

4 Chapter 4: General Statements Concerning Entropy Production and rates of Irreversible Processes

$$\frac{d_i S}{dt} = \sum_k J_k X_k > 0 \quad (1)$$

Eg., entropy production due to a chemical reaction

$$\frac{d_i S}{dt} = J_{ch} X_{ch} \quad J_{ch} = v, \quad X_{ch} = \frac{A}{T} \quad (2)$$

Uniqueness of flows and forces?

Consider system in which two isomerizations take place



Corresponding affinities

$$A_1 = \mu_A - \mu_B, \quad A_2 = \mu_B - \mu_C \quad (4)$$

Change per unit time of the mole numbers

$$\frac{dn_A}{dt} = -v_1; \quad \frac{dn_B}{dt} = v_1 - v_2; \quad \frac{dn_C}{dt} = v_2 \quad (5)$$

Corresponding entropy production;

$$T \frac{d_i S}{dt} = A_1 v_1 + A_2 v_2 > 0 \quad (6)$$

Chemical changes could equally well be described by



which are linear combinations of (3). New affinities

$$A'_1 = \mu_A - \mu_C = A_1 + A_2 \quad (8)$$

$$A'_2 = \mu_B - \mu_C = A_2 \quad (9)$$

For corresponding changes of mole numbers

$$\frac{dn_A}{dt} = -v'_1; \quad \frac{dn_B}{dt} = -v'_2; \quad \frac{dn_C}{dt} = v'_1 + v'_2 \quad (10)$$

Comparing eqn. (5) with (10) give

$$v_1 = v'_1 \quad (11)$$

$$v_2 = v'_1 + v'_2 \quad (12)$$

Note that the transformation law for the reaction rates is complementary to that for the affinities such that the entropy production remains invariant

$$T \frac{d_i S}{dt} = A_1 v_1 + A_2 v_2 = A'_1 v'_1 + A'_2 v'_2 \quad (13)$$

From a thermodynamic point of view, therefore, the descriptions of the reactions are *equivalent* and such systems are called *equivalent systems*.

Generalization:

Can introduce a new set of forces X'_k which are linear combinations of the old ones, and a new set of flows J'_k chosen in such a way that the entropy production remains invariant

$$\sum_k J_k X_k = \sum_k J'_k X'_k \quad (14)$$

The description (J_k, X_k) is macroscopically equivalent to that in terms of (J'_k, X'_k) .

Alternatively, could choose a new set of J'_k which are linear combinations of the old ones, and then determine the new X'_k in order to satisfy eqn. (14).

Eg.

Consider entropy production due to heat flow and diffusion of matter.

$$d_i S = d_i^I \phi \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) - \sum_\gamma \left(\frac{\mu_\gamma^I}{T^I} - \frac{\mu_\gamma^{II}}{T^{II}} \right) d_e n_\gamma^I \quad (15)$$

then

$$\frac{d_i S}{dt} = JX + \sum_\gamma J_\gamma X_\gamma \quad (16)$$

with

$$J = -\frac{d_i^I \phi}{dt} = \frac{d_i^{II} \phi}{dt}; \quad J_\gamma = -\frac{d_e n_\gamma^I}{dt} = \frac{d_e n_\gamma^{II}}{dt} \quad (17)$$

$$X = \frac{1}{T^{II}} - \frac{1}{T^I} = \Delta \left(\frac{1}{T} \right); \quad X_\gamma = -\left(\frac{\mu_\gamma^{II}}{T^{II}} - \frac{\mu_\gamma^I}{T^I} \right) = -\Delta \left(\frac{\mu_\gamma}{T} \right) \quad (18)$$

Now introduce new fluxes

$$J' = J - \sum_\gamma h_\gamma J_\gamma \quad (19)$$

$$J'_\gamma = J_\gamma \quad (20)$$

Using the invariance relation

$$JX + \sum_\gamma J_\gamma X_\gamma = J'X' + \sum_\gamma J'_\gamma X'_\gamma \quad (21)$$

one can show that

$$X' = X = \Delta \left(\frac{1}{T} \right) \quad (22)$$

$$X'_\gamma = X_\gamma + h_\gamma X = -\Delta \left(\frac{\mu_\gamma}{T} \right) + h_\gamma \Delta \left(\frac{1}{T} \right) \quad (23)$$

Using

$$\Delta \left(\frac{x}{y} \right) = \frac{\partial(x/y)}{\partial x} \Delta x + \frac{\partial(x/y)}{\partial y} \Delta y \quad (24)$$

can show that

$$\Delta \left(\frac{\mu_\gamma}{T} \right) = \frac{\partial(\mu_\gamma/T)}{\partial T} \Delta T + \frac{(\Delta \mu_\gamma)_T}{T} \quad (25)$$

and using eqn. (4.22), X'_γ becomes

$$X'_\gamma = -\frac{(\Delta\mu_\gamma)_T}{T} \quad (26)$$

Use of the forces X' , X'_γ has the advantage over the set X , X_γ is that it is well defined numerically while X_γ , still containing h_γ (see eqn. (25) and (4.22)) contains an arbitrary additive constant (see 3.16).

