Final Report of the IUPAC Taskgroup

PHYSISORPTION OF GASES, WITH SPECIAL REFERENCE TO THE EVALUATION OF SURFACE AREA AND PORE SIZE DISTRIBUTION

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY INCLUDING CATALYSIS*

REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984)

Prepared for publication by the Subcommittee on Reporting Gas Adsorption Data

Consisting of

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The recommendations given in this 1984 report have been broadly followed and referred to by the scientific and industrial community and has meanwhile more than 4000 citations according to Web of Science!

*Membership of the Commission during the period (1981—85) in which the report was prepared was as follows:

Chairman: 1981—83 J. Lykiema (Netherlands); 1983—85 K. S. W. Sing (UK); Vice-Chairman: 1981—85 J. Haber (Poland); Secretary: 1981—83 M. Kerker (USA); 1983—85 A. Wolfram (Hungary); Members: J. H. Block (FRG; Titular 1983—85, Associate 1981—83); N. V. Churaev (USSR; Associate 1981—85); D. H. Everett (UK; National Representative 1981—85); G. F.

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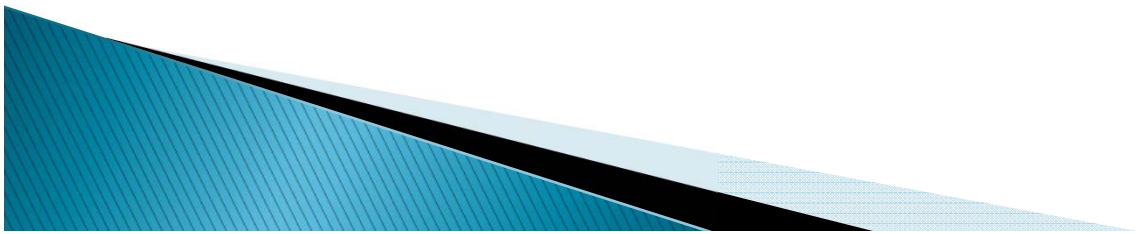
Need for Revisions/Update of 1985 Recommendations

- In the past 25 years major advances have been made in the development of nanoporous materials with uniform, tailor-made pore structures (e.g. mesoporous molecular sieves, carbon nanotubes and nanohorns, microporous-mesoporous carbons and silicas with hierarchical pore structures).

$\Rightarrow$ The characterization of these novel materials has required the development and refinement of high resolution experimental protocols for adsorption of various subcritical fluids (e.g., nitrogen at 77K, argon at 87K, carbon dioxide at 273 K)

$\Rightarrow$ Need for advancing the methods of analysis and interpretation of adsorption data (e.g. development of microscopic methods based on statistical mechanics based on DFT and molecular simulation)

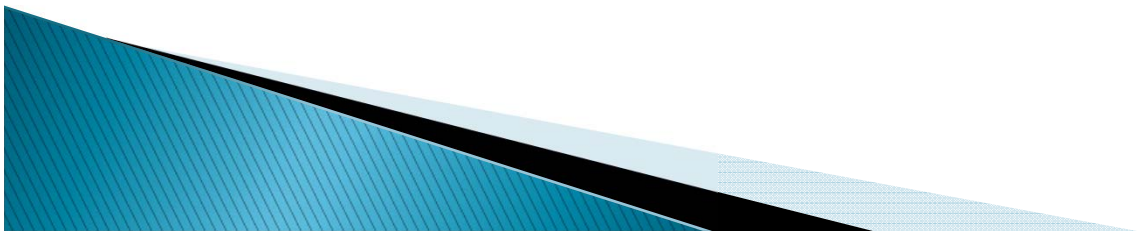


Objectives of the IUPAC Task Group

(i) To provide authoritative, up-to-date guidance on gas physisorption methodology

(ii) To draw attention to the advantages and limitations of using physisorption techniques for studying solid surfaces and pore structures with particular reference to the determination of surface area and pore size distribution.

