

Kinetics of Materials and Linear Irreversible Thermodynamics

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Based on:

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Linear Irreversible Thermodynamics (LIT), coupling between forces and fluxes.

The first law of thermodynamics is a consequence of the existence of a conserved internal energy¹ and is well understood. Contrary, the origins of the entropy are not well known and its existence as a state function is explained as a consequence of the second law of thermodynamics.² To consider the irreversible processes, LIT, one has to introduce also the fundamental concept of local equilibrium [2]. In the following we will derive basic relations of LIT.

The foundation of the classical thermodynamics form the concepts of the internal energy conservation and of the entropy. They are combined in the fundamental canonical equation of thermodynamics (CET):

$$U = U(S, \Omega, m_1, \dots, m_r). \quad (1)$$

where U , S , Ω and m_1, \dots, m_r are the overall internal energy, entropy and mass of the components.

1. INTERNAL ENERGY.

We begin with derivation of the Gibbs relations. To compute the changes of the internal energy of the mixture we differentiate the CET, Eq. (1), and the differential form of the Gibbs equation and definitions of pressure, temperature and chemical potential follow:

$$dU = TdS - pd\Omega + \sum_i \mu_i^{ch} dm_i \quad [kgm^2/s^2], \quad (2)$$

where the term in the brackets shows the dimension of the equation. Note, that above equation does not imply that system is closed, i.e., the energy, volume and the mass of components may depend on time. Chemical potential, μ_i^{ch} , depends upon the energetics of the chemical interactions that occur when a i -component (particle or atom) is added to the system and can be expressed as a general function of the components mass or molar fraction:

$$\mu_i^{ch} = \mu_i^0 + RT \ln(\gamma_i N_i), \quad (3)$$

$$\mu_i^{ch} = \mu_i^0 + RT \ln(\gamma_i^m N_i^m) \quad (4)$$

where $N_i = n_i / \sum_i n_i$ and $N_i^m = m_i / \sum_i m_i$ are the molar and mass fractions respectively. The activity coefficients γ_i and γ_i^m generally depend on respective fractions but, according to Raoult's law, are approximately equal one for pure substances: $N_i^m = N_i^M = 1$.

One can integrate Eq. (2) and obtain the integral form of Gibbs relation:

$$U = TS - p\Omega + \sum_i \mu_i^{ch} m_i \quad [kg m^2/s^2]. \quad (5)$$

Above equations are often sufficient in a case of equilibrium. The kinetic of the arbitrary processes implies the changes at every point of the system (i.e., in its every elementary volume). Thus, all variables depend on the time and position and one has to reformulate Eqs. (2) – (5). The all extensive variables (U, S, Ω, m_i) must now be expressed by their volume

¹The numerical values of a system's energy are always specified with respect to a reference energy.

²Despite numerous attempts, not much progress has been made in this area since Boltzmann. Arguments explaining the origins of entropy concept are provided by statistical mechanics, where the entropy is related to the number of microscopic states available at a fixed energy. A state-counting methods are known to compute entropy for a systems at equilibrium. However, no such method is generally available for the irreversible case discussed here.

densities (per unit volume) or by density per mass unit. The first form is helpful in description and understanding of the fluxes, the density per mass unit is useful in identification and computing of the forces and volume effects.

Gibbs relation expressed as the energy per mass unit. By replacing in Eq. (5): $U = mu$, $S = ms$, $\Omega = \Omega^m m$, where $m = \sum_i m_i$, the differential form of the Gibbs relation expressed as energy per mass unit becomes³:

$$du = Tds - p d\Omega^m + \sum_i \mu_i^{ch} dN_i^m, \quad (6)$$

$$u = Ts - p\Omega^m + \sum_i \mu_i^{ch} N_i^m, \quad (7)$$

where u , s , Ω^m and μ_i^{ch} are expressed as energy per mass unit.

We consider the multicomponent systems and it is convenient to express characteristic volume (volume per mass unit, Ω^m , or molar volume, Ω^M) by Euler relations [2,3], for example:

$$\Omega^m(N_1^m, \dots, N_r^m; p, T) = \sum_i \Omega_i^m(p, T) N_i^m. \quad (8)$$

The Euler relation, Eq. (8), allows to write integral form of the Gibbs relations in the form:

$$u = Ts - p \sum_i \Omega_i^m N_i^m + \sum_i \mu_i^{ch} N_i^m \quad (9)$$

or introducing the mechano chemical potential also:

$$u = Ts + \sum_i \mu_i N_i^m \quad \text{where} \quad \mu_i = \mu_i^{ch} - p\Omega_i^m. \quad (10)$$

The differential form of the Gibbs relation, Eq. (6), is expressed now by the following equivalent relations:

$$du = Tds - p d\left(\sum_i \Omega_i^m N_i^m\right) + \sum_i \mu_i^{ch} dN_i^m \quad (11)$$

or

$$du = Tds - p \sum_i N_i^m d\Omega_i^m + \sum_i \mu_i dN_i^m. \quad (12)$$

Gibbs relation expressed by energy density (per volume unit). By multiplying the Eq. (6)

by the overall density of mass, ρ , we obtain the densities of internal energy, $u^v = \rho u$, entropy, $s^v = \rho s$, and mass, $\rho_i = \rho N_i^m$:

$$\rho du = T \rho ds - p \rho d\Omega^m + \sum_i \mu_i^{ch} \rho dN_i^m. \quad (13)$$

³It is easy to show that Eq. (2) becomes: $d(mu) = Td(ms) - pd(\Omega^m m) + \sum_i \mu_i^{ch} d(mN_i^m)$.

By differentiation and dividing by overall mass we get:

$$du = Tds - p d\Omega^m + \sum_i \mu_i^{ch} dN_i^m - \left(u - Ts + p\Omega^m - \sum_i \mu_i^{ch} N_i^m\right) \frac{dm}{m} \quad \text{and}$$

$$du = Tds - p d\Omega^m + \sum_i \mu_i^{ch} dN_i^m - \left(U - TS + p\Omega - \sum_i \mu_i^{ch} m_i\right) \frac{dm}{m^2}. \quad \text{From integral form of the}$$

Gibbs relation, Eq. (4), the term in brackets equals zero and consequently we get:

$$du = Tds - p d\Omega^m + \sum_i \mu_i^{ch} dN_i^m.$$

Using identity ($d(xy) = xdy + ydx$) and subsequent rearranging results in:

$$du^v = Tds^v - pd(\Omega^m \rho) + \sum_i \mu_i^{ch} d\rho_i + (u - Ts + p\Omega^m - \sum_i \mu_i^{ch} N_i^m) d\rho, \quad (14)$$

$$du^v = Tds^v - pd(\Omega^m \rho) + \sum_i \mu_i^{ch} d\rho_i \quad (15)$$

which using the integral Gibbs and the Euler ($\Omega^m \rho = 1$) relations becomes:

$$du^v = Tds^v + \sum_i \mu_i^{ch} d\rho_i \quad (16)$$

or introducing Eq. (8) also

$$du^v = Tds^v - p \sum_i \rho_i d\Omega_i^m + \sum_i \mu_i d\rho_i. \quad (17)$$

