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ADSORPTION ISOTHERM AND SURFACE AREA
DETERMINATION BELOW THE TRIPLE POINT

ANALYZED

BY

G. G. LITVAN

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L'ISOTHERME D'ADSORPTION ET LA DETERMINATION DE L'AIRES SUPERFICIELLE AU-DESSOUS DU TRIPLE POINT

SOMMAIRE

On attire l'attention sur les conséquences de la découverte que les substances adsorbées sont comme à l'état liquide à des températures au-dessous de leur point de congélation apparent (bulk freezing point). Si la pression relative se fonde sur la pression de vapeur de saturation du liquide sous-refroidi, les différences entre les aires superficielles de N_2 et de Kr et celles entre les aires de BET et de Dubinin-Raduskevich deviennent minimales. Si l'on applique des valeurs de pression relative inappropriées dans la construction d'isothermes, il peut y avoir sursaturation apparente.

Adsorption Isotherm and Surface Area Determination below the Triple Point

by G. G. Litvan

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Ottawa, Canada (Received March 13, 1972)*

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Attention is drawn to the consequences of the finding that adsorbates are in a liquidlike state at temperatures below their bulk freezing point. If the relative pressure is based on the saturation vapor pressure of the undercooled liquid, differences between the N_2 and Kr surface areas and those between the BET and Dubinin-Raduskevich areas become minimal. On application of inappropriate relative pressure values in constructing isotherms, apparent supersaturation may be indicated.

Adsorptive properties of systems are commonly characterized by isotherms where the experimentally determined amount of adsorbed vapor is plotted against the relative pressure, p/p° (p is the vapor pressure (vp) of the adsorbate and p° , the vp of the substance in the bulk state at the temperature of the experiment). At temperatures, T , above the triple point, T_{tr} , p° is taken as that of the bulk liquid, p°_l , and at $T < T_{tr}$ that of the solid p°_s .

In calorimetric¹⁻⁵ and dilatometric^{5,6} experiments no evidence can be found for "freezing" in the first two adsorbed layers at any T , and recently it has been shown⁷ that even at higher coverages the adsorbate is in a liquidlike state.

The direct consequence of this finding is that in estimating the surface area by the BET method the value of p°_l has to be substituted in the equation even if $T < T_{tr}$. The failure to follow this practice, sug-

gested by the first proponents of the Kr method,⁸ is the reason for the discrepancies observed between the N_2 and Kr surface areas, when the experimental temperature is 77°K, 39° below the T_{tr} of krypton. This is proved by the discovery that the surface area values obtained by the two methods can be brought into alignment when p°_s is substituted with adjustable

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parameters $p^{\circ 9}$ and Q^{10} the value of which was identical with $p^{\circ 1}$ calculated by extrapolation. The authors of ref 9 and 10 take the view, however, that the close agreement between Q and $p^{\circ 1}$ is fortuitous.

The purpose of this note is to show that recognizing the liquidlike state of the adsorbate at $T < T_{tr}$ provides theoretical support for the practice of applying $p^{\circ 1}$ in the krypton surface area calculation and implies that similar practice has to be followed in the case of other adsorbates, *e.g.*, argon, xenon, and methane at liquid nitrogen temperature.

Furthermore, if experimentally determined adsorption data are plotted in terms of inappropriate p° value, (such as $p^{\circ s}$) distortion of the curve results.⁷ For example, in the case of krypton at 77°K, $p^{\circ s} = 1.75$ Torr while $p^{\circ 1} = 2.63$ Torr, thus when $p/p^{\circ s} = 1$ the value of $p/p^{\circ 1}$ is only 0.66. When the pressure in the cell exceeds this value, condensation on the walls of the cell restores it to $p^{\circ s}$. The obtained isotherm, if plotted as a function of $p/p^{\circ s}$, crosses the ordinate at unity relative pressures instead of approaching it asymptotically. This was reported¹⁰ in 1965 and more recently in a study of the adsorption on nonpolar gases on oxide, metal, and salt surfaces.¹¹ It should be emphasized that the phenomenon considered here occurs below T_{tr} and is distinct from that discussed by Brunauer and coworkers.¹²

If nucleation on the walls is delayed, p may exceed $p^{\circ s}$ temporarily, but this phenomenon is not related in

any way to the adsorbent since it is not yet saturated. In the study of xenon adsorption on porous silver at 77.4°K,¹³ $p/p^{\circ s}$ rose temporarily to a value of approximately 1.08 but, if the values are recalculated the true relative pressure was apparently only ~ 0.02 (applying $p^{\circ} = 2.06 \times 10^{-2}$ Torr, obtained by extrapolation¹⁴). Supersaturation is clearly an artefact as shown not only by the above consideration but also by the reasonably good superimposition of the Ar, Kr, and Xe isotherms when they were plotted in terms of $p/p^{\circ 1}$. It is very probable that the differences between the BET and Dubinin-Raduskevich areas will become minimal when the proper $p^{\circ 1}$ values are used. Difficulties are encountered, however, in determining accurate $p^{\circ 1}$ values which, in some cases, are 80° below T_{tr} (xenon at 77°K).

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