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An International Laboratory Comparison Study on Approximating the Enthalpy of Adsorption via the Clausius-Clapeyron Approach

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ABSTRACT

Materials-based gas capture and storage is an increasingly important area of research. Robust and accurate determination of material properties is required for judicial selection of materials for specific applications and for engineering materials-based systems at scale. One key property is the strength of the adsorbate–adsorbent interaction often quantified via the isosteric enthalpy of adsorption. The heat of adsorption can be measured directly through calorimetry; however, a more widely used approach is to apply the Clausius-Clapeyron (CC) equation to adsorption isotherms collected at different temperatures. While this approach appears to be straightforward, there exist multiple variants in the application of the methodologies employed. This raises the question on how these variations may or may not affect the determined results. Presented here is a discussion of the most common methodologies and a comparison of indirect determinations (via CC) of the isosteric enthalpy of adsorption by different laboratories on identical material. Included in that comparison are discussions on the measurement and analysis reproducibility. Importantly, details of the methodologies are shown to be critical when comparing enthalpies among laboratories, and different methodologies contribute to significant discrepancies and artifacts in the results. Recommendations are provided to promote robust determination and the reporting thereof.

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1 | Introduction

Gas adsorption is of increasing importance for a wide variety of ongoing research areas, including hydrogen storage and capture, methane storage and capture, carbon capture, and various gas separation/purification methods [1–4]. These applications lead to a pervasive need for accurate differentiation between promising highly effective adsorption materials and materials that underperform. This need requires robust metrics for comparing the physicochemical properties of sorbents under a diverse set of conditions. The isosteric heat of adsorption, q_{st} , or isosteric enthalpy of adsorption, ΔH_{st} , is one often-used metric for the strength of adsorbate–adsorbent interaction [3]. The research field of hydrogen storage has defined optimal adsorption enthalpy targets for material development based on maximizing usable hydrogen capacity [5–7]; thus, it plays a critical role in defining research directions making accurate determination of ΔH_{st} critical. While the heat of adsorption can be measured directly through calorimetry, a more widely used method applies the Clausius-Clapeyron (CC) equation to adsorption isotherms collected at different temperatures [3, 8, 9]. The heat of adsorption is the heat released when a unit mass of a component in the gas phase transitions to the adsorbed phase; thus, the CC thermodynamic correlations describing the heats of phase-transition are applicable. In effect, the CC equation relates the heat of adsorption to the temperature dependence of the adsorption isotherms. In the literature, the terms isosteric heat of adsorption and isosteric enthalpy of adsorption are often used interchangeably. Herein, we will follow the guidelines provided in ‘Adsorption by Powders and Porous Solids’ [10] and the IUPAC technical report [11]. In the former, the CC calculation is defined as an indirect ‘approximation’ methodology which dictates the use of isosteric enthalpy of adsorption (ΔH_{st}), with the term isosteric heat of adsorption being reserved for calorimetry where the heat released with adsorption is measured directly. The IUPAC technical report discourages the use of heat of adsorption even for calorimetry results.

The CC approximation has been derived in detail elsewhere [12] and is provided below (Equation (1)). In summary, the CC equation correlates the enthalpy of adsorption to the change in the natural log of pressure (P) as a function of temperature (T) at constant moles loading (n).

$$\Delta H_{st} = -RT^2 \left(\frac{\partial \ln(P)}{\partial T} \right)_n = R \left(\frac{\partial \ln(P)}{\partial \left(\frac{1}{T} \right)} \right)_n \quad (1)$$

Deriving the CC equation requires two assumptions that may not be valid under experimental conditions, especially near or at the supercritical regime: (i) The molar volume of the free gas is significantly higher than that of the adsorbed phase and (ii) that the free gas behaves ideally. Relatively large error should be assumed when determining isosteric enthalpy of adsorption values via the CC approximation at experimental conditions where the adsorbate deviates from ideal gas behavior, as demonstrated in previous work [12]. Despite concerns arising from the inherent assumptions of the CC approximation, it is implicitly assumed within the larger research community that the technique is accurate and valid for relative comparison between materials when high-quality isotherms are collected. While this seems to be a logical assumption under conditions where the CC approximations are valid, differences in how the experimental data is processed

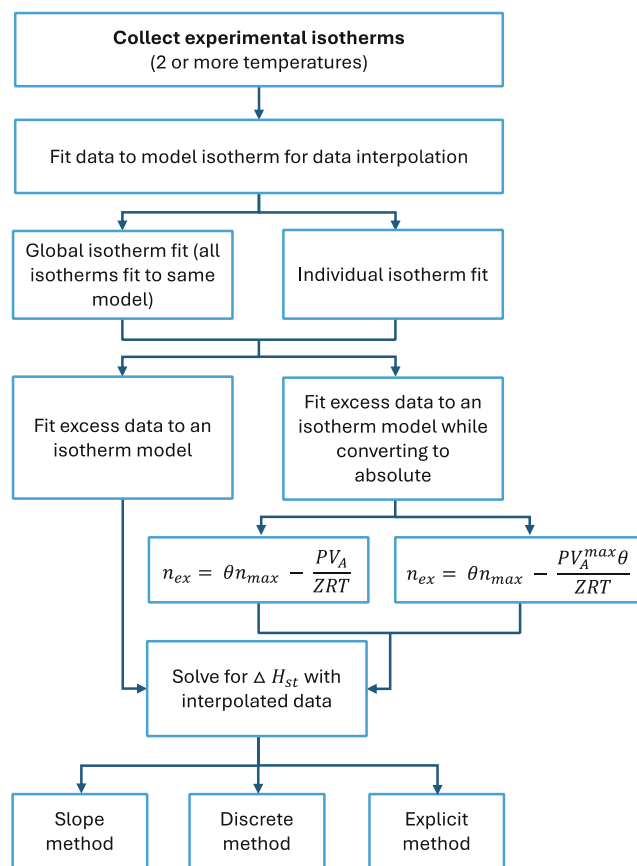


FIGURE 1 | Decision tree for determining isosteric heat/enthalpy of adsorption from adsorption isotherms.

can cause significant discrepancies in the ΔH_{st} values and trends. These errors from data processing would be in addition to any errors arising from experimental conditions not aligning with the assumptions required for the CC equation. A schematic outlining the techniques for implementing CC calculations to determine isosteric enthalpies of adsorption and the inherent decisions, that must be made, is provided in Figure 1. Assuming Equation (1) is used with no further modification or corrections, there are several data processing decisions that affect the resultant ΔH_{st} values (vide infra).