Thus, from Eqs. (7) and (10) the integral forms of Gibbs relation are given by:

$$u^v = Ts^v - p + \sum_i \mu_i^{ch} \rho_i, \quad (18)$$

$$u^v = Ts^v + \sum_i \mu_i \rho_i. \quad (19)$$

Summary:

<p>Per mass unit: m^2/s^2</p> $u = Ts - p \sum_i N_i^m \Omega_i^m + \sum_i \mu_i^{ch} N_i^m$ $du = Tds - pd \sum_i N_i^m \Omega_i^m + \sum_i \mu_i^{ch} dN_i^m$ $du = Tds - p \sum_i N_i^m d\Omega_i^m + \sum_i \mu_i dN_i^m$ $0 = sdT - \Omega^m dp + \sum_i N_i^m d\mu_i^{ch}$	<p>Per volume unit: $kgm^{-1}s^{-2} = \frac{kgm^2}{s^2m^3}$</p> $u^v = Ts^v - p + \sum_i \mu_i^{ch} \rho_i$ $du^v = Tds^v + \sum_i \mu_i^{ch} d\rho_i$ $du^v = Tds^v - p \sum_i \rho_i d\Omega_i^m + \sum_i \mu_i d\rho_i$ $0 = s^v dT - dp + \sum_i \rho_i d\mu_i^{ch}$
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2. ENTROPY AND ENTROPY PRODUCTION

The entropy production (2nd law) must be always positive in an isolated system and leads to a inevitable coupling of the driving forces and corresponding fluxes that are present in a nonequilibrium system. In classical thermodynamics, the value of a system's entropy can be calculated by devising a reversible path from a reference state to the actual system's state⁴ and integrating $dS = Q^{rev} / T$ along that path. For a nonequilibrium system, a reversible path is generally unavailable.

To obtain a local quantification of entropy in a nonequilibrium material, we consider a continuous system that has gradients in temperature, chemical potential, and other intensive thermodynamic quantities. Fluxes of heat, mass, and other extensive quantities will result and proceed till the system approaches equilibrium. Assume that the system volume, $\Omega(t)$, can be divided into the finite number of sub-volumes in which the temperature, pressure, chemical potential, and other thermodynamic potentials can be reasonably accurate expressed by their average values. The local equilibrium assumption implies that the thermodynamic state of each cell is specified (thermalization occurs) and the Gibbs-Duheme relation holds (there is a balance of the local values of thermodynamic potentials). If local equilibrium holds (in such non-equilibrium system) for each sub-space, then the differential form of Gibbs's relation can be used to calculate changes in the local equilibrium states as a result of evolution of the spatial distribution of thermodynamic potentials. Especially in a case of solids it is convenient to generalize the work term in the differential form of Gibbs equation⁵, Eq. (15) and/or (17):

⁴Entropy can not be measured directly.

⁵To simplify the mathematics, from now on we pay no attention here to the volume effects caused by the pressure, the electric field, the surface tension etc. Such simplification is

$$du^v = Tds^v - dw + \sum_i \mu_i^{ch} d\rho_i, \quad (20)$$

dw is internal energy density change due to the work (other than chemical) in the elementary volume, i.e., dw is the work density.

The work density can include all types of (nonchemical) work likely for the system such as:

- the elastic work density caused by small-strain deformation: $dw = -\sum_k \sum_l \sigma_{kl} d\epsilon_{kl}$ (where σ_{kl} and ϵ_{kl} are the stress and strain tensors), which can be further separated into hydrostatic and deviatoric terms: $dw = Pd\Omega - \sum_k \sum_l \tilde{\sigma}_{kl} d\tilde{\epsilon}_{kl}$, where $\tilde{\sigma}$ and $\tilde{\epsilon}_{kl}$ are the deviatoric stress and strain tensors, respectively. The $Pd\Omega$ term represents a work of expansion/compression;
- the electrostatic potential work, $dw_i = -\varphi dq_i$, where φ is the electric potential $q_i = \rho_i Fz_i / M_i$ is the charge density, F, z_i and M_i denote the Faraday constant and the effective charge and the molar mass of i -component;
- the interfacial work, $dw = -\gamma dA$, in systems containing extensible interfaces (where γ is the interfacial energy density and A is the interfacial area);
- the magnetization work, $dw = -\vec{H} \cdot d\vec{b}$ (where \vec{H} is the magnetic field and \vec{b} is the total magnetic moment density, including the permeability of vacuum) and
- the electric polarization work, $dw = -\vec{E} \cdot d\vec{p}$ (where \vec{E} is the electric field given by $\vec{E} = -\text{grad} \varphi$ and \vec{p} is the total polarization density, including the contribution from the vacuum).

If the system can perform other types of work, one must introduce the necessary terms in Eq. (20). The generalized form of Gibbs relation is now:

$$du^v = Tds^v + \sum_j \psi_j d\xi_j, \quad (21)$$

where ψ_j is a j -th generalized intensive quantity and ξ_j its conjugate extensive quantity density⁶. The ψ_j may be scalar, vector, or, generally, tensor quantities; however, each product in Eq. (22) must be a scalar.

When electro-mechano-chemical processes in multicomponent ionic solid are concerned, the sum on r.h.s. of Eq. (21) reads

$$\sum_j \psi_j d\xi_j = -Pd\Omega + \sum_k \sum_l \tilde{\sigma}_{kl} d\tilde{\epsilon}_{kl} + \varphi \frac{Fz_1}{M_1} d\rho_1 + \dots + \varphi \frac{Fz_r}{M_r} d\rho_r + \mu_1^{ch} d\rho_1 + \dots + \mu_r^{ch} d\rho_r. \quad (22)$$

By introducing the electrochemical potential, $\mu_i = \mu_i^{ch} + \varphi Fz_i / M_i$, Eq. (22) becomes:

$$\begin{aligned} \sum_j \psi_j d\xi_j &= -Pd\Omega + \sum_k \sum_l \tilde{\sigma}_{kl} d\tilde{\epsilon}_{kl} + \sum_i \left(\mu_i^{ch} + \frac{Fz_i}{M_i} \varphi \right) d\rho_i \\ &= -Pd\Omega + \sum_k \sum_l \tilde{\sigma}_{kl} d\tilde{\epsilon}_{kl} + \sum_i \mu_i^{e-ch} d\rho_i \end{aligned} \quad (23)$$

The differential terms in (21) are the first-order approximations of the increase of the quantities at a point (in an elementary volume). Such changes may as well represent a quantity changes in time, t , at a given point and may also follow certain trajectory in space. Thus from (21) it follows for example:

allowed in the condensed phases and when density of respective energy field is low when compared with chemical term, for example the $p \sum_i \rho_i d\Omega_i^m$ term in Eq. (17).

