SYMMETRY AND OTHER PROPERTIES OF SECOND-ORDER PHENOMENOLOGICAL COEFFICIENTS AND THEIR SIGNIFICANCE IN A CHEMICAL SYSTEM

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Abstract

Using a second-order phenomenological equation $J_i = \Sigma_j L_{ij} X_j + \Sigma_{j,k} L_{ijk} X_j X_k$ and assuming that the system is at a state near equilibrium, it has been shown that the symmetry of L_{ijk} is retained with respect to the permutations of suffices 'i', 'j' and 'k'. Furthermore, using the second-order flux equations, the thermodynamic stability criterion is expressed. The symmetry is shown to be retained in a reaction scheme representing the 'Template model'. The significance of the stability criterion as expressed by the higher-order phenomenological coefficients is discussed.

In the vicinity of equilibrium, the macroscopic fluxes maintain a linear relation with the forces. As one increases the distance from equilibrium, the fluxes may be related to the forces in a non-linear way. Since non-linear systems, even in their simplest forms, exhibit a number of special dynamic characteristics, it would be interesting to study the behaviour of such systems, the distance from equilibrium remaining small. Firstly, one may look at the symmetry properties of the non-linear phenomenological coefficients. In the case where a higher-order symmetry is obtained for such coefficients, the number of independent parameters of the system would be reduced. This would obviously reduce the number of possible trajectories of the system in the phase space. Another important question related to symmetry of higher-order phenomenological coefficients is the possible existence of one or more critical conditions at which the symmetry may be broken. The present report shows that the breaking of higher-order

symmetry may correspond to some special situation which has no counterpart in the linear domain.

Let us consider a second-order non-linear system in which the fluxes (J) and forces (X) are related as

$$J_i = \sum_k L_{ik} X_k + \sum_{k,l} L_{ikl} X_k X_l \ . \tag{1}$$

Writing $J_i - J_i^{eq} = \delta J_i$ and $X_i - X_i^{eq} = \delta X_i$ and remembering that $J_i^{eq} = X_i^{eq} = 0$ for each i (by definition of equilibrium) [3] we obtain

$$\delta J_i = \sum_k L_{ik} \delta X_k + \sum_{k,l} L_{ikl} \delta X_k \delta X_l \ . \tag{2}$$

The thermodynamic stability criterion can be expressed as [4] (assuming homogeneity)

$$\sum_i \delta J_i \cdot \delta X_i \geqslant 0 \ , \tag{3}$$

i.e.

$$\sum_{i,k} \delta X_i (L_{ik} + \sum_l L_{ikl} \delta X_l) \delta X_k \geqslant 0 \ . \tag{4}$$

Writing

$$\mathcal{O}_{ik} = L_{ik} + \sum_l L_{ikl} \delta X_l \ . \tag{5}$$

eq. (4) can be written in the matrix form as

$$\delta X^T \ \mathcal{O} \ \delta X \geqslant 0 \ . \tag{6a}$$

In other words, the thermodynamic stability criterion can be expressed in terms of the higher-order phenomenological coefficients as

$$\det \| L_{ik} + \sum_l L_{ikl} \delta X_l \| \ \geqslant 0. \tag{6b}$$

The equality sign in eq. (6a,b) prevails only at steady state or equilibrium. Under mass closed conditions, a chemical system, operating in the range of validity of the ideal solution approximation, must exhibit a unique [5] asymptotically stable [4] equilibrium point, This obviously demands $\mathcal{O}$ to be definite, or in other words [6]

$$\mathcal{O}_{ii} > 0; \ \ \mathcal{O}_{ii} \mathcal{O}_{kk} \geqslant \mathcal{O}_{ik}^2 \ . \tag{7a}$$

i.e.

$$(L_{ii} + \sum_l L_{iil} \delta X_l) > 0 \tag{7b}$$

and

$$\sum_{l,m} (L_{ikl} \cdot L_{kim} - L_{iil} \cdot L_{kkm}) \delta X_l \delta X_m - \sum_j (L_{kkj} \cdot L_{ii} + L_{iij} \cdot L_{kk}$$

$$- L_{kij} \cdot L_{ik} - L_{ikj} \cdot L_{ik}) \delta X_j \leqslant (L_{ii} L_{kk} - L_{ik}^2). \tag{7c} \quad (7c)$$

The dependence on the phase space trajectory is expressed by the inequalities expressed in eqs. (7b) and (7c), respectively.

