Intermezzo

Consider the EBR

$$A + A \xrightarrow{k} B + R$$

Corresponding ODE for A?

$$\frac{dA}{dt} = -2kA^2 \quad \text{or} \quad \frac{dA}{dt} = -kA^2$$

Write

(i) $$\frac{dA}{dt} = -cA^2$$

for some $c > 0$ we still have to decide on.

Thought experiment:

Split A-pop. arbitrarily into two groups labelled A_1 and A_2, which remain chemically equivalent.

$$A_1 + A_1 \xrightarrow{k} B + R$$
$$A_1 + A_2 \xrightarrow{k} B + R$$
$$A_2 + A_2 \xrightarrow{k} B + R$$

Then

(ii)
$$\frac{dA_1}{dt} = -cA_1^2 - kA_1A_2$$
$$\frac{dA_2}{dt} = -kA_1A_2 - cA_2^2$$

Since $A = A_1 + A_2$ (concentrations) we have from (i)

(iii) $$\frac{d(A_1+A_2)}{dt} = -c(A_1+A_2)^2 = -cA_1^2 - 2cA_1A_2 - cA_2^2$$

and from (ii)

(iv) $$\frac{d(A_1+A_2)}{dt} = -cA_1^2 - 2kA_1A_2 - cA_2^2$$

Since (iii) and (iv) must be equal for any subdivision A_1, A_2, it follows that $c = k$.

The correct ODEs are therefore

$$\frac{dA}{dt} = -kA^2$$

$$\frac{dB}{dt} = \tfrac{1}{2}kA^2$$

$$\frac{dR}{dt} = \tfrac{1}{2}kA^2$$

(Since from every two A-molecs that disappear only one B and one R molec appears hence the factor $\frac{1}{2}$)

If B happens to be the same as A:

$$\frac{dA}{dt} = -kA^2 + \tfrac{1}{2}kA^2 = -\tfrac{1}{2}kA^2$$

$$\frac{dR}{dt} = \tfrac{1}{2}kA^2$$

(end of intermezzo)