Chapter 3

Experimental Methods and Analysis

1. Equipment

The fundamental basis of quantitative adsorption analysis is the measurement of excess adsorption isotherms. Each isotherm comprises a series of excess adsorption uptake values, measured stepwise at increasing pressures and a constant temperature. At high pressure, the excess adsorption becomes non-monotonic as a function of pressure, after reaching an excess adsorption maximum. A desorption isotherm may be measured in reverse, by starting with a preloaded adsorbent at high pressures and reducing the pressure stepwise. Observed hysteresis between pairs of adsorption and desorption isotherms yields valuable information about the adsorptive system, often indicating the presence of capillary condensation in mesopores.

In this thesis, excess adsorption isotherms were measured by the volumetric method also known as the Sieverts' method using a custom Sieverts apparatus designed and tested for accuracy up to 10 MPa (Figure 1).[1] The Sieverts apparatus comprises a number of rigid, stainless steel, and leak-proof compartments, each interconnected with controllable on-off valves (either hand-turned or pneumatic). The volume of each compartment is known with high precision (± 0.01 mL). For standard adsorption measurements, only two of the compartments are of interest: the manifold and the reactor. The manifold is equipped with a midrange (3000 PSI) MKS Baratron (Model 833) pressure transducer for high-pressure measurements and an MKS Baratron (Model 120AA) for low-pressure measurements of higher resolution. The temperature of the gas in the manifold was measured with platinum resistance thermometers. The temperature of the reactor was monitored with K-type thermocouples. In a preparatory step the adsorbent sample of interest was weighed and sealed within the reactor, which seals by the tightening of a conflat flange with a copper gasket. Additional nickel filter gaskets with a 0.5-micron mesh size prevented the adsorbent from escaping from the reactor. After sealing the reactor, each sample was degassed at ~520 K under a vacuum of less than 10^{-3} Pa prior to testing. The Sieverts apparatus is equipped with a molecular drag pump capable of achieving a vacuum of 10^{-4} Pa and vacuum pressures were verified using a digital cold cathode pressure sensor (I-MAG, Series 423). To obtain low temperature isotherms, the reactor was submerged in a circulated chiller bath or cryogenic bath with temperature fluctuations no larger than ± 0.1 K. High temperature isotherms were obtained by encasing the reactor in a copper heat conductor wrapped with insulating fiberglass heating tape. Using a proportional integral derivative (PID) controller, the reactor temperature was maintained with fluctuations no larger than ± 0.4 K. Prior to measurements, the entire Sieverts was purged multiple times with the gas of interested to eliminate any impurity residues. On each sample, multiple adsorption/desorption isotherms were taken to ensure complete reversibility and identical measurements were found to be reproducible to within 1% error.

