



Letter to the Editors

Thermodynamically consistent thermal energy equation for an adsorbent/fluid system

Wojcik et al. [1] examined, among other things, thermodynamic consistency of some equations expressing energy balance. The authors consider their Eq. (1) taken from the literature to be thermodynamically inconsistent because of the boundary conditions in Eq. (3). In the conclusion they seem to prefer Eq. (4) borrowed from the Thermodynamics of Irreversible Processes.

The discussion of Wojcik et al. is both interesting and important, but, as it seems to me, needs to be supplemented. It is the purpose of this letter to show the balance Eqs. (1) and (4) to immediately follow from a more complete expression by neglecting particular terms. Consequently, these equations are equally inconsistent in a qualitative sense. However, the quantitative treatment provided by the authors [1] is useful in several instances, e.g. if we are to simplify the energy balance.

Assuming each phase to occupy the whole domain (overlapping continua), we start our discussion¹ by writing the local energy balance for an adsorbent/fluid system in the form

$$\frac{\partial}{\partial t} \left(\sum_k \rho_k h_k \right) + \text{div } \vec{q} = \pm \varepsilon_Q \quad (1)$$

where ρ_k represents the partial mass density and h_k the specific enthalpy of the phase k contained in the control volume, and ε_Q stands as a heat source for possible thermal effects arising from interactions of the fluid with the adsorbent. However, we will neglect ε_Q in the present discussion.

The energy flux \vec{q} may be written as

$$\vec{q} = -k \text{ grad } T + \sum_k (h_k \vec{\phi}_k) \quad (2)$$

where k represents an apparent thermal conductivity of the system, T the temperature, and the product $h_k \vec{\phi}_k$ the enthalpy flux at the boundary of the control volume, $\vec{\phi}$ being the mass flux.

¹ Supposing the literature in the field considered was sufficiently studied by Wojcik et al., I have not consulted any further paper. Therefore it is not excluded that similar considerations already exist in the literature.

Combining Eqs. (1) and (2) gives

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) - \sum_k (h_k \text{ div } \vec{\phi}_k) - \sum_k (\vec{\phi}_k \text{ grad } h_k) - \sum_k h_k \frac{\partial \rho_k}{\partial t}. \quad (3)$$

The system considered consists of three phases: bulk fluid (liquid or gas, G), adsorbed fluid (film, F) and adsorbent (solid, S). In what follows the adsorbent is assumed to possess a constant density and to be fixed in the coordinate system, thus $\vec{\phi}_S = 0$ and $\partial \rho_S / \partial t = 0$. Then, Eq. (3) gives

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) - (\vec{\phi}_G \text{ grad } h_G + \vec{\phi}_F \text{ grad } h_F) - h_G \left(\frac{\partial \rho_G}{\partial t} + \text{div } \vec{\phi}_G \right) - h_F \left(\frac{\partial \rho_F}{\partial t} + \text{div } \vec{\phi}_F \right) \quad (4)$$

In the case that the fluid phases do not undergo any phase change, their continuity equations

$$\frac{\partial \rho_G}{\partial t} + \text{div } \vec{\phi}_G = 0, \quad (5)$$

$$\frac{\partial \rho_F}{\partial t} + \text{div } \vec{\phi}_F = 0 \quad (6)$$

simplify Eq. (4) giving

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) - (\vec{\phi}_G \text{ grad } h_G + \vec{\phi}_F \text{ grad } h_F). \quad (7)$$

However, when a phase change is taking place, the amount of one phase increases at the expense of the other one. This interaction can be taken into account by introducing a source term ε , thus

$$\frac{\partial \rho_G}{\partial t} + \text{div } \vec{\phi}_G = -\varepsilon_G, \quad (8)$$

$$\frac{\partial \rho_F}{\partial t} + \text{div } \vec{\phi}_F = +\varepsilon_F, \quad (9)$$

if a phase change occurs from the gas towards the film (adsorption).

