

Calculation of Pressure-Varying Langmuir and Brunauer-Emmett-Teller Isotherm Adsorption Parameters

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Abstract : Gas-solid physical adsorption methods are central to the characterization and optimization of the effective surface area, pore size and porosity for applications such as heterogeneous catalysis, and gas separation and storage. Properties such as adsorption uptake, capacity, equilibrium constants and Gibbs free energy are dependent on the composition and structure of both the gas and the adsorbent. However, challenges remain, in accurately calculating these properties from experimental data. Gas adsorption experiments involve measuring the amounts of gas adsorbed over a range of pressures under isothermal conditions. Various constant-parameter models, such as Langmuir and Brunauer-Emmett-Teller (BET) theories are used to provide information on adsorbate and adsorbent properties from the isotherm data. These models typically do not provide accurate interpretations across the full range of pressures and temperatures. The Langmuir adsorption isotherm is a simple approximation for modelling equilibrium adsorption data and has been effective in estimating surface areas and catalytic rate laws, particularly for high surface area solids. The Langmuir isotherm assumes the systematic filling of identical adsorption sites to a monolayer coverage. The BET model is based on the Langmuir isotherm and allows for the formation of multiple layers. These additional layers do not interact with the first layer and the energetics are equal to the adsorbate as a bulk liquid. This BET method is widely used to measure the specific surface area of materials. Both Langmuir and BET models assume that the affinity of the gas for all adsorption sites are identical and so the calculated adsorbent uptake at the monolayer and equilibrium constant are independent of coverage and pressure. Accurate representations of adsorption data have been achieved by extending the Langmuir and BET models to include pressure-varying uptake capacities and equilibrium constants. These parameters are determined using a novel regression technique called flexible least squares for time-varying linear regression. For isothermal adsorption the adsorption parameters are assumed to vary slowly and smoothly with increasing pressure. The flexible least squares for pressure-varying linear regression (FLS-PVLR) approach assumes two distinct types of discrepancy terms, dynamic and measurement for all parameters in the linear equation used to simulate the data. Dynamic terms account for pressure variation in successive parameter vectors, and measurement terms account for differences between observed and theoretically predicted outcomes via linear regression. The resultant pressure-varying parameters are optimized by minimizing both dynamic and measurement residual squared errors. Validation of this methodology has been achieved by simulating adsorption data for n-butane and isobutane on activated carbon at 298 K, 323 K and 348 K and for nitrogen on mesoporous alumina at 77 K with pressure-varying Langmuir and BET adsorption parameters (equilibrium constants and uptake capacities). This modeling provides information on the adsorbent (accessible surface area and micropore volume), adsorbate (molecular areas and volumes) and thermodynamic (Gibbs free energies) variations of the adsorption sites.

Keywords : Langmuir adsorption isotherm, BET adsorption isotherm, pressure-varying adsorption parameters, adsorbate and adsorbent properties and energetics

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