<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 3</td>
<td>1</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>7</td>
</tr>
<tr>
<td>Chapter 10</td>
<td>14</td>
</tr>
<tr>
<td>Chapter 11</td>
<td>19</td>
</tr>
<tr>
<td>Chapter 12</td>
<td>35</td>
</tr>
<tr>
<td>Chapter 13</td>
<td>63</td>
</tr>
<tr>
<td>Chapter 14</td>
<td>76</td>
</tr>
<tr>
<td>Chapter 15</td>
<td>97</td>
</tr>
<tr>
<td>Chapter 16</td>
<td>105</td>
</tr>
<tr>
<td>Chapter 17</td>
<td>112</td>
</tr>
<tr>
<td>Chapter 18</td>
<td>112</td>
</tr>
<tr>
<td>Chapter 20</td>
<td>113</td>
</tr>
<tr>
<td>Chapter 21</td>
<td>113</td>
</tr>
<tr>
<td>Chapter 22</td>
<td>114</td>
</tr>
<tr>
<td>Chapter 23</td>
<td>114</td>
</tr>
</tbody>
</table>
CHAPTER 3

1. Denoting \( \text{CH}_3 \)- groups by \( \text{Me} \) for simplicity we have

\[
\text{Me}_2\text{C}-\text{N}=\text{N}-\text{CMe}_2 \rightarrow 2 \text{Me}_2\text{C} \cdot + \text{N}_2
\]

\[
\text{Me}_2\text{C} \cdot + \text{H}_2\text{C}=\text{CHO}\text{CMe} \rightarrow \text{Me}_2\text{C}-\text{CH}_2\text{C} \cdot \text{O}\text{CMe}
\]

\[
\text{Me}_2\text{C}-\text{CH}_2\text{C} \cdot \text{O}\text{CMe} + \text{H}_2\text{C}=\text{CHO}\text{CMe} \rightarrow \text{Me}_2\text{C}-\text{CH}_2\text{CHCH}_2\text{C} \cdot \text{O}\text{CMe}\text{O}\text{CMe}
\]

\[
\text{Me}_2\text{C}\left(\text{CH}_2\text{C}\text{O}\text{CMe}_{n-1}\text{O}\text{CMe}\right) + \text{H}_2\text{C}=\text{CHO}\text{CMe} \rightarrow \text{Me}_2\text{C}\left(\text{CH}_2\text{C}\text{O}\text{CMe}_{n}\text{O}\text{CMe}\right)
\]

\[
\text{Me}_2\text{C}\left(\text{CH}_2\text{C}\text{O}\text{CMe}_{n}\text{O}\text{CMe}\right) + \text{YZ} \rightarrow \text{Me}_2\text{C}\left(\text{CH}_2\text{C}\text{O}\text{CMe}_{n}\text{O}\text{CMe}\right) + \text{Z} \cdot
\]

\[
\text{Me}_2\text{C}\left(\text{CH}_2\text{C}\text{O}\text{CMe}_{n-1}\text{O}\text{CMe}\right) + \text{CH}_2\text{C} \left(\text{CHCH}_2\right)\text{CMe}_2 \rightarrow \text{over}
\]
A completely analogous mechanism applies to methyl methacrylate,

\[
\begin{align*}
\text{H}_2\text{C} &= \text{C} - \text{C} - \text{OMe} \\
&\quad \text{Me}
\end{align*}
\]

If CCl₄ is added to the system, a chain transfer reaction, namely,

\[
\begin{align*}
\begin{array}{c}
\text{Me}_2\text{C} \\
\text{OCMe}
\end{array} &\quad \begin{array}{c}
\text{CH}_2\text{CH} \\
\text{OCMe}
\end{array} &\quad \begin{array}{c}
\text{H} \\
\text{O}
\end{array} &\quad \begin{array}{c}
\text{Cl} \\
\text{O}
\end{array} + \text{CCl}_4 + \begin{array}{c}
\text{Me}_2\text{C} \\
\text{OCMe}
\end{array} &\quad \begin{array}{c}
\text{CH}_2\text{CH}_{2}\text{OCMe} \\
\text{O}
\end{array} &\quad \cdot \text{CCl}_3
\end{array}
\]

takes place. Since this transfer reaction stops further growth of the polymeric radical, the average molecular weight is reduced. The same effect occurs in the case of methyl methacrylate.
2. Free-radical addition to \( \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \) is favored at the position shown because the radical so produced has the tertiary structure. After six such additions, the propagating radical will be

```
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{R} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 & \\
\text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \\
\end{align*}
```

(a)

Addition of a free radical to the other double bond can also occur with formation of a radical of secondary structure. Suppose the above propagating radical encounters a propagating radical containing four monomer units and instead of a termination reaction occurring, the latter radical adds to the vinyl group of the former, labeled (a), with the result

```
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2 & \quad \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 & \\
\text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} & \\
\text{Me} - \text{C} - \text{CH} = \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \\
\text{Me} - \text{C} - \text{CH} = \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \\
\end{align*}
```

Further addition can now occur at the two radical sites marked by which leads obviously to a branched polymer.

3. \( 10^{-6} < k_i = 1.0 \times 10^{14} e^{-\frac{35000}{RT}} < 10^{-5} \text{ sec}^{-1} \)
Solving for \( T \) gives

\[ 382K < T < 403K \]

So \( \Delta T_{\text{useful}} = 109-130^\circ C \)

4. The initiating radicals, \( R' \), at the moment of formation are contained in a solvent cage. Let us represent these caged radicals by ( ). The mechanism of initiation may then be written:

\[
\begin{align*}
I & \rightarrow (2R') + N2 \\
(2R') & \rightarrow 2R' \\
(2R') & \rightarrow R_2' \\
2R' & \rightarrow R_2' \\
R' + M & \rightarrow R_1
\end{align*}
\]

(1) Initiator dissociation

(2) Escape from solvent cage

(3) Cage recombination

(4) Recombination outside of cage

(5) Initiation

Processes (3) and (4) which waste initiating radicals compete with initiation. As the monomer concentration is increased, the initiation (5) becomes more probable and \( f \) increases. At the limit of \( f = 0.65 \), [M] is so large that recombination outside of the cage, (4), has been completely eliminated. However, the cage recombination, (3), cannot be eliminated, even though the cage consists of monomer molecules.

