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Development of Energy Balances for Fixed-Bed Adsorption Processes: Thermodynamic Paths, Heat Capacities and Isosteric Heats

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Abstract. This paper provides a simplified treatment of the method of Walton and LeVan (2003) for the development of energy balances for bidisperse particles in fixed-bed adsorption using thermodynamic paths. When adsorbed-phase enthalpy is properly defined, terms involving reference states cancel out of the energy balance, and only gas-phase heat capacities appear in the equation. Calculations show that adsorbed-phase heat capacities may deviate significantly from gas-phase heat capacities when the isosteric heat has a relatively small temperature dependency. Thus, special attention should be given to the path used to derive the energy balance to avoid inconsistencies in heat capacity definitions.

Keywords: energy balance, thermodynamic path, heat capacity, isosteric heat

1. Introduction

Many different forms of the energy balance have been used in the mathematical description of non-isothermal adsorption processes, and various assumptions can be applied to simplify process simulations. A common simplifying assumption is that adsorbent particles are in thermal equilibrium with the interstitial fluid in the bed (e.g., Mahle et al., 1996), in which case only one energy balance is needed. For a process in which the heat of adsorption is high and the adsorption isotherm is steep, the difference between the particle temperature and the interstitial-fluid temperature can be important, which would necessitate a particle energy balance (Brunovská et al., 1978). If the particles are bidisperse in nature with nanoporous domains characterized by a thermal diffusivity to mass diffusivity ratio that is less than 10 (Sun and Meunier, 1987), then temperature gradients within the particle can be significant, and the model should account for heat and mass transfer in the nanoporous domain as well.

In our previous work (Walton and LeVan, 2003), detailed material and energy balances were developed for adsorption in bidisperse particles. A three-domain system was considered: nanoporous domains, macropore space, and interstitial fluid. The energy balance was obtained by defining the enthalpy of the fluid phase and enthalpy of the adsorbed phase from thermodynamic paths using an appropriate reference state. The equations were developed for a general case and thus are applicable for non-ideal, multicomponent gas-solid systems.

This paper discusses briefly the thermodynamic paths used to define fluid-phase and adsorbed-phase enthalpies and calls attention to the proper heat capacities that should be used in the energy balance based on these paths. A simplified model is given to demonstrate the effect of the thermodynamic paths on the final material and energy balance equations. A simple relation for the heat capacity of the adsorbed phase follows naturally as a result of the enthalpy definitions, although this heat capacity need never be defined for certain thermodynamic paths. This relation then is used to illustrate the effect of a temperature-dependent isosteric

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heat on the calculated adsorbed-phase heat capacity for methane, ethane, propane, and n-butane on BPL activated carbon.

2. Definition of Thermodynamic Paths

By definition, enthalpy and internal energy are generally not absolute measurable quantities and therefore must be evaluated relative to some reference state. Both are state variables and are independent of the path chosen to evaluate them; thus, many different paths may be defined. For a fluid phase, we choose a path that first heats the gas isobarically from the reference temperature, T_{ref}, to the final temperature, T_f, and then isothermally changes the pressure from P_{ref} to P_f. The enthalpy of the gas phase, h_g is then given by

$$h_g = \sum_i y_i h_{\text{ref}_i} + \int_{T_{\text{ref}}}^{T_f} \sum_i y_i C^{\circ}_{pg_i} dT + H_T^R \quad (1)$$

Two convenient paths for evaluating the enthalpy of the adsorbed phase are shown in Fig. 1. Along path 1, the gas phase is heated from T_{ref} to the final system temperature at constant P_{ref} and then pressurized to the final system pressure at constant temperature. Both of these steps are performed on the adsorbable components while they are still in the gas phase; thus, the resulting heat capacity is a property of the gas phase. The final step of path 1 adsorbs the gas to the final loading, n, at constant pressure and temperature. The enthalpy change for this step is the isosteric heat of adsorption, λ, and is in general a function of the system temperature and adsorbent loadings. Neglecting the volume of the adsorbed phase, the internal energy of the adsorbed phase is equal to the enthalpy of the adsorbed phase, h_a, and is given by

