# 7  Chapter 6: Stationary Non-equilibrium States

## 7.1  Thermodynamic Significance of Stationary Non-equilibrium States

Have seen example of a typical stationary non-equilibrium state
    – thermomolecular pressure difference:
transport of matter $J_m$ is zero but the transport of energy between the two phases at different temperature , as well as the entropy production, are different from zero.

Another example, various chemical reactions among various components. The system receives a component M from the outside and transforms it into a final product F which is returned to the external environment. Stationary state arises when the concentrations of the intermediate components no longer varies with time.

Now will see that the stationary state may be characterized by an extremum principle, – the entropy production has its minimum value compatible with the external constraints.

Eg. Thermomolecular pressure difference – constraint is the difference in temperature between phase I and II.

Eg. Chemical reactions, – constraint is the concentrations of M and F in the external environment.

## 7.2  States of Minimum Entropy Production

Consider the transfer of matter and energy between two phases at different temperatures;

$$\frac{d_i S}{dt} = J_{th}X_{th} + J_m X_m > 0 \tag{1}$$

with the phenomenological laws

$$J_{th} = L_{11}X_{th} + L_{12}X_m \tag{2}$$
$$J_m = L_{21}X_{th} + L_{22}X_m \tag{3}$$

For the stationary state

$$J_m = L_{21}X_{th} + L_{22}X_m = 0 \tag{4}$$

Now we will show that eqn. (4) gives the condition that the entropy production is a minimum for a given value of $X_{th}$.

We have

$$L_{12} = L_{21} \tag{5}$$

so that eqn. (1) becomes

$$\frac{d_i S}{dt} = L_{11}X_{th}^2 + 2L_{21}X_{th}X_m + L_{22}X_m^2 > 0 \tag{6}$$

Taking derivative of this eqn. with respect to $X_m$ at constant $X_{th}$ gives

$$\frac{\partial}{\partial X_m}\left(\frac{d_iS}{dt}\right) = 2(L_{21}X_{th} + L_{22}X_m) = 2J_m = 0 \tag{7}$$

Thus the two conditions

$$J_m = 0 \quad or \quad \frac{\partial}{\partial X_m}\left(\frac{d_iS}{dt}\right) = 0 \tag{8}$$

are completely equivalent as long as the linear relations (3) are valid.

Argument can be generalized to the case of $n$ independent forces $X_1 \dots X_n$ of which a certain number $k$, $X_1 \dots X_k$ are kept constant. In the stationary state

$$J_{k+1} = \dots = J_n = 0 \tag{9}$$

These conditions are equivalent to the minimum conditions for the entropy production

$$\frac{\partial}{\partial X_j}\left(\frac{d_iS}{dt}\right) = 0 \quad (j = k+1, \dots, n) \tag{10}$$

Note that since $d_iS/dt$ is a definite positive quadratic expression, the extremum condition defined by (10) refers to a minimum.

## 7.3   Consecutive Chemical Reactions

Consider open system undergoing sequence of $r$ consecutive reactions

$$M \;\; \to \;\; N \quad (1) \tag{11}$$
$$N \;\; \to \;\; O \quad (2) \tag{12}$$
$$\vdots \tag{13}$$
$$P \;\; \to \;\; F \quad (r) \tag{14}$$

Only components $M$ and $F$ can be exchanged with the environment, so

$$\frac{dn_M}{dt} = \frac{d_en_M}{dt} - v_1; \;\; \frac{dn_N}{dt} = v_1 - v_2; \;\; \frac{dn_F}{dt} = \frac{d_en_F}{dt} + v_r \tag{15}$$

For the stationary state, the flows $dn_i/dt$ are zero so the above implies,

$$\frac{d_en_M}{dt} = v_1 = v_2 \dots = v_r = -\frac{d_en_F}{dt} \tag{16}$$

The internal entropy production, including the two transport processes

$$M(\text{outside world}) \to M \text{ (system)}$$
$$F(\text{outside world}) \to F \text{ (system)}$$
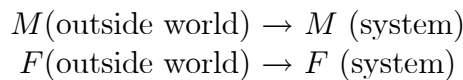
is given by

$$T\frac{d_iS}{dt} = A_M\frac{d_en_M}{dt} + \sum_{\rho=1}^{r} A_\rho v_\rho + A_F\frac{d_en_F}{dt} > 0 \tag{17}$$

where $A_F$ and $A_M$ are the forces or "affinities" corresponding to the transport of the components $M$ and $F$, and $A_\rho$ is the affinity of the $\rho^{th}$ reaction.