5. (a) \[
\ln \frac{\%\text{Comb}}{\%\text{Disp}} = \ln \frac{A_C}{A_D} + \ln \frac{E_D - E_C}{RT}
\]

Plot \( \ln \frac{\%\text{Comb}}{\%\text{Disp}} \) vs. \( \frac{1}{T} \). The slope is \( E_D - E_C \) and the value obtained is:

\( E_D - E_C = 4.52 \text{ kcal/mole} \). From the intercept

4
\[ \frac{A_C}{A_D} = 7.13 \times 10^{-4} \]

(b) From (a) \[ \frac{\%\text{Comb}}{\%\text{Disp}} = 7.13 \times 10^{-4} e^{\frac{4530}{RT}} \]

For termination 90\% by combination, \[ \frac{\%\text{Comb}}{\%\text{Disp}} = 9 \]. Substituting and solving for \( T \) gives

\[ T = 241 K = -32\degree C. \]

6. (a) Plot \( \ln \frac{\%C}{\%D} \) as in (5). From the slope

\[ E_D - E_C = 5.85 \text{ kcal/mole} \]

and from the intercept \[ \frac{A_C}{A_D} = 4.18 \times 10^{-4} \]

Thus \[ \frac{\%C}{\%D} = 4.18 \times 10^{-4} \ e^{\frac{5850}{RT}} \]

(b) \[ 1 = 4.18 \times 10^{-4} \ e^{\frac{5850}{RT}} \]

from which \( T = 378K = 105\degree C. \)

\[
C_2H_5Ag \rightarrow C_2H_4 + Ag
\]
\[
k_1 = 5.0 \times 10^8 e^{\frac{-14200}{RT}} < 10^{-5}
\]

Thus \[10^{-6} < 5.0 \times 10^8 e^{\frac{-14200}{RT}} < 10^{-5}\]

From which \(211K < T < 227K\)

Or \(-62^\circ C < T < -46^\circ C\).

8. A free-radical chain termination is a pairwise destruction of two chain centers as in the process

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{CH}_2\text{C} \cdot \\
X
\end{array}
\begin{array}{c}
\cdot \text{C} \cdot \text{CH}_2
\end{array}
\begin{array}{c}
\rightarrow
\end{array}
\begin{array}{c}
\text{CH}_2\text{CH} \cdot \text{CH} \cdot \text{CH}_2
\end{array}
\begin{array}{c}
\text{X} \\
\text{X}
\end{array}
\]

while the termination of a particular growing free radical can occur without destruction of a chain center such as in the chain transfer process to CHCl₃.

\[
\begin{array}{c}
\text{H}
\end{array}
\begin{array}{c}
\text{CH}_2\text{C} \cdot \\
X
\end{array}
\begin{array}{c}
+ \text{CHCl}_3
\end{array}
\begin{array}{c}
\rightarrow
\end{array}
\begin{array}{c}
\text{CH}_2\text{CH}_2\text{X}
\end{array}
\begin{array}{c}
+ \cdot \text{CCl}_3
\end{array}
\]

Note the growing free radical is terminated but the chain is not since this process is followed by

\[
\begin{array}{c}
\text{Cl}_3\text{C} \cdot \\
X
\end{array}
\begin{array}{c}
+ \text{CH}_2=\text{CHX}
\end{array}
\begin{array}{c}
\rightarrow
\end{array}
\begin{array}{c}
\text{Cl}_3\text{C} \cdot \text{CH}_2
\end{array}
\begin{array}{c}
\text{C} \cdot \\
X
\end{array}
\]

6
CHAPTER 5

4. \( \frac{d[R]}{dt} = 2 \Phi q \) where \( q \) is the rate of absorption of photons per unit volume.

Comparison with eqn. (5.5) shows

\[
q = \frac{I_0}{L} (1 - e^{-\kappa L E_1 N_2}) = \frac{I_0}{L} (1 - e^{-2.303 \kappa L E_1 N_2})
\]

Inserting the data given

\( q = 4.3 \times 10^{14} \) quanta/cm\(^2\)-sec

5. The initiation reaction is: \( \text{Et-N} = \text{N-Et} + \text{hv} \to 2\text{Et} + \text{N}_2^* \). Therefore the actual change in concentration of azoethane is

\[
\Delta[\text{Et}_2\text{N}_2] = \frac{n_{\text{N}_2^*}}{V_{\text{reactor}}} = \left( \frac{PV_{\text{N}_2^*}}{RT} \right) \frac{1}{\pi R^2 L} = 2.87 \times 10^{-7} \text{ moles/liter}
\]

\[
= 1.73 \times 10^{14} \text{ molecules/cm}^3
\]

(a) So little of the azoethane has decomposed we may assume that \([\text{Et}_2\text{N}_2]\) is a constant during the time of reaction. Then Eqn. 5.5 may be written

\[
\cdot \frac{d[\text{Et}_2\text{N}_2]}{dt} = \frac{\Delta[\text{Et}_2\text{N}_2]}{\Delta t} = \Phi q = 4.3 \times 10^{14} \Phi
\]

\[
\Delta[\text{Et}_2\text{N}_2] = 4.3 \times 10^4 \times 15 \times 60 \Phi = 3.87 \times 10^{17} \Phi = 1.73 \times 10^{14}
\]

\( \Phi = 4.5 \times 10^{-4} \)
(b) \( \frac{d[E^*]}{dt} = 2\Phi q = 3.9 \times 10^{11} \text{radicals/cm}^3\text{-sec} = 6.4 \times 10^{-10} \text{moles/liter-sec} \)