⁶The generalized intensive and extensive quantities may be regarded as generalized potentials and displacements, respectively.

$$\text{grad } u^v = T \text{ grad } s^v + \sum_j \psi_j \text{ grad } \xi_j, \quad (24)$$

$$\frac{\partial u^v}{\partial t} = T \frac{\partial s^v}{\partial t} + \sum_j \psi_j \frac{\partial \xi_j}{\partial t}, \quad (25)$$

$$\left. \frac{Du^v}{Dt} \right|_v = T \left. \frac{Ds^v}{Dt} \right|_v + \sum_j \psi_j \left. \frac{D\xi_j}{Dt} \right|_v, \quad (26)$$

where $\left. \frac{Dy}{Dt} \right|_v = \frac{\partial y}{\partial t} + v \cdot \text{grad } y$, denotes the Lagrange derivative⁷ of quantity y .

The change in the overall molar entropy in the system, S , can be calculated by summing the entropies in each sub-space, s^v , i.e., by integrating over the entire system volume.⁸

Equation (21) was derived from the canonical equation of thermodynamics. As s , u , and the ξ_j are state variables, the **Gibbs relation holds if all quantities refer to a sub-volume under the local equilibrium assumption**. When s^v is considered as the dependent variable, from the Gibbs relation we get how s^v varies with changes in the independent variables, u and ξ_j :

$$ds^v = \frac{1}{T} du^v - \frac{1}{T} \sum_j \psi_j d\xi_j. \quad (27)$$

In equilibrium thermodynamics and when internal energy is fixed, the entropy maximization determines equilibrium. Entropy increase plays a central role in LIT where open systems and multivalued fields are often analyzed, e.g., electro-mechano-chemistry. Since energy, heat, and mass may flow during processes, they cannot be treated as isolated systems, and application of the second law must be generalized. Namely, must take account of the production and transport of entropy, e.g., by means of the components diffusion.

We now will consider entropy as a flowing quantity in a system (like energy, mass and charge). Mass, charge, and energy are conserved quantities and, if they are not formed by reactions, the basic form of the continuity equation holds: $\partial \rho_i / \partial t + \text{div}(\rho_i v_i) = 0$.

Entropy is not conserved as it can be created or destroyed locally (in the chemical reactions, by diffusion, etc). Entropy flux, J^s , and the consequences of entropy production are developed in the next section.

2.1. Entropy Production

The local rate of entropy creation per unit volume is denoted by A^s . The total rate of entropy production in a volume $\Omega(t)$ equals $\int_{\Omega(t)} A^s dx$, for example in an isolated (closed) system the

overall produced entropy is given by: $\frac{d}{dt} \int_{\Omega(t)} s^v dx = \int_{\Omega(t)} A^s dx$. However, in open system or

when we consider sub-space where transport processes occur, the entropy balance depends upon how much entropy is produced within it and upon how much entropy flows through its boundaries. By 2nd law of thermodynamics the overall entropy of the mass contained by $\Omega(t)$ is affected by the heat flow and the local entropy sources:

⁷When velocity of the point equals material drift velocity, $\left. \frac{D\rho_i}{Dt} \right|_{v^{drift}} = \frac{\partial \rho_i}{\partial t} + v^{drift} \cdot \text{grad } \rho_i$, the

Lagrange derivative is called material (or substantial) derivative.

⁸Note that s^v is the entropy of a sub-space (per elementary volume), S is the entropy of the entire system, and s is the entropy per mass unit.

$$\frac{d}{dt} \int_{\Omega(t)} s \rho \, dx = \int_{\Omega(t)} \left(A^s - \frac{1}{T} \operatorname{div} J_Q \right) dx, \quad (28)$$

where J^q denotes the heat flux, which is given by the proper constitutive formulae, $s^v = s\rho$ is the entropy density and A^s a sum of all local sources of entropy (due to friction, diffusion, etc.). Applying the continuity equation (Liouville theorem) Eq. (28) becomes:

$$\int_{\Omega(t)} \left(\frac{\partial s^v}{\partial t} + \operatorname{div}(s^v \nu^m) \right) dx = \int_{\Omega(t)} \left(A^s - \frac{1}{T} \operatorname{div} J_Q \right) dx \quad (29)$$

or

$$\int_{\Omega(t)} \left(\frac{\partial s \rho}{\partial t} + \operatorname{div}(s \rho \nu^m) \right) dx = \int_{\Omega(t)} \left(A^s - \frac{1}{T} \operatorname{div} J^q \right) dx. \quad (30)$$

Integrals in (29) and (30) can be omitted and the local entropy production rate at the fixed position equals [2]:

$$\frac{\partial s^v}{\partial t} + \operatorname{div}(s^v \nu^m) = A^s - \frac{1}{T} \operatorname{div} J_Q \quad (31)$$

$$\frac{\partial s \rho}{\partial t} + \operatorname{div}(s \rho \nu^m) = A^s - \frac{1}{T} \operatorname{div} J_Q. \quad (32)$$

Including the heat flux into the entropy flow term results in:

$$\frac{\partial s^v}{\partial t} + \operatorname{div} \left(\frac{J_Q}{T} + s^v \nu^m \right) = J_Q \cdot \operatorname{grad} \frac{1}{T} + A^s, \quad (33)$$

$$\frac{\partial s \rho}{\partial t} + \operatorname{div} \left(\frac{J_Q}{T} + s \rho \nu^m \right) = J_Q \cdot \operatorname{grad} \frac{1}{T} + A^s. \quad (34)$$

Using now the mass continuity, the equation (34) can be written as:

$$\rho \frac{\partial s}{\partial t} + \rho \nu^m \cdot \operatorname{grad} s + s \left(\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \nu^m) \right) + \operatorname{div} \frac{J_Q}{T} = A^s - \frac{1}{T^2} J_Q \cdot \operatorname{grad} T \quad (35)$$

and entropy production rate at the centre of mass position⁹ equals:

$$\rho \left. \frac{Ds}{Dt} \right|_{\nu^m} + \operatorname{div} \left(\frac{J_Q}{T} \right) = A^s + J_Q \cdot \operatorname{grad} \left(\frac{1}{T} \right). \quad (36)$$

In Eqs. (33), (34) and (36) we have shown that rate of entropy production does not depend on the frame of reference.

