

Direct Determination of Enthalpies of Sorption Using Pressure-Gradient Differential Scanning Calorimetry: CO₂ Sorption by Cu-HKUST

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Enthalpy of sorption (ΔH) is an important parameter for the design of separation processes using adsorptive materials. A pressure-ramped calorimetric method is described and tested for the direct determination of ΔH values. Combining a heat-flow thermogram with a single sorption isotherm enables the determination of ΔH as a function of loading. The method is validated by studying CO₂ sorption by the well-studied metal-organic framework Cu-HKUST over a temperature range of 288–318 K. The measured ΔH values compare well with previously reported data determined by using isosteric and calorimetric methods. The pressure-gradient differential scanning calorimetry (PGDSC) method produces reliable high-resolution results by direct measurement of the enthalpy changes during the sorption processes. Additionally, PGDSC is less labor-intensive and time-consuming than the isosteric method and offers detailed insight into how ΔH changes over a given loading range.

Porous materials can be utilized for the separation of gaseous mixtures, as well as targeted capture and release of specific gases.^[1] When evaluating the merits of a given porous material for physisorption-based processes (we use “sorption” as a generic term for either adsorption or desorption), it is necessary to consider several important physicochemical factors. These include working capacity, saturation pressure, hysteresis, kinetics, selectivity, enthalpies of sorption, and the temperature-dependence of these phenomena. With the exception of enthalpies of sorption, it is possible to measure these parameters directly by using standard sorption isotherms, which provide uptake capacity as a function of equilibrium gas pressure. Bimbo et al. stated that an accurate determination of the enthalpy of adsorption is essential to a thorough understanding of any sorption-based system and that its reliable measurement is particularly critical for heat management.^[2] Indeed, Chang and Talu demonstrated the importance of managing

thermal effects during sorption since temperature changes affect the working capacity of the material (see the Supporting Information, Figure S4).^[3] Correct accounting for thermal effects can lead to the development of a range of sorption-based technologies, which may include heat pumps and cooling systems.^[4–6]

The enthalpy of sorption (ΔH_{ads} and ΔH_{des} for adsorption and desorption, respectively) is the amount of energy generated per mole of guest entering or leaving a host. Adsorption is an exothermic process with negative enthalpy values, whereas desorption is endothermic with positive enthalpy values. The enthalpy of sorption encompasses both host–guest and guest–guest interaction energies.^[7] However, van der Waals interactions between host and guest are usually the major energetic contributors over the entire loading range.^[8] The two most common methods of determining enthalpies of sorption are (i) the indirect isosteric method by using the Clausius–Clapeyron approximation and (ii) direct measurement by using calorimetry.^[9] We note that enthalpies of sorption can also be determined computationally from grand canonical Monte Carlo simulations, but this method is generally based on the indirect Clausius–Clapeyron approach.^[10]

The isosteric method employs multiple adsorption isotherms (desorption processes are usually overlooked) at different temperatures to determine the isosteric enthalpy of adsorption (ΔH_{ads}). This is commonly reported as Q_{st} ^[11] the isosteric heat of adsorption, which is conventionally defined as a positive quantity (i.e., $Q_{\text{st}} \equiv -\Delta H_{\text{ads}}$). Since heat is not a state function, use of this term has been discouraged and we will therefore refer to enthalpies (ΔH_{ads} or ΔH_{des}) in the remainder of this report.^[12] The Clausius–Clapeyron approach assumes that the adsorbate gas exhibits ideal behavior and that the molar volume of the host adsorbent is negligible.^[2] The isosteric approach is therefore an approximation of the differential enthalpy of sorption (also known as $\Delta_{\text{ads}}\hat{h}$),^[12] which is most reliable at low coverage where guest–guest interactions make a negligible contribution in comparison to host–guest interactions. For this reason, ΔH_{ads} is often quoted for zero-loading, as estimated by extrapolation. The isosteric approach is the most widely used method for determining ΔH_{ads} because of the simplicity and general availability of the required instrumentation. However, the inherent assumptions can lead to poor estimation of the actual value at high loading (typically at high pressures),^[13,14] where guest–guest interactions and guest ordering become more prominent.^[8] An accurate determination of how ΔH_{ads} changes with increased loading or pressure is important

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to assess the ideal working conditions of a given adsorptive material.