1.1 | Data Interpolation

The CC approximation utilizes the pressure as a function of temperature for equivalent moles adsorbed, which necessitates the use of interpolation. Typically, an isotherm model is used to fit the data, such as Langmuir [13], double-site/dual-site (or multisite) Langmuir, Langmuir–Freundlich (i.e., Sips) [14], Toth [15, 16], Unilan [17–19], or an empirical approach such as a Virial equation [8, 20]. Alternatively, the experimental data can be fit to a polynomial or directly interpolated, e.g., using linear interpolation or a cubic spline. Note that while interpolation can be used to great effect, extrapolation beyond the bounds of the experimental conditions should be avoided, as it may lead to significant variations and errors in the results.

If using an isotherm model that explicitly depends on the temperature T , how exactly the temperature dependence enters into

the isotherm model will introduce temperature bias into the enthalpy of adsorption results with questionable physical interpretation. For example, when using a Langmuir model, the Langmuir constant is defined by different researchers with different dependencies on temperature, including $b = Ae^{\frac{E_a}{RT}}$ [13] or $b = \frac{Ae^{\frac{E_a}{RT}}}{\sqrt{T}}$ [21]. Introducing the \sqrt{T} dependency results in a $1/2RT$ bias in the CC enthalpy of adsorption results, a mathematical artifact that falls out from applying the CC equation directly and not necessarily a result of the material properties (Supporting Information Figure S1). For example, the Langmuir model has a single adsorption site with energy E_a and adding extraneous temperature factors appears to either violate that assumption or imply other mechanisms that may or may not be realistic or even physical. This holds for other defined temperature dependencies within other isotherms (including Toth, Langmuir–Freundlich, Unilan, etc.) and must be considered prior to assigning physical meaning to a temperature dependence on the resultant enthalpy of adsorption.

Within an isotherm model, a fit can be achieved either globally, in which all isotherms are fit at once to the same equation with an explicit temperature variable fixed for each isotherm data set, or locally, as a function of pressure for each independent temperature. The advantage of the global fit is that the isotherm model depends explicitly on temperature and the ΔH_{st} can be calculated directly via application of Equation (1). The expectation for the independent analyses is that the data will be fit more accurately (because effectively there are more fit variables) and therefore the ΔH_{st} results should be more accurate. However, independent isotherm fits are impacted by measurement noise whereas a global fit is a more holistic approach to fitting which mitigates the impact of noise, or measurement error, in any single isotherm. Thus, these model choices and how to apply each are distinct decision points.

1.2 | Conversion of Excess to Absolute Adsorption

Derivation of the CC equation assumes absolute adsorption; however, isotherm measurements typically determine excess adsorption via van der Waals gas–solid interactions [22]. This attractive force between the gas and the adsorbent surface causes there to be a higher density of gas near the surface. Excess adsorption is the amount adsorbed in excess of what would be present in the same volume accessible to the gas if the adsorbent did not interact with the adsorbate. In contrast, the absolute amount adsorbed consists of all adsorbate molecules within the adsorption volume, or the volume within which the gas is near enough to the adsorbent surface to interact. Determining the absolute adsorption would require knowing the adsorption volume, and adsorbed phase density, neither of which can be explicitly measured.

The *excess* adsorption data can be fit and used to calculate the ΔH_{st} , or the excess data can be converted to *absolute* adsorption. The intent is for the ‘*absolute*’ adsorption to include all adsorbate molecules within the unknown adsorption volume. This should not be confused with *total* adsorption, which includes all free gas within the material’s envelope volume [9] in addition to the *absolute* adsorption.

The conversion between excess and absolute adsorption has been a topic of discussion for many years [15, 23]. In its most general form, conversion necessitates recognizing that a free-gas component within a volume, which may depend in an unknown way on pressure and temperature, must be added to the excess adsorption to determine the absolute adsorption (Equation (2a)). The simplest approach to move past this dilemma is to assume that either the adsorption volume (V_A) is a constant, independent of pressure and temperature (Equation (2b)), or that it is a simple function of the amount adsorbed (Equations (2c) and (2d)). While the justification for reducing V_A to a constant or a function of amount adsorbed is nebulous at best, how well the excess data is fit with these assumptions can be explored.

$$n_{ex} = n_{ab} - \rho_{fg}(P, T)V_A(P, T) \quad (2a)$$

$$n_{ex} = n_{ab} - \rho_{fg}(P, T)V_A \quad (2b)$$

$$n_{ex} = n_{ab} - \rho_{fg}(P, T)V_A(n_{ab}) \quad (2c)$$

$$n_{ab} = n_{ex} + \rho_{fg}(P, T)V_A(n_{ex}) \quad (2d)$$

In the above equations, n_{ab} is the absolute number of moles adsorbed, n_{ex} is the excess number of moles adsorbed, ρ_{fg} is the free-gas molar density at pressure P and temperature T , and V_A is the volume in which adsorption occurs. Note that it is often assumed that V_A is equivalent to the pore volume V_{pore} (measured from a porosity analyzer instrument, aka BET), which is a reasonable assumption if the pores are small enough for the entire volume to be within the attractive force of the surface. Equations (2b) and (2c) provide a methodology to determine the V_A parameter in these models via fitting the excess data given the expectation that n_{ab} is a monotonically increasing function with pressure and n_{ex} is the free gas component subtracted from the absolute adsorption, n_{ab} . At lower temperatures and higher pressures, the free-gas component is sufficiently large enough that a maximum in the excess isotherm appears with pressure and shows a negative slope thereafter. This allows for a robust fitting of the V_A parameter. At higher temperatures, this maximum is often not observed due to limitations in the maximum pressure for the isotherm measurement and presents more difficulty in determining V_A and the free-gas contribution to absolute adsorption. Equations (2b) and (2c) can be written more explicitly to reflect the data-fitting process, Equations (3) and (4).

$$n_{ex} = n_{max}\theta(P, T, \vec{f}) - \frac{PV_A}{RTz(P, T)} \quad (3)$$

$$n_{ex} = \theta(P, T, \vec{f}) \left[n_{max} - \frac{PV_A^{max}}{RTz(P, T)} \right] \quad (4)$$

In these equations, $\theta(P, T, \vec{f})$ represents an isotherm model function at pressure P , temperature T , and a (possibly multidimensional) fitting-parameter vector, \vec{f} (This function scales between 0 and 1 and represents the adsorption coverage fraction). Additional fitting parameters include n_{max} , which is the moles present at maximum adsorption, V_A^{max} , which is the maximum volume in which the adsorption can occur (which tends to approach the pore volume), and V_A . In Equations (3) and (4), R is the universal gas constant and $z(P, T)$ is the compressibility

factor for the gas (hydrogen). It should be noted that Equation (4) can be equivalent to the model whereby the adsorbed phase is represented by a fluid at constant molar density, ρ_{fl} , in which case, $V_A^{max} = \frac{n_{max}}{\rho_{fl}}$ and ρ_{fl} is a fitted parameter or ρ_{fl} is assumed to be a constant equal to the liquid density (~ 71 g/L for H_2) and V_A then becomes proportional to the amount adsorbed.

