Le Châtelier reciprocal relations[a)]

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(Received 23 December 1981; accepted 22 February 1982)

The Le Châtelier matrix $L_{\alpha\beta}$ describes the response to perturbations of a system in thermodynamic equilibrium. The diagonal elements of this matrix embody Le Châtelier's Principle, and the off-diagonal elements describe the response of one pair of conjugate thermodynamic variables to a perturbation involving another pair. The symmetry of this matrix $L_{\alpha\beta} = L_{\beta\alpha}$ gives rise to the Le Châtelier reciprocal relations.

I. NOTATION

Consider a system S in thermodynamic equilibrium with a reservoir R. The system's internal energy U is a function of the system's extensive thermodynamic variables $E^1, E^2, \ldots, E^n$ (e.g., S, V, N, etc.): $U = U(E^\alpha)$. At equilibrium, the system's intensive thermodynamic variables $i_\alpha = (\partial U/\partial E^\alpha)_E$ (e.g., T, $-P$, μ, etc.) are equal to the reservoir's corresponding intensive variables. The stability properties of S are determined by the positive definite metric tensor[1] $U_{\alpha\beta} = \partial^2 U/\partial E^\alpha \partial E^\beta$. The metric tensor $U_{\alpha\beta}$ and its inverse $U^{\alpha\beta}$ have the properties

$$U_{\alpha\beta} = U_{\beta\alpha}, \quad U^{\alpha\beta} = U^{\beta\alpha} \quad \text{(symmetry)}, \tag{1a}$$

$$\sum_\beta U_{\alpha\beta} U^{\beta\gamma} = \delta^\gamma_\alpha \quad \text{(inverse)}, \tag{1b}$$

$$U_{\alpha\alpha} > 0, \quad U^{\alpha\alpha} > 0 \quad \text{(positive definite)}. \tag{1c}$$

(Throughout we indicate all sums explicitly: the summation convention is not used.) The matrix elements of these tensors ($n \times n$ matrices), which also have a natural interpretation as susceptibility tensors,[2] are defined by

$$\delta i_\alpha = \sum_\beta U_{\alpha\beta}\, \delta E^\beta: \quad U_{\alpha\beta} = \left(\frac{\partial i_\alpha}{\partial E^\beta}\right)_E = \left(\frac{\partial E^\beta}{\partial i_\alpha}\right)_E^{-1}, \tag{2a}$$

$$\delta E^\alpha = \sum_\beta U^{\alpha\beta}\, \delta i_\beta: \quad U^{\alpha\beta} = \left(\frac{\partial E^\alpha}{\partial i_\beta}\right)_i = \left(\frac{\partial i_\beta}{\partial E^\alpha}\right)_i^{-1}. \tag{2b}$$

The subscript $E(i)$ means that all extensive (intensive) variables not explicitly indicated in the partial derivatives have been held constant.

II. THE PERTURBATION

At time $t = 0$, the system is perturbed by changing one of its extensive variables (e.g., $E^\alpha \to E^\alpha + \Delta E^\alpha$, with ΔE^α held constant for all $t > 0$). Within a short time ($t = 0^+$) the system reaches an internal equilibrium with itself, but is not in equilibrium with R. In this state of internal thermodynamic equilibrium, changes in the system's intensive and extensive thermodynamic variables are governed by the susceptibility relations (2). Eventually ($t \to \infty$) S relaxes to a new equilibrium state with R (external equilibrium). Le Châtelier's principle states[1] that

$$|\Delta i_\alpha(0^+)| > |\Delta i_\alpha(\infty)| > 0. \tag{3}$$

We extend Le Châtelier's principle to include the responses of the remaining thermodynamic variables E^β, i_β to the initial perturbation $\Delta E^\alpha \neq 0$.