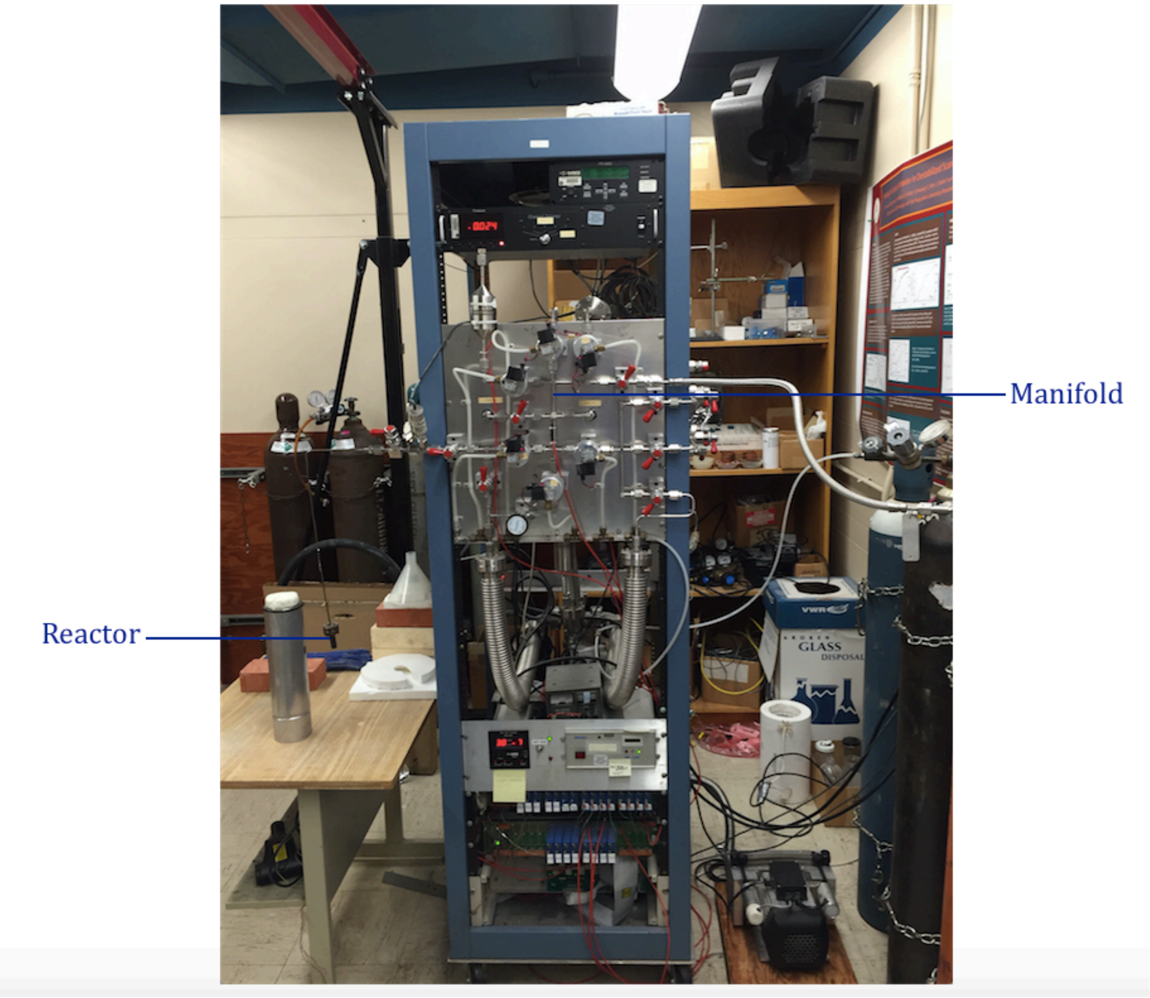

Figure 1. Sieverts Apparatus

2. Methodology

For each isotherm data point, a predetermined pressure of research-grade gas was introduced into and cached in the manifold. Upon reaching equilibrium, the temperature and pressure of this gas were measured with high precision and the gas density was determined from REFPROP data tables[2]. Given that the manifold volume is known, the moles of gas in the manifold were thus determined. Next, a valve was opened to allow the gas to occupy both the manifold and reactor volumes. The reactor housed the porous sample of known mass. Upon opening the valve, the gas was allowed to occupy a volume given by the sum of the manifold and reactor volumes minus the volume of the sample. The volume of the sample was given by the product of the sample mass and the sample skeletal density (obtained by helium pycnometry). Once equilibrium was reestablished, pressure and temperature measurements were taken and a final gas-phase density determined for the step. The moles of gas left in the gas phase were thus calculated. Any quantity of gas introduced into the manifold, but no longer contributing to the gas-phase pressure was considered to be in the adsorbed phase. The sample within the reactor was held at a constant temperature over the course of a successive set of pressure measurements, resulting in an excess adsorption isotherm. Upon completion of an isotherm, the temperature was adjusted for the next isotherm, in order to measure a multitude of isotherms over a wide temperature range.

