# Synthesis and Thermodynamic Studies of Physisorptive Energy Storage Materials

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“Be glad of life,
for it gives you the chance
to love and to work and to play
and to look up at the stars…”
- Henry van Dyke

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## Abstract

Physical adsorption of hydrogen or other chemical fuels on the surface of carbonaceous materials offers a promising avenue for energy storage applications. The addition of a well-chosen sorbent material to a compressed gas tank increases the volumetric energy density of the system while still permitting fast refueling, simplicity of design, complete reversibility, high cyclability, and low overall cost of materials. While physical adsorption is most effective at temperatures below ambient, effective storage technologies are possible at room temperature and modestly high pressure. A volumetric Sieverts apparatus was designed, constructed, and commissioned to accurately measure adsorption uptake at high pressures and an appropriate thermodynamic treatment of the experimental data is presented.

In Chapter 1, the problem of energy storage is introduced in the context of hydrogen as an ideal alternative fuel for future mobile vehicle applications, and with methane in mind as a near-term solution. The theory of physical adsorption that is relevant to this work is covered in Chapter 2. In-depth studies of two classes of materials are presented in the final chapters. Chapter 3 presents a study of the dissociative “hydrogen spillover” effect in the context of its viability as a practical hydrogen storage solution at room temperature. Chapters 4-5 deal with zeolite-templated carbon, an extremely high surface-area material which shows promise for hydrogen and methane storage

applications. Studies of hydrogen adsorption at high pressure (Chapter 4) and anomalous thermodynamic properties of methane adsorption (Chapter 5) on ZTCs are presented. The concluding chapter discusses the impact of and possible future directions for this work.

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# Nomenclature

| Symbol | Description | Default Unit |
|---|---|---|
| t | time | s |
| P | pressure | MPa |
| T | temperature | K |
| V | volume | mL |
| R | gas constant | kJ $K^{-1}$ $mol^{-1}$ |
| n | molar number | mol |
| $n_{ads}$ | molar number adsorbed | mol |
| $n_e$ | specific excess (adsorption) uptake | mmol $g^{-1}$ |
| $n_a$ | specific absolute (adsorption) uptake | mmol $g^{-1}$ |
| U | potential energy | kJ |
| F | Helmholtz free energy | kJ |
| G | Gibbs free energy | kJ |
| μ | chemical potential | kJ $mol^{-1}$ |
| S | entropy | J $K^{-1}$ |
| s | specific entropy | J $mol^{-1}$ $K^{-1}$ |
| H | enthalpy (of adsorption) | kJ |
| h | specific enthalpy (of adsorption) | kJ $mol^{-1}$ |
| Δh | specific differential enthalpy (of adsorption) | kJ $mol^{-1}$ |
| $q_{st}$ | isosteric heat (of adsorption) | kJ $mol^{-1}$ |
| $n_{max}$ | adsorption scaling factor | mmol $g^{-1}$ |
| α | weight factor | - |
| θ | Langmuir surface coverage | - |
| ρ | density | g $mL^{-1}$ |
| $V_a$ | volume of adsorbed molecule | $Å^3$ |
| $V_{ads}$ | specific volume of adsorption layer | mL $g^{-1}$ |
| $V_{max}$ | maximum specific volume of adsorption layer | mL $g^{-1}$ |
| A | (surface) area | $m^2$ |
| $A_{BET}$ | specific BET surface area | $m^2$ $g^{-1}$ |
| $t_{ads}$ | thickness of adsorbed layer | Å |
| $V_s$ | volume of solid sorbent | mL |