The experimental results presented in the previous chapter are subjected to a detailed kinetic analysis in the light of the kinetic expressions derived on the basis of the following reaction schemes, which involves the reactions that are likely to occur.

**REACTION SCHEME**

1. Reaction of manganic ion with the organic substrate to produce primary radical:
   
   (a) Production of primary radical may be through complex formation.
   
   $$\text{Mn}^{3+} + X \rightleftharpoons \text{Complex} \xrightarrow{\text{Fast}} \text{R}^* + \text{Mn}^{2+} + \text{H}^+$$

   where $X$ is the organic substrate and $R^*$ is the primary radical produced from the organic substrate.

   (b) Primary radical may be formed without the formation of intermediate complex.

   $$\text{Mn}^{3+} + X \rightarrow \text{R}^* + \text{Mn}^{2+}$$

2. Reaction of primary radical with Mn$^{3+}$ ion

   $$\text{R}^* + \text{Mn}^{3+} \rightarrow \text{Products}$$

3. Initiation of Polymerization.

   (a) By the primary radical $R^*$

   $$\text{R}^* + \text{M} \rightarrow \text{M}^*$$
(b) By the metal Mn$^{3+}$ ion

\[ \text{Mn}^{3+} + M \xrightarrow{k_i} M^* + \text{Mn}^{2+} + H^+ \]

where $M^*$ is the radical ion of the monomer.

4. Propagation of polymerization

\[ M^* + M \xrightarrow{k_p} M_1^* \]

\[ M_1^* + M \xrightarrow{k_p} M_2^* \]

\[ \ldots \]

\[ M_{n-1}^* + M \xrightarrow{k_p} (M)_n^* \]

5. Termination of polymerization

(a) Termination of mutual combination or disproportionation of polymer radicals.

\[ (M)_n^* + (M)_m^* \xrightarrow{k_{t1}} M_{n+m} \text{ or } (M)_n + (M)_m \]

(b) Linear termination by the Mn$^{3+}$ ion

\[ M_n^* + \text{Mn}^{3+} \xrightarrow{k_{t2}} \text{Polymer} + \text{Mn}^{2+} + H^+ \]
(c) Termination by Mn$^{3+}$ - substrate complex

\[ M_n^* + \text{Complex} \xrightarrow{k_{t3}} \text{Polymer} + X' + \text{Mn}^{2+} \]

where \( X' \) may be the reducing agent itself or an inactive product.

(d) Termination by the primary radical \( R^* \)

\[ M_n^* + R^* \xrightarrow{k_{t4}} \text{Polymer} \]

(e) Termination by reducing agent

\[ M_n^* + X \xrightarrow{k_{t5}} \text{Polymer} \]

**KINETIC RATE EXPRESSIONS**

The reaction scheme outlined above can be used for the derivation of expressions for the rate of polymerization \( R_p \), the rate of manganic ion disappearance \( -R_m \). Various types of kinetic expressions are derived based on the following assumptions.

1. Propagation and termination rate constants are independent of chain lengths.

2. The stationary state conditions are assumed for the free radical chains.
Considering the initiation by the primary radical $R^*$ and termination by mutual combination or disproportionation.

Rate of initiation $R_i = k_i [R][M]$

Rate of propagation $R_p = k_p [M^*][M]$

Rate of termination $R_t = k_{t1} [M^*]^2$

Rate of formation of primary radical $R^*$

$\text{[Complex]} = K[M^{3+}][X]$.  

Therefore

$R^* = k_d [M^{3+}][X]$.

Now the rate of initiation $R_i = k_i k_d K[M^{3+}][X][M]$.

Now applying the steady-state principle

$$\frac{d[R]}{dt} = k_k d[M^{3+}][X] - k_o[R][M^{3+}] - k_i[R][M] = 0 \quad \ldots \quad (1)$$

$$[R] = \frac{k_k d[M^{3+}][X]}{(k_o[M^{3+}] + k_i[M])} \quad \ldots \quad (2)$$

If $R_i = R_t$, then

$$\frac{d[M^*]}{dt} = R_i - R_t = 0 \quad \text{or}$$
Substituting the equation for $R'_n$ in equation (3)

$$\frac{d[M_n^*]}{dt} = k_i[R][M] - k_{t_1} [M_n^*]^2 = 0$$

$$[M_n^*] = \left( \frac{k_i [R][M]}{k_{t_1}} \right)^{1/2} \quad \ldots \quad (3)$$