(c) \( r_i = f \times \frac{d[E] \text{dt}}{dt} = 1.5 \times 10^1 \text{radicals/cm}^3\text{-sec} = 2.6 \times 10^{-10} \text{moles/liter-sec} \)

6. \( r_i = 10^{-7} \text{moles/liter-sec} = f \times \frac{d[R]}{dt} = 2f\Phi q = 6.02 \times 10^{13} \text{radicals/cm}^3\text{sec} \) or
\[ q = 1.40 \times 10^{14} \text{quanta/cm}^3\text{-sec} \]

Suppose we choose a cylindrical cell of radius \( R \) and length \( L \). From eqn (5.5)
\[ q = \frac{I_o}{L} \left( 1 - e^{-\alpha [ABIN]L} \right) \]

For convenience, let's design the system so that \( \alpha [ABIN]L \leq 0.1 \). In this case, (cf equations 5 and 6)
\[ q = I_o \alpha [ABIN] = 2.31 \alpha [ABIN] = 1.40 \times 10^{14} \text{ or } [ABIN] = 6.4 \times 10^{-4} \text{moles/liter} \]

Since \( \alpha [ABIN]L = 2.3 \alpha [ABIN]L \leq 0.1 \)
\[ L \leq 7.14 \text{cm} \]

Suppose we choose \( L = 5.0 \text{cm} \). Since the total volume is 50 cm\(^3\)
\[ R = \sqrt{\frac{V}{\pi L}} = \sqrt{\frac{50}{5\pi}} = 1.78 \text{ cm} \]

A quartz window should be used to transmit the 366 nm light.

7. No. of molecules of MMA polymerized = \( \frac{0.25 \text{ g}}{100 \text{ g/mole}} \times 6.02 \times 10^{23} = 1.51 \times 10^{21} \)

The average rate of polymerization = \( \frac{1.51 \times 10^{21}}{50 \text{ cm}^3 \times 15 \text{ min} \times 60 \text{ sec/min}} \)

= \( 3.3 \times 10^{16} \) molecules/cm\(^3\)-sec

\( q = 1.40 \times 10^{14} \) quanta/cm\(^3\) sec (From Problem 6)

Hence, \( \Phi = \frac{1}{q} \left( -\frac{d[M]}{dt} \right) = \frac{3.3 \times 10^{16}}{1.40 \times 10^{14}} = 236 \) molecules/quantum

8. From the numbers of electrons in the molecules, the concentrations and Eqn 23, there results

(a) \( \varepsilon \) (methylacrylate) = 0.485

(b) \( \varepsilon \) (vinyl bromide) = 0.011

(c) \( \varepsilon \) (styrene) = 0.491

(d) \( \varepsilon \) (methyl acrylate) = 0.509
9. The dose rate to any of the substances from this source is

\[
\frac{dD}{dt} = 1.50 \times 10^6 \text{rad/hr} \times 10^1 \text{ergs/g-rad} \times 10^7 \text{ joules/erg} = 9.4 \times 10^{19} \text{ ev/g-hr}
\]

(a) The energy absorption rate per unit volume in styrene is

\[
\frac{dD}{dt} = 9.4 \times 10^{19} \times \frac{1}{3600} \text{ hr} \times 0.906 \text{g/cm}^3 = 2.4 \times 10^{16} \text{ ev/cm}^3 \text{-sec}
\]

Then \( \tau = \left( \frac{dD}{dt} \right) \frac{G(R)}{100} \times f = (2.4 \times 10^{16}) \left( \frac{0.66}{100} \right)(0.5) = \]

\[
7.8 \times 10^{13} \text{ radicals/cm}^3 \text{-sec} = 1.3 \times 10^{-7} \text{ moles/liter-sec}
\]

(b) \(1.9 \times 10^{-4} \text{ moles/liter-sec}\)

(c) \(8.7 \times 10^{-7} \text{ moles/liter-sec}\)

(d) \(1.3 \times 10^{-4} \text{ moles/liter-sec}\)

10. \[
\frac{dD}{dt} = 1.0 \times 10^6 \times \frac{1}{3600} \times 10^2 \times 10^{-7} \times \frac{1}{1.60 \times 10^{19}} = 1.7 \times 10^{16} \text{ ev/g-sec}
\]

The mass of acrylonitrile/liter is 53 grams/liter and assuming additivity of volumes, the densities of acrylonitrile and benzene may be used to calculate the benzene concentration to be \([C_6H_6]=10.5 \text{ moles/liter}\) and the density of solution to be \(\rho 0.874 \text{g/cm}^3\), so,
\[ \frac{dD'}{dt} = 1.7 \times 10^{16} \times 0.874 = 1.5 \times 10^{16} \text{ev/cm}^3\text{-sec} \]

\[ \varepsilon(\text{acrylonitrile}) = 0.0597 \text{ and } \varepsilon(C_6H_6) = 0.940 \text{ and hence} \]

\[ \tau = f \left[ 0.0597 \left( \frac{G(R)}{100} \right)_{\text{acrylonitrile}} + 0.940 \left( \frac{G(R)}{100} \right)_{\text{benzene}} \right] \]

\[ \tau = 9.8 \times 10^{13} \text{radicals/cm}^3\text{-sec} = 1.6 \times 10^{-7} \text{moles/liter-sec}. \]

11. \(G(-M) = 1500 \text{ molecules/100 ev} = 15 \text{ molecules/ev}\)

From problem 10, \(\frac{dD'}{dt} = 1.5 \times 10^{16} \text{ ev/cm}^3\text{-sec}\)

Hence,

\[ \tau_p = -\frac{d[M]}{dt} = (15)(1.5 \times 10^{16}) \text{ molecules/cm}^3\text{-sec} \]

\[ = 3.8 \times 10^{-5} \text{ moles/liter-sec} \]

