Adsorption (2009) 15: 53–63
DOI 10.1007/s10450-009-9150-4

# Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 2: conservation of mass and energy

**M.-A. Richard · P. Bénard · R. Chahine**

Received: 27 September 2007 / Revised: 23 July 2008 / Accepted: 12 January 2009 / Published online: 7 February 2009

**Abstract** Simulations of the thermal effects during adsorption cycles are a valuable tool for the design of efficient adsorption-based systems such as gas storage, gas separation and adsorption-based heat pumps. In this paper, we present simulations of the thermal phenomena associated with hydrogen, nitrogen and methane adsorption on activated carbon for supercritical temperatures and high pressures. The analytical expressions of adsorption and of the internal energy of the adsorbed phase are calculated from a Dubinin-Astakhov adsorption model using solution thermodynamics. A constant adsorption volume is assumed. The isosteric heat is also calculated and discussed. Finally, the mass and energy rate balance equations for an adsorbate/adsorbent pair are presented and are shown to be in agreement with desorption experiments.

**Keywords** Gas adsorption · Activated carbon · Dubinin-Astakhov · Supercritical · Hydrogen · Nitrogen · Methane · Internal energy · Isosteric heat · Modeling

## 1 Introduction

Physisorption in microporous adsorbents is used in various applications such as gas separation, gas storage, and adsorption heat pumps (Batos-Neto et al. 2005; Cruz et al. 2003; Mota et al. 1997; Teng et al. 1997). The design of physisorption-based systems must take into account not only the mass transfer but also the energy balance and the thermal effects associated with adsorption processes. The objective of this paper is to develop the mass and energy balance equations for hydrogen, nitrogen and methane adsorption on activated carbon valid over a large temperature and pressure range in the supercritical region. The neglecting of the specific volume of the adsorbed phase in the calculation of thermodynamic properties is avoided and the use of the perfect gas assumption is discussed. The contribution of the adsorbed phase in the balance equations can be obtained from an isotherm expressing the adsorbed gas as a function of temperature and pressure. For this purpose, in the companion paper, the Dubinin-Astakhov (D-A) model is adapted to model excess hydrogen and nitrogen adsorption isotherms at high pressure and over a wide range of supercritical temperatures using a constant microporous adsorption volume ($V_a$) to convert excess adsorption data into absolute adsorption (Richard et al. 2009). The total void volume of the adsorbent is divided in two constant contributions: the adsorption volume $V_a$ (the pore volume of the adsorbent subjected to the potential field of the solid) and the gas phase compression volume $V_g$ (the space outside $V_a$). The constant adsorption volume, $V_a$, is determined by model fitting.

The energy ($E$) of an adsorption system is given by:

$$E = n_g u_g + m_s u_s + m_s U_a, \tag{1}$$

where $n_g$ and $u_g$ are the mass and specific internal energy of the bulk gas present in the system, $m_s$ and $u_s$ are the mass and the specific internal energy of the adsorbent, and $U_a$ is the total internal energy of the adsorbed gas per unit mass of adsorbent. The specific internal energy of the adsorbed phase ($u_a$) is usually given by:

$$\frac{U_a}{n_a} = u_a = h_a - P\frac{V_a}{n_a}, \tag{2}$$

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M.-A. Richard (✉) · P. Bénard · R. Chahine
Institut de recherche sur l'hydrogène, Université du Québec
à Trois-Rivières, 3351, boulevard des Forges,
C.P. 500, Trois-Rivières, Québec, G9A 5H7 Canada
e-mail: Marc-andre.richard@uqtr.ca

where $n_a$ represents the normalised mass of adsorbed gas in mol/kg, $V_a$, the adsorbed phased volume in $m^3$/kg, and P, the pressure of the gas phase in equilibrium with the adsorbed phase. Since the adsorption volume is small, the usual approach is to consider $u_a$ equal to $h_a$, the specific adsorbed phase enthalpy (Walton and LeVan 2003). The enthalpy of the adsorbed gas is given by:

$$h_a = h_g + \frac{1}{n_a}\int_0^{n_a} \Delta\bar{h}_a dn_a, \tag{3}$$

where $-\Delta\bar{h}_a$ is the isosteric heat of adsorption obtained from adsorption isotherms and a Clausius-Clapeyron type equation which is given by:

$$\Delta\bar{h}_a = -ZRT^2\left[\frac{\partial \ln P}{\partial T}\right]_{n_a}, \tag{4}$$

where $Z$ is the compressibility factor, generally assumed to equal to 1. The heat of adsorption is generally assumed to be a function of the amount of adsorbed gas ($n_a$) (Myers 2002); however, in simulations, it is often considered to be constant (Basumatary et al. 2005; Cruz et al. 2003; Mota et al. 1997). If the isosteric heat is constant, (3) can be simplified to:

$$h_a = h_g + \Delta\bar{h}_a. \tag{5}$$

Considered as a function of $n_a$ only, a non-constant $\Delta\bar{h}_a$ is also used sometimes in the energy balance equation (Chang and Talu 1996; Mota et al. 2004).

Neglecting the second term of (2) is valid for excess adsorption, where a zero adsorption volume is assumed. Equation (4) is valid within the limit of a negligible adsorption volume or, as demonstrated in the Appendix, for a constant adsorption volume. However, the excess isosteric heat of adsorption has a singularity at high pressure because the excess adsorption reaches a maximum (see companion paper). If a non-zero adsorption volume is assumed, the contribution of the second term of (2) may not be negligible at high pressure. Furthermore, the definition of the adsorbed phase pressure is unclear. A spreading pressure has been defined to take into account the adsorption forces (Steele 1974). Others assert that a pressure of a fluid confined inside a strictly rigid porous material is simply undefined (Myers and Monson 2002). In this paper, we use directly an expression for the total internal energy of the adsorbed gas ($U_a$) and we do not neglect the adsorption volume. This property can be derived by applying solution thermodynamics (Myers and Monson 2002) to the modified D-A model.

The solution thermodynamic formalism for the adsorbed phase is presented in Sect. 2. The calculations of adsorbed phase internal energy and other thermodynamic properties are presented in Sect. 3. The mass and energy conservation equations for the adsorption of hydrogen, nitrogen and methane on activated carbon are presented in Sect. 4. Finally, simulated nitrogen desorption is compared to experiments in Sect. 5.

