

10.F.1. Entropy Production in Multi-Component Systems

For convenience, we declare 1st the following conventions:

$$x = \frac{X}{V} = \text{density of variable } X. \quad V = \text{volume of system.}$$

$$\tilde{x} = \frac{X}{M} = \text{specific (or per unit mass) quantity of } X. \quad M = \text{mass in } V.$$

$$\rightarrow dX = x dV + V dx \quad (\text{a})$$

For a system of N types of particles,

$$X = \sum_{j=1}^N X_j \quad X_j = \text{partial quantity of the extensive variable } X.$$

$$= V \sum_{j=1}^N x_j = \sum_{j=1}^N \tilde{x}_j M_j = V \sum_{j=1}^N \tilde{x}_j \rho_j \quad (\text{b})$$

Consider now a fluid of N types of particles. In the hydrodynamic equations [see (10.33-5)], the fluid is specified by the ρ_j , \mathbf{v} , P & T fields. Therefore, a fluid particle is a microscopically large but macroscopically small system in temporary equilibrium with independent thermodynamic variables ρ_j , P & T . Since the fluid particle is part of the fluid, it can exchange energy, heat and particles with the latter.

The **fundamental equation** [see (2.61) of §2.E] for the fluid particle is

$$U = TS - PV + \sum_{j=1}^N \mu_j n_j$$

where, for the type j particles, μ_j & n_j are the **molar chemical potential** & **number of moles** in V , respectively. Using

$$M_j = m_j n_j = \rho_j V \quad \tilde{\mu}_j = \frac{\mu_j}{m_j}$$

where, for the type j particles, M_j is the total mass, m_j the **molar mass** (or mass per mole), ρ_j the **mass density** and $\tilde{\mu}_j$ the **specific chemical potential**. Thus,

$$U = TS - PV + \sum_{j=1}^N \tilde{\mu}_j M_j \quad (10.165a)$$

Caution: In Reichl's text, the roles of the symbols M_j & m_j are interchanged.

The corresponding **1st law** is

$$dU = \bar{d}Q - PdV + \sum_{j=1}^N \mu_j dn_j$$

$$= \bar{d}Q - PdV + \sum_{j=1}^N \tilde{\mu}_j dM_j \quad (\text{all processes}) \quad (10.165b)$$

$$= TdS - PdV + \sum_{j=1}^N \tilde{\mu}_j dM_j \quad (\text{reversible processes only}) \quad (10.165c)$$

where \bar{d} denotes a path-dependent (or **inexact**) **differential** [see §2.D.2].

In terms of densities, (10.165a) becomes

$$u = Ts - P + \sum_{j=1}^N \tilde{\mu}_j \rho_j \quad (10.165d)$$

while for (10.165c),

$$V du + u dV = T (V ds + s dV) - P dV + \sum_{j=1}^N \tilde{\mu}_j (V d\rho_j + \rho_j dV)$$

$$V \left(du - T ds - \sum_{j=1}^N \tilde{\mu}_j d\rho_j \right) = \left(-u + T s - P + \sum_{j=1}^N \tilde{\mu}_j \rho_j \right) dV$$

$$= 0 \quad [(10.165d) \text{ used. }]$$

$$\therefore du - T ds - \sum_{j=1}^N \tilde{\mu}_j d\rho_j = 0 \quad (\text{rev. processes only}) \quad (10.165)$$

The **Gibbs free energy** is defined in (2.107) as

$$G = U - T S + P V = \sum_{j=1}^N \mu_j N_j = \sum_{j=1}^N G_j$$

where N_j is the number of type j particles. Hence, the chemical potential $\mu_j = \frac{G_j}{N_j}$ is the partial Gibbs free energy per type j particle.

In terms of (10.165a), we have

$$G = \sum_{j=1}^N \tilde{\mu}_j M_j \quad \rightarrow \quad g = \sum_{j=1}^N \tilde{\mu}_j \rho_j = \sum_{j=1}^N g_j$$

The interpretation of $\tilde{\mu}_j$ is not as clear as μ_j .

