A Statistical Mechanical Perspective on the Temperature Dependence of the Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity

Shaheen A. Al-Muhtaseb and James A. Ritter*

Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208

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Statistical mechanical concepts were applied to analyze the temperature dependence of the isosteric heat of adsorption and, consequently, the difference between the adsorbed and gas phase heat capacities for monatomic, diatomic, and linear and nonlinear polyatomic molecules. Expressions were developed at the two extremes of localized and mobile adsorption. Also, the effects of the molecular size and shape on the isosteric heats of adsorption and the dependence on temperature were analyzed. The temperature dependence of the isosteric heat of adsorption was always important, especially for localized adsorption, heavily adsorbed molecules, or relatively low temperatures. At relatively high temperatures, the temperature dependence of the isosteric heat of adsorption became linear with a fixed slope, regardless of the molecular size (for both localized and mobile adsorption) and molecular shape (for mobile adsorption). Depending on the type of molecule and/or temperature, the difference between the adsorbed and gas phase heat capacity could be either negative or positive; and in some cases, significant deviations were exhibited mostly at industrially relevant conditions.

Introduction

Recent analyses[1] have shown that nonisothermal pressure swing adsorption simulations can be very sensitive to variations in thermodynamic properties such as the isosteric heat of adsorption and the adsorbed phase heat capacity, which is related to the temperature dependency of the isosteric heat of adsorption. The isosteric heat of adsorption is typically estimated by applying the Clausius−Clapeyron equation to adsorption isotherm data.[2−4] There are only two published approaches which look for a possible dependency of the isosteric heat of adsorption on temperature. The first and more conventional approach plots the pressure logarithm versus the temperature reciprocal from experimental adsorption equilibria. This approach always resulted in linear plots,[3,4] leading to the assumption of a negligible temperature dependency. However, recent studies, which have adopted the second approach of applying the Clausius−Clapeyron equation to various forms of adsorption isotherm models, have shown that altering the order of the temperature dependency of the parameters in these models to improve their description of adsorption equilibria with temperature,[5−7] or extending these models to account for surface heterogeneity,[8] can indicate different degrees of temperature dependencies of the isosteric heat of adsorption. Surprisingly, when plotting the adsorption equilibria in the Clausius−Clapeyron form (pressure logarithm versus the temperature reciprocal), using statistically optimized correlations that describe the experimental data very well and also indicate a noticeable temperature dependency of the isosteric heat of adsorption,[7] the resulting relationships were highly linear, in agreement with the results obtained from the first more conventional approach. Also, multicomponent isosteric heats of adsorption can be temperature dependent, even when the single-component isosteric heats of adsorption for some of the components in the mixture are not.[5] The temperature independence of the isosteric heat of adsorption also causes the adsorbed phase heat capacity to be equal to the gas phase heat capacity.[9] This fact is disturbing because relatively weak temperature dependencies of the isosteric heat of adsorption can result in about a 20% difference between the adsorbed and gas phase molar heat capacities.[8] Moreover, density functional theory predictions of the isosteric heat of adsorption[10] exhibit weak temperature dependencies that are, in most cases, of the same order as those predicted from correcting the Fowler−Guggenheim model to account for surface heterogeneity with a uniform energy distribution.[8] Although these results tend to suggest that the temperature independent assumption is valid and should give reasonable values for the isosteric heat of adsorption, it can lead to erroneously different values of the adsorbed phase heat capacity,[8] which in turn can impact significantly nonisothermal adsorption process simulations.[1]

Results from the literature have shown that the temperature dependence of the isosteric heat of adsorption is directly related to the adsorbate−adsorbent interactions as represented by a temperature-dependent extension of the Fowler−Guggenheim isotherm to account for adsorption on a heterogeneous surface with a uniform distribution of adsorption energies.[8] Variable temperature dependencies of the isosteric heats of adsorption have also been demonstrated using concepts from gas phase vibrational partition functions[11] and surface energy site distributions.[12] However, these analyses are limited to specific models[8] or specific cases at relatively high temperatures.[11,12]

Molecular simulations can also provide relatively accurate predictions of the derived thermodynamic properties in dense phases when an accurate description of the intermolecular potentials is applied. Hard sphere and Lennard-Jones potentials with different proportions of interaction and repulsion terms are the most widely used potentials.[11] However, molecular simulations are necessarily applied to very specific and simple molecules at specific adsorption conditions. In contrast, simple and idealized statistical mechanical approaches are more suitable

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* To whom all correspondence should be addressed. Phone: (803) 777-3590. Fax: (803) 777-8265. E-mail: ritter@engr.sc.edu.

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for generalizing the roles of different parameters on the temperature dependence of the derived thermodynamic properties; and although they may not be as accurate as molecular simulations in predicting these properties at specific adsorption conditions, statistical mechanical approaches definitely provide the correct trends and magnitudes for the ideal gas adsorption conditions, which are the focus of this study. Therefore, the objective of this work is to further apply the statistical thermodynamic approach to gain more insight into the temperature dependence of the isosteric heat of adsorption from the canonical partition function for the adsorbed and gas phase ensemble.

Different simplifying assumptions and adsorption conditions are evaluated with accordance to their impact on the temperature dependence of the isosteric heat of adsorption and, consequently, the adsorbed phase heat capacity. Although real adsorption systems rarely correspond to either simple localized or nonlocalized (mobile) conditions, this analysis is carried out at these two extreme limits to obtain clear insights into the corresponding boundaries of the temperature dependence of the isosteric heat of adsorption. For all cases, the effects of molecular size and shape are considered and new expressions are presented for predicting both the isosteric heat of adsorption and adsorbed phase heat capacity, on the basis of different statistical mechanical models of the adsorbed and gas phase ensemble.

Theory

The statistical mechanical adsorption isotherm is usually obtained by deriving an expression for the chemical potential of the adsorbed phase and equating it to the gas phase chemical potential at the same conditions.[11,13−15] Applying this approach to localized adsorption results in the popular Langmuir isotherm model[11,13,14] which is given by

$$\theta = \frac{b(T)P}{1 + b(T)P} \quad \text{or} \quad b(T)P = \frac{\theta}{1-\theta} \tag{1}$$

where θ is the fractional surface coverage ($= N/M$), P is the pressure, T is the temperature, M is the number of adsorption sites, and N is the number of adsorbed molecules. The corresponding expression for nonlocalized (mobile) adsorption is derived using a two-dimensional fluid equation of state and is generally given by[12,15]

$$b(T)P = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right) \tag{2}$$

where $b(T)$ is the Henry's law constant and is given in both cases by

$$b(T) = b_0(T)\exp\left(\frac{\epsilon}{RT}\right) \tag{3a}$$

where ϵ refers to the potential energy minimum of an adsorbed molecule and R is the universal gas constant. Here, $b(T)$ can also be extended in both cases with Bragg−Williams-type approximations to account for lateral interactions as

$$b(T) = b_0(T)\exp\left(\frac{\epsilon - z\omega\theta}{RT}\right) \tag{3b}$$

where z is a fixed number, ω is the nearest-neighbor interaction energy, and b_0 is given by

$$b_0(T) = \frac{h^3}{\kappa T(2\pi m\kappa T)^{3/2}}\frac{q(T)}{Q^g_{\text{int}}(T)} \tag{4}$$

where m is the mass of the molecule, h and κ are Planck's and Boltzmann's constants, respectively, $q(T)$ is the molecular partition function of the adsorbed phase, and $Q^g_{\text{int}}(T)$ is the partition function of the internal degrees of freedom (mainly, rotational and vibrational) for the component in the gas phase. A summary of the expressions for $Q^g_{\text{int}}(T)$ and the corresponding gas phase heat capacities is given in the Appendix. Clearly, b_0 is temperature dependent, and its temperature dependency varies with variations in the conditions encountered in the ensemble of the adsorption system, as well as the assumptions that are used in evaluating the partition functions. Typically q is obtained by applying the rigid rotator approximation and harmonic oscillations, which leads to[11,13−14]

$$q = q_{\text{trans}}q_{\text{el}}q_{\text{nucl}}q_{\text{vib}}q_{\text{rot}} \cong \Omega_{\text{el}}q_{\text{trans}}q_{\text{vib}}q_{\text{rot}} \tag{5}$$

where q_{trans}, q_{el}, q_{nucl}, q_{vib}, and q_{rot} are the translational, electronic, nuclear, vibrational, and rotational contributions of the molecular partition function, respectively, and Ω_{el} is the degeneracy for the lowest electron-level energy. These partition functions can be expressed in different alternative forms, depending on the system and corresponding conditions and assumptions.[16] Also, some of these partition functions can overcome the others depending on the degree of the adsorbed phase mobility as shown later in the discussion.