## 2 Thermodynamic formalism

The calculations of the adsorption properties are based on the thermodynamic formalism of Myers and Monson for absolute adsorption (Myers and Monson 2002). For the sake of completeness, we reproduce here among others some of their main equations.[1] The solution thermodynamics is applied to the condensed phase (adsorbent + adsorbed gas), which is noted with the subscript *c*. The assumption of constant adsorption volume $V_a$ is essential to the validity of this procedure, the work related term $PdV_a$ being neglected. The adsorbent is assumed to be rigid and its mass to be fixed. The thermodynamic quantities of the condensed and adsorbed phase are expressed per unit mass of adsorbent for convenience. The internal energy of the condensed phase $U_c$, the Helmholtz free energy $F_c$, and the grand potential $\Omega_c$ are given by:

$$U_c = TS_c - PV + \mu n_a + \mu_s, \tag{6}$$

$$F_c = U_c - TS_c = -PV + \mu n_a + \mu_s, \tag{7}$$

$$\Omega_c = -PV + \mu_s. \tag{8}$$

From which we can express $S_c$ and $U_c$ as:

$$S_c = -\left[\frac{\partial F_c}{\partial T}\right]_{n_a,V}, \tag{9}$$

$$U_c = -T^2\frac{\partial}{\partial T}\left[\frac{F_c}{T}\right]_{n_a,V}. \tag{10}$$

The internal energy and the entropy of the adsorbed gas can be extracted from the internal energy of the condensed phase by subtracting that of the solid adsorbent in vacuum ($u_s$ and $s_s$):

$$U_a = U_c - u_s, \tag{11}$$

$$S_a = S_c - s_s. \tag{12}$$

The grand potential relative to the adsorbent in vacuum, $\omega_s$ is obtained using:

$$\Omega_a = \Omega_c - \omega_s = -\int n_a d\mu$$
$$= -RT\int_0^f \frac{n_a}{f}df \quad (\text{constant } T). \tag{13}$$

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[1] Equations (6)–(10), (13) and (16) correspond to equations (8)–(10), (18), (19), (23) and (27) presented by Myers and Monson (Myers and Monson 2002).

**Table 1** Modified Dubinin-Astakhov model parameters and adsorption volume for 3 adsorption pairs

| Parameters | Adsorbate/Adsorbent pairs | | |
|---|---|---|---|
| | $H_2$/<br>AX-21™ | $N_2$/<br>C034 | $CH_4$/<br>CNS-201™ |
| $n_{\max}$ (mol/kg) | 71.6 | 63.7 | 25.4 |
| $P_0$ (MPa) | 1470 | 11320 | 1850 |
| $\alpha$ (J/mol) | 3080 | 6160 | 11850 |
| $\beta$ (J/mol K) | 18.9 | 24.9 | 7.05 |
| $V_a$ ($m^3$/kg) | 0.00143 | 0.00183 | 0.00085 |

Using (6) to (8), (10) and (11) (see Appendix), $\Delta U_a$ is:

$$\Delta U_a = U_a - n_a u_g^0 = -T^2 \frac{\partial}{\partial T}\left[\frac{\Omega_a}{T}\right]_{n_a,V} - n_a R T^2 \left[\frac{\partial \ln f}{\partial T}\right]_{n_a,V} + n_a R T, \tag{14}$$

where $u_g^0$ is the internal energy of the perfect gas at 1 atm and the same temperature.

Similarly, $\Delta S_a$ is:

$$\Delta S_a = S_a - n_a s_g^0 = -T^2 \frac{\partial}{\partial T}[\Omega_a]_{n_a,V} - n_a R \ln\left(\frac{f}{P^0}\right) + n_a R T \left[\frac{\partial \ln f}{\partial T}\right]_{n_a,V}, \tag{15}$$

where $s_g^0$ is the entropy and the pressure of the perfect gas at 1 atm ($P^0 = 1$ atm) and the same temperature.

The differential energy of adsorption is:

$$\Delta \bar{u}_a = \left[\frac{\partial \Delta U_a}{\partial n_a}\right]_{T,V} = \left[\frac{\partial U_c}{\partial n_a}\right]_{T,V} - u_g^0 = \left[\frac{\partial U_a}{\partial n_a}\right]_{T,V} - u_g^0 = -RT^2\left[\frac{\partial \ln f}{\partial T}\right]_{n_a,V} + RT. \tag{16}$$

If the perfect gas assumption is used, the fugacity can be replaced with pressure. This expression is coherent with the definition of the isosteric heat of adsorption for perfect gas, (4):

$$\Delta \bar{h}_a = \Delta \bar{u}_a - RT = -RT^2\left[\frac{\partial \ln f}{\partial T}\right]_{n_a,V}. \tag{17}$$

We demonstrate in the Appendix that (17) is the real gas isosteric heat (with minus sign) if it is defined using the perfect gas reference state. Therefore, the notation $\Delta \bar{h}_a^0$ will be used for (17) in the remaining of the article.

## 3 Thermodynamics of adsorption

### 3.1 Derivation of thermodynamic properties

The thermodynamic variables in (13) to (17) are calculated using a D-A based fit presented in the companion paper (Richard et al. 2009). The parameters of the model were chosen not only to fit experimental data accurately over a large pressure and temperature range in the supercritical region but also to allow the analytical derivation of the adsorbed phase properties. It is shown to fit the experimental data for hydrogen (over the temperature range 30 K–293 K and pressure range 0–6 MPa) (Bénard and Chahine 2001; Michelsen and Chahine 2005),[2] nitrogen (over the temperature range 93 K–298 K and pressure range 0–6 MPa) (Czerny et al. 2005) and methane (over the temperature range 243 K–333 K and pressure up to 10 MPa) (Bénard and Chahine 1997) on activated carbon. Using this approach, the absolute adsorbed amount per unit mass of adsorbent is:

$$n_a = n_{\max} \exp\left[-\left[\frac{RT}{\varepsilon}\right]^2 \ln^2\left(\frac{P_0}{P}\right)\right]. \tag{18}$$

Contrarily to the original D-A model, $\varepsilon$, the characteristic free energy of adsorption is temperature dependent expressed as the sum of an enthalpic factor ($\alpha$) and of an entropic factor ($\beta T$).

$$\varepsilon = \alpha + \beta T. \tag{19}$$

The parameters ($n_{\max}, \alpha, \beta$ and $P_0$) were solved assuming a constant adsorption volume $V_a$ to convert excess adsorption to absolute adsorption. The values of these parameters for the three adsorbent/adsorbate pairs are presented in Table 1. The same model has also been tested using fugacity as the independent variable without showing noticeable difference in the fit.

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[2] Michelsen, J., Chahine, R.: Private communication (for the 30–77 K temperature range) (2005).

