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► To cite this version:

J. Ocampo, B. Schmitt, J. Klinger. "CHEMICAL" REACTIVITY ON THE DISORDERED SURFACES. THE CASE OF ICE. Journal de Physique Colloques, 1987, 48 (C1), pp.C1-557-C1-563. 10.1051/jphyscol:1987176 . jpa-00226323

HAL Id: jpa-00226323

<https://hal.science/jpa-00226323>

Submitted on 1 Jan 1987

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"CHEMICAL" REACTIVITY ON THE DISORDERED SURFACES. THE CASE OF ICE

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RESUME : La cinétique de clathration du dioxyde de carbone et du krypton sur la surface de la glace a été étudiée. Afin de comprendre le rôle joué par une surface désordonnée sur la clathration la "rugosité" de la surface est caractérisée par sa dimension fractale d . Cette dimension a été calculée de manière indirecte à partir de la diffusion des molécules d'eau pendant le frittage des particules de glace et pendant la clathration. Le fait que $\tilde{d} < 2$ implique que l'exploration est "compacte" ce qui influence fortement le frittage et la clathration.

ABSTRACT : The kinetics of krypton and carbon dioxide clathration on ice surface was studied. In order to understand the role played by a disordered surface in clathration, the surface "roughness" was characterized by the spectral dimension d . This dimension was calculated indirectly from the water diffusion during the sintering and clathration of ice particles. Since $\tilde{d} < 2$ the exploration is "compact" which strongly influences the sintering and clathration.

INTRODUCTION

The clathration by gas-ice reaction has been observed since 1962 [1 to 4]. Barrer and Edge theoretical approach was unique and based on the concept of preexisting cages being filled as Langmuir isotherms.

This paper attempts to apply the physics of fractal structures to the measure of the degree of surface disorder and the clathration kinetics.

During these past few years, the concept of fractal structures developed by Mandelbrot [5] has been of great utility for the description of structures with geometrical and dynamical properties which appear purely random [6]. Avnir and Farin [7] have remarked that the surfaces of most materials are fractals at the molecular scale. Since it is difficult to conceive any dynamic interfacial process that is independent of surface irregularities and defects, the study of gas clathration kinetics on the ice surface seems obviously very important. Catalysis is a phenomenon governed by such surface characteristics and certainly plays an important role in clathration.

EXPERIMENTAL PROCEDURES

The ice powder sample was prepared by deionized water condensation (18 M Ω /cm at 25°C) at 77K. Amorphous ice is obtained. After heating the sample up to 200K amor-

phous ice is transformed into hexagonal ice. From single crystal we have also prepared a powder ice after crushing the ice in vacuum at 77K.

We observed the evolution of specific surface area and heat of adsorption of the powder ice annealed at 195K, by means of krypton adsorption isotherms at 77K. The classical manometric method used is described elsewhere[8]. From this evolution, we have characterized the initial surface by a spectral dimension.

The formation of krypton and carbon dioxide clathrates was done at 195K and monitored in the same way as an adsorption isotherm [9]. The krypton clathration is possible only if the surface contains the germ of another clathrate. The equilibrium pressure was compared to data in the literature (usually obtained from clathrates prepared by freezing of a gas liquid mixture). To confirm the formation of clathrates, the surface reaction was followed qualitatively with an X-ray diffractometer.

RESULTS

Figure 1 shows the evolution of the specific surface area and heat of adsorption for crushed ice measured with krypton at 77K. The sample was annealed at 195K for different time intervals and came back to 77K to avoid evolution and to measure the krypton isotherms.

Figure 1: Specific surface area (S_w) and adsorption heat (ΔQ) evolution. Krypton was used to measure adsorption isotherms at 77K between different annealing periods at 195K.

We can observe a fast evolution of the specific surface area and heat of adsorption in the first hour of the annealing period. The specific surface area decreased from $0.33 \text{ m}^2/\text{g}$ (fresh ice surface) to $0.06 \text{ m}^2/\text{g}$, close to the equilibrium value observed after 30 hours of annealing.