At equilibrium the chemical potential of the gas phase (μ_g) and the adsorbed phase (μ_a) are equal

$$\mu_a = \mu_g \tag{1}$$

By taking the total differential of both sides of Equation 1:

$$-s_a dT + v_a dP = -s_g dT + v_g dP \tag{2}$$

$$\frac{dP}{dT} = \frac{(s_g - s_a)}{(v_g - v_a)} \tag{3}$$

Thus the derivative of pressure with respect to temperature is related to the change in entropy (upon adsorption) divided by the change in volume (upon adsorption). At constant coverage, the difference between the entropy of the adsorbed phase (S_a) and the entropy of the gas phase (S_g) is the isosteric entropy of adsorption (ΔS_{ads}) and is given by Equation 4.

$$\Delta S_{ads} = S_a - S_g \tag{4}$$

$$\Delta S_{ads} = \left(v_g - v_a\right)\frac{dP}{dT} \tag{5}$$

The isosteric entropy of adsorption is in turn related to isosteric enthalpy of adsorption (ΔH_{ads}) by Equation 6

$$\frac{\Delta H_{ads}}{T} = \Delta S_{ads} \tag{6}$$

At constant coverage, the difference between the adsorbed and gas-phase enthalpies is thus given by Equation 7

$$\Delta H_{ads} = T\left(v_g - v_a\right)\frac{dP}{dT} \tag{7}$$

This is the Clapeyron equation, and is fundamental to the calculation of the isosteric enthalpy of adsorption. A number of simplifying assumptions may be made in dealing with the Clapeyron equation. The two most common are as follows:

1. That the volume of the gas phase is significantly larger than that of the adsorbed phase such that the overall change in volume is well approximated as the gas-phase volume.
2. That the gas follows the ideal gas law.

Together these assumptions transform the Clapeyron equation into Equation 8

$$\Delta H_{ads}(n_a) = -\frac{RT^2}{P}\left(\frac{dP}{dT}\right)_{n_a} \tag{8}$$

This may in turn be rearranged into the Van't Hoff form:

$$\Delta H_{ads}(n_a) = R\left(\frac{dln\, P}{d\left(\frac{1}{T}\right)}\right)_{n_a} \tag{9}$$

By plotting ln(P) vs ($1/T$), a Van't Hoff plot is formed. The slope of the Van't Hoff plot multiplied by R gives the isosteric heat. In common practice, adsorption measurements directly determine excess adsorption (n_e), not absolute adsorption (n_a). It is thus common to hold excess adsorption, not absolute adsorption, constant in Equation 9. This results in an isoexcess enthalpy of adsorption that approximates the isosteric enthalpy of adsorption, but only at low gas densities. The previously mentioned assumptions fail when applied broadly to gas data. Thus we must consider alternatives to these oversimplifying assumptions.

First, the ideal gas assumption may be avoided by inserting values from gas data tables directly into the Clapeyron equation. This is the course of action followed in this thesis. Using gas data tables enables thermodynamic calculations outside of the ideal gas regime. Second, the simplified Clausius-Clapeyron equation assumes that the adsorbed phase has virtually zero volume and that the net difference between the molar volume of the gas phase and the adsorbed phase equals the molar volume of the gas phase. In reality, the adsorbed phase has a finite molar volume that approaches that of the liquid phase of the adsorbed species. Thus the assumption of a zero molar volume adsorbed phase may be replaced with one of two options. Either the adsorbed-phase molar volume is assumed to be equal to that of the liquid phase molar volume, or, fit functions are used to approximate the adsorbed-phase molar volume.

In applying the Clapeyron equation, it is necessary to take the derivative of pressure with respect to temperature at constant coverage conditions. Where absolute adsorption is held constant, this determines the isosteric enthalpy of adsorption and where the excess adsorption is held constant, this determines the isoexcess enthalpy of adsorption. In practice, however, neither absolute nor excess adsorption is an experimentally tunable variable. The uptake quantity is never directly selected, rather the pressure is roughly selected. Thus obtaining data points at constant coverage conditions is not simple. In some cases, with sufficient data, constant coverage conditions across a number of temperatures may be achieved for select data points by pure coincidence. This can be thought of as "analysis without fitting". Fortuitously positioned data points, however, are sparse and unreliable.

In general it is necessary to establish an interpolation function to interpolate between the measured data points. Interpolation functions of a variety of forms have been employed in literature. The simplest entails linear interpolation between data points.