The partial differentials of $n_a$ with respect to $T$ and $P$ are:

$$\left(\frac{\partial n_a}{\partial T}\right)_{P,V} = \frac{2\alpha n_a \ln(\frac{n_a}{n_{\max}})}{T(\alpha+\beta T)}, \tag{20}$$

$$\left(\frac{\partial n_a}{\partial P}\right)_{T,V} = \frac{2n_a RT\sqrt{-\ln(\frac{n_a}{n_{\max}})}}{P(\alpha+\beta T)}. \tag{21}$$

Using (18), the pressure is given by:

$$P = P_0 \exp\left[-\frac{(\alpha+\beta T)}{RT}\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right]. \tag{22}$$

Contrarily to (18), the independent variables of (13) to (17) are the temperature and the fugacity. Pressure will be used instead in what follows. The impact of this assumption is discussed in the next section. Substituting the fugacity in (13) with pressure (22), we obtain:

$$\Omega_a = -\frac{n_{\max}(\alpha+\beta T)\sqrt{\pi}}{2}\left[1 - \mathit{Erf}\left(\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right)\right], \tag{23}$$

where *Erf* is the error function. Substituting (23) in (14) yields:

$$\begin{aligned}\Delta U_a &= U_a - n_a u_g^o \\ &= -\frac{n_{\max}\alpha\sqrt{\pi}}{2}\left[1 - \mathit{Erf}\left(\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right)\right] \\ &\quad + n_a\left[RT - \alpha\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right],\end{aligned} \tag{24}$$

for which the partial derivatives with respect to $T$ and $P$ are expressed as:

$$\begin{aligned}\left[\frac{\partial \Delta U_a}{\partial T}\right]_{P,V} &= n_a R + \frac{2\alpha n_a}{T(\alpha+\beta T)}\ln\left(\frac{n_a}{n_{\max}}\right) \\ &\quad \times \left[RT - \alpha\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right],\end{aligned} \tag{25}$$

$$\begin{aligned}\left[\frac{\partial \Delta U_a}{\partial P}\right]_{T,V} &= \frac{2n_a RT}{P(\alpha+\beta T)}\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)} \\ &\quad \times \left[RT - \alpha\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right].\end{aligned} \tag{26}$$

The differential energy of adsorption is obtained by substituting (22) or (24) in (16):

$$\Delta\bar{u}_a = \left[\frac{\partial \Delta U_a}{\partial n_a}\right]_{T,V} = RT - \alpha\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}. \tag{27}$$

The isosteric heat of adsorption, $-\Delta\bar{h}_a^0$, is obtained with:

$$\Delta\bar{h}_a^0 = -RT^2\left[\frac{\partial \ln P}{\partial T}\right]_{n_a,V} = -\alpha\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}. \tag{28}$$

It is a function of $n_a$ only, an assumption often made in the literature (Myers 2002). It is the case without using the perfect gas assumption if the modified D-A model uses fugacity as the independent variable. Hence, the total internal energy of the adsorbed phase, $U_a$, previously calculated using (22), could also be calculated by integrating (27) or (28) from 0 to $n_a$:

$$\begin{aligned}\frac{U_a}{n_a} &= u_g^0 + \frac{1}{n_a}\int_0^{n_a}\Delta\bar{u}_a dn_a \\ &= h_g^0 + \frac{1}{n_a}\int_0^{n_a}\Delta\bar{h}_a^0 dn_a.\end{aligned} \tag{29}$$

Unlike (2) and (3), the adsorption volume is not neglected. The adsorption volume is kept constant and the reference is to the perfect gas enthalpy.

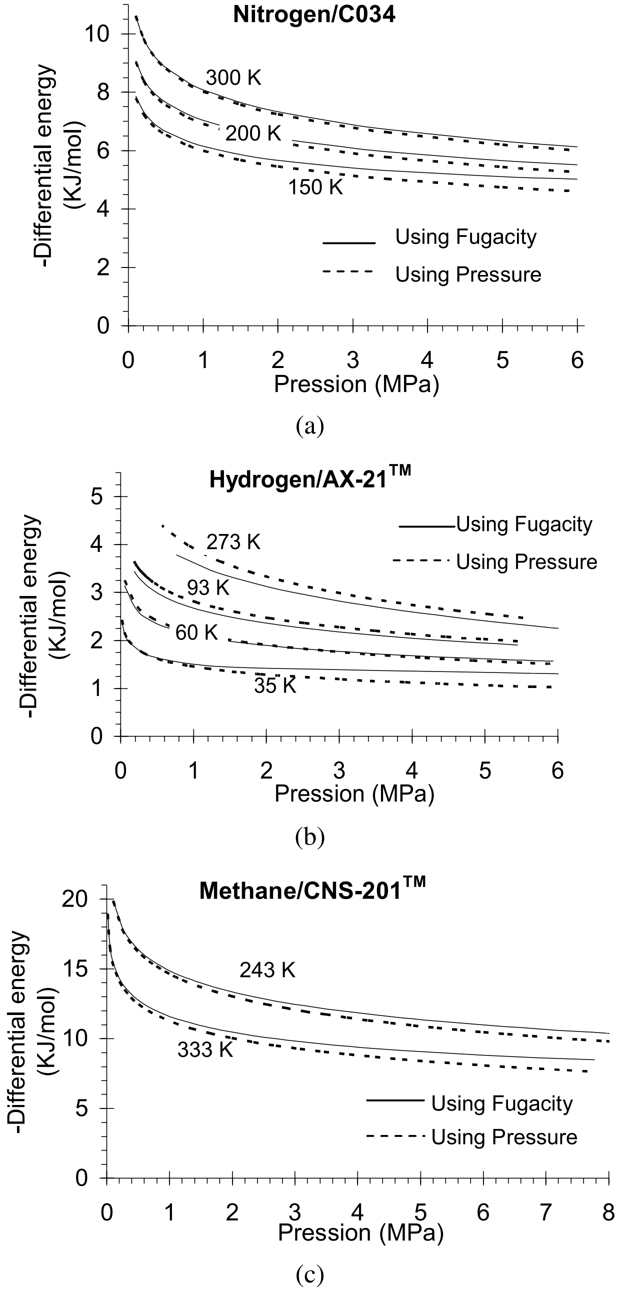
Supporting our interpretation of the temperature dependence of the characteristic free energy of adsorption, the parameter $\alpha$ appears in the energy and enthalpy related terms ((24), (27) and (28)). Whereas the parameter $\beta$ appears in entropy related terms; for example, $\Delta S_a$ is:

$$\begin{aligned}\Delta S_a &= S_a - n_a s_g^o \\ &= \frac{n_{\max}\beta\sqrt{\pi}}{2}\left[1 - \mathit{Erf}\left(\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right)\right] \\ &\quad + n_a\left[\beta\sqrt{-\ln\left(\frac{n_a}{n_{\max}}\right)}\right] + n_a R \ln\left(\frac{P^0}{P_0}\right),\end{aligned} \tag{30}$$

where $P^0$ is the reference state pressure: 1 atmosphere.

