

THE ENTROPY DISSIPATION FUNCTION

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Abstract

Using symmetry relations of a new theory published recently ("Thermokinetics") new thermodynamical functions are introduced called "Entropy Dissipation Functions". The three quantities are close related, $D_S = D_S^i + D_S^f$ and two of them (D_S^i and $-D_S^f$) are Legendre-transformed of each other. The linear phenomenological coefficients of Onsager are showed to be second derivatives of the appropriate Entropy Dissipation (D_S^f), and the Entropy Production is interpreted as second differential of both D_S^i and D_S^f . Usefulness of the concept thermodynamic force is demonstrated in strongly nonlinear cases. Position of the Entropy Dissipation Functions in the unified system of thermodynamic concepts is shown.

1. Introduction

In any sphere of physics some fundamental functions play important roles. In the classical mechanics the Hamilton and Lagrange functions, the kinetic energy, in the thermostatics the entropy, in the thermodynamics the entropy production, Φ and Ψ functions [1] may have similar roles. Using these functions most of the general features of material systems can be formulated in a very concise way.

Some mathematical preliminaries [2].

Let a system be characterized by a set of quantities

$$x_i \quad (i = 1, 2, \dots, n)$$

and let another set of quantities (y_i) be given as invertable functions of the x_i 's:

$$y_i = f_i(x_1, x_2, \dots, x_n)$$

and

$$x_i = g_i(y_1, y_2, \dots, y_n).$$

If the symmetry relations

$$\left(\frac{\partial y_i}{\partial x_j}\right) = \left(\frac{\partial y_j}{\partial x_i}\right) \quad (i, j = 1, 2, \dots, n) \quad (1)$$

hold then

$$\left(\frac{\partial x_i}{\partial y_j}\right) = \left(\frac{\partial x_j}{\partial y_i}\right) \quad (i, j = 1, 2, \dots, n). \quad (2)$$

In such cases one may introduce the functions

$$S^x(x) \quad \text{and} \quad S^y(y)$$

so that

$$y_i = \left(\frac{\partial S^x}{\partial x_i}\right) \quad \text{and} \quad x_i = \left(\frac{\partial S^y}{\partial y_i}\right) \quad (3)$$

and

$$dS^x = \sum_i y_i \cdot dx_i \quad \text{and} \quad dS^y = \sum_i x_i \cdot dy_i \quad (4)$$

are exact differentials.

In this sense S^x and S^y are potential functions and are unique apart from and additive constant.

S^x and S^y are Legendre transforms of each other:

$$S^y(y) = S(x(y), y) - S^x(x) \quad (5)$$

where

$$S(x, y) = \sum_i x_i \cdot y_i, \quad (6)$$

consequently

$$S = S^x + S^y \quad \text{and} \quad dS = dS^x + dS^y. \quad (7)$$

Second differentials:

$$d^2 S^x(x) = \sum_i \sum_j \left(\frac{\partial^2 S^x}{\partial x_i \partial x_j}\right) \cdot dx_i dx_j = \sum_i dy_i \cdot dx_i \quad (8)$$

$$d^2 S^y(y) = \sum_i \sum_j \left(\frac{\partial^2 S^y}{\partial y_i \partial y_j}\right) \cdot dy_i dy_j = \sum_i dx_i \cdot dy_i \quad (= d^2 S^x(x)) \quad (9)$$

$$d^2 S(x, y) = 0. \quad (10)$$

Examples

a. Linear relationship between x_i and y_j :

$$y_i = \sum_j K_{ij} \cdot x_j. \quad (11)$$

If the matrix \mathbf{K} is nonsingular then

$$x_i = \sum_j L_{ij} \cdot y_j \quad (12)$$

where L is the inverse matrix of K .

In this case

$$S^x = 1/2 \cdot \sum_i \sum_j K_{ij} \cdot x_i x_j \quad \text{and} \quad S^y = 1/2 \cdot \sum_i \sum_j L_{ij} \cdot y_i y_j \quad (13)$$

$$S = 2 \cdot S^x = 2 \cdot S^y \quad (14)$$

$$dS = \sum_i \sum_j K_{ij} \cdot x_i dx_j; \quad dS = \sum_i \sum_j L_{ij} \cdot y_i dy_j \quad (15)$$

$$d^2 S^x = \sum_i \sum_j K_{ij} \cdot dx_i dx_j; \quad d^2 S^y = \sum_i \sum_j L_{ij} \cdot dy_i dy_j \quad (16)$$

(see: [2]).

b. y_i 's are homogeneous first order functions of x_i 's [4]:

$$y_i(kx_1, kx_2, \dots, kx_n) = ky_i(x_1, x_2, \dots, x_n). \quad (17)$$

The relationship is not invertable now:

$$\sum_i x_i \cdot dy_i = 0. \quad (18)$$

That means the quantities y_i are not independent of each other.