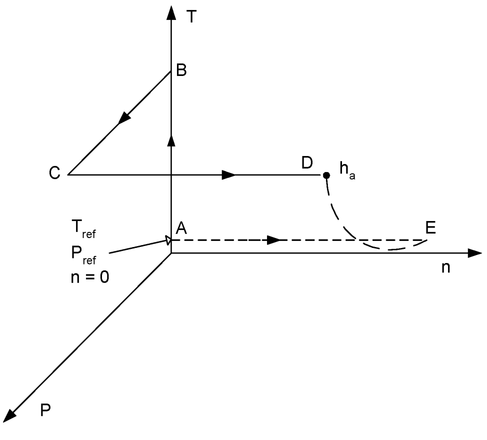


Figure 1. Thermodynamic paths for defining adsorbed-phase enthalpy. Path 1: solid line. Path 2: dashed line.

$$h_{a1} = \sum_i x_i h_{\text{ref}_i} + \int_{T_{\text{ref}}}^{T_f} \sum_i x_i C^{\circ}_{pg_i} dT + H_T^R - \frac{1}{n} \sum_i \int_0^{n_i} \lambda_i(\bar{n}', T) dn'_i \quad (2)$$

where the summation of the integrated isosteric heat in the last term of the equation will later be denoted as Λ_T.

For path 2, components are adsorbed at the reference temperature and pressure and then heated and pressurized to the final system conditions at constant loading. For this case, the heat capacity arising from the temperature change will be an adsorbed-phase property and the isosteric heat will be evaluated at the reference temperature. Neglecting the adsorbed-phase volume, the enthalpy definition for this path is then given by

$$h_{a2} = \sum_i x_i h_{\text{ref}_i} - \frac{1}{n} \sum_i \int_0^{n_i} \lambda_i(\bar{n}', T_{\text{ref}})\, dn'_i + \int_{T_{\text{ref}}}^{T_f} \sum_i x_i C_{pa_i} dT \quad (3)$$

The internal energy of the stationary phase (solid + adsorbate), u_s, can then be defined as

$$u_s = C_{\text{sol}}(T - T_{\text{ref}}) + n h_a \quad (4)$$

3. Simplified Model

Equivalent energy balance equations can be written using the enthalpy definitions from either of the thermodynamic paths. However, equations from path 1 will not contain any reference state terms, and the only heat capacity appearing in the energy balance will be that of the fluid phase. Equations developed from path 2 will contain both adsorbed-phase and fluid-phase heat capacities and reference state terms. There is clearly an advantage to using path 1 because it eliminates the need for defining the adsorbed-phase heat capacity. Path 2 equations, however, require evaluation of the isosteric heat at only the reference temperature, while path 1 equations would require an estimate over the entire temperature range.

To illustrate these arguments, we apply several simplifying assumptions to the general model that will reduce the equations to a more manageable form. The development of the complete general model for nonideal gas adsorption with multicomponent fluxes can be found in Walton and LeVan (2003). The following assumptions are applied to the general model: (1) the particle is monodisperse; (2) the gas phase is ideal; (3) heat capacities are constant; and (4) adsorbed-phase fluxes are neglected. Employing the enthalpy definition from path 1 (Eq. (2)), the energy balance becomes

$$\begin{aligned}
&\chi\left(\sum_i \frac{\partial c_i}{\partial t}\left[h_{\mathrm{ref}_i} + C^{\circ}_{pg_i}(T - T_{\mathrm{ref}})\right] + \sum_i c_i C^{\circ}_{pg_i}\frac{\partial T}{\partial t}\right)\\
&\quad + \rho_p\left(C_{\mathrm{sol}}\frac{\partial T}{\partial t} + \sum_i \frac{\partial n_i}{\partial t}\left[h_{\mathrm{ref}_i} + C^{\circ}_{pg_i}(T - T_{\mathrm{ref}})\right]\right.\\
&\quad \left. + \sum_i n_i C^{\circ}_{pg_i}\frac{\partial T}{\partial t} - \frac{\partial \Lambda_T}{\partial t}\right) = (\chi k_g + \rho_p k_m)\nabla^2 T\\
&\quad - \chi\left(\sum_i \nabla J_i^g\left[h_{\mathrm{ref}_i} + C^{\circ}_{pg_i}(T - T_{\mathrm{ref}})\right]\right.\\
&\quad \left. + \sum_i J_i^g C^{\circ}_{pg_i}\nabla T\right) \qquad (5)
\end{aligned}$$

