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Technical Note

Thermodynamically consistent thermal energy equation for an adsorbent/fluid system

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Abstract

We show that thermodynamically inconsistent results are obtained if a thermal energy equation is used that includes the heat of adsorption in modelling heat and mass transfer of adsorption processes as a surface phenomenon. However, if the heat of adsorption is included in the boundary conditions and not in the thermal energy equation, then the results are thermodynamically consistent. For a simple example, we found significant differences in temperature changes and heat flux for low Lewis numbers. © 2001 Elsevier Science Ltd. All rights reserved.

Fig. 1 shows schematically a vapour/adsorbent system with the enthalpy, heat, and mass flow at the vapour/adsorbent boundary in case of a single desorbing fluid in a one-dimensional coordinate system. The adsorbent has a finite thickness L and is assumed to be isotropic in which only heat and mass transfer is considered. The thermal energy equation that accounts for the heat of adsorption in an adsorbent/fluid system, e.g., water adsorption/desorption in zeolite in some of the literature, e.g. [1–5] (list is not exhaustive), is given by

$$\rho c_\mathrm{p}\frac{\partial T}{\partial t} = k\nabla^2 T + \frac{\partial \rho_\mathrm{w}}{\partial t}\Delta h_\mathrm{ads}. \tag{1}$$

Eq. (1) implies that water adsorbs/desorbs inside the zeolite layer itself. This means that for the mass balance inside the zeolite also a vapour phase should be taken into account. However, the authors in [1–5] assume implicitly that only an adsorbed phase is present, by using a mass diffusion equation for only the adsorbed phase, e.g.,

$$\frac{\partial \rho_\mathrm{w}}{\partial t} = D\nabla^2 \rho_\mathrm{w}. \tag{2}$$

In principle, there is nothing wrong with this assumption for a micropore system but it has certain consequences for a consistent heat balance. Now, Eq. (1) becomes thermodynamically inconsistent because it implies that for the boundary condition the first law of thermodynamics is not obeyed as shown in Fig. 1. The fluid desorbs at the vapour/adsorbent boundary and not sooner. Eq. (2) yields a mass flux $\vec{\Phi}_\mathrm{m} = -D\,\mathrm{grad}\,(\rho_\mathrm{w})$ at the vapour/adsorbent boundary. The specific enthalpy h_v for the vapour fluid is larger than the specific enthalpy h_s for the adsorbed fluid. As a result of this difference in enthalpy and the conservation law of heat, an amount of adsorption heat h_ads $(= h_\mathrm{v} - h_\mathrm{s})$ is withdrawn from the vapour/adsorbent system. This yields for the conservation law of heat at the boundary

$$\begin{aligned} \vec{\Phi}_q + \vec{\Phi}_\mathrm{m} h_\mathrm{v} &= -k\frac{\partial T}{\partial x} + \vec{\Phi}_\mathrm{m} h_s \\ \Rightarrow \vec{\Phi}_q &= -k\frac{\partial T}{\partial x} - \vec{\Phi}_\mathrm{m}\Delta h_\mathrm{ads}. \end{aligned} \tag{3}$$

However, in the literature the "$-\vec{\Phi}_\mathrm{m}\Delta h_\mathrm{ads}$"-term from Eq. (3) is mostly left out, see e.g. [1–5], ([6] is an exception) because of the presence of the $(\partial\rho_\mathrm{w}/\partial t)\Delta h_\mathrm{ads}$-term in Eq. (1) which obeys the conservation law of heat

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Nomenclature

c_p	heat capacity (J kg^{-1} K^{-1})
D	mass diffusivity (m^2 s^{-1})
Fo	Fourier number (dimensionless)
h	specific enthalpy (J kg^{-1})
k	heat conductivity (W m^{-1} K^{-1})
L	adsorbent thickness (m)
Le	Lewis number (dimensionless)
p	dimensionless parameter (dimensionless)
t	time (s)
T	temperature (K)
x	spatial co-ordinate (m)
Greek symbols	
α	thermal diffusivity (m^2 s^{-1})
Δ	difference
∂	partial differential operator
∇^2	nambla operator
λ	eigenvalue (dimensionless)
$\vec{\Phi}_q$	heat flux (W m^{-2})
$\vec{\Phi}_m$	mass flux (kg m^{-2} s^{-1})
ρ	density (kg m^{-3})
τ	dimensionless temperature (dimensionless)
ξ	dimensionless spatial coordinate (dimensionless)
Subscripts	
ads	adsorption
m	mass
n	index number
0	initial value
q	heat
v	vapour
w	adsorbate

for the whole vapour/adsorbent system but violates the conservation law of heat at the adsorbent/vapour boundary.

