1 The energy balance

The derivation of a rigorous energy balance for any real-life system, of which the idealized Plug Flow Reactor (PFR) is one simple example, demands a *tour de continuum mécanique* which definitely is beyond the scope of this little text. But, we cannot ignore the energy balance altogether so we must somehow pick up a model description that is mathematically succinct and at the same time physically correct. The following derivation is a humble attempt to reach a reasonably clear disposition of the subject. Let $U(t, z, \Delta z)$ be the internal energy of a control volume with a single inlet and a single outlet. The material flow into the control volume, and out from it, is assumed to be perpendicular to the control surfaces which are situated at $z$ and $z + \Delta z$. This simplification reduces the formal inner product of the surface normal (vector) and the (vectorial) flows of heat, displacement work, and energy, into their scalar counterparts called $\vec{Q}$, $p\vec{V}$ and $\vec{U}$. Note that we shall only consider the flow of internal energy $U$ while in the general case we might need to include terms for potential energy, kinetic energy, surface energy, electromagnetic energy and so forth. But, because the picture becomes immensely complicated when every possible term is included, it is important to simplify the model as much as possible without losing the grip of reality. According to the aforementioned simplifications, and the principle of energy conservation, we can write

$$\dot{U}(t, z, \Delta z) = U_0 + \int_0^t \left( \dot{U} + p\dot{V} \right)_z d\tau - \int_0^t \left( \dot{U} + p\dot{V} \right)_{z+\Delta z} d\tau + \int_0^t (\dot{Q} - \dot{W}_s) d\tau$$
where $\vec{W}$ is the mechanical “shaft” work applied to the reactor. Normally it is close to zero. Subscripts $z$ and $z+\Delta z$ are used to denote physical properties that are calculated at these two spatial positions. This is not to say that $\vec{U}$ and $p\vec{V}$ are functions of $z$ per se. They are, however, indirectly attached to the spatial co/ordinates defining their proper values at every point in space and time. There are therefore two co/ordinate systems in action at all times: One which is invisible to us describing the thermodynamic state in abstract quantities like $u$ and $s$, and one which is identical to $\mathbb{R}^3$ being the real space. This subtlety is discussed further down the text.

In the current context we may put the integration constant $U_0$ to zero. It implies that a material system with zero mass has zero energy. This is an important thermodynamic consideration which is true for all chemical systems in the absence of strong electromagnetic radiation.

The symbols $\vec{Q}$, $\vec{V}$ and $\vec{U}$ stand for the transported heat, volume and energy (per unit time) and has nothing to do with the derivative of a mathematical function, say $F$, which is defined like:

$$\left( \frac{\partial F}{\partial t} \right) = \lim_{\Delta t \to 0} \left( \frac{F(t + \Delta t) - F(t)}{\Delta t} \right)_{x_1,x_2,\ldots}$$

This means we need to distinguish clearly between the transportation $\vec{F}$ and the time derivative ($\partial F/\partial t$). The scientific units are the same but their interpretations are entirely different\(^1\). In other articles on the same subject you may find that $\dot{F}$ and $\ddot{F}$ are used interchangably for denoting $\vec{F}$. The meaning is the same though.

In the derivation of the energy balance it looks like $U$ and $\vec{U}$, from which $\vec{U}$ is derived, are quite similar, but they do actually measure two different aspects of the internal energy. $U$ is a mathematical construction (we may call it a functional) which has no simple physical description, while $\vec{U}$ is a thermodynamic state function $U(S,V, N_1, N_2, \ldots, N_n)$ depending on the material description but not upon space or time. That is to say $U(x,t_1,z_1) = U(x,t_2,z_2) = \ldots U(x,t_n,z_n)$ for all fixed values of entropy, volume and mole numbers (collected into a single vector $x$). To be a state function $U$ must represent the energy of an isotropic system in equilibrium with respect to certain restricted changes in the state variables $S$, $V$, $N_1$, $N_2$, etc. (the definition of state variables is made broader later in this text). Hence, it is generally true that $(\partial U/\partial t) = \ldots$\(^2\)

