

# Non-ideal Flame equations

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## 1. Continuity Equation

The overall continuity equation for unsteady flame can be <sup>c1</sup>written as

$$\frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \nabla \cdot (\rho\mathbf{V}) = 0 \quad (1)$$

Note that  $D/Dt$  is the substantial derivative, given as

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{V} \cdot \nabla \quad (2)$$

$\mathbf{V}$  is the velocity vector and  $\nabla$  is the divergence operator.

## 2. Momentum Equation

$$\rho \frac{D\mathbf{V}}{Dt} = \rho \left[ \frac{\partial\mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla)\mathbf{V} \right] = \mathbf{f} - \nabla p + \nabla \cdot T' \quad (3)$$

Here  $T'$  is the deviatoric stress tensor.

(Ref: Chemically reacting flows, second edition- Eq. 2.143, page 49)

## 3. Species Continuity Equation

$$\rho \frac{DY_k}{Dt} = -\nabla \cdot \mathbf{j}_k + \omega_k W_k \quad (4)$$

Where  $\mathbf{j}_k$  is the diffusive mass flux vector,

$$\mathbf{j}_k = \rho Y_k \mathbf{V}_k \quad (5)$$

Here  $\mathbf{V}_k$  is the diffusion velocity for species k.

(Ref: Chemically reacting flows, second edition- Sections 3.5 and 3.6)

## 4. Energy Equation

The thermal energy equation is written as

$$\underbrace{\rho \frac{Dh}{Dt}}_I = \frac{Dp}{Dt} + \vec{\nabla} \cdot (\lambda \nabla T) - \sum_{k=1}^K \nabla \cdot h_k \mathbf{j}_k + \Phi \quad (6)$$

<sup>c1</sup>SCD: FYI - I have added a package to enable track changes. You can also 'annotate', 'remove,' 'add', and 'change'

## 4.1 Term I

Now consider the term  $\frac{Dh}{Dt}$  from Eq. 6. Since enthalpy of the mixture depends on the temperature, pressure and composition ( $h = h(T, P, Y_k)$ ), this term can be written as

$$\underbrace{\rho \frac{Dh}{Dt}}_I = \rho \left( \underbrace{\frac{\partial h}{\partial T} \Big|_{p, Y_k} \frac{DT}{Dt}}_A + \underbrace{\frac{\partial h}{\partial p} \Big|_{T, Y_k} \frac{Dp}{Dt}}_B + \underbrace{\sum_1^k \frac{\partial h}{\partial Y_k} \Big|_{T, p} \frac{DY_k}{Dt}}_C \right) \quad (7)$$

### 4.1.1 Term A

Define

$$\frac{\partial h}{\partial T} \Big|_{p, Y_k} = c_{p, \text{mix}} \quad (8)$$

(This term is calculated in a document written for Peng-Robinson EoS).  
Using this definition, the term A in Eq. 7 simplifies to

$$A = \frac{\partial h}{\partial T} \Big|_{p, Y_k} \frac{DT}{Dt} = c_{p, \text{mix}} \frac{DT}{Dt} \quad (9)$$

### 4.1.2 Term B

From Eq. 7, consider the term,

$$\frac{\partial h}{\partial p} \Big|_{T, Y_k} \quad (10)$$

This term can be calculated using Maxwell's relations:

$$dh = Tds + vdp \quad (11)$$

and:

$$\frac{\partial v}{\partial T} \Big|_p = - \frac{\partial s}{\partial p} \Big|_T. \quad (12)$$

Hence

$$\frac{\partial h}{\partial p} \Big|_{T, Y_k} = T \frac{\partial s}{\partial p} \Big|_{T, Y_k} + v, \quad (13)$$

and therefore:

$$\frac{\partial h}{\partial p} \Big|_{T, Y_k} = v - T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \quad (14)$$

Substituting above equation in 7, the term B can be calculated as

$$B = \left[ v - T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] \frac{Dp}{Dt} \quad (15)$$

### 4.1.3 Term C

Consider the term C in Eq. 7

$$C = \sum_1^k \frac{\partial h}{\partial Y_k} \Big|_{T,p} \frac{DY_k}{Dt} \quad (16)$$