12. \(\tau = f \left( \frac{dD}{dt} \right) \rho_{\text{solution}} \left[ \left( \frac{G(R)}{100} \right)_{\text{MMA}} \varepsilon_{\text{MMA}} + \left( \frac{G(R)}{100} \right)_{\text{benzene}} \varepsilon_{\text{benzene}} \right] \)

Substituting the data given and rearranging

\[
\frac{10^{-7} \times 6.02 \times 10^{23}}{(0.5)(0.5 \times 10^4)(10^2)} \left( \frac{1}{3600} \right) \left( \frac{1}{1.60 \times 10^{-16}} \right) = \rho_{\text{solution}} \left[ 0.061 \varepsilon_{\text{MMA}} + 6.6 \times 10^{17} \varepsilon_{\text{benzene}} \right] \]

\[ = 8.7 \times 10^{15} \quad (I) \]
letting \( x \) = concentration of MMA, we have in 1 liter of solution a weight \( W_{\text{MMA}} = 100 \times \text{g/liter} \). If we assume additivity of volumes, then

\[
V_{\text{MMA}} = \frac{100}{0.95} x = 105x \text{cm}^3/\text{liter}
\]

\[
V_{\text{Benzene}} = 1000-105 x \text{ cm}^3/\text{liter}
\]

\[
W_{\text{Benzene}} = (1000-105 x ) \times (0.879)
\]

\[
\left[ C_6H_6 \right] = \frac{(1000-105x)(0.879)}{78.0} = 11.3-1.19 x \text{ moles/liter}
\]

\[
\rho_{\text{solution}} = \frac{W_{\text{MMA}} + W_{\text{Benzene}}}{1000}
\]

\[
\varepsilon_{\text{MMA}} = \frac{54x}{54x+42(11.3-1.19x)}
\]

\[
\varepsilon_{\text{Benzene}} = 1-\varepsilon_{\text{MMA}}
\]

When these latter three expressions are substituted into (1) above and rearranged, one has

\[
x^2 + 116x - 172 = 0
\]

the roots of which are: \( x_1 = 1.47 \text{ moles/liter} \)

\( x_2 = 118 \text{ moles/liter} \)

Obviously, \( x_2 \) is not physically real. Hence

\[
[\text{MMA}] = 1.47 \text{ moles/liter}
\]
For 100 cm$^3$ of solution, we need

$$W_{\text{MMA}} = 1.47 \text{ moles/liter} \times \frac{1}{10} \text{ liter} \times 100 \text{ g/mole}$$

$$= 14.7 \text{ grams}$$
CHAPTER 10

2. According to (9): \( RT \ln(1-\phi) = \Delta H_8 - T\Delta S_8 \)

At 100°C and with \( \Delta S_8 = 28 \text{ cal/deg mole} \) and \( \phi = 0.4 \)

\[ \Delta H_8 = (1.978) (373) \ln 0.6 + (373) (28) = +10.1 \text{ kcal/mole} \]

\[ \Delta G_8 = \Delta H_8 - T\Delta S_8 = -0.38 \text{ kcal/mole} \]

7. It may be shown from (9) that the weight fraction of polymer chains is

\[ \phi = 1 - e^{\frac{\Delta S_8}{R} - \frac{\Delta H_8}{RT}} \]

which upon substitution of the values given for \( \Delta S_8 \) and \( \Delta H_8 \) becomes

\[ \phi = 1 - e^{10.57 e^{\frac{3523}{T}}} \]

(a) A plot of \( \Phi \) as a function of \( T \) is given in Figure 10.1.

(b) At the ceiling temperature, \( \Delta G_8 = 0 \) or \( T_c = \frac{\Delta H_8}{\Delta S_8} \).

Hence \( T_c = \frac{-7000}{-21} = 333^\circ K \)
Figure 10.1

(c) 0.95 = 1 - e^{10.37e^{3523/T}}

Hence T = 260°C

(d) The assumptions are those described in the Gee treatment given in the chapter.

8. From the expressions derived on p.230 for P and \([M_o]\), it is easy to show

\[
K = \frac{[M_o] - [M]}{[M][P]^2}
\]

\[
K_o = \frac{P - 1}{[M][P]} = \frac{1}{[M]}
\]
Using these expressions and the data given, we find the following:

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>K</th>
<th>K₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>267</td>
<td>1.14×10⁻⁸</td>
<td>0.549kg/mole</td>
</tr>
<tr>
<td>167</td>
<td>8.24×10⁻¹²</td>
<td>0.257kg/mole</td>
</tr>
</tbody>
</table>

(a) The equations for the temperature dependence of lnK and lnK₃ given on p.231 can be rearranged to

\[ \Delta H^\circ = \frac{R(T_2)(T_1)}{T_2 - T_1} \ln \frac{(K)_{T_2}}{(K)_{T_1}} \]

Hence

\[ \Delta H^\circ = \frac{(1.987)(540)(440)}{100} \ln \frac{1.14 \times 10^{-8}}{8.24 \times 10^{-12}} = 34.1 \text{ kcal/mole} \]

\[ \Delta H^\circ = \frac{(1.987)(540)(440)}{100} \ln \frac{0.549}{0.275} = 3.26 \text{ kcal/mole} \]

Then \( \Delta S^\circ / R = \ln K + \frac{\Delta H^\circ}{RT} \) and \( \Delta S^\circ / R = \ln K_3 + \frac{\Delta H^\circ}{RT} \)

Using \( \Delta H \) values and data at 267°C, and we obtain

\[ \Delta S^\circ = 26.8 \text{ cal/mole-deg} \]
\[ \Delta S^\circ = 4.85 \text{ cal/mole-deg} \]

(b) Using the values of \( \Delta H^\circ, \Delta H_3^\circ, \Delta S^\circ \) and \( \Delta S_3^\circ \) we may write the Van't Hoff equations as