Converting to absolute adsorption necessitates assumptions and thus introduces an additional source of possible error. The decision on if, as well as how, to convert from excess to absolute adsorption are two additional decision points in the data processing.

1.3 | Enthalpy Determination

The final decision point is which method to use to calculate the ΔH_{st} via the CC equation (Equation (1)). While there can be potentially many techniques, here we focus on the four most common for the calculations:

- i. The model (global) isotherm can explicitly depend on temperature, and the equation solved explicitly (henceforth referred to as the *Explicit method*).
- ii. If isotherms at only two temperatures are being used, a discretized form of the CC equation can be applied, as in Equation (5), which we will refer to as the *Discretized method*. Note that this is equivalent to the slope method below rearranged for two points (Equation (5)).

$$\Delta H_{st} = RT_1 T_2 \left(\frac{\ln\left(\frac{P_2}{P_1}\right)}{T_2 - T_1} \right)_n \quad (5)$$

- iii. When the data is plotted as $\ln(P)$ as a function of $(1/T)$ at equivalent moles adsorbed and fitted to a line, the slope can be taken as equal to $-\Delta H_{st}/R$ (which we will refer to as the *Slope method*). This can be repeated at different coverages to yield ΔH_{st} vs coverage.
- iv. The virial method can be used which generally relies on a double polynomial fit for $\ln(P)$ as a function of adsorption uptake (coverage) with one of the polynomials having a $1/T$ multiplicative prefactor and the other no temperature dependence. The degrees of the polynomials are at the discretion of the analyzer. This is a type of global or explicit fitting, and it is referred to as the *Virial method*. It is unique because the isotherm data is transformed to $\ln(P)$ vs amount adsorbed at each temperature before the global fit. By virtue of the CC equation, the polynomial with the $1/T$ prefactor determines ΔH_{st} vs coverage.

As described earlier, the ΔH_{st} is often treated as a critical parameter for evaluating materials for gas sorption/separation applications. Inaccuracies in reporting their enthalpies can cause promising materials to be prematurely dismissed and/or resources directed to underperforming materials. This necessitates a definitive understanding of the limitations in both accuracy and robustness of the metric reported. Inter-laboratory comparisons have been used previously to reveal discrepancies within the research community in order to formulate best practices for characterization and reporting of the various properties of hydrogen storage materials [5–7]. This allows for the community to define ‘best practices’ so as to avoid ‘black-box syndrome’

confusion through a consensus set of protocols to ensure data is directly comparable between different laboratories as well as between multiple measurements on the same material [8, 9]. Herein are the results from an international multilaboratory study carried out to investigate variation in experimental application of the CC approximation for the determination of ΔH_{st} .

2 | Experimental Section

In order to minimize variables in material preparation, a large single batch of HKUST-1 [24, 25], which is a highly porous coordination polymer $[Cu_3(BTC)_2(H_2O)_3]_n$ where BTC is benzene-1,3,5-tricarboxylate, also known as MOF-199 (where MOF stands for metal-organic framework), was sourced from NuMAT, divided, and sent to 11 different academic, industrial, and government laboratories. The instructions supplied to all participants were to measure the adsorption isotherms at two or more different temperatures and then to apply characterization protocols of their choosing to determine the isosteric enthalpy of adsorption of that material. The as-received enthalpy of adsorption results are compared to understand the current level of consistency within the research community, with additional attention paid to the outliers to elucidate the underlying causes. A consistent method to calculate the ΔH_{st} via the CC-approach was then applied to the isotherms submitted from each lab to understand the impact of data quality on the resultant ΔH_{st} . Finally, the impact of different isotherm model choices was directly evaluated by fitting the NREL isotherms with two different models and analyzing the impact of the ΔH_{st} .

The participants were given the same set of instructions (see Supporting Information Exhibit S1) to maintain a level of consistency. The name and material properties of the sample were not provided to the participants until after the measurements from all laboratories were reported. It was recommended that the labs use the largest mass of the sample possible while still performing high-accuracy, high-precision measurements, to minimize error resulting from small sample mass. The degassing procedure sent to participants directed them to achieve the lowest possible baseline vacuum level prior to heating the sample, and to hold that for an hour. Then, while still under active vacuum, to heat the sample to 150°C at a rate of $5^\circ\text{C}/\text{min}$ and hold at 150°C for 15–24 h, while striving for a final pressure of better than 10^{-3} Pa. The participants were informed that, if possible, the sample should not be exposed to air before starting the hydrogen-capacity measurements.

For determining the isosteric enthalpy of adsorption, at least two isotherms at different temperatures were required, with the temperatures selected close in proximity (within ± 20 K). The specific temperatures for the isotherms were not specified in order to avoid participants deviating from their typical instrumental setup. For example, for a liquid nitrogen bath (which was a commonly selected temperature among the participating laboratories), the precise temperature changes with varying geographic altitude. We requested more than two temperatures for the isotherms if possible and suggested using a wider temperature range for additional pairs of isotherms to look for global temperature dependence. For reporting the isotherm data, the labs were provided with a Data Analysis and Run sheets to fill out and submit (see Supporting Information Exhibits S2 and S3) to ensure that

the methods the various labs used were recorded and would be accounted for in subsequent data analyses. In addition, participants supplied all isotherm data (both excess and absolute if absolute was used) and their final isosteric enthalpy of adsorption values in either tab-delimited text files or Excel spreadsheets. Guidelines were provided that described the data calculations and enthalpy analysis, outlining the decision points along the way as described in the introduction, and following the decision tree shown in Figure 1.