Let  $Y_k$  and  $X_k$  be mass and mole fractions of species  $k$  respectively.

$$X_k = \frac{n_k}{n_T}, Y_k = \frac{n_k W_k}{n_T \bar{W}} = \frac{W_k}{\bar{W}} X_k \quad (17)$$

where  $\bar{W}$  is a mean molecular weight of the mixture. The total mass of the system be  $M (= \bar{W} n_T)$ . Hence,

$$Y_k = \frac{n_k W_k}{M} \quad (18)$$

Since  $Y_k = f(n_k, M, W_k)$ , using chain rule,

$$\frac{\partial h}{\partial Y_k} = \left( \frac{\partial h}{\partial n_k} \frac{\partial n_k}{\partial Y_k} \right) \Big|_{M,T,p} + \left( \frac{\partial h}{\partial M} \frac{\partial M}{\partial Y_k} \right) \Big|_{n_k,T,p} \quad (19)$$

Partial derivative with respect to  $W_k$  is not considered here, since molecular weight  $W_k$  is constant. Also since  $h$  is an intensive property, its derivative with respect to total mass  $M$  is zero. Thus simplifying above equation,

$$\frac{\partial h}{\partial Y_k} \Big|_{T,p} = \frac{M}{W_k} \left( \frac{\partial h}{\partial n_k} \right) \Big|_{M,T,p} + 0 = M \left( \frac{\partial h}{\partial W_k n_k} \right) \Big|_{M,T,p} \quad (20)$$

Since  $m_k = n_k W_k$  and  $W_k$  is constant,

$$\frac{\partial h}{\partial Y_k} \Big|_{T,p} = M \left( \frac{\partial h}{\partial m_k} \right) \Big|_{M,T,p} = \left( \frac{\partial M h}{\partial m_k} \right) \Big|_{T,p} - h \left( \frac{\partial M}{\partial m_k} \right) \Big|_{h,T,p} \quad (21)$$

Mass based individual species enthalpies are defined as

$$h_k = \frac{\partial(Mh)}{\partial m_k} \Big|_{T,p,m_{j \neq k}} \quad (22)$$

Hence,

$$\frac{\partial h}{\partial Y_k} \Big|_{T,p} = h_k - h \left( \frac{\partial M}{\partial m_k} \right) \Big|_{h,T,p} \quad (23)$$

$$\frac{\partial h}{\partial Y_k} \Big|_{T,p} = h_k - h \left( \frac{\partial}{\partial m_k} \sum_1^k m_k \right) \Big|_{h,T,p} = h_k - h \times 1 \quad (24)$$

Hence,

$$\frac{\partial h}{\partial Y_k} \Big|_{T,p} = h_k - h \quad (25)$$

Now considering the term C in Eq. 7 ,

$$C = \sum_1^k \frac{\partial h}{\partial Y_k} \Big|_{T,p} \frac{DY_k}{Dt} = \sum_1^k (h_k - h) \frac{DY_k}{Dt} \quad (26)$$

$$C = \sum_1^k h_k \frac{DY_k}{Dt} - h \sum_1^k \frac{DY_k}{Dt} = \sum_1^k h_k \frac{DY_k}{Dt} - h \frac{D}{Dt} \sum_1^k Y_k \quad (27)$$

Simplifying,

$$C = \sum_1^k h_k \frac{DY_k}{Dt} \quad (28)$$

## 4.2 Term I

Combining Eq.s 9, 15 and 28, the  $Dh/Dt$  term in Eq. 7 simplifies to

$$\frac{Dh}{Dt} = c_{p,\text{mix}} \frac{DT}{Dt} + \left[ v - T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] \frac{Dp}{Dt} + \sum_1^k h_k \frac{DY_k}{Dt} \quad (29)$$

