Unity Lewis Number Model Derivation

1 Governing equations

The two equations from the set of governing equations for reactive flows that are relevant with respect to the current discussion are the conservation equation for species mass fractions (Y_k), Eq. 3.111 in Kee *et al.* [1], and thermal energy, Eq. 3.203 in [1], here expressed in terms of enthalpy (h):

$$\rho \frac{DY_k}{Dt} = -\nabla \cdot \mathbf{j_k} + \dot{\omega}_k W_k \tag{1}$$

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \nabla \cdot (\lambda \nabla T) - \sum \nabla \cdot (h_k \mathbf{j_k}) + \Phi \ , \tag{2}$$

where $\dot{\omega}_k$, W_k, h_k and $\mathbf{j_k}$ are the chemical source term, molecular weight, specific enthalpy and diffusive mass flux for species k, respectively, and λ is the thermal conductivity. The mass density is denoted by ρ and $\frac{D}{Dt}$ is the total derivative. Neglecting the pressure $\left(\frac{Dp}{Dt}\right)$ and viscous dissipation (Φ) terms for the following discussion, the energy equation simplifies to:

$$\rho \frac{Dh}{Dt} = \nabla \cdot (\lambda \nabla T) - \sum \nabla \cdot (h_k \mathbf{j_k}) \ . \tag{3}$$

2 Diffusive mass flux

Introducing the average velocity of species k[1] relative the fixed laboratory frame of reference $\widetilde{\mathbf{V}}_k$ and the mass-averaged velocity $\mathbf{V} = \sum Y_k \widetilde{\mathbf{V}}_k$, the mass flux of species k relative to the mass-averaged velocity is then defined as (Eq. 12.155 in [1])

$$\mathbf{j_k} = \rho Y_k \left(\widetilde{\mathbf{V}}_k - \mathbf{V} \right) = \rho Y_k \mathbf{V}_k \ , \tag{4}$$

where $\mathbf{V}_k$ denotes the mass diffusion velocity of species k relative to the mass-averaged velocity.

2.1 Mixture-averaged formulation

Starting from the Stefan-Maxwell equations (Eq. 12.170 in [1], where the terms due to temperature gradients (Soret effect) and pressure gradients are neglected),

$$\nabla X_k = -\sum \frac{X_k X_j}{\mathcal{D}_{k,j}} \left(\mathbf{V}_k - \mathbf{V}_j \right) \ , \tag{5}$$

[1] i.e. the average over all molecules of species k at a given location

the Hirschfelder-Curtiss approximation [2] for the ordinary diffusion velocity of species k can be derived by applying the simplifying *approximation* that the velocities of all species $j \neq k$ are equal. Here, X_k and $\mathcal{D}_{k,j}$ denote the molar fraction and binary diffusion coefficients. Substituting the approximation

$$\mathbf{V}_j = \mathbf{V}' \quad \forall j \neq k \ ,$$

with $\mathbf{V}'$ denoting the common velocity for all species $j \neq k$, into Eq. (5), and subsequently replacing $\mathbf{V}_k$ with the ordinary diffusion velocity $\hat{\mathbf{V}}_k$, yields

$$\nabla X_k = -X_k \left(\hat{\mathbf{V}}_k - \mathbf{V}' \right) \sum_{j \neq k} \frac{X_j}{\mathcal{D}_{k,j}} \ . \tag{6}$$

Rearranging the constraint $\sum Y_k \mathbf{V}_k = 0$ as

$$\sum_{j \neq k} Y_j \mathbf{V}_j = -Y_k \mathbf{V}_k$$

and applying the same approximation and substitutions as in Eq. (6) yields

$$\mathbf{V}' = -\frac{Y_k \hat{\mathbf{V}}_k}{1 - Y_k} \ . \tag{7}$$

Substituting Eq. (7) into Eq. (6) yields the Hirschfelder-Curtiss approximation for the ordinary diffusion velocity

$$\hat{\mathbf{V}}_k = -\frac{1}{X_k} \frac{1 - Y_k}{\sum_{j \neq k} \frac{X_j}{\mathcal{D}_{k,j}}} \nabla X_k \ , \tag{8}$$

and by defining a mixture-averaged diffusion coefficient[2] (Eq. 12.180 in [1])