A short time after the initial perturbation, S has achieved a state of internal thermodynamic equilibrium but the extensive variables E^β ($\beta \neq \alpha$) have not yet had a chance to respond to the perturbation. The responses of the thermodynamic variables at $t = 0^+$ are therefore

$$\Delta E^\alpha(0^+) = \Delta E^\alpha, \tag{4a}$$

$$\Delta E^\beta(0^+) = 0, \quad \beta \neq \alpha, \tag{4b}$$

$$\Delta i_\alpha(0^+) = \left(\frac{\partial i_\alpha}{\partial E^\alpha}\right)_E \Delta E^\alpha = U_{\alpha\alpha}\Delta E^\alpha, \tag{4c}$$

$$\Delta i_\beta(0^+) = \left(\frac{\partial i_\beta}{\partial E^\alpha}\right)_E \Delta E^\alpha = U_{\beta\alpha}\Delta E^\alpha. \tag{4d}$$

After S reaches thermodynamic equlibrium with R, all intensive variables except i_α have relaxed to their original values. The final state of S can be reached either as described, or quasistatically and reversibly by changing E^α keeping all intensive variables except i_α fixed. The responses of the thermodynamic variables at $t = \infty$ are therefore

$$\Delta E^\alpha(\infty) = \Delta E^\alpha, \tag{5a}$$

$$\Delta E^\beta(\infty) = \left(\frac{\partial E^\beta}{\partial E^\alpha}\right)_i \Delta E^\alpha = (U^{\beta\alpha}/U^{\alpha\alpha})\Delta E^\alpha, \tag{5b}$$

$$\Delta i_\alpha(\infty) = \left(\frac{\partial i_\alpha}{\partial E^\alpha}\right)_i \Delta E^\alpha = (1/U^{\alpha\alpha})\Delta E^\alpha, \tag{5c}$$

$$\Delta i_\beta(\infty) = 0, \quad \beta \neq \alpha. \tag{5d}$$

III. LE CHATELIER'S PRINCIPLE

Le Châtelier's principle (3), in succinct and symmetric form, is [using Eqs. (1c), (4c), and (5c)]

$$U_{\alpha\alpha} U^{\alpha\alpha} > 1 \quad \text{(Le Châtelier's principle)}. \tag{6}$$

IV. LE CHATELIER RESPONSE MATRIX

It remains to consider the responses $\Delta i_\beta(0^+)$ and $\Delta E^\beta(\infty)$ of the remaining thermodynamic variables to the perturbation $\Delta E^\alpha \neq 0$. These responses are all proportional to the original perturbation. Dimensional considerations suggest that we compare the product $\Delta i_\beta(0^+)\Delta E^\beta(\infty)$ with the product $\Delta i_\alpha(\infty)\Delta E^\alpha$. This comparison defines a dimensionless matrix, the Le Châtelier matrix $L_{\beta\alpha}$, as follows:

$$\Delta i_\beta(0^+)\Delta E^\beta(\infty) = L_{\beta\alpha}\Delta i_\alpha(\infty)\Delta E^\alpha. \tag{7}$$

The matrix elements $L_{\beta\alpha}$ are easily determined from

[a)]Work supported in part by NSF Grant PHY810-2977.

Eqs. (4d), (5b), and (5c):

$$L_{\beta\alpha} = U_{\beta\alpha} U^{\beta\alpha} = L_{\alpha\beta} \quad . \tag{8}$$

The diagonal matrix elements are the Le Châtelier ratios $L_{\alpha\alpha} = U_{\alpha\alpha} U^{\alpha\alpha} = \Delta i_\alpha(0^+)/\Delta i_\alpha(\infty) > 1$. The inequality $U_{\alpha\alpha} U^{\alpha\alpha} \geq 1$ follows from the positive definite nature of $U_{\alpha\beta}$ and the Schwartz[3] and Bessel inequalities.[4] The off-diagonal matrix elements $L_{\beta\alpha}$ describe the response of the β variables to a perturbation involving the α variables. This response function is symmetric due to the symmetry of the metric tensor [Eq. (1a)]. This symmetry gives rise to reciprocal relations in the usual way.

