

LETTERS TO THE EDITOR

A COMMENT ON THE ANALYSIS OF
 VOLTERRA MODEL

THE purpose of this short note is to comment on the usual method of analysis of Volterra's model¹ for the population of several interacting species, with special reference to the review paper by Goel, Maitra and Montroll². The n -species competing system is characterized by the system of equations

$$\frac{dN_i}{dt} = k_i N_i + \beta_i^{-1} \sum_{j=1}^n a_{ij} N_i N_j \quad (1)$$

where N_i is the instantaneous population of the i -th species and k_i is its "rate constant". The interaction is represented by the second term on the right side of eq. (1) and corresponds to all possible binary encounters. The antisymmetric coefficients a_{ij} represent the strength of the interactions and the positive quantities β_i^{-1} are the "equivalence numbers".

In the work of Goel *et al.*², the "steady state" of the assembly was characterized by that set of populations $\{N_j\}$ for which

$$dN_j/dt = 0, \text{ for all } j. \quad (2)$$

However we intend to point out here that such a set $\{N_j\}$ for which $dN_j/dt = 0$ for all j , is not a physical solution. It is clear from eqs. (1) and (2) that, not only the first order derivatives $\{dN_i/dt\}$ are zero, but all other finite order derivatives $\{d^m N_i/dt^m\}$ vanish simultaneously; for example from eq. (1)

$$\begin{aligned} \frac{d^2 N_i}{dt^2} &= k_i \frac{dN_i}{dt} + \beta_i^{-1} \sum_{j=1}^n a_{ij} \\ &\times \left(N_i \frac{dN_j}{dt} + \frac{dN_i}{dt} N_j \right), \end{aligned}$$

and each of the term on the right side is zero by eq. (2). Hence

$$\frac{d^2 N_i}{dt^2} = 0.$$

In like manner

$$\frac{d^m N_i}{dt^m} = 0 \quad (\text{all } i \text{ and } m). \quad (3)$$

Thus the set of populations $\{N_j\}$ will be totally flat as a function of time, as can be seen by a (Taylor) series expansion (also for earlier times by analytic continuation). But it is well known that the solution of the Volterra system shows oscillations in $\{N_j\}$ ³ and at no finite time, $\{N_j\}$ is constant. Hence the equations⁽²⁾ defining the "steady state" do not correspond to any

physical solution. However we argue that all the relations derived in the work of Goel *et al.*² are valid, provided we replace the "steady state" population by a long time average population $\{[N_i]\}$ defined by

$$[N_i] = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T N_i(t) dt \quad (4)$$

provided the limit exists. Then we can directly integrate eq. (1) from $t = 0$ to $t = T$, divide by T and take the limit $T \rightarrow \infty$, when we get

$$\begin{aligned} \lim_{T \rightarrow \infty} \beta_i \{T^{-1} \log N_i(T) - T^{-1} \log N_i(0)\} \\ = k_i \beta_i + \sum_{j=1}^n a_{ij} [N_j]. \end{aligned} \quad (5)$$

This was done in the work of Goel *et al.*². However we wish to stress on an important difference. In the cited reference, the conservation condition [eq. (1.9) of ref. (2)] was utilized in the subsequent argument; but the conservation condition itself was derived from the "steady state" definition eq. (2). Our aim here is to derive the basic equation (1.6) of ref. (2) without invoking $dN_i/dt = 0$, for all i . After eq. (5) we argue as follows: $N_i(t)$ cannot be zero at any instant, since if $N_i(t_0) = 0$, then from eq. (1)

$$\frac{dN_i}{dt}(t_0) = 0, \quad (6)$$

and following the same argument which led to eq. (3)

$$\frac{d^m N_i}{dt^m}(t_0) = 0 \quad (\text{all } i, m). \quad (7)$$

Thus the curve must be flat and continuing analytically to $t < t_0$, we see that $N_i(t) = 0$ at all time t (this will be so whenever the population of a species dies off with zero slope), which is an uninteresting situation. Furthermore, $N_i(t)$ cannot blow up, since we assumed, for the physically interesting case, that

$\lim_{T \rightarrow \infty} 1/T \int_0^T N_i(t) dt$ exists. Thus $N_i(t)$ can neither

vanish nor blow up. Hence the left side of eq. (5) vanishes and we have

$$k_i \beta_i + \sum_{j=1}^n a_{ij} [N_j] = 0, \quad (8)$$

which is eq. (1.6) of ref. (2), provided we interpret $q_j = [N_j]$, as was suggested there. Once we derive eq. (1.6) of the cited reference, all the other relations derived therefrom stand valid.