4.1 Rates and Affinities (Flows and Forces)

In thermodynamic equilibrium

$$J_k = 0 \quad \text{and} \quad X_k = 0 \quad (27)$$

Presume that close to equilibrium we have a linear relation between the forces and the flows, eg. Fourier's law for heat flow or Fick's law for diffusion.

Linear laws of this kind called *phenomenological relations*. There is no thermodynamic basis for this presumption. Evidence is empirical.

Eg. Consider case of two simultaneous irreversible processes;

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (28)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \quad (29)$$

L_{ik} are called the *phenomenological coefficients*. L_{ii} may represent the heat conductivity coefficient, the diffusion constant, electrical conductivity, etc. L_{ik} with ($i \neq k$) describe the *interference* of two irreversible processes. Eg. if the two processes are thermal conductivity and diffusion, then L_{ik} is connected with thermodiffusion (appearance of a concentration gradient in an initially homogeneous mixture under the influence of a temperature gradient). L_{ik} are called *interference coefficients*.

Using eqns. (29) in the entropy production gives,

$$\frac{d_i S}{dt} = L_{11}X_1^2 + (L_{12} + L_{21})X_1X_2 + L_{22}X_2^2 > 0 \quad (30)$$

Above has to be positive for all negative or positive values of the variables X_1 , X_2 .

Show that this implies that;

$$L_{11} > 0, \quad L_{22} > 0 \quad (31)$$

and

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22} \quad (32)$$

Hence, the "proper" phenomenological coefficients (L_{11} and L_{22}) are positive. The "mutual" coefficients (L_{12} and L_{21}) may be positive or negative, only their magnitude being limited by eqn. (32).

In agreement with experimental observation that thermal conductivity or electrical conductivity are always positive, while the thermodiffusion coefficient has no definite sign.

Theorem concerning the “mutual” coefficients L_{ik} .
Reciprocity relations of Onsager (1931)

$$L_{ik} = L_{ki} \quad (i, k = 1 \dots n) \quad (33)$$

When the flow, corresponding to the irreversible process i , is influenced by the force X_k of the irreversible process k , then the flow k is also influenced by the force X_i through the same interference coefficient L_{ik} .

Proof based on “fluctuation theory” and *microscopic reversibility* of mechanical equations of motion (see Prigogine). Only demonstrated in conditions of thermodynamic equilibrium.

4.2 Symmetry Requirements on Coupling of Irreversible Processes

Now specify which irreversible processes are capable of mutual interference.

Consider system without thermal diffusion but with heat flow along a geometrical coordinate x and subject at the same time to a chemical reaction.

$$\sigma = -\frac{W_x}{T^2} \frac{\partial T}{\partial x} + \frac{Av_v}{T} > 0 \quad (34)$$

The phenomenological relations are

$$W_x = -\frac{L_{th}}{T^2} \frac{\partial T}{\partial x} + L_{12} \frac{A}{T} \quad (35)$$

$$v_v = -\frac{L_{21}}{T^2} \frac{\partial T}{\partial x} + L_{ch} \frac{A}{T} \quad (36)$$

A first reduction in the number of phenomenological coefficients can be obtained by applying Onsager's reciprocity relations $L_{12} = L_{21}$. However, we can show that in fact $L_{12} = L_{21} = 0$:
Suppose that $\partial T / \partial x = 0$, then

$$W_x = L_{12} \frac{A}{T} \quad (37)$$

so that the scalar cause A/T would produce a vectorial effect W_x . Contrary to the general requirements of symmetry principles: Curie's symmetry principle – macroscopic causes always have fewer elements of symmetry than the effects they produce.

Chemical affinity cannot produce a directed flow of heat and the interference coefficient must necessarily be zero.

In this case, the different irreversible processes must separately both be positive, ie.,

$$-\frac{W_x}{T^2} \frac{\partial T}{\partial x} > 0, \text{ and } \frac{Av_v}{T} > 0 \quad (38)$$