Forms of the Microscopic Energy Balance

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notes begun: March 23, 2005
last updated: March 3, 2010

I. Balance Equations

When one derives the microscopic mass balance, one inevitably obtains the continuity equation,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \left(\rho \mathbf{v} \right) \quad , \tag{1}$$

where ρ is the mass density, $\mathbf{v}$ is the center-of-mass velocity, and t is time. We understand very clearly that the LHS is an accumulation term and the right hand side is a convection term. The only assumption in equation (1) is that mass is not created or destroyed in the system, meaning that there are no nuclear reactions in our system. In our text book, this is equation (3.1-4) on page 77 [1].

When one derives the microscopic mass balance on a single component within a multicomponent system, one typically obtains

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A} \quad , \tag{2}$$

where w_A is the mass fraction of component A, $\mathbf{j}_A$ is the diffusive mass flux of component A relative to the center-of-mass velocity, N_R is the number of independent chemical reactions in the system, and $r_{i,A}$ is the rate of production of component A in reaction i, in units of mass/volume/time. The functional form of $\mathbf{j}_A$ depends on the choice of the form of the constitutive equation, i.e. Fick's law, that one chooses to employ. This diffusive flux can include the Soret effect, in which there is mass transfer due to a temperature gradient. We understand that the LHS is an accumulation term. The first term on the RHS is the convection term, the second term on the RHS is the diffusion term and the third term is the reaction term. Again, this equation neglects nuclear reaction. In our text book, this is equation (19.1-14) on page 584 [1].

When one derives the microscopic momentum balance, one typically obtains

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla (\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi} \quad , \tag{3}$$

where p is the pressure, $\boldsymbol{\tau}$ is the extra stress tensor, and $\hat{\Phi}$ is the specific external field imposed by, for example, gravity. If gravity is the source of the external field then we have $\mathbf{g} = -\nabla \hat{\Phi}$. Again, the functional form of the extra stress tensor must be determined by the choice of constitutive equation. One common constitutive equation is Newton's law of viscosity. We

understand that the LHS is an accumulation term. The first term on the RHS is the convection term, the second term on the RHS represents the momentum transport due to molecular transport due to a gradient in the pressure, the third term is the momentum transport due to molecular transport due to viscous dissipation, and the fourth term is due to an external potential such as gravity. This equation is a the difference of equation (3.2-9) on page 80 of our textbook [1] and the continuity equation , equation(1). There are numerous assumptions in this equation. It assumes that there is no coupling of the momentum and reaction.

When one derives the microscopic energy balance, one obtains

$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \hat{U} + \hat{\Phi} \right)}{\partial t} = -\nabla \cdot \rho \left(\frac{1}{2} v^2 \mathbf{v} + \hat{U} \mathbf{v} + \hat{\Phi} \mathbf{v} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot p \mathbf{v} - \nabla \cdot \left(\mathbf{\tau} \cdot \mathbf{v} \right) \quad , \qquad (4)$$

where $\hat{U}$ is the specific (per mass) internal energy, $\hat{\Phi}$ is the specific potential energy due to an external field, and $\mathbf{q}$ is the heat flux due to conduction. The term on the LHS is the accumulation term. The first term on the RHS is the convection term. The second term on the RHS is the conduction term. The third term on the RHS is the reversible rate of internal energy change per unit change in unit volume. Note that a compression will increase the internal energy. The last term on the RHS is the irreversible rate of internal energy increase per unit volume by viscous dissipation. This is equation (11.1-9) on page 336 in your text book.

We can add other terms to this energy balance to account for reactions and energy loss to the surroundings by other means.

Enthalpy vs. Internal Energy

Equation (4) is written in terms of the internal energy. The internal energy is always the correct thermodynamic function to start with in terms of a derivation. However, we know from experience that sometimes we write the energy balance in terms of the enthalpy. Let's discuss when we use one or the other.

If there is no flow in the system, then the velocity is zero and equation (4) becomes

$$\frac{\partial \rho \left(\hat{U} + \hat{\Phi} \right)}{\partial t} = -\nabla \cdot \mathbf{q} \quad . \qquad (5)$$

In this case, it is very clear that the internal energy is the correct and most convenient thermodynamic function to use.

