Yu. L. KHAIT

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. L. KHAIT

ON THE STATISTICAL THEORY OF RADIATION-CHEMICAL REACTIONS IN CONDENSED BODIES

(Presented by Academician A. V. Topchiev, 10 V 1960)

It is known that radiation-chemical reactions consist of a number of successive stages (formation of ions, free radicals, etc.). Some stages of these reactions are elementary acts of activation processes, in each of which work E' is performed that exceeds certain threshold values $E \gg kT$ (k is Boltzmann' s constant, T is the mean temperature of the system). Under the influence of radiation the reaction rates increase, which cannot be explained by an increase in the mean temperature T caused by irradiation ([1–3]). Attempts to explain this fact by means of the theory of absolute reaction rates, which does not take into account the collective character of the motion of particles of a condensed body, encounter serious difficulties. In ([4]) a method was proposed for calculating the rates of activation processes in condensed bodies that statistically takes into account the collective character of the motion of their particles (without resorting to mechanics).

Below this method is generalized so as to include in the consideration the action of ionizing radiations. Let us first consider a homogeneous equilibrium system with volume V and energy E_0. Divide it into $N = V/l^3$ regions μ_p with mean volume l^3 ($p = 1, 2, \ldots, N$), under the condition that $V^{1/3} \gg l \gg \hbar v/kT = \lambda$ ([10]), where v is the mean rate of energy transfer in the system by the particles (quasiparticles) responsible for the process under consideration. The set M of possible values of the energy U_p of each region μ_p is continuous. We describe the random changes of U (and of the internal parameters f_p) by local random functions $U_p(t, \beta)$ (and $f_p(t, \beta)$), where t is time, β is the number of the realization $U^{(\beta)}(t)$ of the process $U_p(t, \beta)$ ([5,6]). It is usually assumed that the states of an equilibrium system form a homogeneous Markov process possessing the ergodic property, while the fluctuations are described by a Gaussian distribution ([7]). In accordance with this, let us assume that the N processes $U_p(t, \beta)$ (or $f_p(t, \beta)$) form an N-dimensional stationary normal ergodic random vector function $\mathbf{U}(t, \beta)$ (or $\mathbf{f}(t, \beta)$) ([6]), differentiable everywhere except for a finite set of points. For stationary processes the distributions for $U_p(t, \beta)$ and $\dot{U}_p(t)$ are independent ([8,9]). Therefore $\sigma^2 = [\dot{U}_p(t)]^2$ does not depend on the values of

$U_p(t,\beta)$ and is equal to $\sigma = \omega_0\alpha$ ([8,9]), where $\alpha^2 = \overline{(U(t,\beta)-\bar{U})^2}$; ω_0 is a quantity with the dimension of frequency, depending on l, and the bar denotes averaging. The mean change $\overline{\Delta U(\tau)}$ of the energy U over the time τ is equal to $\overline{\Delta U(\tau)} \simeq \sigma\tau = \omega_0\alpha\tau$ ([6,8]). Choose l in such a way that the conditions

$$\overline{\Delta U(\tau)} < E \ll \bar{U}_0, \tag{1}$$

are satisfied, where $\bar{U}_0 = nkT$; $n = \gamma l^3/d^3$; γ is the number of degrees of freedom in the volume d^3 falling to one particle. The dependence $\omega_0(l)$ is not known in general form. Therefore we shall use the uncertainty relation $\overline{\Delta U(\tau)}\,\tau \gtrsim \hbar$ and, with the aid of (1), find

$$l^2 \lesssim d^2\frac{E}{kT}\frac{d}{\lambda\gamma}; \qquad l^3 \gg \frac{E}{kT\gamma}d^3; \qquad \left(\frac{E}{\gamma kT}\right)^{1/2} \gg \left(\frac{\lambda}{d}\right)^{3/2}; \qquad \lambda = \frac{\hbar v}{kT}. \tag{2}$$

The regions μ_ρ, bounded by conditions (1) and (2), are closed with sufficient accuracy over the intervals τ.