## 4.3 Energy equation: Revisited

Substituting Eq. 29 in Eq. 6, the energy equation becomes

$$\rho \left[ c_{p,\text{mix}} \frac{DT}{Dt} + \left[ v - T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] \frac{Dp}{Dt} + \sum_1^k h_k \frac{DY_k}{Dt} \right] = \frac{Dp}{Dt} + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K \nabla \cdot h_k j_k + \Phi \quad (30)$$

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} + \rho \left( \sum_1^k h_k \frac{DY_k}{Dt} \right) = \frac{Dp}{Dt} \left[ 1 - \rho v + \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K \nabla \cdot h_k j_k + \Phi \quad (31)$$

Note that  $\rho v = 1$ ,

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} + \rho \left( \sum_1^k h_k \frac{DY_k}{Dt} \right) = \frac{Dp}{Dt} \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K \nabla \cdot h_k j_k + \Phi \quad (32)$$

The species continuity equation can be given as

$$\rho \frac{DY_k}{Dt} = -\nabla \cdot j_k + \dot{\omega} W_k \quad (33)$$

Substituting Eq. 33 in energy equation,

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} + \sum_1^k h_k (-\nabla \cdot j_k + \dot{\omega} W_k) = \frac{Dp}{Dt} \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K \nabla \cdot h_k j_k + \Phi \quad (34)$$

Now expanding enthalpy-flux term on the right hand side as

$$\sum_{k=1}^K \nabla \cdot h_k j_k = \sum_{k=1}^K j_k \cdot \nabla h_k + \sum_{k=1}^K h_k \nabla \cdot j_k \quad (35)$$

The energy equation becomes

$$\begin{aligned} & \rho c_{p,\text{mix}} \frac{DT}{Dt} + \sum_1^k h_k (-\nabla \cdot j_k + \dot{\omega} W_k) \\ &= \frac{Dp}{Dt} \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K j_k \cdot \nabla h_k - \sum_{k=1}^K h_k \nabla \cdot j_k + \Phi \end{aligned} \quad (36)$$

Canceling common terms from both sides,

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} + \sum_1^k h_k (\dot{\omega} W_k) = \frac{Dp}{Dt} \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K j_k \cdot \nabla h_k + \Phi \quad (37)$$

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} = \frac{Dp}{Dt} \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p, Y_k} \right] - \sum_1^k h_k (\dot{\omega} W_k) + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K j_k \cdot \nabla h_k + \Phi \quad (38)$$

Now consider the enthalpy flux term from Eq. 38,

$$\sum_{k=1}^K \mathbf{j}_k \cdot \nabla h_k \quad (39)$$

This term can be written as Since  $h_k = f(p, T, n_i), i = 1, 2, \dots, K$ , this term can be written as

$$\sum_{k=1}^K \mathbf{j}_k \cdot \nabla h_k = \sum_{k=1}^K \mathbf{j}_k \cdot \left[ \left( \frac{\partial h_k}{\partial T} \right) \nabla T + \left( \frac{\partial h_k}{\partial p} \right) \nabla p + \sum_{i=1}^K \left( \frac{\partial h_k}{\partial n_i} \right) \nabla n_i \right] \quad (40)$$

Since

$$h_k = \left. \frac{\partial(Mh)}{\partial m_k} \right|_{T, p, m_{j \neq k}} \quad (41)$$

The last term in Eq. 40 can also be represented as

$$\sum_{i=1}^K \left( \frac{\partial h_k}{\partial n_i} \right) \nabla n_i = \sum_{i=1}^K \frac{\partial}{\partial m_k} \left( \frac{\partial(Mh)}{\partial m_i} \right) \nabla m_i = \sum_{i=1}^K \frac{\partial h_i}{\partial m_k} \nabla m_i \quad (42)$$

Since  $m_i$  does not depend on  $m_k$ , this term simplifies to

$$\sum_{i=1}^K \left( \frac{\partial h_k}{\partial n_i} \right) \nabla n_i = \frac{\partial}{\partial m_k} \sum_{i=1}^K h_i \nabla m_i \quad (43)$$

