Derive an expression for the rate of photochemical decomposition of HI.

Solution. Photochemical decomposition of hydrogen iodide proceeds according to the scheme:

(1) $HI \rightarrow H^{\cdot} + I^{\cdot}$ (k_1);

(2) $H^{\cdot} + HI \rightarrow H_2 + I^{\cdot}$ (k_2);

(3) $I_2 + H^{\cdot} \rightarrow HI + I^{\cdot}$ (k_3);

(4) $2I^{\cdot} + M \rightarrow I_2 + M$ (k_4).

We will use the method of quasi-stationary concentrations of Bodenstein.
Intermediate particles are the hydrogen radical and the iodine radical, then we write the following:
$\frac{dC_{H^{\cdot}}}{dt} = k_1 C_{HI} - k_2 C_{H^{\cdot}} C_{HI} - k_3 C_{H^{\cdot}} C_{I_2}$=0. Then we will express the concentration of hydrogen radicals from this equation: $C_{H^{\cdot}}=\frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}}$;
Now we will express the concentration of the radical iodine from the equation:
$\frac{dC_{I^{\cdot}}}{dt} = k_1 C_{HI} + k_2 C_{I_2} C_{H^{\cdot}} + k_3 C_{I_2} C_{H^{\cdot}} - k_4 C_{I_2}^2 C_M = 0$, $C_{I_2}^2=\frac{k_1 C_{HI}+k_2 C_{I_2} C_{H^{\cdot}}+k_3 C_{I_2} C_{H^{\cdot}}}{k_4 C_M}$. We substitute the expression for the concentration of the hydrogen radical in this last formula, we get:
$C_{I_2}^2 = \frac{k_1 C_{HI}+k_2 C_{I_2} C_{H^{\cdot}}+k_3 C_{I_2} C_{H^{\cdot}}}{k_4 C_M} = \frac{k_1 C_{HI}+\frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_2 C_{I_2}+\frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_3 C_{I_2}}{k_4 C_M}$.
Now we write the kinetic equation for the decomposition of hydrogen iodide:
$\frac{dC_{HI}}{dt} = -k_1 C_{HI} + k_2 C_{H^{\cdot}} C_{HI} - k_3 C_{I_2} C_{H^{\cdot}} - k_4 C_{I_2}^2 C_M$. Now we will substitute the expressions for the concentrations of hydrogen and iodine radicals that we derived earlier into this equation, we will get the final equation:

$$\frac{dC_{HI}}{dt} = -k_1 C_{HI} + k_2 \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} C_{HI} - k_3 C_{I_2} \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} - k_4 \frac{k_1 C_{HI}+\frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_2 C_{I_2}+\frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_3 C_{I_2}}{k_4 C_M} C_M .$$

After simplification we get: $\frac{dC_{HI}}{dt} = -2k_1 C_{HI} + k_2 \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} C_{HI} - 2k_3 C_{I_2} \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} - \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_2 C_{I_2}$.

Answer: $\frac{dC_{HI}}{dt} = -2k_1 C_{HI} + k_2 \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} C_{HI} - 2k_3 C_{I_2} \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} - \frac{k_1 C_{HI}}{k_2 C_{HI}+k_3 C_{I_2}} k_2 C_{I_2}$.