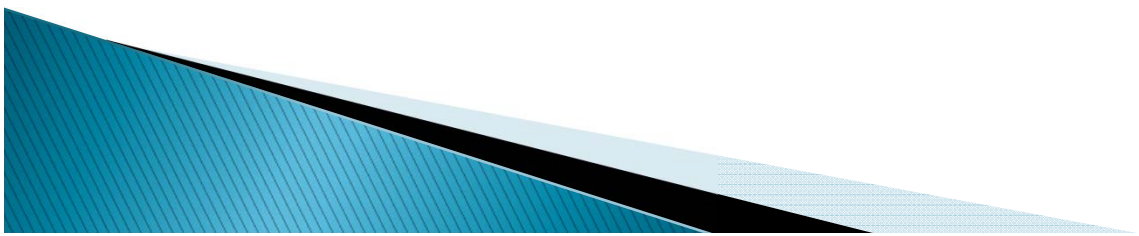
(iii) To publish this work as a IUPAC Technical Report, which should be considered as the update of the 1985 report.



OUTLINE OF PROPOSED TECHNICAL REPORT

1. INTRODUCTION
2. GENERAL DEFINITIONS AND TERMINOLOGY
3. METHODOLOGY AND EXPERIMENTAL PROCEDURES
4. EVALUATION OF ADSORPTION DATA
5. DETERMINATION OF SURFACE AREA
6. ASSESSMENT OF MICROPOROSITY
7. ASSESSMENT OF MESOPOROSITY
8. ASPECTS OF GAS ADSORPTION ON NON-RIGID ADSORBENTS

9 GENERAL CONCLUSIONS



Section 2: Classification of Pore Sizes

Nanopores : pore widths < 100 nm

Within the range of nanopores:

Micropores < 2 nm

Mesopores: 2- 50 nm

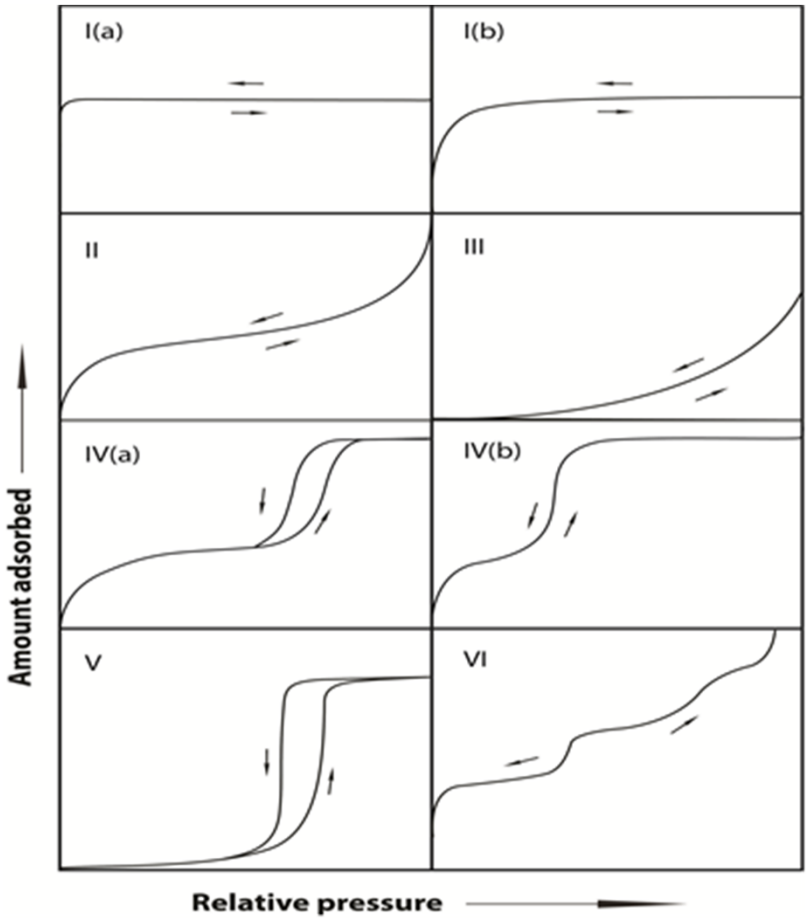
Macropores: > 50nm

Subclassification of Micropores:

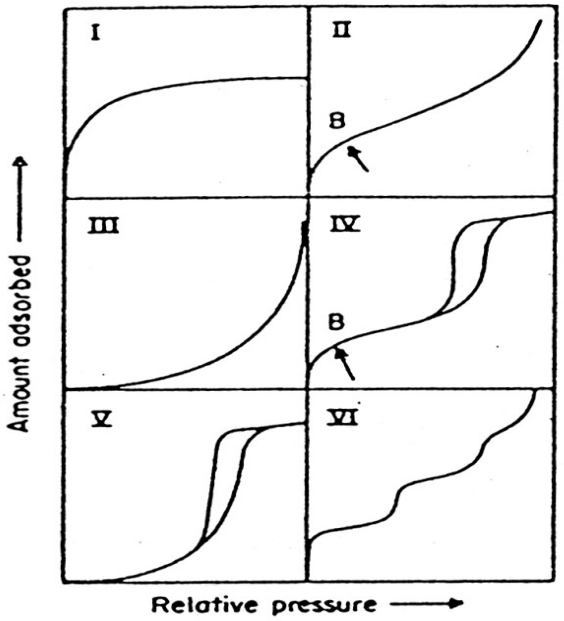
Narrow micropores ***< 0.7nm*** , often called *ultramicropores*