According to the thermodynamics of irreversible processes, see e.g. [7,8], the thermal energy equation is given by

$$\rho c_p \frac{\partial T}{\partial t} = k\nabla^2 T - \vec{\Phi}_m \operatorname{grad}(h_s), \quad \vec{\Phi}_m = -D \operatorname{grad}(\rho_w) \tag{4}$$

with heat flux at the vapour/adsorbent boundary given by Eq. (3). Eqs. (3) and (4) obey the conservation law at the boundary and for the whole system. Although the authors in [6] use also the boundary condition as given in Eq. (3), they neglect the "$-\vec{\Phi}_m \operatorname{grad}(h_s)$"-term. This term is known as Ackermann's "*effect of the diffusing heat capacites*" [7, p. 84]. An important property is that h_s depends on the adsorbed amount [2], which results in a gradient of h_s similar in shape with the concentration gradient of the adsorbed fluid ρ_w. Here we will also neglect this term for simplicity reasons in order to yield a simple algebraic solution, but it should not be left out if numerical routines are used to solve the partial differential equations. For the same reason, we also make other simplifications, such as, e.g., constant effective diffusivities D and α, a uniform surface area at the vapour/adsorbent interface and a one-dimensional system. We demonstrate here the fundamental differences between the two Eqs. (1) and (4), by showing a simple example for the heat flux and temperature changes in the adsorbent.

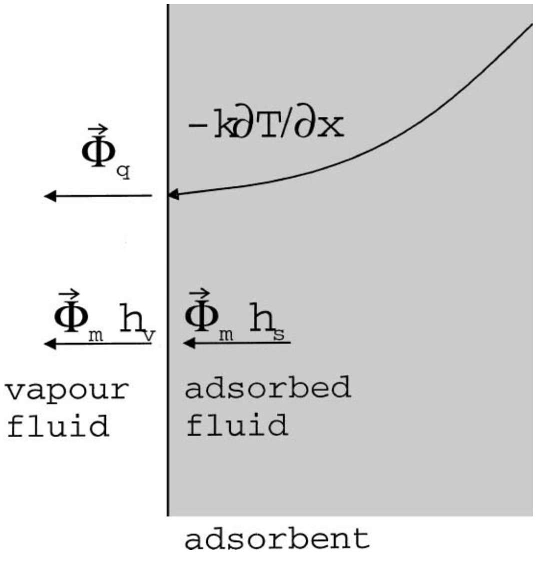

Fig. 1. Enthalpy, heat, and mass flow at the vapour/adsorbent boundary.

The boundary conditions are given by

$$T_{x=0} = T_0, \quad \rho_{w_{x=0}} = \rho_0, \quad \frac{\partial T}{\partial x}_{x=L} = 0, \quad \frac{\partial \rho_w}{\partial x}_{x=L} = 0. \tag{5}$$

The origin, $x = 0$, of the horizontal coordinate axis x is located at the vapour/adsorbent boundary. The initial conditions are given by

$$T(x)_{t=0} = T_0 + \Delta T, \quad \rho_w(x)_{t=0} = \rho_0 + \Delta\rho. \tag{6}$$

The analytical solutions for the thermal energy equations (1) and (4) with mass diffusion given by Eq. (2) are given by (8) and (9), respectively. The main approximations are that ρ remains constant which is valid for small changes in ρ_w ($<0.5\%$ of ρ), and that the specific enthalpy h_s of the adsorbed fluid is a constant value ($\operatorname{grad} h_s = 0$).

For the given boundary conditions, the exact solution for Eq. (2) is given by

$$\begin{aligned}\rho &= \rho_0 + \Delta\rho\sum_{n=1}^{\infty}\frac{2}{\lambda_n}\mathrm{e}^{-(\lambda_n^2/L^2)Dt}\sin\left(\lambda_n\frac{x}{L}\right),\\ \lambda_n &= \frac{(2n-1)\pi}{2}.\end{aligned} \tag{7}$$

The exact solution for Eq. (1) is given by

$$\begin{aligned}T = T_0 + \Delta T\sum_{n=1}^{\infty}\Bigg[&\frac{2}{\lambda_n}\mathrm{e}^{-(\lambda_n^2/L^2)\alpha t}\sin\left(\lambda_n\frac{x}{L}\right)\\ &- p\frac{2}{\lambda_n}D\frac{\mathrm{e}^{-(\lambda_n^2/L^2)Dt}-\mathrm{e}^{-(\lambda_n^2/L^2)\alpha t}}{\alpha - D}\sin\left(\lambda_n\frac{x}{L}\right)\Bigg],\\ p = \frac{\Delta\rho_{\mathrm{w}}\Delta h_{\mathrm{ads}}}{\Delta T\rho c_{\mathrm{p}}}&.\end{aligned} \tag{8}$$