If there is flow in the system, then we can recall the definition of the specific enthalpy,

$$\hat{H} = \hat{U} + p\hat{V} = \hat{U} + \frac{p}{\rho} \quad . \qquad (6)$$

If we examine the pressure term in equation (4) we can introduce the necessary density factor

$$-\nabla \cdot p\mathbf{v} = -\nabla \cdot \frac{\rho}{\rho} p\mathbf{v} = -\nabla \cdot \rho \left(\frac{p}{\rho} \mathbf{v} \right) \quad , \qquad (7)$$

We substitute equation (7) into equation (4) to obtain

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{U}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \rho\left(\frac{p}{\rho}\mathbf{v}\right) - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \ , \quad (8)$$

Rearranging we have

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{U}\mathbf{v} + \frac{p}{\rho}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \ , \quad (9)$$

We can substitute equation (6) into the convection term of equation (9):

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \ . \quad (10)$$

So, it is straightforward to obtain the enthalpy in the convection term. However, we still have the internal energy in the accumulation term. If we substitute equation (6) into the accumulation term of equation (9) we have

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{H} - \frac{p}{\rho} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \ , \quad (11)$$

Rearranging we have,

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)}{\partial t} - \frac{\partial p}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2 \cdot \mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \ , \quad (12)$$

So, the change from internal energy to enthalpy dictates that the time derivative of the pressure appear explicitly. If the system is at steady state, then the time derivative terms drop out. Otherwise, we need both of them.

One other general trick is to cancel those terms that equate to the continuity equation, equation (1). We use the product rule on the accumulation and convection terms of equation (12),

$$\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)\frac{\partial \rho}{\partial t} + \rho \frac{\partial\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)}{\partial t} - \frac{\partial p}{\partial t} =$$
$$-\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)\cdot\nabla\rho\mathbf{v} - \rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right) - \nabla\cdot\mathbf{q} - \nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v})$$

(13)

The first term on the LHS and first term on the RHS cancel because of the continuity equation, leaving

$$\rho\frac{\partial\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)}{\partial t} - \frac{\partial p}{\partial t} = -\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right) - \nabla\cdot\mathbf{q} - \nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) \quad .$$

(14)

II. Thermodynamic Descriptions for Pressure and Enthalpy

II.A. Pressure

At this point we have an energy balance, but ultimately we need a PDE that has derivatives exclusively in terms of the unknowns density, composition, velocity and temperature. All terms that are not variables in equations (1), (2), (3) and (14) must be replaced by functions of these unknowns. The transport properties and reaction rates will be replaced by constitutive equations. The thermodynamic properties, pressure and enthalpy, must also be replaced by functions from equilibrium thermodynamics. Remember, the ultimate goal is to create an energy balance that provides an evolution equation for the temperature.

We begin with the pressure. Temporal and spatial derivatives of the pressure can be eliminated by introducing an equation of state and differentiating using the chain rule. What does the time derivative of the pressure look like? In general we have

$$p = f(\rho, T, \underline{w})$$

(15)

The temporal derivative of this pressure can be determined using the chain rule,

$$\frac{\partial p}{\partial t} = \left(\frac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\frac{\partial \rho}{\partial t} + \left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1}\left(\frac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\frac{\partial w_i}{\partial t}$$

(16)

The spatial derivative is completely analogous

$$\frac{\partial p}{\partial z} = \left(\frac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\frac{\partial \rho}{\partial z} + \left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\frac{\partial T}{\partial z} + \sum_{i=1}^{N_c-1}\left(\frac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\frac{\partial w_i}{\partial z}$$

(17)

The three partial derivatives of the pressure that appear on the RHS of equations (16) and (17) are thermodynamic properties. They can be evaluated for any equation of state. The temporal

derivatives of density and composition in equation (16) are already known and given in equations (1) and (2). They can be substituted in to yield

$$\frac{\partial p}{\partial t} = -\left(\frac{\partial p}{\partial \rho}\right)_{T,\underline{w}} \nabla \cdot (\rho \mathbf{v}) + \left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c - 1}\left(\frac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\left(-\rho \mathbf{v} \cdot \nabla w_i - \nabla \cdot \mathbf{j}_i + \sum_{k=1}^{N_R} r_{k,i}\right) \quad (18)$$

Several examples follow. For a single-component ideal gas, we have

$$p = \frac{\rho R T}{m} \quad (19)$$

so the time derivative of the pressure is

$$\frac{\partial p}{\partial t} = \frac{RT}{m}\frac{\partial \rho}{\partial t} + \frac{\rho R}{m}\frac{\partial T}{\partial t} = -\frac{RT}{m}\nabla \cdot (\rho \mathbf{v}) + \frac{\rho R}{m}\frac{\partial T}{\partial t} \quad (20)$$

where we substituted in the continuity equation to get the final result. The energy balance will be converted into a differential equation for temperature, so the form of equation (16) is acceptable.

