

On the Choice of Inter-Action Rate Constants

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Phenomenological rate equations are used as axioms in the formalism of irreversible thermodynamics^{1,2,3}. The theoretical⁴ and the experimental^{5,6} studies of a number of phenomena have gone to establish that beyond certain magnitudes of the applied forces the rate constants i.e. the proportionality constants of linear laws do not behave as constants. Recently it has been suggested by Van Rysselberghe⁷ that in the formalism of irreversible thermodynamics the proportionality constants of linear laws should be introduced in the interaction rate constants in order to increase their constancy. The main advantage of this modification lies in the fact that the proportionality constants are to a better extent constants with respect to local variables. The modification, mentioned above has been found to hold good in cases of thermal diffusion⁸ and electro-osmosis.⁹ The purpose of this note is to examine its validity in respect of thermo-osmosis.

The phenomenological rate equation for thermo-osmosis relating to the transport of matter J_M , the temperature and pressure gradients ΔT and ΔP across the membrane, respectively, at a mean temperature T is written⁴ as

$$J_M = L_{11} (-v \cdot \Delta P / T) + L_{12} (-\Delta T / T^2) \quad \dots \quad (1)$$

where L_{ij} ($i=1,2$; $j=1,2$) are the phenomenological rate constants and v is the specific volume of the transported matter. The modified equation for the phenomenon according to Blokhra¹⁰ is written as

$$J_M, \eta^{\frac{1}{2}} T^{-\frac{1}{2}} = (-D \cdot v \cdot \eta^{-\frac{1}{2}} \cdot T^{-\frac{1}{2}}) \cdot \Delta P + L (-\Delta T / T) \quad \dots \quad (2)$$

In eq. (2) η is the viscosity of the liquid, $D=L_{11} (\eta/T)$ and L is the modified interaction rate constant. Comparison of eqs. (1) and (2) gives

$$L = L_{12} (T^{-3/2} \cdot \eta^{\frac{1}{2}}) \quad \dots \quad (3)$$

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Both L and L_{12} have been calculated from the recent experimental data¹¹ on thermo-osmosis of conductivity water through cellophane membrane at different mean temperatures for the fixed temperature gradient $\Delta T = (9 \pm 0.2)^\circ$. Since the units of L and L_{12} are different, their comparative constancy have been analyzed by the differential method^{8,9} in order to get a clear answer. The fractional changes considered in the analysis for the two cases are for $\delta t = 1^\circ$.

The results on the constancy of L and L_{12} in respect of the variation with the mean temperature, T , at a constant temperature gradient, $\Delta T = (9 \pm 0.2)^\circ$, have been obtained graphically. The average variation in L is found to be 0.68% only of that of the variation in L_{12} ; the minimum and maximum limits being 0.56% and 0.73% respectively in the temperature range, 40° - 60° . These results are in agreement with those of Van Rysselberghe⁷ and Blokhra¹⁰. It is worthwhile mentioning, however, that the results obtained from the analysis of the data of Rastogi, Blokhra and Agarwal¹², on thermo-osmosis, do not support them.

Eq. (2) presupposes Onsager's reciprocity relation. This may not be true under all circumstances. However, following the method of Colman and Truesdell¹³, the relation may be shown to be valid even with the modified fluxes and forces.

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