Nomenclature

A	surface
D	mass diffusivity
h	specific enthalpy
k	thermal conductivity
\vec{q}	heat flux vector
t	time
T	temperature
$\vec{\phi}$	mass flux vector

ε	source
ρ	mass density

Indices

F	adsorbed phase (film)
G	bulk phase (gas)
k	phase k

Since the mass of one phase increases while the mass of the other phase decreases by the same amount, it is $\varepsilon_G = \varepsilon_F = \varepsilon$. Furthermore, as the quantity ε represents the mass flow rate per unit volume due to phase change, we may set it equal to the time derivative of the film density, $\varepsilon = \partial\rho_F/\partial t$. This step becomes obvious if we, for instance, write the continuity equation for the fluid (both phases) of a system containing an evaporating liquid droplet (or a droplet growing by condensation) that is completely enclosed by the vapour, thereby assuming the control surface not to intersect the interface.

Thus, Eq. (4) takes the form

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) - (\vec{\phi}_G \text{ grad } h_G + \vec{\phi}_F \text{ grad } h_F) + (h_G - h_F) \frac{\partial \rho_F}{\partial t} \quad (10)$$

expressing a local energy balance for a system undergoing a phase change, the last term representing a heat source (for $\partial\rho_F/\partial t > 0$, heat sink for $\partial\rho_F/\partial t < 0$) due to the phase change. This equation, deduced from Eq. (1) without making any assumption, is complete inasmuch as Eq. (1) accounts for the terms important for the energy balance.

Now, neglecting the term $\vec{\phi}_G \text{ grad } h_G$ (that is, supposing $\vec{\phi}_G \perp \text{ grad } h_G$, or $\vec{\phi}_G = 0$, or $\text{grad } h_G = 0$) and, in addition, setting

$$\vec{\phi}_F = -D_F \text{ grad } \rho_F, \quad (11)$$

which postulates the film flow to occur by diffusion only, D_F being a diffusion coefficient, we find

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) + D_F \text{ grad } \rho_F \cdot \text{grad } h_F + (h_G - h_F) \frac{\partial \rho_F}{\partial t}. \quad (12)$$

By the next assumption the relationship $\text{grad } \rho_F \cdot \text{grad } h_F = 0$ should hold (which requires $\text{grad } \rho_F \perp \text{grad } h_F$ or $\text{grad } \rho_F = 0$, or $\text{grad } h_F = 0$) and obtain from Eq. (12)

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) + (h_G - h_F) \frac{\partial \rho_F}{\partial t}, \quad (13)$$

which is the Eq. (1) of Wojcik et al. [1].

On the other hand, setting $\partial\rho_F/\partial t = 0$ or $h_G - h_F = 0$, which implies no phase change accompanied by a thermal effect, Eq. (12) delivers

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = \text{div}(k \text{ grad } T) + D_F \text{ grad } \rho_F \cdot \text{grad } h_F \quad (14)$$

which is the Eq. (4) in the paper under the discussion.

As is obvious from the derivations above, Eq. (13) disregards the (sensible) enthalpy change of the phases flowing in the control volume, whereas Eq. (14) accounts for only the (sensible) enthalpy change of the film phase; the latter disregards even the latent heat arising from the phase change. Consequently, neither Eq. (13) nor Eq. (14) (that is, none of Eqs. (1) and (4) in [1]) does satisfy the first principle of thermodynamics. The conclusions of Wojcik et al. regarding their Eq. (4) that should obey the conservation law (at the boundary and in the whole system), sensitively contradict the present finding.

The last expression in the chain of our derivation that is consistent regarding the energy conservation is the Eq. (10). It also satisfies the boundary conditions at the interface (Eq. (3) in [1]) which follows from the above Eq. (4) by taking the interface to be a mathematical surface allowing us to omit all the capacity terms. Then, our Eq. (4) reduces to

$$\text{div}(k \text{ grad } T - h\vec{\phi}) = \text{div}(k \text{ grad } T - (h_G\vec{\phi}_G + h_F\vec{\phi}_F)) = 0 \quad (15)$$

or, by involving the Gauss theorem, to

$$\int_A ((k \text{ grad } T - h\vec{\phi}) \cdot d\vec{A}) = 0 \quad (16)$$

where the surface A encloses the interface. If the integrand does not change over the interface, the integration

may at once be performed. The same immediately follows also from Eq. (15).

Reference

- [1] A.M.W. Wojcik, J.C. Jansen, Th. Maschmeyer, Thermodynamically consistent thermal energy equation for an absorbent/fluid system, *Int. J. Heat Mass Transfer* 44 (2001) 2379–2383.

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