One of us (TKD) wishes to acknowledge financial support from the Council of Scientific and Industrial Research, India. He further wishes to thank Prof. B. Bhattacharya for making it possible for him to work as a pool officer at Jadavpur University.

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April 23, 1977.

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RELAXATION TIMES AND ACTIVATION ENERGIES OF SOME SUBSTITUTED PHENOLS

RELAXATION times of four polar substituted phenols namely (A) 3, 5 dimethyl phenol, (B) 2, 3, 5 trimethyl phenol, (C) 2, 4, 6 trimethyl phenol and (D) 2, 4, 6 trichlorophenol have been measured in the dilute solution of benzene at 20, 25, 30 and 35°C at S-band. The free energies of activation for the process of dipole orientation and viscons flow have been calculated using Eyring's theory¹ of

rate process. The results have been analysed in the light of molecular motions of the system and it is concluded that dipole orientation is contributed by both molecular as well as intramolecular rotation.

Dielectric studies of polar solutes in the non-polar solvent throw considerable light on various molecular and intramolecular forces. Magee and Walker^{2,3} have investigated the relaxation times of some substituted phenols in a number of non-polar solvents. LeFerve⁴ and Hiremath⁵ have investigated the dielectric behaviour of phenols in the dilute solution of non-polar solvents and concluded that hydroxyl relaxation plays dominant role in the relaxation process of the phenols.

Due to their wide industrial and pharmaceutical applications the present study forms a significant contribution to the existing knowledge of the dielectric behaviour of some di and tri substituted phenols.

The dielectric constant (ϵ') and dielectric loss (ϵ'') have been measured on a S-n and microwave bench⁶ by a technique, due to Roberts and Von Hippel⁷, later modified by Dekin and Works⁸. The relaxation time (τ) has been evaluated using Gopalakrishna fixed frequency method⁹. The compounds obtained from B.D.H., England, were of pure quality. The solvent (A.R.) was distilled before use.

The values of relaxation times and thermodynamic parameters are reported in Table I. It

TABLE I
Relaxation times and activation energies
($\lambda = 9.80$ cm)

Molecule	Temp. °K	$\tau \times 10^{12}$ sec	ΔF_e Kcal/ mol	ΔH_e Kcal/ mol	ΔS_e Cal/ mol	ΔF_η Kcal/ mol	ΔH_η Kcal/ mol	ΔS_η Cal/ mol
3, 5 Dimethyl phenol	293	21.2	2.83	1.90	-3.17	2.90	2.52	-1.29
	298	20.1	2.86	1.90	-3.22	2.91	2.52	-1.30
	308	17.4	2.89	1.90	-3.21	2.93	2.52	-1.33
2, 4, 6 trichlorophenol	298	21.1	2.88	1.41	-4.93	2.90	2.52	-1.29
	303	19.8	2.91	1.41	-4.95	2.91	2.52	-1.30
	308	19.0	2.94	1.41	-4.96	2.93	2.52	-1.33
2, 4, 6 trimethylphenol	293	11.1	2.4	1.09	-4.64	2.90	2.52	-1.29
	298	10.6	2.5	1.09	-4.75	2.91	2.52	-1.30
	308	10.0	2.6	1.09	-4.74	2.92	2.52	-1.30
2, 3, 5 trimethylphenol	293	18.0	2.73	1.63	-3.75	2.90	2.52	-1.29
	298	16.9	2.75	1.63	-3.75	2.91	2.52	-1.30
	303	15.9	2.77	1.63	-3.76	2.92	2.52	-1.32
	308	15.3	2.88	1.63	-3.83	2.93	2.52	-1.33