For an ideal gas binary mixture, we have

$$p = \frac{N}{V}RT = cRT = \left(\frac{w_A}{M_A} + \frac{w_B}{M_B}\right)\rho RT = \left(\frac{w_A}{M_A} + \frac{1 - w_A}{M_B}\right)\rho RT \quad , \quad (21)$$

in which case the time derivative of the pressure can be expressed in terms of the fundamental variables as

$$\frac{\partial p}{\partial t} = \left(\frac{w_A}{M_A} + \frac{1 - w_A}{M_B}\right)\rho R\frac{\partial T}{\partial t} + \left(\frac{w_A}{M_A} + \frac{1 - w_A}{M_B}\right)RT\frac{\partial \rho}{\partial t} + \rho RT\left(\frac{1}{M_A} - \frac{1}{M_B}\right)\frac{\partial w_A}{\partial t} \quad . \quad (22)$$

It we again want to have the expression in terms of the time derivative of the temperature only, we have to substitute in the continuity equation and the material balance for component A, equation (2) to obtain

$$\frac{\partial p}{\partial t} = \left(\frac{w_A}{M_A} + \frac{1 - w_A}{M_B}\right)\rho R\frac{\partial T}{\partial t} - \left(\frac{w_A}{M_A} + \frac{1 - w_A}{M_B}\right)RT\nabla \cdot (\rho \mathbf{v})$$

$$+ \rho RT\left(\frac{1}{M_A} - \frac{1}{M_B}\right)\left(-\mathbf{v} \cdot \nabla w_A - \frac{1}{\rho}\nabla \cdot \mathbf{j}_A\right) \quad , \quad (23)$$

where we have ignored the possibility of chemical reaction.

A similar treatment must be done for any equation of state. For example, for the single component van der Waal's equation of state, we have

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT}{\frac{m}{\rho} - b} - \frac{a}{\left(\frac{m}{\rho}\right)^2} = \frac{\rho RT}{m - \rho b} - \frac{a\rho^2}{m^2} \tag{24}$$

so the time derivative of the pressure is

$$\frac{\partial p}{\partial t} = \frac{\rho R}{m - \rho b} \frac{\partial T}{\partial t} + \left(\frac{RT}{m - \rho b} + \frac{b\rho RT}{(m - \rho b)^2} - \frac{2a\rho}{m^2} \right) \frac{\partial \rho}{\partial t} \tag{25}$$

Eliminating the time derivative of the density through the continuity equation, we have

$$\frac{\partial p}{\partial t} = \frac{\rho R}{m - \rho b} \frac{\partial T}{\partial t} - \left(\frac{RT}{m - \rho b} + \frac{b\rho RT}{(m - \rho b)^2} - \frac{2a\rho}{m^2} \right) \nabla \cdot (\rho \mathbf{v}) \tag{26}$$

II.B. Enthalpy

We can now perform the same analysis for the enthalpy. In order to do this, we require a thermodynamic equation for the enthalpy. We accept that the specific enthalpy of a mixture is a function of the thermodynamic state,

$$\hat{H}_{mix} = f(\rho, T, \underline{w}) \tag{27}$$

The temporal derivative of this enthalpy can be determined using the chain rule,

$$\frac{\partial \hat{H}_{mix}}{\partial t} = \left(\frac{\partial \hat{H}_{mix}}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} + \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c - 1} \left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial t} \tag{28}$$

The spatial derivative is completely analogous

$$\frac{\partial \hat{H}_{mix}}{\partial z} = \left(\frac{\partial \hat{H}_{mix}}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial z} + \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial z} + \sum_{i=1}^{N_c - 1} \left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial z} \tag{29}$$