where k_g and k_m are thermal conductivities for the gas and solid, respectively, c_i is the concentration of component i in the gas phase, and J_i is the molar flux of the gas phase.

Examining this equation term-by-term, we see that all reference state terms appearing in the equation (i.e., terms in the square brackets) multiply terms that sum to zero in the material balance and hence, will cancel out of the equation. Therefore, it is not necessary to assign them numerical values. Alternatively, if the path 2 enthalpy definition (Eq. (3)) is used to write the energy balance, the equation becomes

$$\begin{aligned}
&\chi\left(\sum_i \frac{\partial c_i}{\partial t}\left[h_{\mathrm{ref}_i} + C^{\circ}_{pg_i}(T - T_{\mathrm{ref}})\right] + \sum_i c_i C^{\circ}_{pg_i}\frac{\partial T}{\partial t}\right)\\
&\quad + \rho_p\left(C_{\mathrm{sol}}\frac{\partial T}{\partial t} + \sum_i \frac{\partial n_i}{\partial t}\left[h_{\mathrm{ref}_i} + C_{pa_i}(T - T_{\mathrm{ref}})\right]\right.\\
&\quad \left. + \sum_i n_i C_{pa_i}\frac{\partial T}{\partial t} - \frac{\partial \Lambda_{T_{\mathrm{ref}}}}{\partial t}\right)\\
&\quad = (\chi k_g + \rho_p k_m)\nabla^2 T - \chi\left(\sum_i \nabla J_i^g\left[h_{\mathrm{ref}_i}\right.\right.\\
&\quad \left.\left. + C^{\circ}_{pg_i}(T - T_{\mathrm{ref}})\right] + \sum_i J_i^g C^{\circ}_{pg_i}\nabla T\right) \qquad (6)
\end{aligned}$$

For this case, only the reference state enthalpy will cancel out of the equation because of the adsorbed-phase heat capacity appearing in the square brackets of the second line. Consequently, the reference temperature must be explicitly defined.

For pure-component adsorption, Eq. (5) reduces to

$$\begin{aligned}
&\chi c C^{\circ}_{pg}\frac{\partial T}{\partial t} + \rho_p\left(C_{\mathrm{sol}}\frac{\partial T}{\partial t} + n C^{\circ}_{pg}\frac{\partial T}{\partial t} - \frac{\partial \Lambda_T}{\partial t}\right)\\
&\quad = (\chi k_g + \rho_p k_m)\nabla^2 T \qquad (7)
\end{aligned}$$

Adsorbed-phase heat capacities are sometimes used in energy balances like Eq. (7), but clearly, one cannot simply substitute an adsorbed-phase heat capacity for the gas-phase heat capacity in the third term of Eq. (7) because it would be inconsistent with the enthalpy definitions from thermodynamic paths. If one desires to use C_{pa} in non-isothermal calculations, then Eq. (6) must be used. For pure-component adsorption, Eq. (6) becomes

$$\begin{aligned}
&\chi\left(c C^{\circ}_{pg}\frac{\partial T}{\partial t} + C^{\circ}_{pg}(T - T_{\mathrm{ref}})\frac{\partial c}{\partial t}\right) + \rho_p\left(C_{\mathrm{sol}}\frac{\partial T}{\partial t}\right.\\
&\quad \left. + C_{pa}(T - T_{\mathrm{ref}})\frac{\partial n}{\partial t} + n C_{pa}\frac{\partial T}{\partial t} - \frac{\partial \Lambda_{T_{\mathrm{ref}}}}{\partial t}\right)\\
&\quad = (\chi k_g + \rho_p k_m)\nabla^2 T \qquad (8)
\end{aligned}$$

where Λ_{Tref} is the integrated isosteric heat evaluated at the reference temperature. Because of the thermodynamic paths, if the isosteric heat is independent of temperature, then $C_{pa} = C_{pg}$ and Eq. (8) collapses to Eq. (7).