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\(^1\)A formal argument can be raised against the derivative conjecture as it is stated in the text above. Consider the functional $\mathcal{F}$ which describes the amount of energy, mass or any other extensive property that has passed the control surface at $z$ over the time period $[0,t]$. Then $\mathcal{F}(t,z) = \int_0^t A \vec{f} \, d\tau$ where $\vec{f}$ is the flux (amount per unit area and time) of $F$, and $A$ is the cross-sectional area of the transport. The time derivative of $\mathcal{F}$ is $\left( \frac{\partial \mathcal{F}}{\partial t} \right)_{z} = A \vec{f} \equiv \vec{F}$. So, in a sense $\vec{F}$ is really a partial derivative, but it must be understood that $\mathcal{F}$ has no explicit (and time independent) function expression like e.g. the thermodynamic and the kinetic models we are using. Many students have problems in understanding this difference between $dF/dt$ and $(\partial F/\partial t)$ and I therefore hesitate in calling $\vec{F}$ a time derivative because it will bring even more confusion into the subject.

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0 whilst \((\partial U/\partial t) \neq 0\). To proceed, we introduce from thermodynamic theory that \(H \equiv U + pV\). This definition also works for the transported enthalpy:

\[
\tilde{H} = \tilde{U} + p\tilde{V}
\]  

(1)

It works because \(p\) (the pressure) is an intensive state variable which is independent of the magnitude of the volume flow. At the same time we want to integrate the total heat flux over the external surface of the reactor section

\[
\bar{Q} = z + \int_{z}^{z+\Delta z} C\bar{q}\,d\zeta,
\]

(2)

where \(C\) is the circumference of the reactor and \(\bar{q}\) is the heat flux (per unit time and surface area). Note that \(d\zeta\) rather than \(dz\) is acting as an integrator for \(\bar{q}\). We use this convention (Greek integrator–Latin variable) to make sure we do not mix up the integrator symbol with the symbol of either the upper or the lower limit of the integral\(^2\). This makes the integral a function of \(z\) while \(\zeta\) is consumed during the integration.

The axial heat flow can usually be neglected in a chemical reactor which is why the heat integral is carried out over the outer surface only. However, strictly speaking there is an order-of-magnitude analysis missing here but this is left as an exercise for the reader. The internal energy of the control volume is then:

\[
\mathcal{U}(t, z, \Delta z) = \int_{0}^{t} (\tilde{H}_z - \tilde{H}_{z+\Delta z}) \,d\tau + \int_{0}^{t} \int_{z}^{z+\Delta z} C\bar{q}\,d\zeta \,d\tau
\]

This states the energy balance of a simple plug flow reactor. On the form given it is particularly useful for testing and verifying the accuracy of numerical integrators used in dynamic simulation studies, but this is not our goal. We will proceed here by calculating the partial derivative \(\mathcal{U}\) at a fixed spatial position \(z\) with respect to time:

\[
\left(\frac{\partial \mathcal{U}}{\partial t}\right)_{z,\Delta z} = \tilde{H}_z - \tilde{H}_{z+\Delta z} + \int_{z}^{z+\Delta z} C\bar{q}\,d\zeta
\]

(3)

On the current form Eq. 3 leads to a partial differential equation (PDE) in time and space which must be viewed upon as a hard numerical task. But, there are relevant simplifications. In particular we want to study the behaviour of closed systems without throughput of mass and steady state (time independent) systems.

\(^2\)Dealing mostly with closed and definite integrals we may not even realise the problem, but as we move on to indefinite integrals (antiderivatives) the symbol clash becomes very noticeable. In thermodynamics we define for example the residual function \(G^*(p) \equiv \int_{0}^{p} (V(\pi) - V^*(\pi)) \,d\pi\) where \(\pi\) is an integrator (over pressure) and \(p\) is the system pressure. The convolution integral \(F(t) = \int_{0}^{t} \phi(\tau)\psi(t - \tau) \,d\tau\) used in signal theory is another example. The mutual roles of \(\tau\) and \(t\) must here be sorted out beforehand.
1.1 First law of thermodynamics

A special form of the energy balance in Eq. 3 applies to closed systems. Here, closed means \( \vec{H}_z = \vec{H}_{z+\Delta z} = 0 \). This appears to be outside the scope of our PFR model but it is still in reach of the thermodynamic formalism. In a system of this kind energy changes solely because heat is expelled to, or brought in from, the environment. For the change of \( \mathcal{U} \) we can then write:

\[
(\mathrm{d}\mathcal{U})^{cs} = \int_z^{z+\Delta z} C\vec{q}\,\mathrm{d}\zeta\,\mathrm{d}t
\]

