~~ON~~
CONFIDENTIAL - 2

EFFECS OF SURFACE WATER ON THE ADSORPTION OF INERT GASES

R. B. Gammage and H. F. Holmes

By acceptance of this article, the publisher or recipient acknowledges the U. S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering the article.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, sub-contractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

429

EFFECTS OF SURFACE WATER ON THE ADSORPTION OF INERT GASES*

R. B. Gammage and H. F. Holmes
Oak Ridge National Laboratory

ABSTRACT

Molecular water on mildly outgassed open oxide surfaces can, under special circumstances, significantly reduce the monolayer capacity for inert gas molecules. Non-porous thorium and cubic europium are two examples. The special proviso is that the surface be sufficiently uniform to permit the formation of a well structured, ice-like surface with non-polar character. This type of behavior reaches an extreme for a non-porous ground calcite; surface water converts a Type II isotherm for krypton into a Type III. These structured layers of adsorbed water adsorb nitrogen in a manner very similar to that found for various types of ice. For open oxide surface in a more thoroughly outgassed condition, the BET specific surface area does not generally vary with outgassing temperature at and above 150°C. The area occupied by an inert gas molecule does not change, therefore, with varying hydroxyl ion content of the surface.

I. INTRODUCTION

Even the serious reader of the literature on inert gas adsorptions by oxides and other polar solids is likely to be baffled by claims made for the effects of residual water. Karasz et al.(1) were among the first to demonstrate that molecular water on standard anatase surface significantly lowers the uptake of nitrogen and argon; adsorption of argon onto a sample of silver iodide, however, was not affected by the presence or absence of molecular water.

There is also confusion as to whether or not the concentration of surface hydroxyl groups can influence the apparent specific surface area. The few available examples given in Table 1 suggest that sometimes it does, sometimes it doesn't; in each instance the author claims that the deviations in specific surface, where they occur, arise from a changing occupancy area of the adsorbed nitrogen molecule.

*Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corporation.

TABLE 1

Effect of Outgassing Temperature on the Specific Surface Area by Nitrogen or Argon Adsorption for Several Different Oxides

Outgas. Temp. (°C)	Specific Surface (M ² /g)									
	Silica Gel		Silica SB (Ref.3) N ₂	Silica SL (Ref.3) N ₂	Rutile		Lunar Fines Apollo 16 (Ref.4) N ₂	ThO ₂ Sample I (Refs.6,7) N ₂ Ar		Cubic Europium Oxide N ₂
	KSK-2 (Ref.2) N ₂	Ar			(Ref.5) N ₂	Ar				
25					32	32	0.42	2.39	2.38	5.36
50					32	32	0.43			
100			334	593	32	32		2.74	2.52	
150	320	316			35	34				
200			341	611	36	36	(0.39)	2.70	-	
250					37	36				
300			337	637			0.50	2.70	-	5.72
350					37	37				
400	320	316	339	646			0.56			
450					37	36				
500							0.50	2.70	2.69	
600	320	-			17	17	0.50			
700					10	10	0.45			
800	314	319								

In studying polar solids [thoria (7), europia (8), lunar fines (4) and calcium carbonate (9)] we have been faced with the problem of deciding whether or not, and by how much, water or the elements of water are affecting the adsorption of nitrogen, argon and krypton. The purpose of this paper is to shed more light on these problems and pinpoint the circumstances under which surface water alters the adsorption characteristics. Several new, and several previously published, results are given in order to achieve this purpose.

II. EXPERIMENTAL

The oxides and calcium carbonate examined in this study were all low, or relatively low-area ($< 10 \text{ m}^2 \text{g}^{-1}$), non-porous solids. The criteria for non-porosity were a reversible inert gas adsorption isotherm with rapid kinetics of adsorption and t-plots which extrapolated to the origin. In the case of the thoria sample I, heat of immersion data in water confirmed the non-porous nature (10).

The thoria, I-ThO₂ (11), originated from thorium oxalate and was calcined at 1200°C. The cubic europia was obtained from the Molybdenum Company of America in high purity form. The lunar fines 63321 were returned from the Apollo 16 mission. They were rich in feldspar (~ 30% Al₂O₃) and had "matured" through the combined effects of solar wind radiation damage and meteorite bombardment (12). The calcium carbonate sample was an Iceland spar ball-milled for 1000 hours, whose properties have been extensively studied (13)(14).