Denoting the system itself by I and the external environment by II, then

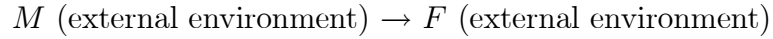$$A_M = \mu_M^I - \mu_M^{II}; \qquad A_F = \mu_F^I - \mu_F^{II} \tag{18}$$

In the stationary state, eqn. (16) implies

$$T\frac{d_i S}{dt} = (A_M + \sum_\rho A_\rho - A_F)v = Av > 0 \tag{19}$$

where $v$ is the common value of the partial rates, eqn. (16), and $A$ is the resultant affinity

$$A = A_M + \sum_\rho A_\rho - A_F \tag{20}$$

corresponding to the global process

$$M \text{ (external environment)} \to F \text{ (external environment)}$$

This affinity can often be written in the simple form (see eqn. (5.13))

$$A = RT \log \frac{K(T)}{C_M^{-1} C_F} \tag{21}$$

and depends essentially on the concentrations $C_M$ and $C_F$ in the outside environment.
*Show that this is correct.*

We now show that conditions (16) that the net flows $dn_i/dt = 0$ in the stationary state give the condition of minimal entropy production for *a given value of the resultant affinity*. Using the phenomenological laws, eqn. (17) may be written

$$T\frac{d_i S}{dt} = \sum_{\rho=1}^{r+2} \sum_{\rho'=1}^{r+2} L_{\rho\rho'} \frac{A_\rho}{T} \frac{A'_\rho}{T} > 0 \tag{22}$$

Now must determine minimum of (22) given a fixed value of the resultant affinity (20). Can be done by method of Lagrange's undetermined multipliers. Must determine the extremum of the function

$$\Phi = \sum_{\rho=1}^{r+2} \sum_{\rho'=1}^{r+2} L_{\rho\rho'} \frac{A_\rho}{T} \frac{A'_\rho}{T} - 2\lambda \sum_\rho \frac{A_\rho}{T} \tag{23}$$

where $\lambda$ is the Lagrange multiplier. The extremum conditions of (23) are

$$\frac{\partial \Phi}{\partial(A_\rho/T)} = 2\sum_{\rho'} L_{\rho\rho'} \frac{A'_\rho}{T} - 2\lambda = 0 \tag{24}$$

or

$$v_\rho = \lambda \quad (\rho = 1, 2, \ldots r + 2) \tag{25}$$

which is precisely the condition of stationary flows, eqn. (16).

## 7.4 More Complicated Systems of Chemical Reactions

Consider a more complicated system of chemical reactions. Synthesis of hydrobromic acid.

$$
\begin{array}{rlr}
Br_2 & \rightarrow 2Br & (1) \\
Br + H_2 & \rightarrow HBr + H & (2) \\
Br_2 + H & \rightarrow HBr + Br & (3)
\end{array}
\tag{26, 27, 28}
$$

The macroscopic stotiometric equation is

$$
Br_2 + H_2 \rightarrow 2HBr \quad (2) + (3) \tag{29}
$$

For convenience, we ignore the affinities of the transport processes. The stationary state now corresponds to an extremum of entropy production for a given value of the resultant affinity

$$
A = A_2 + A_3 \tag{30}
$$

*Show that the extremum conditions of entropy production are given by*

$$
v_1 = 0 \quad v_2 = v_3 \tag{31}
$$

It is easy to see that these conditions give that the time variation of the concentrations inside the system are zero

$$
\frac{dn_H}{dt} = v_2 - v_3 = 0 \tag{32}
$$

$$
\frac{dn_{Br}}{dt} = 2v_1 - v_2 + v_3 = 0 \tag{33}
$$

So, here again, the stationary conditions are equivalent to the conditions of minimum production of entropy.

## 7.5 Time Variation of Entropy Production - Stability of Stationary States

Will show that irreversible processes occurring inside a thermodynamic system always lower the value of the entropy production per unit time. Define

$$
\mathcal{P} \equiv \frac{d_i S}{dt} \tag{34}
$$

Consider a system with two simultaneous chemical reactions. Entropy production per unit time is

$$
\mathcal{P} = L_{11} \left( \frac{A_1}{T} \right)^2 + 2L_{12} \frac{A_1 A_2}{T^2} + L_{22} \left( \frac{A_2}{T} \right)^2 > 0 \tag{35}
$$

