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Hydrogen cryo-adsorption; comparing low pressure and isosteric heats[1]

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The two criteria for effective physisorbents for hydrogen storage are high surface area and high adsorption heats. There are two heats that can be determined readily from the sorption isotherm. At very low pressures corresponding to low surface coverages, we can consider the differential enthalpy at zero coverage, determined from the temperature dependence of the Henry's Law constant which is in turn determined by the low pressure isotherm slope. The differential enthalpy can also be determined from isosteric heat measurements from the same data, provided that data is taken over a higher pressure range that includes the saturation limit. We have found that the two quantities are of similar magnitude, and while the direct measurement of the differential enthalpy is the easiest to perform, the requirements necessary in determining the isosteric heat yield the most useful data. 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. Consequently, this value drops as a function of pressure. The consequence of this is that materials that show initially high sorption values at low pressure, do not typically yield high gravimetric saturation values. We will discuss this behavior in metal organic frameworks, activated carbons and carbon aerogels. All of these materials can have high surface area but the adsorption heats are typically 4–7 kJ/mole. We have measured the highest gravimetric hydrogen sorption in an activated carbon.

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