Problems 1-7, 9-13 Chapter 12, Allcock and Lampe

ANSWER KEY

1. $k_p$ = 74 L/mol-sec; $k_t$ = 3.3 x10$^6$ L/mol-sec; $r_i$ = 10$^{-6}$ mol/L-sec

(a) $$[R] = \left(\frac{r_i}{2k_t}\right)^{1/2} = 3.89\times 10^{-7}\ \frac{\text{mol}}{\text{L}}$$

(b) $$\frac{d[R]}{dt} = r_i - r_t = r_i - 2k_t[R]^2$$

Separate variables and expand into partial fractions:

$$\int \frac{d[R]}{r_i - 2k_t[R]^2} = \frac{1}{2\sqrt{2k_t r_i}}\left(\int \frac{\sqrt{2k_t}}{\sqrt{r_i}+[R]\sqrt{2k_t}}d[R] + \int \frac{\sqrt{2k_t}}{\sqrt{r_i}-[R]\sqrt{2k_t}}d[R]\right) = \int dt$$

$$\frac{1}{2\sqrt{2k_t r_i}}\left[\ln\left(\sqrt{r_i}+[R]\sqrt{2k_t}\right) - \ln\left(\sqrt{r_i}-[R]\sqrt{2k_t}\right)\right] = t$$

$$\ln\frac{\sqrt{r_i}+[R]\sqrt{2k_t}}{\sqrt{r_i}-[R]\sqrt{2k_t}} = 2\left(2k_t r\right)^{1/2} t$$

Or:

$$[R] = \left(\frac{r_i}{2k_t}\right)^{1/2}\tanh\left(2k_t r_i\right)^{1/2} t = \left(\frac{r_i}{2k_t}\right)^{1/2}\frac{e^{(2k_t r_i)^{1/2}t} - e^{-(2k_t r_i)^{1/2}t}}{e^{(2k_t r_i)^{1/2}t} + e^{-(2k_t r_i)^{1/2}t}}$$

Now, find $t$ at $[R] = 0.95\left(\frac{r_i}{2k_t}\right)^{1/2}$

$$t = \frac{\ln\frac{\sqrt{r_i}+[R]\sqrt{2k_t}}{\sqrt{r_i}-[R]\sqrt{2k_t}}}{2\sqrt{2k_t r_i}} = \frac{\ln\frac{\sqrt{r_i}+0.95\sqrt{r_i}}{\sqrt{r_i}-0.95\sqrt{r_i}}}{2\sqrt{2k_t r_i}} = \frac{\ln\frac{1.95}{0.05}}{2\sqrt{2k_t r_i}} = 0.713\ \text{s}$$

(c) Integrate the free-radical polymerization rate equation with respect to monomer ($r_i$ = constant).

$$r_p = \frac{-d[M]}{dt} = \left(\frac{k_p^2}{2k_t}\right)^{1/2} r_i^{1/2}[M] \quad\Rightarrow\quad \ln\frac{[M]_o}{[M]} = \left(\frac{k_p^2}{2k_t}\right)^{1/2} r_i^{1/2} t$$

Find $t$ for which $[M] = 0.8[M]_o$:

$$t = \left(\frac{k_p^2}{2k_t}\right)^{-1/2} r_i^{-1/2}\ln\frac{[M]_o}{[M]} = 7.75\times 10^3\ \text{s}$$

(d) Instead of assuming the steady-state concentration from the beginning of the reaction, utilize the expression for [R] as a function of time developed in section (b) above. $[R]_{SS}$ = steady-state radical concentration.

$$\frac{-d[M]}{dt} = k_p\left(\frac{r_i}{2k_t}\right)^{1/2}[M]\tanh\left(2k_t r_i\right)^{1/2} t$$

