

Physical Adsorption of Gases on Pyrex Glass Evidence for Superactivity

J. R. H ROSS AND M. W. ROBERTS

*From the Department of Chemistry, The Queen's University of Belfast,
Northern Ireland*

Received January 20, 1965

Pyrex glass has been shown to be capable of developing during use a superactivity for the physical adsorption of the gases Xe, Kr, N₂, and O₂ at -195°C. This superactivity has been analyzed by applying the BET equation to the adsorption isotherms of krypton and xenon and has been shown to be comparable to the activity of some metal films in physical adsorption. The possible reason for and the significance of this superactivity in both adsorption measurements and the determination of the cross-sectional areas of adsorbed molecules are discussed briefly.

The surface coverage of oxygen on Pyrex glass at 10⁻³ mm pressure and -195°C was about 10% of the xenon monolayer; this is in good agreement with Hobson's nitrogen data. The superactive glass was about 15 times more active under the same conditions.

INTRODUCTION

The use of the physical adsorption of krypton and xenon for determining the surface area of metal films has been discussed recently in detail (1-5). In this connection the assignment of values to σ_{Kr} and σ_{Xe} , the cross-sectional areas of adsorbed krypton and xenon molecules, is important and the usual procedure has been to assume the generally accepted value of 19.5 Å² for σ_{Kr} and to determine σ_{Xe} by comparing the number of molecules in the monolayer, V_m , for a given surface with the two gases. The surfaces used have ranged from evaporated metal films to glass (6). Field-emission data (7, 8) suggest that cross-sectional areas estimated in this way have little significance since it is the topographical nature of the surface which determines the adsorption and so one might expect an equal number of molecules of xenon and krypton to be adsorbed (1). At higher pressures than used in field-emission work close-packing of the molecules might however be expected. By applying the Singleton-Halsey equation to the adsorption of krypton on iron films (12)

it was shown that the interaction energy only became comparable with multilayer values at θ values greater than 0.8. This suggested that much stronger adsorption forces existed at small krypton coverages than near the monolayer. Recent data (1, 4) obtained from studies of the adsorption of both krypton and xenon on metal films appear to support the concept of topographic specificity.

During the course of using physical adsorption measurements over a period of years we have known isolated cases where blank measurements with nitrogen and krypton with a Pyrex reaction vessel maintained at -195°C indicated extensive adsorption. At a nitrogen pressure of about 10⁻⁴ mm (relative pressure $\sim 10^{-7}$) adsorption corresponded to multilayers on the glass surface if it was assumed to have a roughness factor of unity. Replacing the reaction vessel by another of identical dimensions resulted in the more usual negligible uptake of nitrogen. More recently in a study of the interaction of oxygen with nickel films at -195°, an unexpectedly large fraction of the gas appeared to be physically adsorbed at an

oxygen pressure of about 10^{-2} mm and this stimulated us to investigate the effect in detail.

This article therefore describes a study of the activity of glass for the adsorption of xenon and krypton at -195°C and also of the more chemically active gas oxygen, which would be less likely to be physically adsorbed at the low pressures ($\sim 10^{-2}$ mm) and temperature used in our adsorption experiments. The participation of glass in extensive physical adsorption could conceivably result in appreciable error in the monolayer values of metal films which have areas close to the geometric area of the glass envelope. This point does not appear to have been considered in detail, probably on the grounds that it is very unlikely that the free energy of adsorption, ΔG , of krypton or xenon on glass will approach that with a metal film so that the coverage on the glass under the conditions where a monolayer has formed on the film will be negligible. If the ΔG values are comparable then some caution would have to be exercised in the interpretation of physical adsorption data on metal films.

