Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.17021

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Volume 138, No. 2

PHYSICAL CHEMISTRY

M. G. KAGANER

ADSORPTION OF NITROGEN, ARGON, AND KRYPTON ON VARIOUS SURFACES AND DETERMINATION OF SURFACE AREA

(Presented by Academician M. M. Dubinin, 15 XII 1960)

The adsorption of nitrogen on various surfaces has been studied comparatively well over a wide range of relative pressures. Nitrogen is often used in determining specific surface area by the BET method. Recently the author proposed ([1]) a new method for determining surface area from adsorption in the monomolecular region, based on the use of the equation of M. M. Dubinin and L. V. Radushkevich. In that work nitrogen was also used as the adsorbate.

The main purpose of the present work was to investigate the adsorption of other gases, in particular argon and krypton, over a wide range of pressures and to test the possibility of using them to determine surface area by the new method. The adsorption of N_2, Ar, and Kr was measured* at 90° K and at pressures from $1 \cdot 10^{-4}$ to 500 mm Hg on four adsorbents: silica gel, silica aerogel, alumogel, and activated carbon. The measurements were carried out on an apparatus described earlier ([1]). The experimental data are presented in Figs. 1–4 in logarithmic coordinates.

According to the potential theory of adsorption, the adsorption potential ε is determined by the relation:

$$\varepsilon = RT\ln(p_s/p),$$

where R is the gas constant, p and T are the pressure and temperature of adsorption, and p_s is the pressure of the saturated vapor of the adsorbate. Adsorption isotherms of different vapors on one and the same adsorbent, plotted in coordinates a–ε, where a is the adsorbed amount, should, according to the potential theory, be affine. M. M. Dubinin and D. P. Timofeev ([2]) showed that the affinity coefficient in the first approximation is equal to the ratio of the molar volumes of the condensed phase of the adsorbates.

Fig. 1

Figure 1: Fig. 1

Fig. 2. Adsorption isotherms on silica aerogel. 1 –nitrogen, 2 –argon, 3 –krypton. $T = 90.1^{\circ}$K

Figure 2: Fig. 2. Adsorption isotherms on silica aerogel. 1 –nitrogen, 2 –argon, 3 –krypton. $T = 90.1^{\circ}$K

Fig. 1. Adsorption isotherms on silica gel S-U.
1 –nitrogen, 2 –argon, 3 –krypton. $T = 90.1^{\circ}$ K

Since in the present work all adsorption isotherms were obtained at one and the same temperature, the lines in Figs. 1-4 should be affine. The molar volume of liquid nitrogen at 90° K is greater than that of liquid argon and solid krypton. Consequently, the N_2 isotherm should lie somewhat below the Ar and Kr isotherms. As can be seen from the figures, this relation holds for carbon in the region of relative pressures greater than 0.001; analogous results for carbons were obtained by us with N_2 and Ar ([3]) and with N_2 and Kr ([4]). For the remaining sorbents (Figs. 1-3), the nitrogen isotherms lie considerably above the lines for the other gases, and the discrepancy increases as the pressure decreases. The same dependence was found in the measurements of the adsorption of N_2 and Ar on crystalline substances (see, for example, ([5], [6])). No satisfactory explanation of the nature of this phenomenon has been given.

A distinctive feature of nitrogen molecules, in comparison with the molecules of a number of other gases, is the presence of an appreciable permanent quadrupole moment ([7], [8]). For nitrogen it is equal to $1.5 \cdot 10^{-26}$ CGSE (r), whereas for oxygen it does not exceed $0.5 \cdot 10^{-26}$ CGSE (r), and in monatomic gases it is absent. This moment has no appreciable influence on the forces of interaction between molecules at comparatively large distances, as a result of which gaseous nitrogen is thermodynamically similar to Ar, Kr, O_2, and certain other gases ([9]).

Fig. 2. Adsorption isotherms on silica aerogel. *1* –nitrogen, *2* –argon, *3* –krypton. $T = 90.1^{\circ}$K

Theoretical calculations have shown ([10]) that the energy of interaction of the nitrogen quadrupole with the electrostatic field of the surface of a solid is fairly large and, in some cases, close in magnitude to the dispersion interaction energy. It was established ([8], [11]) that the interaction of quadrupoles with the surface is the reason for the increased heats of adsorption of N_2 and CO compared with Ar and O_2 on crystalline solids at low relative pressures. The increased adsorption of N_2 compared with Ar and Kr on silica gel and alumogel at low relative

---

* G. P. Tikhonova took part in carrying out the experiments.