Integrate:

$$-\int\frac{d[M]}{[M]} = k_p[R]_{SS}\int\frac{e^{at}-e^{-at}}{e^{at}+e^{-at}}dt \qquad where, [R]_{SS} = \left(\frac{r_i}{2k_t}\right)^{1/2}\ and, \quad a = \left(2k_t r_i\right)^{1/2}$$

$$-\ln[M]\Big|_{[M]_o}^{[M]} = k_p[R]_{SS}\frac{1}{a}\ln\left(e^{at}+e^{-at}\right)\Big|_0^t$$

$$\ln\frac{[M]_o}{[M]} = k_p[R]_{SS}\frac{1}{a}\ln\frac{e^{at}+e^{-at}}{2} \quad\Rightarrow\quad \ln\frac{[M]_o}{[M]} = k_p[R]_{SS}\left(2k_t r_i\right)^{-1/2}\ln\frac{e^{(2k_t r_i)^{1/2}t}+e^{-(2k_t r_i)^{1/2}t}}{2}$$

This expression takes the following form at long times ( $t \ge \frac{10}{\sqrt{2k_t r_i}}$ sec or so):

$$\ln\frac{[M]_o}{[M]} = k_p[R]_{SS}\left(t - \frac{\ln 2}{\left(2k_t r_i\right)^{1/2}}\right)$$

According to this equation, the time required to reach 20% conversion is 0.270 s longer than calculated in section (c) above. This amounts to an error of roughly 3 x$10^{-3}$ %.

2. (a) Yes. A plot of $r_p$ vs. $[MMA][AIBN]^{1/2}$ is linear. Also, plots of $r_p$/[MMA] vs. $[AIBN]^{1/2}$ and $r_p/[AIBN]^{1/2}$ vs. [MMA] are linear.

(b) $k_i$ (77°C) = 9.89 x$10^{-5}$ $s^{-1}$; thus, $\left(2\,fk_i\right)^{1/2} = 1.18\times10^{-2}\ \left(\text{mol/L}\cdot\text{s}\right)^{1/2}$.

The slope of the $r_p$ vs. $[MMA][AIBN]^{1/2}$ plot is $\left(\frac{k_p^2}{2k_t}\right)^{1/2}\left(2\,fk_i\right)^{1/2}$. Therefore:

$$\left(\frac{k_p^2}{2k_t}\right)^{1/2} = \text{slope}\times\left(2\,fk_i\right)^{-1/2} = 0.00139\,\frac{\text{L}^{1/2}}{\text{mol}^{1/2}\cdot\text{s}}\times 85.00\,\text{s}^{1/2} = 0.118\,\frac{\text{L}^{1/2}}{\text{mol}^{1/2}\cdot\text{s}^{1/2}}$$

3. (a) The data are in accord with eq. 35. Plots of $r_p$ vs. [MMA] are linear at each temperature (at each temperature, the values of $r_p$/[MMA] are approximately constant).

(b) The slope of a plot of $r_p$ vs. [MMA] (i.e., the average value of $r_p$/[MMA]) is equal to $\left(\frac{k_p^2}{2k_t}\right)^{1/2}(2fk_i)^{1/2}[I]^{1/2}$. Therefore,

$$E_p - \frac{1}{2}E_t + \frac{1}{2}E_i = -R\ln\frac{\text{slope}_{50}}{\text{slope}_{70}}\left(\frac{1}{323}-\frac{1}{343}\right)^{-1} = 19.6\,\frac{\text{kcal}}{\text{mol}}$$

(c) From Table 12.2, for MMA, $E_p - E_t/2$ = 4.9 kcal/mol. Using the answer from (b) above, $E_i$ for benzoyl peroxide = 29.4 kcal/mol.

(d) $\overline{X}_n\ (\overline{DP})$ is proportional to [MMA], as predicted by eqs. (39) and (43). Since $\overline{X}_n \propto \exp\left[\frac{-(E_p - E_t/2 - E_i/2)}{RT}\right]$, and the overall activation energy is negative, $\overline{X}_n$ goes down as temperature goes up.