Suppose that the phenomenological coefficients $L_{ij}$ are constant in time, then

$$
\frac{1}{2} \frac{d\mathcal{P}}{dt} = \left( L_{11} \frac{A_1}{T} + L_{12} \frac{A_2}{T} \right) \frac{d(A_1/T)}{dt} + \left( L_{12} \frac{A_1}{T} + L_{22} \frac{A_2}{T} \right) \frac{d(A_2/T)}{dt} \tag{36}
$$

$$
= v_1 \frac{d(A_1/T)}{dt} + v_2 \frac{d(A_2/T)}{dt} \tag{37}
$$

First, consider a *closed system.* Then $A_1$ and $A_2$ may then be expressed in terms of two independent physical variables (eg. $p$ and $T$), assumed to be constant, and $\xi_1, \xi_2$, so that

$$\frac{1}{2}\frac{d\mathcal{P}}{dt} = \frac{v_1}{T}\left[\left(\frac{\partial A_1}{\partial \xi_1}\right)_{pT}v_1 + \left(\frac{\partial A_1}{\partial \xi_2}\right)_{pT}v_2\right] + \frac{v_2}{T}\left[\left(\frac{\partial A_2}{\partial \xi_1}\right)_{pT}v_1 + \left(\frac{\partial A_2}{\partial \xi_2}\right)_{pT}v_2\right] \quad (38)$$

Now,

$$\left(\frac{\partial A_1}{\partial \xi_2}\right)_{pT} = \left(\frac{\partial A_2}{\partial \xi_1}\right)_{pT} = -\left(\frac{\partial^2 G}{\partial \xi_1 \partial \xi_2}\right)_{pT} \quad (39)$$

*Show that the above is correct.* Therefore, Eqn. (38) may be written in the form

$$\frac{1}{2}\frac{d\mathcal{P}}{dt} = \frac{1}{T}\left(\frac{\partial A_1}{\partial \xi_1}v_1^2 + 2\frac{\partial A_1}{\partial \xi_2}v_1 v_2 + \frac{\partial A_2}{\partial \xi_2}v_2^2\right) \quad (40)$$

Now, it can be shown that $\partial A_\rho / \partial \xi_{\rho'}$ are negative definite (see chapter on Onsarger's reciprocity relations (Chpt. IV Prigogine) when considering fluctuations, and homework). Thus,

$$\frac{1}{2}\frac{d\mathcal{P}}{dt} < 0 \quad (41)$$

Therefore, in a closed system, the entropy production per unit time can only diminish.
*Discuss this fact in relation to the development of an egg.*

The above arguments can be extended to *open systems.*
The affinities can be written as functions of the mole numbers $n_1 \cdots n_c$. Therefore,

$$\frac{dA_1}{dt} = \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{dn_\gamma}{dt} = \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{d_i n_\gamma}{dt} + \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{d_e n_\gamma}{dt}$$

$n_\gamma$ changing internaly due to 2 chemical ractions, and flow from env.

$$= \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\nu_{\gamma 1}\frac{d\xi_1}{dt} + \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\nu_{\gamma 2}\frac{d\xi_2}{dt} + \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{d_e n_\gamma}{dt}$$

$\nu_{\gamma 1}$ is the stotiometric coefficient of componet $\gamma$ in reaction 1
now $\sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\nu_{\gamma 1} = \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{\partial n_\gamma}{\partial \xi_1} = \frac{\partial A_1}{\partial \xi_1}$ remember $d\xi = \frac{dn_\gamma}{\nu_\gamma}$
Therefore,

$$\frac{dA_1}{dt} = \frac{\partial A_1}{\partial \xi_1}v_1 + \frac{\partial A_1}{\partial \xi_2}v_2 + \sum_\gamma \frac{\partial A_1}{\partial n_\gamma}\frac{d_e n_\gamma}{dt}$$

and similarly for $\frac{dA_2}{dt}$.
Using this relation in (37) gives

$$\frac{1}{2}\frac{d\mathcal{P}}{dt} = \frac{1}{T}\left(\frac{\partial A_1}{\partial \xi_1}v_1^2 + 2\frac{\partial A_1}{\partial \xi_2}v_1 v_2 + \frac{\partial A_2}{\partial \xi_2}v_2^2\right) + \frac{1}{T}\sum_\gamma\left(v_1\frac{\partial A_1}{\partial n_\gamma} + v_2\frac{\partial A_2}{\partial n_\gamma}\right)\frac{d_e n_\gamma}{dt} \quad (42)$$