EXPERIMENTAL

The high-vacuum apparatus was of conventional design, manipulation of gases was by means of mercury cutoffs, and the spherical Pyrex reaction vessel was protected from mercury vapor by a trap maintained at -195° . The reaction vessel, trap, and connecting glass tubing were baked at $\sim 400^{\circ}\text{C}$ before studying adsorption and pressures $\ll 10^{-6}$ mm could be attained. The total area of glass maintained at -195° , assuming a roughness factor of unity, was about 300 cm^2 . Pure gases were supplied in sealed ampoules by B.O.C. Ltd. The volumes of krypton, xenon, and oxygen adsorbed are calculated from blank measurements with hydrogen, it being assumed that the latter is not adsorbed on the cold glass surfaces. The value of the saturation pressure, P_0 , of xenon at the temperature of liquid nitrogen was between 2 and 3×10^{-3} mm, the value for krypton at the same temperature was assumed to be 2 mm. All pressures have been corrected for thermomolecular flow (9). The

adsorption isotherms could be reproduced to an accuracy of $\sim 5\%$.

RESULTS AND DISCUSSION

In Fig. 1(a) are plotted adsorption isotherms of krypton and xenon obtained with a Pyrex glass reaction vessel which we have designated "active glass." There is extensive uptake of xenon at pressures of about 10^{-6} mm at -195° and the isotherm obeys the BET relationship [Eq. (1)], really the Langmuir equation in this pressure range, up to a P/P_0 value

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0} \quad (1)$$

of 0.2 [Fig. 1(b)]. The symbols used in this equation have their usual significance. The values of the parameters C and V_m calculated from the xenon BET plot are 370 and 13.5×10^{-3} cc (STP), respectively. With krypton there is extensive adsorption at 10^{-3} mm and the BET equation is obeyed up to a P/P_0 value of 0.01. Values of 1260 and 19.8×10^{-3} cc (STP) were calculated for C and V_m , respectively, from the krypton BET plot. The C values are therefore within the range observed with metal films (see ref. 3).

The "active glass" was shown to adsorb oxygen extensively at -195°C (Fig. 2), and at an oxygen pressure of 10^{-2} mm about 14×10^{-3} cc (STP) were adsorbed. Thus if we assume for the moment that adsorbed oxygen and xenon occupy the same area then about a monolayer of oxygen is apparently formed at a P/P_0 value of about 10^{-4} . This behavior of oxygen is analogous to data obtained some years ago (10) when 15×10^{-3} cc (STP) of nitrogen were adsorbed at a pressure of $\sim 10^{-4}$ mm on a glass reaction vessel maintained at -195° . In this latter case the number of nitrogen molecules adsorbed at a P/P_0 value of $\sim 10^{-7}$ corresponded to about four times that required to form a monolayer on the glass if it had a roughness factor of unity.

When the reaction vessel designated "active glass" was replaced by an unused Pyrex one of identical dimensions, and then degassed, the adsorption isotherms of krypton