Now,

$$S = \sum_{j=1}^N S_j = \sum_{j=1}^N \tilde{s}_j M_j$$

$$\rightarrow dS = \sum_{j=1}^N (M_j d\tilde{s}_j + \tilde{s}_j dM_j)$$

$$= (dS)_{\{M_j\}} + dS' \quad (10.166a)$$

where

$$(dS)_{\{M_j\}} = \sum_{j=1}^N (dS_j)_{\{M_j\}} = \sum_{j=1}^N d(M_j \tilde{s}_j)_{\{M_j\}} = \sum_{j=1}^N M_j d\tilde{s}_j \quad (10.166b)$$

= change in S with all M_j fixed, i.e., no particle exchanges.

$$dS' = \sum_{j=1}^N \tilde{s}_j dM_j = \text{change in } S \text{ due to particle exchanges.} \quad (10.166c)$$

To find an expression for \tilde{s}_j , we use the **enthalpy**, $H = U + P V$, to write (10.165a) as

$$H = T S + \sum_{j=1}^N \tilde{\mu}_j M_j$$

$$\rightarrow \sum_{j=1}^N H_j = \sum_{j=1}^N (T S_j + \tilde{\mu}_j M_j)$$

$$H_j = T S_j + \tilde{\mu}_j M_j$$

$$h_j = T s_j + \tilde{\mu}_j \rho_j$$

$$\tilde{h}_j = T \tilde{s}_j + \tilde{\mu}_j = \text{partial specific enthalpy} \quad (10.167a)$$

Using [see (2.107) of §2.F.4]

$$G = \sum_{j=1}^N \tilde{\mu}_j M_j = \sum_{j=1}^N G_j = \sum_{j=1}^N \tilde{g}_j M_j$$

we see that the **specific chemical potential** $\tilde{\mu}_j$ is just the **partial specific Gibbs free energy** \tilde{g}_j .

Similarly, we can write

$$\bar{d}Q = (\bar{d}Q)_{\{M_j\}} + \bar{d}Q'$$

Assuming

$$\bar{d}Q' = T \sum_{j=1}^N \tilde{s}_j dM_j = \text{heat change due to particle exchanges.} \quad (10.167b)$$

we have

$$\begin{aligned} \bar{d}Q &= (\bar{d}Q)_{\{M_j\}} + T \sum_{j=1}^N \tilde{s}_j dM_j \\ &= (\bar{d}Q)_{\{M_j\}} + \sum_{j=1}^N (\tilde{h}_j - \tilde{\mu}_j) dM_j \end{aligned}$$

we get

$$\bar{d}Q = (\bar{d}Q)_{\{M_j\}} + \sum_{j=1}^N (\tilde{h}_j - \tilde{\mu}_j) dM_j \quad (10.167)$$

(10.168-170) in Reichl's text then follow readily.

However, the assumption (10.167b) cannot be justified for irreversible processes so that the validity of (10.167-170) in Reichl's text is questionable. Fortunately, they are not needed for the following discussion. In fact, we can skip everything after (10.165).

For spontaneous processes, no work is done so that the 1st law becomes

$$\begin{aligned} dU &= \bar{d}Q \\ \rightarrow V(du - \bar{d}q) &= (u - q) dV \end{aligned}$$

Since only the difference $\bar{d}q$ is physically significant, we can set $u = q$ by adjusting the origin of the heat scale without affecting the physical outcome. Hence,

$$du = \bar{d}q \quad \text{for spontaneous processes.} \quad (10.170a)$$

Putting (10.170a) into (10.165) gives

$$T ds = dq - \sum_{j=1}^N \tilde{\mu}_j d\rho_j \quad \text{for spontaneous processes.} \quad (10.171)$$

Note that (10.171) is the estimate of the entropy change of a spontaneous process using a reversible process between the same initial & final states. Thus, $\bar{d}q$ is now written as dq since it is really the exact differential du with value equal to $\bar{d}q$.