Back/substitution of \( \vec{Q} \) from Eq. 2 yields the simpler form: \( \mathrm{d}\mathcal{U} = \vec{Q}\,\mathrm{d}t \). A similar argument holds also for any kind of external work even though it by coincidence has been excluded in Eq. 3. The reason is that the PFR model is not subject to any volume change nor is it equipped with a mechanical stirrer. If we had decided to include external work (positive when work is delivered by the system) the energy equation would have been extended to \( \mathrm{d}\mathcal{U} = \vec{Q}\,\mathrm{d}t - \vec{W}\,\mathrm{d}t \).

Taken a bit further it customary to say that \( \vec{Q}\,\mathrm{d}t = \delta Q \) and \( \vec{W}\,\mathrm{d}t = \delta W \) where \( \delta Q \) and \( \delta W \) stand for the non-exact differentials of \( Q \) and \( W \). Non-exact means that \( \mathcal{U} \) does not depend on \( Q \) and \( W \) in a definite way. I.e. there exists no function \( \mathcal{U}(Q,W) \) such that when \( Q \) and \( W \) are given then \( \mathcal{U} \) is also given. This should be quite intuitive all the time \( \mathcal{U} \) is the energy of a material system where the masses of the chemical constituents must also play a role.

In fact, \( Q \) and \( W \) are path dependent functions of the thermodynamic state, and also of the spatial coordinates, and of time. They are not state functions in any way and they do not constitute a part of the system. Rather, they express the transportation of energy across the system border. Inside the system, however, heat and work can only be stored as internal energy. There are in other words no “heat content” or “energy content” of the system, only the ability to exchange heat and work with the environment. We therefore talk about “heat potential” and “work potential” to stress the fact that energy (the thermodynamic potential) has to be converted back and forth between heat and work all the time.

Finally, before we leave the discussion of the closed system we shall make a precise interpretation of \( \mathcal{U} \) and \( \mathcal{U} \). It has already been stated that \( \mathcal{U} \) is a constructed energy function—a functional—that serves the need of an accumulation term in the energy equation. From the discussion given above it is clear that \( \mathcal{U} \) does not change in a closed system unless there is heat or work exchange with the environment. If there are no interactions of any kind, then all experiments made over the past 200 years indicate that \( \mathcal{U} \) gradually becomes undistinguishable from \( \mathcal{U} \). That is:

\[
\mathcal{U}_{eq} \doteq \lim_{t \to \infty} \mathcal{U} \rightarrow \mathcal{U}
\]

The two functions \( \mathcal{U} \) and \( \mathcal{U} \) are identical whenever their function values are the same over the entire definition domain\(^3\). In this case \( \mathcal{U} \) is constant throughout the experiment

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\(^3\)E.g. the two functions \( f(x) = \cos^2(x) + \sin^2(x) \) and \( g(x) = 1 \) are mathematically identical for \( x \in \mathbb{R} \).
so how can it then be that it *gradually* becomes undistinguishable from $U$? Well, the *experiment* tells us that $U$ does not change in a closed system over time. The *postulate* says that $U$ is identical to $U$ when all the internal agitation and transients have died out. Before that the measurements of any intensive variables like temperature, pressure and chemical potentials give unreliable readings even though the function values are the same at any time. It is only then all the readings are stable we can say that $U \equiv U$ in the mathematical understanding of the statement. We call this the equilibrium state of the system. It has an incredible simple representation in the sense that only $n+2$ macroscopic variables are needed in order to establish the value of $U(S, V, N_1, N_2, \ldots, N_n)$. From a microscopic point of view this is really *incredible* because there are $6N_A \sum N_i$ mechanical degrees of freedom when all the particles in the system are considered as a Newtonian universe. Thermodynamic systems are much simpler, however, because experimentally only the statistically most relevant state is being observed, and since thermodynamics *is* a phenomenological science the observations and theory go hand in hand. This means we can write the energy balance of a closed system as

$$(dU)^{c-s} = \delta Q - \delta W$$

which is precisely the first law of thermodynamics. The energy balance in Eq. 3 fulfills in other words the requirements of the first law of thermodynamics albeit in disguise. It must be understood, however, that the usability of $U = U_{\text{eq}}$ hinges on the fact that the relaxation time of the equilibrium process must be smaller than the time scale of the simulation. This may, or may not, be the case, but for the present purpose we shall assume that $U$ has the meaning of $U$; at least locally for each point in space—if not for the entire system.