The isosteric heat of adsorption can be obtained from the Clausius−Clapeyron equation:

$$q_{\text{st}} = RT^2\left(\frac{\partial \ln P}{\partial T}\right)_\theta \tag{6}$$

Substituting eq 1 or 2 and eq 3 into eq 6 gives the following expression for the isosteric heat of adsorption:

$$q_{\text{st}} = \epsilon - z\omega\theta - RT^2\left(\frac{\partial \ln b_0(T)}{\partial T}\right)_\theta \tag{7}$$

The difference between the differential adsorbed phase and molar gas phase heat capacities is obtained from the temperature dependence of the isosteric heat of adsorption[8] by

$$\Delta\bar{C}p_a = \bar{C}p_a - \tilde{C}p_g = -\left(\frac{\partial q_{\text{st}}}{\partial T}\right)_\theta \tag{8}$$

which, when applied to eq 7, becomes

$$\Delta\bar{C}p_a = RT\left(2\left[\frac{\partial \ln b_0(T)}{\partial T}\right]_\theta - T\left[\frac{\partial \ln b_0(T)}{\partial T}\right]^2_\theta + \frac{T}{b_0(T)}\left[\frac{\partial^2 b_0(T)}{\partial T^2}\right]_\theta\right) \tag{9}$$

Therefore, according to eqs 7 and 9, the temperature dependence of the isosteric heat of adsorption, its deviation from the average adsorption energy ($\epsilon - z\omega\theta$), and the difference between the differential adsorbed phase and molar gas phase heat capacities all depend highly on the temperature dependence of b_0. As b_0 reflects mainly the adsorbate−adsorbent interactions as shown in eq 4, this result agrees with the classical thermodynamic approach,[8] which shows that the temperature dependence appears mainly as a result of interactions between the adsorbate and adsorbent as represented by the surface heterogeneity parameter. However, in that case[8] the heterogeneity parameter was the only parameter reflecting this type of interaction.

Simple formulas for the temperature dependence of b_0 have been considered in the literature by considering the high temperature approximation on the vibrational contribution from the adsorbed phase in both localized[11] and nonlocalized[13] adsorption. The results from these studies show that the isosteric heat of adsorption for a monatomic ideal gas adsorbed at relatively high temperatures is obtained from

$$q_{st} = \epsilon \pm {}^{1}/_{2}RT \tag{10}$$

for the Langmuir isotherm. The negative and positive signs correspond to localized[11] and nonlocalized adsorption,[13] respectively. Equation 10 gives $\Delta\bar{C}p_a = \mp R/2$, with the opposite sign from eq 10. Therefore, nonlocalized adsorption and the high temperature approximation of the adsorbed phase vibrational partition function[13] estimate the differential adsorbed phase heat capacity to be below the molar gas phase heat capacity (negative $\Delta\bar{C}p_a$), which indicates extremely weak adsorption conditions; however, localized adsorption[11] results in a positive $\Delta\bar{C}p_a$.

This brief analysis shows that different treatments of the adsorption ensemble at different conditions can result in remarkably different temperature dependencies of the isosteric heats of adsorption. Clearly, in addition to the effect of the high temperature approximation, the nature of the adsorbed phase and its relative mobility on the surface of the adsorbent have a remarkable effect on the sign and magnitude of the temperature dependency of the isosteric heat of adsorption and the deviation between the differential adsorbed phase and molar gas phase heat capacities. Therefore, different statistical mechanical models of the adsorbed gas phase ensemble, along with different parameters and conditions, are analyzed below to determine each of their impacts on the isosteric heat of adsorption and corresponding adsorbed phase heat capacity.

Results and Discussion

The contribution of b_0 in the predicted temperature dependence of the isosteric heat of adsorption and $\Delta\bar{C}p_a$ results from its own temperature dependency, regardless of the temperature's linear multipliers, as demonstrated below. Therefore, the partition functions in eqs 2 and 5 are subjected to different conditions and scenarios to illustrate their roles on the temperature dependence of b_0 and, hence, the isosteric heat of adsorption and $\Delta\bar{C}p_a$. The analysis covers monatomic, diatomic, and linear and spherical-top nonlinear polyatomic adsorbate molecules in equilibrium with an ideal gas phase, which is assumed to exhibit separable Hamiltonians and negligible intramolecular interactions.[16] Each of these cases is evaluated at the extreme conditions of localized (immobile) and nonlocalized (mobile) adsorption. The effect of temperature in different scenarios is also analyzed.

Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity of a Monatomic Molecule. In this case, in addition to the absence of internal degrees of freedom in the gas phase (see Appendix A1), the rotational contribution in the adsorbed phase is negligible. Therefore, the only factors are the relative contributions from the vibrational and translational partition functions in the adsorbed phase, as shown in eq 2. These factors change with the relative mobility of the adsorbed phase on the surface of the adsorbent.

In the extreme limit of a localized (immobile) adsorbed phase, all of the translational degrees of freedom change into vibrational degrees of freedom.[11] Therefore, for an adsorbed monatomic molecule, there are only three vibrational degrees of freedom in the adsorbed molecule, one normal and two parallel to the plane of the adsorbent surface.[11] As a result of this phenomenon, and assuming almost equal frequencies of vibration in the three directions, eq 5 simplifies to

$$q \cong \Omega_{el} q_{vib}^{3} \tag{11}$$

which leads to

$$b_0 = \frac{\Omega_{el} h^3}{\kappa T (2\pi m \kappa T)^{3/2}} q_{vib}^{3} \tag{12}$$

To obtain the proper form of q_{vib}, the dimensionless adsorbed phase vibrational temperature, τ_{vs}, is introduced here as the ratio of the temperature of the system to the adsorbed phase vibration frequency temperature, or $\tau_{vs} = T/\Phi_{vs}$, where $\Phi_{vs} = h\nu_{vs}/\kappa$ and ν_{vs} is the frequency of vibration. Generally, the vibrational partition function at such a vibration frequency temperature, τ_v, is given explicitly by

$$q_{vib}(\tau_v) = \frac{\exp(1/2\tau_v)}{\exp(1/\tau_v) - 1} \tag{13}$$

which, at a very high τ_v, reduces to

$$q_{vib}(\tau_v) = \tau_v \tag{14}$$

Substituting eqs 11 to 13 in eq 7 gives

$$q_{st} = \epsilon - z\omega\theta - RT\left(\frac{-5}{2} + \frac{3\exp(1/\tau_{vs}) + 1}{2\tau_{vs}\,[\exp(1/\tau_{vs}) - 1]}\right) \tag{15}$$

which, with the high adsorbed phase vibrational temperature (τ_{vs}) approximation, reduces to

$$q_{st} = \epsilon - z\omega\theta - RT/2 \tag{16}$$

Equations 15 and 16 provide analytic expressions for the isosteric heat of monatomic localized adsorption as a function of temperature and the frequency of vibration in the adsorbed phase. Substituting these expressions into eq 8 leads to the following explicit expressions for $\Delta\bar{C}p_a$ at low and high τ_{vs}, respectively:

$$\Delta\bar{C}p_a = R\left(\frac{-5}{2} + \frac{3\exp(1/\tau_{vs})}{\tau_{vs}^{\ 2}\,[\exp(1/\tau_{vs}) - 1]^2}\right) \tag{17}$$

$$\Delta\bar{C}p_a = +R/2 \qquad \text{at high } \tau_{vs} \tag{18}$$

with eqs 16 and 18 satisfying the previously published results.[11]

In the other extreme limit of a nonlocalized (mobile) adsorbed phase, only one translational degree of freedom in the adsorbed phase changes into a vibrational degree of freedom normal to the plane of the adsorbent surface, leaving a two-dimensional translational partition function, along with a one-dimensional vibrational partition function, in eq 2. Therefore, eq 5 reduces in this case to

$$b_0(T) \cong \frac{\Omega_{el} h^3}{\kappa T (2\pi m \kappa T)^{3/2}} q_{trans}^{(2D)} q_{vib} = \frac{\Omega_{el} h a^2}{kT\sqrt{2\pi m \kappa T}} q_{vib} \tag{19}$$

where a^2 is the unit area for the 2-dimensional adsorbed phase translational partition function and q_{vib} is treated as before (see eqs 13 and 14). Substituting eq 19 into eq 7 gives

$$q_{st} = \epsilon - z\omega\theta - RT\left(\frac{-3}{2} + \frac{\exp(1/\tau_{vs}) + 1}{2\tau_{vs}\,[\exp(1/\tau_{vs}) - 1]}\right) \tag{20}$$

which, with the high τ_{vs} approximation, reduces to

$$q_{st} = \epsilon - z\omega\theta + RT/2 \tag{21}$$

Substituting these expressions into eq 8 gives the following explicit expressions for $\Delta\bar{C}p_a$ at low and high τ_{vs}, respectively:

$$\Delta\bar{C}p_a = R\left(\frac{-3}{2} + \frac{\exp(1/\tau_{vs})}{\tau_{vs}^{\ 2}[\exp(1/\tau_{vs}) - 1]^2}\right) \tag{22}$$

$$\Delta\bar{C}p_a = -R/2 \qquad \text{at high } \tau_{vs} \tag{23}$$

Equations 21 and 23 satisfy the results obtained indirectly by Adamson.[13] The difference in signs between eqs 18 and 23 shows the role of the adsorbed phase when it is localized or mobile at high adsorbed phase vibrational temperatures.