Consider now a multi-component fluid in a stationary container. The fluid as a whole is assumed to be stationary but we shall allow spontaneous processes such as particle diffusion and chemical reactions inside it. To keep the entire fluid stationary, the velocity of the center of mass of every fluid particle

must be zero:

$$\mathbf{v} = \frac{1}{M} \sum_{j=1}^N M_j \mathbf{v}_j = \frac{1}{\rho} \sum_{j=1}^N \rho_j \mathbf{v}_j = \frac{1}{\rho} \sum_{j=1}^N \mathbf{J}_j = 0 \quad (10.171a)$$

where $\mathbf{J}_j = \rho_j \mathbf{v}_j$ is the mass flux of type j particles. (10.171) then simplifies to

$$T \frac{\partial s}{\partial t} = \frac{\partial q}{\partial t} - \sum_{j=1}^N \tilde{\mu}_j \frac{\partial \rho_j}{\partial t} \quad (10.172)$$

Consider now the balance equations for the fluid particle.

Since there is no heat source, we have

$$\frac{\partial q}{\partial t} + \nabla_r \cdot \mathbf{J}_q = 0 \quad (10.175)$$

where \mathbf{J}_q is the **heat flux**.

Let σ be the **entropy source**, then

$$\frac{\partial s}{\partial t} + \nabla_r \cdot \mathbf{J}_s = \sigma \quad (10.173)$$

where \mathbf{J}_s is the **entropy flux**.

As discussed in §S2.D.1, if particles of type j are involved in r chemical reactions, then [see (2.241)]

$$d n_j = \sum_{\alpha=1}^r d n_{j\alpha} = \sum_{\alpha=1}^r \nu_{j\alpha} d \xi_{\alpha} \quad (10.174a)$$

where n denotes number of moles. For the α^{th} reaction, $\nu_{j\alpha}$ is the **stoichiometric coefficient** for type j particles and ξ_{α} is the **degree of reaction** [see (2.229) & (2.235)]. Since $V = \text{const}$ for a stationary fluid particle, the rate change in ρ_j due to chemical reactions is

$$\frac{d \rho_j^c}{dt} = \frac{1}{V} \frac{d M_j}{dt} = \frac{m_j}{V} \frac{d n_j}{dt} = \frac{m_j}{V} \sum_{\alpha=1}^r \nu_{j\alpha} \frac{d \xi_{\alpha}}{dt} = \sum_{\alpha=1}^r \tilde{\nu}_{j\alpha} J_{\alpha}^c \quad (10.174b)$$

where

$$\tilde{\nu}_{j\alpha} = m_j \nu_{j\alpha} \quad J_{\alpha}^c = \frac{1}{V} \frac{d \xi_{\alpha}}{dt} \quad (10.174c)$$

The balance equation for ρ_j is therefore

$$\frac{\partial \rho_j}{\partial t} + \nabla_r \cdot \tilde{\mathbf{J}}_j = \sum_{\alpha=1}^r \tilde{\nu}_{j\alpha} J_{\alpha}^c \quad (10.174)$$

where $\tilde{\mathbf{J}}_j$ is the **mass flux** of the type j particles.

Putting (10.173, 4 & 5) into (10.172) gives,

$$T (-\nabla_r \cdot \mathbf{J}_s + \sigma) = -\nabla_r \cdot \mathbf{J}_q - \sum_{j=1}^N \tilde{\mu}_j \left(-\nabla_r \cdot \tilde{\mathbf{J}}_j + \sum_{\alpha=1}^r \tilde{\nu}_{j\alpha} J_{\alpha}^c \right) \quad (10.176)$$

Using

$$\begin{aligned} \frac{\nabla_r \cdot \mathbf{J}_q}{T} &= \nabla_r \cdot \left(\frac{\mathbf{J}_q}{T} \right) - \mathbf{J}_q \cdot \nabla_r \left(\frac{1}{T} \right) \\ \frac{\tilde{\mu}_j \nabla_r \cdot \tilde{\mathbf{J}}_j}{T} &= \nabla_r \cdot \left(\frac{\tilde{\mu}_j \tilde{\mathbf{J}}_j}{T} \right) - \tilde{\mathbf{J}}_j \cdot \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) \end{aligned}$$