### 1.2 Steady state solution

Eq. 3 has another special meaning whenever the physical situation is such that it allows the left hand side to be put to zero. It is the celebrated *steady state* which reduces the differential equation to a time/independent algebraic equation on the form:

$$(\vec{H}_{z+\Delta z} - \vec{H}_z)^{s-s} = \int_z^{z+\Delta z} C\vec{q} d\zeta$$

Despite its simple form the last equation has a wide range of applicability. It is valid for any type of fluid flow, inviscid or not, gas or liquid, one-phase or multi-phase, and with or without chemical reactions.

Just like the displacement work in Eq. 1 was factored into $p\vec{V}$, the transported enthalpy can be factored into the transported mass and a term called the *specific* enthalpy $h$:

$$\vec{H} = h\vec{M}$$

The inherent scaling properties, namely that $\vec{W} = p\vec{V}$ and $\vec{H} = h\vec{M}$, are deeply rooted in thermodynamic theory and are examples of the so-called Euler homogeneous functions.
The energy balance is then reduced to:

\[(h\bar{M})_{z+\Delta z} - (h\bar{M})_z = \int_z^{z+\Delta z} C\bar{q} d\zeta\]

From the mass conservation principle we know that (for steady-state flow):

\[\bar{M}_{z+\Delta z} - \bar{M}_z = 0\]

Division by \(\bar{M}_{z+\Delta z} = \bar{M}_z \equiv \bar{M}\) on both sides of the equation yields:

\[h_{z+\Delta z} - h_z = \int_z^{z+\Delta z} \frac{C\bar{q}}{\bar{M}} d\zeta\]

In the limit of \(\Delta z \to 0\) we get:

\[\lim_{\Delta z \to 0} (h_{z+\Delta z} - h_z) = C\frac{\bar{q}}{\bar{M}} \Delta z\]

or rearranged:

\[\lim_{\Delta z \to 0} \frac{h_{z+\Delta z} - h_z}{\Delta z} = C\frac{\bar{q}}{\bar{M}}\]

We immediately recognize the left hand side as the partial derivative of \(h\) with respect to \(z\). On the right hand side we can make the definition \(q \equiv \bar{q}/\bar{M}\) standing for the specific heat load (energy per unit mass and area). The energy balance for a steady state reactor with only internal energy flow is then:

\[\left(\frac{\partial h}{\partial z}\right)_{s-s} = Cq\]  

(4)

The anti/derivative of the energy balance defines the so-called enthalpy equation (please note the integral on the right side is zero for an adiabatic reactor without external heat load):

\[h(z) = h(0) + \int_0^z C(\zeta)q(\zeta) d\zeta\]

At this point we need to worry about the mathematical notation we are using. The operations are formally correct up to the point where \(\Delta z \to 0\), but here it stops. At some finite value of \(\Delta z\) it becomes smaller than the resolution of the measurement. Or, it may in fact become smaller than the effective size of the molecules comprising the system and on this tiny scale \(h\) loses its meaning since it requires a big number of colliding molecules to establish a thermodynamic state variable. Hence, the derivative
(\partial h/\partial z) does not exist in proper. We have in fact not indicated anything about \( h \) being a continuous property—the only assumption is that \( h \) has different values at the inlet and outlets of the reactor. It is then \( \Delta z \) becomes small we must encompass the theory with an assumption of continuity. It is only the finite difference \( h_{z+\Delta z} - h_z \) that is physically measureable, and then only if \( \Delta z \) is sufficiently large. This is not a practical problem in most cases, but for e.g. high-vacuum systems we must take precautions because the distance covered between two successive collisions of the molecules can be of the order millimeters or even centimeters.

