8 Chapter 8: Non-linear Thermodynamics of Irreversible Processes

8.1 Introduction

Irreversible thermodynamics is based on the Gibbs formula and an evaluation of the entropy production and flow. Gibbs formula was derived for equilibrium conditions and its use in non-equilibrium situations is a new postulate. Must ultimately be justified by methods of statistical mechanics of irreversible processes.

Use of Gibbs formula implies that even without equilibrium conditions, entropy depends on the same independent variables as in equilibrium.
Based on the kinetic theory of gasses, domain of validity of the thermodynamics of irreversible processes is restricted to domain of validity of linear phenomenological laws. (Excludes only cases of rarefied gasses and very low temperature situations where interactions are not numerous enough to maintain a state of local equilibrium.)

For chemical reactions, reaction rate must be sufficiently slow so as not to disturb the Maxwell equilibrium distribution of the velocities of each component. (Excludes only reactions of abnormally low energies of activation.)

For the study of stationary states, we assumed

1. Linear phenomenological laws
2. Validity of Onsager's reciprocity relations
3. Phenomenological coefficients can be treated as constants.

These conditions are more restrictive than conditions for the validity of the Gibbs formula. Eg. In chemical reactions, linear phenomenological laws may not be sufficiently good approximations; in transport processes it may be necessary to account for the variation of the phenomenological coefficients (eg. variation in the coefficient of thermal conductivity with temperature). These effects may be considered as being non-linear.
Purpose of this chapter is to extend the treatment into the non-linear regime. Eg. theorem of minimum entropy production was only proved for the linear regime.

8.2 Variation of the Entropy Production

The entropy production is

$$\mathcal{P} = \frac{d_i S}{dt} = \sum_k J_k X_k \geq 0 \tag{1}$$

Decompose the time change $d\mathcal{P}$ into two parts, one related to the change of forces and the other to the change of flows

$$d\mathcal{P} = d_X\mathcal{P} + d_J\mathcal{P} = \sum_k J_k dX_k + \sum_k X_k dJ_k \tag{2}$$

Will now prove the following theorems

1. Under the restrictive conditions assumed for the study of the stationary state,

$$d_X\mathcal{P} = d_J\mathcal{P} = \frac{1}{2}d\mathcal{P} \tag{3}$$

Proof:

$$d_X\mathcal{P} = \sum_k J_k dX_k = \sum_{kl} L_{kl}X_l dX_k \tag{4}$$

using the reciprocity relations and treating the L_{kl} as constants

$$d_X\mathcal{P} = \sum_{kl} X_l(L_{lk}dX_k) = \sum_l X_l dJ_l = d_J\mathcal{P} \tag{5}$$

2. In the whole domain of the validity of thermodynamics of irreversible processes, the contribution of the time change of the forces to the entropy production is negative or zero

$$d_X\mathcal{P} \leq 0 \tag{6}$$

Holds whenever the boundary conditions are time-independent. This is **the most general result obtained in the thermodynamics of irreversible processes.**
Proof: Will not provide a general proof. Instead, will prove it for chemical reactions; Consider an open system in contact with some external phases in a time-independent state. For each component of the system, one of the following two conditions is realized

(a) it has a time-independent chemical potential determined by the external reservoirs

(b) it cannot cross the boundary of the system

The change in the number of moles of component γ is

$$dn_\gamma/dt = d_e n_\gamma/dt + \sum_\rho \nu_{\gamma\rho}v_\rho \tag{7}$$

multiplying both sides by the time derivative of the chemical potential of component γ gives

$$\dot{\mu}_\gamma(dn_\gamma/dt) = \dot{\mu}_\gamma(d_e n_\gamma/dt) + \sum_\rho \nu_{\gamma\rho}\dot{\mu}_\gamma v_\rho \tag{8}$$