At this point, we require a functional form for $\hat{H}_{mix}$ to proceed further. Let's begin the review with the enthalpy of a pure component fluid. The energy scale is arbitrary and we require a reference point. Typically, one uses the enthalpy of formation at T_{ref} and p_{ref}, $\hat{H}_f(T_{ref}, p_{ref})$, which is a constant that can be looked up for many compounds in table such as those contained in the CRC Handbook of Chemistry and Physics. The enthalpy is a state function. The enthalpy difference from (T_{ref}, p_{ref}) to an arbitrary point (T, p) is independent of the path taken. Therefore, we can imagine a simple path that includes two steps. The first step is an isothermal

expansion/compression from p_{ref} to p at T_{ref}. The second step is an isobaric heating/cooling from T_{ref} to T at p. The enthalpy difference is thus

$$\hat{H}(T,p) = \int_{T_{ref}}^{T} \left(\frac{\partial \hat{H}}{\partial T} \right)_p dT + \int_{p_{ref}}^{p} \left(\frac{\partial \hat{H}}{\partial p} \right)_{T_{ref}} dp + \hat{H}_f(T_{ref}, p_{ref}) \tag{30}$$

There are two integrals on the RHS of equation (30) that account for changes in enthalpy due to the isothermal expansion/compression and the isobaric heating/cooling. The partial derivatives within the integrand must be known from the thermodynamic equation of state. We recognize that one of the derivatives has a common name, the constant pressure heat capacity,

$$\hat{C}_p \equiv \left(\frac{\partial \hat{H}}{\partial T} \right)_p \tag{31}$$

In general this heat capacity is also a function of the thermodynamic state (T and p) for the pure fluid. Frequently one makes the assumption that it is not a function of p. Sometimes, one makes the assumption that it is not a function of T.

We now move onto the specific enthalpy of a mixture. In general, the enthalpy of a mixture is expressed in terms of the partial specific properties. (If the derivation was being done in terms of moles, then it would be the partial molar properties.)

$$\hat{H}_{mix}(\rho, T, \underline{w}) = \sum_{i=1}^{N_c} w_i \overline{H}_i \tag{32}$$

If the mixture is ideal, then we assume that the partial specific properties can be equated to the pure component properties,

$$\overline{H}_i \approx \hat{H}_i \tag{33}$$

where $\hat{H}_i$ is the pure component enthalpy of component i, as given in equation (30), where we now add a subscript i to designate that equation (30) can be written for each component. Equation (33) may not look like a big deal, but it makes a big difference in terms of availability of information, because $\overline{H}_i$ is a mixture property and $\hat{H}_i$ is a pure component property. With the assumption of an ideal mixture, the enthalpy of the mixture is now

$$\hat{H}_{mix}(\rho, T, \underline{w}) = \sum_{i=1}^{N_c} w_i \hat{H}_i \tag{34}$$

Assumption 1: The mixture is an ideal mixture.

If we substitute equation (30) into equation (34) we have

$$\hat{H}_{mix}(\rho, T, \underline{w}) = \sum_{i=1}^{N_c} w_i \left[\int_{T_{ref}}^{T} \left(\frac{\partial \hat{H}_i}{\partial T} \right)_p dT + \int_{p_{ref}}^{p} \left(\frac{\partial \hat{H}_i}{\partial p} \right)_{T_{ref}} dp + \hat{H}_{f,i}(T_{ref}, p_{ref}) \right] \tag{35}$$

This is a reasonable expression for the enthalpy for the mixture, with the only assumption thus far being that the enthalpy behaves as an ideal mixture. We are also now in a position to evaluate the derivatives in equation required in equation (28), which is reprinted below.

$$\frac{\partial \hat{H}_{mix}}{\partial t} = \left(\frac{\partial \hat{H}_{mix}}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} + \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1} \left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,w_{j \neq i}} \frac{\partial w_i}{\partial t} \tag{28}$$

With the ideal mixture approximation,

$$\left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} = \left(\frac{\partial}{\partial w_i} \sum_{k=1}^{N_c} w_k \hat{H}_k \right)_{\rho,T,w_{j \neq i}} = \left(\sum_{k=1}^{N_c} \hat{H}_k \frac{\partial w_k}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} = \hat{H}_i - \hat{H}_{N_c} \tag{36}$$