we can write (10.176) as

$$\begin{aligned}
-\nabla_r \cdot \mathbf{J}_s + \sigma &= -\nabla_r \cdot \left(\frac{\mathbf{J}_q}{T} \right) + \mathbf{J}_q \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \left[-\nabla_r \cdot \left(\frac{\tilde{\mu}_j \tilde{\mathbf{J}}_j}{T} \right) + \tilde{\mathbf{J}}_j \cdot \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) + \frac{1}{T} \sum_{\alpha=1}^r \tilde{\mu}_j \tilde{\nu}_{j\alpha} J_\alpha^c \right] \\
&= -\nabla_r \cdot \left(\frac{\mathbf{J}_q - \sum_{j=1}^N \tilde{\mu}_j \tilde{\mathbf{J}}_j}{T} \right) + \mathbf{J}_q \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) - \sum_{\alpha=1}^r \frac{A_\alpha}{T} J_\alpha^c \quad (10.177)
\end{aligned}$$

where [see (2.238)]

$$A_\alpha = \sum_{j=1}^N \tilde{\mu}_j \tilde{\nu}_{j\alpha} = \sum_{j=1}^N \mu_j \nu_{j\alpha} = \text{affinity of the } \alpha^{\text{th}} \text{ reaction.} \quad (10.177a)$$

Comparing the two sides of (10.177) gives

$$\mathbf{J}_s = \frac{\mathbf{J}_q - \sum_{j=1}^N \tilde{\mu}_j \tilde{\mathbf{J}}_j}{T} \quad (10.178)$$

$$\sigma = \mathbf{J}_q \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) - \sum_{\alpha=1}^r \frac{A_\alpha}{T} J_\alpha^c \quad (10.178a)$$

$$= T \mathbf{J}_s \cdot \nabla_r \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \tilde{\mu}_j - \sum_{\alpha=1}^r \frac{A_\alpha}{T} J_\alpha^c \quad [(10.178) \text{ used.}]$$

$$= -\frac{1}{T} \mathbf{J}_s \cdot \nabla_r T - \frac{1}{T} \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \tilde{\mu}_j - \sum_{\alpha=1}^r \frac{A_\alpha}{T} J_\alpha^c \quad (10.179)$$

$$\rightarrow T \sigma = -\mathbf{J}_s \cdot \nabla_r T - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \tilde{\mu}_j - \sum_{\alpha=1}^r A_\alpha J_\alpha^c \quad (10.179a)$$

Owing to the Gibbs-Duhem equation, (2.62), the natural independent variables of μ_j are the intensive ones. Since it is reasonable to assume that $\mu_{k \neq j}$ has no effect on μ_j , we have

$$\tilde{\mu}_j = \frac{\mu_j}{m_j} = \tilde{\mu}_j(T, P_j) = \tilde{\mu}_j(T, P, x_j) \quad (10.179b)$$

where

P_j = partial pressure of type j particles

$x_j = \frac{n_j}{n} = \frac{M_j}{M}$ = molar fraction of type j particles

As an example, see (2.242) of §S2.D.1 for μ_j in an ideal gas mixture.

For a system with independent variables T, P & $\{M_k\}$, we have

$$d \left(\frac{\tilde{\mu}_j}{T} \right) = \frac{(d \tilde{\mu}_j)_T}{T} + \left[\frac{\partial}{\partial T} \left(\frac{\tilde{\mu}_j}{T} \right)_{P, \{M_k\}} \right] dT \quad (10.180a)$$

where effects of dP and dM_k are lumped in $(d \tilde{\mu}_j)_T$. The Gibbs-Duhem equation [see (2.62)]

$$S dT - V dP + \sum_{j=1}^N n_j d\mu_j = 0 = S dT - V dP + \sum_{j=1}^N M_j d\tilde{\mu}_j$$

$$\rightarrow s dT - dP + \sum_{j=1}^N \rho_j d\tilde{\mu}_j = 0 = -dP + \sum_{j=1}^N (s_j dT + \rho_j d\tilde{\mu}_j) \quad (10.180b)$$

$$\therefore \left(\frac{\partial \tilde{\mu}_j}{\partial T} \right)_{P, \{M_k\}} = -\frac{s_j}{\rho_j} = -\tilde{s}_j$$

$$\frac{\partial}{\partial T} \left(\frac{\tilde{\mu}_j}{T} \right)_{P, \{M_k\}} = \frac{1}{T} \left(\frac{\partial \tilde{\mu}_j}{\partial T} \right)_{P, \{M_k\}} - \frac{\tilde{\mu}_j}{T^2} = -\frac{1}{T^2} (\tilde{\mu}_j + T \tilde{s}_j) = -\frac{\tilde{h}_j}{T^2} \quad [(10.167a) \text{ used.}]$$