In order to quantify the local entropy production, A^s , in Eq. (36), we will now assume purely diffusional mass and energy transport¹⁰ and use the differential form of the Gibbs relation. From Eq. (21), the time derivative of entropy density in a cell is

$$\frac{\partial s^v}{\partial t} = \frac{1}{T} \frac{\partial u^v}{\partial t} - \frac{1}{T} \sum_j \psi_j \frac{\partial \xi_j}{\partial t}. \quad (37)$$

Using conservation principles (continuity equations) in Eq. (37),¹¹

⁹The point moving with the velocity of the local mass centre, ν^m .

¹⁰We neglect the thermal expansion, stresses and Kirkendall effect due to not balanced mass fluxes.

¹¹Here, all the extensive densities are treated as conserved quantities. This is not the general case. For example, polarization and magnetization density are not conserved. It can be shown that for nonconserved quantities, additional terms will appear on the right-hand side of Eq. (42).

$$\frac{\partial s^v}{\partial t} = -\frac{1}{T} \operatorname{div} J^u + \sum_j \frac{\psi_j}{T} \operatorname{div} J_j. \quad (38)$$

Because for a scalar a and a vector B we have the following identity:

$$\operatorname{div}(aB) = B \cdot \operatorname{grad} a + a \operatorname{div} B \quad (39)$$

and the Eq. (38) can be written

$$\frac{\partial s^v}{\partial t} + \operatorname{div} \left(\frac{J^u}{T} - \sum_j \frac{\psi_j}{T} J_j \right) = J^u \cdot \operatorname{grad} \frac{1}{T} - \sum_j J_j \cdot \operatorname{grad} \frac{\psi_j}{T}. \quad (40)$$

Comparison terms in Eqs. (33) and (40) allows identifying the entropy flux and entropy production:

$$J^s = \frac{1}{T} \left(J^u - \sum_j \psi_j J_j \right), \quad (41)$$

$$A^s = J^u \cdot \operatorname{grad} \frac{1}{T} - \sum_j J_j \cdot \operatorname{grad} \frac{\psi_j}{T}. \quad (42)$$

The entropy flux is related to the sum of all potentials multiplying their conjugate fluxes. The local entropy production is due to the heat flow and is produced by all fluxes, i.e., the every process of diffusive mass transport results in energy dissipation (heat is produced locally).

Internal energy and heat fluxes. Equation (42) can have more suitable form by introducing the flux of heat, J_Q . From the generalized form of the Gibbs relation, Eq. (21), we have

$$du^v = dQ^v + \sum_j \psi_j d\xi_j, \quad (43)$$

where dQ is the amount of heat transferred to an elementary volume and we have assumed the local equilibrium, $dQ^v = T ds^v$.

The time derivative of internal energy density in an unit volume is

$$du^v = dQ^v + \sum_j \psi_j d\xi_j \Rightarrow \frac{\partial u^v}{\partial t} = \frac{\partial Q^v}{\partial t} + \sum_j \psi_j \frac{\partial \xi_j}{\partial t}. \quad (44)$$

Using conservation principles (continuity equations) in Eq. (44) we get

$$\operatorname{div} J^u = \operatorname{div} J_Q + \sum_j \psi_j \operatorname{div} J_j. \quad (45)$$

Using the identity (39), Eq. (45) becomes

$$\operatorname{div} J^u = \operatorname{div} \left(J_Q + \sum_j \psi_j J_j \right) - \sum_j J_j \cdot \operatorname{grad} \psi_j. \quad (46)$$

The terms on r.h.s. denote the overall internal energy flux and work by the generalized forces. Thus, we may conclude that the overall internal energy flux when the local equilibrium condition holds is given by:

$$J^u = J_Q + \sum_j \psi_j J_j. \quad (47)$$

Combining Eqs. (42) and (47): $\begin{cases} A^s = J^u \cdot \operatorname{grad} T^{-1} - \sum_j J_j \cdot \operatorname{grad} (\psi_j / T), \\ J^u = J_Q + \sum_j \psi_j J_j, \end{cases}$ results in

$$A^s = J_Q \cdot \operatorname{grad} \frac{1}{T} - \frac{1}{T} \sum_j J_j \cdot \operatorname{grad} \psi_j. \quad (48)$$

2.2 Conjugated Forces and Fluxes

Multiplying Eq. (48) by T gives

$$TA^s = -\frac{J_Q}{T} \cdot \operatorname{grad} T - \sum_j J_j \cdot \operatorname{grad} \psi_j. \quad (49)$$

Every term on the right-hand side of Eq. (49) is the scalar product of a flux and a gradient of its conjugate force. Furthermore, each term has the same units as energy dissipation

density, $\text{J m}^{-3} \text{s}^{-1}$, and is a flux multiplied by a thermodynamic potential gradient. Each term that multiplies a flux in Eq. (49) is therefore a force for that flux. The paired forces and fluxes in the entropy production rate can be identified in Eq. (49) and are termed conjugate forces and fluxes. Basic examples are listed in Table 1 for heat, component i , and electric charge. These are Fourier's law of heat flow, a Nernst-Planck diffusion flux for mass diffusion at constant temperature¹², and Ohm's law for the electric current density at constant temperature. The mobility, B_i , is defined as the velocity of component i induced by a unit force, K is the thermal conductivity; B_i the i -component mobility and k_q the electrical conductivity.

Table 1: Selected conjugate forces, fluxes, and empirical diffusion constitutive relations (force-flux relations) for systems with unconstrained components, i .

Extensive Quantity	Flux	Conjugate Force	Constitutive flux equation
Heat	J_Q	$-\frac{1}{T} \text{grad } T$	Fourier's: $J_Q = -K \text{grad } T$
Component i	J_i^d	$-\text{grad } \mu_i^{ch}$	Nernst-Planck: $J_i^d = -B_i c_i \text{grad } \mu_i^{ch}$
Charge	J_q	$-\text{grad } \varphi = -\text{grad } V$	Ohm's: $J_q = -k_q \text{grad } \varphi$

These forces and fluxes have been defined as an unconstrained extensive quantities (i.e., the differential extensive quantities in Eq. (22) can vary independently). However, many systems have constraints relating changes in their extensive quantities, and these constrained cases are not analyzed here. Besides, we often assume; for simplicity, that the material is isotropic and that forces and fluxes are parallel. This assumption is not valid for anisotropic materials.

2.3. The Consequences of the Basic Postulate of Irreversible Thermodynamics.

The basic postulate of irreversible thermodynamics is that, near equilibrium; the local entropy production is nonnegative:

$$A^s \equiv \frac{\partial s}{\partial t} + \text{div } J^s \geq 0. \quad (50)$$

Using the empirical laws displayed in Table 1, the entropy production is easy to identify for an elementary process. For instance, if only heat flow is occurring, then, using Eq. (49) and Fourier's heat-flux law,

$$J_Q = -K \text{grad } T, \quad (51)$$

results in

$$TA^s = \frac{K |\text{grad } T|^2}{T}, \quad (52)$$

which predicts (because of Eq. (50)) that the thermal conductivity will always be positive.