Measurements of the adsorption of nitrogen and argon were made on microbalance systems suited to the handling of low area solids (15), while the sorption onto calcium carbonate was measured volumetrically using ⁸⁵Kr - labeled krypton (16).

III. RESULTS AND DISCUSSION

A. Molecular Adsorbed Water

The adsorption of nitrogen and argon onto standard anatase is increasingly reduced by the first, second and third layers of preadsorbed water (1). This section of the present paper is addressed to ionic adsorbents outgassed at, or slightly above, room temperature. Can molecular surface water not removed in the mild outgassing significantly reduce the adsorption of an inert gas compared to adsorption on the well outgassed surface? It will be shown that the answer is yes, in special circumstances, but that the magnitude of the effect depends on the nature of the adsorbent and the structural perfection of the adsorbed water.

We have experienced two unambiguous examples of drastic effects of surface molecular water on the magnitude and energetics of inert gases adsorbed on two different kinds of non-porous, ionic materials.

The first example is a ground calcite which had been structurally degraded in plastic flow processes (13). Although extremely reactive, because of a high density of imperfections including 2% by weight of buried water taken up during the milling for 1000 hours, the flowed grains had been rendered non-porous to inert gas molecules (14). The hitherto unpublished isotherms of krypton shown in Fig. 1 were measured on the same specimen of this ground calcite. One isotherm was measured immediately after, the other 48 hours after cessation of prolonged outgassing in vacuo at 150°C. The effect of the time delay of 48 hours on the subsequent adsorption of krypton was depression of the BET c constant from a value of 800 to 2 (Type II → Type III isotherm). A similar, but less

Fig. 1. Krypton adsorbed at 77°K on a single sample of calcite ground for 1000 hours; the solid was frozen either immediately after, or after 48 hours at room temperature, following outgassing at 150°C.

pronounced, change in the adsorption, Fig. 2, was observed with an identically outgassed sample of precipitated calcite with 3% by weight of occluded water. The c constant this time was reduced to 21. In both instances the most probable cause of the changes in adsorption behavior is water diffusing from the bulk to the surface after cessation of the outgassing at 150°C with structuring to present an annealed, or partially annealed, ice-like exterior to the adsorbing krypton.

In general, for various specimens of calcium carbonate containing water, unless the well outgassed solid was frozen immediately to prevent diffusion of water, anomalous adsorption behavior and erroneous and varying specific surface

Fig. 2. Krypton adsorbed at 77°K on a single sample of precipitated calcite; the solid was frozen either immediately after, or after 48 hours at room temperature, following outgassing at 150°C.

measurement would ensue. However, adsorption of krypton on ten aliquots of the ground calcite (1000 hours) in the well outgassed condition yielded a specific surface of 6.92 m²/g, constant within a standard deviation of 3%.

Adsorptions of butane at 0°C have already been reported (13) for the ground calcite (1000 hours). In very much the

same way as for krypton adsorption, there was a conversion from a Type II to a Type III isotherm. At that time the resemblance to the isotherm for alkanes adsorbed on the surface of liquid water (17) was noted.

The second example concerns high-fired (1200°C), non-porous, low specific surface thorium oxide (sample I of reference 7) possessing a considerable degree of surface homogeneity. In addition to reversible, stepped isotherms of nitrogen and argon (7), net differential heats of adsorption, derived from heat of immersion measurements, indicate two distinct layers of molecular water bound to the fully hydroxylated surface with net enthalpy values of -8.6 and -1.8 kcal/mole (10). The formation of these discrete layers of water occurs very rapidly in aqueous media (10). Reaching the equilibrium state through adsorption of water vapor is, in contrast, a very laborious process requiring many sorption cycles to relative pressures approaching saturation (18). The apparent specific surface, determined by nitrogen adsorption, is 2.39 m²/g after carefully equilibrating with water vapor and outgassing at 25°C (7) compared to 2.70 m²/g for the surface outgassed at 500°C, a 13% increase. Slightly lesser amounts of irreversibly bound and less well-structured molecular water give intermediate values for the specific surface; 2.51 m²/g was an earlier published result (19) where less effort was made to ensure the equilibrium condition.