### 3.2 Pressure vs fugacity

To verify the impact of the use of pressure as an independent variable, the modified D-A model was parameterised with the same experimental excess adsorption data (Bénard and Chahine 1997, 2001; Michelsen and Chahine 2005; Czerny et al. 2005) using fugacity instead of pressure. Figure 1 presents the differential energy of adsorption (25) for both cases. The overall difference between the results of the two models is small, particularly far from the critical temperature. This approximation is still reasonable in cases where the fugacity differs significantly from pressure and where the perfect gas assumption is not valid anymore (such as hydrogen at 35 K and pressure above 1 MPa). Therefore, in the studied range, as long as the reference is to the



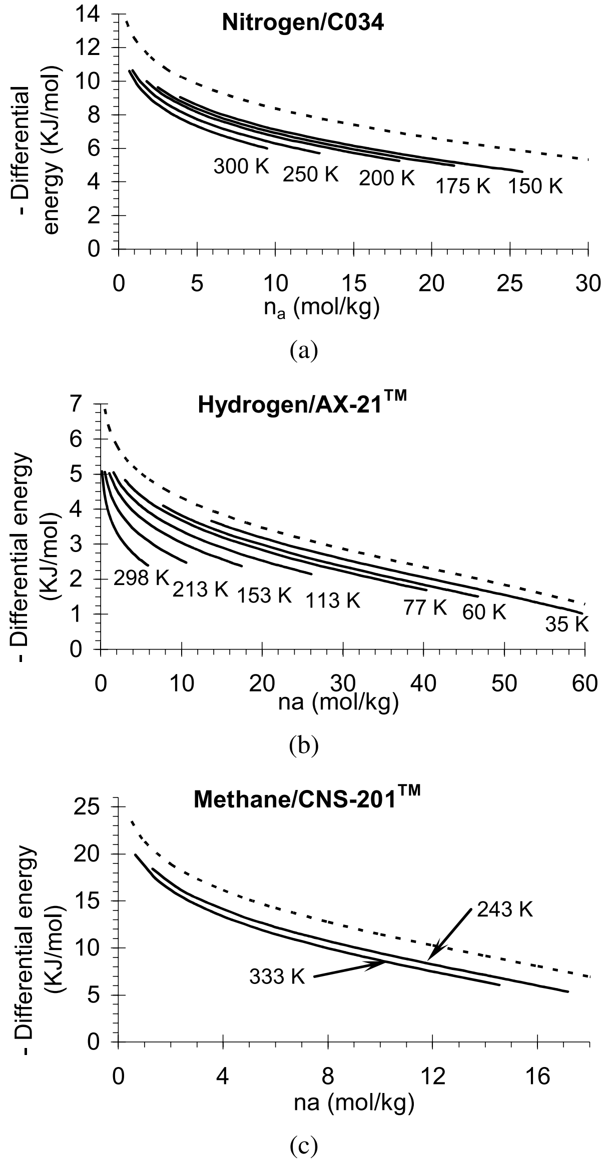
(a)

(b)

(c)

**Fig. 1** Differential energy of adsorption ($\Delta\bar{u}_a$) as a function of pressure for nitrogen/C034 (**a**), hydrogen/AX-21™ (**b**) and methane/CNS-201™ (**c**). It is calculated using pressure (*dashed line*) and fugacity (*solid line*)

perfect gas state, the thermodynamic properties calculated with pressure as the independent variable in (21) to (26) are equivalent to those with the real gas assumption. At very high pressure (above 6 MPa) and temperatures approaching critical point, it may be more appropriate to use fugacity as the independent variable (using the modified D-A modeled isotherms with fugacity).



(a)

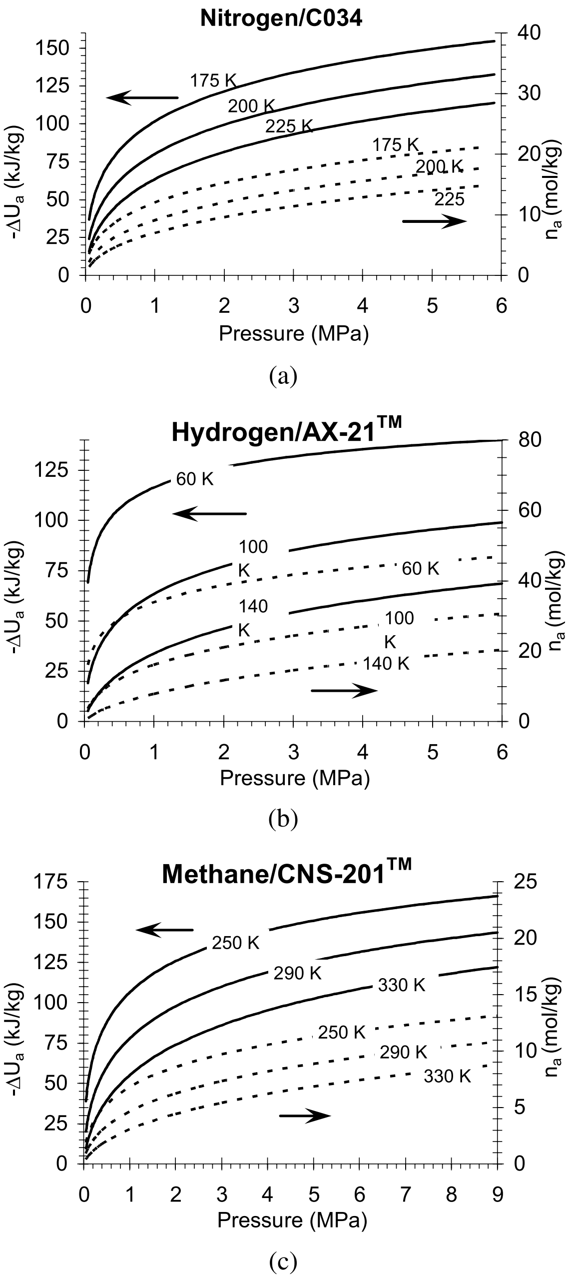
(b)

(c)

**Fig. 2** Differential energy of adsorption $\Delta\bar{u}_a$ (*solid lines*) and isosteric heat (*dashed lines*) as a function of loading for nitrogen/C034 (**a**), hydrogen/AX-21™ (**b**) and methane/CNS-201™ (**c**)