4. $W_n = X_n \frac{n}{\overline{X}_n}$

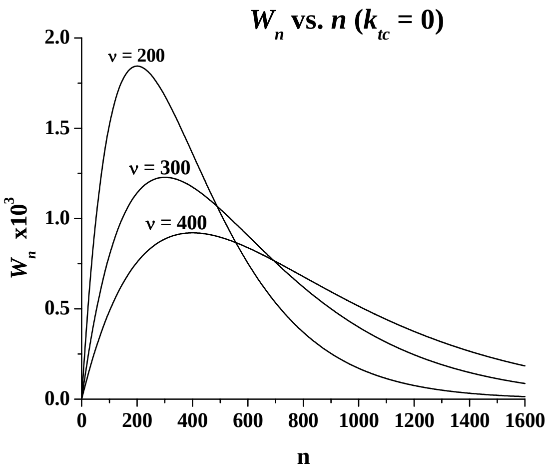
$W_n$ is the weight fraction of polymer chains containing exactly $n$ repeat units.
$X_n$ is the mole fraction of polymer chains containing exactly $n$ repeat units.
$\overline{X}_n$ is the average degree of polymerization of the polymer.
And, $\overline{X}_n = 2\nu\frac{k_{tc}+k_{td}}{k_{tc}+2k_{td}}$ (eq. (43)).

Combination of eq. (66) and (43) with the equation at the top of this problem yields:

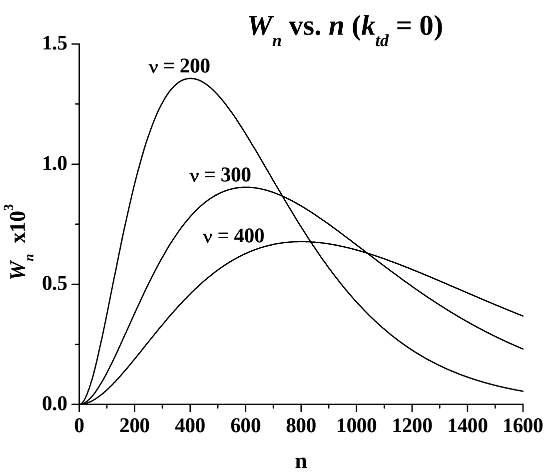
$$W_n = \frac{1}{\nu}\left(1+\frac{1}{\nu}\right)^{-n}\frac{(n-1)/\nu + 2(k_{td}/k_{tc})}{1+2(k_{td}/k_{tc})}\left(\frac{n}{2\nu}\right)\frac{1+2(k_{td}/k_{tc})}{1+(k_{td}/k_{tc})}$$

$$W_n = \frac{n}{2\nu^2}\left(1+\frac{1}{\nu}\right)^{-n}\frac{(n-1)/\nu + 2(k_{td}/k_{tc})}{1+(k_{td}/k_{tc})}$$

5. (a) For $k_{tc} = 0$, $W_n = \dfrac{n}{\nu^2}\left(1+\dfrac{1}{\nu}\right)^{-n}$




(b) For $k_{td} = 0$, $W_n = \dfrac{n(n-1)}{2\nu^3}\left(1+\dfrac{1}{\nu}\right)^{-n}$




6. Apply steady-state approximation to radicals of degree of polymerization, n:

$$\frac{d[R_n]}{dt} = k_p[M][R_{n-1}] - k_p[M][R_n] - 2k_t[R_n][R] - \left(k_M[M] + k_S[S] + k_Y[Y]\right)[R_n] = 0$$

Introduce, $\gamma = C_M + C_S\dfrac{[S]}{[M]} + C_Y\dfrac{[Y]}{[M]}$, to yield:

$$\frac{d[R_n]}{dt} = k_p[M][R_{n-1}] - k_p[M][R_n] - 2k_t[R_n][R] - k_p[M][R_n]\gamma = 0 \qquad \text{6-1}$$

Rearrange:

$$\frac{[R_n]}{[R_{n-1}]} = \left(\frac{k_p[M] + 2k_t[R] + k_p[M]\gamma}{k_p[M]}\right)^{-1} = \left(1 + \frac{1}{\nu} + \gamma\right)^{-1} \qquad 6\text{-}2$$