The *n* value plots for nitrogen and argon adsorbed on the most carefully equilibrated water-thoria system are shown in Fig. 3. The isotherms are striking for their overlap; the slight divergence below a P/P_0 of 0.4 is associated with the lower BET *c* constant of 22 for argon compared to 33 for nitrogen. That one is, in effect, measuring inert gas adsorption on ice is confirmed by inclusion in Fig. 3 of the nitrogen isotherm measured by Adamson *et al.* on a non-annealed ice, designated 2A (20), for which the BET *c* constant was a comparable value of 39. The coincidence is nearly exact. It was, in fact, Adamson and Dormant (21) who first recognized the similarity between isotherms of nitrogen for ice and water covered anatase (1) mentioned previously.

Fully annealed ice samples studied by the Adamson group (20) produced Type III isotherms of the sort obtained for krypton adsorbed on water-covered, ground calcite (Fig. 1). The degree of ordering of the molecular water on the polar surface (oxide or carbonate) seems to control the extent to which the inert gas adsorption isotherm is changed. To bring the specific surface of the water covered thoria (2.39 m²/g) into line with the "real" specific surface of 2.70 m²/g, obtained after high temperature outgassing, requires a value

Fig. 3. n -plots of nitrogen and argon adsorbed at 77°K on uniform, non-porous thoria (Sample I) with an equilibrium amount of surface water for the 25°C outgassed condition, together with an n -plot for nitrogen on an ice which exhibits a like BET c constant (ice 2A of ref. 20).

of $18.3 \text{ \AA}^2$ per nitrogen molecule. Another example of larger than the normal cross-sectional area of $16.2 \text{ \AA}^2$ for nitrogen is the well known $20 \text{ \AA}^2$ for graphitized carbon (22).

To demonstrate vividly the effect on adsorption of changing from the non-polar, ice-like substrate to the highly polar thorium surface outgassed at 500°C , n -plots of argon and nitrogen are shown in Fig. 4, and should be compared against those shown in Fig. 3. The slight step structure in the nitrogen isotherm we attribute to surface homogeneity. Reasons for

Fig. 4. n -plots of nitrogen and argon adsorbed at 77°K on uniform, non-porous thorium and cubic europium outgassed at 500°C .

the stepped structure of the argon isotherm lie beyond the scope of this paper.

Another example of inert gas adsorption being influenced by adsorbed molecular water is the absorption on a non-porous, cubic europium oxide, again with some homogeneous surface character. The effects, however, were less pronounced than those with the thorium oxide sample I. Increase in outgassing temperature from 25° to 300°C produced an apparent increase in specific surface of 7% (from 5.36 to 5.72 m²/g) compared to 1% for the thorium oxide example which has been discussed. One surmises that the degree of oxide surface homogeneity and degree of structural perfection in the adsorbed water layer is less for the europia than the thoria.

Confirming the non-porous character of the europia, the isotherms of the nitrogen and argon were reversible over the entire range of relative pressure. The n-plots of nitrogen and argon are reproduced in Fig. 4. The validity of the steps and the reproducibility were checked in repeated isotherm measurement. The europia had been subjected in a prior experiment to adsorption of water vapor at 25°C. This was followed by "clean-up" in oxygen at 300° or 500°C. The similarities to the n-plots obtained for the thorium oxide are quite striking. In spite of these characteristics and the apparently firm indication that surface molecular water is reducing the monolayer capacity for nitrogen, we choose not to confer the same high degree of "unambiguousness" that we attach to the thoria and ground calcite examples. This is because a quite massive interaction with adsorbed water vapor had taken place with irreversible binding of water to the extent of 70 OH/100 Å² on (100) faces of the cubic europium oxide (23). The issue is clouded because of possible real area changes occurring in the extensively hydrated oxide substrate upon increase of the outgassing temperature.