While simple, this approach fails to accurately capture the adsorption behavior, leading to scatter and errors. In this thesis research I employ a superposition of Langmuir isotherms as the fitting function of choice. Specifically, starting from the definition of excess adsorption (n_e):

$$n_e = n_a - V_a\rho(P,T) \tag{10}$$

I fit the absolute adsorption (n_a) and the volume of the adsorption layer (V_a) with superpositions of Langmuir isotherms with appropriate prefactors:

$$n_a(P,T) = n_{max}\sum_i a_i\left(\frac{K_iP}{1+K_iP}\right) \tag{11}$$

$$V_a(P,T) = V_{max}\sum_i a_i\left(\frac{K_iP}{1+K_iP}\right) \tag{12}$$

where a_i is the respective weight of the i^{th} isotherm$(\sum_i \propto_i = 1)$, P is the pressure, and K_i is an equilibrium constant given by an Arrhenius-type equation such that:

$$K_i = \frac{A_i}{\sqrt{T}}e^{\frac{-E_i}{RT}} \tag{13}$$

where A_i is a prefactor and E_i is an energy of the i^{th} isotherm. Altogether the fit function becomes:

$$n_e(P,T) = (n_a - V_{max}\rho(P,T))\sum_i a_i\left(\frac{K_iP}{1+K_iP}\right) \tag{14}$$

One particular advantage of this fitting procedure is that the absolute adsorption is easily accessible. It is one of the quantities that is directly fitted and given by Equation 11.

Absolute adsorption is a more fundamental quantity than excess adsorption, and its determination is critical for in-depth analysis of the adsorption physics.

In addition to producing high quality fits, the dual-Langmuir fitting method used in this thesis gives physically realistic fitting parameters. In particular the n_{max} and v_{max} parameters have been found to be in reasonable agreement with independently determined physical data (See Chapter 9). The n_{max} parameter gives the maximum possible absolute adsorption as determined by fits. This is directly comparable to an estimate of the maximum possible adsorption as obtained by multiplying the measured micropore volume by the liquid density of the adsorptive species[2]. Here we assume that the entirety of the micropores is filled with adsorbate at a density equal to the liquid density (upon maximal adsorption). Furthermore, the v_{max} parameter indicates the maximum possible volume of the adsorbed phase, which may be directly compared to the measured micropore volume of the adsorbent.

While the isosteric enthalpy of adsorption (ΔH_{ads}) is a popularly cited proxy metric of binding site energy, a more fundamental metric exists in the adsorbed-phase molar enthalpy (H_a) given by Equation 15. The isosteric enthalpy of adsorption is the difference between the adsorbed-phase and gas-phase (H_g) molar enthalpies and thus retains a dependence on gas-phase properties.

$$H_a = H_g + \Delta H_{ads} \tag{15}$$

For nonideal gas conditions, this dependence can obscure interesting phenomenon occurring strictly within the adsorbed phase. The gas-phase enthalpy is obtained from reference tables[2]. The adsorbed-phase enthalpy gives critical insight into the nature of the adsorbent-adsorbate binding-site energy. Moreover, the constant pressure molar heat capacity of the adsorbed phase (C_P) follows directly from the adsorbed-phase enthalpy (Equation 16):

$$C_P = \left.\frac{dH_a}{dT}\right|_P \tag{16}$$

The adsorbed-phase molar heat capacities provide critical qualitative insight into the adsorbed-phase layer. For a monatomic gas like krypton, comparison to theoretical estimates of the heat capacity provides further means to peer into the underpinnings of the adsorbed-phase thermodynamics. Furthermore, the isosteric entropy of adsorption (ΔS_{ads}) is directly accessible from the isosteric enthalpy of adsorption:

$$\Delta S_{ads} = \frac{\Delta H_{ads}}{T} \tag{17}$$

By adding the isosteric entropy of adsorption to the gas-phase molar entropy (from REFPROP[2]), we obtain the adsorbed-phase molar entropy (S_a).

$$S_a = S_g + \Delta S_{ads} \tag{18}$$

References:

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2. Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP,* version 8.0; National Institute of Standards and Technology: Gaithersburg, MD, 2007; CD-ROM.