Before we consider an actual chemical system to decipher the implications of the stability criterion expressed in terms of L_{ij} and L_{ijk}, let us consider some general properties of the second-order phenomenological coefficients. Let us assume that the second-order non-linear system is in a state close to equilibrium. The distance from equilibrium is to some extent an arbitrary concept. By 'closeness' to equilibrium, we may not necessarily mean 'linearity'. This perhaps is most relevant in chemical systems which are intrinsically non-linear in nature. In states close to equilibrium, macroscopic reversibility (MR) [1,3,7] must be valid. If $\Delta \xi$ represents a vector, each component of which are α-type macroscopic variables representing the deviation of a given thermodynamic parameter from its corresponding equilibrium value, MR can be written as [1,2]

$$\overline{\Delta \xi_i(t) \Delta \xi_k(t+\tau)} = \overline{\Delta \xi_i(t+\tau) \Delta \xi_k(t)}, \tag{8}$$

where the bar indicates time average. Furthermore, we assume the validity of the condition [1]

$$\overline{\Delta \xi_i X_j} = K \delta_{ij}. \tag{9}$$

Expanding $\Delta \xi_i(t+\tau)$ at 't' up to second-order terms, we obtain

$$\Delta \xi_i(t+\tau) = \Delta \xi_i(t) + \tau \Delta \dot{\xi}_i(t) + \tfrac{1}{2} \tau^2 \Delta \ddot{\xi}_i(t). \tag{10}$$

Subtracting $\Delta \xi_i(t) \Delta \xi_k(t)$ from both sides of eq. (8) and using eq. (10), we obtain

$$M_{ik} = M_{ki}, \tag{11a}$$

where

$$M_{ik} = \overline{\tau \Delta \xi_i \Delta \dot{\xi}_k} + \tfrac{1}{2} \tau^2 \overline{\Delta \xi_i \Delta \ddot{\xi}_k}. \tag{11b}$$

Since we have chosen a second-order equation connecting J_i and X_i, the corresponding equation connecting J_i and $\Delta\xi_i$ can be written as

$$J_i = \Delta\dot{\xi}_i = \sum_j A_{ij}\Delta\xi_j + \sum_{j,k} A_{ijk}\Delta\xi_j\Delta\xi_k . \tag{12}$$

where A_{ij} and A_{ijk} are rate coefficients of first- and second-order variation of rates.

Differentiating both sides of eq. (12) with respect to times.

$$\Delta\ddot{\xi}_i = \sum_j A_{ij}\Delta\dot{\xi}_j + \sum_{j,k} A_{ijk}(\Delta\xi_j\Delta\dot{\xi}_k + \Delta\dot{\xi}_j\Delta\xi_k). \tag{13a}$$

Using eq. (12) in (13a),

$$\Delta\ddot{\xi}_i = \sum_{j,m} A_{ij}A_{jm}\Delta\xi_m + \sum_{j,m,l} (A_{ij}A_{jml} + A_{ilj}A_{jm} + A_{ijl}A_{jm})\Delta\xi_m\Delta\xi_l . \tag{13b}$$

Writing $B_{im} = \Sigma_j A_{ij}A_{jm}$ and negecting the third-order product terms of $\Delta\xi_i$'s, we obtain from eqs. (1), (11a), (11b), (12) and (13b):

$$\tau\Delta\xi_i\left(\sum_j L_{kj}X_j + \sum_{j,l} L_{kjl}X_jX_l\right) + \tfrac{1}{2}\tau^2\sum_j B_{kj}\Delta\xi_i\Delta\xi_j = M_{ik} = M_{ki} . \tag{14}$$

Comparing each power of τ from the expression of M_{ik} and M_{ki}, and furthermore assuming the validity of eq. (9) and that of Onsager symmetry ($L_{kj} = L_{jk}$) [1,2], one obtains the symmetry condition (for the first power of τ):

$$G_{ik} = \overline{\sum_{j,l} L_{kjl}X_jX_l\Delta\xi_i} = \overline{\sum_{j,l} L_{ijl}X_jX_l\Delta\xi_k} = G_{ki} . \tag{15}$$

Assuming that p represents Einsteinian fluctuation probability, we know that $p = \exp(\Delta S/k)$, where $\Delta S = S - S_{eq}$ and S represents the entropy of the system. Using the definition

$$X_i = \frac{\partial\Delta S}{\partial\Delta\xi_i} .$$

we have the following:

$$\overline{\Delta\xi_k X_j X_l} = \int_{\xi_1}\cdots\int_{\xi_n}\Delta\xi_k \frac{\partial k\ln p}{\partial\Delta\xi_j} X_l \, d\Delta\xi_1 \ldots d\Delta\xi_n$$

$$= k\int_{\xi_1}\cdots\int_{\xi_{j-1}}\int_{\xi_{j+1}}\cdots\int_{\xi_n} X_l \, d\Delta\xi_i \ldots d\Delta\xi_{j-i}\, d\Delta\xi_{j+i}$$

$$\int\Delta\xi_k \frac{\partial p}{\partial\Delta\xi_j} \, d\Delta\xi_j . \tag{16}$$