The last term on the right appears the only Nc-1 of the mass fractions are independent. The last one is simply

$$w_{N_c} = 1 - \sum_{i=1}^{N_c-1} w_i \tag{37}$$

so that

$$\frac{\partial w_k}{\partial w_i} = \begin{cases} 1 \, if \, k = i \\ -1 \, if \, k = N_c \\ 0 \, otherwise \end{cases} \tag{38}$$

This makes sense because, if you have a binary mixture and you increase the mole fraction of A then you must decrease the mole fraction of B a proportional amount so that the net change in the enthalpy of the mixture is

$$\left(\frac{\partial \hat{H}_{mix}}{\partial w_A} \right)_{\rho,T} = \hat{H}_A - \hat{H}_B \tag{39}$$

We can also evaluate the derivatives of the mixture enthalpy with respect to temperature and density. We shall do the temperature first,

$$\left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho, \underline{w}} = \sum_{i=1}^{N_c} w_i \left(\frac{\partial \hat{H}_i}{\partial T} \right)_{\rho, \underline{w}}$$

$$= \sum_{i=1}^{N_c} w_i \left(\frac{\partial}{\partial T} \left[\int_{T_{ref}}^{T} \left(\frac{\partial \hat{H}_i}{\partial T} \right)_p dT + \int_{p_{ref}}^{p} \left(\frac{\partial \hat{H}_i}{\partial p} \right)_{T_{ref}} dp + \hat{H}_{f,i}(T_{ref}, p_{ref}) \right] \right)_{\rho, \underline{w}} \tag{40}$$

The enthalpy of formation will drop out since it is a constant. The other two terms require differentiation under the integral. At this point it is necessary to recall Leibniz's rule for differentiation under the integral sign.

$$\frac{d}{dz} \int_{a(z)}^{b(z)} f(z,x) dx = \int_{a(z)}^{b(z)} \frac{df(z,x)}{dz} dx + f(z,b(z)) \frac{db(z)}{dz} - f(z,a(z)) \frac{da(z)}{dz} \tag{41}$$

We apply Leibniz's rule to the integral over temperature first. Only the upper limit is a function of temperature, so only the second term in the RHS of Leibniz rule remains, yielding

$$\left(\frac{\partial}{\partial T} \int_{T_{ref}}^{T} \left(\frac{\partial \hat{H}_i}{\partial T} \right)_p dT \right)_{\rho, \underline{w}} = \left(\frac{\partial \hat{H}_i}{\partial T} \right)_p = \hat{C}_{p,i} \tag{42}$$

We next apply Leibniz's rule to the integral over pressure. Again, only the upper limit is a function of temperature, so only the second term in the RHS of Leibniz rule remains, yielding

$$\left(\frac{\partial}{\partial T} \int_{p_{ref}}^{p} \left(\frac{\partial \hat{H}_i}{\partial p} \right)_{T_{ref}} dp \right)_{\rho, \underline{w}} = \left(\frac{\partial \hat{H}_i}{\partial p} \right)_{T_{ref}} \left(\frac{\partial p}{\partial T} \right)_{\rho, \underline{w}} \tag{43.a}$$

The derivative of the enthalpy with respect to pressure must be simplified,

$$\left(\frac{\partial \hat{H}_i}{\partial p} \right)_{T_{ref}} \left(\frac{\partial p}{\partial T} \right)_{\rho, \underline{w}} = \left(\frac{\partial \hat{U}_i}{\partial p} \right)_{T_{ref}} \left(\frac{\partial p}{\partial T} \right)_{\rho, \underline{w}} + \left(\frac{\partial \frac{p_i}{\rho_i}}{\partial p} \right)_{T_{ref}} \left(\frac{\partial p}{\partial T} \right)_{\rho, \underline{w}} \tag{43.b}$$

This equation contains the partial pressure of component i and the density of component i. The derivative of the pressure over the density can be simplified

$$\left(\frac{\partial \frac{p_i}{\rho_i}}{\partial p}\right)_{T_{ref}} = \frac{1}{\rho_i}\left(\frac{\partial p_i}{\partial p}\right)_{T_{ref}} - \frac{p_i}{\rho_i^2}\left(\frac{\partial \rho_i}{\partial p}\right)_{T_{ref}} = \frac{x_i}{\rho_i} - \frac{p_i}{\rho_i^2}\left(\frac{\partial \rho_i}{\partial p}\right)_{T_{ref}} \qquad (43.c)$$