16
\[
\ln K = 13.5 - \frac{1.72 \times 10^4}{T}
\]

\[
\ln K_3 = 2.44 - \frac{1.64 \times 10^3}{T}
\]

and plots are shown in Figure 10.2

![Figure 10.2](image)

Figure 10.2

(c) From the expressions for \(K\) and \(K_3\) in (b)

\[
K = 1.18 \times 10^{-10}
\]

\[
K_3 = 0.358
\]

and 200°C. It was shown earlier in this problem that for long chains

\[
K_3 = \frac{1 + KP^2}{[M_o]}
\]
Thus

\[ P = \sqrt{\frac{[M_a]K_1 - 1}{K}} \]

and hence at 200°C, \( P = 5.79 \times 10^4 \)

\[ [M] = \frac{[M_a]}{1 + KP^2} = 2.79 \text{ moles/kg} \]
CHAPTER 11

1. \( M_w = \frac{\sum w_i M_i}{\sum w_i} = \sum W_i M_i = 83,300 \text{ grams/mole} \)

\( M_a = \frac{\sum n_i M_i}{\sum n_i} = \sum X_i M_i = 57,100 \text{ grams/mole} \)

where \( W_i = \) weight fraction of polymer of molecular weight \( M_i \)

\[ = \frac{w_i}{\sum w_i} \]

and \( X_i = \) mole fraction of polymer of molecular weight \( M_i \)

\[ = \frac{n_i}{\sum n_i} = \frac{(w_i/M_i)}{\sum (w_i/M_i)} \]

2. Assume that the molecular weight of each fraction is the mid-point of the specified range of \( M \). Then, as in Problem 1,

\( M_w = \sum W_i M_i = 137,400 \text{ grams/mole} \)

\( M_a = \sum X_i M_i = 108,600 \text{ grams/mole} \)
3. (a) \( \overline{M_w} = M_o \left( \frac{1+P}{1-P} \right) \)

Solving for \( P \) with \( M_o = 100 \) one obtains \( P = 0.989 \)

(b) \( \overline{M_n} = \frac{\overline{M_w}}{1+P} = \frac{18,400}{1,989} = 9,250 \text{ grams/mole} \)

(c) \( \overline{N_{su}} = \frac{\overline{M_n}}{M_o} = 92.5 \)

(d) The probability of exactly twice the average number of structural units is

\[ \text{Prob}(2\overline{N_{su}}) = P^{2\overline{N_{su}}-1} (1-P) \]

or

\[ \text{Prob}(185) = (0.989)^{184} (1-0.989) = 1.44 \times 10^{-3} \]

4. The structural unit and repeating unit of this polymer is

\[ \overline{\text{NH-CH}_2\left(\text{CH}_2\right)_4\text{CH}_2\text{O}} \]

with a molecular weight of \( M_o = 127 \text{ a.m.u.} \) The molecular weight of the polymer is 12,718 g/mole so

\[ M = nM_o + 18 = 12,718 \text{ g/mole} \]

and \( n = 100 \)
(a) The reaction is

$$100 \ H_2N\left(\text{CH}_2\right)_6\text{COOH} \rightarrow 100 \ H\left[\text{NH}\left(\text{CH}_2\right)_6\text{C}^+\text{OH} + 99 \ H_2O$$

(b) From the Arrhenius equation for a rate constant, \(k = A e^{-\frac{E}{RT}}\) we may write for the ratio of rate constants at two temperatures,

$$\frac{k(T_1)}{k(T_2)} = e^{\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Solving for \(E\) and using the values of \(k\) at the two given temperatures one obtains

\(E = 34.6\) kcal/mole

On substitution of \(E\) into the Arrhenius equation, \(A\) may be evaluated, the result is

\(A = 7.55 \times 10^{14}\) kg/mole-min

To the proper number of significant figures:

\(E = 35\) kcal/mole

\(A = 7.6 \times 10^{14}\) kg/mole-min

(c) \(\overline{M_a} = \frac{M_a}{1-P} + 18\)

Solving for \(P\), one obtains \(P = 0.970\) or a conversion of 97.0 %.
(d) \[ \overline{M_\infty} = M_0 \left( \frac{1+P}{1-P} \right) \]

from which \( P = 0.989 \) or a conversion of 98.9%.

5. (a) The second order rate equation gives

\[ \frac{1}{1-P} = \frac{\overline{DP}}{1+\kappa_2 [\text{COOH}]} t = 1+9.04 \times 10^2 t \] where \( t \) is in minutes.

If caproic acid was present at a level of 0.65% in the amino acid, then, for 1 mole total, we have 1 mole of COOH and 0.9935 moles of NH\(_2\) groups. NH\(_2\) groups are limiting so we define \( P \) as the fraction of NH\(_2\) groups reacted. Then \( rP \) is the fraction of COOH groups reacted, where

\[ r = \frac{N_{\text{NH}_2}}{N_{\text{COOH}}} = 0.9935 \]

According to (59)

\[ \frac{\overline{DP}}{2r(1-P)+1-r} \quad \text{or} \quad \frac{1}{1-P} = \frac{2\overline{DP}}{1+\kappa_2 [\text{NH}_2]} = 1+\kappa_2 [\text{NH}_2] t \]

Solving for \( \overline{DP} \) we obtain

\[ \overline{DP} = \frac{1+k_2 [\text{NH}_2] t}{1+\left( \frac{1-r}{1+r} \right) k_2 [\text{NH}_2] t} = 1+8.98 \times 10^2 t \]

where \( t \) is in minutes.
(b) For the case in which \([\text{COOH}]_0 = [\text{NH}_2]_0\), i.e. no caproic acid present.

\[ \overline{M}_n = M_0 (1+k_2 [\text{COOH}]_0 t) = 6340 \]