Substituting the equation for $R'$ in equation (3)

$$[M_n^*] = \left( \frac{k_i k_d [M] [Mn^{3+}][X]}{k_{t_1} (k_o [Mn^{3+}] + k_i [M])} \right)^{1/2} \quad \ldots \quad (4)$$

The rate of polymerization is given by

$$R_p = -\frac{d[M]}{dt} = k_p [M_n^*][M]$$

Substituting the equation for $[M_n^*]$ from previous equation

$$R_p = k_p \left( \frac{k_i k_d [Mn^{3+}][X][M]}{(k_o [Mn^{3+}] + k_i [M])k_{t_1}} \right)^{1/2} [M] \quad \ldots \quad (5)$$

or

$$R_p = k_p M^{3/2} \left( \frac{k_i k_d [Mn^{3+}][X]}{k_{t_1} \left\{ (k_o/k_i) [Mn^{3+}] + [M] \right\}^{1/2}} \right)^{1/2} \quad \ldots \quad (5)$$

$$R_p = \frac{k_p k_i^{1/2} (k_d [Mn^{3+}][X]^{1/2}[M]^{3/2}}{k_{t_1}^{1/2} (k_o [Mn^{3+}] + k_i [M])^{1/2}}$$
The rate of manganic ion disappearance is given by

\[-R_M = K k_d [\text{Mn}^{3+}] [\mathcal{X}] + k_o [\text{Mn}^{3+}] [\mathcal{R}] \] ... (6)

Substituting for $[\mathcal{R}]$ into the above equation and rearranging we get

\[-R_m = K k_d [\text{Mn}^{3+}] [\mathcal{X}] \left(1 + \frac{k_o [\text{Mn}^{3+}]}{k_i [\mathcal{M}] + k_o [\text{Mn}^{3+}]}ight) \] ... (7)

**Case-2**

When the initiation is by the primary radical $\mathcal{R}^*$ and termination by the Mn$^{3+}$ ions

Rate of initiation $R_i$ : $k_i [\mathcal{R}] [\mathcal{M}]$

Rate of propagation $R_p$ : $k_p [\text{Mn}^*] [\mathcal{M}]$

Rate of termination $R_t$ : $k_t [\text{Mn}^*] [\text{Mn}^{3+}]$

The expression for $[\mathcal{R}]$ is the same as in equation (2)

\[[\mathcal{R}] = \frac{K k_d [\text{Mn}^{3+}] [\mathcal{X}]}{(k_o [\text{Mn}^{3+}] + k_i [\mathcal{M}])} \] ... (2)

If $R_i = R_t$ i.e

\[k_i [\mathcal{R}] [\mathcal{M}] = k_{t2} [\text{Mn}^*] [\text{Mn}^{3+}] \] ... (8)

\[\frac{d[\text{Mn}^*]}{dt} = k_i [\mathcal{R}] [\mathcal{M}] - k_{t2} [\text{Mn}^*] [\text{Mn}^{3+}] = 0 \] ... (9)
Substituting the equation (2) \([R]\) in the above equation, we get

\[
[M_n^+] = \frac{k_d [X][M]}{k_{t_2}} \frac{k_i [M]}{(k_i[M] + k_o[M_n^{3+}])} ... (11)
\]

The rate of polymerization \(R_p\) is given by

\[
R_p = \frac{-d[M]}{dt} = k_p [M_n^+][M]
\]

\[
R_p = \frac{k_p[M] k_d k_i[X][M]}{k_{t_2} (k_i[M] + k_o[M_n^{3+}])}
\]

Rearranging the above equation

\[
R_p = \frac{k_p k_d [X][M]^2}{k_{t_2} \left\{([M] + (k_o/k_i)[M_n^{3+}])_b\right\}} ... (12)
\]

The expression for the rate of manganic ion disappearance, is given by

\[
-R_m = k_d [M_n^{3+}][X] + k_o[M_n^{3+}][R] + k_{t_2} [M_n^{3+}][M_n^+] ... (13)
\]

Substituting the expressions for \([M_n^+]\) and \([R]\) from equation (2) and (9), \(-R_m\) is given by

\[
-R_m = 2k_d[M_n^{3+}][X] \quad ... (14)
\]

Case-3

Initiation by the primary radical and termination by \(Mn^{3+}\) - Reducing agent complex
Rate of initiation \( R_i \) : \( k_i[R][M] \)

Rate of propagation \( R_p \) : \( k_p[M^*][M] \)

Rate of termination \( R_t \) : \( k_{t3} \) [Complex]