First term on right hand side vanishes by the boundary conditions. Summing up all components and taking account that the temperature and pressure are assumed constant in time

$$\sum_\gamma \dot{\mu}_\gamma \frac{dn_\gamma}{dt} = \sum_\gamma\sum_{\gamma'}\left(\frac{\partial\mu_\gamma}{dn_{\gamma'}}\right)_{pT}\frac{dn_\gamma}{dt}\frac{dn_{\gamma'}}{dt} = \sum_{\rho\gamma}\nu_{\gamma\rho}\dot{\mu}_\gamma v_\rho \tag{9}$$

Introducing the affinity A_ρ

$$A_\rho = -\sum_\gamma \nu_{\gamma\rho}\mu_\gamma \tag{10}$$

gives

$$\sum_\gamma\sum_{\gamma'}\left(\frac{\partial\mu_\gamma}{dn_{\gamma'}}\right)_{pT}\frac{dn_\gamma}{dt}\frac{dn_{\gamma'}}{dt} = -\sum_\rho v_\rho\frac{dA_\rho}{dt} \tag{11}$$

Now, equilibrium stability conditions involve the inequality (see eqn. (4.28) in section of fluctuations in book of Prigogine)

$$\sum_{\gamma}\sum_{\gamma'}\left(\frac{\partial\mu_\gamma}{dn_{\gamma'}}\right)_{pT} x_\gamma x_{\gamma'} \geq 0 \tag{12}$$

whatever the quantities $x_1, \ldots, x_c$. Theorem of classical thermodynamics and is analogous to the theorem that specific heat at constant volume is positive. Applying this theorem to eqn. (11) gives (can be applied because we assume that the chemical potentials have the same functional dependence on the n_γ as in equilibrium)

$$\sum_{\rho} v_\rho dA_\rho = T d_X \mathcal{P} \leq 0 \tag{13}$$

since the generalized flows are v_ρ and the forces are A_ρ. Which completes the proof.

Note that by combining eqn. (13) with eqn. (5) gives the theorem of minimum entropy production valid in the linear region

$$d\mathcal{P} \leq 0 \tag{14}$$

An important feature of the inequality $d_X\mathcal{P} \leq 0$ is that it can be extended to include flow processes in inhomogeneous systems as well (proved elsewhere). Therefore,

$$d\Phi = \int dV \sum_k J'_k dX'_k \leq 0 \tag{15}$$

where the integral is over the volume of the system and where the forces X'_k and the flows J'_k now include mechanical processes such as convection terms. For time-independent boundary conditions inequality (15) is so general that it may be called a *universal* evolution criterion valid throughout the whole range of macroscopic physics.

Note, however, that $d\Phi$ is not a total differential. Therefore it does not imply the existence of a universal potential (eg. like entropy), however, will see that it leads to the concept of a "local potential" which is nevertheless of great interest.

8.3 Steady States and Entropy Production

Note that even though $d_X\mathcal{P}$ is not a total differential, it can still be used in a manner similar to the use of the entropy production to describe the equilibrium of chemical reactions, but now in the steady state;
Consider first

$$T d_i S = \sum_\rho A_\rho d\xi_\rho \geq 0 \tag{16}$$

The condition of chemical equilibrium

$$A_\rho = -\sum_\gamma \nu_{\gamma\rho}\mu_\gamma = 0 \tag{17}$$

is independent of the existence of of thermodynamic potentials. Eqn. (13) can be treated in a similar way.

The condition for a time independent situation is

$$\sum_{\rho} v_\rho dA_\rho = 0 \tag{18}$$

for all independent variations of the affininties. Suppose that the steady state can be characterized by the concentrations $X_1, \ldots X_c$ of the different components. Equation (18) implies the following conditions between the reaction rates

$$\sum_{\rho} v_\rho \frac{\partial A_\rho}{\partial X_\gamma} = 0 \tag{19}$$

Show that the above is true. (Remember that

$$\frac{\partial}{\partial X_m}\left(\frac{d_i S}{dt}\right) = 0 \tag{20}$$

)
Which is a restatement of the usual relations between the reaction rates at the steady state. To see this, consider the following example of a sequence of reactions

$$\begin{array}{ccc} A \overset{1}{\rightleftharpoons} & X & \overset{2}{\rightleftharpoons} B \\ & 3 \parallel & \\ & M & \end{array} \tag{21--23}$$