The lunar fines also fall into the category of being less than totally satisfactory in exemplifying definite effects on apparent specific surface caused by molecular water. There are three reasons. The specific surface of the fines 63321 is about 0.5 m²/g and the anticipated maximum variation with outgassing temperature of about 10% is only 0.5 m²/g. Since the experimental error is ± 0.02 m²/g the changes we seek are barely discernible from experimental inaccuracy. The BET c constant is about 150 for surface outgassed at 25°C, which hardly approaches the value of 2 for the ground calcite with its annealed, ice-like layer of surface water. The layer of adsorbed water on lunar fines is, in all probability, insufficiently ordered to produce a more open than normal monolayer of adsorbed nitrogen molecules. Finally, lunar fines are rich

in buried solar wind, principally hydrogen in the form of small gas bubbles (12). This gas diffuses out of the grains at $> 150^{\circ}\text{C}$ and poses the possibility of real surface area changes taking place due to structural alteration.

The data in Table 1 for rutile (5) are also regarded as unsatisfactory for explanation in terms of well-structured water layers. The acknowledged porosity leaves a possibility that micropores may be present which can remain blocked by water in an outgassing at 100°C . The $\sim 15\%$ increase in apparent specific surface after outgassing at 200°C would then come about from an opening up of these micropores.

It is of value to discuss these various findings with respect to the now commonly used standard or universal isotherm of nitrogen on non-porous oxides. In the general case of a high specific surface, oxide having a heterogeneous but still non-porous surface, it would be unlikely for firmly bound molecular water to become sufficiently ordered and non-polar to affect significantly the standard nitrogen isotherm. This, in our judgment, is one of the reasons for the successful operation of the α_s (24) and t-plot methods of analysis (25). However, as a general principle, it is advisable to use well-outgassed surfaces for obtaining reference isotherms. There is then no possibility of well-structured water layers being present to give unusual behavior in the adsorption of nitrogen.

B. Surface Hydroxyl Groups

Molecular water strongly adsorbed in the micropores of a finely pored oxide blocks the entry of adsorbed inert gas molecules and reduces the apparent specific surface area. To drive off this molecular water completely requires outgassing temperatures ranging from about 200°C for microporous samples of silica (26), calcium sulphate (27) and alumino-silicates of lunar origin (28), to about 400°C for a microporous thorium oxide (29). Where any increase in specific surface of an oxide is noted one cannot attribute the increase to changes in the specific interactions between hydroxyl groups and nitrogen molecules unless one is certain there are no micropores to complicate the issue. We now consider the data of Table 1 with this proviso in mind, especially the data relating to outgassing temperatures of 150°C or more. At 150°C all, or a major fraction, of strongly bound surface molecular water will be removed from the open surfaces of these oxides. The surfaces will still have essentially their full complement of surface hydroxyl groups.

The silica SL increases its apparent specific surface area by approximately 10% with stripping of surface hydroxyls. Whalen argues (3) that real surface area changes are not occurring and that changes in surface structure are responsible (changing occupancy area of the nitrogen molecule?). Although this author states that there is no "significant evidence" for microporosity, an initially very large discrepancy between the nitrogen and benzene derived areas leaves room for doubt, in our opinion. For this reason, silica SL will be dropped from our further discussions of whether or not the packing of adsorbed nitrogen (or argon) molecules is influenced by the hydroxyl group content of the oxide surface. Within an experimental error of a few percent, the remaining oxide samples have invariant specific surfaces until the outgassing temperatures become high enough to cause loss of surface area by sintering. The argon data, though much more limited than the nitrogen data, also suggests invariance with the hydroxyl group content of the surface. These argon specific surfaces were all derived using $16.6 \text{ \AA}^2$ per argon atom and the saturation pressure of the supercooled liquid argon, a procedure with which we have found the most satisfaction (7).

IV. SUMMARY

In special circumstances molecular water remaining on an outgassed non-porous solid can significantly alter the adsorption of an inert gas such as nitrogen, argon or krypton. The special requirement for an oxide, such as thoria, is that the oxide surface be sufficiently uniform to permit the formation of a well structured, ice-like layer of water which can then present a non-polar surface to the adsorbing inert gas. The reduction in the BET specific surface can be as much as 13% and presumably is caused by an abnormally open packing of adsorbate molecules in the monolayer. An extreme example of this phenomenon is offered by ground calcite where the presence of molecular surface water changes a Type II adsorption isotherm of krypton into a Type III. It is logical to suppose that with the typical oxide sample, the degree of surface heterogeneity is high enough to disrupt the water structure and produce a polar rather than a non-polar exterior. The effect we describe does not, therefore, have general occurrence. Hence the general success of the reference isotherm in α_s (24) or t-plot (25) characterizations.