$$D'_{k,m} := \frac{1 - Y_k}{\sum_{j \neq k} \frac{X_j}{\mathcal{D}_{k,j}}} \ , \tag{9}$$

we obtain a Fickian expression for the ordinary diffusion velocity expressed in terms of the mole fraction gradient (Eq. 12.179 in [1]):

$$\hat{\mathbf{V}}_k = -\frac{1}{X_k} D'_{k,m} \nabla X_k \ . \tag{10}$$

The mass diffusion velocity of species k is then defined as (Eq. 12.182 in [1])

$$\mathbf{V}_k = \hat{\mathbf{V}}_k + \mathbf{V}_c \ , \tag{11}$$

where $\mathbf{V}_c$ is a correction velocity [3, 4] to ensure that the net species diffusion flux is zero ($\sum \mathbf{j_k} = 0$) and is defined by (Eq. 12.183 in [1])

$$\mathbf{V}_c = -\sum Y_k \hat{\mathbf{V}}_k \ . \tag{12}$$

[2]adopting the notation by Kee *et al.* [1] (Chapter 12.7.4)

Diffusive mass flux: Finally, substituting Eqs. (10)–(12) into Eq. (4) yields the following expression for the diffusive mass flux in terms of the mole fraction gradient:

$$
\begin{aligned}
\mathbf{j_k} &= \rho Y_k \mathbf{V}_k \\
&= \rho Y_k \left(\hat{\mathbf{V}}_k - \sum Y_k \hat{\mathbf{V}}_k \right) \\
&= \rho Y_k \left(-\frac{1}{X_k} {D'}_{k,m} \nabla X_k + \sum Y_k \frac{1}{X_k} {D'}_{k,m} \nabla X_k \right) \\
&= \rho \left[-\frac{W_k}{\overline{W}} {D'}_{k,m} \nabla X_k + Y_k \left(\sum \frac{W_k}{\overline{W}} {D'}_{k,m} \nabla X_k \right) \right] ,
\end{aligned} \tag{13}
$$

where the identity $Y_k/X_k = W_k/\overline{W}$ has been used to obtain an equivalent formulation for a stable numerical implementation. The mean molecular weight $\overline{W}$ is defined as $\overline{W} = \left(\sum Y_k/W_k\right)^{-1}$.

Mass fraction gradient: The diffusive mass flux can alternatively be formulated in terms of mass fraction gradient by expressing the ordinary diffusion velocity (Eq. 10) as

$$
\begin{aligned}
\hat{\mathbf{V}}_k &= -\frac{1}{Y_k} \frac{W_k}{\overline{W}} {D'}_{k,m} \nabla \left(\frac{Y_k}{W_k} \overline{W} \right) \\
&= -\frac{1}{Y_k} \frac{1}{\overline{W}} {D'}_{k,m} \left(\overline{W} \nabla Y_k + Y_k \nabla \overline{W} \right) \\
&= -\frac{1}{Y_k} {D'}_{k,m} \nabla Y_k - \frac{1}{\overline{W}} {D'}_{k,m} \nabla \overline{W} \ .
\end{aligned} \tag{14}
$$

The diffusive mass flux in terms of mass fraction gradient reads then

$$
\begin{aligned}
\mathbf{j_k} &= \rho Y_k \mathbf{V}_k \\
&= \rho Y_k \left(\hat{\mathbf{V}}_k - \sum Y_k \hat{\mathbf{V}}_k \right) \\
&= \rho Y_k \Bigg[\qquad -\frac{1}{Y_k} {D'}_{k,m} \nabla Y_k - \frac{1}{\overline{W}} {D'}_{k,m} \nabla \overline{W} \\
&\qquad - \sum Y_k \left(-\frac{1}{Y_k} {D'}_{k,m} \nabla Y_k - \frac{1}{\overline{W}} {D'}_{k,m} \nabla \overline{W} \right) \Bigg] \\
&= -\rho {D'}_{k,m} \nabla Y_k \\
&\quad - \rho Y_k \left[\frac{1}{\overline{W}} {D'}_{k,m} \nabla \overline{W} + \sum Y_k \left(-\frac{1}{Y_k} {D'}_{k,m} \nabla Y_k - \frac{1}{\overline{W}} {D'}_{k,m} \nabla \overline{W} \right) \right] \\
&= -\rho {D'}_{k,m} \nabla Y_k \\
&\quad - \rho Y_k \left[{D'}_{k,m} \frac{\nabla \overline{W}}{\overline{W}} - \sum {D'}_{k,m} \nabla Y_k - \frac{\nabla \overline{W}}{\overline{W}} \left(\sum {D'}_{k,m} Y_k \right) \right] \ .
\end{aligned} \tag{15}
$$