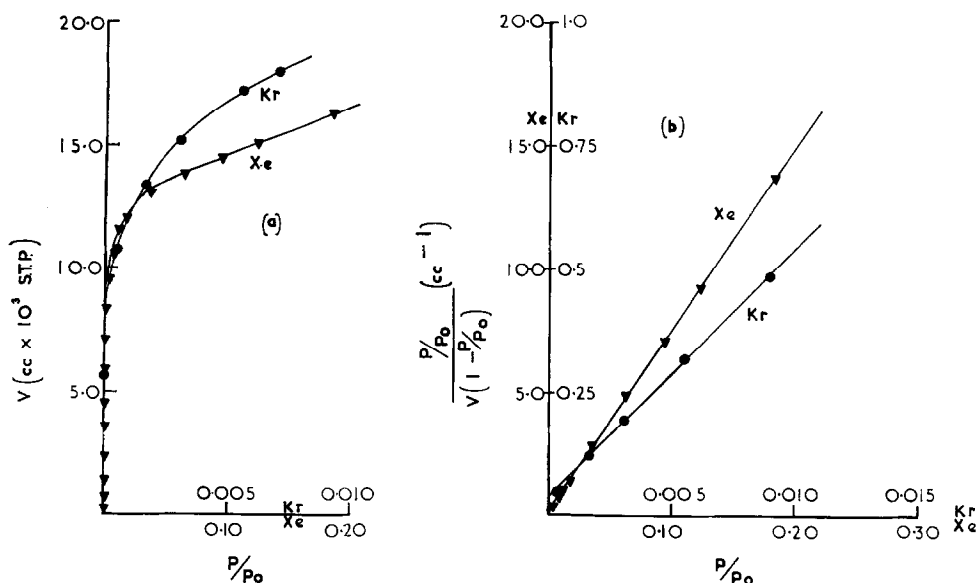


Fig. 1. (a) Adsorption of krypton (●) and xenon (▼) on "active glass" at -195°C as a function of the relative pressure P/P_0 . BET plots for krypton (●) and xenon (▼) adsorption on "active glass."

and xenon were as shown in Fig. 3(a). Adsorption was much less extensive over the whole range of P/P_0 studied, but the difference between this "inactive glass" and "active glass" is particularly marked at low P/P_0 values. From the appropriate BET

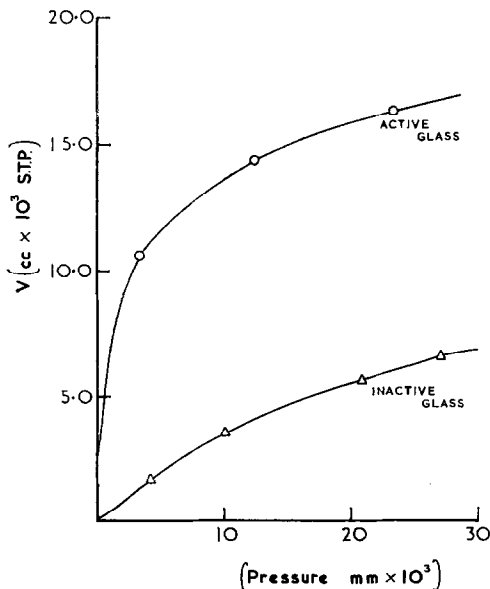


Fig. 2. Adsorption of oxygen on "active glass" (○) and "inactive glass" (Δ) at -195°C .

plots [Fig. 3(b)] the values calculated for C and V_m are 52.5 and 4.65×10^{-3} cc (xenon) and 114 and 10.7×10^{-3} cc (krypton). There is therefore a drastic reduction in the monolayer values, and the C values which are related to ΔG the free energy of adsorption decrease by factors of 7 and 10 with xenon and krypton, respectively.

Adsorption of oxygen by this "inactive glass" was also much smaller than with the "active glass" (Fig. 2). For example, at a pressure of 10^{-2} mm about 3.5×10^{-3} cc (STP) of oxygen were adsorbed, which compares with $\sim 14 \times 10^{-3}$ cc (STP) on the active glass. This change in activity for oxygen adsorption is paralleled by a comparable change in the xenon monolayer (13.5×10^{-3} cc to 4.65×10^{-3} cc).

A significant feature of our data is therefore the very high sorption capacity of the "active glass." At a P/P_0 value of 0.004 about 75% of the xenon required to form a monolayer (V_m) has been adsorbed, this compares with a P/P_0 value of 0.005 for complete coverage with xenon on tungsten films (1, 4). Similarly, with krypton the respective P/P_0 values are 0.0025 (glass) and about 0.005 (tungsten film, 1, 4). We have evidence that much of the activity of