The obtained data from each laboratory was assigned a numerical designation, which is kept consistent throughout the manuscript. NREL's data is explicitly labeled as such. The majority of the uptake measurements were collected with a volumetric 'Sieverts-type' apparatus except for one participant who reported gravimetric data. Six of the laboratories used low-pressure (exclusively under 2 bar) isotherms to extract isosteric enthalpies, while the other five labs collected high-pressure (up to 100 bar) isotherms. While each laboratory reported their calculated adsorption enthalpy (denoted 'as-reported'), each set of isotherms was also analyzed with a chosen particular methodology to investigate the sensitivity of the isosteric heat calculation on the measured excess uptake isotherm data.

3 | Results and Discussion

3.1 | Excess Gravimetric Capacity

The participants' liquid nitrogen temperature hydrogen excess uptake measurement results are shown in Figure 2a,b at high and low pressure, respectively. All data shown were obtained with volumetric Sieverts apparatuses; the gravimetric data did not include measurement of excess uptake at liquid nitrogen temperatures. Laboratories with multiple isotherm measurements at the same temperature have letters to denote duplicate measurements. Of the liquid nitrogen isotherms, five laboratories measured isotherms above 1 bar, while the other 6 laboratories measured uptake only up to 1 bar pressure. Two outliers were identified (Lab1 and Lab4), and there could be several possible explanations such as insufficient sample activation, sample degradation, or headspace measurement errors [23, 26]. Specifically, with Lab1, the sample was initially degassed in a vacuum oven at 120°C for 12 h, and again while on the measurement instrument (2 h at 120°C), but was briefly exposed to air during the transfer to the measurement instrument. That exact sequence may have contaminated the open metal sites or degraded the sample even though the sample is expected to be relatively resilient to air exposure. Based on the current analysis, it would be approximately a 25% degradation. For Lab4, the researchers used a cold finger cryostat which has since been found to be inadequate for maintaining isothermal conditions especially at higher pressures where the heat conduction and convection of the gas result in larger thermal gradients. Additionally, the increased downward slope after the maximum compared to the other labs' isotherms could indicate that the headspace used in the mole-balance calculation was too large and this is compounded by the smaller sample mass used for this measurement (84.5 mg) that makes extremely accurate headspace calibrations critical.

Eleven laboratories reported excess isotherms at sub-ambient pressures, with eight of the 11 laboratories having excess uptake

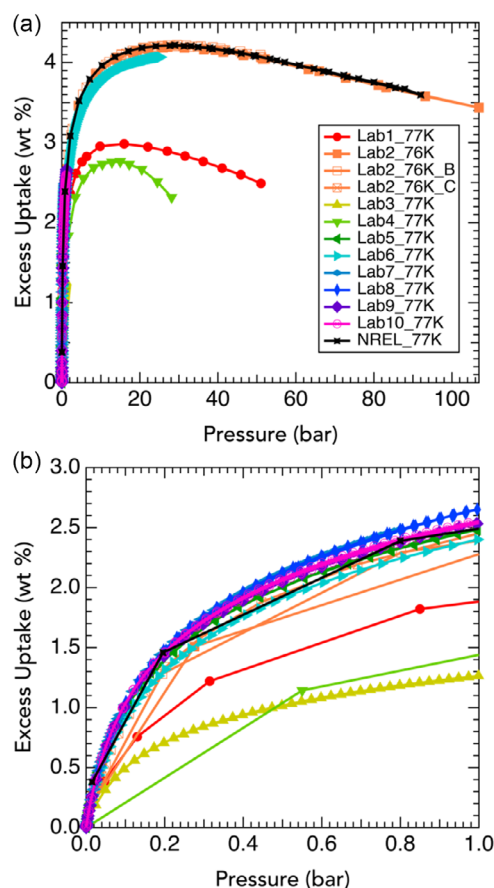


FIGURE 2 | As-reported excess hydrogen uptake isotherms from (a) laboratories at up to 100 bar and (b) 1 bar, measured at liquid N₂ temperatures.

measurements in close agreement. The three outliers (Lab1, Lab3, and Lab4) reported decreased values relative to the other eight labs. Lab1 and Lab4 were the two outliers at higher pressures, where decreased values were also reported.

3.2 | As-Reported Enthalpies of Adsorption

A summary of the decisions each laboratory made when determining ΔH_{st} is provided in Table 1. The as-reported isosteric enthalpies of adsorption from all laboratories are shown in Figure 3a, showing the full range of coverage reported by each lab, including results determined directly from the excess isotherms and results determined from isotherms converted to absolute adsorption. The results at low coverage are provided in Figure 3b. Lab1 ($-\Delta H_{st} = \sim 7.5$ to ~ 9 kJ/mol) and Lab4 ($-\Delta H_{st} = \sim 3.5$ to ~ 5.25 kJ/mol) have the highest and lowest reported adsorption enthalpy values, respectively. Both of these labs' excess adsorption isotherms were outliers, reporting lower capacities (Figure 2a). Of particular interest is Lab3, which also measured lower excess uptake measurements than most other laboratories yet reported an adsorption enthalpy consistent with other reported values. In the Henry's Law regime (Figure 3b), Lab10 reported a sharply decreasing enthalpy of adsorption not present in the other labs' results.