Now,

$$\int_{\xi_j} \Delta\xi_k \; \frac{\partial p}{\partial \Delta\xi_j} \; d\Delta\xi_j = p\,\Delta\xi_k\big|_0^\infty - \int_{\xi_j} p \; \frac{\partial \Delta\xi_k}{\partial \Delta\xi_j} \; d\Delta\xi_j = -\delta_{kj} \int_{\xi_j} p\, d\Delta\xi_j \;. \qquad (17)$$

From eqs. (16) and (17),

$$\overline{\Delta\xi_k \, X_j \, X_l} = -k\delta_{kj} \int_{\xi_1} \dots \int_{\xi_n} X_l \, p \, d\Delta\xi_1 \dots d\Delta\xi_n \;. \qquad (18)$$

Since, in eq. (16), j and l are interchangeable, equation (18) can also be written as

$$\overline{\Delta\xi_k \, X_j \, X_l} = -k\delta_{kl} \int_{\xi_1} \dots \int_{\xi_n} X_j \, p \, d\Delta\xi_1 \dots d\Delta\xi_n \;. \qquad (19a)$$

or

$$\overline{\Delta\xi_k \, X_j \, X_l} = -k\delta_{kj}\bar{X}_l = -k\delta_{kl}\bar{X}_j \;. \qquad (19b)$$

From eqs. (15) and (19), we obtain

$$k^{-1}G_{ik} = -\sum_{j,l} L_{kjl}\delta_{ij}\bar{X}_l = -\sum_{j,l} L_{kjl}\delta_{il}\bar{X}_j \qquad (20a)$$

$$k^{-1}G_{ki} = -\sum_{j,l} L_{ijl}\delta_{kj}\bar{X}_l = -\sum_{j,l} L_{ijl}\delta_{kl}\bar{X}_j \qquad (20b)$$

and

$$\sum_j L_{kji}\bar{X}_j = \sum_j L_{kij}\bar{X}_j = \sum_j L_{ikj}\bar{X}_j = \sum_j L_{ijk}\bar{X}_j \;. \qquad (21)$$

Since X_j's are linearly independent, equation (21) will hold good provided

$$L_{kji} = L_{kij} = L_{ikj} = L_{ijk} \;. \qquad (22a)$$

Since we have chosen i, j and k arbitrarily, equation (22) will also imply

$$L_{kji} = L_{jki} = L_{jik} \;. \qquad (22b)$$

Writing eq. (22a) together with eq. (22b), one obtains the symmetry relations

$$L_{ijk} = L_{ikj} = L_{jki} = L_{jik} = L_{kij} = L_{kji} \;. \qquad (23)$$

Thus, the phenomenological coefficients L_{ijk}'s retain symmetry for all possible permutations with i, j and k.

There exists a special situation when the symmetry as expressed by eq. (23) is broken. Such a condition can be written as

$$\sum_{j} (L_{kji} - L_{kij}) \bar{X}_j = 0 \tag{23a}$$

$$\sum_{j} a_j^{ki} \bar{X}_j = 0 \tag{23b}$$

for each k and i, where

$$a_j^{ki} = L_{kji} - L_{kij} . \tag{23c}$$

Thus, one obtains for each (i) the condition

$$\sum_{j=1}^{n} a_j^{kl} \bar{X}_j = 0$$

$$\sum_{j=1}^{n} a_j^{ki} \bar{X}_j = 0$$

$$\sum_{j=1}^{n} a_j^{kn} \bar{X}_j = 0 . \tag{23d}$$

Similarly, one obtains $'n'$ such equations for each $'k'$. Thus, one obtains $'n^2'$ equations of the form (23d), i.e. there are $'n^2'$ conditions for which the symmetry $L_{ijk} = L_{ikj}$ can be broken. Thus, for a 2D system (i.e. a system having two independent fluxes), there are four symmetry-breaking conditions and for a 3D system, there are nine symmetry-breaking conditions. This symmetry has no parallelism in the first-order phenomenological equation. In fact, it is not possible to obtain such conditions in the domain of validity of the linear laws.

