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APPLICATION OF THE TEMPERATURE-JUMP RELAXATION TECHNIQUE TO VERIFICATION OF THE ONSAGER RECIPROCAL RELATIONS

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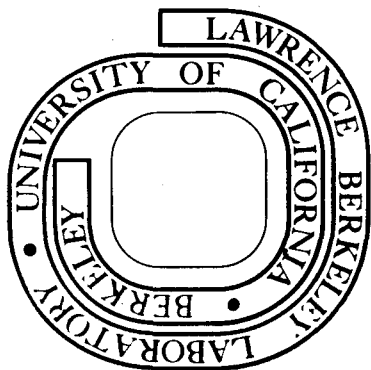# APPLICATION OF THE TEMPERATURE-JUMP RELAXATION TECHNIQUE TO VERIFICATION OF THE ONSAGER RECIPROCAL RELATIONS
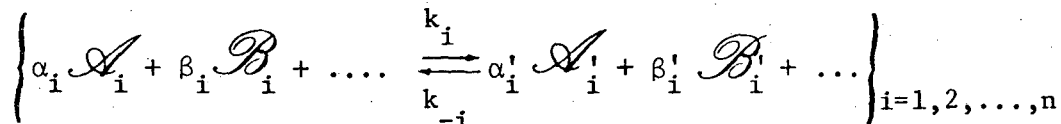
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The Onsager reciprocal relations[1] which play a central role in the theory of coupled irreversible processes[2-5] were derived by L. Onsager in 1931. These relations have been verified experimentally for several irreversible processes.[6,7] However, verification of the relations for coupled irreversible chemical reactions although of great importance in biological and other systems, has apparently not been achieved except for the case of the so-called mono-molecular triangular reactions through verification of the Wegscheider relation.[8-10]

The purpose of this communication is to suggest the method of temperature-jump relaxation[11,12] to verify the Onsager reciprocal relations for a variety of coupled chemical reactions. In this method the temperature of a small cell containing one or more chemical reactions at equilibrium (usually occurring in solution) is raised by a few degrees in a very short time. The temperature jump is carried out by electric discharge through the solution. The variations in the concentrations are then followed by optical methods while the system is approaching its new equilibrium position corresponding to the new temperature of the cell. Analysis of the data so obtained gives the relaxation times of all the different reactions. The relaxation time of a reaction, initially displaced from equilibrium, is the time in which the displacement from equilibrium drops to 1/e of its initial value (e being the

base of the natural logarithm).

Consider the set of coupled chemical reactions

$$\left\{ \alpha_i \mathscr{A}_i + \beta_i \mathscr{B}_i + \ldots \; \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \; \alpha_i' \mathscr{A}_i' + \beta_i' \mathscr{B}_i' + \ldots \right\}_{i=1,2,\ldots,n}$$

where α_i, β_i,... and α_i', β_i',... are the stoichiometric coefficients of the chemical components $\mathscr{A}_i, \mathscr{B}_i,\ldots$ and $\mathscr{A}_i', \mathscr{B}_i',\ldots$, respectively, in the ith reaction. Suppose now that each member of the set is slightly perturbed from its equilibrium position. It can be shown that the rate of the internal entropy production of the system due to approach to the equilibrium is[2]

$$\frac{d\sigma}{dt} = \frac{1}{T} \sum_{i=1}^{n} A_i \, v_i \tag{1}$$

where $\frac{d\sigma}{dt}$ is the time derivative of the total internal entropy of the system, σ. T is the absolute temperature and A_i and v_i are the affinity and rate of the reaction "i", respectively. If the displacement from equilibrium is small (in terms of the degree of advancement or extent of reaction, $\dot{\xi}$, introduced by Th. DeDonder[13]) then the rate of each reaction can be written as a linear combination of the affinity of the reaction divided by the absolute temperature (at constant temperature)[2,14] i.e.