### 3.3 Differential energy of adsorption and heat of adsorption

Figure 2 presents the differential energy and the isosteric heat of adsorption as function of $n_a$. The isosteric heat values fall within the same range of published for nitrogen (Czerny et al. 2005; Zhou et al. 2001), hydrogen (Poirier et al. 2006; Zhou and Zhou 1996; Roussel et al. 2006) and methane (Himeno et al. 2005; Pribylov et al. 2000; Zhou et al. 2001) adsorption on carbon. It decreases rapidly with the amount adsorbed. At the limit of zero pressure, the differential energy and the isosteric heat are infinite. This singularity originates from the D-A model which has no Henry's law limit. However, the contribution of the singu-



(a)

(b)

(c)

**Fig. 3** Internal energy of adsorption $-\Delta U_a$ (*solid line*) and adsorbed amount $n_a$ (*dashed line*) for nitrogen/C034 (**a**), hydrogen/AX-21™ (**b**) and methane/CNS-201™ (**c**)

larity to the integral value is negligible and the total internal energy of the adsorbed phase can be calculated from the D-A model.

The variations of $\Delta U_a$ as a function of $P$ and $T$ are shown in Fig. 3 for nitrogen, hydrogen and methane on activated carbons. The internal energy of the adsorbed gas will depend on the definition of the adsorbed amount ($n_a$). However, the total internal energy of the adsorbent/adsorbate system is independent of the approach used to model the adsorption process.

## 4 Adsorption process simulations

### 4.1 Mass conservation

We assume that the molar flux in and out of a volume element is only composed of gas. If the adsorption or desorption rate are sufficiently slow so that the diffusion effects in pores can be neglected, the adsorbate mass conservation equation can be written as:

$$\frac{dn_{tot}}{dt} = \dot{n}_{in} - \dot{n}_{out}, \tag{31}$$

where $\dot{n}_{in}$ and $\dot{n}_{out}$ are the gas mass flow rate entering or leaving the volume. The total amount of adsorbate in the system, $n_{tot}$, is composed the bulk gas in $V_g$ and the adsorbed gas in $V_a$. The volume $V_g$, expressed in $\mathrm{m}^3/\mathrm{kg}$ of adsorbent, is determined by subtracting $V_a$ from the void volume of the adsorbent and the adsorption system ($V_{v,sys}$, it includes the pore volume of the adsorbent, the interstitial space and any additional empty space of the system). The volume $V_a$ is a constant found by model fitting and the void space of the adsorbent is calculated using the density of graphite or is measured by helium probing. The assumption of constant $V_a$ and thus constant $V_g$, simplify significantly the conservation equations.

$$n_{tot} = n_g + m_s n_a = m_s[V_g \rho_g + n_a]. \tag{32}$$

Substituting (32) into (31) and taking into account that the densities of the bulk gas and the amount adsorbed gas are function of pressure and temperature, the final mass balance partial differential equation becomes:

$$\begin{aligned} &m_s\left[V_g\left(\frac{\partial \rho_g}{\partial P}\right)_T + \left(\frac{\partial n_a}{\partial P}\right)_{T,V}\right]\frac{dP}{dt} \\ &\quad + m_s\left[V_g\left(\frac{\partial \rho_g}{\partial T}\right)_P + \left(\frac{\partial n_a}{\partial T}\right)_{P,V}\right]\frac{dT}{dt} \\ &= \dot{n}_{in} - \dot{n}_{out}. \end{aligned} \tag{33}$$

Expressions for the derivatives of the variable $n_a$ with respect to temperature and pressure are, respectively, (20) and (21). The real gas properties are taken into account.

### 4.2 Energy conservation

The adsorbent, the adsorbed gas and the gas phase are assumed to be in thermal equilibrium in the control volume and there is no external work. The energy rate balance can therefore be written as:

$$\frac{dE}{dt} = \dot{Q} + \dot{n}_{g,in} h_{g,in} - \dot{n}_{g,out} h_{g,out}, \tag{34}$$

where $\dot{Q}$ is the heat transfer rate over the boundary of the control volume and $h_g$ is the enthalpy of the gas entering or leaving the volume. The control volume energy, $E$, is the sum of that of the bulk gas, the adsorbed gas and the adsorbent:

$$E = m_s[V_g \rho_g u_g + U_a + u_s]. \tag{35}$$

Substituting (34) in (35) yields:

$$m_s\left[V_g \frac{d(\rho_g u_g)}{dt} + \frac{dU_a}{dt} + \frac{du_s}{dt}\right] = \dot{Q} + \dot{n}_{in} h_{in} - \dot{n}_{out} h_{out}. \tag{36}$$

Expressing (36) in terms of $\Delta U_a$ and deriving with respect to pressure and temperature, we finally obtain:

$$\begin{aligned}
&m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial T}\right)_P + u_g\left(\frac{\partial \rho_g}{\partial T}\right)_P\right] + \left(\frac{\partial \Delta U_a}{\partial T}\right)_{P,V}\right.\\
&\qquad\left. + n_a\left(\frac{\partial u_g^0}{\partial T}\right)_P + u_g^0\left(\frac{\partial n_a}{\partial T}\right)_{P,V} + c_s\right]\frac{dT}{dt}\\
&\qquad + m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial P}\right)_T + u_g\left(\frac{\partial \rho_g}{\partial P}\right)_T\right]\right.\\
&\qquad\left. + u_g^0\left(\frac{\partial n_a}{\partial P}\right)_{T,V} + \left(\frac{\partial \Delta U_a}{\partial P}\right)_{T,V}\right]\frac{dP}{dt}\\
&\quad = \dot{Q} + \dot{n}_{in} h_{in} - \dot{n}_{out} h_{out}.
\end{aligned} \tag{37}$$

Expression for the variable $n_a$ is given by (18). The terms for the derivatives of $\Delta U_a$ with respect to temperature and pressure are given by (25) and (26).

Since the derived isosteric heat is function of $n_a$ only, an alternative form of (37) is:

$$\begin{aligned}
&m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial T}\right)_P + u_g\left(\frac{\partial \rho_g}{\partial T}\right)_P\right]\right.\\
&\qquad\left. + (\Delta\bar{h}_a^0 + h_g^0)\left(\frac{\partial n_a}{\partial T}\right)_{P,V} + n_a c_p^0 + c_s\right]\frac{dT}{dt}\\
&\qquad + m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial P}\right)_T + u_g\left(\frac{\partial \rho_g}{\partial P}\right)_T\right]\right.\\
&\qquad\left. + (\Delta\bar{h}_a^0 + h_g^0)\left(\frac{\partial n_a}{\partial P}\right)_{T,V}\right]\frac{dP}{dt}\\
&\quad = \dot{Q} + \dot{n}_{in} h_{in} - \dot{n}_{out} h_{out}.
\end{aligned} \tag{38}$$

Expression for $\Delta\bar{h}_a^0$ is given by (28).