Our second worry is that \( h \) is not a function of the spatial coordinate \( z \). At least not explicitly so. It is rather a function of the densities \( T, v \triangleq V/M, c_1 \triangleq N_1/M, c_2 \triangleq N_2/M, \) etc. when any of the modern pressure explicit equations of state is being used in the modelling (most of them are descendants of the Van der Waals equation of state from 1873). The densities are assumed to be continuous in space. Hence, \((\partial h/\partial z)\) does only exist as a formal expression, but from differential calculus we know that \( d(\partial h/\partial z) \) takes the same numerical value as \((\partial h/\partial z)\) when all the degrees of freedom except one (i.e. \( z \)) are locked. From the total differential of \( h \)

\[
dh = \left( \frac{\partial h}{\partial T} \right)_{v,c_1,c_2,\ldots,c_n} dT + \left( \frac{\partial h}{\partial v} \right)_{T,c_1,c_2,\ldots,c_n} dv + \left( \frac{\partial h}{\partial c_1} \right)_{T,v,c_2,\ldots,c_n} dc_1 + \left( \frac{\partial h}{\partial c_2} \right)_{T,v,c_1,\ldots,c_n} dc_2 + \cdots
\]

we may write:

\[
dh = \partial_T h \cdot dT + \partial_v h \cdot dv + \partial_{c_1} h \cdot dc_1 + \partial_{c_2} h \cdot dc_2 + \cdots
\]

Inventing a new notation “over the night” is not something I usually recommend, but we will run out of paper pretty soon unless we do something about the partial derivatives flourishing all over the place. Dividing by \( dz \) (which is an algebraic quantity remember—making it quite different from \( \partial z \) which is an operator) gives the differential quotient:

\[
\left( \frac{dh}{dz} \right) = \left( \frac{\partial h}{\partial T} \right)_{v,c_1,c_2,\ldots,c_n} \left( \frac{dT}{dz} \right) + \left( \frac{\partial h}{\partial v} \right)_{T,c_1,c_2,\ldots,c_n} \left( \frac{dv}{dz} \right) + \left( \frac{\partial h}{\partial c_1} \right)_{T,v,c_2,\ldots,c_n} \left( \frac{dc_1}{dz} \right) + \left( \frac{\partial h}{\partial c_2} \right)_{T,v,c_1,\ldots,c_n} \left( \frac{dc_2}{dz} \right) + \cdots
\]

or, using our shorter notation:

\[
\nabla h = \partial_T h \cdot \nabla T + \partial_v h \cdot \nabla v + \partial_{c_1} h \cdot \nabla c_1 + \partial_{c_2} h \cdot \nabla c_2 + \cdots
\]

This is precisely the expression we are looking for\(^4\). The crux of the matter is that \( \nabla h \) takes the same numerical value as \((\partial h/\partial z)\). To carry on we must first solve an equation

\(^4\)Note that we have merely askewed from the original problem that \((\partial h/\partial z)\) is not properly defined in the thermodynamic sense. What we now assume is that \( \nabla T, \nabla v \) and \( \nabla c_i \) are meaningful to us—both physically and mathematically. This assumption can be formalized, however, in claiming that Gibbss-Duhem’s equation is fulfilled with time and in space. Hence: \( s(\partial T/\partial t) - v(\partial p/\partial t) + c^T(\partial \mu/\partial t) = 0 \) and \( s\nabla T - v \nabla p + c^T \nabla \mu = 0 \). These are the conditions that must be fulfilled in order to relief us from our second worry.
system that settles the values of $\nabla T$, $\nabla v$, $\nabla c_1$, $\nabla c_2$, etc. This is done by solving the energy, momentum and mass balances simultaneously at the inlet of the reactor, and integrating the solution variables along the spatial coordinate $z$. The how’s and why’s are fully explained in Section ?? entitled Modelling Issues. The implicit nature of the conservation statement is so fundamental to the thermodynamicsist, however, that it really deserves its own introductory example. The internal workings of the so-called Jacobian transformation are explained below.