Calorimetric techniques offer the advantage of directly measuring the amount of heat associated with a gas sorption event.^[7,12] The gas can be introduced either incrementally or continuously and to date only the former approach has been applied to metal–organic frameworks (MOFs). However, using zeolites as model systems, Llewellyn and Maurin^[12] showed that continuous introduction (ramping) of the gas increases the resolution of the heat-flow curve by maintaining the system in a quasi-equilibrium state. Moreover, ramping allows subtle phenomena such as phase changes to be observed.^[12] Herein we describe a direct approach to determining ΔH_{ads} and ΔH_{des} for a gas-sorption system by employing pressure-gradient differential scanning calorimetry (PGDSC). Instead of dosing, the method increases the gas pressure at a steady rate to afford a continuous measurement of the enthalpy profile over the entire loading range. To validate the procedure, we have selected a system for which ΔH_{ads} has been reported several times (Table 1 and Table S7); the adsorption of CO_2 by the well-known MOF Cu-HKUST (Figure 1). Although Cu-HKUST has two major binding sites,^[16] both are filled rapidly and yield a hysteresis-free type I isotherm (Figure S5). For the isosteric method, the reported values range from $\Delta H_{\text{ads}} = -22$ to -35 kJ mol^{-1} (determined for zero-loading over different temperature ranges).

Method	ΔH [kJ mol^{-1}]	Temperature range [K]
Isosteric method	-22 ^[17]	273–295
	$-25.9(4)$ ^[18]	283–343
	-28 ^[19]	276–319
	-29.2 ^[20]	308–343
	-35 ^[21]	120–290
	$-27(1)$ ^[a]	288–318
	$27(2)$ ^[b]	288–318
Calorimetry	-30 ^{[22][c]}	not reported
	-21.3 ^[23]	308
	-29 ^[24]	303
	$-28(2)$ ^[a]	288–318
	$27(1)$ ^[b]	288–318

[a] This study, adsorption data. [b] This study, desorption data. [c] Differential thermal analysis (DTA).

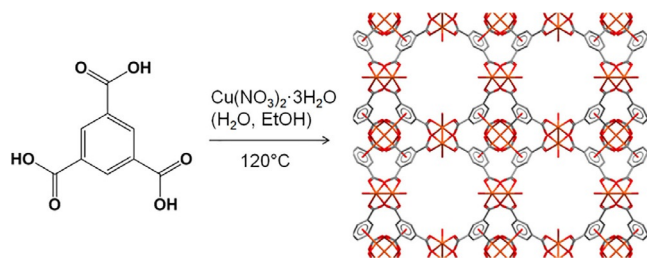


Figure 1. Preparation of Cu-HKUST by using a modification of the procedure reported by Chui et al.^[15]

Both isosteric and PGDSC adsorption–desorption experiments were carried out at four different temperatures (288, 298, 308, and 318 K) to determine ΔH_{ads} and ΔH_{des} values as a function of guest loading. A pressure range from vacuum (2.3×10^{-1} mbar) to 2 bar was used for both types of experiments to yield ΔH_{ads} data over a wide loading range. The isosteric method uses the Clausius–Clapeyron^[21,25] equation [Eq. (1)] for approximating ΔH_{ads} :

$$\frac{dP}{P} = \frac{-\Delta H_{\text{ads}} dT}{R T^2} \quad (1)$$

The integrated form [Eq. (2)] yields linear plots (i.e., isosteres) of $\ln P$ vs. T^{-1} at constant loading, from which ΔH_{ads} can be estimated:

$$\ln P = \frac{-\Delta H_{\text{ads}}}{R} \frac{1}{T} + C \quad (2)$$

Figure 2 shows a plot of ΔH as a function of loading, as determined in this study by using the isosteric method. Our extrapolated zero-loading values for adsorption [$27(1) \text{ kJ mol}^{-1}$]