In this case,

$$S^x = \sum_i y_i x_i = S. \quad (19)$$

This example is realized in the thermostatics.

Here

$$X_i = E_i \quad (\text{extensities})$$

$$y_i = F_i \quad (\text{entropic intensities})$$

$$S^x = S \quad (\text{entropy})$$

$$S = \sum_i F_i \cdot E_i$$

$$d^2 S = \sum_{i,j} \sum \left(\frac{\partial F_i}{\partial E_j} \right) \cdot dE_i dE_j \leq 0.$$

(The matrix of $(\partial F/\partial E)$ is negative semidefinit.) Now y_i 's are not independent:

$$\sum_i x_i dy_i = \sum_i E_i \cdot dF_i = 0 \quad (20)$$

which is the familiar Gibbs-Duhem relation.

c. The Lagrangian mechanical system with general coordinates

$$q_i \quad (i = 1, \dots, n).$$

Here,

$$x_i = \dot{q}_i \quad (\text{velocities})$$

$$S^x = L \quad (\text{the Lagrangian})$$

$$y_i = p_i = \partial L / \partial \dot{q}_i \quad (\text{the momenta})$$

$$S = \sum_i p_i \cdot \dot{q}_i$$

and

$$S^y = H(p_1, \dots, p_n).$$

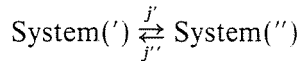
2. Thermokinetics, partial fluxes

Considering a system consisting of two homogeneous subsystems (denoted by system (')) and system (''), respectively), as known, thermodynamic forces (X_i) are regarded as differences of the appropriate potentials (F_i):

$$X_i = F_i'' - F_i' = \Delta F_i. \quad (21)$$

'Thermokinetics' is a theory based on the assumption that there exist partial fluxes j' and j'' so that the thermodynamic net fluxes J_i are given as differences as well:

$$J_i = j_i' - j_i'' = -\Delta j \quad (22)$$



It was proven [5–7] that the partial fluxes vary only with their own potentials:

$$j_i' = j_i'(F_1', F_2', \dots, F_n') \quad (i = 1, 2, \dots, n)$$

$$j_i'' = j_i''(F_1'', F_2'', \dots, F_n'') \quad (i = 1, 2, \dots, n).$$

The permeability properties of the wall separating system (')) and system ('')) are characterized by constant parameters of the $j(F)$ canonical rate equations. These parameters do not depend on the direction of the partial process.

The Law of Detailed Balancing claims that in equilibria

$$F_i' = F_i'' \quad (i = 1, 2, \dots, n)$$

and

$$j_i' = j_i'' \quad (i = 1, 2, \dots, n)$$

must be fulfilled simultaneously.

Consistently with the Law of D.B. one can conclude that

$$j'_i(F_1, \dots, F_n) = j''_i(F_1, \dots, F_n) \quad (23)$$

for every F . Therefore, the canonical constitutive functions must be the same for the two subsystems and we may omit ' and '' when we write the symbols of these functions.

In non-equilibrium values of j' and j'' may differ from each other:

$$j'_i = j_i(F'_1, F'_2, \dots, F'_n)$$

$$j''_i = j_i(F''_1, F''_2, \dots, F''_n).$$

An important example is the mass transport through an energy barrier E :

$$j_m = \text{const} \cdot T^n \cdot \exp(-E/RT) \cdot \exp(\mu/RT)$$

or in isothermal systems (denoting the entropic chemical potential $(-\mu/T)$ by F):

$$j_m = j_m^0(T) \exp(-F/R) \quad (24)$$

(See Figure 1).

Let us consider a small neighborhood of a given state (F_0) in which the constitutive functions $j(F)$ can be regarded as linear.