1.3 Calculation example

Doing matrix algebra by hand is hard work but there is no other way we can get an understanding of how the linearization really works. To gain some insight we will practise on a minimalistic $2 \times 2$ example. Assuming then a problem on the form:

$$H^g(T, V) = C^g T = H_o$$

$$p^g(T, V) = \frac{NRT}{V} = p_o$$

where $N$ is constant, and $H_o$ and $p_o$ are conserved quantities. Let $x = (T, V)$ and $y = (H, p)$. In order to solve $y(x) = y_0$ we must first linearize $y(x)$ and then attempt solving the equations iteratively using e.g. the Newton-Raphson method:

$$y_k + \left( \frac{\partial y}{\partial x} \right)_k (x_{k+1} - x_k) = y_0$$

Rearrangement gives:

$$x_{k+1} = x_k - J_k^{-1}(y_k - y_0)$$

where

$$J_k = \left( \frac{\partial y}{\partial x} \right)_k = \left( \begin{array}{cc} \frac{\partial H}{\partial T} & \frac{\partial H}{\partial V} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial V} \end{array} \right)_k$$

so that:

$$J_k^{-1} = \left( \begin{array}{cc} C^g_R & 0 \\ \frac{NRT}{V^2} & \frac{NRT}{V} \end{array} \right)_k^{-1} = \frac{1}{C^g_P V} \left( \begin{array}{cc} \frac{NRT}{V} & 0 \\ \frac{NRT}{V^2} & C^g_P \end{array} \right)_k = \left( \begin{array}{cc} \frac{1}{C^g_P} & 0 \\ \frac{V}{C^g_P T} & \frac{V^2}{NRT} \end{array} \right)_k$$

The remaining algebra is straightforward:

$$\left( \begin{array}{c} T \\ V \end{array} \right)_{k+1} = \left( \begin{array}{c} T \\ V \end{array} \right)_k - \left( \begin{array}{c} \frac{C^g_P}{C^g_P V^2} & 0 \\ \frac{V}{C^g_P T} & \frac{V^2}{NRT} \end{array} \right)_k \left( \begin{array}{c} C^g_P T \\ \frac{NRT}{V} \end{array} \right)_k - \left( \begin{array}{c} H \\ p \end{array} \right)_o$$

An iteration example follows. Let: $H_o = 10^4 J$, $p_o = 10^6 Pa$, $N = 1$ mol, $C^g_P = \frac{5}{2} R$, $R = 8.3145 J mol^{-1} K^{-1}$:
The Newton-Raphson iteration is a so-called 2nd order method. One characteristic feature of 2nd order methods is that the number of significant digits will double, in each iteration, iff the state is sufficiently close to the solution (iteration 3 onward in this case). This is a superior convergence indicator which should always be verified when solving equations numerically. From the table it is also clear that $T$ converges in a single step whilst $V$ requires 8 iterations. Give a reason for this observation\(^5\). Finally, it should be mentioned that the Newton-Raphson method is sensitive to the starting values. E.g. try to start the iteration at $V = 0.01$ rather than $V = 0.001$. Suggest a possible fix to the algorithm in this case\(^6\).

### 1.4 On differentials and derivatives

I have in this little text sought to establish a fairly rigorous derivation of the energy balance for an idealized plug flow reactor. It is neither highly sophisticated nor does it require advanced mathematics. Still, it is not of a kind that is eagerly agreed upon by the chemical engineering community—be it professors, students or working professionals. Many people find the painstaking calculations of differentials and partial derivatives confusing and of little practical interest, but the latter is definitely wrong. The very fact that $\nabla T$, $\nabla v$ and $\nabla c_i$ are the solution variables of a set of model equation whereas $\partial_{T,h}$, $\partial_{v,h}$ and $\partial_{c_i,h}$ are explicit (or sometimes implicit) state functions establishing the coefficient matrix of the model equations is so important that it can hardly be overemphasized. 

The culprit in this controversy might be the teaching of $\frac{dy}{dx} = y'$ in highschool mathematics. By doing so the students learn that $\frac{dy}{dx}$ is synonymous with $y' \doteq (\partial y/\partial x)$ and that the rest of the story is just syntactic sugar. For one/variable systems I can agree that the difference is subtle, but for many/variable systems it is not. The discussion has much in common with the use of substantial derivatives in fluid mechanics which says: $\frac{dy}{dt} = (\partial y/\partial t) + (\partial y/\partial x_1) \frac{dx_1}{dt} + (\partial y/\partial x_2) \frac{dx_2}{dt} + \cdots$. In this case I think it can hardly be misunderstood that $\frac{dy}{dt}$ and $(\partial y/\partial t)$ are different mathematical objects—and very different ones as well.

\(^5\) A misunderstanding here in both $J$ and $J_H$ is $(A^\top J)H$.

\(^6\) Unphysical volume update step length restriction is necessary.