where the concentrations of A and B are fixed. There are only two independent affinities because of the condition

$$A_1 + A_2 = given \quad or \quad \delta A_1 + \delta A_2 = 0 \tag{24}$$

Therefore, eqn. (18) leads to

$$v_1 = v_2, \quad v_3 = 0 \tag{25}$$

which are indeed the usual steady state conditons (see Chpt. 7.4 notes, discussion of production of hydrobromic acid) and include as a special case the equilibrium condition

$$v_1 = v_2 = 0, \quad v_3 = 0 \tag{26}$$

Now, consider a restatement of eqn. (13) of the following form

$$T d_X \mathcal{P} = d(\sum A_\rho v_\rho) - \sum A_\rho dv_\rho \leq 0 \tag{27}$$

The conditions of the steady state are now

$$\delta\left(\frac{d_i S}{dt}\right) - \sum_{\rho} \frac{A_\rho}{T} \delta v_\rho = 0 \tag{28}$$

and the equations corresponding to (19) are

$$\frac{\partial}{\partial X_\gamma}\frac{d_i S}{dt} - \sum_{\rho} \frac{A_\rho}{T}\frac{\partial v_\rho}{\partial X_\gamma} = 0 \tag{29}$$

These are the general relations which give the steady state concentrations.

Near equilibrium, in the domain of validity of the linear kinetic laws we have

$$\sum_{\rho} \frac{A_\rho}{T} \delta v_\rho = \sum_{\rho} \frac{v_\rho}{T} \delta A_\rho = \frac{1}{2} \delta \left(\frac{d_i S}{dt} \right) \tag{30}$$

Remember that $d_X \mathcal{P} = d_J \mathcal{P} = 1/2 d\mathcal{P}$.
Therefore Eqn. (28) reduces to the theorem of minimum entropy production

$$\delta \left(\frac{d_i S}{dt} \right) = 0 \tag{31}$$

In general, both thermodynamic and kinetic quantities enter into the determination of the steady state through Eqn. (29). It is only near equilibrium that all *explicit* reference to the reaction rates disappears.

Consider again the chemical reactions (23). Asume kinetic laws of the form (all equilibrium and rate constants, as well as RT are set equal to one).

$$v_1 = A - X \quad v_2 = X - B \quad v_3 = X - M \tag{32}$$

Eqn. (29) gives

$$\begin{aligned} \frac{\partial}{\partial X} \frac{d_i S}{dt} &+ \frac{A_1 - A_2 - A_3}{T} = 0 \\ \frac{\partial}{\partial M} \frac{d_i S}{dt} &+ \frac{A_3}{T} = 0 \end{aligned} \tag{33}$$

Using the steady state condition

$$v_1 = v_2, \quad v_3 = 0 \tag{34}$$

and the usual form of the affinities in terms of the concentrations

$$A = log \frac{C^{II}}{C^{I}} \tag{35}$$

gives

$$\frac{\partial}{\partial X} \frac{d_i S}{dt} = -log \frac{4AB}{(A+B)^2} \tag{36}$$

$$\frac{\partial}{\partial M} \frac{d_i S}{dt} = 0 \tag{37}$$

Define

$$1 - \gamma \equiv B/A \tag{38}$$

where γ measures the deviation of the steady state from thermodynamic equilibrium (for which B/A =1). Then Eqn. (36) becomes

$$\frac{\partial}{\partial X} \frac{d_i S}{dt} = -log \frac{4(1-\gamma)}{(2-\gamma)^2} \tag{39}$$

Note that, as expected, the deviations from the theorem of minimum entropy production begin with the terms of second order in γ.