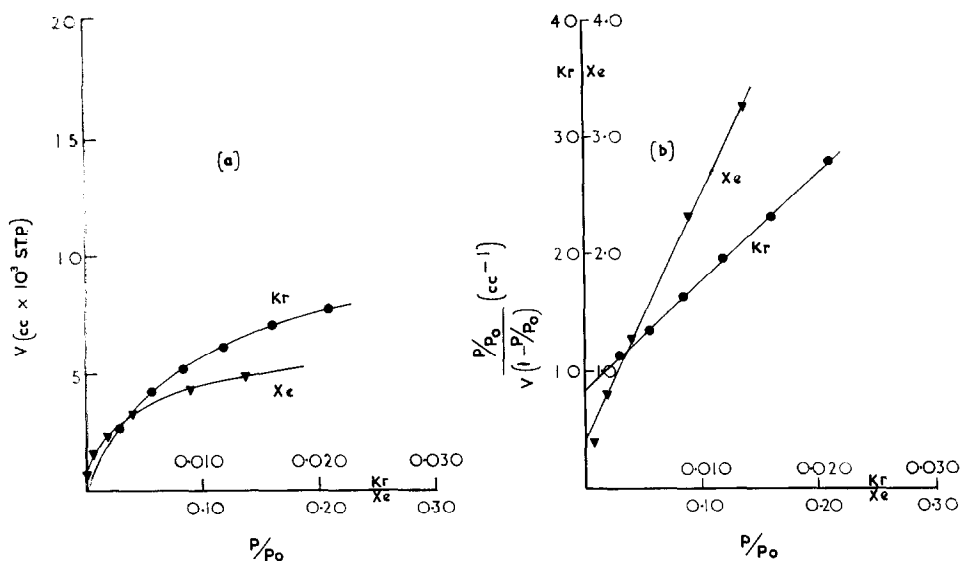


FIG. 3. (a) Adsorption of xenon (\blacktriangledown) and krypton (\bullet) on "inactive glass" at -195°C as a function of the relative pressure P/P_0 . (b) BET plots for krypton (\bullet) and xenon (\blacktriangledown) adsorption on "inactive glass."

the "active glass" is due to repeated heating during glass-blowing. By removing about 10 cm^2 of glass in the region where extensive glass-blowing had been carried out, and which had become slightly opaque in appearance, the extent of the adsorption of both krypton and xenon decreased by a factor of 2. The glass removed represents only about 3% of the total geometric area but causes a 50% decrease in the adsorption activity at -195° . The enhanced activity is therefore probably due to devitrification of the glass during repeated heating and cooling with the formation of a highly porous molecular-sieve-like structure. This could result in cations such as Na^+ present in glass being able to participate extensively in the binding of the inert gas molecules and therefore enhance the polarization of the adsorbed molecules. The entropy of adsorption would also be likely to be very different with this channel-like structure than with the initially planar surface. The much larger C values with the "active glass" can therefore be reconciled with the different nature of the gas-sorbent interaction which can effect an increase in both the partition function and heat of adsorption of the molecules.

With the "active glass" the adsorption isotherms of both xenon and krypton had

sharp "knee" bends and the V_m values are probably realistic. The adsorption of krypton on the "inactive glass" had a rather diffuse "knee" and we believe that the V_m value in this case is unreliable. This may be partly the result of hydrogen being adsorbed itself on the glass and therefore not giving a true blank at high pressures ($\sim 10^{-2}$ mm) which would lead to serious errors for sorbents with small surface areas. This error would of course not arise in the case of the adsorption of xenon. The xenon monolayer (V_m) for the "inactive glass" corresponds to 4.65×10^{-3} cc (STP) which, if we assume that the glass has a roughness factor of unity (300 cm^2), gives a surface concentration of 4×10^{14} molecules cm^{-2} . This value is close to 6.4×10^{14} cm^{-2} which is the nitrogen monolayer estimated by Hobson (11) for Pyrex glass known to have a roughness factor less than 1.4. At a nitrogen pressure of 10^{-3} mm and -195.6°C the surface coverage is only about 15% but Hobson made use of the Dubinin-Radushkevich relationship [Eq. (2)] to estimate the monolayer value V'_m .

$$\log V = \log V'_m - D(\log P/P_0)^2 \quad (2)$$

where V is the number of molecules adsorbed per cm^2 and $D = AT^2$, where A is a constant and T the temperature. Our data for oxygen

adsorption on "inactive glass" (Fig. 2) is therefore comparable with Hobson's nitrogen data since $\sim 4 \times 10^{-4}$ cc (STP) of oxygen are adsorbed at 10^{-3} mm and -195° (Fig. 2) which is about 10% of the xenon monolayer.