Figure 1 shows the effect of τ_{vs} on the relative error included in the assumption of equal differential adsorbed and molar gas phase heat capacities (η), the absolute deviation between the differential adsorbed and molar gas phase heat capacities, and the relative magnitude of the temperature dependency of the isosteric heat of adsorption in terms of RT, for both localized and mobile adsorption. Figure 1a shows that, relative to the monatomic ideal gas phase heat capacity, about ±20% error can result from assuming equal adsorbed and gas phase heat capacities at high τ_{vs}, which is the expected condition of most industrial applications. If lower temperatures or stronger adsorption bonds are encountered, the absolute magnitude of this error can be as high as 60% for nonlocalized adsorption or 100% for localized adsorption. Also, except for localized adsorption at high τ_{vs}, the monatomic adsorbed phase heat capacity is less than the molar gas phase heat capacity, as also shown in Figure 1b. Nonlocalized adsorption exhibits a higher heat capacity than localized adsorption at low τ_{vs}. However, these two curves cross each other at $\tau_{vs} \cong 0.35$ with $\Delta\bar{C}p_a \cong -R$ for each, and the trend inverts at higher τ_{vs} exhibiting a higher adsorbed phase heat capacity for localized adsorption. This point of intersection shows that an intermediate value of τ_{vs} exists where the two vibrational degrees of freedom parallel to the surface of the adsorbent become equivalent to the two-dimensional translational degree of freedom, resulting in equal effects of localized and nonlocalized adsorption on the related thermodynamic properties. The difference between the localized differential adsorbed and molar gas phase heat capacities diminishes at $\tau_{vs} \cong 0.7$; then it begins to deviate again, but in the positive direction, until it reaches a fixed value of $+R/2$ at relatively high temperatures. The corresponding trend for nonlocalized adsorption always stays negative and becomes increasingly closer to the gas phase heat capacity with increasing τ_{vs}, until $\Delta\bar{C}p_a$ reaches a fixed value of $-R/2$.

Figure 1c shows that the temperature dependent monatomic isosteric heat of adsorption always causes a negative deviation from the minimum adsorption potential energy, ϵ, at low τ_{vs}. This deviation disappears for nonlocalized adsorption at $\tau_{vs} \cong 0.4$, and increases thereafter until it reaches the high τ_{vs} limit of $+RT/2$. Since room temperature is expected to be much higher than Φ_{vs}, especially for weak adsorption,[13] high values of τ_{vs} are expected. So clearly the temperature dependence of the isosteric heat of adsorption tends to increase the isosteric heat of adsorption when increasing τ_{vs} except for localized adsorption at relatively high τ_{vs}, where it starts to decrease slightly with increasing τ_{vs}, as indicated by the change in sign of the corresponding $\Delta\bar{C}p_a$. It is noteworthy that this behavior depends only on the vibration frequency in the adsorbed phase; a completely different behavior is realized when the vibration in the gas phase dominates, as demonstrated in the following section.

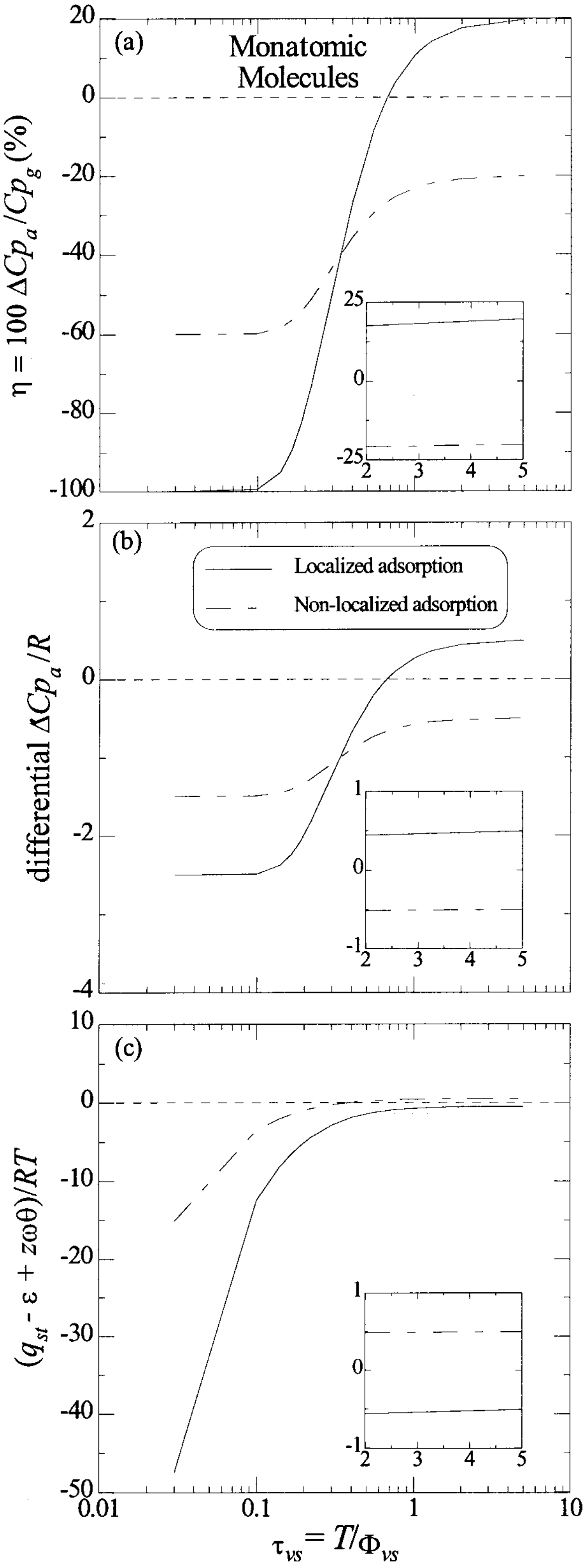

Figure 1. Effect of monatomic adsorbed phase vibrational temperature on the (a) percent error of assuming equal adsorbed and gas phase heat capacities, (b) predicted deviation of the differential adsorbed phase heat capacity from the molar gas phase heat capacity, and (c) magnitude of the temperature dependent term of the isosteric heat of adsorption. The inserts indicate the expected conditions for industrial adsorption processes.

Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity of a Diatomic Molecule. In this case, the internal degrees of freedom of the gas phase contribute to the value of b_0. In contrast to the rotational frequency temperature, the vibrational frequency temperature in the gas phase, Φ_{vg}, can normally be several hundreds or even thousands of degrees Kelvin for diatomic and polyatomic molecules.[16] Therefore, the high gas phase vibrational temperature ($\tau_{vg} = T/\Phi_{vg}$) approximation can be highly misleading unless the system is really considered at extremely high temperatures. The adsorbed phase frequency of vibration is also expected to be orders-of-magnitude less than the gas phase frequency of vibration and, as mentioned previously, room temperature. Therefore, the adsorbed phase vibrational partition function is estimated from the high τ_{vs} approximation, i.e., from eq 14.

As with the monatomic molecule case, when the extreme condition of localized (immobile) adsorption is considered, all of the degrees of freedom in the adsorbed phase change into vibrational degrees of freedom. Therefore, with the high τ_{vs} approximation for the resulting six vibrational degrees of freedom in the adsorbed phase and with the partition function for the internal degrees of freedom of a diatomic gas molecule (see Appendix A2), b_0 is given by

$$b_0 = \sqrt{\frac{h^6 \Phi_{rg}^2 T^5}{8\pi^3 \Phi_{vs}^{12} m^3 \kappa^5}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})} \right) \tag{24}$$

which reduces to

$$b_0 = \sqrt{\frac{h^6 \Phi_{rg}^2\ \Phi_{vg}^2 T^3}{8\pi^3 \Phi_{vs}^{12} m^3 \kappa^5}} \tag{25}$$

upon applying the high τ_{vg} approximation. Substituting eq 24 into eq 7 gives the following expression for the localized, diatomic, isosteric heat of adsorption:

$$q_{st} = \epsilon - z\omega\theta - RT\left(\frac{5}{2} - \frac{\exp(1/\tau_{vg}) + 1}{2\tau_{vg}[\exp(1/\tau_{vg}) - 1]} \right) \tag{26}$$

or when $\tau_{vg} \gg 1$

$$q_{st} = \epsilon - z\omega\theta - 3RT/2 \tag{27}$$

The absolute deviation from the minimum potential energy of adsorption at the high temperature limit has increased by a magnitude of RT, compared to that of the monatomic gas. This higher temperature dependence of the isosteric heat of adsorption is due to the effects of the internal degrees of freedom in the gas phase on the temperature dependence of b_0. Substituting eq 26 into eq 8 gives the following expression for $\Delta\bar{C}p_a$:

$$\Delta\bar{C}p_a = R\left(\frac{5}{2} - \frac{\exp(1/\tau_{vg})}{\tau_{vg}^2\ [\exp(1/\tau_{vg}) - 1]^2} \right) \tag{28}$$

which reduces to $+3R/2$ upon applying the high τ_{vg} approximation.

