



NRC Publications Archive Archives des publications du CNRC

Adsorption isotherm and surface area determination below the triple point

Litvan, G. G.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

The Journal of Physical Chemistry, 76, 18, pp. 2584-2585, 1972-12-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=d848039b-0375-4cfa-9d4e-8b758af9ec50>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=d848039b-0375-4cfa-9d4e-8b758af9ec50>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



Dep.
THI
N21-2
no. 544
C. 2

2758

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

ADSORPTION ISOTHERM AND SURFACE AREA
DETERMINATION BELOW THE TRIPLE POINT

ANALYZED

BY

G. G. LITVAN

REPRINTED FROM
JOURNAL OF PHYSICAL CHEMISTRY
VOL. 76, NO. 18, AUGUST 1972
P. 2584 - 2585

49333

BUILDING RESEARCH
- LIBRARY -
DEC 18 1972
NATIONAL RESEARCH COUNCIL

RESEARCH PAPER NO. 544
OF THE
DIVISION OF BUILDING RESEARCH

OTTAWA

DECEMBER 1972

PRICE 10 CENTS

NRCC 12897

L'ISOTHERME D'ADSORPTION ET LA DETERMINATION DE L'AIRE
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

*Building Materials Section, Division of Building Research, National Research Council of Canada,
Ottawa, Canada (Received March 13, 1972)*

Publication costs assisted by National Research Council of Canada

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 N₂ 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°_1 , 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°_1 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 N₂ 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

- (1) H. P. R. Frederikse, *Physica*, **15**, 860 (1949).
- (2) J. A. Morrison and L. E. Drain, *J. Chem. Phys.*, **19**, 1063 (1951).
- (3) J. A. Morrison, L. E. Drain, and J. S. Dugdale, *Can. J. Chem.*, **30**, 890 (1952).
- (4) K. S. Dennis, E. L. Pace, and Ch. S. Baughman, *J. Amer. Chem. Soc.*, **75**, 3267 (1953).
- (5) G. G. Litvan, *Can. J. Chem.*, **44**, 2617 (1966).
- (6) G. G. Litvan and R. McIntosh, *ibid.*, **41**, 3095 (1963).
- (7) E. W. Sidebottom and G. G. Litvan, *Trans. Faraday Soc.*, **67**, 2726 (1971).
- (8) R. A. Beebe, J. B. Beckwith, and J. M. Honig, *J. Amer. Chem. Soc.*, **67**, 1554 (1945).

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).

Acknowledgment. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

(9) J. M. Haynes, *J. Phys. Chem.*, **66**, 182 (1962).

(10) P. Chenebault and A. Schurenkamper, *ibid.*, **69**, 2300 (1965).

(11) R. H. van Dongen, J. H. Kaspersma, and J. H. DeBoer, *Surface Sci.*, **28**, 237 (1971).

(12) S. Brunauer, J. Skalny, and E. E. Bodor, *J. Colloid Interface Sci.*, **30**, 546 (1969).

(13) J. P. Hobson, *J. Phys. Chem.*, **73**, 2720 (1969).

(14) "Landolt-Börnstein Zahlenwerte und Funktionen," part 2a, Springer-Verlag, Berlin, 1960, p 4.

This publication is being distributed by the Division of Building Research of the National Research Council of Canada. It should not be reproduced in whole or in part without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division may be obtained by mailing the appropriate remittance (a Bank, Express, or Post Office Money Order, or a cheque, made payable to the Receiver General of Canada, credit NRC) to the National Research Council of Canada, Ottawa. K1A 0R6. Stamps are not acceptable.

A list of all publications of the Division is available and may be obtained from the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa. K1A 0R6.