Thus the enthalpy flux term becomes

$$\sum_{k=1}^K \mathbf{j}_k \cdot \nabla h_k = \sum_{k=1}^K \mathbf{j}_k \cdot \left[ \left( \frac{\partial h_k}{\partial T} \right) \nabla T + \left( \frac{\partial h_k}{\partial p} \right) \nabla p + \frac{\partial}{\partial m_k} \sum_{i=1}^K h_i \nabla m_i \right] \quad (44)$$

Define

$$\Phi_k = \sum_{k=1}^K \mathbf{j}_k \cdot \frac{\partial}{\partial m_k} \sum_{i=1}^K h_i \nabla m_i \quad (45)$$

Since expression for  $h_k$  depends on the choice of equation of state (EoS), the term  $\Phi_k$  with partial derivatives of  $h_i$  can not be generalized further. Also calculation of this term at each grid point and for each species is computationally expensive. Instead, evaluating  $h_k$  at each grid point and taking its gradient directly will be more beneficial. <sup>c1</sup>If you want to expand  $\nabla h_k$ , I think there are additional terms, analogous the the expansion of  $Dh/Dt$ , since in general  $h_k = f(T, p, Y_k)$ . However, I don't think this expansion is necessary. When solving this equation, we can always evaluate  $h_k$  from the at each grid point and take the gradient directly. It's only where time derivatives of  $h$  appear that we need to eliminate them in order to have  $T$  as the state variable. <sup>c2</sup>Yes, after Franklin raised the point, Gandhali and I worked out the additional terms here. If I remember correctly, the only term that remained was another pressure term with an expansion coefficient (which we would neglect, at least for now). Gandhali - can you add those extra terms in? Regarding expanding  $\nabla h_k$  vs. evaluating it directly, the only possible concern is that state evaluations can tend to be expensive, for the real gas EoS. Would it be cheaper to evaluate a single state to get  $c_{p,k}$  at an interface, rather than  $h_k$  at each volume center? Not certain, but it is a concern...

<sup>c1</sup>RLS: Text added.

<sup>c2</sup>SCD: Text added.

Now using the definition of specific heat,

$$c_{p,k} = \left. \left( \frac{\partial h_k}{\partial T} \right) \right|_{p, Y_k} \quad (46)$$

Equation 40 can be further simplified as

$$\sum_{k=1}^K \mathbf{j}_k \cdot \nabla h_k = \sum_{k=1}^K c_{p,k} (\mathbf{j}_k \cdot \nabla T) + \sum_{k=1}^K \mathbf{j}_k \cdot \left( \frac{\partial h_k}{\partial p} \right) \nabla p + \Phi_k \quad (47)$$

Hence, the energy equation 38 becomes

$$\begin{aligned} \rho c_{p,\text{mix}} \frac{DT}{Dt} = \left[ \rho T \frac{\partial v}{\partial T} \Big|_{p,Y_k} \right] \frac{Dp}{Dt} - \sum_1^k h_k \dot{\omega} W_k + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K c_{p,k} (\mathbf{j}_k \cdot \nabla T) \\ - \sum_{k=1}^K \mathbf{j}_k \cdot \left( \frac{\partial h_k}{\partial p} \right) \nabla p - \Phi_k + \Phi \end{aligned} \quad (48)$$

Note that the term  $\frac{\partial v}{\partial T} \Big|_{p,Y_k}$  is calculated as

$$\frac{\partial v}{\partial T} \Big|_{p,Y_k} = \frac{\frac{\partial p}{\partial T} \Big|_{v,Y_k}}{\frac{\partial p}{\partial v} \Big|_{T,Y_k}} \quad (49)$$

Also note that volume expansivity (or coefficient of thermal expansion) is defined as

$$\alpha_v = \frac{1}{v} \frac{\partial v}{\partial T} \Big|_{p,Y_k} \quad (50)$$

Using this definition, the energy equation reduces to

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} = (T \alpha_v) \frac{Dp}{Dt} - \sum_1^k h_k \dot{\omega} W_k + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K c_{p,k} \mathbf{j}_k \cdot \nabla T - \underbrace{\sum_{k=1}^K \mathbf{j}_k \cdot \left( \frac{\partial h_k}{\partial p} \right) \nabla p}_{D} - \Phi_k + \Phi \quad (51)$$

