Temperature Effect in a Radiolytic System under Steady Irradiation

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There are two types of temperature effects in a system under irradiation by high-energy radiation; one is a local temperature effect on a microscopic scale, and the other is a gross or macroscopic temperature effect. The former is initially confined to a small region of the system (spur) which cools rapidly.[1] No significant contribution from such effect can be expected in the case of low LET radiations. The latter effect is the temperature rise in the system when a thermally steady state is reached under irradiation; its magnitude depends upon dose rate, properties of the system, and chemical reactions involved. In this note we will describe the gross temperature effect and estimate average temperature rise, the time constant for approach to steady condition, and an effective rate constant in an irradiated system. This consideration is of interest in connection with the conditions under which irradiations can be taken to be isothermal.

Let us consider a spherical system with radius r_m in a thermostat at a constant temperature, T_0.

The temperature of the system as a function of the space (r) and the time (t) is given by:

$$\frac{\partial T(r,t)}{\partial t}=\frac{\kappa}{\rho c_v}\nabla^2 T(r,t)+\frac{1}{\rho c_v}\left(qI+\frac{\partial(\varDelta H)}{\partial t}\right) \tag{1}$$

where T, κ, c_v and ρ are the absolute temperature, the heat conductivity, the specific heat and the density, and qI and $\varDelta H$ are the dose rate and the heat of reaction per unit volume, respectively.

We put:

$$\frac{\partial(\varDelta H)}{\partial t}=h,\quad \theta=\frac{T-T_0}{T_0},$$
$$\tau=\left(\frac{\kappa}{r_m{}^2\rho c_v}\right)t,\quad x=\frac{r}{r_m} \tag{2}$$

We can then solve Eq. 1 by using the boundary condition $T=T_0$ at $r=r_m$. The solution is given by:

$$\theta(x,\tau)=\frac{T(x,\tau)-T_0}{T_0}$$
$$=\frac{\lambda}{6}\Big[1-x^2+\frac{12}{\pi^3 x}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^3}(\sin\pi nx)$$
$$\times\exp(-n^2\pi^2\tau)\Big] \tag{3}$$

where $\lambda=\dfrac{(qI+\mathrm{h})r_m{}^2}{\kappa T_0}$

Since the temperature at a steady state can be defined as that when t approaches to infinity, we get:

$$\theta(x,\infty)=\frac{T(x,\infty)-T_0}{T_0}=\frac{\lambda}{6}(1-x^2) \tag{4}$$

Taking an average over space, we get:

$$\overline{\theta}=\langle\theta(x,\infty)\rangle_{\mathrm{av}}=\frac{\lambda}{15} \tag{5}$$

where $\overline{\theta}$ represents the relative temperature rise of the system at a steady state.

In the case where $qI\gg h$, as is the case with most systems in radiation chemistry, $\overline{\theta}$ is given by:

$$\overline{\theta}\simeq\frac{qIr_m{}^2}{15\kappa T_0} \tag{6}$$

As an example, we have estimated $\overline{\theta}$ for liquid hydrocarbons as a function of the dose rate and the sample size. The results are shown in Fig. 1.

As we can see from Eq. 6, the relative temperature rise is proportional to I and $r_m{}^2$ and inversely proportional to T_0 in the temperature

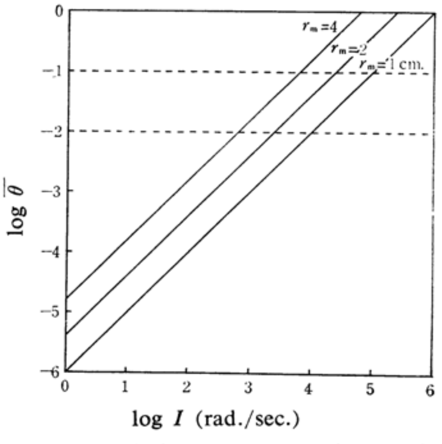

Fig. 1. The relative temperature rise as a function of dose rate and sample size.
$\kappa=4\times10^{-4}$ cal./cm. sec.°C; $\rho=0.8$ g./cm^3
$T_0=300$°K

range in which the physical constants do not change very much. Consequently, a smaller sample at a higher temperature is more favorable for maintaining isothermal conditions in an irradiated system, provided that the system is irradiated uniformly.

The time constant for approach to this steady state is given by the condition that the first term in the series in Eq. 3 falls to 1/e of its initial value:

$$\tau_c = \frac{1}{\pi^2}, \quad \text{or} \quad t_c = \frac{r_m{}^2 \rho c_v}{\pi^2 \kappa} \tag{7}$$

Putting numerical values into Eq. 7, we get:

$$t_c \simeq 100\ r_m{}^2\ \text{(sec.)}$$

where r_m is in unit of cm. and c_v is taken to be 0.5 cal./g.°C.

Let us consider the case where a rate constant is expressed by the Arrhenius equation. We define an effective rate constant as the rate constant averaged over space, since temperature is a function of space. Then, the ratio of the effective rate constant to the rate constant at the temperature T_0 is given by:

$$\frac{k_{eff}}{k_{T_0}} = 3\ \exp\left(\frac{E}{\boldsymbol{R}T_0}\right) \int_0^1 X^2 \times \exp\left[-\frac{E}{\boldsymbol{F}T_0\{1+qIr_m{}^2(1-x^2)/6\kappa T_0\}}\right] \mathrm{d}x \tag{8}$$

where E is an activation energy and $\boldsymbol{R}$ is the gas constant.

The ratio k_{eff}/k_{T_0} calculated using Eq. 8 is shown in Fig. 2. At high dose rates the ratio deviates considerably from unity.

Thus care must be taken in application of simple kinetic techniques to systems irradiated at such high dose rates.

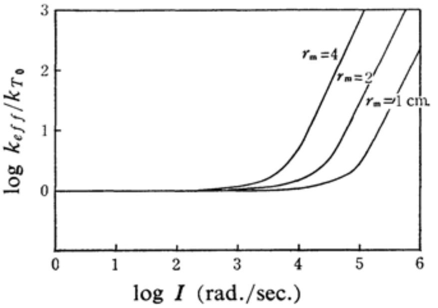

Fig. 2. The effective rate constant as a function of dose rate and sample size.
$E = 6$ kcal./mol.; $T_0 = 300$°K

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[1] J. L. Magee, *Ann. Rev. Phys. Chem.*, **12**, 389 (1961).