

Henry's Law and Isothermic Heats in Physisorbents

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Effective physisorbents require both high surface area and high adsorption enthalpies. There are two enthalpies that can be determined readily from sorption isotherms. The Henry's law region at low pressures yields the differential enthalpy at zero coverage and provides a single convenient enthalpy value. The enthalpy can also be determined from isosteric heat measurements from the same isotherm data, provided that the data is taken over a high-pressure range that includes the surface excess maximum. While the two quantities are similar at low coverage, and while the direct measurement of the Henry's law value is the easiest to determine, the isosteric heat yields the most useful data as it plots enthalpy as a function of hydrogen loading. Ideally, the sorption heats are constant as a function of ad-atom/molecule coverage density. This is typically not the case due to sorption site heterogeneities that are typical of real surfaces, and due to hydrogen-hydrogen interactions that occur at higher pressures. Examples of systems with initially high sorption enthalpies are coordinatively unsaturated metal centers as found in framework structures like Prussian blues and some metal organic frameworks. After the initial high enthalpy site(s) adsorb hydrogen, only surfaces with weaker adsorption enthalpies are then available. We will discuss this behavior in a MOF-74 structure which shows an initially high isosteric enthalpy of 8.8kJ/mole, but which drops to half of that value within 2wt% of gravimetric uptake.