The expression derived for \([R]\) is the same as in the previous cases and is given by

\[
[R] = \frac{k \cdot k_d [Mn^{3+}][X]}{k_o[Mn^{3+}] + k_i[M]} \quad \ldots \quad (2)
\]

When we assume that the rate of initiation is equal to rate of termination; i.e.

\[
k_i[R][M] = k_{t3} [M^*][\text{Complex}]
\]

\[
d[M^*_n]/dt = k_i[R][M] - k_{t3} [M^*][\text{Complex}] = 0 \quad \ldots \quad (15)
\]

\[
[M^*_n] = \frac{k \cdot k_i[R][M]}{k_{t3} \text{[Complex]}} \quad \ldots \quad (16)
\]

Substituting the value for \([R]\) from the above equation

\[
[M^*_n] = \frac{k \cdot k_i \cdot k_d [Mn^{3+}][X][M]}{k_{t3} \text{[Complex]} \cdot (k_o [Mn^{3+}] + k_i[M])} \quad \ldots \quad (17)
\]

Since we know that \([\text{Complex}] = K [Mn^{3+}][X]\)

\[
[M^*_n] = \frac{k_i \cdot k_d [M]}{k_{t3} \cdot (k_o [Mn^{3+}] + k_i[M])} \quad \ldots \quad (18)
\]

As given in the beginning, the rate of polymerization

\[
R_p = k_p [M^*_n][M] \quad \ldots \quad (19)
\]
If we substitute the expression \([M^+_n]\) from equation (18), then

\[
R_p = \frac{k_p k_i k_d[M]^2}{k_{t3} \left( k_o[Mn^{3+}] + (k_i[M]) \right)}
\]

By dividing both the numerator and denominator with \(k_i\),

\[
R_p = \frac{k_p k_d \frac{[M]^2}{k_{t3} \left( (k_o/k_i)[Mn^{3+}] + k_i[M] \right)}}{\ldots \ (20)}
\]

Then, \(-R_m\) the rate of manganic ion disappearance is given by

\[
-R_m = k k_d[Mn^{3+}][X] + k_o[Mn^{3+}][R] + k_{t3} [M^+_n] \text{ Complex}
\]

We know that \(k_i[R][M] = k_{t3} [M^+_n] \text{ Complex}\)

Now

\[
-R_m = k k_d[Mn^{3+}][X] + k_o[Mn^{3+}][R] + k_i[R][M] \text{ or}
\]

\[
-R_m = k k_d[Mn^{3+}][X] + R(k_o[Mn^{3+}] + k_i[M])
\]

Substituting the expression for \([R]\)

\[
-R_m = 2 k k_d[Mn^{3+}][X] \ldots \ (14)
\]

**Case-4**

When both initiation and termination are by the primary radical \(R^*\),

Rate of initiation \(R_i\) : \(k_i[R][M]\)

Rate of propagation \(R_p\) : \(k_p[M^+_n][M]\)
Rate of termination $R_t$ : $k_t \frac{[M_n^*][R^*]}{[R]}$

Rate of formation of $R^*$ : $K \frac{k_d[Mn^{3+}][X]}{[R]}$

Rate of $R^*$ consumption : $k_i[R][M] + k_o[R][Mn^{3+}] + k_{t_4} [R][M_n^*]$

Applying the steady-state principle

$K \frac{k_d[Mn^{3+}][M]}{[K]} = k_i[R][M] + k_o[R][Mn^{3+}] + k_{t_4} [R][M_n^*]$

$\frac{d[R]}{dt} = \frac{K k_d[Mn^{3+}][X]}{[K]} - k_i[R][M] - k_o[R][Mn^{3+}] + k_{t_4} [R][M_n^*]$

We know that $k_i[R][M] = k_{t_4} [R][M_n^*]$ i.e. $R_i = R_t$

Then:

$\frac{d[R]}{dt} = \frac{K k_d[Mn^{3+}][X]}{[K]} - k_o[R][Mn^{3+}] - 2 k_i[R][M] ... (21)$

Therefore

$[R] = \frac{K k_d[Mn^{3+}][X]}{(k_o[Mn^{3+}] + 2 k_i[M])} ... (22)$

If $R_i = R_t$, then

$k_i[R][M] = k_{t_4} [R][M_n^*]$

From

$[M_n^*] = \frac{k_i[R][M]}{k_{t_4} [R]}$ or $\frac{k_i[M]}{k_{t_4}} ... (23)$

The rate of polymerization $R_p = k_p[M_n^*][M]$
Substituting the $[M^*_{n}]$ from the above equation

$$R_p = \frac{k_p k_i[M]^2}{k_{t4}}$$

... (24)