(10.180a) thus becomes

$$\begin{aligned} d \left(\frac{\tilde{\mu}_j}{T} \right) &= \frac{(d \tilde{\mu}_j)_T}{T} - \frac{\tilde{h}_j}{T^2} dT \\ \rightarrow \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) &= \frac{(\nabla_r \tilde{\mu}_j)_T}{T} - \frac{\tilde{h}_j}{T^2} \nabla_r T \\ &= \frac{(\nabla_r \tilde{\mu}_j)_T}{T} + \tilde{h}_j \nabla_r \left(\frac{1}{T} \right) \end{aligned}$$

Putting this into (10.178a) gives

$$\begin{aligned} \sigma &= \left(\mathbf{J}_q - \sum_{j=1}^N \tilde{h}_j \tilde{\mathbf{J}}_j \right) \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \frac{(\nabla_r \tilde{\mu}_j)_T}{T} - \sum_{\alpha=1}^r \frac{A_\alpha}{T} J_\alpha^c \\ \rightarrow T \sigma &= T \mathbf{J}_q' \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot (\nabla_r \tilde{\mu}_j)_T - \sum_{\alpha=1}^r A_\alpha J_\alpha^c \\ &= -\frac{1}{T} \mathbf{J}_q' \cdot \nabla_r T - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot (\nabla_r \tilde{\mu}_j)_T - \sum_{\alpha=1}^r A_\alpha J_\alpha^c \end{aligned} \quad (10.180)$$

where

$$\mathbf{J}_q' = \mathbf{J}_q - \sum_{j=1}^N \tilde{h}_j \tilde{\mathbf{J}}_j \quad (10.180c)$$

Exercise 10.7.

The cyclic set of chemical reactions



provides a textbook example of using the Onsager's relations. Assuming a uniform ideal gas at constant T & P [see §2.D.1], the entropy production (10.179) reduces to

$$T \sigma = - \sum_{\alpha=1}^3 A_\alpha J_\alpha^c \quad (1b)$$

Assume that μ_j is that of an ideal gas mixture.

(a) Show that near equilibrium,

$$J_1^c - J_3^c = L_{11} A_1 + L_{12} A_2$$

$$J_2^c - J_3^c = L_{21} A_1 + L_{22} A_2$$

and find L_{11} , L_{12} , L_{21} and L_{22} .

(b) Show that

$$L_{12} = L_{21}$$

Answer

Using (2.228) of §2.D.1, we have

$$\begin{aligned}
 \alpha = 1: \quad & v_{A1} = -1 & v_{B1} = 1 & v_{C1} = 0 \\
 & \frac{dn_{A1}}{dt} = -k_1 n_A + k_{-1} n_B & & \frac{dn_{B1}}{dt} = k_1 n_A - k_{-1} n_B \\
 & d\xi_1 = -dn_{A1} = dn_{B1} \\
 & A_1 = \sum_{j=A,B,C} v_{j1} \mu_j = -\mu_A + \mu_B
 \end{aligned} \tag{2a}$$

$$\begin{aligned}
 \alpha = 2: \quad & v_{A2} = 0 & v_{B2} = -1 & v_{C2} = 1 \\
 & \frac{dn_{B2}}{dt} = -k_2 n_B + k_{-2} n_C & & \frac{dn_{C2}}{dt} = k_2 n_B - k_{-2} n_C \\
 & d\xi_2 = -dn_{B2} = dn_{C2} \\
 & A_2 = \sum_{j=A,B,C} v_{j2} \mu_j = -\mu_B + \mu_C
 \end{aligned} \tag{2b}$$

$$\begin{aligned}
 \alpha = 3: \quad & v_{A3} = 1 & v_{B3} = 0 & v_{C3} = -1 \\
 & \frac{dn_{C3}}{dt} = -k_3 n_C + k_{-3} n_A & & \frac{dn_{A3}}{dt} = k_3 n_C - k_{-3} n_A \\
 & d\xi_3 = -dn_{C3} = dn_{A3} \\
 & A_3 = \sum_{j=A,B,C} v_{j3} \mu_j = -\mu_C + \mu_A
 \end{aligned} \tag{2c}$$