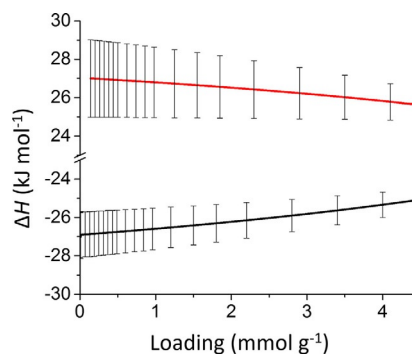


Figure 2. ΔH vs. loading data for CO_2 adsorption (black) and desorption (red) by Cu-HKUST obtained by using the isosteric method. The error bars show errors derived from the isosteres [Eq. (2)].

and desorption [$27(2) \text{ kJ mol}^{-1}$] fall comfortably within the range for adsorption reported previously (to our knowledge, no values have previously been reported for desorption). The decreasing trend (i.e., lower $|\Delta H|$ values with increased loading) is typical for a heterogeneous adsorbent surface.^[12,13] Since the trends are based on use of the ideal gas approximation, ΔH values at higher loading may be unreliable.^[13] The shapes of the isosteres, and treatment thereof, may also introduce additional artefacts. Since estimation of ΔH at zero loading is based on extrapolation of a trend, the large range of reported values may be due to assumptions that sorption isosteres are linear. If the isosteres are nonlinear, the use of widely different temperature ranges can result in different approximations of ΔH . The isosteric approach is susceptible to the choice of experimental conditions, as well as methods of data interpretation.

Values for ΔH_{ads} and ΔH_{des} were also determined directly by measuring heat flow as a function of pressure by using the

PGDSC method. Since the calorimetric method does not yield loading data as a function of pressure, it is necessary to obtain these values from a sorption isotherm recorded at the same temperature. The apparatus shown in Figure 3 consists of a pressure introduction system connected to a differential scanning calorimeter (see Figure S1 in the Supporting Information for a more complete description of the system). The computer-

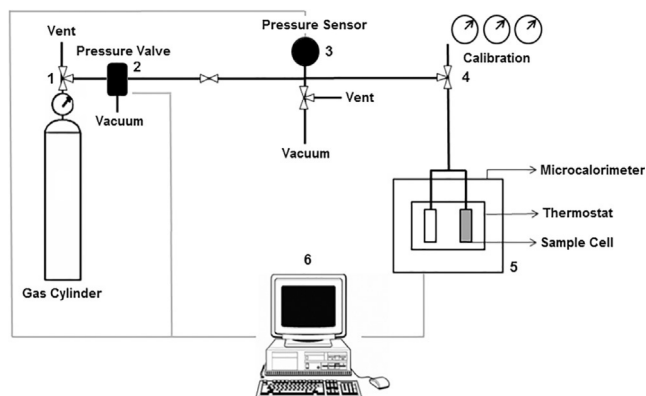


Figure 3. Schematic diagram of the PGDSC setup. Black lines indicate gas reticulation and grey lines indicate electronic control.

controlled pressure valve enables automated introduction and removal of a test gas at a constant pressure gradient, thus yielding high-resolution results. Although the following derivations are given for the exothermic adsorption process, endothermic desorption can be treated similarly. Integration of the PGDSC thermogram over time yields a total (i.e., cumulative) heat value Q_{int} for the sorption process. Differentiating the integral heat with respect to loading (N , obtained from the corresponding sorption isotherm) yields Q_{diff} [Eq. (3)].^[7,26]

$$Q_{\text{diff}} = \frac{dQ_{\text{int}}}{dN} \quad (3)$$

The enthalpy of sorption is calculated by adding an appropriate thermodynamic term (zRT),^[27] where z is the compressibility factor for the gas [taken as 1 for CO_2 at pressures lower than 3 bar; Eqs. (4) and (5)].^[28]

$$-\Delta H_{\text{ads}} = Q_{\text{diff}} + zRT \quad (4)$$

$$\Delta H_{\text{des}} = -(Q_{\text{diff}} + zRT) \quad (5)$$

Figure 4 shows plots of ΔH_{ads} and ΔH_{des} obtained by averaging the data measured at the four different temperatures. The averaging errors are relatively small, demonstrating that the enthalpy data obtained by using the PGDSC method are less temperature dependent than those obtained by using the isosteric method.