The time variation of the entropy production can thus be split into two terms: an internal term which is always negative

$$\frac{1}{2}\frac{d_i\mathcal{P}}{dt} = \frac{1}{T}\left(\frac{\partial A_1}{\partial \xi_1}v_1^2 + 2\frac{\partial A_1}{\partial \xi_2}v_1 v_2 + \frac{\partial A_2}{\partial \xi_2}v_2^2\right) < 0 \tag{43}$$

and an external term of no definite sign

$$\frac{1}{2}\frac{d_e\mathcal{P}}{dt} = \frac{1}{T}\sum_\gamma \left(v_1\frac{\partial A_1}{\partial n_\gamma} + v_2\frac{\partial A_2}{\partial n_\gamma}\right)\frac{d_e n_\gamma}{dt} \tag{44}$$

Conclusion, *internal irreversible processes always operate in such a way that their effect is to lower the value of the internal entropy production per unit time.*

Has implications for the stability of the stationary state. If system is in state of minimum entropy production, it therefore cannot leave this state by a spontaneous irreversible change. If, as a result of some fluctuation, it deviates from the this state, internal changes will take place to bring the system back to its initial state, the *stable state.*

## 7.6   Entropy Flow in Stationary States

In the stationary state, the total entropy is independent of time. Therefore, positive entropy production has to be compensated by a negative flow of of entropy such that,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0 \tag{45}$$

Since

$$\frac{d_i S}{dt} > 0 \tag{46}$$

we must have

$$\frac{d_e S}{dt} < 0 \tag{47}$$

Stationary non-equilibrium states *cannot occur in isolated systems* because a flow of entropy is necessary to maintain the stationary state.

Eg. Consider a system of two subsystems maintained at temperatures $T^I$ and $T^{II}$. Both subsystems are individually open but the system as a whole is closed. The entropy flow from the outside is

$$\frac{d_e S}{dt} = \frac{1}{T^I}\frac{d_e^I Q}{dt} + \frac{1}{T^{II}}\frac{d_e^{II} Q}{dt} \tag{48}$$

where $d_e^I Q$ represents the heat flowing into (or out of) phase $I$ from the external environment. Suppose that $T^I > T^{II}$. Then, in order to maintain the temperature difference, we must have $d_e^I Q > 0$ and $d_e^{II} Q < 0$. Moreover, in the stationary state, the total heat received by the system is zero

$$dQ = d_e^I Q + d_e^{II} Q = 0 \tag{49}$$

and thus

$$\frac{d_e S}{dt} = \frac{d_e^I Q}{dt}\left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) < 0 \tag{50}$$

Negative entropy flow due to fact that the heat received by the system at temperature $T^I$ is returned to the external world at a lower temperature $T^{II}$.

Eg. Consider an open system. Entropy flow to or from external environment has been given by (3.51) (flow of energy $\phi$ and matter $n_\gamma$)

$$d_e S = \frac{d\phi}{T} - \sum_\gamma \frac{\mu_\gamma}{T} d_e n_\gamma \tag{51}$$

Instead of $d\phi/dt$, which is only defined apart from a term $\beta(dm/dt)$ (see section 2.4) where $\beta$ is an arbitrary constant, it is more convenient to use the flux $J'_{th}$ defined in eqn. (4.19). The entropy flow is then

$$\frac{d_e S}{dt} = \frac{1}{T} J'_{th} - \sum_\gamma \frac{\mu_\gamma - h_\gamma}{T} \frac{d_e n_\gamma}{dt} \tag{52}$$

$$= \frac{1}{T} J'_{th} + \sum_\gamma s_\gamma \frac{d_e n_\gamma}{dt} \tag{53}$$

where we have used

$$\mu_\gamma = h_\gamma - T s_\gamma \tag{54}$$

based on the relation $G = H - TS$.

*Show that eqn. (54) is correct.*

Note that in the stationary state, eqn. (53) has to become negative. Consider the limiting case when $J'_{th} = 0$, i.e. when the entropy exchanges with the environment are due solely to an exchange of matter. Then,

$$\frac{d_e S}{dt} = \sum_\gamma s_\gamma \frac{d_e n_\gamma}{dt} < 0 \tag{55}$$

Therefore, the entropy of matter entering the system has to be smaller than the entropy of matter given off by the system to the external world. From a thermodynamic point of view, the open system "degrades" the matter it receives and this degradation maintains the stationary state.