$$\begin{aligned}
 \rightarrow \quad d n_A &= \sum_{\alpha=1}^3 d n_{A\alpha} = \sum_{\alpha=1}^3 v_{A\alpha} d \xi_\alpha = -d \xi_1 + d \xi_3 \\
 d n_B &= \sum_{\alpha=1}^3 d n_{B\alpha} = \sum_{\alpha=1}^3 v_{B\alpha} d \xi_\alpha = d \xi_1 - d \xi_2 \\
 d n_C &= \sum_{\alpha=1}^3 d n_{C\alpha} = \sum_{\alpha=1}^3 v_{C\alpha} d \xi_\alpha = d \xi_2 - d \xi_3
 \end{aligned}$$

Also,

$$A_1 + A_2 + A_3 = 0 \tag{2d}$$

(1b) thus becomes

$$\begin{aligned}
 T \sigma &= - \left[A_1 J_1^c + A_1 J_1^c - (A_1 + A_2) J_3^c \right] \\
 &= - \left[(J_1^c - J_3^c) A_1 + (J_2^c - J_3^c) A_2 \right]
 \end{aligned} \tag{3}$$

Comparing (3) with (10.81) of §10.D.1, we make the following assignment:

$$\begin{aligned}
 \mathcal{J} &= \frac{d\alpha}{dt} \rightarrow (J_1^c - J_3^c, J_2^c - J_3^c) \\
 \mathcal{X} &\rightarrow (A_1, A_2)
 \end{aligned}$$

so that (10.96) becomes

$$\begin{aligned}
 \begin{pmatrix} J_1^c - J_3^c \\ J_2^c - J_3^c \end{pmatrix} &= -\mathbb{L} \cdot \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \\
 &= - \begin{pmatrix} L_{11} A_1 + L_{12} A_2 \\ L_{21} A_1 + L_{22} A_2 \end{pmatrix}
 \end{aligned} \tag{4}$$

From (10.174c), we have

$$\begin{aligned} J_1^c &= \frac{1}{V} \frac{d\xi_1}{dt} = -\frac{1}{V} \frac{dn_{A1}}{dt} = -\frac{1}{V} (-k_1 n_A + k_{-1} n_B) && [(2a) \text{ used.}] \\ &= k_1 c_A - k_{-1} c_B \end{aligned} \quad (5)$$

where

$$c_j = \frac{n_j}{V} = \text{molar concentration of type } j \text{ particles} \quad j = A, B, C$$

Similarly,

$$\begin{aligned} J_2^c &= \frac{1}{V} \frac{d\xi_2}{dt} = -\frac{1}{V} \frac{dn_{B2}}{dt} = -\frac{1}{V} (-k_2 n_B + k_{-2} n_C) = k_2 c_B - k_{-2} c_C \\ J_3^c &= \frac{1}{V} \frac{d\xi_3}{dt} = -\frac{1}{V} \frac{dn_{C3}}{dt} = -\frac{1}{V} (-k_3 n_C + k_{-3} n_A) = k_3 c_C - k_{-3} c_A \end{aligned}$$

At equilibrium,

$$\begin{aligned} J_\alpha^c &= 0 && \forall \alpha \\ \rightarrow \frac{c_{A0}}{c_{B0}} &= \frac{k_{-1}}{k_1} && \frac{c_{B0}}{c_{C0}} = \frac{k_{-2}}{k_2} && \frac{c_{C0}}{c_{A0}} = \frac{k_{-3}}{k_3} \end{aligned} \quad (6)$$

For an ideal gas mixture, we have [see (2.243) of §S2.D.1]

$$G(P, T, \{n_j\}) = G^{(0)} - nRT \ln \frac{T^{5/2}}{P} + RT \sum_j n_j \ln x_j \quad (7)$$

where $G^{(0)}$ is some constant.