In general, it appears that the area of occupancy of adsorbed, inert gas molecules (the best data exists for nitrogen) does not change with varying hydroxyl ion content of an oxide surface. This conclusion is drawn best from work on

low area, non-porous oxide samples. At the very least it is essential to establish the absence of micropores in the oxide being studied otherwise blocking effects by very strongly bound molecular water will lead to erroneous conclusions.

REFERENCES

1. Karasz, F. E., Champian, W. M. and Halsey, G. D., Jr., J. Phys. Chem. 60, 376 (1956).
2. Aristov, B. G., and Kiselev, A. V., Russian J. Phys. Chem. 37, 135 (1963).
3. Whalen, J. W., J. Phys. Chem. 71, 1557 (1967).
4. Gammage, R. B., and Holmes, H. F., to be published in Earth and Planetary Sci. Lett.
5. Isirikyan, A. A. and Kazmenko, I. A., Kolloidnyi Zhurnal 30, 220 (1968).
6. Holmes, H. F., Fuller, Jr., E. L., Gammage, R. B., and Secoy, C. H., J. Colloid and Interface Sci. 21, 405 (1966).
7. Gammage, R. B., Fuller, Jr., E. L., and Holmes, H. F., J. Colloid and Interface Sci. 34, 428 (1970).
8. Holmes, H. F. and Gammage, R. B., to be published.
9. Gammage, R. B., Ph.D. Thesis, Exeter University, England (1964).
10. Holmes, H. F., Fuller, Jr., E. L., and Secoy, C. H., J. Phys. Chem. 72, 2095 (1968).
11. Fuller, Jr., E. L., Holmes, H. F., and Secoy, C. H., J. Phys. Chem. 72, 573 (1968).
12. Maurette, M., and Price, F. B., Science 187, 121 (1975).
13. Gammage, R. B., Holmes, H. F., Fuller, Jr., E. L., and Glasson, D. R., J. Colloid and Interface Sci. 47, 350 (1974).
14. Gammage, R. B., and Gregg, S. J., *Ibid.* 38, 118 (1972).
15. Holmes, H. F., Fuller, Jr., E. L., and Gammage, R. B., Earth and Planetary Sci. Lett. 19, 90 (1973).

16. Aylemore, D. W., and Jepson, W. B., J. Sci. Instr. 38, 156 (1961).
17. Jones, D. C., and Ottewill, R. H., Proc. 2nd Intern. Congr. Surface Activity, London 1, 188 (1957).
18. Holmes, H. F., Fuller, Jr., E. L., and Secoy, C. H., J. Phys. Chem. 72, 2293 (1968).
19. Holmes, H. F., Fuller, Jr., E. L., Gammage, R. B., and Secoy, C. H., J. Colloid and Interface Sci. 28, 421 (1968).
20. Adamson, A. W., Dormant, L. M., and Orem, M., *Ibid.* 25, 206 (1967).
21. Adamson, A. W., and Dormant, L. M., J. Am. Chem. Soc. 88, 2055 (1966).
22. Pierce, C., J. Phys. Chem. 73, 813 (1969).
23. Holmes, H. F., to be published.
24. Carruthers, J. D., Payne, D. A., Sing, K. S. W., and Stryker, L. J., J. Colloid and Interface Sci. 36, 205 (1971).
25. Lippens, B. C., and De Boer, J. H., J. Catal. 4, 319 (1965); De Boer, J. H., Linsen, G. G., and Osinga, Th. J., J. Catal. 4, 643 (1965).
26. Lange, K. R., J. Colloid Sci. 20, 321 (1965).
27. Ridge, M. J., and Molony, B., Trans. Faraday Soc. 65, 1113 (1969).
28. Gammage, R. B., and Holmes, H. F., Proc. 6th Lunar Sci. Conf. 3305 (1975).
29. Gammage, R. B., Fuller, Jr., E. L., and Holmes, H. F., J. Colloid and Interface Sci. 38, 91 (1972).