Substituting \(M_0 = 127\) amu, \(k_2 = 2.74 \times 10^{-2}\) kg/mole-min, and \([\text{COOH}]_0 = 3.3\) moles/liter, we get:

\[ t = 541\] minutes

(c) \(M = 12.718\) g/mole. As shown in Problem 4a, this corresponds to \(\overline{DP} = x = 100\) for this monomer. For the time corresponding to Problem 5b, a polymer of

\[ \overline{M}_n = \frac{M_0}{1-P} + 18 = \frac{6322}{1-P} + 18 \]

Hence \(1-P = 2.009 \times 10^{-2}\)

and \(P = 0.9799\)

The weight fraction of polymer with this value of DP is according to eqn. (44)

\[ w_{100} = 100(2.009 \times 10^{-2})^2 (0.9799)^{100} = 5.41 \times 10^{-3} \]

Since we have a kg of solution, the weight of this polymer is

\[ w_{100} = 1000 \times 5.41 \times 10^{-3} = 5.41\] grams

6. (a) For the uncatalyzed reaction
\[
\left( \frac{1}{1-P} \right)^2 = 1 + 2k_3 [\text{COOH}]_0 t \\
(1-P) = \left( \frac{1}{1 + 2k_3 [\text{COOH}]_0 t} \right)^{1/2} \\
P = \frac{(1 + 2k_3 [\text{COOH}]_0^2 t)^{1/2} - 1}{(1 + 2k_3 [\text{COOH}]_0^2 t)^{1/2}}
\]

Then from eqn. (38), the mole fraction of x-mer is

\[
X_x = \frac{1}{(1 + 2k_3 [\text{COOH}]_0 t)^{1/2}} \left[ \frac{(1 + 2k_3 [\text{COOH}]_0^2 t)^{1/2} - 1}{(1 + 2k_3 [\text{COOH}]_0^2 t)^{1/2}} \right]^{x-1}
\]

(b) For the catalyzed reaction

\[
\frac{1}{1-P} = 1 + k_2 [\text{COOH}]_0 t \\
\text{so} \quad 1-P = \frac{1}{1 + k_2 [\text{COOH}]_0 t} \\
P = \frac{k_2 [\text{COOH}]_0 t}{1 + k_2 [\text{COOH}]_0 t}
\]

and the mole fraction of x-mer is

\[
X_x = \frac{(k_2 [\text{COOH}]_0 t)^{x-1}}{(1 + k_2 [\text{COOH}]_0 t)^x}
\]
In plotting these mole fractions as a function of time, we are interested only in the shapes.

Hence, let

\[ k_2 [\text{COOH}]_0 = 1 \]

\[ 2k_3 [\text{COOH}]_0^2 = 1 \]

and our functions for plotting are then

(a) Uncatalyzed: \( X = \left( \frac{1}{1+t} \right)^{1/2} \left[ \frac{(1+t)^{1/2} - 1}{(1+t)^{1/2}} \right]^{1/2} \)

(b) Catalyzed: \( X = \frac{t^{x-1}}{(1+t)^{x-1}} \left( \frac{1}{1+t} \right) \)

Plots of these two mole fractions versus \( t \) for \( x = 10 \) and \( x = 100 \) are shown on the next page in Figure 11.1.
Figure 11.1
7. This is a further polymerization of an initial equal molar mixture of

$$\text{HO-} \left( \frac{\text{CH}_2}{10} \right) \text{OH} + \text{HOOC-} \left( \frac{\text{CH}_2}{4} \right) \text{COOH}$$

where $t = 0$ corresponds to 82% esterification of the original COOH groups (see Figure 11.2 in the text) and $[\text{COOH}]_0 = 0 = 1.25$ equiv/kg.

For the uncatalyzed reaction we plot $\left( \frac{1}{1-P} \right)^2$, where $P = \frac{\text{% reaction}}{100}$, versus $t$ and for the catalyzed polyesterification we plot $\frac{1}{1-P}$ versus $t$. These plots are shown in the following figures, 11.2 and 11.3.

(a) At $190^\circ\text{C}$. Slope $= 3.93 \times 10^2 \text{min}^{-1} = 2k_3 [\text{COOH}]_0^2$

$k_3 = 1.26 \times 10^2 \text{ kg}^2/\text{equiv-min}$

At $161^\circ\text{C}$. Slope $= 1.39 \times 10^2 \text{min}^{-1} = 2k_3 [\text{COOH}]_0^2$

$k_3 = 4.45 \times 10^3 \text{ kg}^2/\text{equiv-min}$

$$\frac{k(463 \text{K})}{k(434 \text{K})} = e^{\frac{E}{R \left( \frac{1}{463} - \frac{1}{434} \right)}} = 2.82$$

From which $E = 14.3$ kcal/mole

(b) Slope $= 0.121 = k_2 [\text{COOH}]_0$

$$k_2 = 9.71 \times 10^2 \text{ kg/equiv-min}$$

27
8. Combination of Equation (28) with (38) and (44) gives for the two distributions

\[ X_t = \left( \frac{k_2 [\text{COOH}]_0}{1 + k_2 [\text{COOH}]_0 t} \right)^{x-1} \left( \frac{1}{1 + k_2 [\text{COOH}]_0 t} \right) \]

\[ W_t = \left( \frac{x}{(1 + k_2 [\text{COOH}]_0 t)^{x-1}} \right) \left( \frac{k_2 [\text{COOH}]_0 t}{1 + k_2 [\text{COOH}]_0 t} \right)^{x-1} \]

Using the values of \( k = 9.71 \times 10^2 \) kg/equiv-min and \([\text{COOH}]_0 = 1.25\text{equiv/kg}\) from Problem 7, these distributions at \( t = 120 \text{ min} \) and 240 minutes are plotted in Figure 11.4.
Figure 11.4

9. Because of the impurity, \([\text{COOH}]_0 = 0.9915 \ [\text{OH}]_o\) so

\[
r = \frac{[\text{COOH}]}{[\text{OH}]_o} = 0.9915
\]

\[
(\overline{DP})_{\text{max}} = \frac{1+r}{1-r} \frac{1.9915}{0.0085} = 234
\]

\[
(\overline{M}_n)_{\text{max}} = 234M_n + 18 = 234(142) + 18 = 33,246
\]
\[ \left( \bar{M}_w \right)_{\text{max}} = \left( \bar{M}_n \right)_{\text{max}} (1+P)_{\text{max}} = 2 \left( \bar{M}_n \right)_{\text{max}} = 66,492 \]

10. (a) Plots according to 2\textsuperscript{nd} order and 3\textsuperscript{rd} order kinetics are made in the figures 11.6 and 11.7. From the figures, it is clear that the reaction is 3\textsuperscript{rd} order, since a straight-line relationship is obtained (P ≥ 80) when \( \left( \frac{1}{1-P} \right)^2 \) is plotted versus time.