## 7.7 Time Variation of the Entropy

Have shown that

1. entropy flows from a system in a stationary state toward the external environment,

2. during the evolution toward a stationary state the entropy production decreases and takes its lowest value compatible with the external constraints

Will now examine what happens to the *entropy* of the system during this evolution – will find that it often decreases.

Eg. Consider the Knudsen gas (Chpt. 5 sec. 4). Two subsystems connected by an opening of a diameter smaller than the mean free path. The distribution of matter in the stationary state is given by eqn. (6.72),

$$\frac{p^I}{p^{II}} = \sqrt{\frac{T^I}{T^{II}}} \tag{56}$$

The volumes of the two subsystems are assumed to be the same. Will now calculate the entropy of the system in the initial, uniform, state and compare it with the entropy once the system has reached the stationary state – will show that the entropy decreases.

In the initial state, we have one mole of gas in each subsystem

$$n_{in}^I = n_{in}^{II} = 1, \quad n^I + n^{II} = 2 \tag{57}$$

In the stationary state, Eqn. (56) leads to (since $V^I = V^{II} = V$) using $pV = NRT$

$$\frac{n^I}{n^{II}} = \left(\frac{T^{II}}{T^I}\right)^{1/2} = \left(1 + \frac{\Delta T}{T}\right)^{1/2} \tag{58}$$

Thus, the distribution of matter for the stationary state is (because we need $n^I + n^{II} = 2$)

$$n_{st}^I = \frac{2[1 + (\Delta T/T)]^{1/2}}{1 + [1 + (\Delta T/T)]^{1/2}}; \quad n_{st}^{II} = \frac{2}{1 + [1 + (\Delta T/T)]^{1/2}}; \tag{59}$$

In textbooks on thermodynamics, it can be found that the entropy of a perfect gas is

$$S = n\left[\sigma(T) - R\log\frac{n}{V}\right] \tag{60}$$

and that

$$\frac{\partial S}{\partial T} = n\frac{\partial\sigma}{\partial T} = C_v/T \tag{61}$$

The entropy of the system can thus be written

$$S = S^I + S^{II} = n^I\left[\sigma(T) - R\log\frac{n^I}{V}\right] + n^{II}\left[\sigma(T + \Delta T) - R\log\frac{n^{II}}{V}\right] \tag{62}$$

Applying this formula to the initial state and the stationary state, and developing $\sigma(T + \Delta T)$ in powers of $\Delta T/T$ we find that

$$S_{st} - S_{in} = -(1/16)(4C_v + R)\left(\frac{\Delta T}{T}\right)^2 < 0 \tag{63}$$

*Show that the above formula is correct.*
The entropy of the stationary state is thus smaller than that of the initial state. The same is true for thermal diffusion. The separation of matter corresponds to a decrease of entropy in comparison with the initial uniform state.
Note; the above is not always true, entropy may increase in the stationary state.

# 8    Stationary State Coupling of Irreversible Processes

Interference of irreversible processes shown to occur through the existence of interference coefficients $L_{ik}$ $(i \neq k)$ in the phenomenological relations. However, it is possible that in the stationary state, processes which are not connected directly by phenomenological coefficients may be coupled, eg. diffusion and chemical reactions.

Example, open system (phase I) receiving a component $M$ from the external environment (phase II), transforming it into component $N$, which is returned to the external environment. Besides $M$ and $N$, the system receives a component $O$ which does not take part in the chemical reaction (inert component).

The entropy production is

$$T\frac{d_iS}{dt} = A_M\frac{d_en_M}{dt} + A_N\frac{d_en_N}{dt} + A_O\frac{d_en_O}{dt} + A_{ch}v_{ch} > 0 \tag{64}$$

$A_M, A_N$, and $A_O$ are affinities corresponding to the transfer phenomena.

Assume the following phenomenological relations

$$\frac{d_e n_M}{dt} = L_{11}\frac{A_M}{T} + L_{12}\frac{A_O}{T} \tag{65}$$

$$\frac{d_e n_O}{dt} = L_{21}\frac{A_M}{T} + L_{22}\frac{A_O}{T} \tag{66}$$

$$\frac{d_e n_N}{dt} = L_N\frac{A_N}{T} \tag{67}$$

$$v_{ch} = L_{ch}\frac{A_{ch}}{T} \tag{68}$$

Only the transport of components $M$ and $O$ is coupled. What are the consequences of this coupling in the stationary state?