At the other extreme of nonlocalized (mobile) adsorption, only one translational degree of freedom in the adsorbed phase changes into a vibrational degree of freedom. Although some rotational degrees of freedom may change upon adsorption to an intermediate form between vibration and rotation, they are assumed here to be unchanged. Nevertheless, a comparison between eqs 14 and A3 shows that the high temperature approximation for both the adsorbed phase vibrational and rotational partition functions gives similar, linear temperature dependencies; thus, the resulting expressions for the isosteric heat of adsorption are unaffected by distinguishing between these two types of degrees of freedom. After substituting the resulting two-dimensional translational partition function, along with the remaining vibrational and rotational degrees of freedom, into eq 4, b_0 becomes

$$b_0 = \frac{ha^2 \Phi_{rg} \sqrt{T}}{\Phi_{rs} \Phi_{vs}^2 \sqrt{2\pi m \kappa^3}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})} \right) \tag{29}$$

or with the high τ_{vg} approximation

$$b_0 = \frac{ha^2 \Phi_{rg} \Phi_{vg}}{\Phi_{rs} \Phi_{vs}^2 \sqrt{2\pi m \kappa^3 T}} \tag{30}$$

Substituting eq 29 into eq 7 gives the following expression for the diatomic nonlocalized isosteric heat of adsorption:

$$q_{st} = \epsilon - z\omega\theta - RT\left(\frac{1}{2} - \frac{\exp(1/\tau_{vg}) + 1}{2\tau_{vg}\ [\exp(1/\tau_{vg}) - 1]} \right) \tag{31}$$

with the corresponding high τ_{vg} approximation given by

$$q_{st} = \epsilon - z\omega\theta + RT/2 \tag{32}$$

Equations 21 and 32 indicate that when nonlocalized adsorption is considered at relatively high temperatures, the size of the molecule is insignificant to the isosteric heat of adsorption. On the other hand, the isosteric heat of localized diatomic gas adsorption at relatively high temperatures shows a considerable difference from, at least, the isosteric heat of monatomic gas adsorption. These contradicting behaviors at high temperatures are due to the fact that the adsorbed phase in nonlocalized adsorption now has equivalent rotational and vibrational degrees of freedom to substitute for those introduced from the gas phase. Therefore, as they all have the same temperature dependence at high temperatures and the isosteric heat of adsorption is unaffected by distinguishing between these degrees of freedom when they all have the same linear temperature dependence, the isosteric heat of nonlocalized adsorption at high temperatures becomes the same, but only because it is estimated in reference to the gas-phase enthalpy. Nevertheless, the enthalpy of both the gas and adsorbed phases would change in equal magnitudes upon changing the size of the molecule, thereby keeping the difference fixed between the enthalpies of both phases. Substituting eq 31 in eq 8 gives the following expression for $\Delta\bar{C}p_a$ for diatomic nonlocalized adsorption:

$$\Delta\bar{C}p_a = R\left(\frac{1}{2} - \frac{\exp(1/\tau_{vg})}{\tau_{vg}^2\ [\exp(1/\tau_{vg}) - 1]^2} \right) \tag{33}$$

which, at high τ_{vg}, reduces to $-R/2$.

Figure 2 shows the effect of τ_{vg} on the relative error (η) of assuming equal adsorbed and gas phase heat capacities, the magnitude of the deviation between the differential adsorbed and molar gas phase heat capacities, and the magnitude of the temperature dependent part of the isosteric heat of adsorption, all for diatomic molecules with the high temperature approximations applied to the adsorbed phase vibrational partition function and also the rotational partition functions in both phases. Figure 2a shows that the deviation between the differential adsorbed

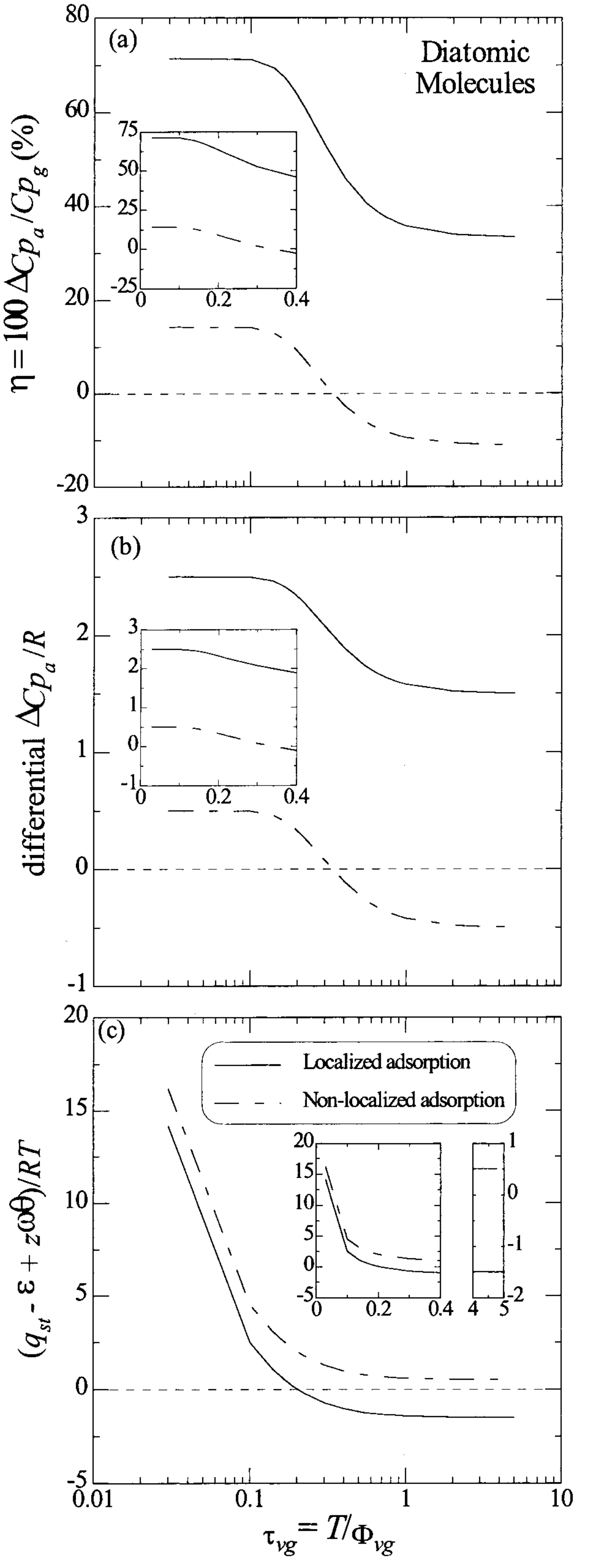

Figure 2. Effect of diatomic gas phase vibrational temperature on the (a) percent error of assuming equal adsorbed and gas phase heat capacities, (b) predicted deviation of the differential adsorbed phase heat capacity from the molar gas phase heat capacity, and (c) magnitude of the temperature dependent term of the isosteric heat of adsorption. The inserts indicate the expected conditions for industrial adsorption processes.

and molar gas phase (see Appendix A2) heat capacities at low τ_{vg} (which are expected in typical industrial applications) can be in the approximate range of 14 to 71% for nonlocalized to localized adsorption, respectively. This shows the increasing importance of the temperature dependence of the isosteric heat of adsorption when increasing the size of the molecule, in comparison to the errors presented in Figure 1a. At high τ_{vg}, the error decreases to -11% for nonlocalized adsorption and 33% for localized adsorption, indicating the importance of the temperature dependence for diatomic gas adsorption, even at high temperatures, and especially if relatively strong interactions between the adsorbent and adsorbate (resulting in localized adsorption) are expected. In nonlocalized adsorption, however, η reaches zero at $\tau_{vg} \cong 0.3$ and deviates after that from the gas phase heat capacity, but in the negative direction. The same behavior is also shown in Figure 2b with respect to $\Delta\bar{C}p_a$. This phenomenon (the cancellation of the temperature dependence of the isosteric heat of adsorption as a result of certain adsorption conditions) has been observed elsewhere[5] and was related to the ratio between different interactions. Moreover, Figure 2b shows that for nonlocalized adsorption of a diatomic molecule at low τ_{vg}, $\Delta\bar{C}p_a$ can be as high as $+R/2$ and decreases with temperature until it reaches $-R/2$; the same trend of $\Delta\bar{C}p_a$ decreasing with increasing τ_{vg} can also be noticed for localized adsorption. Comparing this to the τ_{vs} effect in Figure 1b shows that an increase in the vibration frequency in the gas phase or a decrease in temperature (both resulting in a decrease in τ_{vg}) has a positive effect on $\Delta\bar{C}p_a$; while an increase in the vibration frequency in the adsorbed phase, increasing the adsorbed bond strength or sharply decreasing the temperature (all resulting in a decrease in τ_{vs}), causes a negative effect on $\Delta\bar{C}p_a$. This shows how the internal degrees of freedom of the molecules in the gas and adsorbed phases play different roles on the thermodynamic derived properties. However, the vibration frequency in the gas phase is normally more dominant than that in the adsorbed phase; and, hence, τ_{vg} can be considered as the limiting factor when di- or polyatomic molecules are considered.

Figure 2c shows that the temperature dependent part of the isosteric heat of adsorption can reach more than $+15RT$ when low τ_{vg} conditions are exhibited. However, it drops relatively fast with τ_{vg} increasing and equals zero for localized adsorption at $\tau_{vg} \cong 0.15$, changing from a positive to a negative deviation from ϵ. On the other hand, nonlocalized adsorption always exhibits positive deviations from ϵ at all τ_{vg}. Moreover, the temperature dependent term of the isosteric heat of nonlocalized adsorption tends to invert at high temperatures, switching from a decreasing to an increasing function of τ_{vg}, as indicated by the changing sign of $\Delta\bar{C}p_a$ in Figure 2b. Therefore, no general rule can be formulated regarding the temperature dependence of the isosteric heat of adsorption. In most of the cases, however, the isosteric heat of adsorption decreases with an increase in temperature (or alternatively, τ_{vg}). However, if high mobility of the adsorbed phase is exhibited at high τ_{vg}, the isosteric heat of adsorption can increase slightly with increasing temperature.

Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity of Linear and Spherical-Top Nonlinear Polyatomic Molecules. Polyatomic molecules exhibit different internal degrees of freedom for different molecular sizes and shapes. Linear and nonlinear molecules, for example, exhibit two and three rotational degrees of freedom, respectively. Moreover, the expressions for the rotational and vibrational partition functions are different for different shapes and sizes of polyatomic molecules as shown in Appendix A3.

In the extreme condition of localized adsorption, all degrees of freedom change to an adsorbed phase vibrational partition function which, with the high temperature approximation, is given by eq 14 raised to the power of 3μ where μ is the number of atoms in the molecule. With these considerations and with the appropriate partition function for the internal degrees of freedom in the gas phase (see Appendix A3), the resulting b_0 for a linear polyatomic molecule is given by

$$b_0 = \frac{\sigma h^3 \Phi_{rg} T^{(3\mu-5/2)}}{\Phi_{vs}^{3\mu}\sqrt{8\pi^3 m^3 \kappa^5}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})}\right)^{(3\mu-5)} \tag{34}$$

which, with the high temperature approximation, reduces to

$$b_0 = \frac{\sigma h^3 \Phi_{rg} \Phi_{vg}^{(3\mu-5)} T^{3/2}}{\Phi_{vs}^{3\mu}\sqrt{8\pi^3 m^3 \kappa^5}} \tag{35}$$

and for a spherical-top nonlinear molecule, it is given by

$$b_0 = \frac{\sigma h^3 \Phi_{rg}^{3/2} T^{(3\mu-4)}}{\pi^2 \Phi_{vs}^{3\mu}\sqrt{8 m^3 \kappa^5}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})}\right)^{(3\mu-6)} \tag{36}$$

which, with the high temperature approximation, also reduces to

$$b_0 = \frac{\sigma h^3 \Phi_{rg}^{3/2} \Phi_{vg}^{(3\mu-6)} T^{2}}{\pi^2 \Phi_{vs}^{3\mu}\sqrt{8 m^3 \kappa^5}} \tag{37}$$

The isosteric heat of adsorption for a linear polyatomic molecule is obtained from substituting eq 34 into eq 7, which gives

$$q_{st} = \epsilon - z\omega\theta - RT\left(3\mu - \frac{7}{2} - \frac{3\mu - 5}{2\tau_{vg}}\left(\frac{\exp(1/\tau_{vg}) + 1}{\exp(1/\tau_{vg}) - 1}\right)\right) \tag{38}$$

which, with the high temperature approximation, reduces to

$$q_{st} = \epsilon - z\omega\theta - 3RT/2 \tag{39}$$

and for a spherical-top nonlinear molecule, substituting eq 36 into eq 7 gives

$$q_{st} = \epsilon - z\omega\theta - RT\left(3\mu - 4 - \frac{3\mu - 6}{2\tau_{vg}}\left(\frac{\exp(1/\tau_{vg}) + 1}{\exp(1/\tau_{vg}) - 1}\right)\right) \tag{40}$$

which, with the high temperature approximation, also reduces to

$$q_{st} = \epsilon - z\omega\theta - 2RT \tag{41}$$

The equivalence of eqs 27 and 39, but not eq 41, indicates that the high temperature limit of the isosteric heat of adsorption depends on the molecular shape rather than size. Therefore, the difference that was previously noticed between the monatomic and diatomic molecules is a result of their different shapes rather than their different sizes. Moreover, eqs 39 and 41 are independent of μ, which proves the independence of the isosteric heat of adsorption on the size of the molecule in the high temperature limit. The difference between the isosteric heats of adsorption of linear and nonlinear molecules (i.e., the difference between eqs 38 and 40) is given by

$$q_{st}^{\text{linear}} - q_{st}^{\text{nonlinear}} = \frac{-RT}{2}\left(1 - \frac{\exp(1/\tau_{vg}) + 1}{\tau_{vg}\,[\exp(1/\tau_{vg}) - 1]}\right) \tag{42}$$

which approaches ∞ when $\tau_{vg} \to 0$ and $+RT/2$ when $\tau_{vg} \to \infty$. Therefore, the molecular shape effect on the isosteric heat of localized adsorption makes the isosteric heat of adsorption of linear molecules always higher than that of nonlinear molecules. Equation 42 also shows this to be the case at low τ_{vg}, which is the typically expected condition and usually reflected in either low-to-moderate temperatures or high frequencies of vibration for the molecule in the gas phase.

Substituting eq 40 into eq 8 gives the following analytic expression for $\Delta\bar{C}p_a$ of a linear polyatomic molecule:

$$\Delta\bar{C}p_a = R\left(3\mu - \frac{7}{2} - \frac{(3\mu - 5)\exp(1/\tau_{vg})}{\tau_{vg}^2\,[\exp(1/\tau_{vg}) - 1]^2}\right) \tag{43}$$

which, upon the high temperature approximation, reduces to $+3R/2$. The corresponding $\Delta\bar{C}p_a$ for a spherical-top nonlinear molecule is obtained by substituting eq 42 into eq 8, which gives

$$\Delta\bar{C}p_a = R\left(3\mu - 4 - \frac{(3\mu - 6)\exp(1/\tau_{vg})}{\tau_{vg}^2\,[\exp(1/\tau_{vg}) - 1]^2}\right) \tag{44}$$

which, with the high temperature approximation, reduces to $+2R$. The difference between the differential heat capacities of linear and nonlinear polyatomic molecules is, therefore, given by

$$\bar{C}p_a^{\text{linear}} - \bar{C}p_a^{\text{nonlinear}} = R\left(1 - \frac{\exp(1/\tau_{vg})}{\tau_{vg}^2\,[\exp(1/\tau_{vg}) - 1]^2}\right) \tag{45}$$

which approaches $+R/2$ and $-R/2$ at the low and high temperature limits, respectively, and equals zero at $\tau_{vg} \cong 0.33$. It is clear from eqs 50 and 53 that the shape effect of the polyatomic molecules is related only to the gas phase vibrational temperature, τ_{vg}, regardless of the size of the molecule.

At the other extreme of mobile (nonlocalized) adsorption, it is assumed that there are still two and three rotational degrees of freedom in the adsorbed phase for linear and nonlinear molecules, respectively, and that one translational degree of freedom is changed into a vibrational degree of freedom normal to the plane of the adsorbent surface. This leaves α' vibrational degrees of freedom, where α' equals $(3\mu - 4)$ or $(3\mu - 5)$ for the adsorbed linear and nonlinear molecules, respectively. As explained before, distinguishing between the vibrational and rotational degrees of freedom in the adsorbed phase is unimportant for the purpose of this study, as long as they are all estimated from the high temperature approximation. Therefore, the rotational partition functions are still estimated from eqs A6 and A7 for linear and nonlinear molecules, respectively, and the vibrational partition function in the adsorbed phase is calculated from eq 14 raised to the power of α'. As a result of these considerations, b_0 for a linear polyatomic molecule is given by

$$b_0 = \frac{\sigma h a^2 \Phi_{rg} T^{(3\mu-11/2)}}{\Phi_{rs} \Phi_{vs}^{(3\mu-4)}\sqrt{2\pi m \kappa^3}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})}\right)^{(3\mu-5)} \tag{46}$$

which, with the high τ_{vg} approximation, gives

$$b_0 = \frac{\sigma h a^2 \Phi_{rg} \Phi_{vg}^{(3\mu-5)}}{\Phi_{rs} \Phi_{vs}^{(3\mu-4)} \sqrt{2\pi m \kappa^3 T}} \tag{47}$$

and the corresponding b_0 for a nonlinear polyatomic molecule is given by

$$b_0 = \frac{\sigma h a^2 \Phi_{rg}^{3/2} T^{(3\mu-13/2)}}{\Phi_{vs}^{(3\mu-5)} \sqrt{2\pi m \kappa^3 \Phi_{rs}^3}} \left(\frac{\exp(1/\tau_{vg}) - 1}{\exp(1/2\tau_{vg})} \right)^{(3\mu-6)} \tag{48}$$

which also reduces to

$$b_0 = \frac{\sigma h a^2 \Phi_{rg}^{3/2}\, \Phi_{vg}^{(3\mu-6)}}{\Phi_{vs}^{(3\mu-5)} \sqrt{2\pi m \kappa^3 \Phi_{rs}^3 T}} \tag{49}$$

with the high τ_{vg} approximation. Although eqs 47 and 49 are different functions, they have the same temperature dependence, thus they are expected to exhibit the same isosteric heat of adsorption and $\Delta\bar{C}p_a$. Substituting eq 46 into eq 7 gives the following expression for the isosteric heat of nonlocalized adsorption of a linear polyatomic molecule

$$q_{st} = \epsilon - z\omega\theta - RT\left(3\mu - \frac{11}{2} - \frac{3\mu - 5}{2\tau_{vg}} \left(\frac{\exp(1/\tau_{vg}) + 1}{\exp(1/\tau_{vg}) - 1} \right)\right) \tag{50}$$

and substituting eq 48 into eq 7 gives the following expression for the isosteric heat of nonlocalized adsorption of a nonlinear molecule

$$q_{st} = \epsilon - z\omega\theta - RT\left(3\mu - \frac{13}{2} - \frac{3\mu - 6}{2\tau_{vg}} \left(\frac{\exp(1/\tau_{vg}) + 1}{\exp(1/\tau_{vg}) - 1} \right)\right) \tag{51}$$

As expected, because of the equal temperature dependence of b_0 with the high temperature approximation, eqs 50 and 51 both reduce to eq 32 at the high temperature limit. This result proves the previous conclusion that the high temperature limit of the isosteric heat of nonlocalized adsorption is independent of the molecular size. Moreover, it also provides an additional conclusion that, unlike the case of localized adsorption, it is also independent of the molecular shape.