In order to demonstrate the implications of symmetry relations (eq. (23) between second-order phenomenological coefficients in the chemical system, let us consider the following reaction scheme:

$$
\begin{aligned}
l &\rightleftharpoons X \\
X + X &\rightleftharpoons X_2 \\
X_2 + X &\rightleftharpoons Y_1 \\
X + Y_1 &\rightleftharpoons Y_2 \\
Y_2 &\rightleftharpoons 2X_2 \\
X_2 &\rightleftharpoons F .
\end{aligned}
\tag{R}
$$

The scheme (R) presents the template model $'T'$ which, as proposed by Nicolis and Prigogine [7], describes the synthesis of low-molecular weight homopolymer units such as poly-uridylic or poly-adenylic acids. A precursor l enters into the system to form an active monomer X. The condensation of two monomers then produces the dimeric molecule X_2, which then serves as a template for its own formation through two intermediates Y_1 and Y_2. Finally, X_2 is transformed into the product F through an isomerization reaction. The overall composite reaction is given by $4l = 2F$. The reasons behind the choice of this particular scheme are as follows. Firstly, the reaction-network (R) is stoichiometrically dependent [8] so that all elementary reactions can not proceed independently and hence the first-order off-diagonal phenomenological coefficients (i.e. $(dJ_i/dX_k)_{eq}$) are non-vanishing. Secondly, the kinetic equations are nonlinear and finally, the scheme exhibits an inherent asymmetry in the sense that all the chemical flows do not have symmetrical forms, as shown below.

The reaction-affinities A_i ($i = 1, \ldots, 6$) for such reactions obey the relations

$$A_2 - A_3 - A_4 - A_5 = 0 \quad \text{or} \quad A_2 = A_3 + A_4 + A_5 . \tag{24}$$

The rate of entropy production is given by

$$T\sigma = \sum_{i=1}^{6} A_i v_i . \tag{25}$$

where v_i is the velocity of the ith reaction. From eqs. (24) and (25),

$$T = A_1 v_1 + A_3(v_3 + v_2) + A_4(v_4 + v_2) + A_5(v_5 + v_2) + A_6 v_6 . \tag{26}$$

Hence, we can write

$$
\begin{aligned}
J_1 &= v_1 & \quad \text{and} \quad & X_1 = A_1 \\
J_2 &= v_6 & & X_2 = A_6 \\
J_3 &= v_3 + v_2 & & X_3 = A_3 \\
J_4 &= v_4 + v_2 & & X_4 = A_4 \\
J_5 &= v_5 + v_2 & & X_5 = A_5 .
\end{aligned}
\tag{27}
$$

The expression for J_i's are not symmetrical and hence apparently do not imply the symmetry of second-order phenomenological coefficients. The reaction-affinity A_i can be expressed as

$$A_i = RT \ln \left(\frac{v_i^+}{v_i^-} \right) = RT \ln \left(\frac{v_i + v_i^-}{v_i^-} \right)$$

$$= RT \ln \left[1 + \frac{v_i}{v_i^-} \right] \tag{28}$$

$[v_i = v_i^+ - v_i^-$, where v_i^+ and v_i^- represent the forward and backward reaction-velocity for the ith reaction].

In the neighbourhood of equilibrium, $v_i^+ \to v_i^-$, $v_i \to 0$, and eq. (28) assumes the form

$$A_1 = RT \left[\left(\frac{v_i}{v_i^-} \right) - \frac{3}{2} \left(\frac{v_i}{v_i^-} \right)^2 \right] \quad \text{(neglecting the higher-order terms)},$$

or

$$v_i = \left(\frac{v_i^-}{3} \right) \left[1 \pm \left(1 - \frac{6A_i}{RT} \right)^{1/2} \right] .$$

Considering upto the second-order term, taking the $(-ve)$ sign, and assuming $v_i^- \to (v_i^-)_{eq}$, we obtain

$$v_i = \frac{A_i (v_i^-)_{eq}}{RT} - \frac{3A_i^2}{(RT)^2} (v_i^-)_{eq} . \tag{29}$$

We can write eqs. (24), (27) and (29) as

$$J_1 = \frac{A_1 (v_1^-)_{eq}}{RT} - \frac{3A_1^2}{(RT)^2} (v_1^-)_{eq}$$

$$J_2 = \frac{A_6 (v_6^-)_{eq}}{RT} - \frac{3A_6^2}{(RT)^2} (v_6^-)_{eq} \tag{30}$$

$$J_3 = \frac{1}{RT} [A_3 (v_2^-)_{eq} + (v_3^-)_{eq} + A_4 (v_2^-)_{eq} + A_5 (v_2^-)_{eq}]$$

$$- \frac{3}{(RT)^2} [A_3^2 (v_2^-)_{eq} + (v_3^-)_{eq} - (A_4^2 + A_5^2 + 2A_3 A_4$$

$$+ 2A_4 A_5 + 2A_3 A_5)(v_2^-)_{eq}] .$$

The expressions for J_4 and J_5 can be obtained by exchanging the subscripts 3 and 4 or 3 and 5 in the last equation of (30).