To obtain $[R_n]/[R_1]$:

$$\frac{[R_n]}{[R_1]} = \left(\frac{[R_n]}{[R_{n-1}]}\right)\left(\frac{[R_{n-1}]}{[R_{n-2}]}\right)\left(\frac{[R_{n-2}]}{[R_{n-3}]}\right)\cdots\frac{[R_2]}{[R_1]} = \left(1 + \frac{1}{\nu} + \gamma\right)^{1-n} \qquad 6\text{-}3$$

$f_n$ is defined as the fraction of propagating radicals that has a degree of polymerization $n$. Combine with 6-3:

$$f_n = \frac{[R_n]}{[R]} = \frac{[R_1]}{[R]}\left(1 + \frac{1}{\nu} + \gamma\right)^{1-n} \qquad 6\text{-}4$$

Now, apply the steady-state approximation to [R] and [$R_1$]:

$$\frac{d[R]}{dt} = r_i - 2k_t[R]^2 = 0 \qquad 6\text{-}5$$

$$\frac{d[R_1]}{dt} = r - k_p[M][R_1] - 2k_t[R_1][R] - k_p[M][R_1]\gamma + k_p[M][R]\gamma = 0 \qquad 6\text{-}6$$

The last term in 6-6 accounts for the fact that chain transfer produces (after reaction of the primary radical with monomer) a new radical of degree of polymerization of 1. Combine 6-5 and 6-6:

$$\frac{[R_1]}{[R]} = \frac{2k_t[R] + k_p[M]\gamma}{k_p[M] + 2k_t[R] + k_p[M]\gamma} = \left(\frac{1 + \frac{1}{\nu} + \gamma}{\frac{1}{\nu} + \gamma}\right)^{-1} \qquad 6\text{-}7$$

Combine 6-4 and 6-7 to yield the distribution function.

$$f_n = \frac{[R_n]}{[R]}\left(\frac{1}{\nu} + \gamma\right)\left(1 + \frac{1}{\nu} + \gamma\right)^{-n} \qquad 6\text{-}8$$

The mole fraction of polymer with degree of polymerization of $n$ is represented as $X_n$ and is defined by the rate of formation of polymer with degree of polymerization of $n$, $P_n$, divided the rate of formation of polymer of all degrees of polymerization, $P$.

$$X_n = \frac{d[P_n]}{dt} \Big/ \frac{d[P]}{dt} \qquad 6\text{-}9$$

The rate of formation of *P* is:

$$\frac{d[P]}{dt} = (k_{tc} + 2k_{td})[R]^2 + k_p[M][R]\gamma = \left[(k_{tc} + 2k_{td}) + 2\nu\gamma(k_{tc} + k_{td})\right][R]^2 \qquad \text{6-10}$$

For even *n*,

$$\frac{d[P_n]}{dt} = k_{tnnc}[R_{n/2}][R_{n/2}] + \frac{1}{2}\sum_{\substack{m=1 \\ m\neq n/2}}^{n-1} k_{tnmc}[R_m][R_{n-m}] + 2k_{td}[R_n][R] + k_p[M][R_n]\gamma \qquad \text{6-11}$$

The rate constant for termination of unlike radicals, $k_{tnm}$, is twice that of like radicals, $k_{tnn}$ (i.e., $k_{tnm} = 2k_{tnn} = 2k_t$). (In the absence of an "*nn*" or "*nm*" subscript, $k_t$ is understood to be the rate constant for termination of like radicals.)

$$\frac{d[P_n]}{dt} = k_{tc}\sum_{m=1}^{n-1}[R_m][R_{n-m}](1)^m + 2k_{td}[R_n][R] + k_p[M][R_n]\gamma \qquad \text{6-12}$$

6-12 also holds for odd n. Substitute 6-8.

$$\frac{d[P_n]}{dt} = \left[k_{tc}\left(\frac{1}{\nu}+\gamma\right)^2\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\sum_{m=1}^{n-1}(1)^m + 2k_{td}\left(\frac{1}{\nu}+\gamma\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n} + \frac{k_p[M]}{[R]}\gamma\left(\frac{1}{\nu}+\gamma\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\right][R]^2$$

Combine terms.