If mass diffusion is the only operating process,

$$TA^s = \sum_i B_i c_i |\text{grad } \mu_i^{ch}|^2, \quad (53)$$

implying that each mobility must be always positive.

The local entropy production in a case of heat flow and pure diffusion of mass only.

From differential form of Gibbs equation we have:

¹²Under special circumstances, the Nernst-Planck flux reduces to the classical 1st Fick's law: $J_i^d = -D_i \text{grad } c_i$, where D_i is the mass diffusivity.

$$T \frac{\partial s^v}{\partial t} = \frac{\partial u^v}{\partial t} - \sum_i \mu_i^{ch} \frac{\partial \rho_i}{\partial t}.$$

Introducing the mass continuity and rearranging

$$\frac{\partial s^v}{\partial t} = -\frac{1}{T} \operatorname{div} J^u + \sum_i \left(\frac{\mu_i^{ch}}{T} \right) \operatorname{div} J_i^d,$$

$$\frac{\partial s^v}{\partial t} = -\operatorname{div} \frac{J^u}{T} + \sum_i \operatorname{div} \left(\frac{\mu_i^{ch}}{T} J_i^d \right) + J^u \cdot \operatorname{grad} \frac{1}{T} - \sum_i J_i^d \cdot \operatorname{grad} \frac{\mu_i^{ch}}{T},$$

$$\frac{\partial s^v}{\partial t} + \operatorname{div} \left(\frac{J^u}{T} - \sum_i \left(\frac{\mu_i^{ch}}{T} J_i^d \right) \right) = J^u \cdot \operatorname{grad} \frac{1}{T} - \sum_i J_i^d \cdot \operatorname{grad} \frac{\mu_i^{ch}}{T},$$

and by comparing with Eq. (33):

$$A^s = J^u \cdot \operatorname{grad} \frac{1}{T} - \sum_i J_i^d \cdot \operatorname{grad} \frac{\mu_i^{ch}}{T}. \quad (54)$$

The energy flux, Eq. (47), in the discussed case equals:

$$J^u = J_Q + \sum_i \mu_i^{ch} J_i^d \quad (55)$$

Combining relations (54) and (55) results in:

$$A^s = J_Q \cdot \operatorname{grad} \frac{1}{T} - \frac{1}{T} \sum_i J_i^d \cdot \operatorname{grad} \mu_i^{ch} \quad (56)$$

or

$$TA^s = -\frac{J_Q}{T} \cdot \operatorname{grad} T - \sum_i J_i^d \cdot \operatorname{grad} \mu_i^{ch}. \quad (57)$$

3 LINEAR IRREVERSIBLE THERMODYNAMICS (LIT)

In many materials, a gradient in temperature will produce not only a flux of heat but also a gradient in electric potential. This coupled phenomenon is called the thermoelectric effect. Coupling from the thermoelectric effect works both ways: if heat can flow, the gradient in electrical potential will result in a heat flux. That a coupling between different kinds of forces and fluxes exists is not surprising; flows of mass (atoms), electricity (electrons), and heat (phonons) all involve particles possessing momentum, and interactions may therefore be expected as momentum is transferred between them. A formulation of these coupling effects can be obtained by generalization of the previous empirical force-flux equations.

3.1 General Coupling between Forces and Fluxes

In general, the fluxes may be expected to be a function of all the driving forces acting in the system, F_j ; for instance, the heat flux J_Q can be a function of other forces in addition to its conjugate force F_Q ; that is,

$$J_Q = J_Q(F_Q, F_q, F_1, \dots, F_r).$$

Assuming that the system is near equilibrium and the driving forces are small, each of the fluxes can be expanded in a Taylor series near the equilibrium point $F_Q = F_q = F_1 = \dots = F_r = 0$. To first order:

$$\begin{aligned}
J_Q &= J_Q(F_Q, F_q, F_1, \dots, F_r) = \frac{\partial J_Q}{\partial F_Q} F_Q + \frac{\partial J_Q}{\partial F_q} F_q + \dots + \frac{\partial J_Q}{\partial F_r} F_r, \\
J_q &= J_q(F_Q, F_q, F_1, \dots, F_r) = \frac{\partial J_q}{\partial F_Q} F_Q + \frac{\partial J_q}{\partial F_q} F_q + \dots + \frac{\partial J_q}{\partial F_r} F_r, \\
&\vdots \\
J_r &= J_r(F_Q, F_q, F_1, \dots, F_r) = \frac{\partial J_r}{\partial F_Q} F_Q + \frac{\partial J_r}{\partial F_q} F_q + \dots + \frac{\partial J_r}{\partial F_r} F_r,
\end{aligned} \tag{58}$$

or in abbreviated form,

$$J_\alpha = \sum_\beta L_{\alpha\beta} F_\beta \quad \text{where} \quad \alpha, \beta = Q, q, 1, \dots, r, \tag{59}$$

and

$$L_{\alpha\beta} = \frac{\partial J_\alpha}{\partial F_\beta} \tag{60}$$

is evaluated at equilibrium ($F_\beta = 0$ for all β).¹³ In this approximation, the fluxes vary linearly with the forces.

In Eqs. (58) and (60), the diagonal terms, $L_{\alpha\alpha}$, are called direct coefficients; they couple each flux to its conjugate driving force. The off-diagonal terms are called coupling coefficients and are responsible for the coupling effects (also called cross effects) identified above.

Combining Eqs. (49) and (59) results in a relation for the entropy production that applies near equilibrium:

$$TA^s = \sum_\beta \sum_\alpha L_{\alpha\beta} F_\alpha F_\beta. \tag{61}$$

The connection between the direct coefficients in Eq. (59) and the empirical force-flux laws can be illustrated for heat flow. If a bar of pure material that is an electrical insulator has a constant thermal gradient imposed along it, and no other fields are present and no fluxes but heat exist, then according to Eq. (59) and Table 2.1,

$$J_Q = L_{QQ} \left(-\frac{1}{T} \text{grad } T \right). \tag{62}$$

Comparison with Eq. (51) shows that the thermal conductivity K is related to the direct coefficient L_{QQ} by

$$K = \frac{L_{QQ}}{T} \tag{63}$$

If the material is also electronically conducting, the general force-flux relationships are

$$J_Q = L_{QQ} F_Q + L_{Qq} F_q, \tag{64}$$

$$J_q = L_{qQ} F_Q + L_{qq} F_q. \tag{65}$$

If a constant thermal gradient is imposed and no electrically conductive contacts are made at the ends of the specimen, the heat flow is in a steady state and the charge-density current must vanish. Hence $J_q = 0$ and a force

¹³ Note that the fluxes and forces are written as scalars, consistent with the assumption that the material is isotropic. Otherwise, terms like $J_Q = \frac{\partial J_Q}{\partial F_Q} F_Q$ must be written as rank-two tensors multiplying vectors, and the equations that result can be written as linear relations.

$$F_q = \frac{L_{qQ}}{L_{qq}} F_Q \quad (66)$$

will arise. The existence of the force F_q indicates the presence of a gradient in the electrical potential, $\nabla\Phi$, along the bar. Therefore, using Eqs. (66) and (64),

$$J_Q = \left[L_{QQ} - \frac{L_{Qq}L_{qQ}}{L_{qq}} F_Q \right] F_Q = - \left[\frac{L_{QQ}}{T} - \frac{L_{Qq}L_{qQ}}{TL_{qq}} F_Q \right] \text{grad } T = -K \text{grad } T. \quad (67)$$

In such a material under these conditions, Fourier's law again pertains, but the thermal conductivity K depends on the direct coefficient L_{QQ} , as in Eq. (63), as well as on the direct and coupling coefficients associated with electrical charge flow. In general, the empirical conductivity associated with a particular flux depends on the constraints applied to other possible fluxes.