#### 4.3.1 Term D

Consider the term

$$D = \sum_k \mathbf{j}_k \cdot \left( \frac{\partial h_k}{\partial p} \right) \nabla p \quad (52)$$

As calculated in Sec. 4.1.2,

$$\frac{dh}{dp} \Big|_{T,Y_k} = v - T \frac{\partial v}{\partial T} \Big|_{p,Y_k} \quad (53)$$

Similarly, we have,

$$\frac{dh_k}{dp} \Big|_{T,Y_k} = v_k - T \frac{\partial v_k}{\partial T} \Big|_{p,Y_k} \quad (54)$$

Define coefficient of thermal expansion for a species  $k$  as

$$\alpha_{v,k} = \frac{1}{v_k} \frac{\partial v_k}{\partial T} \Big|_{p,Y_k} \quad (55)$$

Therefore,

$$D = \sum_k \mathbf{j}_k \cdot v_k (1 - T \alpha_{v,k}) \nabla p \quad (56)$$

Since  $v_k = 1/\rho_k$  and  $\mathbf{j}_k = \rho Y_k \mathbf{V}_k$ , we get

$$D = \sum_k \frac{1}{\rho_k} (1 - T\alpha_{v,k}) \rho Y_k \mathbf{V}_k \cdot \nabla p \quad (57)$$

Using  $\rho_k = \rho Y_k$ ,

$$D = \sum_k (1 - T\alpha_{v,k}) \mathbf{V}_k \cdot \nabla p \quad (58)$$

Simplifying,

$$D = \left[ \sum_k \mathbf{V}_k - \sum_k T\alpha_{v,k} \mathbf{V}_k \right] \cdot \nabla p \quad (59)$$

#### 4.4 Energy equation

$$\begin{aligned} \rho c_{p,\text{mix}} \frac{DT}{Dt} = (T\alpha_v) \frac{Dp}{Dt} - \sum_1^k h_k \dot{\omega} W_k + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K c_{p,k} \mathbf{j}_k \cdot \nabla T \\ - \sum_{k=1}^K (1 - T\alpha_{v,k}) (\mathbf{V}_k \cdot \nabla p) + \Phi \end{aligned} \quad (60)$$

For Ideal gas EoS,  $\alpha_v = 1/T$ , hence energy equation in this case becomes

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} = \frac{Dp}{Dt} - \sum_1^k h_k \dot{\omega} W_k + \nabla \cdot (\lambda \nabla T) - \sum_{k=1}^K c_{p,k} j_k \cdot \nabla T - \Phi_k + \Phi \quad (61)$$

Usually at atmospheric conditions,  $\alpha_v \approx 10^{-3}$ . However, in case of near-critical flows, we might need to consider the pressure term. <sup>c1</sup>Handling the case where this is important would be quite an undertaking – this would require solving a compressible formulation of the flame governing equations, which I suspect would lead to some interesting numerical challenges.

<sup>c1</sup>RLS: Text added.

## 5. 1D Flame equations

Consider a one dimensional co-ordinate system with axial direction  $z$ . Using Eq.s 1, 3, 4 and 60 and ignoring other two directions, we get simplified governing equations as follows:

**Continuity equation**

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial z} = 0 \quad (62)$$

**Momentum equation**

$$\rho \frac{\partial u}{\partial t} + \rho u \frac{\partial u}{\partial z} = -\frac{\partial p}{\partial z} + \frac{\partial}{\partial z} \left( 2\mu \frac{\partial u}{\partial z} + \kappa \nabla \cdot \mathbf{V} \right) \quad (63)$$

Using Stokes' hypothesis,

$$\kappa + \frac{2}{3}\mu = 0 \quad (64)$$

$$\rho \frac{\partial u}{\partial t} + \rho u \frac{\partial u}{\partial z} = -\frac{\partial p}{\partial z} + \frac{\partial}{\partial z} \left( \frac{4}{3}\mu \frac{\partial u}{\partial z} \right) \quad (65)$$

**Species continuity equation**

$$\rho \frac{DY_k}{Dt} = -\frac{\partial}{\partial z} j_k + \dot{\omega}_k W_k \quad (66)$$

Where  $j_k$  is the diffusive mass flux in axial direction,

$$j_k = \rho Y_k u_k \quad (67)$$

Here  $u_k$  is the diffusion velocity for species k.

