

A New Classification of Adsorption Isotherms

When a gas comes into contact with a solid surface, molecules of the gas will adsorb (stick) to the surface in quantities that are a function of their partial pressure in the bulk. The measurement of the amount of gas adsorbed over a range of partial pressures at a single temperature results in a graph known as an adsorption isotherm. Many different types of isotherms have been observed in the literature^{1,2}; these isotherms can have very different shapes depending on the type of adsorbent, the type of adsorbate, and intermolecular interactions between the gas and the surface.

The first systematic attempt to interpret adsorption isotherms for gas-solid equilibria was introduced by Brunauer, Deming, Deming, and Teller³ (BDDT) in 1940. These authors classified isotherms into five types. The BDDT classification has become the core of the modern IUPAC classification of adsorption isotherms^{4,5}; these BDDT isotherms and an additional one introduced much later by Sing, which completes the IUPAC classification, are illustrated in Figure 1. Type I isotherms characterize microporous adsorbents. Types II and III describe adsorption on macroporous adsorbents with strong and weak adsorbate-adsorbent interactions, respectively. Types IV and V represent adsorption isotherms with hysteresis. Finally, type VI has steps. The BDDT and IUPAC classifications have two deficiencies: they are incomplete and they give the incorrect impression that adsorption isotherms are always monotonic functions of pressure. This is because the IUPAC classification only takes into account adsorption at subcritical temperatures.

In this project, we analyzed available experimental data and predictions from lattice density functional theory (DFT), a theoretical tool which has been developed by our research group. From this study, we have proposed a new classification of adsorption isotherms. This new classification scheme is shown in Figure 2.

While general, this new classification is meant to be qualitative and does not show all possible details. In this classification, Type I shows adsorption isotherms on microporous adsorbents for subcritical, near critical, and supercritical conditions. Notice that the isotherm is not mono-

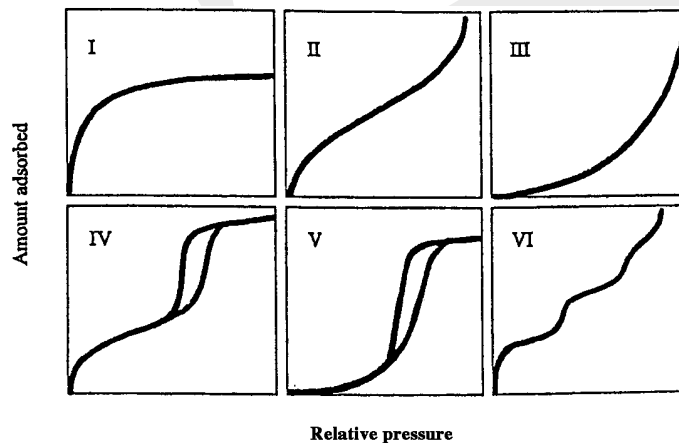


Figure 1: The IUPAC classification for adsorption isotherms.

tonic at supercritical conditions. Types II and III give adsorption isotherms on macroporous adsorbents with strong and weak affinities, respectively. For low temperatures these Types have steps, but increasing temperature transforms them into the smooth monotonic curves which are like those in Types II and III of the IUPAC classification. However, near the critical temperature these isotherms change dramatically to non-monotonic behavior showing sharp maxima, and further increase in temperature leads to isotherms with smooth maxima. Types IV and V characterize mesoporous adsorbents with strong and weak affinities, respectively. For lower temperatures they show adsorption hysteresis.

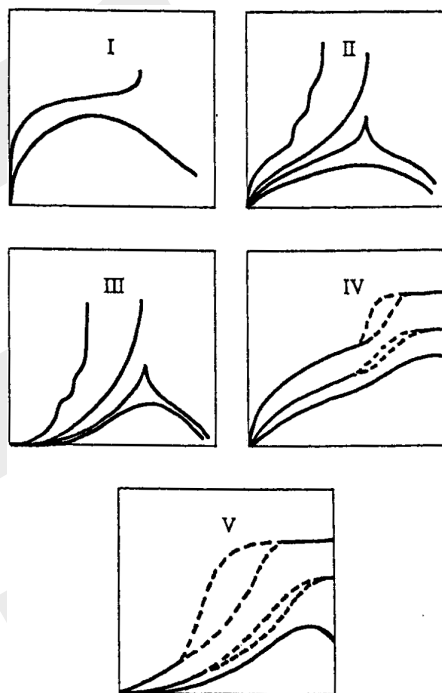


Figure 2: A new classification for adsorption isotherms.

¹Findenegg, G. H. *Fundamentals of Adsorption*; Engineering Foundation: New York, 1984, pp. 207-218.

²Nolan, J. T.; McKeehan, T. W.; Danner, R. P. *J. Chem. Eng. Data* **1981**, 26, 112.

³Brunauer, S.; Deming, L.; Deming, W.; Teller, E. *J. Am. Chem. Soc.* **1940**, 62, 1723.

⁴IUPAC Recommendations *Pure Appl. Chem.* **1985**, 57, 603.

⁵IUPAC Recommendations *Pure Appl. Chem.* **1994**, 66, 1739.