

Notes

Flux-Force Relationship in Oscillatory Reactions

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Flux-force relationship between chemical reaction rate and affinity has been obtained for Lotka-Volterra reaction scheme. The thermodynamic flux equation is found to be complex and non-linear even when affinities tend to zero.

IT has been shown^{1,2} that oscillations cannot occur within the linear domain of irreversible thermodynamics and hence it has been suggested that flux-force relationship in oscillatory processes must be complex. Franck³ has suggested that in oscillatory processes, flux-force relationship would involve autoinhibitory and autocatalytic stages. In order to study oscillatory phenomena in membranes, a deep insight into the nature of flux-force relationship is necessary. Unfortunately experimental studies in this area are few. Quite recently, Rastogi *et al.*⁴ have observed complex relationship between electro-osmotic flux of methanol-water mixture through ion exchange membranes and potential difference. Streaming potential measurements show still more complicated dependence on pressure difference⁵ which can be helpful in understanding oscillatory phenomena in membranes and in biological processes. However, there is need to obtain flux-force relation for a system in which oscillations are known to occur. For this purpose, we shall examine the Lotka-Volterra scheme⁶



where oscillations in the concentration of X and Y have been predicted.

Theoretical: Flux-force relationship for Lotka-Volterra scheme—In reaction systems, thermodynamic forces corresponding to reaction rates are affinities which act as driving forces regardless of the fact whether the system is at equilibrium or far from equilibrium⁷. This should be the case for oscillating reaction systems as well. We shall now try to obtain the thermodynamic fluxes and forces for the above reaction scheme.

The affinity A_1 , A_2 and A_3 of the three reaction steps would be given by

$$A_1 = RT \ln \frac{k_1}{k_{-1}} - RT \ln \frac{X}{A} \quad \dots(1)$$

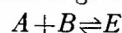
$$A_2 = RT \ln \frac{k_2}{k_{-2}} - RT \ln \frac{Y}{X} \quad \dots(2)$$

$$A_3 = RT \ln \frac{k_3}{k_{-3}} - RT \ln \frac{E}{BY} \quad \dots(3)$$

where k_1 , k_2 and k_3 are the rate constants of the forward steps in sequence of reaction (i), (ii) and (iii) and k_{-1} , k_{-2} and k_{-3} are the rate constants for the corresponding back reactions. R is the gas constant and T is the temperature. The concentration of respective species has been expressed by symbols themselves. The affinity A_i of the overall reaction is given by Eq. (4)

$$A_i = A_1 + A_2 + A_3 = RT \ln \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} \frac{AB}{E} \quad \dots(4)$$

since the net reaction is given by



According to the scheme, since the concentration of A , B and E is kept fixed, out of the three affinities, only two would be independent. If we choose A_1 and A_3 as the independent affinities, we have from Eqs. (1) and (3)

$$X = \frac{k_1 A}{k_{-1}} e^{-A_1} \quad \dots(5)$$

$$Y = \frac{k_{-3}}{k_3 B} e^{A_3} \quad \dots(6)$$

Now, if we neglect all the backward rates, the rates of change of concentration of X and Y with time would be given by