The derivative of the internal energy with respect to the pressure can be simplified

$$\left(\frac{\partial \hat{U}_i}{\partial p}\right)_{T_{ref}} = \frac{p_i - T\left(\frac{\partial p_i}{\partial T}\right)_{\rho_i}}{-\left(\frac{\partial p}{\partial \hat{V}_i}\right)_T} = \frac{p_i - T\left(\frac{\partial p_i}{\partial T}\right)_{\rho_i}}{-\left(\frac{\partial p}{\partial \rho_i}\right)_T\left(\frac{\partial \rho_i}{\partial \hat{V}_i}\right)_T} = \frac{p_i - T\left(\frac{\partial p_i}{\partial T}\right)_{\rho_i}}{\rho_i^2\left(\frac{\partial p}{\partial \rho_i}\right)_T} \qquad (43.d)$$

This form can be easily evaluated with an equation of state for the pressure in terms of the density and temperature, which was the point of the rearrangement. Thus the derivative of the enthalpy with respect to pressure is obtained by substituting (43.d) and (43.c) into (43.b), yielding,

$$\left(\frac{\partial \hat{H}_i}{\partial p}\right)_{T_{ref}}\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}} = -\frac{T\left(\frac{\partial p_i}{\partial T}\right)_{\rho_i}}{\rho_i^2\left(\frac{\partial p}{\partial \rho_i}\right)_T} + \frac{x_i}{\rho_i}\left(\frac{\partial p_i}{\partial T}\right)_{\rho,\underline{w}} \qquad (43.e)$$

Substitution of equation (43.e) and (42) into equation (40) yields

$$\left(\frac{\partial \hat{H}_{mix}}{\partial T}\right)_{\rho,\underline{w}} = \sum_{i=1}^{N_c} w_i\left[\hat{C}_{p,i} + -\frac{T\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}^2}{\rho_i^2\left(\frac{\partial p}{\partial \rho_i}\right)_T} + \frac{1}{\rho_i}\left(\frac{\partial p_i}{\partial T}\right)_{\rho,\underline{w}}\right] = \sum_{i=1}^{N_c} w_i\hat{C}_{p,i} - \frac{T\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}^2}{\rho^2\left(\frac{\partial p}{\partial \rho}\right)_T} + \frac{1}{\rho}\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}$$

$$(44)$$

The partial pressures and component densities can be pulled out of the summation to yield the total pressure and density. Equation (44) is a thermodynamic identity that could have also been obtained directly from, for example, the Bridgman Tables.

We can proceed in an analogous manner for the density derivative that appears in equation (28). We differentiate equation (35) with respect to the density and obtain,

$$\left(\frac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}} = \sum_{i=1}^{N_c} w_i \left(\frac{\partial \hat{H}_i}{\partial \rho}\right)_{T,\underline{w}}$$

$$= \sum_{i=1}^{N_c} w_i \left(\frac{\partial}{\partial \rho}\left[\int_{T_{ref}}^{T}\left(\frac{\partial \hat{H}_i}{\partial T}\right)_p dT + \int_{p_{ref}}^{p}\left(\frac{\partial \hat{H}_i}{\partial p}\right)_{T_{ref}} dp + \hat{H}_{f,i}(T_{ref}, p_{ref})\right]\right)_{T,\underline{w}}$$

(45)

Again, the enthalpy of formation is constant and drops out. The limits of the integral over temperature are not functions of density, so that term drops out. The only remaining term is the integral over pressure. In the integral over pressure, only the upper limit is a function of the density. Applying Leibniz's rule yields

$$\left(\frac{\partial}{\partial \rho}\left[\int_{p_{ref}}^{p}\left(\frac{\partial \hat{H}_i}{\partial p}\right)_{T_{ref}} dp\right]\right)_{T,\underline{w}} = \left(\frac{\partial \hat{H}_i}{\partial p}\right)_{T_{ref}}\left(\frac{\partial p}{\partial \rho}\right)_{T,\underline{w}} = \left(\frac{\partial \hat{H}_i}{\partial \rho}\right)_{T,\underline{w}}$$

(46)