The cross-sectional area of adsorbed xenon calculated from our "inactive glass" data is $\sim 24 \text{ \AA}^2$ and this compares favorably with 27 \AA^2 obtained by Cannon (6) who used a similar procedure. But in view of the variable nature of the sorptive capacity of glass observed in the present work this is clearly an unreliable method for determining cross-sectional areas of adsorbed molecules. The data obtained with the "active glass" gives a σ_{Xe}/σ_{Kr} ratio of 1.46 which if σ_{Kr} is 19.5 \AA^2 gives a value of 28.5 \AA^2 for σ_{Xe} . Although the value is consistent with previous results obtained with metal films and other sorbents ($24 \pm 4 \text{ \AA}^2$ covers all the values) this method of determining cross-sectional areas can be questioned. In this connection it is significant to note that the krypton and xenon isotherms plotted as a function of P/P_0 are not superimposable with either the active or inactive glass. This contrasts with the behavior of metal films (1) and may reflect the rather undefined crystallographic nature of glass surfaces. It is therefore unlikely that one will be able to define regions of "lattice-packed" and "close-packed" monolayers (4) on these surfaces although both low- and high-energy adsorption sites obviously exist, as reflected in the partial reversibility of adsorbed xenon at -195° .

Our data therefore indicate that Pyrex glass which had initially a roughness factor close to unity can develop a superactivity for gas adsorption; for the physical adsorption of krypton and xenon the activity is as high as that of some metal films. This superactivity would be undetected unless frequent blank measurements were made and could result in an overestimate of the extent of adsorption which for metal films of small area (up to five times the geometric area of the glass envelope in the present study) would be serious. Any estimate of surface

coverage of a chemisorbed gas, based on the ratio V_{gas}/V_m , would consequently be smaller than the correct value. The general shape of an adsorption isotherm, supposedly on a metal film, could also be distorted since the "active glass" can participate in extensive adsorption at very low P/P_0 values (0.001). This would be reflected as a step in the adsorption isotherm obtained with a metal film of low adsorption activity, i.e., where appreciable adsorption on the film only occurred at say a P/P_0 value of 0.01 or 0.1. The occurrence of steps in isotherms is usually interpreted as evidence for a phase change of the adsorbed molecules but such an interpretation would be fallacious in this particular case. There is also no reason why this superactivity *per se* could not develop under other experimental conditions and therefore be a factor in gas-phase decomposition or other reactions studied with glass surfaces.

ACKNOWLEDGMENT

One of us (J.R.H.R.) is in receipt of a grant from the Ministry of Education of Northern Ireland.

REFERENCES

1. BRENNAN, D., GRAHAM, M. J., AND HAYES, F. H., *Nature* **199**, 1152 (1963).
2. PRITCHARD, J., *Nature* **194**, 38 (1962).
3. LITTLE, J. G., QUINN, C. M., AND ROBERTS, M. W., *J. Catalysis* **3**, 57 (1964).
4. ANDERSON, J. R., AND BAKER, B. G., *J. Phys. Chem.* **66**, 482 (1962).
5. PONEC, V., AND KNOR, Z., *Collection Czech. Chem. Comm.* **27**, 1091 (1962).
6. CANNON, W. A., *Nature* **197**, 1000 (1963).
7. EHRLICH, G., AND HUDDA, F. G., *J. Chem. Phys.* **35**, 1421 (1961).
8. ROOTSAERT, W. J. M., VAN REIJEN, L. L., AND SACTLER, W. H. M., *J. Catalysis* **1**, 416 (1962).
9. BENNETT, M. J., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **53**, 185 (1957).
10. ROBERTS, M. W., unpublished data.
11. HOBSON, J. P., *J. Chem. Phys.* **34**, 1850 (1961).
12. ROBERTS, M. W., *Trans. Faraday Soc.* **56**, 128 (1960).