APPLICATION OF THE PRIGOGINE–GYARMATI PRINCIPLE FOR AN ELECTROCHEMICAL PROBLEM

By

J. VERHÁS

Department for Physical Chemistry, Polytechnical University Budapest,

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It was PRIGOGINE who primarily assumed the existence of a thermodynamical minimum principle similar to the Gauss principle of mechanics [1]. The problem raised by Prigogine was recently solved by GYARMATI by developing a general variational principle of non-equilibrium thermodynamics [2, 3, 4]. Therefore, it is justified to call this principle the Prigogine–Gyarmati principle. In the sense of the principle

$$C \equiv \frac{1}{2} \sum_{i,k} R_{ik} \left(J_i - \sum_s L_{is} X_s\right)\left(J_k - \sum_r L_{kr} X_r\right) = \text{minimum} \tag{1}$$

where J_i and X_i are the thermodynamic fluxes and forces, respectively, whereas L_{ik} and R_{ik} are the conductivity coefficients and resistances, for which Onsager's reciprocal relations are valid. The (1) minimum principle is similar to the Gauss principle of mechanics, since the minimum of the "constraint" C is zero without restrictions just as in the case of the Gauss principle [3, 4, 5]. In general it can be said, that for the given free forces X_i such irreversible processes are taking place in a system, for which the "constraint" C is minimum. Formulation (1) of the Prigogine–Gyarmati principle will be applied for a constraint problem of electrochemistry.

Let us consider an electrolite of uniform pressure and temperature, however, in which the gradients of chemical potentials of K components exist. Let us also assume that the electric current vanishes in the system. In such a system the diffusional thermodynamic forces (without external forces) are [6]:

$$\mathbf{X} = -\operatorname{grad}(\mu_k - \mu_K), \qquad (k = 1, 2, \ldots, K). \tag{2}$$

The vanishing of the electric current signifies a local constraint, which is represented by the restriction

$$\mathbf{I} = \sum e_i \mathbf{J}_i = 0 \tag{3}$$

where e_i is the specific charge of the ith component, whereas $\mathbf{J}_i$ is the current density of diffusion. The determination of the actual form of Onsager's linear laws owing to restriction (3) is an extremum problem, which can be solved by using the minimum principle (1). Hence such a minimum of (1) shall be determined which is compatible with restriction (3) valid for the diffusion current densities $\mathbf{J}_i$. The problem can be solved by the Lagrangian multiplicator method. Multiplying (3) by a vector multiplicator $\boldsymbol{\lambda}$ and adding it to the quantity C in (1) the derivative over the current density components J_{ia} $(a = x, y, z)$ of the expression obtained shall vanish:

$$\frac{\partial}{J_{i_a}}\left(C + \boldsymbol{\lambda} \sum_i e_i \mathbf{J}_i\right) = 0, \qquad (a = x, y, z). \tag{4}$$

Hence the actual vectorial form of which owing to (1), further due to the reciprocity of the matrices $\mathbf{R}$ and $\mathbf{L}$ will become the following:

$$\sum_k R_{ik} \mathbf{J}_k - \mathbf{X}_i + \boldsymbol{\lambda} e_i = 0, \qquad (i = 1, 2, \cdots, K), \tag{5}$$

from which

$$\mathbf{J}_k = \sum_i L_{ki}(\boldsymbol{\lambda} e_i + \mathbf{X}_i), \qquad (k = 1, 2, \cdots, K). \tag{6}$$

This expression is the linear law belonging to the problem, if we recognize that the negative of multiplicator $\boldsymbol{\lambda}$ is just identical with the electric field strength. Indeed, if $\mathbf{E} \equiv -\boldsymbol{\lambda}$, we obtain

$$\mathbf{J}_k = \sum_i L_{ki}(e_i \mathbf{E} + \mathbf{X}_i), \qquad k = 1, 2, \cdots, K) \tag{7}$$

which is a well known expression. With the aid of the principle hitherto unsolved constraint problems can also be successfully examined.

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Summary

The form of the minimum principle similar to the Gauss principle of mechanics given by I. Gyarmati is applied to the solution of an electrochemical local constraint problem. With the aid of the principle and the use of the Lagrangian multiplicator method we can directly attain the form of linear laws valid in isoterm electrolitic solutions. By means of the principle also other hitherto unsolved local constraint problems can be successfully examined.

References

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József VERHÁS, Budapest XI., Budafoki út 8. Hungary.