12.B.2.1. General Arguments

Consider the total entropy production

$$P = \int d^3 r \, T \, \sigma_s$$

$$= - \int d^3 r \sum_i \mathcal{J}_i \chi_i \geq 0 \qquad \text{[See (12.3-4).]} \qquad (12.17)$$

and its time derivative

$$\frac{dP}{dt} = - \int d^3 r \sum_i \left(\frac{\partial \mathcal{J}_i}{\partial t} \chi_i + \mathcal{J}_i \frac{\partial \chi_i}{\partial t} \right) \qquad (12.18)$$

$$= \frac{\partial_{\mathcal{J}} P}{\partial t} + \frac{\partial_{\chi} P}{\partial t} \qquad (12.18a)$$

where

$$\frac{\partial_{\mathcal{J}} P}{\partial t} = - \int d^3 r \sum_i \frac{\partial \mathcal{J}_i}{\partial t} \chi_i \qquad (12.21a)$$

$$\frac{\partial_{\chi} P}{\partial t} = - \int d^3 r \sum_i \mathcal{J}_i \frac{\partial \chi_i}{\partial t} \qquad (12.20a)$$

In the linear regime [see (12.5)]

$$\mathcal{J}_i = - \sum_j L_{ij} \chi_j \qquad (L_{ij} = \text{const}) \qquad (12.19a)$$

so that

$$\frac{dP}{dt} \leq 0 \qquad \text{[See (12.16).]} \qquad (12.19b)$$

and

$$- \int d^3 r \sum_i \frac{\partial \mathcal{J}_i}{\partial t} \chi_i = \int d^3 r \sum_{i,j} L_{ij} \frac{\partial \chi_j}{\partial t} \chi_i$$

$$= - \int d^3 r \sum_j \frac{\partial \chi_j}{\partial t} \mathcal{J}_j$$

$$= \frac{1}{2} \frac{dP}{dt}$$

$$\leq 0 \qquad \text{[(12.16) used.]} \qquad (12.19)$$

In general, the sign of $\frac{\partial_{\mathcal{J}} P}{\partial t}$ depends on the situation at hand but

$$\frac{\partial_{\chi} P}{\partial t} \leq 0 \qquad (12.20)$$

due to local thermodynamic stability requirements.

Following Reichl, we shall prove (12.20) only for the special case of a chemically reacting system of N types of molecules that is held far from equilibrium, i.e., it has large affinity [see (2.238) of §S2.D.1].

For the sake of simplicity, we shall assume the effects of diffusion, viscosity, and thermal conductivity can be neglected so that both temperature and pressure are uniform throughout the system.

(12.17) simplifies to [see (10.180) of §S10.F.1]

$$P = -\int d^3 r \sum_{\alpha=1}^{\mathbb{r}} J_\alpha^c A_\alpha \qquad (12.22a)$$

where $\mathbb{r}$ is the number of reactions. Since T is uniform, we also have

$$\mathcal{P} \equiv \int d^3 r\, \sigma_s$$

$$= \frac{1}{T} P = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^{\mathbb{r}} J_\alpha^c A_\alpha \qquad \text{[For } T \text{ uniform.]} \qquad (12.22)$$

Note: strictly speaking, $\mathcal{P}$ is the actual entropy production. However, Reichl used the same symbol P for both P & $\mathcal{P}$ so that we had been calling both entropy production.

(12.20a) thus gives

$$\frac{\partial_\chi \mathcal{P}}{\partial t} = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^{\mathbb{r}} J_\alpha^c \frac{\partial A_\alpha}{\partial t} \qquad (12.23)$$

From (2.241) of §S2.D.1, we have

$$\frac{d c_j}{d t} = \frac{1}{V} \frac{d n_j}{d t} = \frac{1}{V} \sum_{\alpha=1}^{\mathbb{r}} \nu_{j\alpha} \frac{d \xi_\alpha}{d t} \qquad \text{[} V = \text{volume of system.]}$$

$$= \sum_{\alpha=1}^{\mathbb{r}} \nu_{j\alpha} J_\alpha^c \qquad \text{[(10.174c) of §10.F.1 used.]} \qquad (12.24)$$

For the α^{th} reaction [see (2.238)],

$$A_\alpha = \sum_{j=1}^{N} \nu_{j\alpha} \mu_j \qquad (12.24a)$$

$$\rightarrow \qquad \frac{\partial A_\alpha}{\partial t} = \sum_{j=1}^{N} \nu_{j\alpha} \frac{\partial \mu_j}{\partial t} \qquad (12.24b)$$

Using (12.24b) on (12.23) gives

$$\frac{\partial_\chi \mathcal{P}}{\partial t} = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^{\mathbb{r}} \sum_{j=1}^{N} J_\alpha^c \nu_{j\alpha} \frac{\partial \mu_j}{\partial t}$$

$$= -\frac{1}{T} \int d^3 r \sum_{j=1}^{N} \frac{d c_j}{d t} \frac{\partial \mu_j}{\partial t} \qquad \text{[(12.24) used.]} \qquad (12.25)$$

Since T & pressure are held constant,

$$\frac{\partial \mu_j}{\partial t} = \sum_{i=1}^{N} \left(\frac{\partial \mu_j}{\partial c_i} \right)_{T,P,\{c_{k\neq i}\}} \frac{d c_i}{d t} \qquad (12.26)$$

so that (12.25) becomes

$$\frac{\partial_\chi \mathcal{P}}{\partial t} = -\frac{1}{T} \int d^3 r \sum_{i,j=1}^{N} \frac{d c_j}{d t} \left(\frac{\partial \mu_j}{\partial c_i} \right)_{T,P,\{c_{k\neq i}\}} \frac{d c_i}{d t} \qquad (12.26a)$$

Using the local stability condition (2.179) of §2.H.2, we have

$$\frac{\partial_\chi \mathcal{P}}{\partial t} \leq 0 \qquad (12.27)$$

as claimed previously.