Then

$$\Delta j_i = \sum_k \left(\frac{\partial j_i}{\partial F_k} \right)_0 \cdot \Delta F_k = -J_i. \quad (25)$$

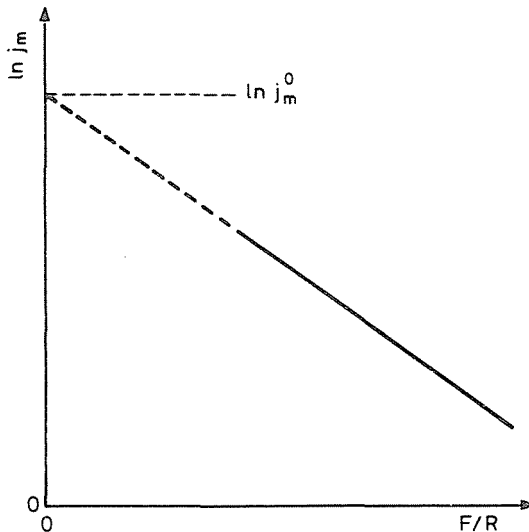


Fig. 1. A typical mass flux versus entropic chemical potential plot

Superscripts ' and '' are by virtue of (23) omitted. (25) shows that the linear phenomenological laws

$$J_i = \sum_k L_{ik} \cdot X_k \quad (26)$$

are now valid and the phenomenological coefficients can be interpreted as

$$L_{ik} = - \left(\frac{\partial j_i}{\partial F_k} \right)_0 \quad (27)$$

In thermokinetics, Onsager's reciprocity relations are reformulated as

$$\left(\frac{\partial j_i}{\partial F_k} \right) = \left(\frac{\partial j_k}{\partial F_i} \right) \quad (28)$$

Here we must stress that j 's mean here partial and not net fluxes (J). Similarly, F 's are potentials and not forces (X)! j 's and F 's equalize but do not vanish in equilibria, in contrast with J 's and X 's. (27) is one of the fundamental relations of the Thermokinetics. From our example (24) follows:

$$L = -(\partial j / \partial F) = j/R \quad (29)$$

which shows the interesting feature that L is proportional to j .

3. The Entropy Dissipation

The symmetry relations (28) of Thermokinetics allow to introduce new fundamental quantities called Entropy Dissipation Functions D_S , D_S^F , D_S^j .

The function D_S is defined as

$$D_S(j, F) = \sum_i j_i \cdot F_i \quad (30)$$

Its differential is

$$dD_S = \sum_i j_i \cdot dF_i + \sum_i F_i \cdot dj_i \quad (31)$$

where both sums on the right side are exact differentials of two quantities D_S^F and D_S^j , respectively.

$$\left(\frac{\partial D_S^F}{\partial F_i} \right) = j_i \quad (32)$$

$$\left(\frac{\partial D_S^j}{\partial j_i} \right) = F_i \quad (33)$$

and

$$\left(\frac{\partial^2 D_S^F}{\partial F_i \partial F_k}\right) = -L_{ik} \tag{34}$$

$$\left(\frac{\partial^2 D_S^j}{\partial j_i \partial j_k}\right) = -L_{ik}^{-1} \tag{35}$$

where L_{ik}^{-1} denote the elements of the inverse matrix of L . Note that relations $j_i(F_1, \dots, F_n)$ are, in general, nonlinear.

In the simple case of (24) (see Fig. 2)

$$j = j^0 \cdot \exp(-F/R); \quad F = -R \cdot \ln\left(\frac{j}{j^0}\right) \tag{36}$$

and

$$dj = -\frac{j}{R} \cdot dF; \quad dF = -R \cdot d \ln j \tag{37}$$

the differentials of the Entropy Dissipation Functions are:

$$dD_S^F = -R \cdot dj \tag{38}$$

$$dD_S^j = -R \cdot \ln\left(\frac{j}{j^0}\right) \cdot dj. \tag{39}$$

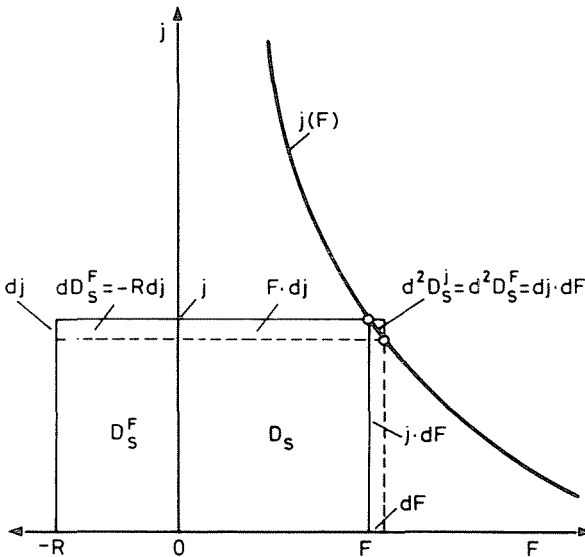


Fig. 2. Entropy Dissipation Functions and their differentials at a given value of F calculated from rate equation $j = j^0 \exp(-F/R)$

Their integrals, assuming that $D_S^F = D_S^j = 0$ if $j = 0$, are the following (see Fig. 3):

$$D_S^F = -R \cdot j \quad (40.a.)$$

$$D_S^j = j \cdot (R + F) \quad (40.b.)$$

$$dD_S = R \cdot \ln j^0 \cdot dj - R \cdot d(j \cdot \ln j) \quad (41)$$

$$D_S = j \cdot (\Psi^0 - R \cdot \ln j) \quad (42)$$

where

$$\Psi^0 = R \cdot \ln j^0 \quad (43)$$

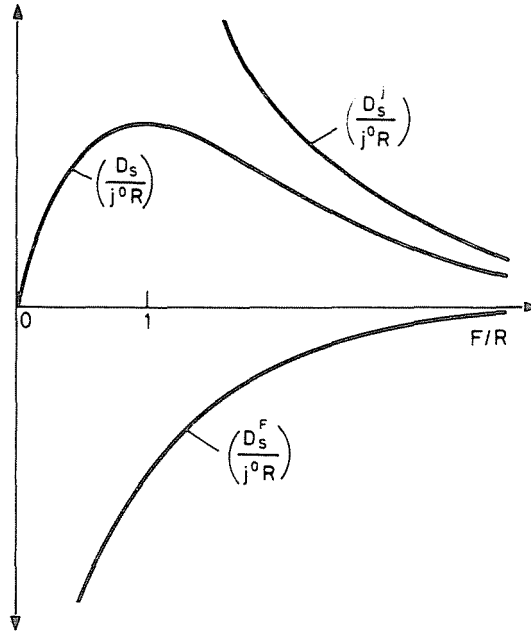


Fig. 3. Entropy Dissipation Functions versus entropic chemical potential

which reminds us to the k 'th "chemical potential-term" of the entropy:

$$x_k \cdot (-\mu_k/T) = -x_k \cdot (\mu_k^0/T + R \cdot \ln x_k)$$

where x_k denotes the k 'th mole fraction.

The second differentials are, by virtue of (9) and (10)

$$d^2 D_S^F = \sum_i dj_i \cdot dF_i = d^2 D_S^j \quad (44)$$

and

$$d^2 D_S = 0. \quad (45)$$

We postulate—temporarily—that the second differentials in (44) are non-positive

$$d^2 D_S^F = d^2 D_S^j \leq 0 \quad (46)$$

for example

$$j_i \cdot \dot{F}_i \leq 0 \quad (47)$$

(46) means that the canonical rate equations have the properties as follows: the j_i partial fluxes are monotonic decreasing functions of the F_i 's (see Fig. 2). For example, the mass partial flux j increases if $F = -\mu/T$ decreases, i.e. the concentration increases.

Calculating with (24) and (36)

$$d^2 D_S^F = d^2 D_S^j = -R \frac{(dj)^2}{j} \leq 0. \quad (48)$$

4. Entropy Dissipation and Entropy Production

Up to this point we have dealt mainly with equilibrium systems. As usual, in nonequilibrium open systems the rate of change of the entropy (\dot{S}) can be written as sum of an external (\dot{S}_{ext}) and of an internal (\dot{S}_{int}) part [8–9]:

$$\dot{S} = \dot{S}_{\text{ext}} + \dot{S}_{\text{int}} \quad (\text{open system}) \quad (49)$$

where \dot{S}_{ext} is the entropy flux due to processes between the system and its surroundings. Considering an isolated system \dot{S}_{ext} vanishes and the entropy change reduces to the internal one:

$$\dot{S} = \dot{S}_{\text{int}} = P_S \geq 0 \quad (\text{closed system}). \quad (50)$$

