LETTERS TO THE EDITOR

ON THE FEASIBILITY OF OSCILLATORY FLUXES IN MEMBRANE TRANSPORT IN THE LINEAR REGION

STUDY of oscillatory processes has aroused considerable interest in recent years,[1-3] on account of its biological implications. The conclusion arrived at from the discussion[3,4] of the stability of steady states is that oscillations are possible only in the non-linear region. Caplan and Mikulecky[5] have shown that oscillations in the linear region can be possible only if the cross phenomenological coefficients have signs opposite to each other. Now the question arises if it is possible to create conditions in the linear region such that the cross phenomenological coefficients have signs opposite to each other which means violating Onsager's reciprocal relations. It is this question that has been examined in the present communication using the formalism of Network Thermodynamics[6] and it has been concluded that oscillatory fluxes are not possible in a purely dissipative system in the linear region. It may be mentioned here that some workers like Bresler and Wendt[7] have raised some doubts on the general validity of Onsager's reciprocal relations while some others[8,9] have contradicted it and pointed out inaccuracies in their argument.

A dissipative two flux-two force irreversible process described by the linear phenomenological relations

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \quad (1)$$

between fluxes J_1, J_2 and conjugate thermodynamic forces X_1, X_2 where the coefficients L_{ik} are the phenomenological coefficients, can be represented by a two port Δ-network shown in Fig. 1. Ys in Fig. 1 are conductances. From simple network considerations we can write Ys in terms of phenomenological coefficients *i.e.*

$$Y_1 = L_{11} + L_{12} \quad (2)$$

$$Y_2 = -L_{12} \quad (3)$$

$$Y_3 = L_{22} + L_{12} \quad (4)$$

Now if $L_{12} \neq L_{21}$, the network shown in Fig. 1 should have a constant current source $I = (L_{21} - L_{12}) X_1$ (shown by the dotted lines in Fig. 1), which means that the linear phenomenological relations (1) would no longer represent a purely dissipative process. The conclusion therefore is that for a purely dissipative irreversible process the Onsager's relations,

$$L_{12} = L_{21} \quad (5)$$

have to be obeyed in the linear region. Since irreversible transport processes through membranes have to be dissipative processes the condition

$$L_{12}\ L_{21} < 0 \quad (6)$$

for oscillatory fluxes cannot arise in the linear region.

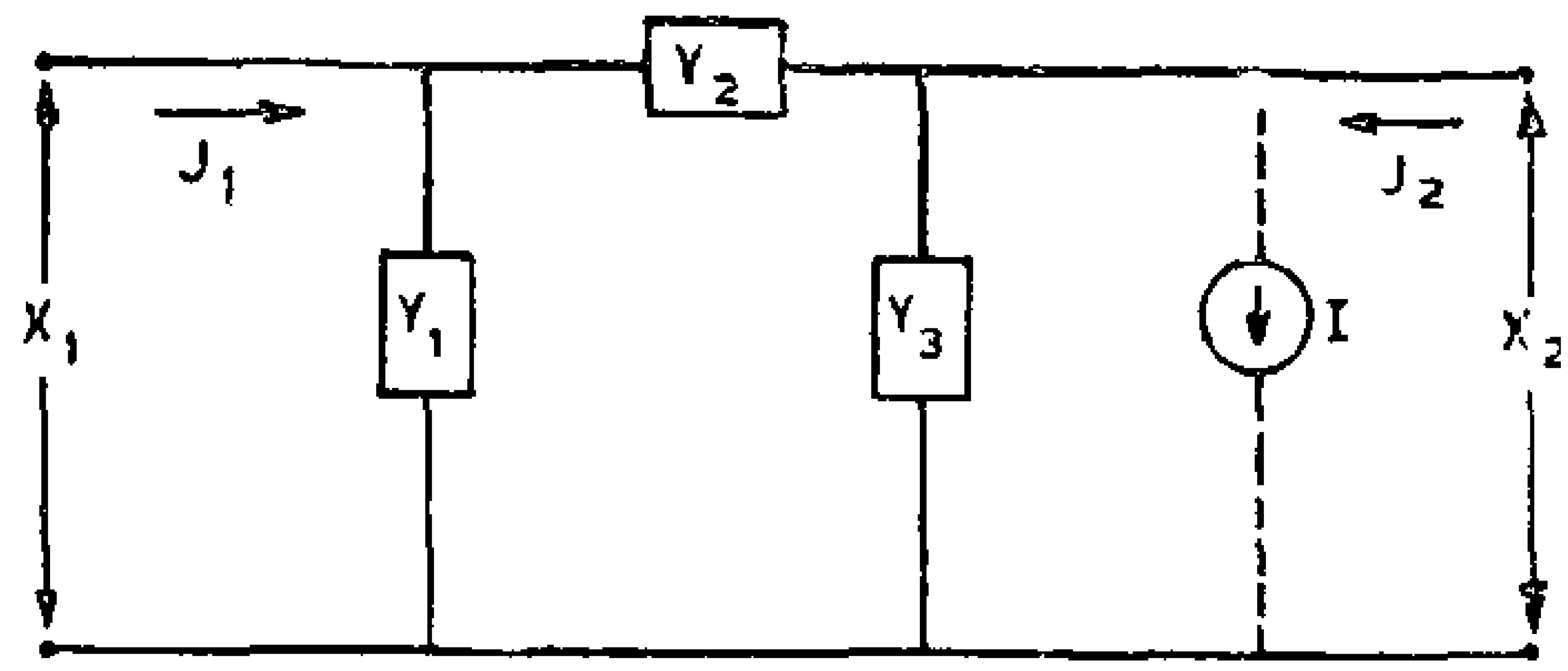

FIG. 1. A Δ-network representation for the linear phenomenological relations (equation 1).

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1. Higgins, J., *Ind. Engg. Chem.*, 1959, 59, 19.
2. Chance, B., Pye, E. K., Ghosh, A. K. and Hess, B., eds., *Biological and Biochemical Oscillators*, Academic Press, New York, 1973.
3. Nicolis, G. and Portnow, J., *Chem. Rev.*, 1973, 73, 365.
4. Nicolis, G., In : *Advances in Chemical Physics*, Vol. 19 (ed. I. Prigogine and S. A. Rice), Wiley–Interscience, 1971, p. 209.
5. Caplan, S. R. and Mikulecky, D. C., In *Ion Exchange* (ed. J. A. Marinsky) Vol. I, Chapter I. Marcel Dekkar Inc., New York, 1966.
6. Oster, G., Perelson, A. and Katchalsky, A.; *Nature*, 1971, 234, 393.
7. Bresler, E. H. and Wendt, R. P., *J. Phys. Chem.*, 1969, 73, 264.
8. Smit, J. A. M. and Starverman, A. J., *Ibid.*, 1970, 74, 966.
9. Srivastava, R. C. and Rajpal, J. *Indian Chem. Soc.*, 1972, 49, 305.