The rate expression for the disappearance of manganic ion is

$$-R_m = K \left( k_d [M^{3+}][X] + k_o[M^{3+}] [R^*] \right)$$

Substituting the expression for $[R^*]$ in the above equation, $-R_m$ is given as

$$-R_m = K k_d[M^{3+}][X] \left( \frac{1 + k_o[M^{3+}]}{(k_o[M^{3+}] + 2 k_i[M])} \right)$$

... (25)

Case-5

Considering the initiation by the primary radical $R^*$ and termination by the reducing agent or the organic substrate 'X' itself

Rate of initiation $R_i$ : $k_i[R^*][M]$  
Rate of propagation $R_p$ : $k_p[M^*_{n}][M]$  
Rate of termination $R_t$ : $k_t[M^*_{n}][X]$

The rate expression for $R^*$ is the same as in equation (2) i.e.,

$$[R^*] = \frac{K k_d[M^{3+}][X]}{(k_o[M^{3+}] + k_i[M])}$$

By applying the steady-state principle
\[ \frac{d[M_n^*]}{dt} = k_i[R][M] - k_{t5}[M_n^*][X] = 0 \] \hfill (26)

\[ R_i = R_t \text{ or } k_i[R][M] = k_{t5}[M_n^*][X]. \]

\[ [M_n^*] = \frac{k_i[R][M]}{k_{t5}[X]} \] \hfill (27)

Substituting the value \([R]\) in the above equation and rearranging,

\[ [M_n^*] = \frac{k_i[R][M]}{k_{t5}} \left\{ \left( \frac{k_o}{k_i} [M_n^{3+}] \right) + [M] \right\} \] \hfill (28)

The rate of polymerization \(R_p\) is given by

\[ R_p = k_p[M_n^*][M] \]

Substitution the expression for \([M_n^*]\)

\[ R_p = \frac{k_p k d[M_n^{3+}][M]^2}{k_{t5}} \left\{ \left( \frac{k_o}{k_i} [M_n^{3+}] \right) + [M] \right\} \] \hfill (29)

The expression for \(-R_m\) is

\[ -R_m = k d[M_n^{3+}][X] + k_o[M_n^{3+}][R] \]

Substituting for \([R]\) into the above equation and rearranging, we get

\[ -R_m = k d[M_n^{3+}][X] \left( \frac{1 + k_o[M_n^{3+}]}{(k_i[M] + k_o[M_n^{3+}])} \right) \] \hfill (30)
Case-6

When initiation is by both primary radical $R^\cdot$ and $\text{Mn}^{3+}$ simultaneously and termination by mutual combination or disproportionation of polymer radicals:

Rate of initiation $R_i$ : \[ k_i[R^\cdot]M + k_i^*[\text{Mn}^{3+}]M \]

Rate of propagation $R_p$ : \[ k_p[M^\cdot]M \]

Rate of termination $R_t$ : \[ k_t[M_n^\cdot]^2 \]

The rate expression for $[R^\cdot]$ is the same as in Case-1 and is given by

\[
[R^\cdot] = \frac{K k_d[\text{Mn}^{3+}][X]}{(k_o[\text{Mn}^{3+}] + k_i[M])} \quad \text{... (2)}
\]

If $R_i = R_t$ (or)

\[ (k_i[R^\cdot] + k_i^*[\text{Mn}^{3+}])[M] = k_t[M_n^\cdot]^2 \]

Applying the steady-state principle

\[
\frac{d[M_n^\cdot]}{dt} = k_i[R^\cdot][M] + k_i^*[\text{Mn}^{3+}][M] - k_t[M_n^\cdot]^2 = 0 \quad \text{... (31)}
\]

\[
[M_n^\cdot] = \left\{ (k_i[R^\cdot][M] + k_i[\text{Mn}^{3+}][M]/k_t) \right\}^{1/2}
\]

Substituting the expression for $R^\cdot$ into the above equation

\[
[M_n^\cdot] = \left( \frac{K k_d[\text{Mn}^{3+}][X][M]}{k_t \left[ \frac{1}{(M + (k_o/k_i)[\text{Mn}^{3+}])} + \frac{k_i^*[\text{Mn}^{3+}][M]}{k_t} \right]^{1/2} \right)
\]

\text{... (32)}
The rate of polymerization is
\[ R_p = k_p[M_n^*][M] \]