Consider now the action of a catalyst on reaction (23). Specificaly, assume the following rate equation for v_1

$$v_1 = (1 + \alpha M)(A - X) \tag{40}$$

Here M is assumed to be the catalyst. Will see that the steady state concentration of M increases as a result of its catalytic action. Using Eqn. (40) together with Eqn. (32) and the steady state conditions (34) gives

$$\begin{aligned} M = X &= \frac{1}{2\alpha}[\alpha A - 2 + [4 + 4\alpha A(1-\gamma) + \alpha^2 A^2]^{\frac{1}{2}}] \\ &\to \frac{1}{2}(A+B) \quad for \quad \alpha \to 0 \\ &\to A \quad for \quad \alpha \to \infty \end{aligned} \tag{41}$$

If A is less than B then the concentration of M has increased due to the catalytic activity. This increase in concentration can be large if more complicated reactions of the following form are considered.

$$A \rightleftharpoons X_1 \rightleftharpoons X_2 \rightleftharpoons \ldots \rightleftharpoons \quad X_n \quad \rightleftharpoons B \tag{42}$$

$$\| \tag{43}$$

$$M \tag{44}$$

For n large, we find that in the steady state in the absence of catalytic activity ($\alpha \to 0$)

$$X_n = M = B + O(\frac{1}{n}) \tag{45}$$

while if M acts as a catalyst for all reactions leading to X_n and for ($\alpha \to \infty$)

$$X_n = M = A \tag{46}$$

Thus the amplification of the steady state concentration can take arbitrarily large values if the ratio B/A is sufficiently small. Note that this amplification is a typical non-equilibrium process since in equilibrium $B/A = 1$.

Consider now the entropy production of the sequence of chemical reactions (23)

$$\frac{d_i S}{dt} = (A - X)(1 + \alpha M)\log\frac{A}{X} + (X - B)\log\frac{X}{B} + (X - M)\log\frac{X}{M} \tag{47}$$

(from $\frac{d_i S}{dt} = \sum vA$)
At the steady state, using (41)

$$\left(\frac{d_i S}{dt}\right)_{\alpha \to 0} = \frac{A - B}{2}\log\frac{A}{B} = -\frac{A}{2}\gamma\log(1-\gamma) \tag{48}$$

and

$$\left(\frac{d_i S}{dt}\right)_{\alpha \to \infty} = -A\gamma\log(1-\gamma) \tag{49}$$

Note that the entropy production is larger for $\alpha \to \infty$ than for $\alpha \to 0$.

Will now show that the entropy production as a function of M has a minimum which shifts to larger values of M as a result of the catalytic activity. In the steady state, we have $X = M$ (41).

$$\frac{\partial}{\partial M}\frac{d_iS}{dt} = -\frac{A+B-2M}{M} - \log\frac{AB}{M^2} - \alpha\left[(A-M) - (A-2M)\log\frac{A}{M}\right] \tag{50}$$

The exact positions of the steady state concentrations of M can be obtained by using (50) with eqns. (29). However, to simplify the analysis and for a qualitative understanding, we assume the condition of minimum entropy production, i.e.

$$\frac{\partial}{\partial M}\frac{d_iS}{dt} = 0 \tag{51}$$

Using this, and the steady state conditions eqns. (41), it can be shown that the catalytic activity moves the minimum of the entropy production from $M = 1 - (\gamma/2)$ to 1.

Such a result may shed light on the problem of the occurance of complicated biological molelcules in steady state concentrations which are of orders of magnitude larger than the equilibrium concentrations.

Thus, for steady states sufficiently far from equilibrium, kinetic factors (like catalytic activity) may compensate for thermodynamic improbability and thus lead to an amplification of the steady state concentrations. Note that this is a non-equilibrium effect. Near equilibrium, catalytic action would not be able to shift in an appreciable way the position of the steady state.

8.4 Evolution Criterion and Velocity Potential

As mentioned, the general evolution criterion $Td_X\mathcal{P} \leq 0$ does not lead in general to a classical potential. Can be expected because the existence of a potential implies the possibility of the system to forget its initial conditions (Eg. an isolated system tends to a state of maximum entropy regardless of the initial conditions. Similarly, in domain of validity of theorem of minimum entropy production, the final state is independent of the initial specification of the system compatible with the given constraints.)

Here we will see systems which cannot forget the initial perturbation and their evolution cannot be described in terms of any potential in the classical sense.

However, a description in terms of a generalized potential may still be useful.