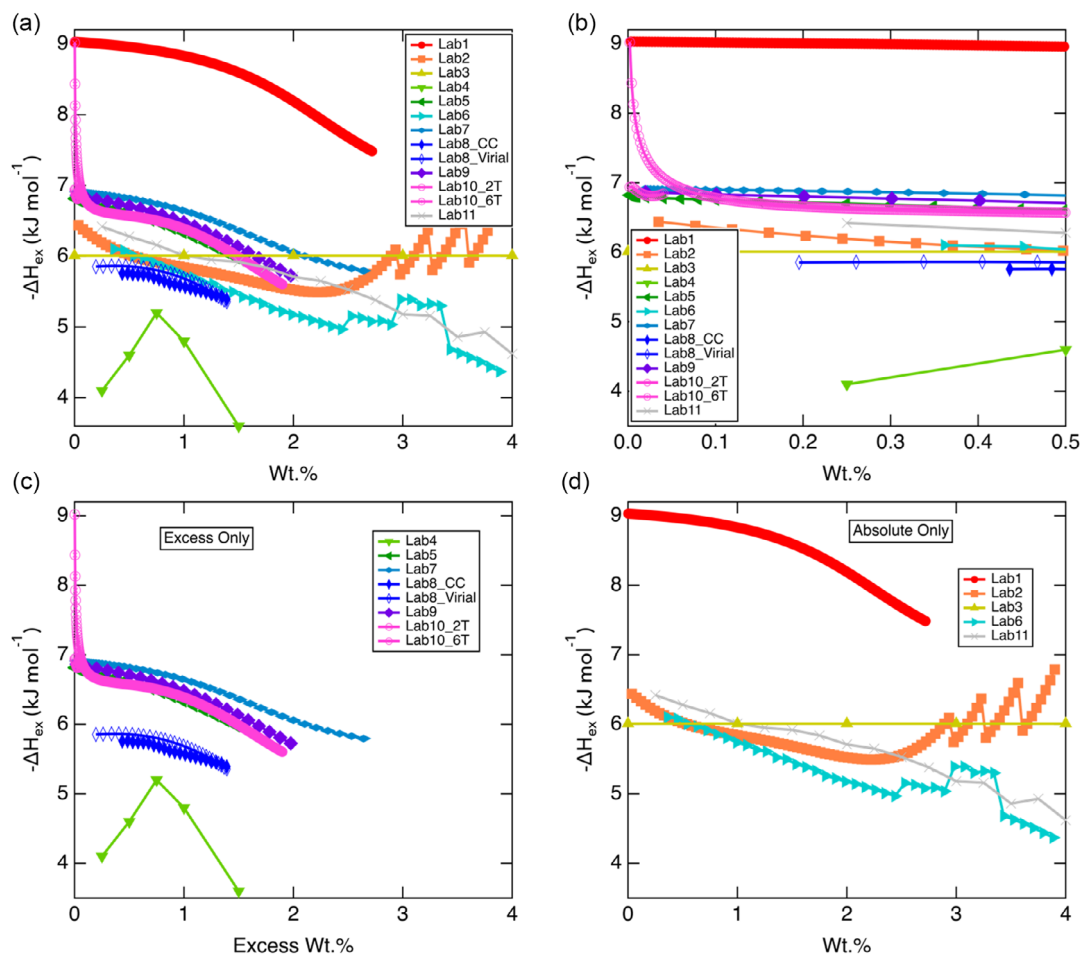
Figure 3c,d shows as-reported values for isosteric enthalpies of adsorption calculated directly from excess isotherms (termed

TABLE 1 | Summary of enthalpy of adsorption determination decisions for all participants.

Lab #	Meas. type	Temperatures, K	Fitting equation	Fit type—global, local, interpolation	Conversion to “absolute”	Isosteric enthalpy calc. method (# of temperatures)
Lab1	Vol.	77, 87, 97	D.L.	Local fit	V_{pore} from BET*	CC: slope (3)
Lab2	Vol.	77, 87, 97, 107, 117	Virial	Local fit	Equation (2d)	CC: slope (5)
Lab3	Vol.	77, 87	Langmuir	Global fit	V_{pore} from BET*	CC: discretized
Lab4	Vol.	53, 77, 99, 124.8, 150	N/A	Linear/spline interp.	No conv. (HP)	CC: slope (3 or 4)
Lab5	Vol.	77, 82, 87, 93, 103, 113, 123, 133	Sips/L.-F.	Global fit	No conv. (LP)	CC: slope (4)
Lab6	Vol.	77, 87, 97, 111, 127, RT	N/A	Linear/spline interp.	Equation (2d)	CC: slope (5)
Lab7	Vol.	70, 77, 87, 100	D.L.	Global fit	No conv. (LP)	CC: explicit (4)
Lab8	Vol.	77, 87, 97, 213, 223, 233	Virial	Global fit	No conv. (LP)	CC: slope (3)
Lab9	Vol.	77, 87	Sips/L.-F.	Global fit	No conv. (LP)	CC: discretized
Lab10	Vol.	77, 87, 113, 157, 175, 195	D.L.	Local fit	No conv. (LP)	CC: slope (2 or 6)
Lab11	Grav.	120, 130, 140, 150, 160	N/A	Cubic interp.	V_{pore} from BET*	CC: slope (5)

Abbreviations: CC, Clausius-Clapeyron; D.L., double Langmuir; Grav., gravimetric; HP, high pressure; interp., interpolation; L.-F., for Langmuir-Freundlich; LP, low pressure; Vol., volumetric.

*Porosity analyzer instrument.

**FIGURE 3** | As-reported isosteric enthalpies of adsorption from (a) all labs, full uptake range, (b) all labs at low loading (0 to 0.5wt%), (c) labs reporting isoexcess enthalpies using excess uptake isotherms, and (d) labs reporting isosteric enthalpies from calculated absolute uptake isotherms.

isoexcess enthalpy of adsorption) and from isotherms converted to absolute adsorption, respectively. Excluding the outliers (Lab1, Lab4, and Lab8), as-reported isoexcess adsorption enthalpies

clustered around values ≈ 0.5 – 1 kJ/mol higher than the isosteric enthalpies of adsorption. All reported isoexcess enthalpies were obtained using sub-ambient excess isotherms (except Lab4) while

all reported isosteric enthalpies were calculated from above-ambient absolute isotherms (except Lab3). Note: Lab11 used a gravimetric apparatus and reported isosteric enthalpies consistent with other laboratories. Lab2 and Lab6 reported isosteric enthalpies with significant discontinuities at high coverage (between 2 and 4 wt%). Direct interpolation techniques can cause discontinuities if the capacity versus pressure isotherm data is insufficient; large spacing between the data points causes the interpolation to result in different linear slopes at the same pressure. Another cause of this phenomenon is using the slope method whereby the number of isotherms at different temperatures contributing to the line fits changes as a function of coverage [27, 28]. Higher temperature isotherms successively “drop out” of the fits and cause the apparent discontinuities. It has been confirmed that the latter is the cause of the discontinuities reported here as both labs used the slope method and the discontinuities occur at the coverages where isotherms drop out of the analysis.

3.3 | Universal Double-Site Isoexcess and Isosteric Adsorption Enthalpies

To compare the results when using excess isotherm data to those obtained using isotherms converted to absolute data, the same

isotherms from each lab were used to calculate isoexcess adsorption enthalpies (from excess data) and isosteric enthalpies (from absolute data). Figure 4 shows adsorption enthalpies from collected isotherms using a fit to the excess data and those from data converted to absolute uptake isotherms. A decision tree is provided in Supporting Information Figure S2 for the analysis methods used to calculate both isosteric and isoexcess adsorption enthalpies with the CC equation. A double-site Langmuir global fit (Supporting Information Equation (S1)) was used to fit the raw experimental data, with fitting parameters provided in Supporting Information Table S1. The isoexcess heat in Figure 4a,b was obtained using the excess fit as an interpolation function (with pressure spacings of 0.001 bar) for isotherm pairs 77 K–87 K (or closest measured isotherm to 77 K), and applying the CC equation to the interpolated excess data. Plots were truncated where the excess uptake reached a maximum value. Figure 4c,d is obtained using the same double-site Langmuir fit as above, but using the calculated absolute uptake with the Clausius-Clapeyron equation for 77 K–87 K isotherm pairs.

