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**Corrections to "Equilibrium Studies of Polyanions. II. Polyborates in NaClO<sub>4</sub> Medium"\***  
NILS INGRI, GÖSTA LAGERSTRÖM, MINA FRYDMAN and LARS GUNNAR SILLÉN

*Department of Inorganic Chemistry,  
The Royal Institute of Technology,  
Stockholm 70, Sweden*

- P. 1043, Table 2  
 $v_1 = 7.13$ , stands  $E = 753.66$ ,  
read 753.46
- P. 1044, Table 3  
 $B = 0.02$  M,  $Z = 0.513$ , stands  
 $-\log h = 9.996$ , read 8.996
- P. 1045, Table 3  
 $B = 0.400$  M,  $Z = 0.990$ , stands  
 $-\log h = 11.583$ , read 11.683
- P. 1047, Table 4, column 10  
" $\Delta(1-E)$ " should be lowered  
half a step so that the figures  
come in between those of column  
11, "R".

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**On the Possibility of Periodic Transformations of Enzymes during their Action as Catalysts**

J. A. CHRISTIANSEN

*Københavns Universitets Fysisk-Kemiske  
Institut, Copenhagen, Denmark*

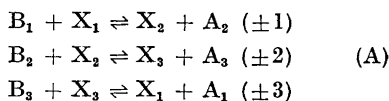
Against the existence of periodic chemical reactions one may argue that chemical reactions have no inertia, and that for this reason periodic phenomena cannot occur during their advancement. This argument evidently is based on an analogy with mechanical systems like pendulums.

It is, however, not true that inertia is a necessary condition for periodicity in all mechanical systems. *E. g.* an Archimedean screw acting as a motor delivers water periodically and in equally great portions to the lower basin with a well defined frequency. But this frequency is evidently determined by circumstances which have nothing to do with the inertia of the system. Consequently this argument is not valid.

Another argument seems, however, at a first glance to be conclusive. To fix our ideas, let us assume that an irreversible overall reaction (B)



is catalyzed by an enzyme according to the sequence (A)



(In preparation for a future paper the A's and B's of Ref.<sup>5</sup> have been interchanged.) The B's and the A's are intended to symbolize the "substrates" while  $X_1$ ,  $X_2$  and  $X_3$  mean three different forms of the enzyme or complexes of the enzyme with the substrates. The affinity of the overall reaction (B) then compels the enzyme to perform cyclic transformations in the direction 1231. The question now is whether the partition fractions of the enzyme on three forms become steady asymptotically or whether they perform periodic variations around certain mean values. By application of well known ideas one arrives at a system of three linear equations between

the three partition fractions and their first derivatives with respect to time. The solutions of this system are certainly aperiodic and by the way, the two decay constants become so large, that steady state is asymptotically arrived at in minute fractions, e. g.  $10^{-8}$ , of a second.

Thus periodic variations should be excluded. However, from nerve physiology it is known with certainty that periodic synchronous phenomena actually occur in certain nerves or rather in their end-organs. As now living organisms have so far as known only chemical reactions as ultimate causes of all observable events which take place in them, we may state with a probability approaching certainty that periodic chemical changes actually occur in nature.

To solve this dilemma one might look for mechanisms of the Volterra<sup>1</sup> type, which allow the appearance of periodic changes. This has been done, *i. a.* by Bonhoeffer<sup>2</sup> and Prigogine<sup>3,4</sup>, but such mechanisms must be so artificial that it is hardly possible to believe in their occurrence, e. g. in living organisms.

We are therefore turned back on mechanisms of the type described above. Now in solving the corresponding equations we have implicitly assumed, that concentrations and their derivatives with respect to time can be determined simultaneously so accurately as we please. But this may not be true. We can certainly, e. g. by means of a "flash" method, determine the concentrations of the forms of the enzyme accurately, at a certain time. But the determination of the derivatives requires a second observation after the lapse of a certain not too short time interval, during which the concentrations may have varied in some unknown way, the more so as the first "flash" to give an observable effect must have changed the state of the enzyme and may have caused some chemical change. Therefore the more accurately we try to determine the concentrations by making the time interval short, the less accurate becomes the determination of the rate of change and *vice versa*.

We thus arrive at the result, that the validity of our system of differential equations can neither be proved nor disproved by direct experiments that is, they are physically unrealistic.

Therefore the occurrence of rhythmic chemical changes in the partition fractions need not surprise us, neither be it surprising that it is actually possible, as shown

elsewhere<sup>5</sup>, to calculate a frequency of oscillations with time in the values of these fractions.

We have only to remember that the aperiodic and the oscillatory treatment of the kinetic problem mutually exclude each other although separately both are possible.

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## Distillation Head for the Distillation of Small Amounts of Liquids

ARNE B:SON GROTH

*Department of Applied Organic Chemistry,  
Royal Institute of Technology,  
Stockholm, Sweden*

A distillation head suitable for semi-micro distillation columns has been designed and tested. Above all the author has tried to attain the following results:

1. As small a volume of liquid as possible that will adhere to the walls of the distillation head and the condenser.
2. Absence of stopcocks and ground glass joints.
3. Adjustable and continuous outlet.
4. Fitness for use in distillations at atmospheric pressure as well as under vacuum.

One of the difficulties encountered in the distillation of small amounts of liquid in a column provided with an ordinary distillation head, is the fact that a major part of the liquid to be distilled will remain in the condenser and on the walls of the tube connecting the condenser to the receiver. Usually, this tube has an internal diameter of 1.5–2 mm. Part of this remaining liquid will be in a state of