$$J_1 = \frac{dX}{dt} = k_1 AX - k_2 XY \quad \dots(7)$$

$$J_2 = \frac{dY}{dt} = k_2 XY - k_3 BY \quad \dots(8)$$

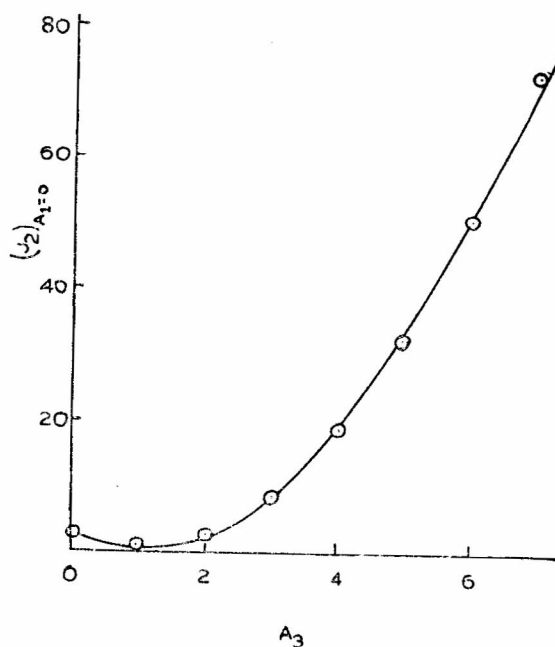
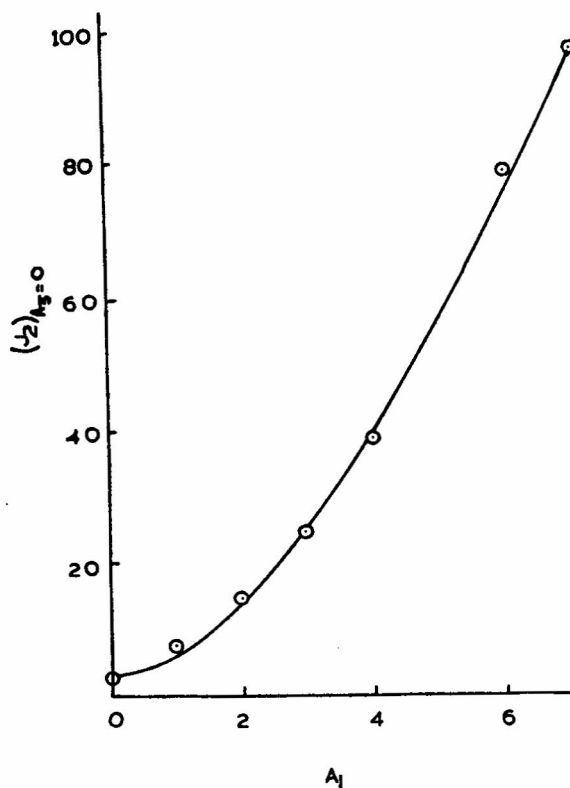
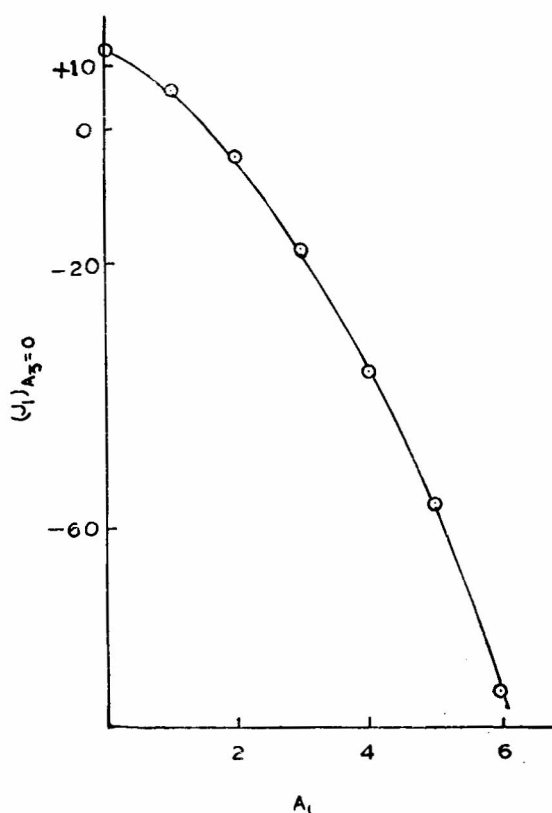
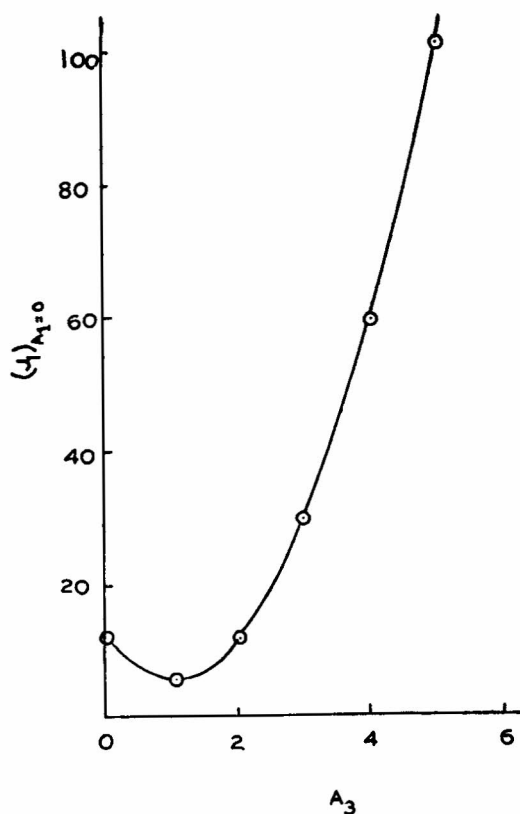


Fig. 1 — Dependence of J_2 on A_3 when $A_1 = 0$


 Fig. 2 — Dependence of J_2 on A_1 when $A_3 = 0$

 Fig. 4 — Dependence of J_1 on A_1 when $A_3 = 0$

 Fig. 3 — Dependence of J_1 on A_3 when $A_1 = 0$

These are the two independent reaction rates. Substituting the values of X and Y from Eqs. (5) and (6) in Eqs. (7) and (8) we get

$$J_1 = A^2 e^{-A_1} - \frac{A}{B} e^{A_3 - A_1} \quad \dots(9)$$

$$J_2 = \frac{A}{B} e^{-A_1 + A_3} - e^{A_3} \quad \dots(10)$$

where we have put all the rates equal to unity.

Obviously the reaction between fluxes J and affinities A are complex and these cannot be reduced to linear relations when $A_1 \rightarrow 0$ or $A_3 \rightarrow 0$. Since no suitable experimental data are available, we shall draw hypothetical curves. Thus J_1 and J_2 have been plotted in Figs. 1-4 by keeping $A_1 = 0$ or $A_3 = 0$ using hypothetical values of A and B . The flux-force relations are typically non-linear.

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