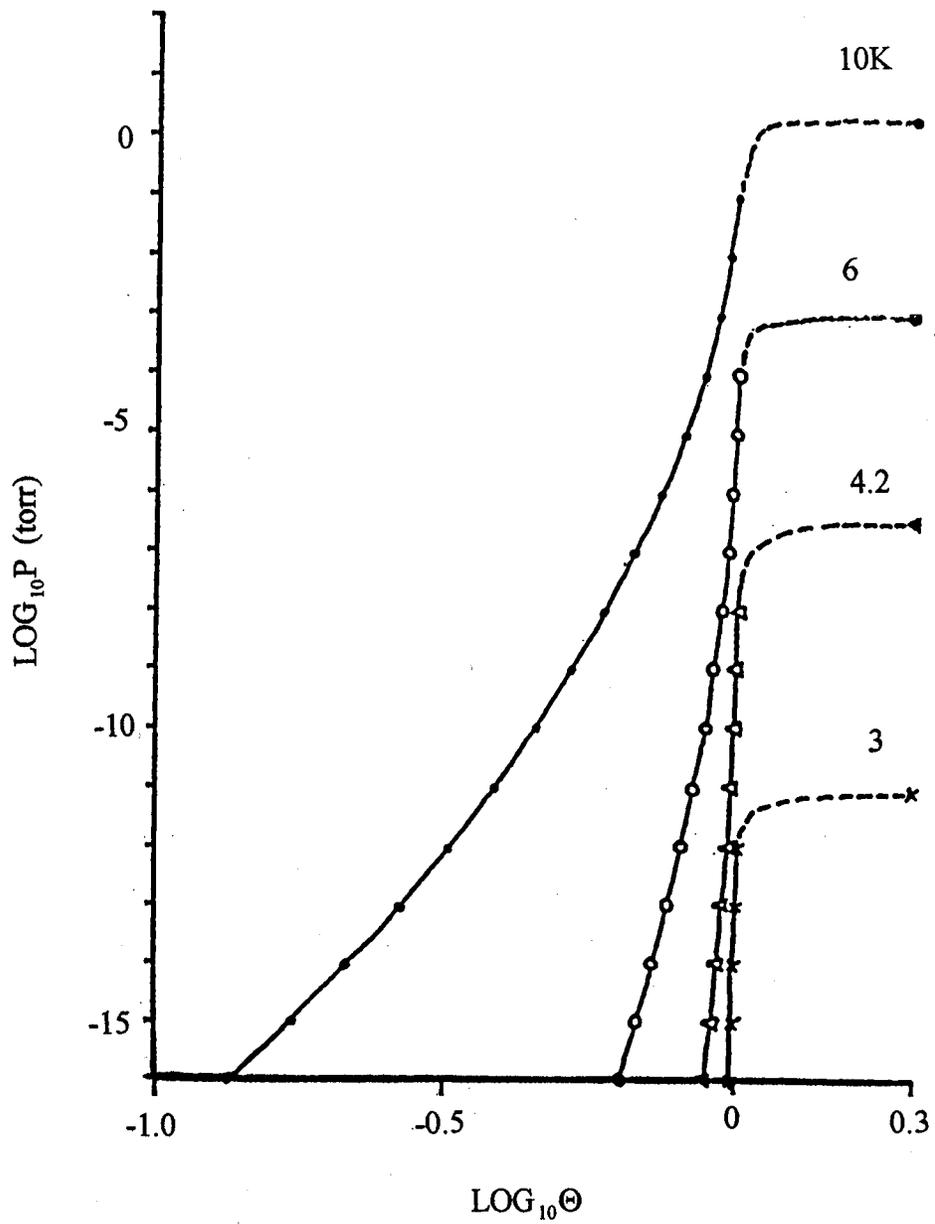


FIG 8