Let us divide the observation time into nonoverlapping intervals $\tau_s = \tau$ ($s = 1,2,...$). To each τ_s we assign N infinitely differentiable functions $\{\delta_\rho(\tau_s,t)\}$, equal to zero outside the intervals τ_s and normalized by the conditions

$$\int_{-\infty}^{\infty}\delta_\rho(\tau_s,t)\,dt = 1.$$

With their aid we construct generalized random processes [11]

$$U_\rho(\tau_s,\beta) = \int_{-\infty}^{\infty}\delta(\tau_s,t)U_\rho(t,\beta)\,dt = \hat{\delta}_\rho(\tau_s)U_\rho(t,\beta),$$

which we regard as the action of the operator $\hat{\delta}_\rho(\tau_s)$ on the argument t. We introduce an operator $\hat{R}$, acting on the variable β, which we define by the formula $\hat{R}U_\rho(t,\beta) = U_\rho^{(\beta)}(t)$, and moreover $\hat{R}\hat{\delta}_\rho(\tau_s) - \hat{\delta}(\tau_s)\hat{R} = 0$, since the two operators act in different spaces. We divide the set M into nonoverlapping intervals $\Delta_r \simeq \Delta U(\tau)$ ($r = 1,2,...$). During each τ_s the values $U = U_\tau$ lie on average in some interval Δ_r and are equal to

$$U_\tau \simeq U_\rho^{(\beta)}(\tau_s) = \hat{\delta}_\rho(\tau_s)\hat{R}U_\rho(t,\beta).$$

Using the concept of a generalized vector function [12] and the quasi-closedness of the regions μ_ρ, we write the law of conservation of energy

$$\hat{\delta}(\tau_s)\hat{R}U(t,\beta) = \sum_\rho U_\rho^{(\beta)}(\tau_s) = E_0,$$

where $\hat{\delta}(\tau_s)$ is a vector operator with components $\hat{\delta}_\rho(\tau_s)$. The state of the system during the interval τ_s can be determined by specifying the occupation numbers b_r of the intervals Δ_r, whose mean values $\bar{b}_r$ can be found (without considering the mutual correlations of the regions μ_ρ) by the methods set forth in work [13]. On the other hand, the state of the system represents a homogeneous random Gaussian field [6], defined on the three-dimensional set of regions μ_ρ, which corresponds to considering the fluctuations as functions of the coordinates [7], while $U(t, \beta)$ describes the evolution of these states in time.

Let us consider a nonequilibrium system in which a thermal activation process is possible, but other processes are absent. Noticeable changes in the mean values $\overline{U}_\rho(t, \beta)$ occur over intervals $\Delta t > 1/w$, where w is the probability, referred to unit time, of an elementary act in the region μ_ρ. Therefore, during small time intervals the quantity $\overline{U}(t)$ is a linear function of time, and such a system can be described by means of a random process with stationary increments [6,11], which over intervals of order $1/w$ may be regarded as stationary, and to which the description given above may be applied. The energy U_τ is randomly distributed among n degrees of freedom of the region μ_ρ, to which there corresponds some distribution function and entropy $S(U_\tau)$. There exists a conditional probability $w(E/U_\tau)\tau_s$ that, during the time τ_s, an energy $E' \geq E$ will be concentrated on particular degrees of freedom (entropy $S(U_\tau - E)$) owing to a noticeable change in the state of the remaining degrees of freedom of the region μ_ρ (an act of a discontinuous random process [5]).* This probability is determined through the statistical weights of the corresponding states [4]

$$w\left(\frac{E}{U_\tau}\right) \simeq \frac{kT\,(U_\tau - E)}{\hbar} \exp\left\{\frac{S(U_\tau - E) - S(U_\tau)}{k}\right\}. \tag{3}$$

A similar result can be obtained for each τ_s and U_τ, while w is found by averaging $w(E/U_\tau)$ over time, which, by virtue of the ergodicity of the processes $U_\rho(t, \beta)$, is replaced by averaging over probability

* We note that from (2) there follow the inequalities $\tau \ll t_0 \ll 1/w$, which make it possible to describe the processes $U_\rho(t, \beta)$ by means of a discrete set of values [17], and also to neglect correlations between elementary acts in one region and in different regions μ_ρ (t_0 is the "radius" of autocorrelation).

