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APPENDIX A

Radiation Dosimetry

Quantitative studies in radiation chemistry require a knowledge of the amount of energy transferred from the radiation field to the absorbing material.

The absorbed dose or total dose is the quantity generally sought and is the amount of energy absorbed per unit mass of irradiated material. The official unit of absorbed dose is the rad, which is defined as an energy absorption of 100 erg g^{-1} or $10^{-2} \text{ J Kg}^{-1}$. The absorbed dose is a direct measure of the energy transferred to the irradiated material and capable of producing chemical or physical change in it; it is determined both by the composition of the material and characteristics of the radiation field.

The absorbed dose rate is the absorbed dose per unit time and has the unit rads, eV g^{-1} , eV cm^{-3} , or grays per unit time, e.g. rads/min, grays/min, $\text{eV g}^{-1}/\text{min}$.

Techniques for measuring ionizing radiation can be divided into absolute and secondary methods. Absolute methods involve direct determination of exposure or absorbed dose from physical measurements of, for example, the energy absorbed (by calorimetry), the ionization

produced in a gas, or the charge carried by a beam of charged particles of known energy. The absolute methods are often not suited to routine use and, in practice, secondary dosimeters (eg. thimble ionization chambers and chemical dosimeters), whose response to radiation is known from comparison with an absolute dosimeter, are generally used.

1. Calorimetry

The most direct way of determining the amount of energy carried by a beam of radiation is to measure the increase in temperature of a block of material placed in the beam, the method originally used by Curie and Laborde to measure the rate of energy release by the radioactive decay of radium. The material must be such that all the absorbed energy is converted to heat, none, for example, being used to initiate chemical reaction. Good thermal conductivity is also necessary and in practice graphite or metals are generally used for this purpose. If the block is of sufficient size to completely absorb the radiation, the rate of temperature increase is related directly to the energy flux density or intensity ($\text{erg cm}^{-2} \text{sec}^{-1}$) of the beam. With low intensity radiation, such as that normally available from x- and γ - ray sources, the temperature rise is very small and it is important as a check on other, less direct, methods, since the results are obtained directly in energy units.

Radak and Markovic give the range of absorbed dose rate that can be measured in this way as $10^{-7} W g^{-1}$ (36 rads hr^{-1}) to $10 W g^{-1}$ (10^6 rads sec^{-1}). Absorbed dose measurements with calorimeter in which water is the absorbing material have been used to calibrate the Fricky and other aqueous chemical dosimeters described later in this chapter.

2. Chemical Dosimetry

In chemical dosimetry the radiation dose is determined from the chemical change produced in a suitable substrate. Calculation of the dose requires a knowledge of the G value for the reaction or product estimated, which is found by comparing the chemical system with some form of absolute dosimeter. Chemical dosimeters are therefore secondary dosimeters and are used because of their greater convenience. In order to facilitate this conversion and to reduce errors, the dosimeter system is usually chosen so as to have the same atomic composition and density as the sample to be irradiated, as far as this is possible. Aqueous dosimeters, for example, are used if the sample is an aqueous solution, biological material, or organic substance.

For a dosimeter in which radiation induces a chemical change, the mean absorbed dose (D_d) over the volume occupied by the dosimeter is derived as follows. For any system, by definition, $G(\text{product})$ is the number of molecules

of product formed per 100 eV energy absorbed and 1 rad corresponds to an energy absorption of 0.01 J Kg⁻¹. Then

$$\begin{aligned}
 D_d &= \text{moles of product formed per kg} \frac{(\text{mol})}{(\text{kg})} \\
 &\quad \times 6.02 \times 10^{23} \frac{(\text{molecules})}{(\text{mole})} \times \frac{100}{G(\text{product})} \frac{(\text{eV})}{(\text{molecule})} \\
 &\quad \times 1.602 \times 10^{-19} \frac{(\text{J})}{(\text{eV})} \times 100 \frac{(\text{kg rad})}{(\text{J})} \\
 &= 9.647 \times 10^8 \times \frac{\text{moles of product formed per kg}}{G(\text{product})} \text{ rads} \quad (\text{A-1})
 \end{aligned}$$

or

$$D_d = 9.647 \times 10^8 \times \frac{\text{moles of product formed per liter}}{\rho G(\text{product})} \text{ rads} \quad (\text{A-2})$$

where ρ is the density of the system (g-cm⁻³). Very often the yield of product will be determined spectrophotometrically when, assuming Beer's Law to be obeyed,

$$\text{moles of product formed per liter} = \frac{\Delta A}{\Delta \epsilon l} \quad (\text{A-3})$$

and

$$D_d = 9.647 \times 10^8 \times \frac{\Delta A}{\epsilon l \rho G(\text{product})} \text{ rads} \quad (\text{A-4})$$

where ΔA is the difference in absorbance (or optical density) between the irradiated solution, ϵ is the difference in molar extinction coefficient (liter mol⁻¹ cm⁻¹) of

reactant and product at the wavelength being used, and l (cm) is the optical path length (i.e., sample thickness) used when determining the absorbances.

2.1 Fricky (Ferrous Sulfate) Dosimetry

The reaction involved in the Fricky dosimeter is the oxidation of an acid solution of ferrous sulfate to the ferric salts, in the presence of oxygen and under the influence of radiation. The standard dosimeter solution is one containing about 10^{-3} M ferrous sulfate or ferrous ammonium sulfate and 10^{-3} M sodium chloride in air-saturated (2.5×10^{-4} M O_2) 0.4 M sulfuric acid (pH 0.46). The quantities required to prepare such a solution are 0.28 g $FeSO_4 \cdot 7H_2O$ [or 0.39 g $Fe(NH_4)_2(SO_4)_3 \cdot 6H_2O$] 0.06 g NaCl and 22 ml concentrated (95-98%) H_2SO_4 per liter of solution; the solution slowly oxidized and should not be stored longer than a few days.

To determine the absorbed dose (in 0.4 M sulfuric acid) using the Fricke dosimeter, a sample of the dosimeter solution in a container thick enough to ensure electronic equilibrium is placed in the radiation field for measured length of time, and then the yield of ferric ions measured. To avoid undue wall effects (i.e. so that practically all the secondary electrons contributing to the energy absorption originate of at least 8 mm when γ -radiation is being determined; Burlin using a modified cavity theory, has calculated that with a silica cell and Co^{60} -rays a

diameter of 6 cm is needed to reduce the wall effect to below 0.1%. The most common method of measuring the ferric ions formed is by spectrophotometric analysis, comparing the absorbance of the irradiated and nonirradiated dosimeter solutions at the wavelength at which ferric ions show maximum absorption (about 304). The optical readings should be taken soon after the irradiation, so that adventitious oxidation of the solutions is minimized. The mean absorbed dose (D_d) for the volume occurred by the dosimeter solution is given by Eq. A-3 (56).

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