Substituting eqs 50 and 51 into eq 8 gives the following expressions for $\Delta\bar{C}p_a$ for linear and nonlinear nonlocalized adsorbed molecules, respectively:

$$\Delta\bar{C}p_a = R\left(3\mu - \frac{11}{2} - \frac{(3\mu - 5)\exp(1/\tau_{vg})}{\tau_{vg}^2\,[\exp(1/\tau_{vg}) - 1]^2}\right) \tag{52}$$

$$\Delta\bar{C}p_a = R\left(3\mu - \frac{13}{2} - \frac{(3\mu - 6)\exp(1/\tau_{vg})}{\tau_{vg}^2\,[\exp(1/\tau_{vg}) - 1]^2}\right) \tag{53}$$

Equations 52 and 53 both reduce to $\Delta\bar{C}p_a = -R/2$ upon applying the high τ_{vg} approximation, which also agrees with the high temperature isosteric heat of adsorption being independent of both molecular shape and size when nonlocalized adsorption is exhibited. Also, it is clear by comparing eqs 52 and 53 to eqs 43 and 44, respectively, that localized and nonlocalized isosteric heats of adsorption and adsorbed phase heat capacities for the same molecular shape both become independent of the molecular size and τ_{vg}. The localized differential adsorbed phase heat capacity is always $2R$ ($-2RT$, for q_{st}) and $5R/2$ ($-5RT/2$, for q_{st}) higher than that of the nonlocalized adsorption for linear and nonlinear molecules, respectively. The fixed deviation in the case of polyatomic linear molecules also applies to the diatomic molecules at all τ_{vg}. This difference reflects the ideal energy barrier between localized and nonlocalized adsorption. The shape effect, however, depends on τ_{vg} for each kind of adsorption. Nevertheless, comparing the shape effects between each of the localized and nonlocalized adsorption cases, eqs 42 and 45 are always $+RT/2$ and $-R/2$, respectively, higher than the corresponding equations for nonlocalized adsorption. This is considered as the fixed shape effect contribution of linear and spherical-top nonlinear molecules to the energy barrier between localized and nonlocalized adsorption. Although the shape effect in each kind of adsorption depends on τ_{vg}, as shown in eqs 42 and 45, its contribution to the energy barrier between localized and nonlocalized adsorption is fixed, regardless of μ or τ_{vg}.

Figure 3 shows the molecular size and shape effects on the relative error resulting from the assumption of equal adsorbed and gas phase heat capacities for both localized and nonlocalized adsorption. Figure 3a shows that for the special case of $\tau_{vg} \gg 1$, which normally corresponds to very high temperatures, η slowly approaches 0% when increasing μ. This is only a relative effect because $\tilde{C}p_g$ increases successively with μ, reflecting a relative decrease in η. Even with this effect, η in the approximate range of -2 to $+7$% for nonlocalized to localized adsorption, respectively, can be expected with relatively large molecules. Moreover, considering low-to-moderate temperatures can significantly increase these errors, as demonstrated before. As supporting evidence of this behavior, Figure 3b shows that for low τ_{vg}, which is the expected case, η always increases with μ for different molecular shapes and types of adsorption, as indicated by the positive sign of its slope. However, a slight decrease of η might be expected for localized adsorption when μ increases at $\tau_{vg} > 0.5$. Nevertheless, $\Delta\bar{C}p_a$ always increases when increasing μ, as shown by the positive slope in Figure 4a. This slope is independent of both molecular shape and degree of localization. Therefore, the increase of $\Delta\bar{C}p_a$ with increasing μ is a pure molecular size effect without any interference from any other factors, and, from the definition of $\Delta\bar{C}p_a$, the temperature dependence of the isosteric heat of adsorption becomes higher when increasing μ. This latter result agrees with the recent literature[5−7] which shows an increase in the temperature dependence for more heavily adsorbed species. However, the size effect on $\Delta\bar{C}p_a$ or, alternatively, the temperature dependence of the isosteric heat of adsorption, diminishes when increasing τ_{vg} until it reaches almost zero at $\tau_{vg} \cong 5$.

Figure 4b shows the shape effect on the adsorbed phase heat capacity as a function of the gas phase vibrational temperature, τ_{vg}. Clearly, when nonlocalized adsorption is considered, there is no equivalence point between the adsorbed phase heat capacity of linear and nonlinear molecules except at extremely high τ_{vg}. Therefore, at low-to-moderate τ_{vg} and nonlocalized adsorption, linear molecules always exhibit higher adsorbed phase heat capacities. In localized adsorption, however, the adsorbed phase heat capacity for linear molecules is higher than that for nonlinear molecules for $\tau_{vg} < 0.3$ and lower for $\tau_{vg} > 0.3$. Nevertheless, the shape effects on the adsorbed phase heat capacity in both localized and nonlocalized adsorption are always parallel, with a fixed spacing of $R/2$, which is considered as the shape effect contribution to the energy barrier between localized and nonlocalized adsorption, as explained before.

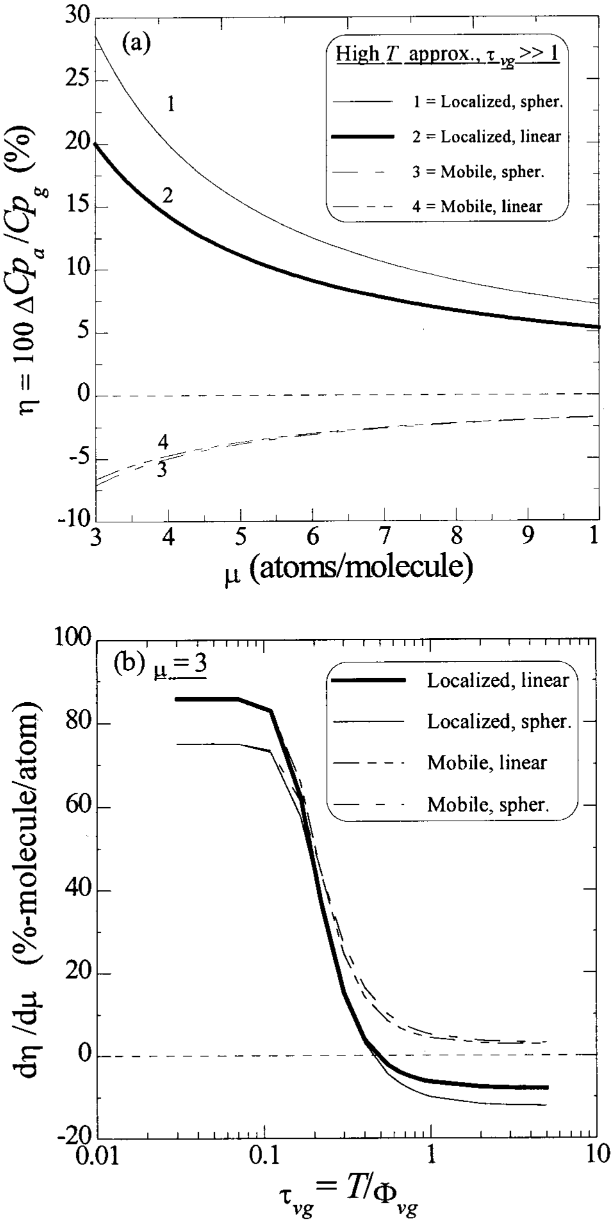

Figure 3. Effect of polyatomic molecule size on the (a) percent error of assuming equal adsorbed and gas phase heat capacities at a very high temperature and (b) rate of change in this error at lower (more typical) temperatures and a triatomic molecule. Relative to τ_{vg}, μ has only a minor effect on dη/dμ.