The exact solution for Eq. (4) is given by

$$T = T_0 + \Delta T\sum_{n=1}^{\infty}\frac{2}{\lambda_n}\mathrm{e}^{-(\lambda_n^2/L^2)\alpha t}\sin\left(\lambda_n\frac{x}{L}\right),\quad \alpha = \frac{k}{\rho c_{\mathrm{p}}}. \tag{9}$$

The exact solutions can easily be verified by substitution in the original equations. After using the dimensionless numbers $\tau = (T - T_0)\Delta T$, $Le = \alpha/D$, $\xi = x/L$, and $Fo = \alpha t/L^2$, the difference between Eqs. (8) and (9) is then given by

$$\begin{aligned}\Delta\tau &= \tau_{\mathrm{Eq.(9)}} - \tau_{\mathrm{Eq.(8)}}\\ &= p\sum_{n=1}^{\infty}\frac{2}{\lambda_n(Le-1)}\left(\mathrm{e}^{-\lambda_n^2(Fo/Le)} - \mathrm{e}^{-\lambda_n^2 Fo}\right)\sin(\lambda_n\xi).\end{aligned} \tag{10}$$

This difference becomes significant at low Lewis numbers as shown in Fig. 2 for $\xi = 1$. Fig. 2 clearly shows that the use of Eq. (1) yields for these Lewis numbers a much faster temperature change than using Eq. (4). Both solutions are identical for $D = 0$ and/or $p = 0$ which means no mass diffusion, and/or no heat of adsorption ($\Delta h_{\mathrm{ads}} = 0$).

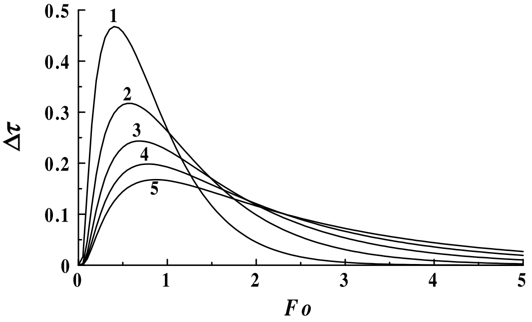

Fig. 2. Difference between the two models discussed. Δτ according to Eq. (10) at $\xi = 1$, vertical axis, as a function of Fourier number *Fo*, horizontal axis, for five different Lewis numbers *Le* from 1 to 5. Other parameter values: $p = 1$ and ∞ is approximated by "30".

For the given boundary conditions the heat flux at the adsorbent/vapour boundary are derived. If Eq. (1) is used, then follows from Eq. (8):

$$\begin{aligned}\vec{\Phi}_q &= -k\frac{\partial T}{\partial x}\bigg|_{x=0}\\ &= -k\Delta T\frac{2}{L}\sum_{n=1}^{\infty}\left[\mathrm{e}^{-\lambda_n^2 Fo} - \frac{p}{Le-1}\left(\mathrm{e}^{-\lambda_n^2(Fo/Le)} - \mathrm{e}^{-\lambda_n^2 Fo}\right)\right]\end{aligned} \tag{11}$$

and if Eq. (4) is used, then follows from the Eqs. (3), (7) and (9):

$$\begin{aligned}\vec{\Phi}_q &= -k\frac{\partial T}{\partial x}\bigg|_{x=0} + D\Delta h_{\mathrm{ads}}\frac{\partial\rho_{\mathrm{w}}}{\partial x}\bigg|_{x=0}\\ &= -k\Delta T\frac{2}{L}\sum_{n=1}^{\infty}\left[\mathrm{e}^{-\lambda_n^2 Fo} - \frac{p}{Le}\mathrm{e}^{-\lambda_n^2(Fo/Le)}\right].\end{aligned} \tag{12}$$

The total amount of heat exchanged at the vapour side from $t = 0$ until $t = \infty$ is the same for both cases. However, the calculation of the relative difference between the two Eqs. (11) and (12) yields $(\vec{\Phi}_{q,\mathrm{Eq.(11)}} - \vec{\Phi}_{q,\mathrm{Eq.(12)}})/\vec{\Phi}_{q,\mathrm{Eq.(12)}} = p/Le$ at $Fo = 0$. This relative difference becomes significant at low Lewis numbers and/or high p values.

Although we only gave here one example, it is clear that, when Eq. (1) is used, the error in heat transfer and temperature is significant for low Lewis numbers. Other examples may yield also errors for large Lewis numbers. With this technical note we demonstrate that there is a difference in temperature and heat transfer affect between adsorption/desorption at the vapour/adsorbent boundary and adsorption/desorption inside the adsorbent itself. If it is plausible that a substantial amount of vapour is present inside the adsorbent and Eq. (1) is used for modelling adsorption/desorption inside the adsorbent itself, then it is better to use also a mass diffusion equation for the vapour phase inside the adsorbent.

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