

EXPERIENCE WITH EVALUATION OF THE ISOSTERIC ADSORPTION HEATS BY STUDENTS USING CLAUSIUS-CLAPEYRON APPROACH

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Abstract

This study analyses the approaches and problem-solving strategies employed by students in calculating the isosteric heat of adsorption Q_{st} for carbon dioxide on coal, utilizing adsorption isotherms and employing the Clausius-Clapeyron approach. Student problem-solving approaches play a critical role in mastering complex topics in physical chemistry, including adsorption processes. Research has shown that student strategies often vary based on their prior knowledge, instructional guidance, and available resources. To better understand these dynamics, this study analyzes the methodologies employed by students in their calculation of isosteric heats and evaluates how these methods reflect their problem-solving preferences. To classify the problem-solving strategies employed by students, their methods were categorized into four groups: a) extracting pressures from original adsorption data; b) deducing pressures from the graphical representation of isotherms; c) calculating pressures through linear regression of isotherms; and d) calculating pressures using a second-order polynomial regression of isotherms. Moreover, the Freundlich adsorption model was evaluated for its potential to approximate isotherm trends. All methods yielded similar isosteric heats (approximately 31 kJ mol^{-1}) for adsorption uptakes (v_a) greater than 2.5 ml g^{-1} , yet significant disparities in Q_{st} were observed at lower surface coverages. When determining the most suitable fit for the adsorption data, analysis of the residues is recommended rather than comparison of the values of the coefficient of determination, R^2 . The second-order polynomial fit, specifically in the coordinates v_a versus $\ln(p)$, demonstrated the tightest course with the experimental adsorption data across the entire range of adsorption and can thus be recommended as the appropriate numerical approximation of the isotherm trends. The classification was based on the students' submitted calculations and their explanations during follow-up discussions. Each approach was further analyzed for its replicability and accuracy. The observed variability in the students' results underscores the importance of providing clear guidelines for data analysis in chemistry education. By engaging in these tasks, students developed critical thinking skills and an appreciation for the impact of methodological choices on scientific outcomes.

Keywords: *Higher education, physical chemistry, problem-solving, adsorption, critical thinking.*

1. Introduction

Heat of adsorption is a crucial parameter for evaluating the energetics of the adsorption process. Isosteric heats of adsorption (Q_{st}) are commonly calculated from adsorption isotherms, which are collected over a wide range of pressures (p) and at various temperatures (T) (Atkinson & Curthoys, 1978). These isotherms allow for the plotting of $\ln(p)$ versus $1/T$ dependencies at constant adsorption uptake, known as isosteres. The isosteric heat Q_{st} for a specific surface coverage is then determined from the slope of the isostere by applying the Clausius-Clapeyron equation (1):

$$Q_{st} = -R \left(\frac{d \ln p}{d(1/T)} \right), \quad (1)$$

where R represents the ideal gas constant.

Linearity of the $\ln(p)$ versus $1/T$ isosteres is an approximation in principle, however, it has been broadly validated by numerous authors. For example (Bülow, Shen, & Jale, 2002) in their study on the adsorption of gases on zeolites, reported remarkably straight lines across a wide temperature range of 90°C . As a result, invariance of the isosteric heat in the given range of temperatures can be assumed.

To construct isosteres, it is essential to determine the pressures under isosteric conditions from the adsorption isotherms. Such principal requirement is mentioned in the textbook of Physical Chemistry (Atkins, 2002) as well as literature specialised on adsorption (Gregg & Sing, 1982). However, no further recommendation for evaluation of Q_{st} is provided. Recently, (Nuhnen & Janiak, 2020) introduced a practical guide for calculating isosteric heats for metal-organic frameworks (MOFs), which, in addition

to the Clausius-Clapeyron method, examines virial analysis, thereby offering a more comprehensive approach to processing adsorption data.

This paper summarises seven years of experience in student calculations of isosteric heat, Q_{st} , using known data of adsorption isotherms at three temperatures and the Clausius-Clapeyron approach.