$w(U)\,dU$ (normal distribution). Such an approach makes it possible to find the rates of processes under thermal excitation of the regions μ_p (4, 15)*. We shall now take into account the influence of ionizing radiation. Suppose that a particle with energy $\varepsilon_0 \gg E$ and velocity v_0 enters the system. Let us assume that its interaction with the body leads to the release of energy ΔE in a volume Q and that the occurrence of particular elementary acts with threshold energy E in the volume Q is determined by the statistical weights of the states of this volume, expressed through its entropy. This assumption would be a good approximation if the volume Q had many degrees of freedom and equilibrium in it were established before its interaction with the remaining parts of the system

became appreciable**. We restrict the volume Q by conditions analogous to (1), but taking into account the action of the radiation:

$$\overline{\Delta U_j(\tau_j)} < E < U_0 + \Delta E; \qquad \frac{U_0 + \Delta E}{m} = aE, \quad 0 < a \leqslant 1, \tag{4}$$

where $m = \gamma Q/d^3$. Thermal excitations in the regions Q are considered in the same way as in the subsystems μ_p. The last of inequalities (4) follows from the fact that the concentration of products of the activation process in the volume Q may be regarded as quasistationary when the energy of motion in individual degrees of freedom becomes less than the threshold energy E. Even if equilibrium is established incompletely, one should expect that the statistical description will give an upper bound for the number of elementary acts performed.

Let us consider a set of volumes Q which are simultaneously subjected to excitation by ionizing particles, and consider the state of statistical equilibrium between direct and reverse acts. With the aid of the principle of detailed balance, in the same way as was done in (4) for thermal excitations of the regions μ_p, we obtain the formula

$$w\left(\frac{E}{U_f}\right) = q\,\frac{kT}{\hbar}(U_f - E)\exp\left\{\frac{S(U_f - E) - S(U_f)}{k}\right\}, \tag{5}$$

analogous to (3), for the conditional probability per unit time $w(E/U_f)$ of the formation in the volume Q_f of an excitation $E' \geq E$ which leads to the reaction of interest. In contrast to (3), in formula (5) the quantity $U_f = U_\tau + \Delta E$ is the total energy of the degrees of freedom considered in the volume Q_f; U is their energy at the moment when the ionizing particle enters the volume Q_f. The desired mean probability w_r (per unit time) of the occurrence of a single act in the region Q is found by averaging the quantity $w(E/U_f)$ over all possible values of U_f according to the formula

$$w_r = \frac{1}{b}\iint w(U_f)\,w\left(\frac{E}{U_f}\right)\tau_j\,dU\,d(\Delta E), \tag{6}$$

where $w(U_f)\,dU\,d(\Delta E) = w(U)p(\Delta E)\,dU\,d(\Delta E)$ is the probability (per unit time) of the concurrence of two independent events: 1) that, at the moment when the ionizing particle enters the volume Q, its energy is equal to U; 2) that the ionizing particle will give the energy ΔE to the volume Q. The probability of the latter event is

$$p(\Delta E) = \int \varphi(\varepsilon_0)\,p(\varepsilon_0, \Delta E)\,d\varepsilon_0 = j\int \varphi(\varepsilon_0)\,\Sigma(\varepsilon_0, \Delta E)\,d\varepsilon_0 = j\overline{\Sigma(\Delta E)}, \tag{7}$$

where j is the flux density of ionizing particles incident on the volume Q_f; $\varphi(\varepsilon_0)$ is the energy distribution function in this flux; $p(\varepsilon_0, \Delta E)$ is the probability (per unit time) that a particle with energy ε_0 will give to the volume

---

* If degrees of freedom of different types contribute to each elementary act, these contributions should be considered as joint random events, considering partial entropies, etc. When the temperature and other conditions change, the role of these contributions changes.

** The situation here is in a certain sense analogous to that in the statistical theory of multiple meson production (18).