$$\frac{d[P_n]}{dt} = \left(\frac{1}{\nu}+\gamma\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\left\{\left[\left(\frac{1}{\nu}+\gamma\right)(n-1) + 2\nu\gamma\right]k_{tc} + (2+2\nu\gamma)k_{td}\right\}[R]^2$$

Divide by 6-10 and introduce $\alpha = k_{td}/k_{tc}$.

$$X_n = \frac{\left(\frac{1}{\nu}+\gamma\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\left[\left(\frac{1}{\nu}+\gamma\right)(n-1) + 2\nu\gamma + (2+2\nu\gamma)\alpha\right]}{1+2\nu\gamma+(2+2\nu\gamma)\alpha}$$

Rearrange.

$$X_n = \left(\frac{1+\nu\gamma}{\nu}\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\left[\frac{(n-1)\left(\frac{1+\nu\gamma}{\nu}\right) + 2\nu\gamma\left(1+\alpha+\frac{\alpha}{\nu\gamma}\right)}{1+2\nu\gamma\left(1+\alpha+\frac{\alpha}{\nu\gamma}\right)}\right]$$

The following obtains for $k_{td} = 0$ (i.e., a = 0):

$$X_n = \left(\frac{1+\nu\gamma}{\nu}\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}\frac{(n-1)\left(\frac{1+\nu\gamma}{\nu}\right) + 2\nu\gamma}{1+2\nu\gamma}$$

7. The following obtains for $k_{tc}$= 0:

$$X_n = \left(\frac{1+\nu\gamma}{\nu}\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}$$

9. [M] = 4 M; [I] = 0.05 M; T = 60°C (333K); $k_i$ = 1.20 x$10^{-6}$ $s^{-1}$; $f$ = 0.75; $k_{tc}$ = 0.

$$r_i^{1/2} = (2\,fk_i)^{1/2}[I]^{1/2} = 3.0\times10^{-4}\left(\frac{\mathrm{M}}{\mathrm{s}}\right)^{1/2}$$

From the chapter:

$$k_p = 1.0\times10^3\ \mathrm{M^{-1}s^{-1}} \quad \text{and} \quad k_t = 3.2\times10^7\ \mathrm{M^{-1}s^{-1}};$$

therefore, $$\left(\frac{k_p^2}{2k_t}\right)^{1/2} = 0.125\left(\frac{L}{mol\cdot s}\right)^{1/2}$$

(a) $$r_p = \left(\frac{k_p^2}{2k_t}\right)^{1/2}(2\,fk_i)^{1/2}[I]^{1/2}[M] = 1.5\times10^{-4}\left(\frac{\mathrm{M}}{\mathrm{s}}\right)$$

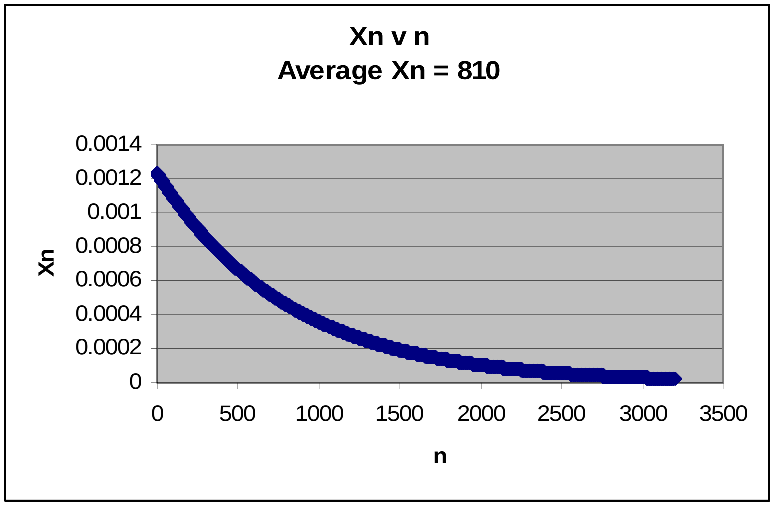
(b) $$\nu = \left(\frac{k_p^2}{2k_t}\right)^{1/2}\frac{[M]}{r_i^{1/2}} = 1.67\times10^3$$