Wide micropores ***> 0.7 nm***, often called *supermicropores*

Section 4 : Updated Classification of Isotherm Types

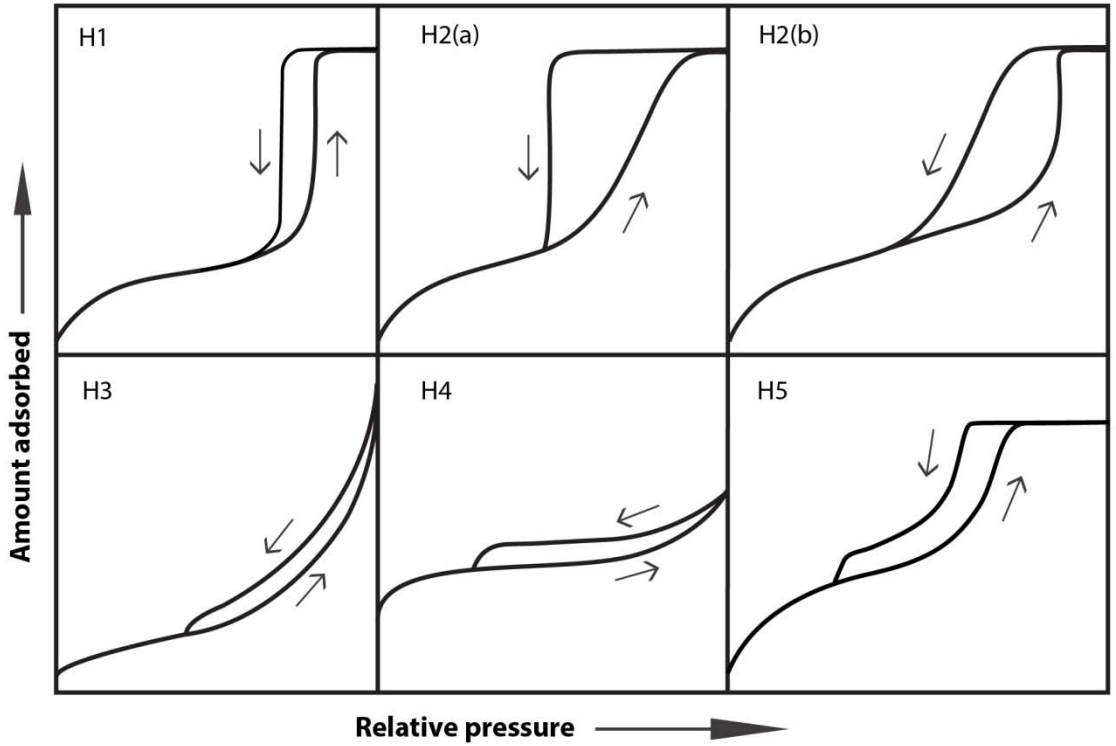


2014: Proposed classification of isotherm types

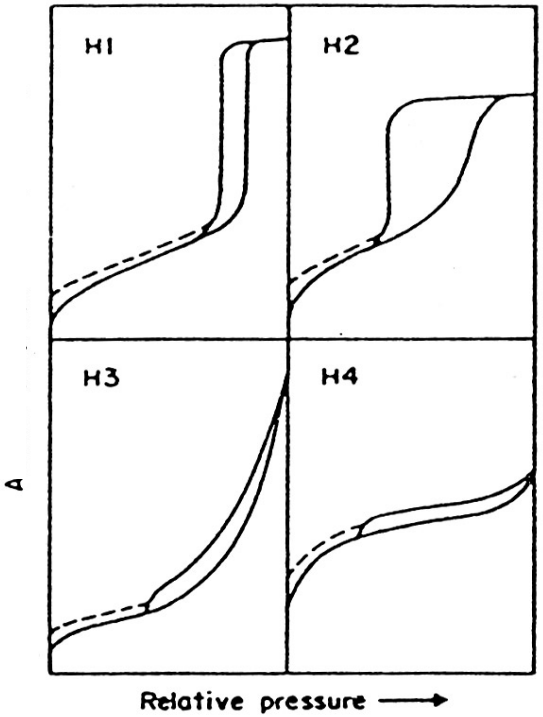


1984 recommendations

Section 4: Updated Classification of Hysteresis Loops



2014: Proposed classification of hysteresis loop types



1984 recommendations

Section 5: Surface Area Determination

●The Brunauer-Emmett-Teller (BET) method continues to be the most widely used procedure for evaluating the surface area of porous and finely-divided materials

●Under certain carefully controlled conditions, the BET-area of a non-porous, macroporous or a mesoporous solid (i.e. giving a well-defined Type II or a Type IVa isotherm) can be regarded as the probe accessible surface area

● In the presence of micropores (ie. Type I isotherms and combinations of Types I and II or Types I and IV isotherms) the application of the BET method only leads to an apparent surface area (i.e ***BET Area***) which serves as a useful "fingerprint" of the adsorbent.

In this case the linear range of the BET plot may be difficult to locate. A useful procedure suggested by Rouquerol et. al permits to overcome this difficulty and improves the reproducibility of the method.

Section 5 and 6: Surface Area, Micropore Analysis : *Choice of Adsorptive*

- **Pore Size/Volume characterization of microporous materials with polar surfaces, e.g. zeolites, MOFs**