Figure 5 shows the predicted values of η, $\Delta\bar{C}p_a$ and the temperature dependent part of q_{st}, respectively, as functions of μ and τ_{vg}. As expected, Figure 5a shows that η always increases when increasing μ at low-to-moderate τ_{vg}; however, at high τ_{vg}, $\Delta\bar{C}p_a$ becomes independent of μ while $\tilde{C}p_g$ continues to increase slowly when increasing μ. This causes a slight decrease of η when increasing μ at relatively high temperatures as shown previously in Figure 3a. Here, η for localized adsorption is always positive (never equals zero) and higher than that for nonlocalized adsorption. Nonlocalized adsorption, however, exhibits the same dependence of η on μ, but with a much weaker dependence at high τ_{vg}. Also, at $\tau_{vg} > \sim 2$, nonlocalized adsorption exhibits slightly negative η values of around -5%. However, the small insert in Figure 5a shows that in the expected range of low-to-moderate τ_{vg}, η is more likely to be always positive and with considerable magnitudes for all conditions. Except for nonlocalized adsorption at high τ_{vg}, linear molecules always exhibit higher η than nonlinear molecules, and this shape effect on η becomes more pronounced at low τ_{vg}. Figure 5b shows the same behavior, and it also shows that the dependence of $\Delta\bar{C}p_a$ on μ at a specific τ_{vg} is almost constant, regardless of μ or the nature of adsorption. This effect is also manifest in Figure 4a, which shows the pure dependence of the rate of change of $\Delta\bar{C}p_a$ with μ on only τ_{vg}. Moreover, both Figures 5a and 5b demonstrate the previously noticed behavior at high τ_{vg} where the size effects cancel out for all adsorption conditions and the shape effect also disappears for nonlocalized adsorption. This equality, as explained before, results from the equal contributions from the molecular size and molecular shape (only in nonlocalized adsorption) to the partition functions in both the adsorbed and gas phases. The shape effect remains important in localized adsorption because all of the internal degrees of freedom in the adsorbed phase are assumed to be vibrational and, hence, do not distinguish between linear and nonlinear molecules. On the other hand, the internal degrees of freedom in the gas phase are always affected by the molecular shape. Therefore, as a result of these different behaviors, the ratio between the internal degrees of freedom in the gas and localized adsorbed phases is always affected by the shape of

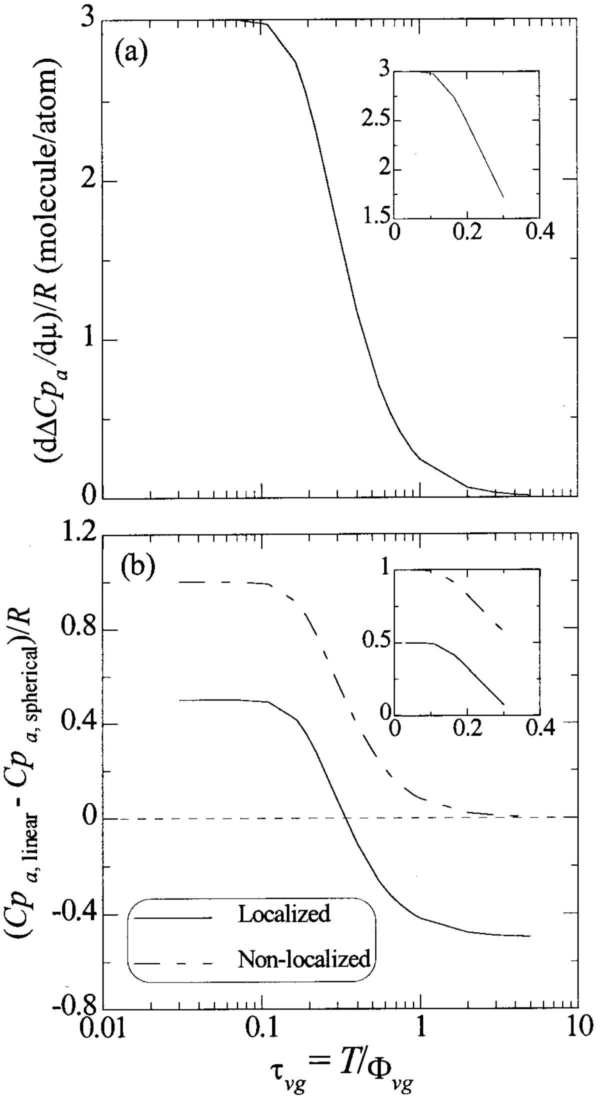

Figure 4. Effect of polyatomic gas phase vibrational temperature on the (a) molecule size dependence of and (b) molecule shape effect on the deviation of the differential adsorbed phase heat capacity from the molar gas phase heat capacity. The inserts indicate the expected conditions for industrial adsorption processes.

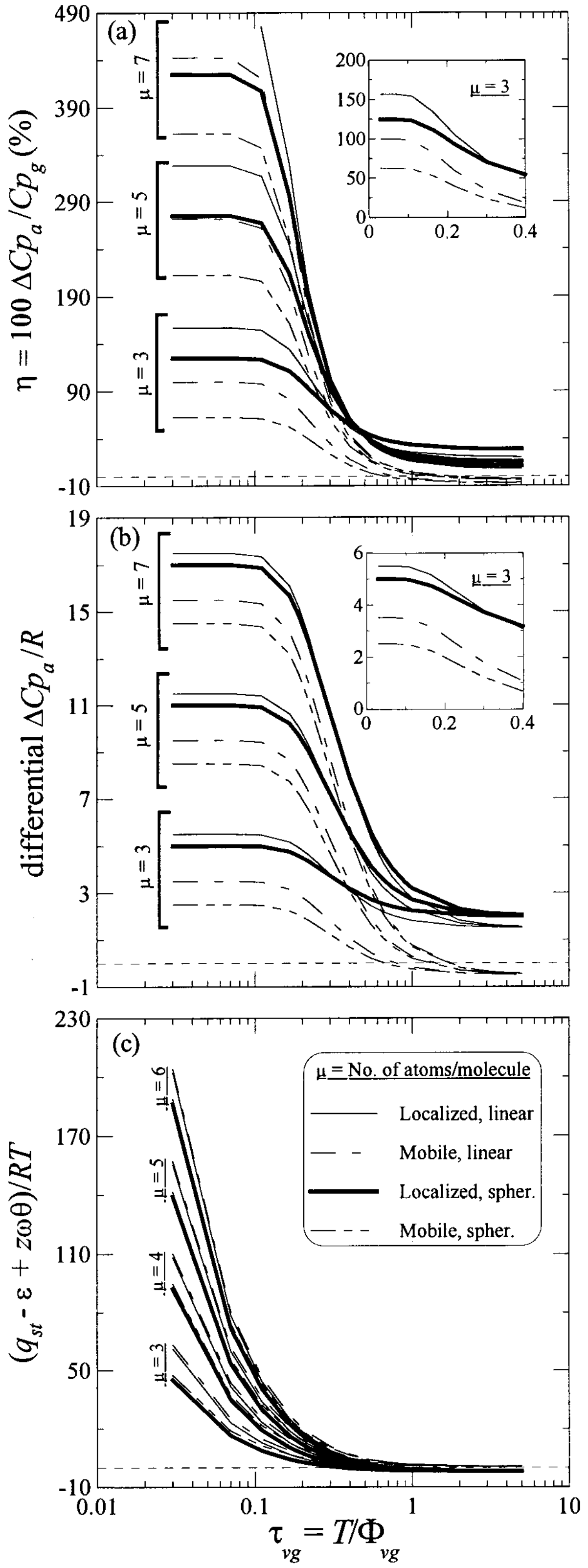

Figure 5. Effect of polyatomic molecule size and gas phase vibrational temperature on the (a) percent error of assuming equal adsorbed and gas phase heat capacities, (b) predicted deviation of the differential adsorbed phase heat capacity from the molar gas phase heat capacity, and (c) magnitude of the temperature dependent term of the isosteric heat of adsorption. The inserts indicate the expected conditions for industrial adsorption processes.

the molecule. Nevertheless, although the internal degrees of freedom in the gas and nonlocalized adsorbed phases are unequal, they are of the same kind and, therefore, change in the same way with μ when the high temperature approximation is considered for both of them.

Figure 5c shows the magnitude of the temperature dependent term of the isosteric heat of adsorption as a function of the τ_{vg}, molecular size and shape, and nature of adsorption. Clearly, the temperature dependence of the isosteric heat of adsorption is at its maximum at low τ_{vg}, where all the other effects are also pronounced. At this condition, μ plays a very important role on the temperature dependence of the isosteric heat of adsorption, which always increases in the positive direction when increasing μ. This agrees with the previously noticed behavior of $\Delta\bar{C}p_a$ and the recently published results[5-7] of the temperature dependence of the isosteric heat of adsorption and its increasing importance when increasing the adsorption affinity of the molecule. The effect of increasing adsorption affinity can be mimicked here with either decreasing τ_{vg} or increasing μ, both resulting in an increasing temperature dependence of the isosteric heat of adsorption. For a fixed molecular size, however, and at low τ_{vg}, the molecular shape effect is more important in determining the temperature dependence of the isosteric heat of adsorption than the nature of adsorption. Therefore, at every μ in Figure 5c, the curves for the temperature dependence of the isosteric heat of adsorption are grouped in two bundles, one for linear and another one for nonlinear molecules, with the linear molecules exhibiting a higher temperature dependence of the isosteric heat of adsorption, as also noticed in Figure 5b. At the high temperature limit, however, the temperature dependence of the isosteric heat of adsorption becomes dependent only on the nature of the adsorption and also slightly on the molecular shape in the case of localized adsorption, as shown previously in eqs 32, 39 and 41.