2.2 Lewis number approximation

The Lewis number is defined as the ratio of the thermal and mixture-averaged diffusion coefficient of specie k as

$$
Le_k = \frac{\alpha}{{D'}_{k,m}} \ , \tag{16}
$$

where $\alpha = \lambda/(c_p\rho)$ denotes the thermal diffusion coefficient and c_p being the heat capacity of the mixture at constant pressure. The diffusive mass flux (Eq. 15) can thus be written as

$$\mathbf{j_k} = -\rho\frac{\alpha}{Le_k}\nabla Y_k - \rho Y_k\alpha\left[\frac{1}{Le_k}\frac{\nabla\overline{W}}{\overline{W}} - \sum\frac{\nabla Y_k}{Le_k} - \frac{\nabla\overline{W}}{\overline{W}}\left(\sum\frac{Y_k}{Le_k}\right)\right] . \quad (17)$$

It is readily seen that in case of equal Lewis numbers for all species ($Le_k = Le$), such as in case of the unity Lewis number assumption ($Le_k = 1$), the second term on the right hand side vanishes and the diffusive mass flux simplifies to

$$\mathbf{j_k} = -\rho\frac{\alpha}{Le}\nabla Y_k . \quad (18)$$

2.2.1 Unity Lewis number model properties

The model transport equations for the species mass fractions and thermal energy that follow from the equal Lewis number approximation are obtained by substituting Eq. (18) into Eqs. (1) and (3):

$$\begin{aligned}\rho\frac{DY_k}{Dt} &= \nabla\cdot\left(\rho\frac{\alpha}{Le}\nabla Y_k\right) + \dot{\omega}_k W_k \\ \rho\frac{Dh}{Dt} &= \nabla\cdot(\lambda\nabla T) + \nabla\cdot\left[\rho\frac{\alpha}{Le}\left(\sum h_k\nabla Y_k\right)\right] \\ &= \nabla\cdot\left[\lambda\nabla T + \rho\frac{\alpha}{Le}\left(\sum h_k\nabla Y_k\right)\right] .\end{aligned}$$

Using the identities $\nabla(h_k Y_k) = h_k\nabla Y_k + Y_k\nabla h_k$ and $dh_k = c_{p,k}dT$ further yields

$$\begin{aligned}\rho\frac{Dh}{Dt} &= \nabla\cdot\left[\lambda\nabla T + \rho\frac{\alpha}{Le}\left(\sum\nabla(h_k Y_k) - \sum Y_k c_{p,k}\nabla T\right)\right] \\ &= \nabla\cdot\left[\lambda\nabla T + \rho\frac{\alpha}{Le}(\nabla h - c_p\nabla T)\right] \\ &= \nabla\cdot\left[\left(1 - \frac{1}{Le}\right)\lambda\nabla T + \rho\frac{\alpha}{Le}\nabla h\right] .\end{aligned}$$

With the unity Lewis number assumption ($Le = 1$) the transport equations further simplify to

$$\rho\frac{DY_k}{Dt} = \nabla\cdot(\rho\alpha\nabla Y_k) + \dot{\omega}_k W_k \quad (19)$$

$$\rho\frac{Dh}{Dt} = \nabla\cdot(\rho\alpha\nabla h) . \quad (20)$$

A key property of the unity Lewis number model is thus that $\frac{Dh}{Dt} = 0$ if $\nabla h = 0$.

References

1. Kee, R. J., Coltrin, M. E. & Glarborg, P. *Chemically Reacting Flow: Theory and Practice* (John Wiley & Sons, 2003).
2. Hirschfelder, J. O. & Curtiss, C. F. Theory of Propagation of Flames. Part I: General Equations. *Symposium on Combustion and Flame, and Explosion Phenomena* **3,** 121–127 (1948).
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