Using the Bridgman Tables, we find the thermodynamic identity

$$\left(\frac{\partial \hat{H}_i}{\partial \rho}\right)_{T,\underline{w}} = -\frac{w_i}{\rho_i^2} T\left(\frac{\partial p_i}{\partial T}\right)_{\rho,\underline{w}} + \frac{1}{\rho}\left(\frac{\partial p_i}{\partial \rho_i}\right)_{\rho,\underline{w}}$$

(47)

Substituting equation (47) into equation (45) yields

$$\left(\frac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}} = \sum_{i=1}^{N_c} w_i \left[-\frac{w_i}{\rho_i^2} T\left(\frac{\partial p_i}{\partial T}\right)_{\rho,\underline{w}} + \frac{1}{\rho}\left(\frac{\partial p_i}{\partial \rho_i}\right)_{\rho,\underline{w}}\right] = -\frac{1}{\rho^2} T\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}} + \frac{1}{\rho}\left(\frac{\partial p}{\partial \rho}\right)_{\rho,\underline{w}}$$

(48)

At this point, we have all the missing partial derivatives in equation (28) given in equations (36), (44) and (48). Equation (28) becomes

$$\frac{\partial \hat{H}_{mix}}{\partial t} = \left(\frac{1}{\rho^2} T\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}} + \frac{1}{\rho}\left(\frac{\partial p}{\partial \rho}\right)_{\rho,\underline{w}}\right)\frac{\partial \rho}{\partial t}$$

$$+ \left(\sum_{i=1}^{N_c} w_i \hat{C}_{p,i} - \frac{T\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}^2}{\rho^2\left(\frac{\partial p}{\partial \rho}\right)_T} + \frac{1}{\rho}\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\right)\frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1}\left(\hat{H}_i - \hat{H}_{N_c}\right)\frac{\partial w_i}{\partial t}$$

(49)

If the either an ideal gas or a liquid, we may be able to assume that the enthalpy is not a function of density. In this case the derivative of the enthalpy with respect to density is zero and equation (49) becomes

$$\frac{\partial \hat{H}_{mix}}{\partial t} = \left(\sum_{i=1}^{N_c} w_i \hat{C}_{p,i} \right) \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1} \left(\hat{H}_i - \hat{H}_{N_c} \right) \frac{\partial w_i}{\partial t} \tag{50}$$

Assumption 2: The enthalpy is not a function of density.

Equation (50) can also be written for the spatial derivatives in an analogous form to what has been given for the temporal derivative.

III. Energy Balance in terms of a temporal derivative of Temperature

If our goal is to express the energy balance in terms of temperature, we can remind ourselves of the energy balance in equation (14)

$$\rho \frac{\partial \left(\frac{1}{2} v^2 + \hat{H} + \hat{\Phi} \right)}{\partial t} - \frac{\partial p}{\partial t} = -\rho \mathbf{v} \nabla \cdot \left(\frac{1}{2} v^2 + \hat{H} + \hat{\Phi} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \quad . \tag{14}$$

And recognize that we need time derivatives for the pressure and enthalpy from equations (16) and (28).

$$\frac{\partial p}{\partial t} = \left(\frac{\partial p}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} + \left(\frac{\partial p}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1} \left(\frac{\partial p}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial t} \tag{16}$$

$$\frac{\partial \hat{H}_{mix}}{\partial t} = \left(\frac{\partial \hat{H}_{mix}}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} + \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_c-1} \left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial t} \tag{28}$$

Substitution of (16) and (28) into (14) yields

$$\rho \frac{1}{2} \frac{\partial v^2}{\partial t} + \rho \left(\frac{\partial \hat{H}_{mix}}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} + \rho \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} + \rho \sum_{i=1}^{N_c-1} \left(\frac{\partial \hat{H}_{mix}}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial t}$$

$$+ \rho \frac{\partial \hat{\Phi}}{\partial t} - \left(\frac{\partial p}{\partial \rho} \right)_{T,\underline{w}} \frac{\partial \rho}{\partial t} - \left(\frac{\partial p}{\partial T} \right)_{\rho,\underline{w}} \frac{\partial T}{\partial t} - \sum_{i=1}^{N_c-1} \left(\frac{\partial p}{\partial w_i} \right)_{\rho,T,w_{j \neq i}} \frac{\partial w_i}{\partial t} \qquad . \tag{51}$$