On a macroscopic scale, the amount of adsorbed gas is determined by its interaction with the gas phase. There is no adsorbed gas flux across the control volume and the adsorption volume $V_a$ is assumed constant. In this context, only the internal energy of the adsorbed gas is required, the enthalpy of adsorption does not need to be defined.

### 4.3 Conservation equations with adsorption kinetics

For very high desorption or adsorption rate with large adsorbent particles, the adsorption kinetics inside the pore should be considered. The chemical potential driving force model, the Fickian diffusion model, or the simpler Linear Driving Force (LDF) model were developed for this purpose (Sircar and Hufton 2000). However, these models require the experimental determination of diffusion factors or the mass transfer coefficients that are functions of temperature and amount adsorbed. The LDF model equation is:

$$\frac{d\bar{n}_a}{dt} = k_L(n_a^* - \bar{n}_a), \tag{39}$$

where $n_a^*$ is the equilibrium adsorbed gas (given by (18) and noted $n_a$ until now), $\bar{n}_a$ is the average amount adsorbed in the pores and $k$ is the effective LDF mass transfer coefficient (to be experimentally determined). The mass conservation equation becomes:

$$\begin{aligned}
&m_s V_g\left(\frac{\partial \rho_g}{\partial P}\right)_T \frac{dP}{dt} + m_s V_g\left(\frac{\partial \rho_g}{\partial T}\right)_P \frac{dT}{dt} + \frac{d\bar{n}_a}{dt}\\
&\quad = \dot{n}_{in} - \dot{n}_{out},
\end{aligned} \tag{40}$$

and the energy balance equation becomes:

$$\begin{aligned}
&m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial T}\right)_P + u_g\left(\frac{\partial \rho_g}{\partial T}\right)_P\right] + \bar{n}_a c_p^0 + c_s\right]\frac{dT}{dt}\\
&\qquad + (\Delta\bar{h}_a^0 + h_g^0)\frac{d\bar{n}_a}{dt}\\
&\qquad + m_s\left[V_g\left[\rho_g\left(\frac{\partial u_g}{\partial P}\right)_T + u_g\left(\frac{\partial \rho_g}{\partial P}\right)_T\right]\right]\frac{dP}{dt}\\
&\quad = \dot{Q} + \dot{n}_{in} h_{in} - \dot{n}_{out} h_{out}.
\end{aligned} \tag{41}$$

## 5 Comparison with experimental data

We compare the solution of the equilibrium mass and energy equations, (30) and (34), with experimental nitrogen desorption data previously published by (Czerny 2005). In their experiments, the system consisted of a three litre stainless steal cylinder filled with one kilogram of granular activated carbon C034, the same carbon used in reference (Czerny et al. 2005) for the model parameterization. The reservoir, filled with nitrogen to an initial equilibrium state of 3.5 MPa and 271 K, was emptied in 4.5 minutes while monitoring the temperature and the pressure inside. The data are shown in Fig. 4. Heat leaks from the ambient to the activated carbon reservoir were present. However, the discharge period being relatively short these experiments constitute a reasonable comparison basis for simulating adiabatic desorption. Due to rapid desorption, the diffusion rate outside

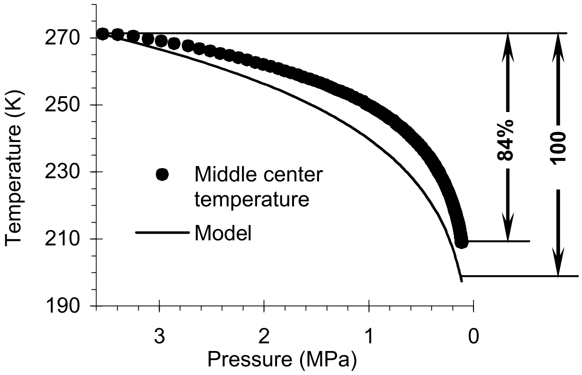


**Fig. 4** Simulated (*solid line*) and experimental (*dots*) nitrogen desorption from activated carbon C034

the pore is not negligible (in their data, atmospheric pressure is reached in 4.5 minutes but the lowest temperature is reached in 6.5 minutes). However, the final temperatures constitute a good basis of comparison for local equilibrium simulations.

The mass and energy balance equations, (33) and (37), were calculated with the COMSOL Multiphysics™ software. The nitrogen gas phase properties were calculated from the NIST12 software package (Lemmon et al. 2000) and the heat transfer rate was set to zero. The specific heat of activated carbon was calculated with the Tarasov equation using three Debye temperatures (Pyda et al. 1998). Figure 4 illustrates the results of desorption test from 3.5 MPa and 271 K and the corresponding numerical simulation.

The total temperature drop measured during experiments is about 84% of the temperature drop obtained with the corresponding adiabatic desorption simulation. This is very reasonable considering the experimental error and the fact that the system suffers from heat leaks.

## 6 Summary and conclusions

Expressions for the mass and energy balance equations for hydrogen, nitrogen and methane adsorption on activated carbon over large temperature and pressure ranges in the supercritical region are developed. We use directly the internal energy of the adsorbed gas in the energy rate balance without neglecting the adsorption volume or referring to the adsorbed gas pressure and enthalpy.

The expressions for the internal energy, grand potential, differential energy of adsorption and specific heat are derived using solution thermodynamics (Myers and Monson 2002). To be rigorous, these derivations require the assumption of constant adsorption volume. The independent variable fugacity was replaced with pressure, a valid approximation for the supercritical temperature range studied, even when fugacity differs significantly from pressure. The thermodynamic variables were calculated using a modified Dubinin-Astakhov micropore-filling model developed for this purpose (Richard et al. 2009). The relative simplicity of the five-parameter model is an advantage for the derivation of the thermodynamic properties.

The resulting expressions are functions of pressure and temperature, ready to include in the conservation equations. The isosteric heat of adsorption (defined with the perfect gas enthalpy as the reference state) is a function of adsorption loading only. Hence, the total internal energy of the adsorbed phase can also be calculated from the perfect gas enthalpy and the integral of the isosteric heat from 0 to the amount adsorbed.

The mass and energy rate balance equations for an adsorbate/adsorbent pair were obtained for both equilibrium and rapid adsorption (adsorption kinetics is calculated using the Linear Driving Force model). Considering that there is only bulk gas flux out of the control volume and that the adsorption volume is constant, only knowledge of the adsorbed gas internal energy is required. Finally, simulations are shown to be in agreement with nitrogen desorption experiments.