Substituting the value of \([M_n^*]\)

\[ R_p = k_p[M]^{3/2} \left( \frac{K k_d[M^{3+}][X]}{k_{t1} \{[M] + (k_o/k_i)[M^{3+}]\}} + \frac{k_i^* [M^{3+}]}{k_{t1}} \right)^{1/2} \]

The expression for \(-R_m\) is

\[ -R_m = K k_d[M^{3+}][X] + k_o[R]^* + k_i^* [M^{3+}][M] \]

Substituting the value of \([R]^*\) from equation (2)

\[ -R_m = K k_d[M^{3+}][X] \left( 1 + \frac{k_o [M^{3+}]}{k_i^*[M] + k_o[M^{3+}]} \right) + k_i^* [M^{3+}][M] \]

... (34)

Case-7

Considering the initiation by the primary radical \(R^*\) and \(Mn^{3+}\) ions alone:

Rate of initiation \(R_i\) : \(k_i[R][M] + k_i^*[M^{3+}][M]\)

Rate of propagation \(R_p\) : \(k_p[M_n^*][M]\)

Rate of termination \(R_t\) : \(k_{t2}[M_n^*][M^{3+}]\)

The rate of formation \(R^*\) is the same as in the Case-1 and the expression for \(R^*\) is
\[
[R^*] = \frac{K \cdot k_d[Mn^{3+}][X]}{k_o[Mn^{3+}] + k_i[M]}
\]

If \( R_i = R_t \), then

\[
k_i[R][M] + k_i^*[Mn^{3+}][M] = k_{t2} [M_n^*[Mn^{3+}] \quad \ldots \quad (35)
\]

Applying the steady-state principle

\[
\frac{d[M_n^*]}{dt} = k_i[R][M] + k_i^*[Mn^{3+}][M] - k_{t2} [M_n^*[Mn^{3+}] = 0
\]

\[
[M_n^*] = \frac{k_i[R][M] + k_i^*[Mn^{3+}][M]}{k_{t2}[Mn^{3+}]}
\]

\[
[M_n^*] = \frac{k_i[R][M]}{k_{t2}[Mn^{3+}]} + \frac{k_i^*[M][Mn^{3+}]}{k_{t2}[Mn^{3+}]} = \frac{[M]}{k_{t2}} \left( \frac{k_i[R]}{[Mn^{3+}]} + k_i^* \right)
\]

Substituting the value of \([R^*]\) from equation (2)

\[
[M_n^*] = \frac{[M]}{k_{t2}} \left( \frac{k_i \cdot k_d[Mn^{3+}][X]}{k_o[Mn^{3+}] + k_i[M][Mn^{3+}] + k_i^*} \right)
\]

Rearranging the above equation, we get

\[
[M_n^*] = [M]k_{t2} \left( \frac{k \cdot k_d[X]}{(k_o/k_i) [Mn^{3+}] + [M]} + k_i^* \right) \quad \ldots \quad (36)
\]

The expression for \( R_p \) is given by

\[
R_p = k_p[M_n^*][M]
\]

Substituting the value of \([M_n^*]\) from the above equation
The expression for $-R$ is

$$-R_m = K_k d_{Mn^{3+}}[M] + k_i^*[M^{3+}][M] + k_o[Mn^{3+}][R^*] + k_t^2[Mn^{3+}][M^*_n]$$

From equation (35) and (1)

$$-R_m = 2K_k d_{Mn^{3+}}[X] + 2k_i^*[M^{3+}][M]$$

$$= 2[M^{3+}](K_k d_{[X]} + k_i^*[M])$$

... (38)

Case-8

Initiation by $R^*$ and $Mn^{3+}$ and termination by the complex

Rate of initiation $R_i$ : $k_i^* [K][M] + k_i^* [M^{3+}][M]$

Rate of propagation $R_p$ : $k_p[M]^*[M]$

Rate of termination $R_t$ : $k_t^3[M][Complex]$ or

$$k_t^3[M^*_n](K[Mn^{3+}][X])$$

The expression for $[R^*]$ as given in the Case-1 is,

$$[R^*] = \frac{K_k d_{[Mn^{3+}][X]}}{k_o[Mn^{3+}] + k_i^*[M]}$$

If $R_i = R_t$

$$k_i^* [K][M] + k_i^* [M^{3+}][M] = k_t^3[M^*_n](K[Mn^{3+}][X])$$

... (39)
Applying stationary state principle

\[
\frac{d[M_n^*]}{dt} = k_i[M] + k_i^*[M^{3+}] - k_{t_3} [M_n^*]\text{[Complex]}
\]

\[
[M_n^*] = \frac{k_i[M] + k_i^*[M^{3+}]}{k_{t_3}}
\]