The enthalpy of adsorption data is reasonably consistent with the same analysis algorithm applied to all of the excess adsorption data. Lab1 and Lab4 remain as outliers in the universal analysis method, with analysis on Lab1 showing a higher isosteric enthalpy than reported from the lab. The universal analysis

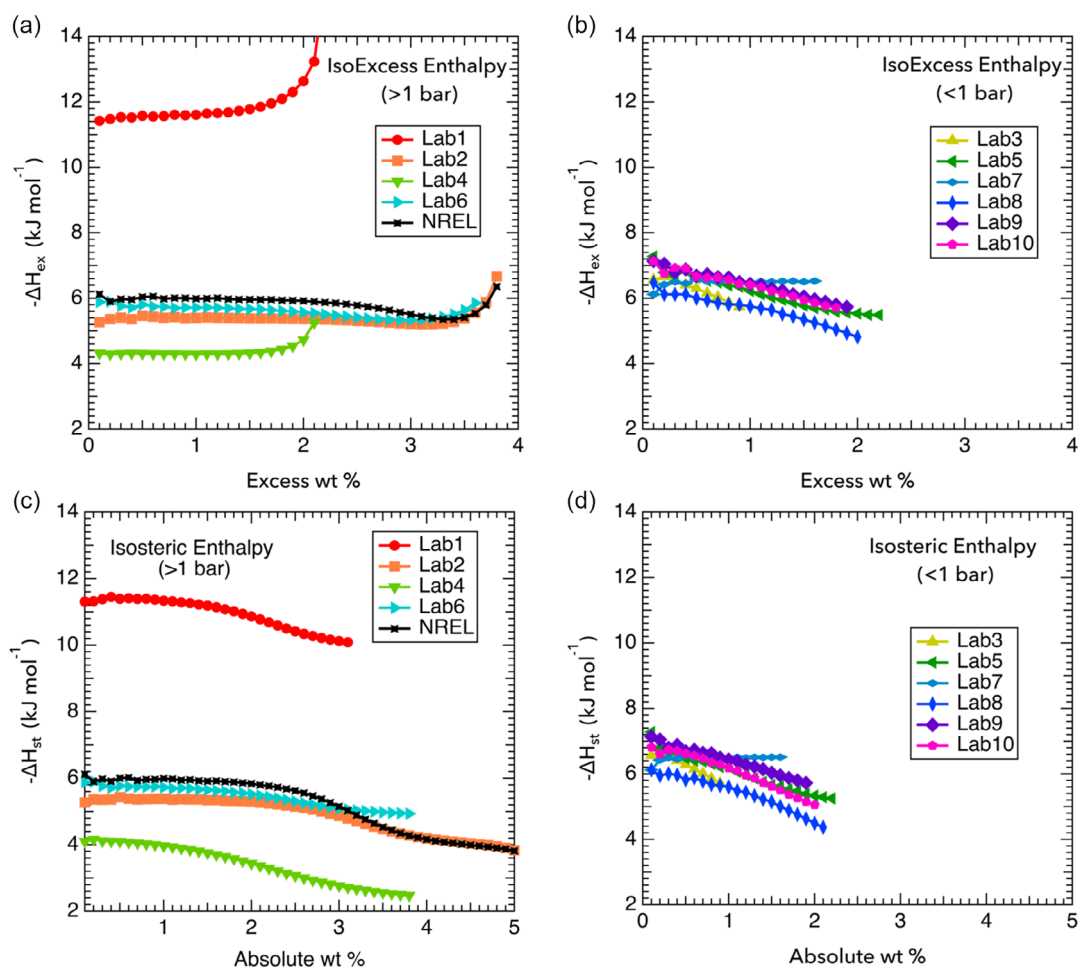


FIGURE 4 | Adsorption enthalpies calculated consistently for all labs using isotherms collected between 77K–100K via the isoexcess method on isotherms collected above 1 bar (a), isotherms collected below 1 bar (b), and the discrete absolute uptake method on isotherms collected above 1 bar (c) and isotherms collected below 1 bar (d).

method shows consistent results between the isoexcess and isosteric enthalpy calculations up to ~ 1.5 wt%. It should be noted that at low pressures, excess and absolute adsorptions are approximately equal and no conversion between the two is generally needed. All high-pressure isoexcess data show an upwards trend above 2 wt%, and is caused by the significant difference between excess and absolute capacities at high pressures. This can be modeled by Equations (3) or (4), and applying CC analysis to the model reveals the upturn. The downward trend of isosteric adsorption enthalpies at high absolute uptake is an inherent feature of the double-site Langmuir isotherm and the CC equation at high coverage.

4 | Discussion

Commonly used isotherm models for extracting thermodynamic adsorption data have built-in assumptions about the nature of the adsorption binding site distributions. These assumptions directly influence both the temperature dependence and shape of the extracted adsorption enthalpies from the fits. In order to evaluate this more fully, we took our own NREL data, and in Figure 5a,b shows two adsorption models, the Unilan and double-site Langmuir isotherm, applied to the same collected HKUST-1 excess uptake data. Both models fit the collected data reasonably

well between 77 K and 140 K. Figure 5c,d shows the resulting enthalpies of adsorption from the Unilan (Supporting Information Equation (S2), Table S2) and double-site Langmuir (Supporting Information Equation (S1)) fits. The Unilan model assumes a uniform distribution of binding energies while the double-site Langmuir assumes two fixed energy delta functions for the binding-site distributions. As a result, the Unilan-calculated isosteric adsorption enthalpy has a negative slope with binding-site coverage, with low-coverage values (<1 wt%) above the double-site Langmuir. The double-site Langmuir isosteric enthalpy has reduced dependence on site coverage, however two levels are observed, due to filling of the two energetic sites. Both isosteric enthalpy values average to between 5–6 kJ/mol when considering all adsorption sites, but with different features. Without other experimental input such as calorimetry measurements or neutron diffraction data, the isotherm model selection may unduly influence both the adsorption enthalpy shape and low coverage limits, even with well-fitted isotherms.