**Acknowledgements** We gratefully acknowledge the support of Natural Resources Canada, Le Fond Québécois de la recherche sur la nature et les technologies and of the Natural Sciences and Engineering Research Council of Canada. We thank Annalise Czerny and Ricardo Paggiaro for useful discussions.

## Appendix

Isosteric heat: assumptions

The isosteric heat expression in its final form (4) originates from the following Clausius-Clapeyron type equation (Gregg and Sing 1982; Steele 1974):

$$\left(\frac{dP}{dT}\right)_{n_a} = \frac{\Delta \bar{h}_a}{T\left[\left(\frac{\partial V_a}{\partial n_a}\right)_{T,P} - v_g\right]}, \tag{42}$$

where the isosteric heat $(-\Delta \bar{h}_a)$ is defined in reference to the equilibrium bulk gas enthalpy,

$$\begin{aligned} \Delta \bar{h}_a &\equiv \left[\left(\frac{\partial H_a}{\partial n_a}\right)_{T,P} - h_g\right] \quad \text{or} \\ \Delta \bar{h}_a &= T\left[\left(\frac{\partial S_a}{\partial n_a}\right)_{T,P} - s_g\right]. \end{aligned} \tag{43}$$

To obtain the final form (4), it is assumed that,

$$\left(\frac{\partial V_a}{\partial n_a}\right)_{T,P} \approx 0. \tag{44}$$

This assumption is generally made by arguing that the specific volume of the adsorbed phase is negligible compared to the specific volume of the gas (Gregg and Sing

1982; Steele 1974). At high pressure and relatively low temperature, this assumption may not be verified. However, we argue that if the adsorption volume is considered constant in the calculation of the absolute adsorption (like it is done in the companion paper), (44) is valid, no matter what is the value of the specific volume of the adsorbed gas. Hence, (42) becomes:

$$T\left(\frac{dP}{dT}\right)_{n_a} = -\frac{\Delta\bar{h}_a}{v_g}. \tag{45}$$

If the perfect gas assumption is used, (45) can be simplified into (46):

$$\Delta\bar{h}_a = -RT^2\left(\frac{d\ln P}{dT}\right)_{n_a}. \tag{46}$$

In cases where the perfect gas assumption is not valid, the second option is to use the compressibility factor. Hence, we get (4):

$$\Delta\bar{h}_a = -ZRT^2\left(\frac{d\ln P}{dT}\right)_{n_a}, \tag{4 or 47}$$

however, since the compressibility factor depends on temperature and pressure, this expression becomes difficult to integrate in (3).

### Isosteric heat: an alternative definition

We propose to use the fugacity to describe the specific volume of the real gas,

$$v_g = RT\left(\frac{\partial \ln f}{\partial P}\right)_T. \tag{48}$$

Hence,

$$\left(\frac{dP}{dT}\right)_{n_a} = \frac{\Delta\bar{h}_a}{-RT^2\left(\frac{\partial \ln f}{\partial P}\right)_T}. \tag{49}$$

An alternative definition for the isosteric heat of adsorption would be to use the perfect gas enthalpy at 1 atm as the reference instead of the bulk gas enthalpy,

$$\Delta\bar{h}_a^0 \equiv \left[\left(\frac{\partial H_a}{\partial n_a}\right)_{T,P} - h_g^0\right]. \tag{50}$$

Hence,

$$\Delta\bar{h}_a = \Delta\bar{h}_a^0 - (h_g - h_g^0). \tag{51}$$

Using fugacity, the second term of (51) can be formulated as

$$h_g - h_g^0 = -RT^2\left(\frac{\partial \ln f}{\partial T}\right)_P. \tag{52}$$

From (49), (51) and (52), the Clausius-Clapeyron type equation becomes:

$$\left(\frac{dP}{dT}\right)_{n_a} = \frac{\Delta\bar{h}_a^0 + RT^2\left(\frac{\partial \ln f}{\partial T}\right)_P}{-RT^2\left(\frac{\partial \ln f}{\partial P}\right)_T}. \tag{53}$$

From (53),

$$\Delta\bar{h}_a^0 = -RT^2\left[\left(\frac{\partial \ln f}{\partial P}\right)_T\left(\frac{dP}{dT}\right)_{n_a} + \left(\frac{\partial \ln f}{\partial T}\right)_P\right]. \tag{54}$$

From the differential of the logarithm of fugacity, and since the pressure of the bulk gas in equilibrium can be express as a function of $n_a$ and $T$,

$$\left(\frac{\partial \ln f}{\partial T}\right)_{na} = \left(\frac{\partial \ln f}{\partial P}\right)_T\left(\frac{dP}{dT}\right)_{n_a} + \left(\frac{\partial \ln f}{\partial T}\right)_P. \tag{55}$$

Hence, the alternative isosteric heat can be expressed as:

$$\Delta\bar{h}_a^0 = -RT^2\left[\left(\frac{\partial \ln f}{\partial T}\right)_{n_a}\right]. \tag{56}$$

This form of isosteric heat is coherent with the thermodynamic formalism used in this article.

$$\Delta\bar{h}_a^0 = \Delta\bar{u}_a - RT = -RT^2\left[\left(\frac{\partial \ln f}{\partial T}\right)_{n_a}\right]. \tag{57}$$

The real gas assumption has two consequences: the reference state is of the perfect gas and the isosteric heat is calculated using fugacity. As demonstrated in Sect. 3.2, even in cases were they are very different, using the pressure instead of the fugacity does not affect significantly the differential energy of adsorption in the range studied, thus, the isosteric heat value.

### Determination of the internal energy of adsorption from the grand potential

$$\Omega_a = \Omega_c - \omega_s, \tag{58}$$

where $\omega_s$ is the grand potential of the clean adsorbent in vacuo.

$$f_s = \omega_s. \tag{59}$$

From (7) and (8):

$$F_c = \Omega_c + \mu n_a. \tag{60}$$

From (58), (59) and (60), the Helmholtz free energy is

$$F_c = \Omega_a + n_a\mu + \mathrm{f}_s. \tag{61}$$

From (10) and (61), the internal energy of the condensed phase is:

$$U_c = -T^2 \frac{\partial}{\partial T}\left[\frac{F_c}{T}\right]_{n_a,V} = -T^2 \frac{\partial}{\partial T}\left[\frac{\Omega_a}{T}\right]_{n_a,V} - n_a T^2 \frac{\partial}{\partial T}\left[\frac{\mu}{T}\right]_{n_a,V} + u_s. \quad (62)$$