Fig. 3. Adsorption isotherms on active alumogel. 1 —nitrogen, 2 —argon, 3 —krypton. $T = 90.1$°K

Figure 3: Fig. 3. Adsorption isotherms on active alumogel. 1 —nitrogen, 2 —argon, 3 —krypton. $T = 90.1$°K

Fig. 4. Adsorption isotherms on SKT carbon. 1—nitrogen, 2—argon, 3—krypton. $T = 90.1$°K

Figure 4: Fig. 4. Adsorption isotherms on SKT carbon. 1—nitrogen, 2—argon, 3—krypton. $T = 90.1$°K

pressures can also be explained by the interaction of the quadrupole with the surface, since these adsorbents have hydroxyl groups on their surface possessing a considerable dipole moment. Activated carbon is amorphous carbon; the interaction in adsorption here is caused mainly by dispersion forces. Therefore the N_2 isotherm on carbon is close to the Ar and Kr isotherms (Fig. 4). The deviation appearing at values of the degree of coverage $\theta < 0.3$ is evidently explained by the presence of a certain number of active sites with a sharply expressed structural heterogeneity.

Fig. 3. Adsorption isotherms on active alumogel. *1* —nitrogen, *2* —argon, *3* —krypton. $T = 90.1$°K

The presence of special features in nitrogen adsorption forces one to examine critically the method, based on it, for determining surface area. Comparative determination of surface area from the adsorption of N_2, Ar, Kr, and other gases has been carried out in a number of works (^{12}–^{18}). In these, as the initial quantity for the calculations, the area of the nitrogen molecule was taken, calculated from the density of the liquid and equal to 16.2 $Å^2$ at 77.4°K. Measurements showed that, in order to obtain data agreeing with the values found from nitrogen adsorption, it is necessary to take for the cross section of the molecules of other gases a value 1.2-1.5 times larger than ⋯

calculated from the density of the adsorbate in the condensed state. The calculated ratio of the area occupied by an adsorbate molecule to the area of an N_2 molecule, σ_x/σ_{N2}, is, at 77.4°K, 0.88 for Ar and 0.94 for Kr, whereas the experimental adsorption data give values of σ_x/σ_{N2} of 0.95—1.05 for Ar and 1.20—1.35 for Kr. In the opinion of a number of investigators, the reason is that adsorbate molecules occupy larger areas on a solid surface than in the condensed phase.

Fig. 4. Adsorption isotherms on SKT carbon. 1—nitrogen, 2—argon, 3—krypton. $T = 90.1$°K

The results of determining the surface from the adsorption isotherms shown in Figs. 1—4 are given in Table 1. Values are also given here for AG-2 carbon, calculated by us from the data of work (^{3}). a_m is the amount of nitrogen adsorbed in the monomolecular layer. The surface area of the adsorbent is readily determined from this quantity in the usual way. The values of σ_x/σ_{N2} were calculated by dividing the value of a_m for N_2 by the same value for Ar and Kr.

First of all it should be noted that calculations by the BET method and by the new method proposed by the author (^{1}) agree well with one another, the discrepancies not exceeding 3%. Consequently, for determining the surface by the new method, adsorption isotherms not only of N_2, but also of Ar and Kr, can be used.

Table 1

Results of surface determination from adsorption of N_2, Ar, and Kr at 90°K

Adsorbent	a_m, mmol/g: nitrogen, BET method	a_m, mmol/g: nitrogen, new method	σ_x/σ_{N2}: argon, BET method	σ_x/σ_{N2}: argon, new method	σ_x/σ_{N2}: krypton, BET method	σ_x/σ_{N2}: krypton, new method
Silica gel S-U	3.87	3.89	1.01	1.04	1.13	1.16
Silica aerogel	1.19	–	0.99	–	1.25	–
Activated alumina	1.09	1.12	1.00	0.97	1.23	1.24
SKT carbon	–	15.1	–	0.84	–	0.94
AG-2 carbon (^{3})	8.45	8.35	0.86	0.86	–	–

Processing of experimental data of other authors (^{3,6}) has shown that the new method gives surface-area values agreeing with the BET method also in the case of O_2 and Xe.

The values of σ_x/σ_{N2} for the first three adsorbents fall within the above-mentioned limits found by other authors, with the exception of the values for Kr on silica gel S-U. The values for carbons, however, are close to the quantities calculated from the density of the adsorbate. The data of work (^{4}) on adsorption on carbons of N_2, Kr, Xe, and other gases give analogous results.

The value of σ_{Kr}/σ_{Ar} is, on the average, both according to our data and according to previously published data, 1.25, whereas for silica gel S-U it is 1.15 and for

SKT carbon 1.12. This may be explained by the phenomenon of ultraporosity, since both adsorbents are very finely porous.

the mean pore radius, calculated by the formula $r = 2v/s$, is 10 Å for silica gel S-U, and 8 Å for SKT carbon.