Using the ideal gas equations

$$PV = nRT \quad P_j V = n_j RT$$

where P_j is the partial pressure of the type j particles, we have

$$\frac{P_j}{P} = \frac{n_j}{n} = x_j = \text{molar fraction of type } j \text{ particles}$$

(2.242) then gives

$$\mu_j(P_j, T) = \mu_j^{(0)} - RT \ln \frac{T^{5/2} P_0}{T_0^{5/2} P_j} = \mu_j^{(0)} - RT \ln \frac{T^{5/2} P_0}{T_0^{5/2} x_j P} \quad (8)$$

where

$$\mu_j^{(0)} = \mu_j(P_0, T_0)$$

(2a,b,c) then gives

$$\begin{aligned} A_1 &= -\mu_A + \mu_B = -\mu_A^{(0)} + \mu_B^{(0)} - RT \ln \frac{x_B}{x_A} = -\mu_A^{(0)} + \mu_B^{(0)} - RT \ln \frac{c_B}{c_A} \\ A_2 &= -\mu_B + \mu_C = -\mu_B^{(0)} + \mu_C^{(0)} - RT \ln \frac{x_C}{x_B} = -\mu_B^{(0)} + \mu_C^{(0)} - RT \ln \frac{c_C}{c_B} \\ A_3 &= -\mu_C + \mu_A = -\mu_C^{(0)} + \mu_A^{(0)} - RT \ln \frac{x_A}{x_C} = -\mu_C^{(0)} + \mu_A^{(0)} - RT \ln \frac{c_A}{c_C} \end{aligned} \quad (9)$$

Near equilibrium, we set

$$c_j = c_{j0} + \alpha_j \quad \text{with} \quad |\alpha_j| \ll |c_{j0}|$$

With

$$A_1^{(0)} = -\mu_A^{(0)} + \mu_B^{(0)} - RT_0 \ln \frac{c_{B0}}{c_{A0}}$$

(9) becomes

$$\begin{aligned}
 A_1 &= -\mu_A^{(0)} + \mu_B^{(0)} - R T \ln \frac{c_{B0} (1 + \alpha_B / c_{B0})}{c_{A0} (1 + \alpha_A / c_{A0})} \\
 &\approx A_1^{(0)} - R T \ln \frac{1 + \alpha_B / c_{B0}}{1 + \alpha_A / c_{A0}} \\
 &\approx A_1^{(0)} - R T \left(\frac{\alpha_B}{c_{B0}} - \frac{\alpha_A}{c_{A0}} \right) \\
 \rightarrow \quad \Delta A_1 &= A_1 - A_1^{(0)} \approx -R T \left(\frac{\alpha_B c_{A0} - \alpha_A c_{B0}}{c_{B0} c_{A0}} \right)
 \end{aligned}$$

and similarly for A_2 & A_3 .

Using (6), (5) becomes

$$\begin{aligned}
 J_1^c &= k_1 (c_{A0} + \alpha_A) - k_{-1} (c_{B0} + \alpha_B) \\
 &= k_1 \alpha_A - k_{-1} \alpha_B \\
 &= k_1 \left(\alpha_A - \frac{c_{A0}}{c_{B0}} \alpha_B \right) \\
 &= \frac{k_1 c_{A0}}{R T} \Delta A_1
 \end{aligned} \tag{10}$$

By symmetry, we have

$$\begin{aligned}
 J_2^c &= \frac{k_2 c_{B0}}{R T} \Delta A_2 \\
 J_3^c &= \frac{k_3 c_{C0}}{R T} \Delta A_3 = -\frac{k_3 c_{C0}}{R T} (\Delta A_1 + \Delta A_2) \quad [(2d) \text{ used. }]
 \end{aligned}$$

Hence,

$$J_1^c - J_3^c = \frac{k_1 c_{A0} + k_3 c_{C0}}{R T} \Delta A_1 + \frac{k_3 c_{C0}}{R T} \Delta A_2 \tag{11}$$

$$J_2^c - J_3^c = \frac{k_3 c_{C0}}{R T} \Delta A_1 + \frac{k_2 c_{B0} + k_3 c_{C0}}{R T} \Delta A_2 \tag{12}$$

Hence, (4) should be modified by replacing A_α with ΔA_α , giving

$$\mathbb{L} = \begin{pmatrix} \frac{k_1 c_{A0} + k_3 c_{C0}}{R T} & \frac{k_3 c_{C0}}{R T} \\ \frac{k_3 c_{C0}}{R T} & \frac{k_2 c_{B0} + k_3 c_{C0}}{R T} \end{pmatrix} \quad \text{QED.}$$