

### 10.F.3. Thermal Diffusion

If, in the dilute solution considered in §10.F.2, we allow a temperature gradient in the mixture, the entropy production (10.180) or (10.181) becomes

$$\begin{aligned}
 T \sigma &= -\frac{1}{T} \mathbf{J}_q' \cdot \nabla_r T - \sum_{j=W,S} \tilde{\mathbf{J}}_j \cdot (\nabla_r \tilde{\mu}_j)_{T,P} \\
 &= -\frac{1}{T} \mathbf{J}_q' \cdot \nabla_r T - \tilde{\mathbf{J}}_W \cdot (\nabla_r \tilde{\mu}_W)_{T,P} - \tilde{\mathbf{J}}_S \cdot (\nabla_r \tilde{\mu}_S)_{T,P} \\
 &= -\frac{1}{T} \mathbf{J}_q' \cdot \nabla_r T - \tilde{\mathbf{J}}_S^D \cdot (\nabla_r \tilde{\mu}_S)_{T,P} \quad [ \text{See (10.183).} ] \quad (10.186)
 \end{aligned}$$

The generalized Ohm's law (10.96) becomes [c.f. (10.184)]

$$\begin{aligned}
 \begin{pmatrix} \tilde{\mathbf{J}}_S^D \\ \mathbf{J}_q' \end{pmatrix} &= -\tilde{\mathbf{L}}_S \cdot \begin{pmatrix} (\nabla_r \tilde{\mu}_S)_{T,P} \\ \nabla_r T \end{pmatrix} \\
 &= -\begin{pmatrix} \tilde{L}_{SS} & \tilde{L}_{Sq} \\ \tilde{L}_{qS} & L_{qq} \end{pmatrix} \cdot \begin{pmatrix} (\nabla_r \tilde{\mu}_S)_{T,P} \\ \nabla_r T \end{pmatrix} \\
 &= -\begin{pmatrix} \tilde{L}_{SS} & \tilde{L}_{Sq} \\ \tilde{L}_{qS} & L_{qq} \end{pmatrix} \cdot \begin{pmatrix} \left( \frac{\partial \tilde{\mu}_S}{\partial X_S} \right)_{T,P} \nabla_r X_S \\ \nabla_r T \end{pmatrix} \quad [ \text{See (10.184).} ] \\
 &= -\begin{pmatrix} \tilde{L}_{SS} & \tilde{L}_{Sq} \\ \tilde{L}_{qS} & L_{qq} \end{pmatrix} \cdot \begin{pmatrix} \left( \frac{\partial \tilde{\mu}_S}{\partial c_S} \right)_{T,P} \nabla_r c_S \\ \nabla_r T \end{pmatrix} \quad (10.188)
 \end{aligned}$$

where  $c_S = c X_S$  and  $c = c_W + c_S$  is a constant since the fluid particle is stationary.

Note that  $\tilde{\mathbf{J}}_S^D$  is a mass flux but  $\mathbf{J}_q'$  is a particle flux, which is why we have denoted  $(\tilde{\mathbf{L}}_S)_{q,q}$  as  $L_{qq}$ . To avoid confusions, one may consider instead  $\begin{pmatrix} \mathbf{J}_S^D \\ \mathbf{J}_q' \end{pmatrix}$  or  $\begin{pmatrix} \tilde{\mathbf{J}}_S^D \\ \tilde{\mathbf{J}}_q' \end{pmatrix}$ .

Comparing (10.188) with (10.185) gives the diffusion coefficient

$$D = \frac{1}{m_S} \tilde{L}_{SS} \left( \frac{\partial \tilde{\mu}_S}{\partial c_S} \right)_{T,P} \quad (10.188a)$$

Comparing with the thermal conduction equation [see (10.29)]

$$\mathbf{J}_q' = -K \nabla_r T$$

gives the **coefficient of thermal conductivity** as

$$K = L_{qq} \quad (10.188b)$$

In experiments, it is found that

$$\tilde{L}_{Sq} = \tilde{L}_{qS} \propto c_S$$

Thus, the particle flux

$$\mathbf{J}_S^D = \frac{\tilde{\mathbf{J}}_S^D}{m_S} = -\frac{\tilde{L}_{SS}}{m_S} \left( \frac{\partial \tilde{\mu}_S}{\partial c_S} \right)_{T,P} \nabla_r c_S - \frac{\tilde{L}_{Sq}}{m_S} \nabla_r T \quad [ (10.188) \text{ used.} ]$$

$$= -D \nabla_r c_s - \frac{\tilde{L}_{sq}}{m_s} \nabla_r T \quad [ (10.188a) \text{ used. } ]$$

can be put into a more symmetric form if we set

$$\tilde{L}_{sq} = m_s c_s D^T \quad (10.188c)$$

so that

$$\mathbf{J}_s^D = -D \nabla_r c_s - c_s D^T \nabla_r T \quad (10.189)$$

where  $D^T$  is called the **coefficient of thermal diffusion** and characterizes the diffusion flux caused by a temperature gradient.

In the steady state,

$$\begin{aligned} \mathbf{J}_s^D &= 0 \\ \rightarrow \nabla_r \ln c_s &= -\frac{D^T}{D} \nabla_r T \\ &= -S_T \nabla_r T \end{aligned}$$

where the **Soret coefficient**

$$\begin{aligned} S_T &\equiv \frac{D^T}{D} = \frac{\tilde{L}_{sq}}{m_s c_s D} \quad [ (10.188c) \text{ used. } ] \quad (10.189a) \\ &= \frac{|\nabla_r \ln c_s|}{|\nabla_r T|} \end{aligned}$$

is a measure of the strength of the thermal diffusion flux relative to the diffusion flux caused by the concentration gradient. Usually,  $S_T \approx 10^{-2} \sim 10^{-3}$ .

Thermal diffusion can be used to separate isotopes in the gaseous phase.