4. Calculation of Heat Capacities

In the preceding section, the two energy balances were shown to differ only when the isosteric heat is a function of temperature, resulting in adsorbed-phase heat capacities that are not equal to those of the gas phase. We show some simple calculations to examine the effect of temperature-dependent isosteric heats on C_{pa}. Equating the two enthalpy definitions and solving for the heat capacity of the adsorbed phase leads to the following expression for the mean heat capacity:

$$\bar{C}_{pa} = \frac{1}{(T - T_{\text{ref}})}\left[\int_{T_{\text{ref}}}^{T} C_{pg}^{\circ} dT' + \Lambda(n, T_{\text{ref}}) - \Lambda(n, T)\right] \tag{9}$$

For calculations, we consider the adsorption of methane, ethane, propane, and n-butane on BPL carbon at loadings of 0.2, 0.6, 1.0, and 1.0 mol/kg, respectively. To maintain some generality, we consider a parameter, α, defined by

$$\alpha \equiv \left.\frac{\partial \Lambda}{\partial T}\right|_{T_{\text{ref}}} \tag{10}$$

to represent the constant change in isosteric heat with a temperature change of $T - T_{\text{ref}}$. This is a reasonable assumption over the temperature range under consideration ($\Delta T = 50$ K). It is well known that for adsorption on an energetically heterogeneous surface, the isosteric heat decreases with increasing temperature. Therefore, α will be less than zero, and C_{pa} approaches the gas-phase value as α approaches zero. A group-contribution theory (GCT) (Russell and LeVan, 1996; LeVan and Pigorini, 2000; Walton et al., 2004) is used to predict approximate values of α for all four components at specific loadings on BPL carbon. Figure 2 shows the effect of temperature on the heat capacity of the adsorbed phase for different values of α for methane and ethane as calculated from Eq. (9). The closed symbols are calculations at GCT-predicted values of α.

Significant variations from the gas-phase heat capacity can be seen for small temperature dependencies in the isosteric heat. Methane is above its critical temperature, so comparisons can only be made with C_{pg}. The GCT prediction shows that for methane on BPL carbon at 0.2 mol/kg, C_{pa} is more than one and a half times the gas-phase value (Fig. 2(a)). At a loading of 0.6 mol/kg, GCT prediction for ethane shows a similar deviation from C_{pg} (Fig. 2(b)), and C_{pL} is much higher than C_{pa}, especially near the critical temperature.

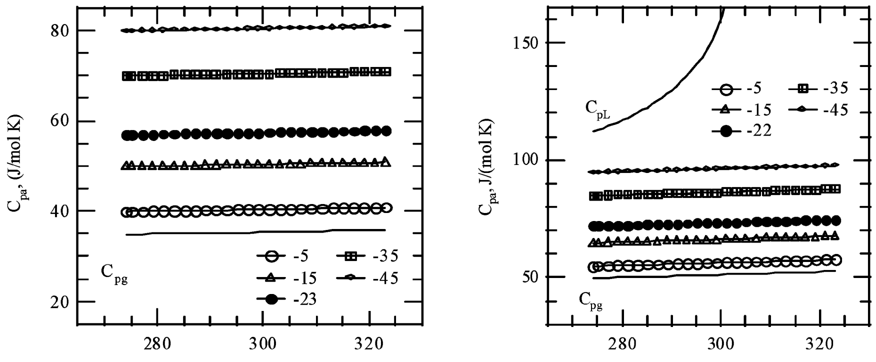
Figure 3 shows calculations using Eq. (9) for propane and n-butane on BPL carbon. The closed symbols are calculations at GCT-predicted values of α for loadings of 1.0 mol/kg. For both gases, C_{pa} lies between the gas-phase and liquid-phase values. From Figs. 2 and 3, we see that methane, ethane, and propane have similar temperature dependencies in the isosteric heat, as reflected in GCT predictions of α, while the isosteric heat for butane is seen to have a smaller temperature dependence. Calculated values of C_{pa} from Eq. (9) for GCT-predicted values of α are shown in Table 1. C_{pa}, C_{pg}, and Λ correspond to 323.15 K.