There is no difficulty if one deals with only one or two independent variables. Eg. for a single independent chemical reaction

$$\begin{aligned} Td_X\mathcal{P} &= v(A)dA \\ &= dD \leq 0 \end{aligned} \tag{52}$$

The right hand side may be considered as the differential of some function D - to be called a velocity potential. Therefore,

$$v = \partial D/\partial A \tag{53}$$

In the stationary state

$$v = \partial D/\partial A = 0 \tag{54}$$

and the stability condition for this state is that D is a minimum

$$\partial^2 D/\partial A^2 > 0 \tag{55}$$

This minimum condition has to be realized, if not, the slightest fluctuation would permit the system to leave this state (see (52)). As an example, consider the reactions

$$A \overset{1}{\rightleftharpoons} X \overset{2}{\rightleftharpoons} B \tag{56}$$

Assume that the concentrations of A and B are given and time independent. Therefore, the total affinity for the two reactions

$$\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2 = \log \frac{A}{X} + \log \frac{X}{B} \tag{57}$$

will also be time-independent. We therefore have a single independent process and we can write

$$Td_X\mathcal{P} = (v_2 - v_1)d\mathcal{A}_2 \leq 0 \tag{58}$$

We now assume the following expressions for the reaction rates corresponding to auto-catalytic reactions

$$v_1 = X^n(A - X); \quad v_2 = X^n(X - B) \tag{59}$$

We then easily find that the velocity potential has the form

$$D = \frac{2}{n+1}X^{n+1} - \frac{1}{n}(A + B)X^n = function\ independent\ of\ X \tag{60}$$

Giving two stationary states

$$X = 0 \tag{61}$$

and

$$X = \frac{A + B}{2} \tag{62}$$

The second state corresponds to a minimum of D and therefore to a stable situation. However, the first corresponds to a maximum of D. Has an obvious physical reason, the smallest fluctuation starting from (61) will increase the rates (59) and therefore again increase the value of X until the stable state (62) is reached.

Consider now, two independent reactions

$$A \overset{1}{\rightleftharpoons} X \overset{2}{\rightleftharpoons} Y \overset{3}{\rightleftharpoons} B \tag{63}$$

We take the simplest possible kinetic laws

$$\begin{aligned} v_1 &= A - X \\ v_2 &= X - Y \\ v_3 &= Y - B \end{aligned} \tag{64}$$

Assume again that A and B are given and constant. Therefore,

$$\begin{aligned} d_X\mathcal{P} &= \sum_\rho v_\rho dA_\rho \\ &= (A - X)d\log\frac{A}{X} + (X - Y)d\log\frac{X}{Y} + (Y - B)d\log\frac{Y}{B} \\ &= \left(\frac{X - A}{X} - \frac{Y - X}{X}\right)dX + \left(\frac{Y - X}{Y} - \frac{B - Y}{Y}\right)dY \end{aligned} \tag{65}$$

We will now see that this is not a total differential. The existence of a velocity potential would imply

$$\frac{\partial D}{\partial X} = \frac{X - A}{X} - \frac{Y - X}{X} \qquad \frac{\partial D}{\partial Y} = \frac{Y - X}{Y} - \frac{B - Y}{Y} \tag{66}$$

But this is clearly impossible since

$$\frac{\partial^2 D}{\partial X \partial Y} = -\frac{1}{X} \neq \frac{\partial^2 D}{\partial Y \partial X} = -\frac{1}{Y} \tag{67}$$

Therefore, (65) is not in general a total differential. It is only so when we can replace X by Y by the same steady state values.

Now, at the steady state Eqns. (64) give

$$X = \frac{B + 2A}{3}; \quad Y = \frac{A + 2B}{3} \tag{68}$$

Thus X will be near to Y if the ratio of A/B is near to 1, but then the total affinity of the reactions will be near to zero. Thus, near equilibrium a velocity potential indeed exists, it is just the entropy production. *Show that for the example above this is true.*

(Note that we could have introduced an integrating factor to satisfy the total integrability condition. However, this cannot be done for more than two independent variables and has therefore no great interest.)