Analysis of the experimental data, taking into account what has been set out above, permits the supposition that the main reason for the discrepancies in measurements of surface area from the adsorption of N_2 and other gases is the denser packing of N_2 molecules on surfaces containing dipoles and ions, owing to the interaction of the latter with the quadrupoles of nitrogen. This packing corresponds, apparently, to packing in solid rather than liquid nitrogen. Consequently, the calculated value of the area of an N_2 molecule must be considerably reduced. An analogous suggestion was recently made on the basis of comparative measurements of surface area by adsorption and electron-microscopic methods (^{16}).

Table 2

Areas occupied by molecules on a solid surface

Adsorbate	Area occupied by one molecule, Å^2 (90° K, from adsorption data)	Area occupied by one molecule, Å^2 (90° K, from density in the condensed state)	Area occupied by one molecule, Å^2 (78° K, from adsorption data)	Area occupied by one molecule, Å^2 (78° K, from density in the condensed state)
Argon	14.4	14.4	13.8	–
Nitrogen	14.4*	14.6***	13.7*	14.6***
Nitrogen	17.0**	17.0	16.1**	16.2
Krypton	18.0	17.5****	17.0	17.5****
Krypton				15.2
Oxygen	13.7	14.1	13.3	13.5

* Polar surfaces.
** Nonpolar surfaces.
*** Density in the solid state at the melting temperature.
**** Density in the liquid state at the melting temperature.

As the initial value it is more correct to take the area of a molecule of a monatomic adsorbate, for example Ar, which does not depend on the type of surface. It is more convenient to carry out the measurements at 90°, and not at 78° K, because argon solidifies at 84° K, whereas according to some data (^{19}) the adsorbed film is apparently in the liquid state even at 78° K. The value of the area of an argon molecule at 90° K, calculated from the density of the liquid, is 14.4 Å^2.

According to adsorption data, the area of an N_2 molecule is approximately equal to the area of an Ar molecule, which corresponds to packing in crystals of solid nitrogen. This strongly confirms the supposition expressed above. The values of molecular areas given in Table 2, calculated from adsorption data on the basis of the indicated area for Ar, are recommended for use in determining surface area. They agree well with the values determined from the density of the condensed phase.

I express my gratitude to A. I. Moroz for valuable advice in discussing the work.

All-Union Scientific Research Institute
of Oxygen Machinery

Received
15 XII 1960

REFERENCES

1. M. G. Kaganer, ZhFKh, **33**, 2202 (1959).
2. M. M. Dubinin, D. P. Timofeev, ZhFKh, **21**, 1213 (1947).
3. V. G. Fastovskii, A. E. Rovinskii, Tr. Vsesoyuzn. elektrotekhn. inst., issue 61, 485 (1958).
4. K. M. Nikolaev, M. M. Dubinin, Izv. AN SSSR, OKN, 1958, 1165.
5. A. G. Keenan, J. M. Holmes, J. Phys. Coll. Chem., **53**, 1309 (1949).
6. J. M. Honig, L. H. Reyerson, J. Phys. Chem., **56**, 140 (1952).
7. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, N. Y., 1954, p. 1028.
8. G. L. Kington, A. C. Macleod, Trans. Farad. Soc., **55**, 1799 (1959).
9. M. G. Kaganer, ZhFKh, **30**, 2691 (1956).
10. L. E. Drain, Trans. Farad. Soc., **49**, 650 (1953).
11. L. E. Drain, J. A. Morrison, Trans. Farad. Soc., **49**, 654 (1953).
12. R. A. Beebe, J. B. Beckwith, J. M. Honig, J. Am. Chem. Soc., **67**, 1554 (1945).
13. P. H. Emmett, M. Cines, J. Phys. Coll. Chem., **51**, 1248 (1947).

SovietRxiv

14. M. L. Corrin, J. Am. Chem. Soc., **73**, 4061 (1951).
15. H. L. Pickering, H. C. Eckstrom, J. Am. Chem. Soc., **74**, 4775 (1952).
16. K. Kodera, J. Onishi, Bull. Chem. Japan, **32**, 356 (1959).
17. M. M. Dubinin, E. G. Zhukovskaya et al., Izv. AN SSSR, OKN, 1960, 588.
18. G. L. Gaines, P. Cannon, J. Phys. Chem., **64**, 997 (1960).
19. V. Daneš, J. Nováková, Coll. Czechosl. Chem. Commun., **24**, 874 (1959).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.