The zero-loading ΔH values determined calorimetrically for both adsorption and desorption compare well to the range of the isosteric method, as well as with the values obtained using calorimetric measurements (Table 1 and Table S7). However, it should be noted that it is not possible to accurately determine

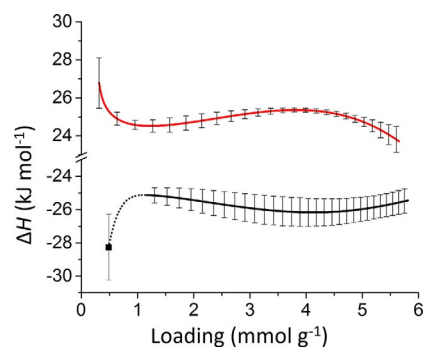


Figure 4. Plots of ΔH_{ads} (black) and ΔH_{des} (red) vs. CO_2 loading by Cu-HKUST obtained by using the calorimetric method (PGDSC). The error bars are based on averaging errors between the various temperatures. The dotted line indicates an extrapolation of data to near-zero loading.

the zero-loading value of ΔH_{ads} directly by using PGDSC, especially during adsorption (although it can be approximated by extrapolation). This can be problematic when the plot of ΔH vs. loading deviates significantly from linearity as it approaches zero-loading. It is then more feasible to use a single pulse of gas pressure in the very low pressure range to approximate near-zero loading. This is important to determine the amount of energy (i.e., zero-loading Q_{st}) required to completely remove a guest species from a host material. Approximation of the zero-loading values for adsorption required a dose from 0 to 0.1 bar to acquire the initial total heat associated with the sorbate-sorbent interaction (Table S4). This was necessary because of a slight lag in recording the heat flow in the scanning mode (Figure S12). For the purposes of heat management, it is also relevant to accurately account for the energy profile throughout the working range of the material, both for adsorption and desorption.

Since the generation of heat is measured directly, the PGDSC method offers a more accurate determination of the enthalpies of sorption with loading. Figure 4 shows that $|\Delta H|$ values for CO_2 @Cu-HKUST are at a maximum at zero loading and decrease rapidly (by approximately 3 kJ mol^{-1}) as loading approaches 1 mmol g^{-1} . This is commonly observed for heterogeneous adsorbents where the interaction energies are the strongest when the gas comes into initial contact with the host surface, that is, the zero-loading value.^[9,12,21] Furthermore, the shape of Figure 4 offers high-resolution information on how ΔH changes over a set loading range due to being derived from direct heat measurements. Since the adsorption and desorption isotherms are superimposed for non-hysteretic type I sorption processes (Figure S5),^[29,30] the Clausius-Clapeyron approach should yield corresponding enthalpies of the same magnitude. Indeed, this is also the case (within error) for the data plotted in Figures 2 and 4, which further validates our approach.

In conclusion, we have demonstrated that the PGDSC method produces reliable temperature-independent ΔH data. Our PGDSC approach uses direct and continuous measurement of heat flow, whereas the isosteric method implements energy values derived from approximated thermodynamic expressions

and the assumption that the bulk gas exhibits ideal behavior. Moreover, the calorimetric method involves recording a single sorption isotherm and a single PGDSC thermogram to obtain ΔH data and offers detailed insight into how ΔH relates to loading. Notably, determining the loading-dependent enthalpies by PGDSC required less than half the time required for the isosteric approach. The improved resolution of the PGDSC method is particularly important for materials that exhibit structural flexibility (e.g., gate-opening events). Finally, it has become commonplace to report ΔH extrapolated to zero loading as a measure of the strength of adsorbent–adsorbate interactions. However, it is equally beneficial to consider ΔH values over the entire loading range for a given adsorbent to assess how the value changes with loading. Since heat plays an important role in sorption, this information is critical for efficient management of thermal effects in systems that are employed for separation and storage technologies.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: adsorption · calorimetry · enthalpies · metal-organic frameworks · porous materials

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