3.2 Force-Flux Relations when Extensive Quantities are Constrained

In many cases, changes in one extensive quantity are coupled to changes in others. This occurs in the important case of substitutional components in a crystal devoid of sources or sinks for atoms, e.g., dislocations, pores, etc. We do consider here the components that are constrained to lie on a fixed network of sites (i.e., the crystal structure), where each site is always occupied by one of the components of the system. Whenever one component leaves a site, it must be replaced. This is called a network constraint (i.e., lattice sites conservation). For example, in the case of substitutional diffusion by a vacancy-atom exchange mechanism, the vacancies are one of the components of the system; every time a vacancy leaves a site, it is replaced by an atom. As a result of this replacement constraint, the fluxes of components are not independent of one another.

This type of constraint will be nonexistent in amorphous materials because the components can be added/removed anywhere in the material without exchanging with any other components. The dN_i will also be independent for interstitial solutes in crystalline materials that lie in the interstices between larger substitutional atoms, as, for example, carbon atoms in body-centered cubic (b.c.c.) Fe. In such a system; carbon atoms can be added or removed independently in a dilute solution.

When a network constraint is present,

$$\sum_i dN_i = 0. \quad (68)$$

Solving Eq. (68) for dN_r and putting the result into Eq. (20) yields

$$Tds = du + dw - \sum_{i=1}^{r-1} (\mu_i^{ch} - \mu_r^{ch}) dc_i \quad (69)$$

Starting with Eq. (69) instead of Eq. (20) and repeating the procedure that led to Eq. (49), the conjugate force for the diffusion of i -component in a network-constrained crystal takes the new form

$$F_i = -\text{grad}(\mu_i^{ch} - \mu_r^{ch}). \quad (70)$$

The conjugate force for the diffusion of a network-constrained i -component depends now upon the gradient of the difference between the chemical potential of i -component and r -component rather than on the chemical potential gradient of i -component alone. If in the case of substitutional diffusion by the vacancy exchange mechanism, the vacancies are taken as the component N_r , the driving force for i -component depends upon the gradient of the difference between the chemical potential of i -component and that of the vacancies. The difference arises because, during migration, a site's state changes from occupancy by an atom of type i to occupancy by a vacancy. This result has been derived and extended by Larche and Cahn, who

investigated coherent thermomechanical equilibrium in multicomponent systems with elastic stress fields [4].

In the development above, the choice of the N_r -th component in a system under network constraint is arbitrary. However, the flux of each component in Eq. (59) must be independent of this choice [2,4]. This independence imposes conditions on the $L_{\alpha\beta}$ coefficients. To demonstrate, consider a three-component system at constant temperature in the absence of an electric field, where components A, B, and C correspond to $i = 1, 2,$ and $3,$ respectively. If component C is the N_r -th component, Eqs. (59) and (70) yield

$$\begin{aligned} J_A &= -L_{AA} \text{grad}(\mu_A^{ch} - \mu_C^{ch}) - L_{AB} \text{grad}(\mu_B^{ch} - \mu_C^{ch}), \\ J_B &= -L_{BA} \text{grad}(\mu_A^{ch} - \mu_C^{ch}) - L_{BB} \text{grad}(\mu_B^{ch} - \mu_C^{ch}), \\ J_C &= -L_{CA} \text{grad}(\mu_A^{ch} - \mu_C^{ch}) - L_{CB} \text{grad}(\mu_B^{ch} - \mu_C^{ch}). \end{aligned} \quad (71)$$

On the other hand, if B is the N_r -th component,

$$\begin{aligned} J'_A &= -L_{AA} \text{grad}(\mu_A^{ch} - \mu_B^{ch}) - L_{AC} \text{grad}(\mu_C^{ch} - \mu_B^{ch}), \\ J'_B &= -L_{BA} \text{grad}(\mu_A^{ch} - \mu_B^{ch}) - L_{BC} \text{grad}(\mu_C^{ch} - \mu_B^{ch}), \\ J'_C &= -L_{CA} \text{grad}(\mu_A^{ch} - \mu_B^{ch}) - L_{CC} \text{grad}(\mu_C^{ch} - \mu_B^{ch}). \end{aligned} \quad (72)$$

Because J_i must be the same as J'_i and the gradient terms are not necessarily zero, Eqs. (71) and (72) imply that

$$\begin{aligned} L_{AA} + L_{AB} + L_{AC} &= 0, \\ L_{BA} + L_{BB} + L_{BC} &= 0, \\ L_{CA} + L_{CB} + L_{CC} &= 0, \end{aligned} \quad (73)$$

or generally,

$$\sum_j L_{ij} = 0. \quad (74)$$

If the lattice network defines the coordinate system in which the fluxes are measured and lattice sites are conserved, the network constraint requires that

$$\sum_i J_i = 0 \quad (75)$$

and this imposes the further condition on the L_{ij} that

$$\sum_i L_{ij} = 0. \quad (76)$$

In other words, the sum of the entries in any row or column of the matrix L_{ij} is zero.

The conjugate forces and fluxes that are obtained when the only constraint is a network constraint are listed in Table 2. However, there are many cases where further constraints between the extensive quantities exist. For example, suppose that component 1 is a nonuniformly distributed ionic specie that has no network constraint. Each ion will experience an electrostatic force due to the local electric field, as well as a force due to the gradient in its chemical potential. This may be demonstrated in a formal manner by using Eq. (22), noting that dq_1 in this case is not independent of $d\rho_1$ but, instead, $dq_1 = \frac{Fz_1}{M_1} d\rho_1$, where Fz_1 is the electrical charge per mol assuming that all electric current is carried by ion showing z_1 -effective charge. Thus dq_1 and $d\rho_1$ can be combined as in Eq. (22) into a single term $\left(\mu_1^{ch} + \frac{Fz_1}{M_1} \varphi\right) d\rho_1$, and when this term is carried through the process leading to Eq. (49), the ion flux, J_1 , is found to be conjugate to an ionic force

$$F_1 = -\text{grad} \left(\mu_1^{ch} + \frac{Fz_1}{M_1} \varphi \right). \quad (77)$$

The potential that appears in the total force expression is the sum of the chemical potential and the electrical potential of the charged ion and is generally called the electrochemical potential. The other must be added to the chemical potential force if, for example, the particle possessed a magnetic moment and a magnetic field were present, etc.