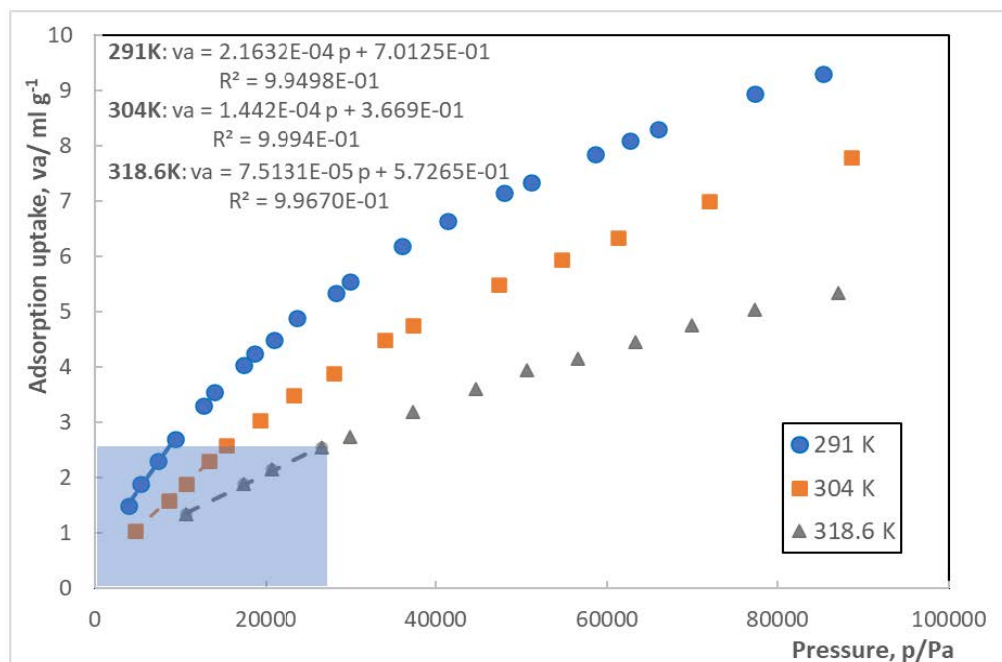
2. Methodology, adsorption data

The evaluation of isosteric heats from known adsorption isotherms constituted a homework assignment for students enrolled in the "Analytical Chemistry of Solid Phase" master's program at Ostrava University, within the course "Energetics and Calorimetry of Heterogeneous Processes." This elective course was taken by forty students over a span of seven years.

All students received detailed instructions on the principles of constructing isosteres and calculating isosteric heat. However, no specific guidelines were provided on how to determine the pressures under isosteric conditions. The students had previously learned data fitting techniques in mandatory courses: "Statistics" during their bachelor's studies, and "Chemometrics" in their master's program. Consequently, the individual experience and skill of each student were thus respected in processing the adsorption data.

The study analyzed adsorption isotherms of carbon dioxide on bituminous coal at temperatures of 291K, 304K, and 318.6K. This adsorption system is significant due to its relevance to gas outburst phenomena. The coal sample, characteristic of the Upper Silesian Coal Basin, had an analytical basis carbon content of 68.4% and a total pore volume of $0.041 \text{ cm}^3 \text{ g}^{-1}$ (Żółcińska-Jezińska & Lasoń, 1981). The adsorption isotherms were measured at the Polish Academy of Sciences using a volumetric apparatus, with an estimated measurement repeatability of approximately 5%. The students received the adsorption data in a tabulated format, including pressure (p) in torr and CO_2 adsorption uptake (v_a) in $\text{cm}^3 \text{ g}^{-1}$ (STP). To convert pressure from torr to pascal, the relation $1 \text{ torr} = 133.322 \text{ Pa}$ was utilized, and the adsorbed amount (v_a) was expressed in the original units of $\text{cm}^3 \text{ g}^{-1}$. A graphical representation of the analyzed isotherms is provided in Figure 1.

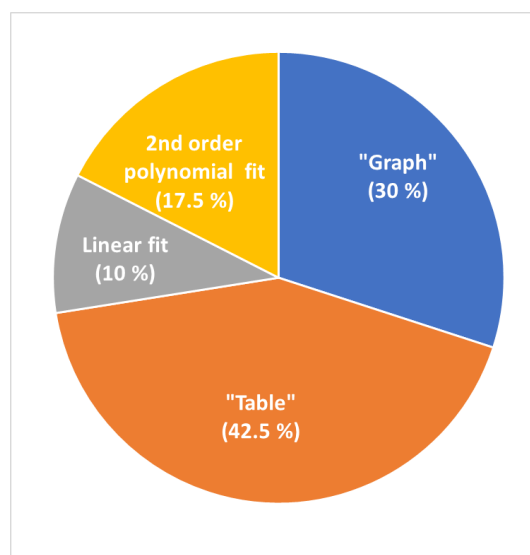
Figure 1. Adsorption isotherms of CO_2 on natural coal to be analysed. Blue area denotes Henry's region with linear development of the isotherms. Equations in the left upper side express linear fit of the isotherms within the Henry's region.



3. Results

In principle, the students employed four distinct methods to determine the pressures under isosteric conditions: a) directly reading the "isosteric" pressures from the original table containing adsorption data; b) determining the "isosteric" pressures through analysis of the graphical representation of the isotherms; c) calculating a linear fit of the isotherms; d) calculating a second-order polynomial fit of the isotherm developments. Figure 2 presents the distribution of these four methods.

Figure 2. Frequency of the procedures used by students to determine isosteric adsorption heats.



The results of the students' calculations were evaluated formatively way during the "evaluation lesson" at the end of the semester. Students received feedback on how the method of approximation of the adsorption isotherms can affect the resulting dependence of Q_{st} versus v_a . Previously, students considered the coefficient of determination R^2 to be the definitive indicator of fit quality. The students thus were introduced to the analysis of residues, which assesses the integrity of the fit across the entire range of surface coverages.

4. Conclusions

The investigations conducted offer valuable insights for educators focusing on the topic of isosteric adsorption heat. Key takeaways include:

- Utilizing graphical representation of adsorption data is a straightforward method to derive rather isolated Q_{st} values at specific adsorption uptakes or surface coverages. The relative standard deviation for such calculations is approximately 6%_{rel}.
- Numerical fits and adsorption model approximations of adsorption isotherms facilitate the generation of continuous Q_{st} series as functions of surface coverage. Notably, these approaches may yield significant variances in Q_{st} values, especially at lower surface coverages.
- For higher adsorption uptakes (here, beyond v_a of 2.5 ml g⁻¹), a general stabilization or only minor decline in Q_{st} values can be anticipated.
- To ascertain the most suitable fit for adsorption data, residue analysis is advised. Ideal fits exhibit random residuals—both positive and negative—across the entire spectrum of surface coverages, as opposed to systematic deviations.
- The second-order polynomial fit in coordinates v_a vs. $\ln p$ demonstrated the closest alignment with experimental adsorption data throughout the entire range of adsorption, thus emerging as the preferred numerical approximation for evaluating isosteric adsorption heats.

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