(c) $C_M$ (vinyl acetate at 60°C) = 2.5 x$10^{-4}$
$C_S$ (vinyl acetate in benzene) = 2.2 x$10^{-4}$
From the densities, and assuming additivity of volumes, [benzene] = 7.0 M
For $k_{tc}$ = 0,

$$\left(\overline{X}_n\right)^{-1} = C_M + C_S\frac{[S]}{[M]} + \frac{1}{\nu} = 1.24\times10^{-3}$$

$$\overline{X}_n = 8.10\times10^2$$

(d) $$X_n = \left(\frac{1+\nu\gamma}{\nu}\right)\left(1+\frac{1}{\nu}+\gamma\right)^{-n}$$




(e) $$\bar{\tau}_s = \frac{k_p}{2k_t}\left(\frac{[M]}{r_p}\right) = 0.42 \text{ s}$$

(f) $$\bar{\tau}_{s,15} = \frac{\bar{\tau}_s}{\nu} = 2.5\times10^{-4} \text{ s}$$

10. [M] = 8.6 M; [$CCl_4$] = 0.1 M; T = 0°C (273K); ν = 1000.
From the activation data in Table 12.3,
$C_{CCl_4,273K} = 1.75\times10^{-3}$ and $C_{M,273K} = 4.4\times10^{-6}$.
From the activation data in Table 12.2, $\left(\frac{k_p^2}{2k_t}\right)^{1/2}_{273K} = 3.28\times10^{-3}\left(\frac{\text{L}}{\text{mol}\cdot\text{s}}\right)^{1/2}$

(a) $$r_{i,273K} = \left(\frac{k_p^2}{2k_t}\right)\left(\frac{[M]}{\nu}\right)^2 = 8.0\times10^{-10}\ \frac{\text{M}}{\text{s}}$$

(b) From the data in Problem 6, Chap. 3, activation of the rate constant ratio $k_{tc}/k_{td}$ is given by ln ($k_{tc}/k_{td}$) = -7.77 + 5.8 kcal/mol/RT (i.e., ln ($A_{tc}/A_{td}$) = -7.77, $E_{tc}$-$E_{td}$ = -5.8 kcal/mol). Therefore, at 273K, $k_{tc}/k_{td}$ = 20.

$$\left(\bar{X}_n\right)^{-1} = C_{CCl_4}\frac{[CCl_4]}{[M]} + C_M + \frac{k_{tc}+2k_{td}}{2\nu\left(k_{tc}+k_{td}\right)} = 5.5\times10^{-4}$$

$$\bar{X}_n = 1.8\times10^3$$

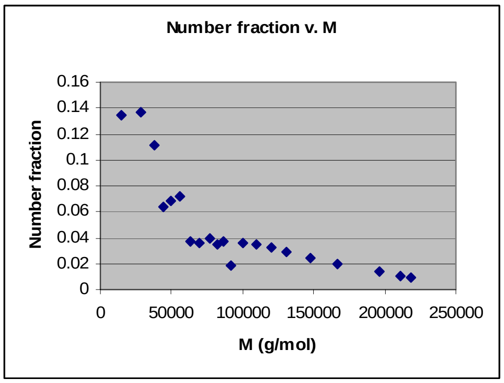
(c) Assuming that $r_i$ stays the same (i.e., the rate of photochemical initiation is temperature independent),

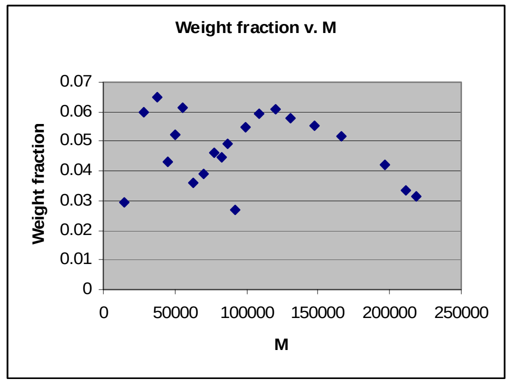
$$\nu_{373K} = \nu_{273K}\left(\frac{k_p^2}{2k_t}\right)_{373}^{1/2}\left(\frac{k_p^2}{2k_t}\right)_{273}^{-1/2} = 2.6\times 10^4$$