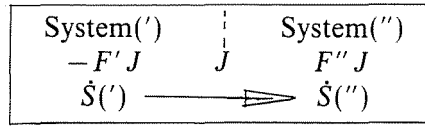
This part of the change is called “Entropy Production” (P_S), an important thermodynamic quantity being always positive in non-equilibrium systems and equal to zero only in equilibria. Regarding the most simple non-equilibrium system consisting of two subsystems System(′) and System(″), separated with a permeable wall and denoting the i 'th extensity by E_i

$$\begin{aligned} \dot{S}(′) &= \sum_i \dot{E}_i' \cdot F_i' = -\sum_i J_i \cdot F_i' \\ \dot{S}(″) &= \sum_i \dot{E}_i'' \cdot F_i'' = \sum_i J_i \cdot F_i'' \end{aligned} \quad (51)$$

We have taken the fluxes J_i positive in the direction System(′) → System(″).

The Entropy Production is the sum of the internal entropy gains

$$P_S = \dot{S}(') + \dot{S}('') = \sum_i J_i \cdot (F_i'' - F_i') = \sum_i J_i \cdot X_i \quad (52)$$



Taking into account that the net fluxes can be regarded as differences (see eqn. 22), the Entropy Production can be written as a sum of four contributions of the overall entropy change each of them being an Entropy Dissipation.

$$\dot{S}_{int} = P_S = \sum_i (j_i' - j_i'') \cdot (F_i'' - F_i') = - \sum_i \Delta j_i \cdot \Delta F_i. \quad (53)$$

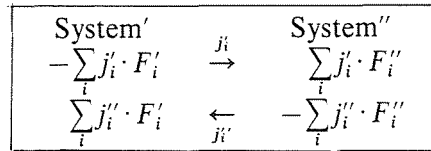
The physical meanings of these dissipation terms are the rate of change of the entropy:

$$\sum_i j_i' \cdot F_i' = D_S(j', F') = -\dot{S}_{11} \quad (\text{in System}' \text{ due to } j')$$

$$\sum_i j_i' \cdot F_i'' = D_S(j', F'') = \dot{S}_{12} \quad (\text{in System}'' \text{ due to } j')$$

$$\sum_i j_i'' \cdot F_i' = D_S(j'', F') = \dot{S}_{21} \quad (\text{in System}' \text{ due to } j'')$$

$$\sum_i j_i'' \cdot F_i'' = D_S(j'', F'') = -\dot{S}_{22} \quad (\text{in System}'' \text{ due to } j'')$$



The two terms in (52) can be interpreted as

$$\begin{aligned} \sum_i F_i' \cdot J_i &= \sum_i F_i' \cdot (j_i' - j_i'') = \\ &= - \int_{j'}^{j''} dD_S^j = D_S^j(j', F') - D_S^j(j'', F'') = - \Delta_j' D_S^j \\ \sum_i F_i'' \cdot J_i &= \sum_i F_i'' \cdot (j_i' - j_i'') = \\ &= - \int_{j'}^{j''} dD_S^j = D_S^j(j', F'') - D_S^j(j'', F'') = - \Delta_j'' D_S^j \\ P_S &= \Delta_j' D_S^j - \Delta_j'' D_S^j = - \Delta_F (\Delta_j D_S^j). \end{aligned} \quad (54)$$

The four contributions can be arranged in another way. In the extreme case if j_i'' can be neglected beside j_i' (e.g. "initial" rate of a chemical process), the "forward initial" entropy production is given as

$$\begin{aligned} \sum_i j_i' \cdot X_i &= \sum_i j_i' \cdot (F_i'' - F_i') = \\ &= \int dD_S^F = D_S^F(', '') - D_S^F(', ') = \Delta_F' D_S^F \end{aligned}$$

The "backward initial" entropy production is in a similar way

$$\begin{aligned} \sum_i j_i'' \cdot X_i &= \sum_i j_i'' \cdot (F_i'' - F_i') = \\ &= \int dD_S^F = D_S^F('', ') - D_S^F('', '') = \Delta_F'' D_S^F. \end{aligned}$$

The overall entropy production is equal to the difference of the differences above:

$$P_S = \Delta_F' D_S^F - \Delta_F'' D_S^F = -\Delta_j (\Delta_F D_S^F). \quad (55)$$

In the near-equilibrium limiting case,

$$\begin{aligned} F' &= F \\ F'' &= F + dF \\ j' &= j \\ j'' &= j + dj \end{aligned}$$

the relations between the Entropy Production and the Entropy Dissipation Functions are

$$P_S = -\sum_i dj_i \cdot dF_i = -d^2 D_S^F = -d^2 D_S^j \geq 0 \quad (56)$$

which means that inequality (46) is consistent with the positivity of the Entropy Production.