**Energy equation**

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} = (T\alpha_v) \frac{Dp}{Dt} - \sum_1^k h_k \dot{\omega}_k W_k + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) - \sum_{k=1}^K c_{p,k} j_k \frac{\partial T}{\partial z} + \Phi \quad (68)$$

The dissipation function  $\Phi$  can be given as

$$\Phi = (2\mu + \kappa) \left( \frac{\partial u}{\partial z} \right)^2 = \frac{4}{3}\mu \left( \frac{\partial u}{\partial z} \right)^2 \quad (69)$$

(Ref: Chemically reacting flows, second edition- Eq. 3.201, page 113)

At very high pressures, the pressure derivative is often small and can be neglected. The dissipation rate  $\Phi$ , being very small can also be ignored.

$$\rho c_{p,\text{mix}} \frac{DT}{Dt} = -\sum_1^k h_k \dot{\omega}_k W_k + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) - \sum_{k=1}^K c_{p,k} j_k \frac{\partial T}{\partial z} \quad (70)$$



## 6. Appendix

### 6.1 Molar and mass based enthalpies and specific heats

Let mass and molar based mixture enthalpies be  $h$  and  $\bar{h}$ . The mixture molecular weight is  $\bar{W}$ . Converting to mass based quantities,

$$h = \frac{\bar{h}}{\bar{W}} \quad (71)$$

Define mass based individual enthalpy as

$$h_k = \left. \frac{\partial(Mh)}{\partial m_k} \right|_{p,V,m_j \neq m_k} = \frac{1}{W_k} \left. \frac{\partial(n_T \bar{W} h)}{\partial n_k} \right|_{p,V,n_j \neq n_k} \quad (72)$$

Using Eq. 71,

$$h_k = \frac{1}{W_k} \left. \frac{\partial(n_T \bar{h})}{\partial n_k} \right|_{p,V,n_j \neq n_k} \quad (73)$$

Hence,

$$h_k = \frac{\bar{h}_k}{W_k} \quad (74)$$

Define specific heat capacities at constant pressure as

$$\bar{c}_{p,k} = \left. \frac{\partial \bar{h}_k}{\partial T} \right|_{p,V,n_j}, c_{p,k} = \left. \frac{\partial h_k}{\partial T} \right|_{p,V,m_j} \quad (75)$$

Consider

$$c_{p,k} = \left. \frac{\partial h_k}{\partial T} \right|_{p,V,m_j} = \frac{\partial}{\partial T} \left( \frac{\bar{h}_k}{W_k} \right) \quad (76)$$

$$c_{p,k} = \frac{1}{W_k} \frac{\partial \bar{h}_k}{\partial T} = \frac{1}{W_k} \bar{c}_{p,k} \quad (77)$$

### 6.2 Derivative of $\bar{W}$

The mean molecular weight of the mixture is given as

$$\bar{W} = \sum_{i=1}^K \frac{n_i}{n_T} W_i \quad (78)$$

$$\frac{\partial \bar{W}}{\partial n_k} = \frac{\partial}{\partial n_k} \sum_{i=1}^K \frac{n_i}{n_T} W_i = \frac{\partial n_k}{\partial n_k} \frac{W_k}{n_T} + \frac{\partial n_T}{\partial n_k} \sum_{i=1}^K \frac{-n_i}{n_T^2} W_i \quad (79)$$

$$\frac{\partial \bar{W}}{\partial n_k} = \frac{W_k}{n_T} - \frac{1}{n_T} \bar{W} \quad (80)$$