The equations in (30) obey the symmetry relations

$$L_{11k} = L_{1k1} = L_{k11} = 0$$

$$k = 1, 2, \ldots, 5 \qquad (31a)$$

$$L_{22k} = L_{2k2} = L_{k22} = 0$$

$$L_{jjk} = L_{jkj} = L_{kjj} = \frac{6}{(RT)^2} \, (v_2^-)_{eq} \quad \begin{matrix} j = 3, 4, 5 \\ k = 3, 4, 5 \end{matrix} \quad j = k \qquad (31b)$$

and

$$L_{ijk} = L_{jik} = L_{ikj} = L_{jki} = L_{kij} = L_{kji} = - \frac{6}{(RT)^-} \, {}^{'}v_2^-)_{eq} \qquad (31c)$$

(when $i, j, k = 3, 4, 5$ and $i = j = k$)

$$= 0 \qquad \text{(when any of the subscripts represent 1 or 6)} \, .$$

Let us now consider the significance of the stability criterion expressed in eq. (7b). For reaction-scheme (R), this criterion yields

$$L_{ii} + \sum_{k=1}^{5} L_{iik} \, \delta X_k \geqslant 0 \, . \qquad (32)$$

For $i = 1$ and 2, $L_{iik} = 0$ as seen from (31a) and hence the stability criterion (32) does not impose any additional restriction on the system. For $i = 3$, from eq. (30),

$$L_{33} + \sum_{k=1}^{5} L_{33k} \, \delta X_k = \frac{(v_2^-)_{eq} + (v_3^-)_{eq}}{RT} - \frac{6}{(RT)^2} \, [(v_2^-)_{eq} + (v_3^-)_{eq} \delta A_3$$

$$+ (v_2^-)_{eq} \, \delta A_4 + (v_2^-)_{eq} \, \delta A_5] \geqslant 0 \, .$$

Putting

$$\alpha_k = \frac{(v_2^-)_{eq}}{(v_2^-)_{eq} + (v_k^-)_{eq}} \, ,$$

we obtain the inequalities

$$\delta A_3 + \alpha_3 \, \delta A_4 + \alpha_3 \, \delta A_5 \leqslant RT/6 \qquad (33a)$$

$$\alpha_4 \, \delta A_3 + \delta A_4 + \alpha_4 \, \delta A_5 < RT/6 \qquad (33b)$$

$$\alpha_5 \, \delta A_3 + \alpha_5 \, \delta A_3 + \delta A_5 < RT/6 \, . \qquad \cdot \quad (33c)$$

Similarly, the stability criteria expressed in eq. (7c) yields some other inequalities which impose additional constraints on the trajectory of the phase-space constructed from δA_3, δA_4 and δA_5, which comprises of the cyclic part of the scheme (R). However, there is no such restriction on the trajectories of δA_1 and δA_6. It is worth emphasizing that δA_i in eq. (33) represents the deviation of the ith reaction-affinity from equilibrium. The symmetry-breaking conditions, for which the stability criteria (33a – 33c) are no longer valid, can yield some threshold values for δA_3, δA_4 and δA_5, and hence can specify the boundary of the near-equilibrium regime, beyond which the symmetry relations will not be valid. The stability criterion expressed in terms of the first-order equation can not give any such quantitative idea about the transition of the system from the thermodynamic to the dissipative branch.

Acknowledgements

References

[1]   L. Onsager, Phys. Rev. 37(1931)405.
[2]   L. Onsager, Phys. Rev. 38(1931)2265.
[3]   A. Katchalsky and P.F. Curran, *Non-Equilibrium Thermodynamics in Biophysics* (Harvard University Press, Cambridge, MA, 1967).
[4]   P. Glansdorff and I. Prigogine, *Thermodynamics of Structure, Stability and Fluctuations* (Wiley, New York, 1971).
[5]   D.B. Shear, J. Chem. Phys. 48(1968)4144.
[6]   J.J. Tyson, J. Chem. Phys. 62(1975)1010.
[7]   G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium Systems* (Wiley, New York, 1977).
[8]   S. Lengyel and I. Gyramati, J. Chem. Phys. 75(1981)2384.