Table 2: Conjugate Forces and Fluxes for Systems with Network-Constrained r -Components

Quantity	Flux	Conjugate Force
Heat	J_Q	$-\frac{1}{T} \text{grad } T$
Component i	J_i	$-\text{grad}(\mu_i^{ch} - \mu_r^{ch})$
Charge	J_q	$-\text{grad } \varphi$

3.3. The Diffusion Potential

Any potential that accounts for the storage of energy due to the addition of a component determines the driving force for the diffusion of that component. The sum of all such supplemental potentials, including the chemical potential, gives the total conjugate force for a diffusing component and is called the diffusion potential for that component and is represented by the symbol μ_i .¹⁴ The conjugate force for the flux of i -component will always have the form

$$F_i = -\text{grad } \mu_i, \quad (78)$$

For the case of electrochemical, mechano-chemical and electro-mechano-chemical potential expressed as energy per mol we have respectively,

$$\begin{aligned} \mu_i &= \mu_i^{ch} + Fz_i\varphi, \\ \mu_i &= \mu_i^{ch} - p\Omega_i^M, \\ \mu_i &= \mu_i^{ch} - p\Omega_i^M + Fz_i\varphi, \end{aligned} \quad (79)$$

where Ω_i^M is the partial molar volume.

When we express the diffusion potential as energy per mass unit the diffusion velocities due the potentials shown in Eq. (79) are given by:

$$\begin{aligned} v_i^d &= -B_i \text{grad} \left(\mu_i^{ch} + \frac{Fz_i}{M_i} \varphi \right), \\ v_i^d &= -B_i \text{grad} \left(\mu_i^{ch} - p\Omega_i^m \right), \\ v_i^d &= -B_i \text{grad} \left(\mu_i^{ch} - p\Omega_i^m + \frac{Fz_i}{M_i} \varphi \right), \end{aligned} \quad (80)$$

where B_i [s] is the mobility that can be visualized as an average time during which the i -component will reach its diffusion velocity.

¹⁴The potential μ_i is an aggregate of all reversible work terms that can be transported with the species i . Using Lagrange multipliers, Cahn and Larche derive a potential that is a sum of the diffusant's elastic energy and its chemical potential, i.e., Cahn and Larche invent the term diffusion potential to describe this sum.

It is easy to show that in a case of ideal solid solution ($\mu_i = \mu_i^0 + RT \ln N_i$ and $c = const$) and when diffusion potential is chemical potential only (effects of pressure and electrical field are negligible) from Eq. (79) and previous relations the diffusion flux is given by:

$$\begin{cases} J_i^d := c_i v_i^d \text{ where } v_i^d = B_i F_i, \\ F_i = -\text{grad } \mu_i^{ch}, \\ \mu_i^{ch} = \mu_i^0 + RT \ln N_i = \mu_i^0 + RT \ln \frac{c_i}{c} \text{ where } c = \sum_i c_i = const, \end{cases} \quad (81)$$

which upon substituting becomes:

$$\begin{cases} J_i^d = -B_i c_i \text{ grad } \mu_i^{ch}, \\ \text{grad } \mu_i^{ch} = RT \text{ grad} (\ln c_i - \ln c) = RT \text{ grad } \ln c_i = RT c_i^{-1} \text{ grad } c_i, \end{cases} \quad (82)$$

and finally:

$$J_i^d = -B_i RT \text{ grad } c_i = D_i \text{ grad } c_i. \quad (83)$$

Equation (83) is called 1st Fick's law where we have shown also that diffusivity and mobility of the component are related by the Nernst-Einstein relation. This relation, when mobility is expressed per atom, is usually used in the form:

$$D_i = B_i kT. \quad (84)$$

3.4 Onsager's Symmetry Principle

Three postulates were utilized to derive the relations between forces and fluxes:

1. The rate of entropy change and the local rate of entropy production can be inferred by invoking equilibrium thermodynamic variations and the assumption of local equilibrium.
2. The entropy production is nonnegative.
3. Each flux depends linearly on all the driving forces.

Above postulates do not follow from statements of the 1st and 2nd laws of thermodynamics.

Onsager's principle supplements these postulates and follows from the statistical theory of reversible fluctuations [5]. Onsager's principle states that when the forces and fluxes are chosen so that they are conjugate, the coupling coefficients are symmetric:

$$L_{\alpha\beta} = L_{\beta\alpha}, \quad (85)$$

which simplifies the coupled force-flux equations and has led to experimentally verifiable predictions [6] and guarantees that all the eigenvalues of Eq. (59) will be real numbers. Also, the quadratic form in Eq. (61) together with Eq. (50) implies that the kinetic matrix ($L_{\alpha\beta}$) will be positive definite - all the eigenvalues are nonnegative.¹⁵ Equation (85) can be rewritten

$$\frac{\partial J_\alpha}{\partial F_\beta} = \frac{\partial J_\beta}{\partial F_\alpha}. \quad (86)$$

This equation shows that the change in flux of some quantity caused by changing the direct driving force for another is equal to the change in flux of the second quantity caused by changing the driving force for the first. These equations resemble the Maxwell relations from thermodynamics.

¹⁵Positive definite means that the matrix when left- and right-multiplied by an arbitrary vector will yield a nonnegative scalar. If the matrix multiplied by a vector composed of forces is proportional to a flux, it implies that the flux always has a positive projection on the force vector. Technically, one should say that $L_{\alpha\beta}$ is nonnegative definite but the meaning is clear.

The statistical-mechanics derivation of Onsager's symmetry principle is based on microscopic reversibility for systems near equilibrium. That is, the time average of a correlation between a driving force of type α and the fluctuations of quantity β is identical with respect to switching α and β [6].