The situations are visualized on Fig. 4. From the non-linear character of the canonical rate equations $j_i(F_1, \dots, F_n)$ one may draw an important conclusion. As in Fig. 4 it is demonstrated, in strongly non-linear cases the net rates ($J_i = -\Delta j_i$) are not unambiguous functions of the forces ($X_i = \Delta F_i$). Consequently, in such cases the concept "force" may be used only cautiously or is to be abandoned. Thus we recommend to calculate with F and j terms of Thermokinetics instead of X 's and J 's.

Matrix G may be regarded as second differential of the entropy and matrices $-L$ and $-L^{-1}$ as second differentials of the Entropy Dissipation

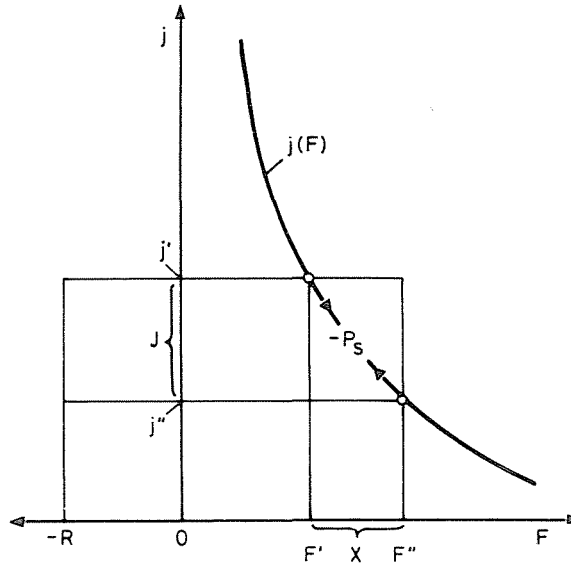


Fig. 4. Entropy production of a nonlinear system being far from equilibrium. A j - F plot

Functions D_S^F and D_S^j , respectively. Such as the existence of the entropy is consistent with Maxwell's symmetry relations, the existence of the Entropy Dissipation Functions are consistent with the symmetry relations of the Thermokinetics. Because of the lack of symmetry of matrix D no third kind of dissipation function can be found. (See the next page for matrix D .)

Both matrices are negative definite, consequently, the two analogous second differentials have to be nonpositive ones:

$$d^2 S = \sum_i dF_i \cdot dE_i \leq 0$$

$$d^2 D_S^j = d^2 D_S^F = \sum_i dj_i \cdot dF_i \leq 0.$$

If differential operator "d" means differentiation with respect to time (d/dt) the inequalities above take the form

$$d^2 S^t \equiv \sum_i \dot{F}_i \cdot \dot{E}_i \leq 0$$

$$d^2 D_S^t \equiv \sum_i j_i \cdot \dot{F}_i \leq 0$$

vanishing in steady states.

5. Entropy Dissipation in the Unified System of thermodynamical quantities

The Unified System which involves the fundamental quantities of the three thermodynamic disciplines—thermostatics, thermokinetics and non-equilibrium thermodynamics—can be set up on three set of quantities:

- the extensities (or densities) (E_i),
- the potentials (F_i) and
- the “traffics” (partial fluxes) (j_i).

Three set of constitutive relationships exist between them:

$$F_i \leftrightarrow E_i \quad (\text{state eqns of thermostatics})$$

$$j_i \leftrightarrow F_i \quad (\text{“canonical” rate eqns})$$

$$j_i \leftrightarrow E_i \quad (\text{non-canonical rate eqns})$$

(See Figs 5 and 6, upper part).

