Brunauer–Emmett–Teller (BET) surface area analysis: brief theory and instrumentation

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Outline

1. Definition-discovery & what technique does

2. Definition-theory of BET, adsorption vs. desorption and adsorbates

3. Types of pores

4. Equipment

5. Sample preparation

6. Results obtained from instrument/software
Definition

- Discovered by Stephen Brunauer, Paul Hugh Emmett and Edward Teller in 1938
- Studies physical adsorption of gas molecules on a solid surface
- Can therefore be used to study surface area & pore size distribution in given material
- Depends on $T$, $P$, surface energy distribution and surface area
<table>
<thead>
<tr>
<th>Surface area</th>
<th>BET, Langmuir, Temkin, Freundlich</th>
<th>Can be calculated from section of isotherm (generally $P/P_0=0.05-0.35$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Pore Volume</td>
<td>Kelvin equation</td>
<td>Generally carried out at $P/P_0 = 0.99 - 0.998$ although theoretically all pores should be full at $P/P_0=0.995$</td>
</tr>
<tr>
<td>Mesopore volume, area, and distribution</td>
<td>BJH, Dollimore-Heal</td>
<td>Requires full adsorption and desorption isotherms</td>
</tr>
<tr>
<td>Micropore distribution</td>
<td>Dubinin-Radushkevich and Astakhov, Horvath-Kawazoe, Saito-Foley, Cheng-Yang, MP method</td>
<td>Requires full adsorption isotherm</td>
</tr>
<tr>
<td>Pore size modeling</td>
<td>Density Functional Theory</td>
<td>Requires full adsorption isotherm</td>
</tr>
<tr>
<td>Surface energy</td>
<td>Density Functional Theory</td>
<td>Requires full adsorption isotherm</td>
</tr>
</tbody>
</table>
Definition

• Gases that adsorb onto material surface are called adsorbates

• These gases should not chemically react with material surfaces

• Most common adsorbate is $N_2$
  • Ar, CO, CO$_2$, and O$_2$ may also be used
  • Volume of gas adsorbed is measured at boiling point of nitrogen (-196 °C)
Definition

- **Adsorption vs. desorption:**
  - **Adsorption** is the sticking of gas molecules onto the surface of a solid.
  - **Desorption** is the removal of gas molecules from the surface of a solid.
  - These include surfaces inside open pores.
Definition

• When the interaction between a surface and an adsorbate is relatively weak only \textbf{physisorption} takes place

• When electrons available for chemical bond formation on surface atoms, \textbf{chemisorption} occurs

• activation energy-adsorbate molecules must overcome an energy barrier
Pore classification

- Microporous <2nm
- Mesoporous 2-50nm
- Macroporous >50nm
Definition

• Assumptions:

1. Homogeneous surface- adsorption occurs across entire surface with no preference for one or more sites
   • Each site is either unoccupied or occupied by a single adsorbate molecule
   • Once adsorbed, molecule can act as sorption site for another gas molecule
Definition

• Assumptions:

2. All sites on the surface are equal

3. No lateral interactions between molecules

4. Adsorbate molecule is immobile

5. The rate of adsorption is equal to the rate of desorption
Equipment

- Programmable two-station degas system
- Isothermal jacket
- Vacuum cold trap
- Long-duration Dewar (more than 72 hours)
Equipment

- Chemi analysis port
- Mass Spec port and cooling fan
- Dual vacuum pump system (inside)
- Chemi furnace
- Vapor inlet
- Six gas inlet ports (Physisorption)
- Six gas inlet ports (Chemisorption)
- Degas backfill inlet
- Free-space helium inlet
- Chemi exhaust and furnace cooling system
Sample preparation

- Clean, pure & dry sample
- Measurement of sample mass
- Degassing the sample using heat & vacuum
- Heating releases water vapor
- Measuring adsorption
- Analyzing measurement
Sample preparation

Measuring surface area with BET

1 - Degas
   Heat and evacuate (or add N₂)

2 - Evacuate
   Apply vacuum to tubes

3 - Volume
   Measure dead volume with He

4 - Evacuate
   Apply vacuum to tubes

5 - Adsorption
   Add N₂ for adsorption isotherm

6 - Desorption
   Evacuate N₂ for desorption isotherm

OPTIONAL
Isotherms

- 6 isotherms & BET applicable to:
  - type II (disperse, nonporous or macroporous solids)
  - type IV (mesoporous solids; pore diameter 2-50 nm)
The BET linear equation

\[
\frac{1}{W \left( \left( \frac{P_0}{P} \right) - 1 \right)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right)
\]

- \( W \) = weight of gas adsorbed
- \( P/P_0 \) = relative pressure
- \( W_m \) = weight of adsorbate as monolayer
- \( C \) = BET constant
<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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<tbody>
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</table>
Results obtained
Results obtained

BET Surface Area Report
BET Surface Area: 49.5820 ± 0.7249 m²/g
Slope:  0.087270 ± 0.001264 g/cm³ STP
Y-Intercept: 0.000528 ± 0.000221 g/cm³ STP
C: 166.425263
Qm: 11.3898 cm³/g STP
Correlation Coefficient: 0.9991614
Molecular Cross-Sectional Area: 0.1620 nm²

<table>
<thead>
<tr>
<th>Relative Pressure (P/P₀)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(P₀/P - 1)]</th>
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<tbody>
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</table>
Conclusions

• BET can be used for:

1. Fibers

2. Nanocatalysts (chemisorption)

3. Nanotubes

4. Polymer membranes
References

https://www.iitk.ac.in/che/pdf/resources/BET-TPX-Chemi-reading-material.pdf


https://andyjconnelly.wordpress.com/2017/03/13/bet-surface-area/