Substituting for \([R]\) from equation (2) and \(K[M^{3+}][X]\) for complex into the above equation

\[
[M_n^*] = \frac{k_i k_d[M]}{k_{t_3} (k_o[M^{3+}] + k_i[M])} + \frac{k_i^* [M]}{k_{t_3} k[X]}
\]

\[
[M_n^*] = \frac{k_i k_d}{k_{t_3} (k_o[M^{3+}] + k_i[M])} + \frac{k_i^* [M]}{k_{t_3} k[X]}
\]

On rearranging

\[
[M_n^*] = \frac{[M]}{k_{t_3}} \left( \frac{k_d}{(k_o/k_i)[M^{3+}] + [M]} + \frac{k_i^* [M]}{k[X]} \right) \quad ... \quad (40)
\]

The rate of polymerization \(R_p\) is given by

\[
R_p = k_p [M_n^*][M]
\]

Substituting for \([M_n^*]\)

\[
R_p = \frac{k_p [M]^2}{k_{t_3}} \left( \frac{k_d}{(k_o/k_i)[M^{3+}] + [M]} + \frac{k_i^* [M]}{k[X]} \right) \quad ... \quad (41)
\]

The rate of disappearance of manganic ion is

\[
-R_m = K k_d[M^{3+}][X] + k_o[M^{3+}][R] + k_i^*[M^{3+}][M] + \frac{k_{t_3} [M_n^*][\text{Complex}]}{}
\]
From equation (39) and (1), we get

\[ -R_m = 2K_k d[Mn^{3+}] [X] + 2k_i^* [Mn^{3+}] [M] \]

\[ -R_m = 2[Mn^{3+}] (K_k d[X] + k_i^* [M]) \]

... (42)

Case-9

Initiation is by both primary radical \( R^* \) and \( Mn^{3+} \) ions and termination by the same primary radical \( R^* \)

Rate of initiation \( R_i \) : \( k_i [R] [M] + k_i^* [Mn^{3+}] [M] \)

Rate of propagation \( R_p \) : \( k_p [M_n^*] [M] \)

Rate of termination \( R_t \) : \( k_t [M_n^*] [R] \)

Rate of formation \( R^* \) : \( k_k d[Mn^{3+}] [X] \)

Rate of \( R^* \) consumption : \( k_i [M] [R] + k_o [Mn^{3+}] [R] + k_t [M_n^*] [R] \)

Applying the steady-state principle

\[ \frac{d[R^*]}{dt} = K_k d[Mn^{3+}] [X] - k_i [M] [R] - k_o [Mn^{3+}] [R] - k_t [M_n^*] [R] \]

... (43)

\[ [R] = \frac{K_k d[Mn^{3+}] [X]}{(k_i [M] + k_o [Mn^{3+}] + k_t [M_n^*])} \]

... (44)

Rearranging the above equation
If \( R_i = R_t \)
Then
\[
M^* = \frac{k_i[M][X] - k_i^*[M]}{k_{t4}[R^*]} \quad \cdots (45)
\]

Applying the steady-state principle
\[
\frac{d[M_n^*]}{dt} = k_i[R][M] + k_i^*[M^3+] [M] - k_{t4} [M_n^*][R] = 0 \quad \cdots (46)
\]
\[
M_n^* = \frac{k_i[M] + k_i^*[M^3+][M]}{k_{t4}[R]} \quad \cdots (47)
\]

Equating the equation (45) and (47) and rearranging
\[
[R^*] = \frac{[M^3+](K - k_i^*[M])}{2k_i[M] + k_o[M^3+]} \quad \cdots (48)
\]

Substituting the value of \([R^*]\) from equation (48) into the equation (47) and rearranging
\[
M_n^* = \frac{k_i[M]}{k_{t4}} + \frac{k_i^*[M][2k_i[M] + k_o[M^3+]}}{k_{t4}(K - k_i^*[M])} \quad \cdots (49)
\]

The rate of polymerization \( R_p \) is given by
\[
R_p = k_p[M_n^*][M]
\]

Substituting the value of \([M_n^*]\)
The rate of manganic ion disappearance is

\[-R_m = K_k \left[ \text{Mn}^{3+} \right] \left[ \text{X} \right] + k_o^{*} \left[ \text{Mn}^{3+} \right] \left[ \text{R} \right] + k_i^{*} \left[ \text{Mn}^{3+} \right] \left[ \text{M} \right] \]