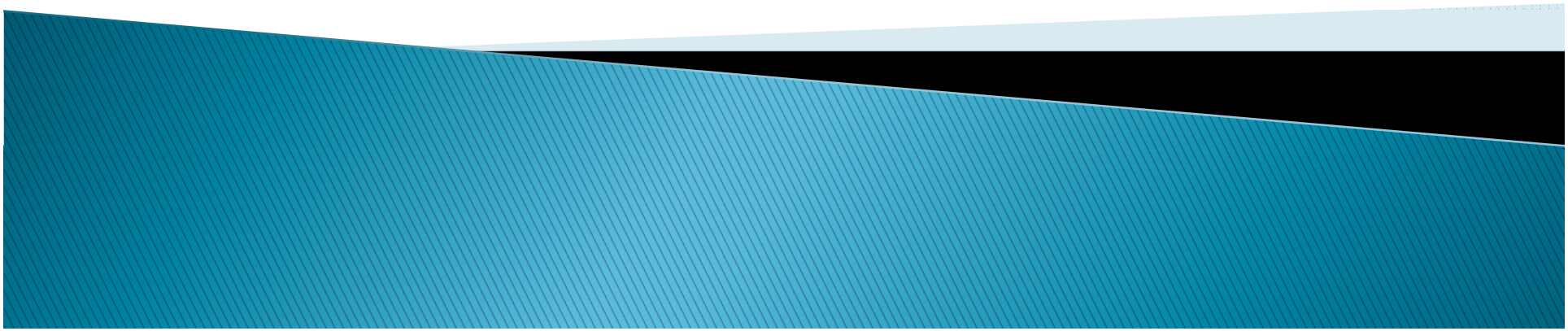
  ⇒ ***Argon 87 K***

- **Pore Size/Volume characterization of nanoporous carbons**

  ⇒ ***Combination of Carbon Dioxide (273K) with Nitrogen/Argon (at 77 K/87K)***

- **Surface area and pore size analysis of materials with ultra-low surface area (e.g. thin films) or**

  ⇒ ***Krypton adsorption at 77 K***



Sections 6 and 7 : Pore Size/Volume Analysis of Micro- and Mesopores

Classical, macroscopic methods

Micropores : e.g., Dubinin-Radushkevitch , Horvath-Kawazoe (HK), Saito-Foley (SF) , comparison plot methods (alpha-s method, t-method, Gurvich rule.

Meso/Macropores : e.g., Kelvin equation based methods such as BJH (Barrett,Joyner, Halenda), or BDB (Brockhoff & de Boer), Gurvich rule

Classical Methods underestimate the pore size for pores of diameters < 10 nm up to 20 – 30 % !

Modern, microscopic methods, based on statistical mechanics describe configuration of adsorbed molecules on a molecular level : e.g., *Density Functional Theory* (DFT), *Molecular Simulation*.

An accurate pore size analysis over the complete micro-and mesopore size range can be performed with a single method!

Section 9: General Conclusions

1 Major advances in adsorption science over the past 30 years include :

i. Preparation of nanoporous materials with uniform pore structures, which are now used as model adsorbents ;

ii. Introduction of high resolution adsorption techniques and reliable commercial instrumentation;

iii. Application of density functional theory (DFT) and molecular simulation.

2 The original IUPAC classifications of physisorption isotherms and hysteresis loops have been extended and refined to include new characteristic types, which are associated with certain well-defined adsorption systems.

Section 9: General Conclusions (Cont.)

3. Caution is required in applying the Brunauer-Emmett-Teller (BET) method for the assessment of surface area.

Use of a recommended procedure improves the reproducibility of the method when micropores are present, but one then obtains an apparent surface area (ie. ***BET area***) which serves as a useful "fingerprint" of the adsorbent.

4 The choice of adsorptive is crucial in the characterization of porous materials. Nitrogen at 77 K has been widely used, but the interpretation of the isotherm data is not always straightforward.

For various reasons, argon adsorption at 87 K is considered to be more reliable and is now recommended - particularly for micropore size analysis.

5 It is now evident that pore size analysis of narrow mesopores cannot be reliably achieved by the application of procedures based on the Kelvin equation, such as the Barrett-Joyner-Halenda (BJH) method. This traditional approach may still be useful, however, for routine work.

Section 9: General Conclusions (Cont.)

6. Density functional theory (DFT) based computational procedures are available in software packages and provide a reasonably reliable assessment of the nanopore size distribution (i.e. for both micro- and mesopores), provided that the given nanopore structure is compatible with the chosen DFT kernel.

7. The characterization of poorly ordered nanoporous and non-rigid adsorbents (e.g. certain MOFs) represents a major challenge. More work is also required on the development of new certified reference materials and improved procedures for routine data analysis.