(b) The slope of the straight line in the third-order plot is

\[ \lambda = \frac{278-50}{1300-300} = 0.228 \text{ min}^{-1} \]

0.228 \text{ min}^{-1} = 2k_3 [\text{COOH}]_0^2

and

\[ k_3 = \frac{0.228 \text{ min}^{-1}}{2[\text{COOH}]_0^2} \]

\( \text{M (adipic acid)} = 146 \text{ g/mole} \)

\( \text{M (ethylene glycol)} = 62 \text{ g/mole} \)

Therefore, in a 1:1 mixture that weighs 1 kg we have

\[ n = \frac{1000 \text{ g}}{208 \text{ g/mole}} = 4.81 \text{ moles of acid/kg.} \]
Then \[ [\text{COOH}]_0 = 9.62 \text{ equiv/kg} \]

and \[ k_3 = 0.00120 \text{ (kg/equiv)}^2 \text{-min}^{-1} \]

(c)

\[
\begin{align*}
\text{t = 270 min} & \quad \text{t = 1370 min} \\
P & = 0.8500 & P & = 0.9405 \\
1-P & = 0.1500 & 1-P & = 0.0595 \\
W_x & = (1-P)^2 x P^{x-1} & W_x & = (0.0035)(0.9405)^{x-1} x \\
W_x & = (0.0225)(0.85)^{x-1} x & W_x & = (0.0035)(0.9405)^{x-1} x
\end{align*}
\]

These functions are shown plotted in Figure 11.5.
Figure 11.6

According to the Carother's Equation \( P_e = \frac{2}{F_{Av}} \)

\[ F_{Av} = (0.40)(2) + (0.50)(2) + (0.10)(2) = 2.10 \]

Hence \( \bar{P}_{OH} = \frac{2}{2.10} = 0.952 \) = average conversion

\[ P_{OH} = \frac{20}{21} P_e = 0.907 \quad P_{\text{COOH}} = \frac{11}{10} P_{OH} = 0.998 \]

According to the Flory treatment
\[ \alpha_c = \frac{P^2_{COOH} p}{r - P^2_{COOH} (1 - p)} = \frac{1}{2} \]

where \( p = \frac{(0.1)(3)}{(0.4)(2) + (0.1)(3)} = \frac{3}{11} \)

\[ r = \frac{N_{OH}}{N_{COOH}} = \frac{(0.4)(2) + (0.1)(3)}{(0.5)(2)} = \frac{11}{10} \]

Substituting these values into expression for \( \alpha_c \) and solving for \( P^2_{COOH} \), one obtains

\[ P^2_{COOH} = 0.864 \]
\[ P_{COOH} = 0.930 \]
13. The (b) diol could add with either end first, and this would give an irregular spacing of the bulky —C(CH₃)₂— segments along the chains.
1. 

\[
\text{CH}_2=\text{CH-} \rightarrow \text{CH}_2=\text{CH-} \_{n}
\]

\( t = 60^\circ \text{C} \)

\( k_p = 176 \text{ liter/mole-sec} \)

\( k_i = 3.0 \times 10^6 \text{ liter/mole-sec} \)

\( n_i = 10^{-6} \text{ moles/liter-sec} \)

(a) \( r_i = r_i = 2k_i[R]^2 \)

\[
[R] = \left( \frac{r_i}{2k_i} \right)^{1/2} = \left( \frac{10^{-6}}{2(3 \times 10^6)} \right)^{1/2} = 4.1 \times 10^7 \text{ moles/liter}
\]

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

or \( \int \frac{d[R]}{r_i - 2k_i[R]^2} = \int dt = t + \text{Constant} \)

The integral to be evaluated is of the form \( \int \frac{dx}{a^2 - b^2x^2} \), where \( a^2 = r_i \) and \( b^2 = 2k_i \).

\( x = [R] \). Also, at the steady state: \( [R]_{\text{max}}^2 = \frac{r_i}{2k_i} \) so \( x_{\text{max}}^2 = \frac{a^2}{b^2} \) or \( b^2x^2 \leq a^2 \). For this case the integral (from tables) is: \( \frac{1}{ab} \tanh^{-1} \frac{bx}{a} \). Thus
\[
\frac{1}{ab} \tanh^{-1} \frac{bx}{a} = t + C.
\]

At \( t = 0 \), \( [R] = 0 = x \) or \( C = 0 \)

Then \( \tanh^{-1} \frac{bx}{a} = abt \)

\[
x = \frac{a}{b} \tanh abt
\]

or in terms of the original variables,

\[
[R] = \left( \frac{s}{2k_i} \right)^{1/2} \tanh \left( 2k_i r_i \right)^{1/2} t
\]

or \( [R] = [R]_a \tanh \left( 2k_i r_i \right)^{1/2} t \)

An equivalent form is

\[
[R] = [R]_a \frac{1 - e^{-\left(4k_i r_i\right)^2 t}}{1 + e^{-\left(4k_i r_i\right)^2 t}}
\]

Thus, \( \frac{[R]}{[R]_a} = \tanh \left( 2k_i r_i \right)^{1/2} t = \frac{1 - e^{-\left(4k_i r_i\right)^2 t}}{1 + e^{-\left(4k_i r_i\right)^2 t}} \)

And a plot of this is shown in Figure 12.1.