A demonstration of the role of microscopic reversibility in the symmetry of the coupling coefficients can be obtained for a system consisting of three isomers, A, B, and C [7, 8]. Each isomer can be converted into either of the other two, without any change in composition. Assuming a closed system containing these molecules at constant temperature and pressure, the rate of conversion of one type into another is proportional to its number, with the constant of proportionality being a rate constant, K (Fig. 2.1). The rates at which the numbers of A, B, and C change are then

$$\begin{aligned}\frac{dN_A}{dt} &= -(K_{AC} + K_{AB})N_A + K_{BA}N_B + K_{CA}N_C, \\ \frac{dN_B}{dt} &= K_{AB}N_A - (K_{BC} + K_{BA})N_B + K_{CB}N_C, \\ \frac{dN_C}{dt} &= K_{AC}N_A + K_{BC}N_B - (K_{CA} + K_{CB})N_C.\end{aligned}\quad (87)$$

At equilibrium, the time derivatives in Eq. (87) vanish. Solving for equilibrium in a closed system ($N_A + N_B + N_C = N^{tot} = \text{const.}$) yields

$$N_A^{eq} = \frac{K_\alpha N^{tot}}{K_\alpha + K_\beta + K_\gamma}, \quad N_B^{eq} = \frac{K_\beta N^{tot}}{K_\alpha + K_\beta + K_\gamma}, \quad N_C^{eq} = \frac{K_\gamma N^{tot}}{K_\alpha + K_\beta + K_\gamma}, \quad (88)$$

where

$$\begin{aligned}K_\alpha &\equiv K_{BA}K_{CA} + K_{BA}K_{CB} + K_{BA}K_{BC}, \\ K_\beta &\equiv K_{CB}K_{AB} + K_{CB}K_{AC} + K_{AB}K_{CA}, \\ K_\gamma &\equiv K_{AC}K_{BC} + K_{AC}K_{BA} + K_{BC}K_{AB}.\end{aligned}\quad (89)$$

For the system near equilibrium, let Y_A be the difference between the number of A and its equilibrium value, $Y_A = N_A - N_A^{eq}$. Introducing this relationship and similar ones for B and C into Eq. (87),

$$\frac{dY_A}{dt} = -(K_{AC} + K_{AB})Y_A + K_{BA}Y_B + K_{CA}Y_C, \quad (90)$$

with similar expressions for B and C.

If Henry's law is obeyed, the activity coefficient is constant and expanding the chemical potential (Eq. (3)) near equilibrium (small Y_A / N_A^{eq}) yields

$$\Delta\mu_A^{ch-eq} \equiv \mu_A^{ch} - \mu_A^{ch-eq} = kT \ln\left(1 + \frac{Y_A}{N_A^{eq}}\right) \approx \frac{kTY_A}{N_A^{eq}}. \quad (91)$$

Substituting Eq. (91) into Eq. (90) and carrying out similar procedures for B and C,

$$\begin{aligned}\frac{dY_A}{dt} &= -\frac{(K_{AC} + K_{AB})N_A^{eq}}{kT} \Delta\mu_A^{ch-eq} + \frac{K_{BA}N_B^{eq}}{kT} \Delta\mu_B^{ch-eq} + \frac{K_{CA}N_C^{eq}}{kT} \Delta\mu_C^{ch-eq}, \\ \frac{dY_B}{dt} &= \frac{K_{AB}N_A^{eq}}{kT} \Delta\mu_A^{ch-eq} - \frac{(K_{BC} + K_{BA})N_B^{eq}}{kT} \Delta\mu_B^{ch-eq} + \frac{K_{CB}N_C^{eq}}{kT} \Delta\mu_C^{ch-eq}, \\ \frac{dY_C}{dt} &= \frac{K_{AC}N_A^{eq}}{kT} \Delta\mu_A^{ch-eq} + \frac{K_{BC}N_B^{eq}}{kT} \Delta\mu_B^{ch-eq} - \frac{(K_{CA} + K_{CB})N_C^{eq}}{kT} \Delta\mu_C^{ch-eq}.\end{aligned}\quad (92)$$

These constitute a set of linear relationships between the potential differences $\mu_i^{ch} - \mu_i^{ch-eq}$, which drive the Y_i toward equilibrium and their corresponding rates, dY_i/dt . In terms of the Onsager coefficients, they have the form

$$\begin{aligned}\frac{dY_A}{dt} &= L_{AA}F_A + L_{AB}F_B + L_{AC}F_C, \\ \frac{dY_B}{dt} &= L_{BA}F_A + L_{BB}F_B + L_{BC}F_C, \\ \frac{dY_C}{dt} &= L_{CA}F_A + L_{CB}F_B + L_{CC}F_C.\end{aligned}\tag{93}$$

When microscopic reversibility is present in a complex system composed of many particles, every elementary process in a forward direction is balanced by one in the reverse direction. The balance of forward and backward rates is characteristic of the equilibrium state, and detailed balance exists throughout the system. Microscopic reversibility therefore requires that the forward and backward reaction fluxes be equal, so that

$$\begin{aligned}\frac{K_{BA}}{K_{AB}} &= \frac{N_A^{eq}}{N_B^{eq}} = \frac{K_\alpha}{K_\beta} = \frac{K_{BA}K_{CA} + K_{BA}K_{CB} + K_{CA}K_{CB}}{K_{CB}K_{AB} + K_{CB}K_{AC} + K_{AB}K_{CA}}, \\ \frac{K_{CB}}{K_{BC}} &= \frac{N_B^{eq}}{N_C^{eq}} = \frac{K_\beta}{K_\gamma} = \frac{K_{CB}K_{AB} + K_{CB}K_{AC} + K_{AB}K_{CA}}{K_{AC}K_{BC} + K_{AC}K_{BA} + K_{BC}K_{AB}}, \\ \frac{K_{AC}}{K_{CA}} &= \frac{N_C^{eq}}{N_A^{eq}} = \frac{K_\gamma}{K_\alpha} = \frac{K_{AC}K_{BC} + K_{AC}K_{BA} + K_{BC}K_{AB}}{K_{BA}K_{CA} + K_{BA}K_{CB} + K_{CA}K_{BC}}.\end{aligned}\tag{94}$$

Comparison of Eq. (93) with Eqs. (92) and (94) shows that $L_{ij} = L_{ji}$ and therefore demonstrates the role of microscopic reversibility in the symmetry of the Onsager coefficients.

References

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- [1] R. W. Balluffi, S. M. Allen and W. C. Carter, „Kinetics of Materials” (A. J. WILEY & Sons. Inc., 2008).
 - [2] S. R. De Groot and P. Mazur, Non-Equilibrium Thermodynamics (North-Holland, Amsterdam, 1962).
 - [3] M. Danielewski and B. Wierzba, *Phil. Mag.*, **89** (2009) 331.
 - [4] F.C. Larche and J.W. Cahn, The interactions of composition and stress in crystalline solids, *Acta Metall.*, **33** (1984) 331-367.
 - [5] L. Onsager, Reciprocal relations in irreversible processes, *Phys. Rev.*, **38** (1931) 2265-2279.
 - [6] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics, Part 1.* (Pergamon Press, New York, 1980), p. 365ff.
 - [7] K. Denbigh, *The Principles of Chemical Equilibrium* (Cambridge University Press, New York, 1971).
 - [8] W. Yourgrau, A. van der Merwe and G. Raw, *Treatise on Irreversible and Statistical Thermodynamics*, (Dover Publications, New York, 1982).