differences between their means for the different variates can be easily obtained.

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October 3, 1944.

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'*ZERO ORDER*' REACTIONS UNDER ELECTRIC DISCHARGE

1. As ordinarily formulated the law of Mass Action implies thermal changes. Its wider significance is, however, indicated by the fact that the Mass law expressions hold for the kinetics of photochemical, especially photocatalytic reactions; spontaneous recombination of opposite ions in gases; radioactive changes including both consecutive and Wegscheider type simultaneous reactions; equilibria in the ionisation of weak electrolytes and of others at low concentrations; decrease of the micellar 'primaries' as envisaged in Smoluchowski's theory of coagulation, etc.[1] It is now suggested that the progress of a discharge reaction may also be considered, under certain conditions, from the standpoint of the Mass law.

2. For a reaction of the *n*th order, it is shewn that,

$$k = \frac{1}{t\,(n-1)} \left\{ (a-x)^{-(n-1)} - a^{-(n-1)} \right\} \qquad \text{(i)}$$

$$= \frac{a^{-(n-1)}}{t\,(n-1)} \left\{ \left(1 - \frac{x}{a}\right)^{-(n-1)} - 1 \right\} \qquad \text{(ii)}$$

where the various symbols have their familiar significance. If now t is such that the corresponding fractional change x/a is small, we can write to a sufficient approximation,

$$.k = \frac{1}{t\,(n-1)\,a^{(n-1)}} \left\{ 1 + (n-1)\,\frac{x}{a} - 1 \right\} \qquad \text{(iii)}$$

$$t = \frac{1}{k \cdot a^{(n-1)}} \cdot \frac{x}{a}\,;\ \frac{x}{a} = k.t.a^{(n-1)} \qquad \text{(iv)}$$

(iv) may also be obtained directly from the Mas law expression for the average velocity $\Delta x/\Delta t = k(a-x)^n$; the simplifying approximation giving (iii) may then be introduced. (iv) leads to the familiar method of determining the 'order' of a reaction from observation of the influence of the initial concentration a upon time t corresponding to given x/a, and *vice versa*. *The derivation* (i-iv) not found in the literature, gives a theoretical basis for this method; its applicability is limited by conditions implied in the approximation leading to (iii). In actual practice x/a as high as 0·5 would appear to be permissible.

3. Putting $n = 0$ in (iv) yields the empirical test for a 'zero order' reaction. It is that for a given t, x/a increases directly as, or what is the same thing, that the absolute rate of change is independent of, a. These reactions occur almost entirely on either the walls of the reaction vessel or/and on a catalyst surface;[2] loss in this amount of the reactant material during reaction is made good by adsorption from the homogeneous phase.[2] Changes in the concentration of the latter will not affect sensibly the amount adsorbed and, therefore, the corresponding nett rate of the reaction.[2]

The frequent occurrence under electrical discharge of the 'clean up' and allied phenomena suggest that the type of effects leading to consequences as indicated above might well obtain in discharge reactions. It is instructive here to cite certain results on the newly observed light-effect,[1,6,3,4,7] *viz.*, Δi an instantaneous and reversible change on exposure to an *external* radiation of the discharge current i. It is found that Δi varies appreciably due to 'ageing' under the discharge,[1,3,4] and, that its time-rate depends markedly on the nature of any pre-treatment to which the discharge tube was subjected.[1] By giving appropriate coats on the container walls, it has been possible not only to alter very markedly the magnitude but the *sign* of the light-effect.[1] These results point to a variable adsorption-like layer as an important determinant of the phenomenon.[1,5] The subsequent observation of a periodic effect[1,5] in the nitrous oxide, hydrogen interaction under discharge showing not only a rhythmic variation of the rate of change but (during certain stages) of its direction is easily explicable, on the assumption of an intermittent formation and break up of a layer on the electrodes, producing a variation of the surface gradient, of the 'threshold potential' V_m[1,6,7,5] and, therefore, of the corresponding electrical quantities during the reaction as observed.[1,6,7,5] It follows, therefore, that (*a*) a large surface : volume ratio as in an ozoniser type discharge tube would favour the occurrence of such a periodic effect and that (*b*) this surface action leading to 'zero order' changes need not necessarily be confined to ordinary adsorption, *viz.*, that produced in absence of an external electrical field. Work is in progress to investigate the limits of the validity of (*a*); (*b*) is to be anticipated from general considerations of the discharge phenomena.

4. Alternatively to, or what is more likely, simultaneously with the mechanism considered in para 3, the change may be caused photochemically by the *internal* radiation produced in the reaction space under discharge. It is considered that adsorption as in para 3 of the reactant material and its activation in the discharge increases its optical absorption. This last towards the *internal* radiation may be total or feeble; the order of the corresponding change, therefore, would be zero or one respectively.

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