$$\frac{\partial \bar{W}}{\partial n_k} = \frac{W_k - \bar{W}}{n_T} \quad (81)$$

## 7. RLS Note: Energy Equation Term C

I think there are a couple of issues in the derivation of the energy equation, specifically involving term C in Eq. 7. First, I think there is a problem with what is held constant when taking  $\partial h/\partial Y_k$ , and the inconsistency in trying to hold all other mass fractions constant and also satisfying  $\sum Y_k = 1$ . As an alternative, the specific enthalpy  $h$  can be considered as a function of species masses  $m_k$  rather than mass fractions  $Y_k$ :

$$h = h(p, T, m_1, \dots, m_K) \quad (82)$$

The substantial derivative of the enthalpy can then be written as:

$$\underbrace{\rho \frac{Dh}{Dt}}_I = \rho \left( \underbrace{\left. \frac{\partial h}{\partial T} \right|_{p, m_1, \dots, m_K} \frac{DT}{Dt}}_A + \underbrace{\left. \frac{\partial h}{\partial p} \right|_{T, m_1, \dots, m_K} \frac{Dp}{Dt}}_B + \underbrace{\sum_{k=1}^K \left. \frac{\partial h}{\partial m_k} \right|_{T, p, m_{i \neq k}} \frac{Dm_k}{Dt}}_C \right) \quad (83)$$

which avoids the inconsistency of trying to take derivatives with respect to  $Y_k$  while holding all other mass fractions constant and also satisfying the constraint that  $\sum Y_k = 1$ .

For the purpose of evaluating term C, we can write:

$$H = mh = \left( \sum_{k=1}^K m_k \right) h \quad (84)$$

$$h_k \equiv \left. \frac{\partial H}{\partial m_k} \right|_{T, p, m_{i \neq k}} = \frac{\partial}{\partial m_k} \left[ \left( \sum_{k=1}^K m_k \right) h \right]_{T, p, m_{i \neq k}} \quad (85)$$

$$= m \left. \frac{\partial h}{\partial m_k} \right|_{T, p, m_{i \neq k}} + \left. \frac{\partial m}{\partial m_k} \right|_{T, p, m_{i \neq k}} h \quad (86)$$

$$h_k = m \left. \frac{\partial h}{\partial m_k} \right|_{T, p, m_{i \neq k}} + h \quad (87)$$

Therefore, the first part of term C can be written as

$$\left. \frac{\partial h}{\partial m_k} \right|_{T, p, m_{i \neq k}} = \frac{h_k - h}{m} \quad (88)$$

We can also write

$$\frac{Dm_k}{Dt} = m \frac{DY_k}{Dt} \quad (89)$$

Then term C becomes:

$$C = \sum_{k=1}^K \left. \frac{\partial h}{\partial m_k} \right|_{T, p, m_{i \neq k}} \frac{Dm_k}{Dt} \quad (90)$$

$$= \sum_{k=1}^K (h_k - h) \frac{DY_k}{Dt} \quad (91)$$

$$= \sum_{k=1}^K h_k \frac{DY_k}{Dt} - h \sum_{k=1}^K \frac{DY_k}{Dt} \quad (92)$$

$$= \sum_{k=1}^K h_k \frac{DY_k}{Dt} \quad (93)$$

with the last step utilizing the constraint that  $\sum DY_k/Dt = 0$ . So, in the end, term C works out to be the same thing, but not in quite the same way.

As an aside, the way I approached this was from trying to resolve some confusion I had about Eq. 26, which does not seem to work out even in the case of a simple ideal mixture of two components. For example, let

$$h = aY_a + bY_b \quad (94)$$

for which the partial species enthalpy of species a is simply  $h_a = a$ . The right hand side of Eq. 26 is then

$$h_a - h = a - (aY_a + bY_b) \quad (95)$$

We can evaluate  $\partial h/\partial Y_a$  either holding  $Y_b$  constant or holding  $\sum Y_k$  constant. For these two methods, we get:

$$\left. \frac{\partial h}{\partial Y_a} \right|_{Y_b} = a \quad (96)$$

$$\left. \frac{\partial h}{\partial Y_a} \right|_{\sum Y} = a - b \quad (97)$$

Neither of which are equivalent to Eq. 95. Instead,  $\partial h/\partial Y_k$  can be found from:

$$h_k \equiv \left. \frac{\partial H}{\partial m_k} \right|_{T,p,m_{i \neq k}} = \frac{\partial}{\partial m_k} \left[ \left( \sum_{i=1}^K m_i \right) h \right]_{T,p,m_{i \neq k}} \quad (98)$$

$$= m \left. \frac{\partial h}{\partial Y_k} \right|_{T,p,m_{i \neq k}} \frac{\partial Y_k}{\partial m_k} \Big|_{T,p,m_{i \neq k}} + h \quad (99)$$