Furthermore,

$$\mu = \mu^0 + RT \ln \frac{f}{f^o}, \quad (63)$$

where the superscript 0 refers to the 1 atm reference state. The standard enthalpy of the bulk gas is:

$$h_g^0 = -T^2 \frac{\partial}{\partial T}\left[\frac{\mu^0}{T}\right], \quad (64)$$

and

$$h_g^0 = u_g^0 + RT. \quad (65)$$

Finally, from (62) to (65):

$$\Delta U_a = U_c - u_s - n_a u_g^0 = -T^2 \frac{\partial}{\partial T}\left[\frac{\Omega_a}{T}\right]_{n_a,V} - n_a R T^2 \left[\frac{\partial \ln f}{\partial T}\right]_{n_a,V} + n_a RT. \quad (14 \text{ or } 66)$$

## Nomenclature

| | |
|---|---|
| $c_p^0$ | Specific heat of the perfect gas at 1 atm and temperature $T$ (J/mol K) |
| $c_s$ | Specific heat of the adsorbent (J/kg K) |
| $E$ | Total energy of the adsorption system (J) |
| $f$ | Fugacity of the bulk gas in equilibrium with the adsorbed phase (Pa) |
| $f_s$ | Specific Helmholtz free energy of the adsorbent (J/kg) |
| $F_c$ | Helmholtz free energy of the condensed phase (per unit mass of adsorbent) (J/kg) |
| $h_a$ | Specific adsorbed phase enthalpy (J/mol) |
| $-\Delta\bar{h}_a$ | Isosteric heat of adsorption (J/mol) |
| $h_g$ | Specific enthalpy of the bulk gas (J/mol) |
| $h_g^0$ | Specific enthalpy of the perfect gas at 1 atm and temperature $T$ (J/mol) |
| $h_{g,in}$ | Specific enthalpy of the gas entering the adsorption system (J/mol) |
| $h_{g,out}$ | Specific enthalpy of the gas leaving the adsorption system (J/mol) |
| $k$ | Effective LDF mass transfer coefficient (1/s) |
| $m_s$ | Mass of the adsorbent (kg) |
| $n_a$ | Absolute adsorption (per unit mass of adsorbent) (mol/kg) |
| $n_a^*$ | Equilibrium amount of absolute adsorbed gas used in adsorption kinetic simulations (per unit mass of adsorbent) (mol/kg) |
| $\bar{n}_a$ | Average amount of absolute adsorbed gas in the pores used in adsorption kinetic simulations (per unit mass of adsorbent) (mol/kg) |
| $n_g$ | Mass of the bulk gas in equilibrium with the adsorbed phase (mol) |
| $n_{ex}$ | Excess adsorption (mol/kg) |
| $n_{\max}$ | Limiting adsorption, corresponding to the maximum filling of the entire volume of adsorption space (adsorption model) (mol/kg) |
| $n_{tot}$ | Total amount of adsorbate introduced in the system (mol) |
| $\dot{n}_{in}$ | Flow rate of the gas entering the adsorption system (mol/s) |
| $\dot{n}_{out}$ | Flow rate of the gas leaving the adsorption system (mol/s) |
| $P$ | Equilibrium pressure (Pa) |
| $P_0$ | Saturation pressure of the vapour at temperature $T$ or pseudo-saturation pressure (adsorption model) (Pa) |
| $P^0$ | Reference state pressure: 1 atmosphere |
| $\dot{Q}$ | Heat transfer rate over the boundary of the control volume (J/s) |
| $R$ | Universal gas constant (8.314 J/mol K) |
| $\Delta S_a$ | Entropy of the adsorbed gas relative to the entropy of the perfect gas state at 1 atm and the same temperature (per unit mass of adsorbent) (J/kg K) |
| $S_c$ | Entropy of the condense phase (adsorbent + adsorbed gas; per unit mass of adsorbent) (J/kg K) |
| $s_g^0$ | Specific entropy of the perfect gas at 1 atm and temperature $T$ (J/mol K) |
| $T$ | Equilibrium temperature (K) |
| $u_a$ | Specific internal energy of the adsorbed phase (J/mol) |
| $\Delta\bar{u}_a$ | Differential energy of adsorption (J/mol) |
| $U_a$ | Internal energy of the adsorbed gas (per unit mass of adsorbent) (J/kg) |
| $\Delta U_a$ | Internal energy of the adsorbed gas relative to the energy of the perfect gas state at 1 atm and the same temperature (per unit mass of adsorbent) (J/kg) |
| $U_c$ | Internal energy of the condense phase (adsorbent + adsorbed gas; per unit mass of adsorbent) (J/kg) |
| $u_g$ | Specific internal energy of the bulk gas (J/mol) |

| | |
|---|---|
| $u_g^0$ | Specific internal energy of the perfect gas at 1 atm and temperature $T$ (J/mol) |
| $u_s$ | Specific internal energy of the adsorbent (J/kg) |
| $V$ | Volume of the condensed phase (constant) (per unit mass of adsorbent) ($\mathrm{m}^3/\mathrm{kg}$) |
| $V_a$ | Adsorption volume (per unit mass of adsorbent) ($\mathrm{m}^3/\mathrm{kg}$) |
| $V_g$ | Volume of the bulk gas phase (per unit mass of adsorbent) ($\mathrm{m}^3/\mathrm{kg}$) |
| $V_{v,sys}$ | Total void volume of the adsorption system (including the pore volume of the adsorbent, the interstitial space, and any additional empty space) ($\mathrm{m}^3/\mathrm{kg}$) |
| $Z$ | Compressibility factor |
| $\alpha$ | Enthalpic contribution to characteristic free energy of adsorption ($\varepsilon = \alpha + \beta T$) (adsorption model) (J/mol) |
| $\beta$ | Entropic contribution to characteristic free energy of adsorption ($\varepsilon = \alpha + \beta T$) (adsorption model) (J/mol K) |
| $\varepsilon$ | Characteristic free energy of adsorption (D-A model) (J/mol) |
| $\mu$ | Chemical potential of the equilibrium bulk gas (J/mol) |
| $\mu_s$ | Chemical potential of the adsorbent (J/kg) |
| $\rho_g$ | Density of the bulk gas in equilibrium with the adsorbed phase ($\mathrm{mol}/\mathrm{m}^3$) |
| $\Omega_a$ | Grand potential of the adsorbed phase (per unit mass of adsorbent) (J/kg) |
| $\Omega_c$ | Grand potential of the condensed phase (adsorbent + adsorbed gas; per unit mass of adsorbent) (J/kg) |
| $\omega_s$ | Specific grand potential of the clean adsorbent in vacuum (J/kg) |

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