In the as-reported data, a few of the laboratories reported initial high adsorption enthalpies in the Henry's Law regime (where adsorption is approximately linear with pressure), which rapidly decreased at low coverage. Figure 6 shows that this feature can be introduced as an interpolation artifact, when using the two-temperature CC equation (Equation (5), the Discretized method) interpolated with insufficient pressure points or spacings at low

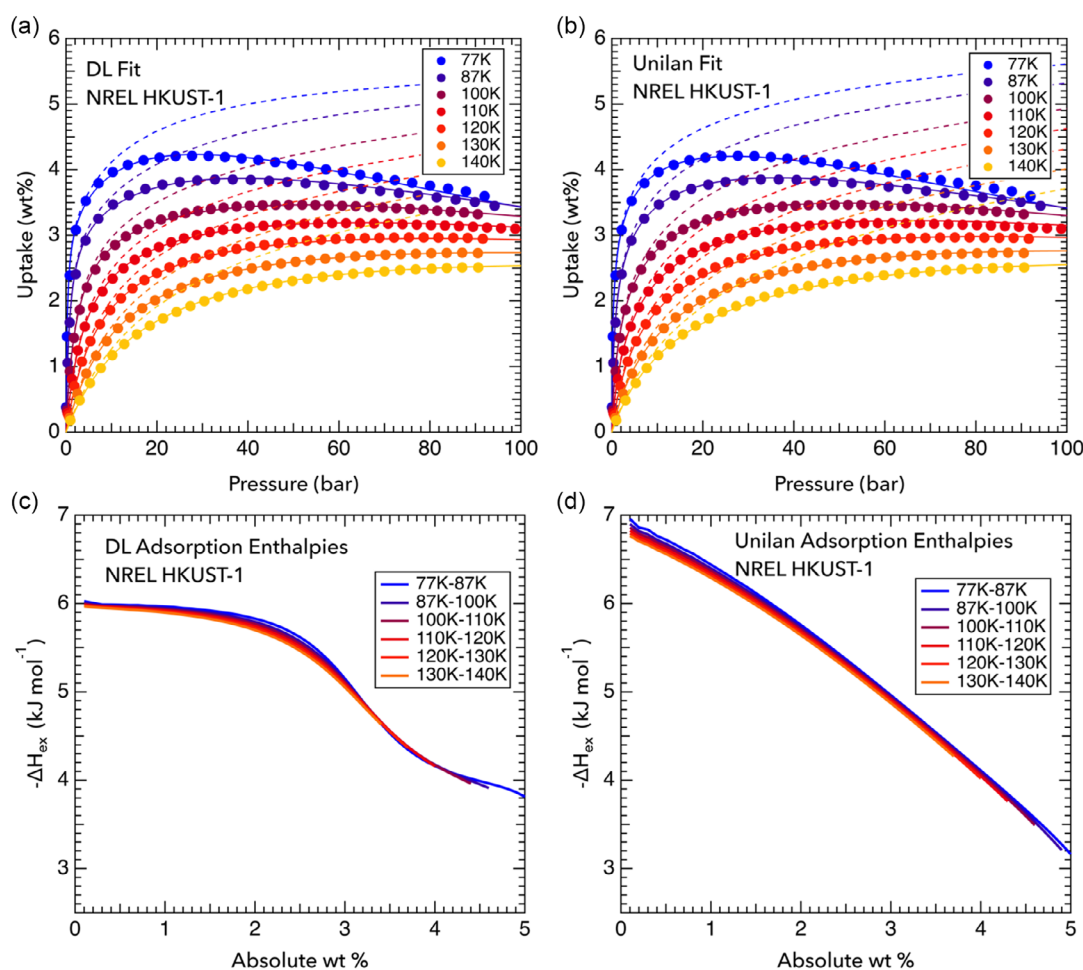


FIGURE 5 | Fitted excess uptake isotherm measurements between 77 K–110 K using double-site Langmuir (a) and Unilan (b) isotherm models, with resulting isosteric adsorption enthalpies for double-site (c) and Unilan (d). Dotted lines denote absolute uptake fits.

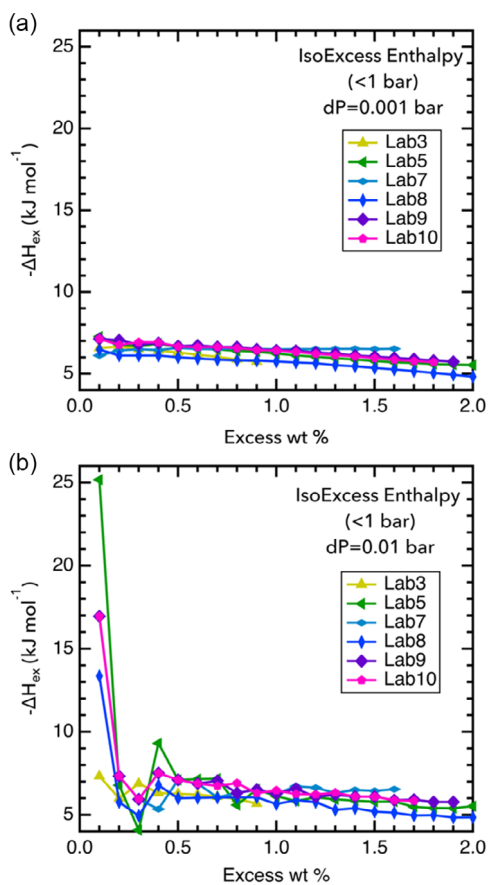


FIGURE 6 | Isoexcess adsorption enthalpies using the same fit with interpolated pressure spacings of (a) 0.001 and (b) 0.01 bar.

coverage where uptake rapidly increases with pressure (Figure 6b). With a decreased spacing between the pressures (such as 0.001 bar, as in Figure 6a), these artifacts disappear. These artifacts could be erroneously interpreted as highly energetic binding sites without careful consideration.