Conclusions

Statistical mechanical concepts were applied to analyze and obtain expressions for the isosteric heat of adsorption and its dependence on temperature. The analysis was held at the two extremes of localized and mobile adsorption for monatomic, diatomic, and linear and nonlinear polyatomic molecules. The temperature dependence of the isosteric heat of adsorption was most severe for localized adsorption, low temperature conditions, heavily adsorbed species, and increasing linearity of the polyatomic molecules at low-to-moderate temperatures, and vice versa at high temperatures. However, the most important determining factor on the temperature dependence of the isosteric heat of adsorption was the gas phase vibrational temperature, exhibiting a higher temperature dependence of the isosteric heat of adsorption at lower dimensionless gas phase vibrational temperatures. The adsorbed phase vibrational temperature was also important; but it could always be assumed to be relatively low at room temperature and, hence, could always be assumed to exhibit a fixed linear temperature dependence. Unlike the gas phase vibrational temperature, this always simplified the adsorption system in the high temperature approximation, but only with respect to the frequencies in the adsorbed phase.

For a fixed molecular shape, the difference in the adsorbed phase heat capacities between localized and nonlocalized adsorption was always constant regardless of the molecular size or adsorption conditions. The deviation between the differential adsorbed phase and molar gas phase heat capacities was in the approximate ranges of 27 to 67% and −10 to 10% for localized and mobile diatomic adsorption, respectively. The upper limits of these ranges corresponded to low temperatures and the lower limits corresponded to the high temperature approximation. At low-to-moderate temperatures, these deviations always increased with increasing linearity of the polyatomic molecules (in localized adsorption) or when increasing the number of atoms in each molecule. The increase in this relative deviation became almost negligible at very high numbers of atoms; however, the absolute deviation between the adsorbed and gas phase heat capacities increased continuously with the number of atoms per molecule. The rate of this increase was independent of the degree of localization and the molecular size and shape. However, a maximum rate of increase of the absolute deviation between the adsorbed and gas phase heat capacities was exhibited at low temperatures. The effect of polyatomic molecular shape could be substituted with either intermediate or relatively high temperatures when localized or mobile adsorption conditions were exhibited, respectively. The temperature dependence of the difference between the differential adsorbed and molar gas phase heat capacities was much less important than that of the isosteric heat of adsorption. Moreover, at relatively high temperatures and for localized adsorption, this difference exhibited constant values of $R/2$, $3R/2$, and $2R$ for monatomic, diatomic and linear polyatomic, and nonlinear polyatomic molecules, respectively, and $-R/2$ for mobile adsorption.

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Appendix

The Gas Phase Partition Function and Ideal Gas Phase Heat Capacities. *A1. Monatomic Gas Molecules.* In monatomic gas molecules the vibrational and rotational partition functions do not exist, therefore

$$Q_{\text{int}}{}^{g}(T) = 1 \tag{A1}$$

Substituting eq A1 into the appropriate expression for the total partition function gives the following expression for the ideal gas phase heat capacity:

$$Cp_g = Cv_g + R = 5R/2 \tag{A2}$$

A2. Diatomic Gas Molecules. In this case, the three main contributors are the one vibrational and two rotational degrees of freedom. The rotational frequency temperature, Φ_{rg} (expressed as $h^2/8\pi^2 I\kappa$, where I is the moment of inertia), is typically much lower than room temperature.[16] Therefore, the high rotational temperature approximation ($\tau_{\text{rg}} = T/\Phi_{\text{rg}} \gg 1$) is a fairly good approximation for most industrial conditions and is applied here for all rotational partition functions in the gas and adsorbed phases. This allows $Q^g_{\text{int}}(T)$ to be estimated from the product of the rotational and vibrational partition functions in the gas phase. This also allows the rotational partition function in the gas and adsorbed phases to be estimated from

$$q_{\text{rot}}(\tau_{\text{r}}) = \tau_{\text{r}} \tag{A3}$$

The vibrational frequency temperature in the gas phase, Φ_{vg}, can normally be several hundreds or even thousands of degrees Kelvin for diatomic and polyatomic molecules.[16] Therefore, the high gas phase vibrational temperature ($\tau_{\text{vg}} = T/\Phi_{\text{vg}}$) approximation was not considered in this study as a default assumption. Under these circumstances, eq 13 should provide a more accurate description for the gas phase vibrational partition function than eq 14; nevertheless, both equations are applied here to the di- and polyatomic molecules. With these considerations for a diatomic molecule, the partition function for the internal degrees of freedom in the gas phase is given by

$$Q^g_{\text{int}}(T) = q^g_{\text{rot}}\, q^g_{\text{vib}} = \frac{\tau_{\text{rg}} \exp(1/2\tau_{\text{vg}})}{\exp(1/\tau_{\text{vg}}) - 1} \tag{A4}$$

and the corresponding molar ideal gas phase heat capacity is given by

$$\tilde{C}p_g = R\left(\frac{7}{2} + \frac{\exp(1/\tau_{\text{vg}})}{\tau^2_{\text{vg}}\,[\exp(1/\tau_{\text{vg}}) - 1]^2}\right) \tag{A5}$$

which, at high τ_{vg}, reduces to $9R/2$.

A3. Polyatomic Gas Molecules. Unrestrained molecules in the gas phase always exhibit three translational degrees of freedom, leaving α vibrational degrees of freedom, where α equals ($3\mu - 5$) or ($3\mu - 6$) for linear and nonlinear molecules, respectively, and μ is the number of atoms in the molecule. The high temperature rotational partition functions for linear and spherical-top nonlinear molecules are given respectively by[16]

$$q^{\text{linear}}_{\text{rot}}(\tau_{\text{r}}) = \tau_{\text{r}}/\sigma \tag{A6}$$

$$q^{\text{nonlinear}}_{\text{rot}}(\tau_{\text{r}}) = \frac{\sqrt{\pi}}{\sigma}\tau_{\text{r}}^{3/2} \tag{A7}$$

where σ is a symmetry factor. Assuming equal vibrational frequencies, the unrestrained vibrational partition function is given by either eq 13 or 14 raised to the power of α. With these considerations, the ideal gas phase molar heat capacity for a linear polyatomic molecule is given by

$$\tilde{C}p_g = R\left(\frac{7}{2} + \frac{(3\mu - 5)\exp(1/\tau_{\text{vg}})}{\tau^2_{\text{vg}}\,[\exp(1/\tau_{\text{vg}}) - 1]^2}\right) \tag{A8}$$

which, at high τ_{vg}, reduces to

$$\tilde{C}p_g = 3R(\mu - 1/2) \tag{A9}$$

and for a spherical-top nonlinear molecule, it is given by

$$\tilde{C}p_g = R\left(4 + \frac{(3\mu - 6)\exp(1/\tau_{\text{vg}})}{\tau^2_{\text{vg}}\,[\exp(1/\tau_{\text{vg}}) - 1]^2}\right) \tag{A10}$$

which also reduces to

$$\tilde{C}p_g = R(3\mu - 2) \tag{A11}$$

at high τ_{vg}.

References and Notes

(1) Liu, Y.; J. A. Ritter, *Adsorption* **1998**, *4*, 159.

(2) Valenzuela, D. P.; Myers, A. M. *Adsorption Equilibrium Data Handbook*; Prentice-Hall: Englewood Cliffs, New Jersey, 1989.

(3) Sircar, S.; Rao, M. B. In *Surfaces of Nanoparticles and Porous Materials*; Schwarz, J. A., Contescu, C. I., Eds.; Dekker: New York, 1999, p 501.

(4) Bülow, M.; Shen, D. In *Proceedings of the Sixth International Conference of Fundamentals of Adsorption*; Meunier, F., Ed.; Elsevier: Amsterdam, The Netherlands, 1998; p 87.

(5) Al-Muhtaseb, S. A.; Ritter, J. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 684.

(6) Al-Muhtaseb, S. A.; Ritter, J. A. *Langmuir* **1998**, *14*, 5317.

(7) Al-Muhtaseb, S. A.; Ritter, J. A. In *Proceedings of the Sixth International Conference of Fundamentals of Adsorption*; Meunier, F., Ed.; Elsevier: Amsterdam, The Netherlands, 1998; p 339.

(8) Al-Muhtaseb, S. A.; Ritter, J. A. *J. Phys. Chem. B* **1999**, *103*, 2467.

(9) Sircar, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1527.

(10) Pan, H.; Ritter, J. A.; Balbuena, P. B. *Ind. and Eng. Chem. Res.* **1998**, *37*, 1159.

(11) Clark, A. *The Theory of Adsorption and Catalysis*; Academic Press: New York, 1970.

(12) Rudzinski, W.; Everett, D. H. *Adsorption of Gases on Heterogeneous Surfaces*; Academic Press: London, 1992.

(13) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley & Sons: New York, 1990.

(14) de Boer, J. H. *The Dynamical Character of Adsorption*, 2nd ed.; Oxford University Press: London and New York, 1968.

(15) Young, D. M.; Crowell, A. D. *Physical Adsorption of Gases*; Butterworth & co.: London, 1962.

(16) McQuarrie, D. A. *Statistical Mechanics*; Harper Collins Publishers: New York, 1976.