From these simple calculations, we can deduce that even a small temperature dependence in the isosteric heat may cause considerable deviations of adsorbed-phase heat capacities from gas and liquid values.

Table 1. Calculations from Eq. (9) for GCT-predicted values of α.

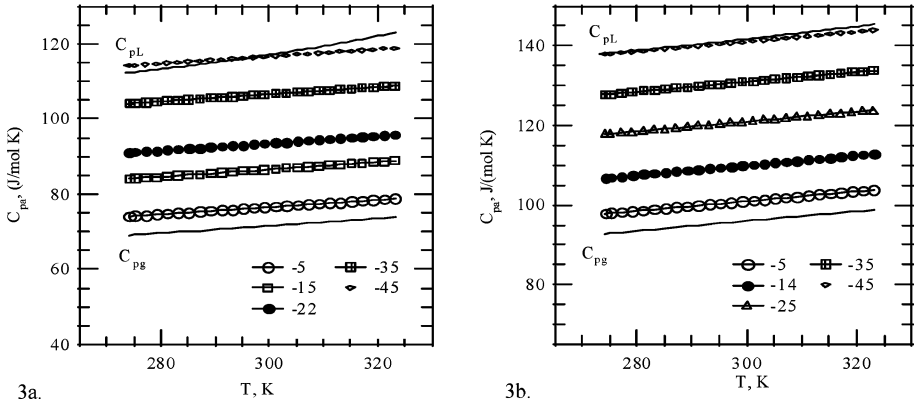
Component	$\Lambda_{\text{Tref}*}$ (J/mol)	$\Lambda_{\text{T}*}$ (J/mol)	C_{pa} (J/mol K)	C_{pg} (J/mol K)	α (J/mol K)
Methane	20400	19250	58.8	35.8	−23
Ethane	27500	26400	74.6	52.6	−22
Propane	37900	36800	95.8	73.8	−22
Butane	44000	43300	112.8	98.8	−14

$^*T_{\text{ref}} = 273.15$ K; T = 323.15 K.



2a. 2b.

Figure 2. Plot of adsorbed-phase heat capacity as a function of temperature for different changes in isosteric heat. (a) methane. (b) ethane. Each curve is calculated for different values of α. Closed symbols are for α estimated from GCT.



3a.

3b.

Figure 3. Plot of adsorbed-phase heat capacity as a function of temperature for different changes in isosteric heat. (a) propane. (b) n-butane. Each curve is calculated for different values of α. Closed symbols are for α estimated from GCT.

Therefore, care should be taken when defining heat capacities in adsorption simulations, so that they are consistent with the thermodynamic paths used to evaluate the enthalpy.

5. Conclusions

Fluid-phase and adsorbed-phase enthalpies have been defined from thermodynamic paths. The path chosen to develop the energy balance identifies the proper heat capacity that should be used in non-isothermal adsorption models. Selecting a path that heats adsorbable components while still in the gas phase will lead to an energy balance containing only gas-phase heat capacities and no reference states. Calculations of an adsorbed-phase heat capacity for methane, ethane, propane, and n-butane on BPL carbon show that small temperature dependencies of the isosteric heat may result in significant deviations from gas-phase heat capacities. As a result, adsorbed-phase heat capacities should not be substituted for gas-phase heat capacities and should only be used in an energy balance developed from the appropriate path, so that inconsistencies are avoided.

Nomenclature

C_{pg}	Fluid-phase heat capacity (J/mol/K)
C_{sol}	Heat capacity of the solid (J/kg/K)
H_R	Enthalpy departure function (J/mol)
χ	Porosity of the particle
ρ_p	Particle density (kg/m^3)
λ	Isosteric heat of adsorption (J/mol)

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