V. G. Firsov and B. V. Ershler

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. G. Firsov and B. V. Ershler

ON THE APPLICABILITY OF ALLEN' S MODEL TO THE RADIOLYSIS OF AQUEOUS SOLUTIONS

(Presented by Academician A. I. Alikhanov, January 23, 1961)

The equations of radiolysis in aqueous solutions are, as a rule, written on the basis of the model of the irradiated solution that was first clearly formulated by A. O. Allen (^{1}). According to this model, H and OH radicals arise at sites of high ionization density (“hot spots,” in Allen' s expression) and then partly recombine, forming molecules of H_2, H_2O_2, and H_2O, and partly diffuse into the bulk of the solution, avoiding recombination. The initial yields of H_2, H_2O_2, H, and OH for Co^{60} γ-radiation, determined by this primary process, were also first reliably established by Allen (^{2}, ^{3}).

In applying Allen' s model, equations of homogeneous chemical kinetics are usually used; thereby, obviously, the following two approximations are admitted: 1) the yields of H_2, H_2O_2, H, and OH are regarded as independent of the composition and concentration of the solution; 2) the nonuniformity of the spatial distribution of the primary products of radiolysis is ignored, i.e., it is assumed that H_2, H_2O_2, H, and OH are distributed uniformly in the solution.

Approximation 1) for dilute solutions of many weak radical acceptors for x-ray and γ-radiation is supported rather well both by experiment and by theoretical calculations of Allen' s model carried out by a number of authors ((^{4}-^{7}) and others)*. However, the validity of approximation 2) has never been tested experimentally, and theoretically it has been considered only in the work of B. V. Ershler and G. G. Myasishcheva on the radiolysis of solutions containing H_2O_2, H_2, and O_2.

One of us has shown (^{8}) that, if Allen's model and the equations of homogeneous chemical kinetics are valid for radiolytic processes, the following two regularities must be observed: 1) if, for the stationary state of an irradiated solution, curves of the dependence of the logarithm of the concentration of all particles present in the solution on the logarithm of the concentration of any one of them have been found at a certain intensity I_1 of the absorbed radiation, then, on transition to the intensity I_2, all these curves, without changing shape, will shift parallel to themselves by the amount $\lg(I_2/I_1)^{1/2}$ along both axes; 2) if, for a radiolytic process, at intensity I_1, a curve has been found for the dependence of the yield of

Figure 1

Figure 1: Figure 1

some particle on the logarithm of the concentration of another particle, then at intensity I_2 this curve, without changing shape, will shift along the logarithmic axis parallel to itself by the amount $\lg[(I_2/I_1)^{1/2}]$. These two "$I^{1/2}$-regularities" must be observed for any reactions in the irradiated solution that obey Allen' s model, provided that the stationary concentrations or yields in this solution are single-valued functions of the concentration of any one particle. Other cases are considered in more detail in ([8]).

* These theoretical calculations, moreover, showed that Allen' s model also explains well the dependence of the magnitude of the initial yields on the ionization density of the radiation.

In the present work we attempted, on the basis of such $I^{1/2}$-regularities, to determine the applicability of approximation 2) of Allen' s model to the radiolysis of titanium salt solutions, assuming that approximation 1) is applicable to them in the same way as has been established for many other solutions of weak acceptors.

Figure 1 gives two curves for the dependence of the yield of radiolytic oxidation of solutions of trivalent titanium sulfate on $\lg[\mathrm{Ti}^{3+}]$, obtained in the absence of oxygen under irradiation in a cobalt source. Curve 1 was taken at radiation intensity $I_1 = 0.0364 \cdot 10^{19}$ eV/l • sec, curve 2 at $I_2 = 1.00 \cdot 10^{19}$ eV/l • sec. The measurements showed that the oxidation yield at first increases slowly with concentration and then falls comparatively steeply. As is seen from Fig. 1, the curves obtained at two different intensities

Fig. 1. Fulfillment of the $I^{1/2}$-regularity in solutions of Ti^{3+} salts. Curves of the dependence of G (the number of oxidized Ti^{3+} ions per 100 eV) on $\lg[\mathrm{Ti}^{3+}]$, taken at intensities $I_1 = 0.0364 \cdot 10^{19}$ eV/l • sec (1) and $I_2 = 1.00 \cdot 10^{19}$ eV/l • sec (2)

do in fact agree rather accurately in shape, are parallel, and the distance between them along the logarithmic axis fluctuates between 0.70 and 0.72, which with good accuracy is equal to the value $\lg(I_2/I_1)^{1/2} = 0.72$. The presence of the $I^{1/2}$-regularity in this case shows that, for solutions of salts of trivalent titanium, Allen' s model is a good approximation.

The dependence of the yield on the radiation intensity is an evident direct indication of interaction between particles born in different tracks, and the detection of the $I^{1/2}$-regularity indicates that this interaction in the present case is well described by the equations of homogeneous kinetics. It is obviously desirable, on the basis of $I^{1/2}$-regularities, to carry out a broader investigation of Allen' s model and by this method to identify those systems, as well as the concentration and intensity intervals, in the study of which it can be used for analysis of the mechanisms of radiolytic processes. Work in this direction is being carried out by us.

Institute of Theoretical and Experimental Physics
Academy of Sciences of the USSR

Received
23 I 1961

REFERENCES

1. A. O. Allen, *J. Phys. and Coll. Chem.*, **52**, 479 (1948).
2. A. O. Allen, C. J. Hochanadel, J. A. Ghormley, T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).
3. A. O. Allen, *Rad. Res.*, **1**, 85 (1954).
4. A. H. Samuel, J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).
5. S. C. Ganguly, J. L. Magee, *J. Chem. Phys.*, **25**, 129 (1956).
6. P. J. Dyne, J. M. Kennedy, *Canad. J. Chem.*, **36**, 1518 (1958).
7. P. J. Dyne, J. M. Kennedy, *Canad. J. Chem.*, **38**, 61 (1960).
8. B. V. Ershler, *DAN*, **129**, 866 (1959).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.