Substituting the value of \([\text{R}]\) from equation (48) and rearranging

\[-R_m = \left[ \text{Mn}^{3+} \right] \left( K_k \left[ \text{X} \right] + k_i^{*} \left[ \text{M} \right] + \frac{k_o^{*} \left[ \text{Mn}^{3+} \right] \left( K_k \left[ \text{X} \right] - k_i^{*} \left[ \text{M} \right] \right)}{2 k_i^{*} \left[ \text{M} \right] + k_o^{*} \left[ \text{Mn}^{3+} \right]} \right) \]

... (51)

Case-10

Initiation by both \(R\) and \(\text{Mn}^{3+}\) ions and termination by the reducing agent

Rate of initiation \(R_i\) : \(k_i \left[ R \right] \left[ M \right] + k_i^{*} \left[ \text{Mn}^{3+} \right] \left[ M \right] \)

Rate of propagation \(R_p\) : \(k_p \left[ \text{M} \right] \left[ \text{Mn}^{3+} \right] \left[ \text{M} \right] \)

Rate of termination \(R_t\) : \(k_{t_5} \left[ \text{M}^{*} \right] \left[ \text{X} \right] \)

The rate expression for \([\text{R}]\) is the same as in equation (2) when \(R_i = R_t\) and applying the steady-state principle

\[ \frac{d\left[ \text{M}^{*} \right]}{dt} = k_i \left[ \text{R} \right] \left[ \text{M} \right] + k_i^{*} \left[ \text{Mn}^{3+} \right] \left[ \text{M} \right] - k_{t_5} \left[ \text{M}^{*} \right] \left[ \text{X} \right] \]

... (52)
\[ k_i[R][M] + k_i^*[Mn^{3+}][M] = k_{t_5} [M_n^*][X] \]

\[ [M_n^*] = \frac{k_i[R][M] + k_i^*[Mn^{3+}][M]}{k_{t_5} [X]} \] ...

Substituting the value of \([R]\)

\[ [M_n^*] = \frac{k_i \frac{k_d}{k_{t_5}} [Mn^{3+}][M][X]}{[X](k_o[k_i][Mn^{3+}] + k_i[M])} + \frac{k_i^* [Mn^{3+}][M]}{k_{t_5} [X]} \]

on rearranging

\[ [M_n^*] = \frac{k_d [Mn^{3+}][M]}{k_{t_5} \left\{ (k_o/k_i) [Mn^{3+}] + [M] \right\}} + \frac{k_i^* [Mn^{3+}][M]}{k_{t_5} [X]} \]

The rate of polymerization \(R_p = k_p [M_n^*][M]

\[ R_p = \frac{k_p [M]^2 [Mn^{3+}]}{k_{t_5}} \left( \frac{k}{k_d} + \frac{k_i^*}{[X]} \right) \] ...

The rate of manganic ion disappearance is

\[ -R_m = k_d [Mn^{3+}][X] + k_o[R][Mn^{3+}] + k_i^* [Mn^{3+}][M] \]

Substituting the value of \([R]\) from equation (2)

\[ -R_m = k_d [Mn^{3+}][X] \left( 1 + \frac{k_o [Mn^{3+}]}{k_i[M] + k_o [Mn^{3+}]} \right) + k_i^* [Mn^{3+}][M] \] ...

(54)
Case-11

When initiation is by the primary radical and termination by \( \text{Mn}^{3+} \) ion and \( \text{Mn}^{3+} \) - reducing agent complex simultaneously

Rate of initiation \( R_i \) : \( k_i [R][M] \)

Rate of propagation \( R_p \) : \( k_p [M_n^*][M] \)

Rate of termination \( R_t \) : \( k_{t_2} [\text{Mn}^{3+}][M_{n}^*] + k_{t_3} [M_{o}^*][\text{Complex}] \)

The expression for \( [R^*] \) is the same as equation (2) in case when \( R_i = R_t \)

\[
k_i [R][M] = k_{t_2} [\text{Mn}^{3+}][M_{n}^*] + k_{t_3} [M_{o}^*][\text{Complex}] \quad \ldots \quad (56)
\]

Applying the steady-state principle

\[
\frac{d[M_{n}^*]}{dt} = k_i [R][M] - k_{t_2} [\text{Mn}^{3+}][M_{n}^*] - k_{t_3} [M_{o}^*][\text{Complex}]
\]

\[
[M_{n}^*] = \frac{k_i [R][M]}{k_{t_2} [\text{Mn}^{3+}] + k_{t_3} [\text{Complex}]}
\]