The krypton clathration was done when the heat of adsorption equilibrium was fully attained and after clathration and decomposition with air. A germ of air clathrate is suspected to exist after this decomposition and to serve as a nuclei for the krypton clathration.

In the case of carbon dioxide, the heat of adsorption is constant for several hours. The incubation time seems linked with this phenomenon.

Figure 2 and 3 show the evolution of carbon dioxide and krypton clathration. No incubation time is observed for krypton. The equilibrium pressure at 195K for the clathrates was 253 mbar and 280 mbar for krypton and carbon dioxide respectively.

Figure 2 : Carbon dioxide clathration (n) and evolution of the reaction rate constant (K) at 195K.

Figure 3 : Krypton clathration (n) and evolution of the reaction rate constant (K) at 195K.

The reaction rates constants shown in these figures were calculated from pressure P evolution towards the equilibrium pressure P_{eq} by the following equation :

$$K = (dP/dt) / (P - P_{eq})$$

We observe a time dependent behaviour of the reaction rate constant for both krypton and carbon dioxide, even far from the saturation.

DISCUSSION

The essential features of our results may be interpreted in the following way:

Our sample preparation method creates a great number of surface defects which are randomly distributed, therefore making a soft surface. The instability of both broken (or non compensated) hydrogen bonds and high surface energy probably causes the evolution of the specific surface area. This evolution seems to take place in a "sintering" fashion probably by short range migration of diffusing elements as we will see below.

The average number of "sintering or fusion sites" in a fractal space which have been visited by a random walker from the start until the time t , before its capture is [1]) :

$$N(t) = N_0 t^{\tilde{d}/2} \quad (1)$$

where $\tilde{d}$ is the fracton(or spectral) dimension.

The differential equation which governs the chemical reaction between two molecules A and B is :

$$- \dot{n}_A = - \dot{n}_B = K n_A n_B \quad (2)$$

where n is the concentration before capture and

$$K = K_0 N(t) / t \quad (3)$$

When fusion occurs : $n_A = n_B = A S_w$ (proportional to specific surface area). Then, from equations (1) to (3) we obtain :

$$S_w = (\tilde{d} t^{-\tilde{d}/2}) / (2 K_0 N_0 A) \quad (4)$$

and from the graph slope of $\log S_w$ vs $\log t$ we found : $\tilde{d} = 0.37$.

It means that the exploration in this space is "compact" ($\tilde{d} < 2$) [11] in the sense that it strongly influences the capture laws. If our system is considered as a percolation one [6] the fractal dimension would be : $\tilde{d} = 0.52$, which satisfies the relation : $d > \tilde{d} > \bar{d}$.

The value of 0.52 confirms our hypothesis of "adhesion points" existence where the sintering takes place in short range diffusion paths.

In order to identify the nature of diffusing elements, we have estimated the activation energies of the rates : (dS_w/dt) and $(d\Delta Q/dt)$ as the average rates at the beginning of the evolution.

The rate of decreasing surface area has an activation energy of $E_w = -0.05$ eV for temperatures lower than 213K and the rate of decreasing adsorption heat has an activation energy of $E_a = -0.16$ eV for temperatures lower than 258K. These energies are probably due to defect migration on the ice surface (as OH or self interstitials [12][13]). The adsorption decrease was already seen in this range of temperatures and is probably due to the creation of a "proton surface" [14].

At temperatures near the melting point of ice, the rate of decreasing adsorption heat has an activation energy of $E_s = 1.12$ eV which is similar to the surface self-diffusion energy.

The carbon dioxide clathration at 195K starts after an incubation period during which there is no capture. At this time, the number of captured molecules grows slowly. From the beginning germination a self-catalytic process maintains the reaction. About the time dependent rate constant K for krypton and carbon dioxide we note that this anomalous reaction law depends on the "cleaness" of the surface (absence of germ), the host molecule nature and the equilibrium pressure.