<sup>c1</sup> <sup>c2</sup> <sup>c3</sup> We can find  $\partial Y_k/\partial m_k$  by writing:

$$Y_k \equiv \frac{m_k}{\sum_{i=1}^K m_i} \quad (100)$$

$$\left. \frac{\partial Y_k}{\partial m_k} \right|_{T,p,m_{i \neq k}} = \frac{1}{m} - \frac{m_k}{m^2} = \frac{1 - Y_k}{m} \quad (101)$$

From which it follows that

$$h_k = \left. \frac{\partial h}{\partial Y_k} \right|_{T,p,\sum Y} (1 - Y_k) + h \quad (102)$$

$$\left. \frac{\partial h}{\partial Y_k} \right|_{T,p,\sum Y} = \frac{h_k - h}{1 - Y_k} \quad (103)$$

which is clearly not the same as Eq. 26. In addition, this equation does work with the EOS given in Eq. 94.

## 8. RLS: Enthalpy flux term

I think the species partial enthalpy  $h_k$  (Is there a more correct term for this? I would say “partial molar enthalpy” if we were working on a molar basis, but we’re not) is also dependent on  $m_k$  or  $Y_k$ , and so these gradients also need to be included in the expansion of the enthalpy flux term (assuming that you want to expand it in the first place). Consider a binary mixture with an interaction term:

$$h = aY_a + bY_b + \alpha Y_a Y_b \quad (104)$$

<sup>c1</sup> *gkoge*: The term  $dY_k/dm_k$  in Eq. 87 is evaluated at constant m (product rule in Eq.87). Hence, right-hand side of Eq. 89 becomes  $(1/m)$ . This eventually gives back Eq. 28.

<sup>c2</sup> *RLS*: I disagree. The partial species enthalpy is defined with the mass of all other species held constant, not at constant total mass.

<sup>c3</sup> *SCD*: Gandhali and I met, and we agree with you, Ray. There was a slight confusion on our end that we cleared up, by meeting.

To find  $h_a$ , write this in terms of actual masses:

$$h = a \frac{m_a}{m_a + m_b} + b \frac{m_b}{m_a + m_b} + \alpha \frac{m_a m_b}{(m_a + m_b)^2} \quad (105)$$

$$H = (m_a + m_b)h = am_a + bm_b + \alpha m_a m_b (m_a + m_b)^{-1} \quad (106)$$

$$h_a \equiv \frac{\partial H}{\partial m_a} = a + \alpha m_b (m_a + m_b)^{-1} - \alpha m_a m_b (m_a + m_b)^{-2} \quad (107)$$

$$h_a = a + \alpha Y_b - \alpha Y_a Y_b \quad (108)$$

So, in general,  $h_k = f(T, p, Y_1, \dots, Y_K)$  and the expansion of  $\nabla h_k$  by the chain rule is something like

$$\nabla h_k = \frac{\partial h_k}{\partial T} \Big|_{p, Y_i} \nabla T + \frac{\partial h_k}{\partial p} \Big|_{T, Y_i} \nabla p + \sum_{j=1}^K \frac{\partial h_k}{\partial Y_j} \Big|_{p, T, Y_{i \neq j}} \nabla Y_j \quad (109)$$

Which again leaves us with the conflicting demands of satisfying both  $\sum Y_k = 1$  and holding the other  $Y_i$  constant. In any case, calculating the derivatives of  $h_k$  with respect to  $T$ ,  $p$ , and  $Y_j$  (or perhaps  $m_j$ ) is an additional burden that I imagine we would like to avoid.