V. EXAMPLE

The metric tensor $U_{\alpha\beta}$ and its inverse $U^{\alpha\beta}$ for a simple single component substance ($n=2$) are[3,4]

$$U_{\alpha\beta} = \begin{bmatrix} \frac{1}{C_V/T} & \frac{-1}{\Gamma_V/T} \\ \frac{-1}{\Gamma_V/T} & \frac{1}{V\beta_S} \end{bmatrix}, \quad U^{\alpha\beta} = \begin{bmatrix} \frac{C_P}{T} & V\alpha_P \\ V\alpha_P & V\beta_T \end{bmatrix} \quad . \tag{9}$$

The Le Châtelier matrix is

$$L_{\alpha\beta} = \begin{bmatrix} \frac{C_P}{C_V} & \frac{-TV\alpha_P}{\Gamma_V} \\ \frac{-TV\alpha_P}{\Gamma_V} & \frac{\beta_T}{\beta_S} \end{bmatrix} \quad . \tag{10}$$

From Eq. (10) we determine immediately $C_P > C_V > 0$, $\beta_T > \beta_S > 0$, and the reciprocal relations

$$\Delta S \neq 0: \ -\Delta P(0^+)\Delta V(\infty) = -\frac{TV\alpha_P}{\Gamma_V}\Delta T(\infty)\Delta S \quad , \tag{11a}$$

$$\Delta V \neq 0: \ \Delta T(0^+)\Delta S(\infty) = -\frac{TV\alpha_P}{\Gamma_V}[-\Delta P(\infty)]\Delta V \quad . \tag{11b}$$

In these equations, $-\Delta P$ is conjugate to ΔV.

VI. REMARKS

The following points are worth emphasizing:

(1) Le Châtelier's principle is embodied in the diagonal elements of the Le Châtelier matrix.

(2) The Le Châtelier matrix is real, symmetric, dimensionless, and positive definite. The matrix elements in any row or column sum to one [use Eqs. (8), (1a), and (1b)]. These properties are all consequences of the fact that $U_{\alpha\beta}$ is positive definite and $U^{\alpha\beta}$ is its inverse.

(3) Although Δi_α has the same sign as the perturbation ΔE^α, the responses $\Delta i_\beta(0^+)$, $\Delta E^\beta(\infty)$ ($\beta \neq \alpha$) generally have opposite signs. This follows from

$$\sum_{\beta, \beta\neq\alpha} L_{\beta\alpha} = 1 - L_{\alpha\alpha} < 0 \quad . \tag{12}$$

For $n=2$, $L_{12} < 0$, as shown in the example.

(4) The Le Châtelier matrix for a system described by n independent variables is an $n\times n$ matrix with $n(n-1)/2$ independent matrix elements. These may conveniently be taken as the off-diagonal matrix elements. Then nontrivial relations exist among the Le Châtelier ratios. For $n=2$, since $L_{11} = 1 - L_{12}$ and $L_{22} = 1 - L_{21}$, $C_P/C_V = L_{11} = L_{22} = \beta_T/\beta_S = 1 + (TV\alpha_P/\Gamma_V)$. For $n=3$ we find [use Eq. (12)]:

$$L_{11} - L_{23} = L_{22} - L_{31} = L_{33} - L_{12} = 1 - (L_{12} + L_{23} + L_{31}) \quad . \tag{13}$$

This result is a consequence of the fact that $U_{\alpha\beta}$ and $U^{\alpha\beta}$ are matrix inverses.

(5) The generalized Le Châtelier principle described above is more generally applicable than to thermodynamic systems alone. It is valid for any physical system possessing the following two properties:

(i) The system is either linear or linearizable about a static or dynamic equilibrium point, and its stability is described by a bilinear form

$$\Delta V = \sum_\alpha \delta x^\alpha \delta y_\alpha \quad , \tag{14a}$$

where displacements in the variables δx^α, δy_β are related by the susceptibility tensor $G_{\alpha\beta}$:

$$\delta y_\alpha = \frac{\partial}{\partial x^\alpha}\Delta V = \sum_\beta G_{\alpha\beta}\delta x^\beta \quad . \tag{14b}$$

The variables x^α, y_α are conjugate, the function V may be either a potential or Lyapunov function, and the susceptibility tensor $G_{\alpha\beta}$ is positive definite but need not be symmetric.