Graphically, the velocity field in the space of the thermodynamic variables (X and Y) can be represented in the following manner.

Case (a) referes to the case in which a velocity potential exists. The velocity lines are orthogonal to the surface corresponding to a given value of the velocity potential. Case (b) is the case in which ther is no velocity potential. We have then in general a turning motion of the velocity lines in the approach to the steady state S. In extreme cases this turning motion can become a rotation around the steady state. To be seen in the following section.

8.5 Rotation around the Stationary State

Consider now in more detail rotations around the stationary state (chemical oscillations). As in the example of eqn. (64) with concentrations of A and B kept constant, consider case of two independent chemical reactions. Develop the rates in the neighborhood of the stationary state. Eg.

$$\begin{aligned} v_a &= v_1 - v_2 \\ v_b &= v_2 - v_3 \end{aligned} \tag{69}$$

Remember that these rates vanish in the stationary state.

We no develop the rates in terms of the affinities in the neighborhood of the stationary state

$$\begin{aligned} v_a &= L_{aa}\delta A_a + L_{ab}\delta A_b \\ v_b &= L_{ba}\delta A_a + L_{bb}\delta A_b \end{aligned} \tag{70}$$

where δA_a and δA_b are the differences between the affinities and their values at the stationary state.

If the stationary state is far from equilibrium, which corresponds to an affinity large with respect to RT (remember that $A = RT\log(K/C_A^{-1}C_B)$) then the phenomenological coefficients no longer satisfy Onsager's relations

$$L_{ab} \neq L_{ba} \tag{71}$$

As an extreme case, we will examine the particular situation in which the matrix L is purely anti-symmetric

$$L_{aa} = L_{bb} = 0, \qquad L_{ab} = -L_{ba} \tag{72}$$

then

$$\begin{aligned} v_a &= L_{ab}\delta A_b \\ v_b &= -L_{ab}\delta A_a \end{aligned} \tag{73}$$

giving

$$-T\frac{d_X\mathcal{P}}{dt} = -L_{ab}\left[\left(\delta A_b\frac{dA_a}{dt}\right) - \left(\delta A_a\frac{dA_b}{dt}\right)\right] \tag{74}$$

Introducing polar coordinates θ, ρ in the plane A_a, A_b gives

$$-T\frac{d_X\mathcal{P}}{dt} = -L_{ab}\rho^2\frac{d\theta}{dt} \geq 0 \tag{75}$$

Therefore we have a rotation and this inequality determines the direction of rotation around the stationary state. Similar results can be shown for an arbitrary number of reactions. Note that rotation is permitted around a non-equilibrium stationary state while it is not permitted around an equilibrium state. The rotation around the stationary state, even if it introduces negative contribution to the entropy production, is possible as long as the total entropy production remains positive.

8.6 Local Potentials and Fluctuations

A generalized, "local" potential can be useful in resolving non-linear problems.

Eg. Consider the case of heat conduction in solids. The equation of energy conservation is

$$\rho\frac{\partial e}{\partial t} = -\frac{\partial W_j}{\partial x_j} \tag{76}$$

where ρ is the density and e is the energy per unit mass. W is the heat flow. Multiplying (76) by $\partial T^{-1}/\partial t$ gives for the left-hand side

$$\psi = \rho\frac{\partial T^{-1}}{\partial t}\frac{\partial e}{\partial t} = -\rho\frac{1}{T^2}\frac{\partial T}{\partial t}\frac{\partial e}{\partial t}\left[\frac{\partial t}{\partial T}\frac{\partial T}{\partial t}\right] = -\rho\frac{C_v}{T^2}\left(\frac{\partial T}{\partial t}\right)^2 \leq 0 \tag{77}$$

This quantity has a well defined sign because $C_v = \partial e/\partial T$ is always positive.