At 373K, $k_{tc}/k_{td}$ = 1.12, $C_M$ = 2.15 x10$^{-4}$, $C_{CCl_4}$ = 2.07 x10$^{-2}$. Therefore,

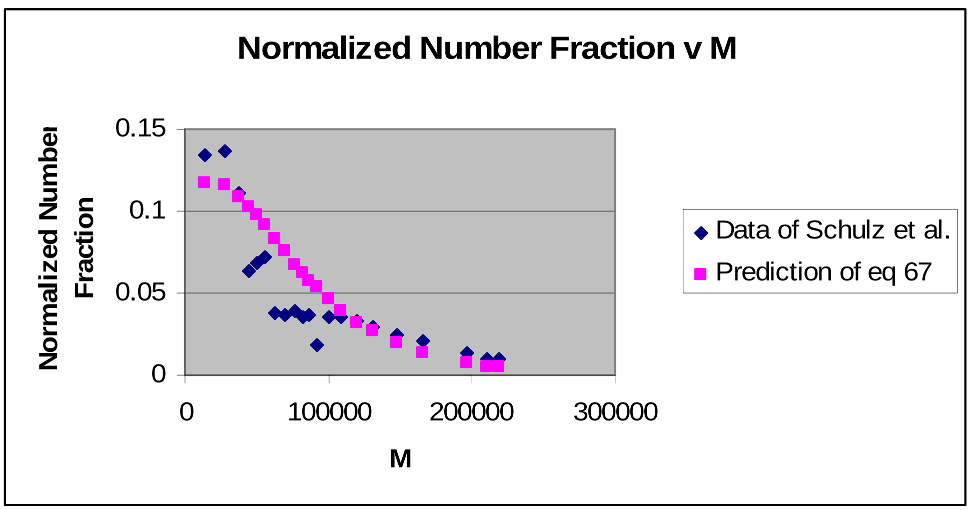
$\overline{X}_n = 2.07\times 10^3$

11. Assume $k_{td}/k_{tc}$ = 0.24. From the data, $\overline{X}_n = 626$ and, $\nu = 374$.




The following chart plots the experimental number distribution data above, against the theoretical prediction of eq 66 (plotted as $X_n$ v. M ). The agreement between data and theory is fair.




12. $M_1$ = vinyl acetate; $M_2$ = vinyl chloride
$[M_1]$ = 3.5 M ; $[M_2]$ = 1.5 M
$r_1$ = 0.23 ; $r_2$ = 1.68

(a) $$\gamma = \frac{f_1}{f_2} = \frac{1+r_1([M_1]/[M_2])}{1+r_2([M_2]/[M_1])} = 0.893$$

$f_1 = 0.47;\ f_2 = 0.53$

(b) $\bar{m}_{M_1} = 1 + r_1 \frac{[M_1]}{[M_2]} = 1.54$

$\bar{m}_{M_2} = 1 + r_2 \frac{[M_2]}{[M_1]} = 1.72$

(c) $R = \frac{200}{\bar{m}_{M_1} + \bar{m}_{M_2}} = 61.4$

(d) $P_{M_1}(8) = P_{11}^{8-1} P_{12} = 4.1 \times 10^{-4}$

13. (a)

acrylonitrile (1) – butadiene (2)

$r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1(e_1 - e_2)\right] = 0.017$

$r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2(e_2 - e_1)\right] = 0.375$

(b) $r_1$ (methyl acrylate) = 7.51
$r_2$ (vinyl chloride) = 0.113

(c) $r_1$ (methyl vinyl ketone) = 0.207
$r_2$ (*p*-methoxystyrene) = 0.182

(d) $r_1$ (styrene) = 0.942
$r_2$ (*p*-methoxystyrene) = 0.964