Q_f the energy ΔE, and $\Sigma(\varepsilon_0, \Delta E) = p(\varepsilon_0, \Delta E)/j$ is the cross section of this process. Taking into account that $w(U)$ is a normal distribution, and using the method also applied in (15), we expand $S(U_f - E)$ in powers of E and integrate over dU, obtaining, with the aid of (5) and (6), the relation

$$w_r \approx \frac{jqk\tau_j}{b\hbar} \int \overline{\Sigma(\Delta E)}\, T(U_f) \exp\left\{\frac{E^2}{2\alpha^2}\right\} \exp\left\{-\frac{E}{kT_{ef}}\right\} d(\Delta E), \qquad (8)$$

where c is the heat capacity of the degrees of freedom under consideration in the volume Q, and $T_{ef} \approx T + \Delta E/c$. It follows from (8) that the probabilities of elementary acts are determined not by the mean temperature T, but by the local temporary temperature $T_{ef} > T$ of the regions Q. For not too small ΔE and small c, the "addition" $\Delta T = \Delta E/c$ may prove large. In particular, a substantial lowering of T leads to a not very strong slowing of radiation-chemical reactions, since in this case c is small, while $\Delta T \approx \Delta E/c$, and therefore T_{ef} will not be small. If $(\Delta E/cT)^2 \ll 1$, then (8) may be rewritten in the form

$$w_r = \frac{j\tau_j qk}{b\hbar} \int \overline{\Sigma(\Delta E)}\, T(U_f) \exp\left\{\frac{E^2}{2\alpha^2}\right\} \exp\left\{\frac{E\Delta E}{kT^2 c}\right\} \exp\left\{-\frac{E}{kT}\right\} d(\Delta E). \qquad (9)$$

It follows from (8) and (9) that an increase in E may cause an increase in the rates of radiation-chemical processes or, at any rate, relatively small decreases in them. In the calculation it was assumed that $\Delta E \ll \overline{U}$ and $\Sigma(\varepsilon_0, \Delta E)\tau_i j \ll 1$. To obtain the total number of elementary acts, one should sum the quantity w_r over all volumes Q that were simultaneously subjected to radiation excitation, and then sum the result over time. The values of the quantities ΔE, l, and Q must be found from experiment.*

In conclusion, I express my sincere gratitude to L. S. Polak, and also to Yu. S. Lazurkin, for discussion of the work and critical comments, and to A. Ya. Temkin and M. A. Mokulskii for useful discussions.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
10 V 1960

REFERENCES

1. M. A. Makul' skii, Yu. S. Lazurkin et al., DAN, **125**, 1007 (1959).
2. N. M. Tikhomirova, Yu. M. Malenskii, V. Ya. Karpov, DAN, **130**, No. 5, 1081 (1960).
3. M. A. Makul' skii, *High-Molecular Compounds*, No. 1 (1960).
4. Yu. L. Khait, *Izv. AN SSSR, ser. fiz.*, **24**, 202 (1960).
5. B. V. Gnedenko, *A Course in Probability Theory*, 1954.
6. A. M. Yaglom, *Uspekhi Matematicheskikh Nauk*, **7**, No. 5 (1952).
7. M. A. Leontovich, *Statistical Physics*, 1944.
8. Bartlett, *Introduction to the Theory of Random Processes*, IL, 1958.
9. B. R. Levin, *Theory of Random Processes and Its Application in Radio Engineering*, 1957.
10. L. E. Gurevich, *Fundamentals of Physical Kinetics*, 1940.
11. I. M. Gel' fand, DAN, **100**, 853 (1955).
12. I. M. Gel' fand, G. E. Shilov, *Generalized Functions*, vol. 1, 1958.
13. E. Schrödinger, *Statistical Thermodynamics*, 1948.
14. L. D. Landau, E. M. Lifshitz, *Statistical Physics*, 1951.
15. S. Z. Roginskii, Yu. L. Khait, DAN, **130**, No. 2 (1960).
16. L. D. Landau, E. M. Lifshitz, *Electrodynamics of Continuous Media*, 1957.
17. Yu. K. Belyaev, *Theory of Probability and Its Applications*, **4**, 437 (1959); A. A. Kharkevich, *Radiotekhnika*, No. 8 (1958).
18. E. Fermi, *Elementary Particles*, IL, 1953; L. D. Landau, *Izv. AN SSSR,*

ser. fiz., **17**, 51 (1953).

* Let us note that at a distance r from the trajectory of a charged particle the spectrum of the field contains mainly frequencies $\nu \sim v_0/r$ (16). Therefore, at distances $r \lesssim v_0 h/E$, frequencies $\nu > E/h$, capable of causing excitation $E' \geq E$, make an appreciable contribution to the spectrum.

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