Based on both the as-reported and the universal fitting method, adsorption enthalpy calculations are sensitive to the overall shape of the excess uptake isotherm and the range of absolute uptake used for fitting. Both the isoexcess and isosteric adsorption enthalpies obtained from low-pressure isotherm data (<1 bar) show higher values in the Henry's Law regime and a steeper slope with coverage as compared to enthalpies obtained from high-pressure isotherms. With high pressure adsorption data, the double-site Langmuir equation fits isotherm points over a larger range of coverage than the low-pressure data, thus including more lower energy binding sites and weighting the fitting parameter for the two energies accordingly. This trend is also observed with the as-reported values from the laboratories, excluding the outlier data sets. Of note, using extrapolated isotherm data beyond what was experimentally collected in the CC approach introduces additional deviation and is not recommended (Supporting Information Figure S3). The extrapolated values are solely determined by the isotherm choice and their respective resultant fitted parameters. With low coverage data fitting, there is no reliability that the enthalpies obtained from the extrapolated sorption isotherm data is accurate at high coverage. Ultimately, the amount of data that is fit (and whether high-coverage data is included in that) has a significant impact on the resulting adsorption enthalpies.

The reported excess uptake measurements in the adsorption enthalpy outlier data sets (Lab1 and Lab4) are lower than the other data sets and also show different functional shapes of the measured uptake. However, a laboratory reporting consistently higher or lower isotherms that can be fixed with a vertical scaling factor (such as inaccurate mass measurements) can still obtain a comparable value for the isosteric enthalpy due to the functional form of the CC equation. This is observed for Lab3, which reported adsorption isotherms lower than other laboratories, but reported reasonable values for the adsorption enthalpy due to correct isotherm shape. The obtained enthalpy values will correspond to incorrect adsorption uptake values, which will result in an isoexcess coverage offset (horizontal shift in the plot). This is not observed in Figure 3 because Lab3 used a single-site Langmuir for their isotherm equation, and a global fit, which results in a single adsorption enthalpy independent of coverage.

5 | Conclusion

The enthalpy of adsorption (ΔH_{st}) is an often-used metric for the evaluation of materials for hydrogen storage applications. This enthalpy is typically indirectly calculated via the CC approximation using isotherm data. This paper illustrates that it is critical for the research community to understand the limitations and inherent inaccuracies of this approach in order to fairly compare/contrast materials' physiochemical properties. A dozen laboratories participated in a study on the reproducibility of calculated enthalpies across the adsorption community. Two outliers were identified, which reported the largest deviations in adsorption enthalpies due to discrepancies in isotherm measurements relative to other laboratories. Adsorption enthalpy calculations were consistent between the other laboratories to within 1 kJ/mol. Differences in enthalpy trends with uptake were observed due to the pressure range of the uptake data measurements, insufficient data points used for interpolation schemes, isotherm interpolation approaches, and conversion to absolute adsorption as opposed to using excess data directly. Careful consideration must be made when comparing ΔH_{st} results reported in literature, especially across different laboratories. Isotherm models introduce inherent biases to the isosteric enthalpy calculation, which can lead to artifacts that are misappropriately attributed to material adsorption properties. When calculating isosteric enthalpy of adsorption, the following best practices should be used:

1. Sufficient quantity of sample should be used—as much as is feasible, which depends on the measurement apparatus. Ideally over 200 mg and more for materials that are expected to adsorb poorly. Larger sample sizes minimize the impact of measurement noise or experimental error on isotherm quality.
2. Collect high-quality, well-equilibrated isotherm data with as many data points as is reasonably possible.
3. Ensure isotherm shape is physically reasonable and consistent across temperatures.
4. Employ identical fitting approach including isotherm model choice and conversion to absolute (or use excess data) when comparing ΔH_{st} results.
5. Only report enthalpy of adsorptions as a function of coverage for coverages experimentally collected with isotherm

data. Don't extrapolate isosteric enthalpy of adsorption outside the pressure/coverage range of the data collected.

- When publishing enthalpies of adsorption, report all details of the methodology used explicitly in the paper or SI. The decision tree used here, and provided as a resource, can serve as a template.
- When comparing enthalpies among laboratories, realize that different methodologies will contribute to significant discrepancies and artifacts in the resultant enthalpies of adsorption.

Many questions and concerns remain regarding the accuracy and reproducibility of isosteric enthalpy calculations. While this study demonstrated an approximate 1 kJ/mol deviation in reported values for HKUST-1, it should not be assumed that this error applies to other adsorbent/adsorbate pairs. Investigation of a material/gas pair with a higher adsorption enthalpy would need to be conducted to discern the enthalpy calculation uncertainty in systems with stronger gas binding. This study focused on the reproducibility of ΔH_{st} calculations across the several laboratories, and not the validity of using adsorption enthalpy calculations as isosteric heats of adsorption. Determination of physical adsorption heats remains challenging due to errors and uncertainties in direct heat measurement techniques, such as adsorption calorimeters. While there exists a validation lab for adsorption uptake measurements, there is currently not a national facility for the validation of adsorption heats. This work is intended to complement recent IUPAC guidelines and contribute towards future international standardization efforts in adsorption thermodynamics.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Supporting Fig. S1:** Isothermic enthalpy from the Langmuir isotherm model as a function of temperature using calculations from the CC equation when the Langmuir has different explicit temperature dependencies. In one case, the result is a constant, independent of temperature, while in the other, a linear dependency given a $\frac{1}{2}$ RT factor. Given that a Langmuir generally is considered a homogeneous site model with adsorption enthalpy E_a , the $\frac{1}{2}$ RT factor introduces a temperature-dependent bias that is not originally present in the classical Langmuir equation. This prefactor choice therefore adds temperature dependencies to the isotherm, and can have consequences, including model-dependent temperature trends, to the enthalpy calculation results. **Supporting Fig. S2:** Decision tree (with choices in solid orange for isothermic and dotted orange for isoexcess) for calculating adsorption enthalpies for Figures 4, 5, and 6. **Supporting Fig. S3:** Extrapolated isothermic adsorption enthalpies, using the low-pressure isotherm fits from Table S1 for experimental data collected below 1 bar. Enthalpy is calculated using the calculated absolute uptake, up to 100 bar, using the discrete Clausius-Clapeyron method with temperature pairs (77 K–87 K, or closest temperature pair to 77 K). Vertical dotted lines denote the limit of the experimentally fitted data for each laboratory isotherm. **Supporting Table S1:** Fitting coefficients for the double-site Langmuir equation using the global fit method for isotherms measured between 77 K and 100 K (77 K–140 K for NREL data) (Figures 4 and 5a in main text). **Supporting Table S2:** Fitting coefficients for the

UNILAN equation using the global fit method for isotherms measured between 77K and 140K (Figure 5b in main text).