Stationary state conditions are;

$$\frac{dn_M}{dt} = \frac{d_e n_M}{dt} - v_{ch} = 0; \quad \frac{dn_N}{dt} = \frac{d_e n_N}{dt} + v_{ch} = 0; \quad \frac{dn_O}{dt} = \frac{d_e n_O}{dt} = 0 \tag{69}$$

or

$$v_{ch} = \frac{d_e n_M}{dt} = -\frac{d_e n_N}{dt}; \quad \frac{d_e n_O}{dt} = 0 \tag{70}$$

Using the phenomenological equations (68) and Onsagers reciprocity relation, gives

$$A_M = \frac{T}{L_{11} - (L_{12}^2/L_{22})}v_{ch}; \quad A_N = -\frac{T}{L_N}v_{ch}; \quad A_O = \frac{-T(L_{21}/L_{22})}{L_{11} - (L_{12}^2/L_{22})}v_{ch} \tag{71}$$

The last formula shows that in the stationary state a difference in concentration in the inert component $O$ has appeared.

$$A_O = RT\log\frac{K(T)}{(C_O^{II})^{-1}(C_O^{I})} = \frac{-T(L_{21}/L_{22})}{L_{11} - (L_{12}^2/L_{22})}v_{ch} \tag{72}$$

The concentration of $O$ in the open system may be higher or lower than in the external environment, accroding to the sign of the phenomenological coefficient $L_{21}$. This effect is proportional to the rate of the chemical reaction. Thus, an interference between transport phenomena and chemical reaction occurs even though the two processes are not directly coupled by phenomenological laws. Such a coupling is called *stationary coupling*.

As a consequence of the positive definite value of the entropy production, it is easy to show that

$$L_{11} - \frac{L_{12}^2}{L_{22}} > 0 \tag{73}$$

is always positive, so that the affinity $A_M$ has always the same sign as the reaction rate $v_{ch}$. If component $M$ is consumed in the reaction then $v_{ch} > 0$ , and therefore $A_M > 0$, meaning that the concentration inside the system is lowered with respect to the environment.

But, this is not always the case.

Consider the more general phenomenological laws

$$\frac{d_e n_M}{dt} = L_{11}\frac{A_M}{T} + L_{12}\frac{A_O}{T} + L_{13}\frac{A_N}{T} \tag{74}$$

$$\frac{d_e n_O}{dt} = L_{21}\frac{A_M}{T} + L_{22}\frac{A_O}{T} + L_{23}\frac{A_N}{T} \tag{75}$$

$$\frac{d_e n_N}{dt} = L_{31}\frac{A_M}{T} + L_{32}\frac{A_O}{T} + L_{33}\frac{A_N}{T} \tag{76}$$

$$v_{ch} = L_{ch}\frac{A_{ch}}{T} \tag{77}$$

We find that, instead of (72),

$$A_M = \frac{T}{D}(L_{22}L_{33} - L_{12}L_{23} - L_{23}^2 + L_{13}L_{22})v_{ch} \tag{78}$$

where $D$ is the determinant of $L_{ij}$

$$D \equiv \begin{vmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{vmatrix} > 0 \tag{79}$$

Since the entropy production due to the coupled flows is positive, (Eqn. (64)), the determinant must be positive also.
*Show that this is true.*
It may happen that the numerator in Eqn. (78) is negative. There would then be in the stationary state a flow of $M$ (the reacting constituent) against its concentration gradient as a result of the stationary state coupling between transport phenomena and chemical reaction.

Eg. In a living cell at a stationary state, may have a non-equilibrium distribution of matter which differs from that in its environment by amounts determined by the rate of metabolism in the cell.

# 9   Applications to Biology

The transport of a compound against its concentration gradient could take place for the following reasons

1. The existence of a force which compensates the gradient of the chemical potential. Eg. charged particles influenced by an electric potential.

2. Coupling by means of phenomenological relations. Eg. thermomolecular pressure difference, thermodiffusion.

3. Stationary state coupling as seen above.

All these effects may be operating in living organisms. Irreversible processes related to internal degrees of freedom may also play a part.

May consider a living organism as evolving under constant constraints, eg. fixed concentrations of components in the environment which are transformed within the organism.

The stationary state may probably, to a good approximation, be considered as a state of minimum production of entropy per unit time. Fits well with some striking characteristics of living organisms.

1. Well documented stability against external pertubation.

2. Living organisms show a decrease in entropy production during their life span ... leading to the stationary state.

3. Organization also increases during this evolution – corresponds to a decrease in entropy as found in section 7.

It has always been difficult to reconcile living organisms with thermodyanmics. However, the situation looks much more plausible from this new perspective of open systems and stationary states.