$$= -\rho \mathbf{v} \nabla \cdot \left(\frac{1}{2} v^2 + \hat{H} + \hat{\Phi} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v})$$

which simplifies to

$$
\rho\frac{1}{2}\frac{\partial v^2}{\partial t}+\left[\rho\left(\frac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}}-\left(\frac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\right]\frac{\partial \rho}{\partial t}+\left[\rho\left(\frac{\partial \hat{H}_{mix}}{\partial T}\right)_{\rho,\underline{w}}-\left(\frac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\right]\frac{\partial T}{\partial t}
$$

$$
+\sum_{i=1}^{N_c-1}\left[\rho\left(\frac{\partial \hat{H}_{mix}}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}-\left(\frac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\right]\frac{\partial w_i}{\partial t}+\rho\frac{\partial \hat{\Phi}}{\partial t}=-\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot(\tau\cdot\mathbf{v})
$$

$$\tag{52}$$

The time derivative of the temperature can be isolated on the LHS,

$$
\frac{\partial T}{\partial t}=\frac{\left\{\begin{array}{l}-\rho\mathbf{v}\nabla\cdot\left(\dfrac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot(\tau\cdot\mathbf{v})-\rho\dfrac{1}{2}\dfrac{\partial v^2}{\partial t}-\rho\dfrac{\partial \hat{\Phi}}{\partial t}\\[4mm]-\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}}-\left(\dfrac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\right]\dfrac{\partial \rho}{\partial t}-\sum_{i=1}^{N_c-1}\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}-\left(\dfrac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\right]\dfrac{\partial w_i}{\partial t}\end{array}\right\}}{\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial T}\right)_{\rho,\underline{w}}-\left(\dfrac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\right]}\tag{53}
$$

The time derivatives of the density, velocity and composition that appear on the RHS can be eliminated by substituting in the mass, composition and momentum balances. The time derivative of the center of mass potential energy must be provided as input. Thus the only unknown time derivative is the temperature time derivative.

If there is no flow, the equation reduces to

$$
\frac{\partial T}{\partial t}=\frac{\left\{-\nabla\cdot\mathbf{q}-\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}}-\left(\dfrac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\right]\dfrac{\partial \rho}{\partial t}-\sum_{i=1}^{N_c-1}\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}-\left(\dfrac{\partial p}{\partial w_i}\right)_{\rho,T,w_{j\neq i}}\right]\dfrac{\partial w_i}{\partial t}\right\}}{\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial T}\right)_{\rho,\underline{w}}-\left(\dfrac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\right]}\tag{54}
$$

In addition if the material is a single component, the equation further reduces to

$$
\frac{\partial T}{\partial t}=\frac{\left\{-\nabla\cdot\mathbf{q}-\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial \rho}\right)_{T,\underline{w}}-\left(\dfrac{\partial p}{\partial \rho}\right)_{T,\underline{w}}\right]\dfrac{\partial \rho}{\partial t}\right\}}{\left[\rho\left(\dfrac{\partial \hat{H}_{mix}}{\partial T}\right)_{\rho,\underline{w}}-\left(\dfrac{\partial p}{\partial T}\right)_{\rho,\underline{w}}\right]}\tag{55}
$$

If addition, if the material is incompressible, the equation further reduces to

$$\frac{\partial T}{\partial t} = \frac{-\nabla \cdot \mathbf{q}}{\left[\rho \left(\frac{\partial \hat{H}_{mix}}{\partial T} \right)_{\rho, \underline{w}} - \left(\frac{\partial p}{\partial T} \right)_{\rho, \underline{w}} \right]} \tag{56}$$

We recognize that the internal energy is in the denominator

$$\frac{\partial T}{\partial t} = \frac{-\nabla \cdot \mathbf{q}}{\rho \left(\frac{\partial \hat{U}_{mix}}{\partial T} \right)_{\rho, \underline{w}}} = \frac{-\nabla \cdot \mathbf{q}}{\rho \hat{C}_V} \tag{57}$$

This expression relates the change in temperature of a material as a result of heat conduction due to a temperature gradient.

References

1. Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*. Second ed. 2002, New York: John Wiley & Sons, Inc.