The differentials of these quantities (Figure 5, lower part) form three sets

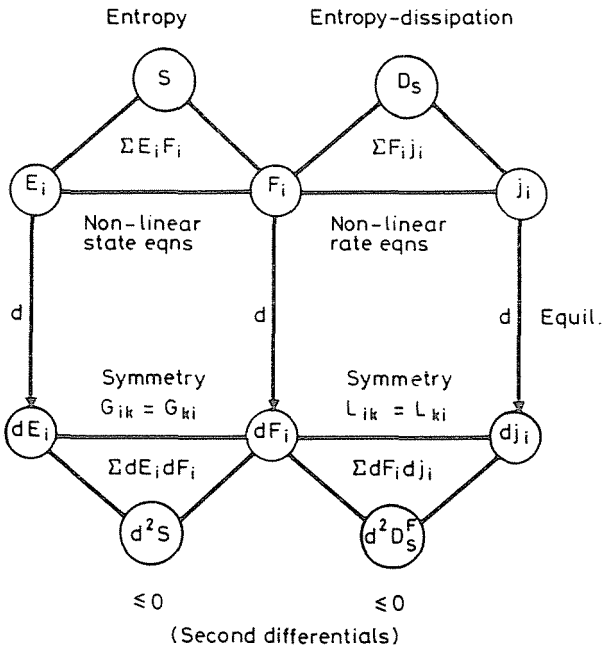


Fig. 5. Unified system of thermodynamic quantities and their differentials

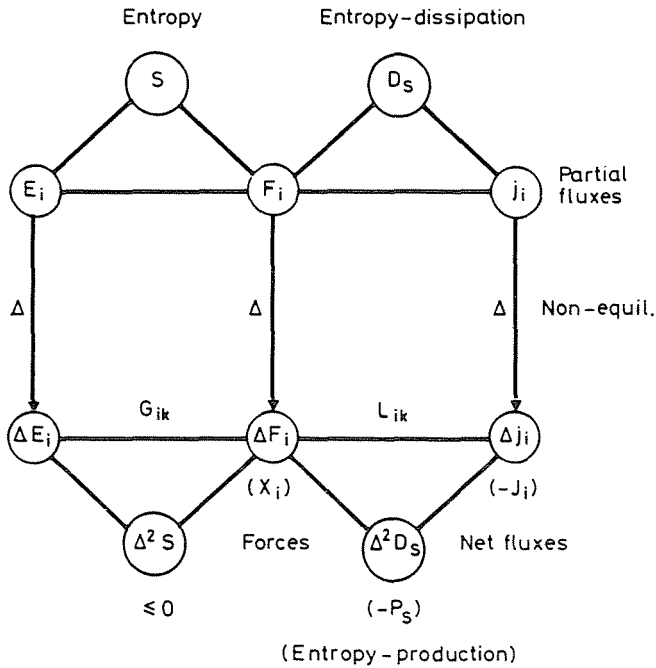


Fig. 6. Unified system of thermodynamic quantities and their differences

of perfect differentials:

$$dF_i = \sum_k G_{ik} \cdot dE_k \quad G_{ik} = G_{ki} \text{ (Maxwell)}$$

$$dj_i = - \sum_k L_{ik} \cdot dF_k \quad -L_{ik} = -L_{ki} \text{ (Onsager—Oláh)}$$

$$dj_i = \sum_k D_{ik} \cdot dE_k$$

where

$$D = -L \cdot G.$$

In non-equilibria, instead of differentials, differences can be introduced between properties of two phases (see Fig. 6, lower part).

These differences mean

ΔE_i : deviations from equilibria,

$X_i = \Delta F_i$: "forces"

$-J_i = \Delta j_i$: "net" fluxes

$$\Delta^2 S \equiv \sum_i \Delta F_i \cdot \Delta E_i \leq 0$$

$$\Delta^2 D_s \equiv \sum_i \Delta j_i \cdot \Delta F_i \leq 0.$$

Close to equilibria (Onsager's linear theory) $\Delta \rightarrow d$ and the relationships to the differences are the same as the appropriate relationships to the differentials.

Far from equilibria both forces and net fluxes may be defined though no unique relationship exists between them. In this case the Entropy Production cannot be expressed as a function of the forces alone (or of the net fluxes alone), but only with potentials and partial fluxes in the sense of (53), using quantities of Thermokinetics instead of ones of the classical non-equilibrium thermodynamics.

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