The right-hand side of (76) gives

$$\psi = -\frac{\partial W_j}{\partial x_j}\frac{\partial T^{-1}}{\partial t} = \frac{\partial}{\partial x_j}\left(-W_j\frac{\partial T^{-1}}{\partial t}\right) + W_j\frac{\partial}{\partial t}\left(\frac{\partial T^{-1}}{\partial x_j}\right) \leq 0 \tag{78}$$

Integrating over the volume gives, for time-independent boundary conditions,

$$\int \psi dV = \int dV W_j\frac{\partial}{\partial t}\frac{\partial T^{-1}}{\partial x_j} \leq 0 \tag{79}$$

Show that the first term in eqn. (78) is zero after doing the integral Hint: Use Gauss's Law.
Inequality (79) is a special case of (15) with the thermodynamic force given by

$$X_j = \frac{\partial(1/T)}{\partial x_j} \tag{80}$$

and the flow

$$J_j = W_j \tag{81}$$

Using Fourier's law $W_x = -(L/T^2)\partial T/\partial x = -L\partial T^{-1}/\partial x_j$ in (79) gives

$$\int dV\lambda(T)T^2\frac{\partial T^{-1}}{\partial x_j}\frac{\partial}{\partial t}\frac{\partial T^{-1}}{\partial x_j} \leq 0 \tag{82}$$

where $\lambda(T) = -L/T^2$.

Now, consider the Fourier equation for temperature (see Chpt. 4)

$$\frac{\partial T}{\partial t} = \lambda(T)\frac{\partial^2 T}{\partial x_j^2} \tag{83}$$

Let $T_0(x)$ be the solution of the time-independent Fourier equation

$$0 = \lambda(T)\frac{\partial^2 T}{\partial x_j^2} \tag{84}$$

We can also replace $\lambda(T)T^2$ by $\lambda_0 T_0^2$. Eqn. (82) still remains valid but now we can write (using $\partial F^2/\partial t = 2F\partial F/\partial t$).

$$\frac{1}{2}\frac{\partial}{\partial t}\int dV \lambda(T_0)T_0^2 \left(\frac{\partial T^{-1}}{\partial x_j}\right)^2 \leq 0 \tag{85}$$

The integral

$$\phi(T, T_0) = \frac{1}{2}\int dV \lambda(T_0)T_0^2 \left(\frac{\partial T^{-1}}{\partial x_j}\right)^2 \tag{86}$$

is the *local potential* appropriate to heat conduction in the time-independent case. The essential point is that it is a function of *both* T and T_0. This splitting of the variable T "in two" has (we will see below) a simple physical meaning: T_0 is the average distribution of the temperature T. T is considered as a fluctuating (or random) quantity. The properties of $\phi(T, T_0)$ are;

1. $\phi(T, T_0)$ decreases in time until it reaches its minimum value of $\phi(T_0, T_0)$; and

2. $$\phi(T_0, T_0) = \frac{1}{2}\frac{d_i S}{dt}$$

   (See Eqns. (5.1), (5.2) and (5.76) in book of Prigogine).

The local potential therefore appears as a generalization of the usual thermodynamic entropy production.

We now minimize (86) with respect to T (at constant T_0) giving (note that the minimization of an integral is a standard mathematical problem leading to the so-called Euler-Lagrange equation of variational calculus)

$$\left(\frac{\delta\phi}{\delta T}\right)_{T_0} = 0, \qquad \frac{\partial}{\partial x_j}\lambda_0 T_0 \left(\frac{\partial T^{-1}}{\partial x_j}\right) = 0 \tag{87}$$

If, moreover, after the minimization we use the subsidiary condition

$$T = T_0 \tag{88}$$

we obtain that the divergence

$$\frac{\partial W}{\partial x_j} = 0 \tag{89}$$

(see Eqn. (5.2) and (5.3) in book of Prigogine).
In this way we derive the steady state condition (89) as an extremum condition of our local potential. *Provide the derivation of equations (87) and (89).*

The two functions T and T_0 which appear in the local potential have both a simple and important physical meaning: T_0 is the average temperature and $T = T_0 + \delta T$ is a fluctuating temperature whose probability can be calculated using the Einstein-Boltzmann formula (Eqn. (4.33) in book of Prigogine)

The method permits the treatment of all dissipative processes through variational techniques in conjunction with an appropriate local potential which is itself a generalized entropy production.