$$v_i = \frac{d\xi_i}{dt} = L_{i1} \frac{A_1}{T} + L_{i2} \frac{A_2}{T} + L_{i3} \frac{A_3}{T} + \ldots + L_{in} \frac{A_n}{T},$$

$$i = 1,2,\ldots,n \tag{2}$$

In which the constants L_{ij} $(i,j = 1,2,....,n)$ are the phenomenological

coefficients. In the matrix-vector notation Eq. (2) can be written as

$$
\begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \cdot \\ \cdot \\ \cdot \\ v_n \end{pmatrix} = \frac{1}{T} \begin{pmatrix} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \\ \cdot & \cdot & & \\ L_{n1} & \cdots & & L_{nn} \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ \cdot \\ \cdot \\ \cdot \\ A_n \end{pmatrix} \tag{3}
$$

The objective is to verify the symmetry of the matrix of the phenomeno-

logical coefficients, experimentally.

Consider the simplest case:

$$ A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \qquad\qquad \text{Reaction 1} $$

$$ C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D \qquad\qquad \text{Reaction 2} $$

where k_i and k_{-i} are the forward and reverse rate constants for reaction

i. The relaxation times t_i^* (after slight displacement from equilibrium)

are given by[15]

$$ t_1^* = \frac{1}{k_1 + k_{-1}} , \qquad t_2^* = \frac{1}{k_2 + k_{-2}} $$

and the rates of approach to equilibrium by

$$v_1 = -(k_1 + k_{-1})\Delta X_B$$
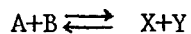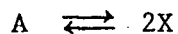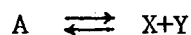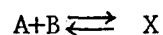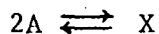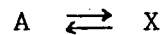
$$v_2 = -(k_2 + k_{-2})\Delta X_D$$

where ΔX_B and ΔX_D are the displacements (in moles) from equilibrium at the commencement of approach to equilibrium, i.e. $\Delta X_i = X_i - X_i^e$. Using the foregoing relationships we can write

$$-\frac{\Delta X_B}{t_1^*} = L_{11} \frac{A_1}{T} + L_{12} \frac{A_2}{T} \tag{4}$$

$$-\frac{X_D}{t_2^*} = L_{21} \frac{A_1}{T} + L_{22} \frac{A_2}{T} \tag{5}$$

By letting the two reactions (1 and 2) take place in the temperature-jump cell, one at a time, and also simultaneously, and thus measuring the corresponding relaxation times and concentrations, one can find all the quantities necessary to calculate L_{12} and L_{21} from Eqs. (4) and (5). This can be done as follows. In the independent study of each reaction the cross terms of Eqs. (4) and (5) drop out. Therefore, measurements of the relaxation times and the initial and final concentrations (corresponding to the old and new chemical equilibria of the system, respectively) and also the temperature of the cell (after the jump), provides enough information to calculate L_{11} and L_{22}. These quantities and a new independent set of measurements of the foregoing quantities when the reactions are coupled make it possible to calculate the values of L_{12} and L_{21}, and thus test the relation $L_{12} = L_{21}$ which is equivalent to the symmetry of the corresponding matrix.

It should be stated that this technique can be applied to any set of coupled reactions from a variety of reactions of the form[15]

$$A \rightleftharpoons X$$

$$2A \rightleftharpoons X$$

$$A+B \rightleftharpoons X$$

$$A \rightleftharpoons X+Y$$

$$A \rightleftharpoons 2X$$

$$A+B \rightleftharpoons X+Y$$

since for all such reactions equations similar to Eqs. (4) and (5) can be derived, provided that the displacements from equilibrium are small.

The temperature jump relaxation technique is suitable for testing the Onsager reciprocal relations because displacements from equilibrium can be made very small by making the temperature jumps small so that the validity of Eqs. (2) and (3) is assured. Furthermore, this method would allow collection of a large amount of data for test of the theory in a reasonably short time.

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