Substituting for \( [R^*] \) and for \( [\text{Complex}] \)

\[
[M_{n}^*] = \frac{k_i \kappa k_d [\text{Mn}^{3+}][X][M]}{(k_i [M] + k_o [\text{Mn}^{3+}])k_{t_2} [\text{Mn}^{3+}] + k_{t_3} \kappa [\text{Mn}^{3+}][X]} \quad \ldots \quad (57)
\]
The rate of polymerization \( R_p \) is
\[
R_p = k_p [M_n^*][M]
\]
Substituting the value of \([M_n^*]\) from equation (57), we get
\[
R_p = \frac{k_p k_{i} k_{d} [Mn^{3+}][X][M]^2}{(k_p[M] + k_o[Mn^{3+}]) (k_{t_2}[Mn^{3+}] + k_{t_3} k [Mn^{3+}][X])}
\]
... (58)

The rate of manganic ion disappearance \(-R_m\) is
\[
-R_m = k k_d[Mn^{3+}][X] + k_o[Mn^{3+}][X] + k_{t_2}[M_n^*][Mn^{3+}] + k_{t_3} [M_n^*][Complex]
\]
... (59)

From equation (1) and (56),
\[
-R_m = 2 k (k_d[Mn^{3+}][X])
\]
... (60)

Case-12

Initiation by \( R^* \) and termination by substrate and \( Mn^{3+} \) simultaneously
\[
R_i = k_i[R^*][M], \ R_p = k_p[M_n^*][M], \ R_t = k_{t_2}[M_n^*][Mn^{3+}] + k_{t_5}[M_n^*][X]
\]
Since the initiation is by the primary radical, the expressions for primary radical is the same as in Case-1, i.e.
\[
[R^*] = \frac{k d[Mn^{3+}][X]}{k_o[Mn^{3+}] + k i[M]}
\]
If \( R_i = R_t \)

\[
[\text{M}^n] = \frac{k_i[M]}{k_{t_2}[\text{Mn}^3+] + k_{t_5}[X]} 
\]

Substituting the value for \( R^* \) in the above equation

\[
[\text{M}^n]^* = \frac{k_i k_d[\text{Mn}^3+] [X][M]}{(k_o/[\text{Mn}^3+] + [M])(k_{t_2}[\text{Mn}^3+] + k_{t_5}[X])} 
\]

Rearrangement of the above equation gives

\[
[\text{M}^n]^* = \frac{K k_d[\text{Mn}^3+] [X][M]}{(k_o/[\text{Mn}^3+] + [M])(k_{t_2}[\text{Mn}^3+] + k_{t_5}[X])} 
\]

The expression for \( R_p \) is given by

\[
R_p = k_p[\text{M}^n][M] 
\]

Substituting the value for \( [\text{M}^n]^* \) into the above equation

\[
R_p = \frac{k_p k_d[\text{Mn}^3+] [X][M]^2}{(k_o/[\text{Mn}^3+] + [M])(k_{t_2}[\text{Mn}^3+] + k_{t_5}[X])} 
\]

Assuming

\[
(k_o/k_i)[\text{Mn}^3+] + [M] = A \quad \text{and} \\
[k_{t_2}[\text{Mn}^3+] + k_{t_5}[X] = B 
\]
Then $A \times B$

$$= \left( \frac{k_o}{k_i} \right)_{k_t} [Mn^{3+}]^2 + \left( \frac{k_o}{k_i} \right)_{k_t} [Mn^{3+}] [X] +$$

$$k_{t_2} [M][Mn^{3+}] + k_{t_5} [M][X]$$

Rearranging this

$$A \times B$$

$$= [Mn^{3+}] \left\{ \left( \frac{k_o}{k_i} \right)_{k_t} [Mn^{3+}] + \left( \frac{k_o}{k_i} \right)_{k_t} [X] +$$

$$k_{t_2} [M] + \left( k_{t_5} [M][X] / [Mn^{3+}] \right) \right\}$$

when

$$k_{t_2} [M] \gg \left( \frac{k_o}{k_i} \right)_{k_t} [X], \left( \frac{k_o}{k_i} \right)_{k_t} [Mn^{3+}]$$

and

$$\left( k_{t_5} [M][X] / [Mn^{3+}] \right)$$

The expression for $R_p$ then reduces to

$$R_p = \frac{K_k_{p} [X][M]}{k_{t_2}} \quad \ldots \quad (63)$$

It is possible to get a wide variety of rate expressions on assuming different initiations and different type of terminations that take place simultaneously. However only a few expressions are derived to indicate the complexity of the situation and stress the range of possibility.