The surface where clathration occurs is certainly very disordered and we can verify its fractal character in the same way as we did for the specific surface area.

From the differential equation (2) and if we consider that : $n_A \ll n_B$ (supertrapping process and far from the saturation), we can have a solution :

$$n_A = n_A^0 \exp(-2k_B n_B^0 t^{\tilde{d}/2} / \tilde{d}) \quad (5)$$

In our case of clathration, the pressure is proportional to the concentration in the gas phase : $n_A = \alpha P$. Moreover, the water molecule concentration ($n_B = n_{\text{water}}$) is considered as an infinite reservoir. Then from :

$$\log(|\dot{P}| / P) = \log k_B n_B^0 + (\frac{\tilde{d}}{2} - 1) \log t$$

we found for krypton clathration : $\tilde{d} = 1.28$. For a percolation system, the fractal dimension would be : $\tilde{d} = 1.79$.

Then the reaction for the krypton clathration seems to occur in quasi-linear paths. The diffusion constant estimated is : $D_{kr} = 3 \cdot 10^{-13} \text{ cm}^2/\text{s}$.

In the case of carbon dioxide clathration, following the incubation period we can observe a first order reaction with a diffusion constant and an activation energy of:

$$D_s = 10^{-9} \text{ cm}^2/\text{s} \quad E_s = -1.13 \text{ eV}$$

After this evolution the reaction rate decreases as a zero order reaction with a diffusion constant and activation energy of:

$$D_v = 10^{-14} \text{ cm}^2/\text{s} \quad E_v = -0.7 \text{ eV}$$

Those values which are very similar to surface self-diffusion and bulk self-diffusion of water molecules in the ordinary hexagonal ice show that the diffusive element seems to be the water molecule.

The phase transformation from hexagonal to cubic clathrate structure is then started by the capture of the adsorbed gas molecule by water molecules migration. For krypton it was necessary to have a residual clathrate of another gas in order to start the clathration. The reaction constant attains a constant value after some time and illustrates a transition from fractal kinetics to classical ones.

CONCLUSION

The ice powder surface was considered as a fractal space and then characterized by a spectral dimension. A kinetics criterion, based on adsorption sites diminution and clathration was used to calculate the spectral dimension.

The ice particles "punctual sintering" seems to occur in a space where the spectral dimension is : $\tilde{d} = 0.37$, probably by surface defects migration in order to compensate the broken hydrogen bonds and to diminish the surface energy.

On the other hand the capture of gas molecules in clathration seems to occur in a fractal space where the spectral dimension is $\bar{d} = 1.28$; The diffusion on ice surface is realized by the water molecules and respects a quasi-linear paths. The apparent bulk diffusion of the gas molecules is possibly due to existing free cages in the clathrate structure and to bulk self-diffusion of water molecules.

The natural occurrence of gas hydrates has been mentioned in the past. Miller[15] has commented their possible occurrence in the solar system. Carbon dioxide hydrate seems to exist on Mars and in comets. The first reported natural occurrence of clathrate hydrates on the Earth is the air hydrate in Antarctic ice-cores [16]. Glaciological and astrophysical applications of this study are described elsewhere[17].

ACKNOWLEDGEMENTS

Financial support by the "Institut Français des Sciences de l'Univers" ATP grant N° 5724 is gratefully acknowledged.

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COMMENTS

P.L.M. PLUMMER

Have you done your fractal analysis in higher dimensions and if so were your results similar as to the fractal dimensions of the process? If you have not carried out the analysis would you care to speculate on the results?

Answer :

No. At lower temperatures and in microporous ice we will have may be a fractal dimension between 2 and 3.

J.P. DEVLIN

We find that polar molecules (such as ethylene oxide) are much more effective in inducing clathrate hydrate formation. Do you have any comparative rate data for polar vs. nonpolar molecules.

Answer : no.

J.S. TSE

What was the gas pressure in your adsorption experiment ?

Answer :

For CO₂ at 195 K not higher than one bar. Always in the phase diagram region for clathrate formation.