(ii) The system possesses two intrinsic time scales of interest, τ_s and T_L, with $\tau_s \ll T_L$. A short time $t \gtrsim \tau_s$ after a perturbation, the system reaches an internal equilibrium state in which the responses $\delta x^\alpha(t)$, $\delta y_\beta(t)$ are related by Eq. (14b), but the system is not in equilibrium with its surroundings. After a time $t \gtrsim T_L \gg \tau_s$ the system relaxes back to an equilibrium state with its surroundings (external equilibrium).

For such systems, the generalized Le Châtelier matrix is $L_{\alpha\beta} = G_{\alpha\beta}(G^{-1})^{\alpha\beta}$. This matrix inherits the symmetry properties of the susceptibility tensor $G_{\alpha\beta}$. Three nonthermodynamic examples follow.

(6) Passive electrical systems involving (a) multiple conductors, (b) multiple capacitors, or (c) multiple inductors are described by the following Lyapunov functions:[5]

$$F = \frac{1}{2}\sum_{\alpha,\beta} G_{\alpha\beta} V_\alpha V_\beta = \frac{1}{2}\sum_{\alpha,\beta} R_{\alpha\beta} I_\alpha I_\beta \quad , \tag{15a}$$

$$V = \frac{1}{2}\sum_{\alpha,\beta} S_{\alpha\beta} Q_\alpha Q_\beta = \frac{1}{2}\sum_{\alpha,\beta} C_{\alpha\beta} V_\alpha V_\beta \quad , \tag{15b}$$

$$T = \frac{1}{2}\sum_{\alpha,\beta} M_{\alpha\beta} I_\alpha I_\beta = \frac{1}{2}\sum_{\alpha,\beta} \Gamma_{\alpha\beta} \Phi_\alpha \Phi_\beta \quad . \tag{15c}$$

Here I_α, V_α, Q_α, Φ_α, respectively, represent the current through, voltage across, charge on, and flux linked by the αth circuit element. The conductance tensor $G_{\alpha\beta}$ is the inverse of the resistance tensor $R_{\alpha\beta}$. The tensor $S_{\alpha\beta}$ and the mutual capacitance tensor $C_{\alpha\beta}$ are inverses, as are the tensor $\Gamma_{\alpha\beta}$ and the mutual inductance tensor $M_{\alpha\beta}$. All tensors are real, symmetric, and positive definite, and, in addition, $G_{\alpha\beta} \leq 0$ ($\alpha \neq \beta$) and

$C_{\alpha\beta} \le 0$ $(\alpha \ne \beta)$. Lenz's law is equivalent to the statement $M_{\alpha\alpha}\Gamma_{\alpha\alpha} > 1$.

(7) In a passive linear electrical network, the voltages V_α and currents I_β are related by the admittance $(Y_{\alpha\beta})$ and impedance $(Z_{\alpha\beta})$ tensors[6]

$$I_\alpha = \sum_\beta Y_{\alpha\beta} V_\beta \quad , \qquad V_\alpha = \sum_\beta Z_{\alpha\beta} I_\beta \quad . \tag{16}$$

The Le Châtelier matrix and the generalized Lenz's law for such systems are $L_{\alpha\beta} = Y_{\alpha\beta} Z_{\alpha\beta}$ and $L_{\alpha\alpha} > 1$, respectively.

(8) Irreversible thermodynamics is governed by the Lyapunov function

$$\dot{S} = \sum_\alpha J_\alpha X_\alpha \quad . \tag{17a}$$

The fluxes J_α and forces X_α are related by the kinetic coefficients $K_{\alpha\beta}$:

$$J_\alpha = \sum_\beta K_{\alpha\beta} X_\beta \quad , \tag{17b}$$

with $K_{\alpha\beta}(\mathrm{H}) = K_{\beta\alpha}(-\mathrm{H})$.[7] The Le Châtelier matrix $L_{\alpha\beta} = K_{\alpha\beta}(K^{-1})_{\alpha\beta}$ inherits the symmetry of the kinetic coefficients: $L_{\alpha\beta}(\mathrm{H}) = L_{\beta\alpha}(-\mathrm{H})$. Irreversible systems obey Le Châtelier as well as Onsager reciprocal relations.

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