(c) \( [M] = 5 \) moles/liter

\[
r_p = \frac{d[M]}{dt} = k_p [M][R]
\]
Assume $[R]$ is constant at $[R]_{ss}$. Then

$$\frac{[R]}{[R]_{ss}}$$

\[ \text{Time (sec)} \]

For $[R]/[R]_{ss} = 0.95$

\[ t = 1.06 \text{ sec} \]

Figure 12.1

$$\int \frac{d[M]}{[M]} = \int k_p [R] dt$$

$$\ln [M] = -k_p [R] t + C$$

$$t = 0 \quad \begin{cases} \text{So, } \ln [M]_0 = C \end{cases}$$

$$[M] = [M]_0$$

and

$$\frac{[M]}{[M]_0} = e^{-k_p t}$$

For 20% polymerization, $[M]/[M]_0 = 0.8$
\[ \ln 0.8 = -k_p [R] t \]

\[ t = -\frac{\ln 0.8}{k_p [R]} = -\frac{\ln 0.8}{(176)(4.1\times10^{-7})} = 3.1\times10^3 \text{ seconds} = 52 \text{ minutes} \]

(d) Denoting steady-state by subscript ss, we define \( a \) as

\[ a = \left( \ln \frac{[M]_s}{[M]} \right)_{ss} = k_p [R]_{ss} t \]

The exact rate equation (not assuming steady-state) is

\[ \frac{d[M]}{dt} = k_p [M][R] = k_p [M][R] \tanh (2k_r t)^{1/2t} \]

or \[ -\int \frac{d[M]}{[M]} = k_p [R] \int \tanh (2k_r t)^{1/2t} \]

integration from table of integrals gives

\[ \left( \ln \frac{[M]_s}{[M]} \right)_{\text{exact}} = \frac{k_p [R]}{(2k_r t_i)^{1/2}} \ln \cosh(2k_r t_i)^{1/2} \]

where \( \cosh x = (1/2)(e^x + e^{-x}) \). Define \( \beta \) as

\[ \beta = \left( \ln \frac{[M]_s}{[M]} \right)_{\text{exact}} = \frac{k_p [R]}{(2k_r t_i)^{1/2}} \ln \frac{e^{(2k_r t_i)^{1/2}} - e^{-(2k_r t_i)^{1/2}}}{2} \]

38
Consider the ratio \( \frac{\beta}{\alpha} = \left( \frac{\ln \left[ \frac{[M]}{[M]_0} \right]}{\ln \left[ \frac{[M]}{[M]_0} \right]_{ss}} \right) = \left( \frac{1}{2k_i r_i} \right)^{1/2} \frac{1}{t} \ln \left( \frac{e^{(2k_i r_i)^{1/2} t} - e^{-(2k_i r_i)^{1/2} t}}{2} \right) \)

These ratios show the error in \( \ln \left[ \frac{[M]}{[M]_0} \right] \) as calculated by the steady-state assumption.

The error in \( \frac{[M]}{[M]_0} \) is given by \( e^{\frac{[M]}{[M]_0}} \Delta \left( \ln \frac{[M]}{[M]_0} \right) \). The % error in \([M]/[M]_0\) so calculated is shown as a function of log % conversion of monomer in Figure 12.2. According to this figure, when we deal with the kinetics of free-radical polymerization for conversion above 1 %, the error associated with use of the steady-state approximation is less than 0.5%.

Figure 12.2
2. (a) Eqn. 35 states

\[
\frac{r_p}{[I]^{1/2}} = \left(2kf_i\right)^{1/2} \left(\frac{k_p^2}{2k_i}\right)^{1/2} [M]
\]

Thus a plot of \(r_p/[I]^{1/2}\) versus \([M]\) will be a straight line if the rate law is obeyed. Alternatively, we may calculate the ratios \(r_p/[I]^{1/2}[M]\) and see if it is constant for all conditions. The value so calculated are:

<table>
<thead>
<tr>
<th>[M]</th>
<th>(r_p/[I]^{1/2} [M] \times 10^2)</th>
<th>[M]</th>
<th>(r_p/[I]^{1/2} [M] \times 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.04</td>
<td>8.38</td>
<td>4.75</td>
<td>8.54</td>
</tr>
<tr>
<td>8.63</td>
<td>8.23</td>
<td>4.22</td>
<td>8.13</td>
</tr>
<tr>
<td>7.19</td>
<td>8.64</td>
<td>4.17</td>
<td>7.77</td>
</tr>
<tr>
<td>6.13</td>
<td>8.37</td>
<td>3.27</td>
<td>8.41</td>
</tr>
<tr>
<td>4.96</td>
<td>8.13</td>
<td>2.07</td>
<td>8.28</td>
</tr>
</tbody>
</table>

Average = 8.23±0.27×10^{-2} liter\(^{1/2}\)/moles\(^{1/2}\)-min

= 1.37±0.04×10^{-3} liter\(^{1/2}\)/moles\(^{1/2}\)-sec

There is no trend in data. Hence the rate law is in accord with the data.

(b) According to (35)

\[
\left(2kf_i\right)^{1/2} \left(\frac{k_p^2}{2k_i}\right)^{1/2} = 1.37\times10^{-3}
\]
\[
\left( \frac{k_p^2}{2k_i} \right)^{1/2} = \frac{1.37 \times 10^{-3}}{(2fk_i)^{1/2}} = \frac{1.37 \times 10^{-3}}{2 \times 10^{15.2} e^{1.587x330}}^{1/2} = 0.803
\]

3. \[ r_p = (2fk_i)^{1/2} \left( \frac{k_p}{2k_i} \right)^{1/2} [I]^{1/2} [M] \]

In these experiments, \([I]\) = a constant = 0.0413 M. Hence, \(\frac{r_p}{[M]}\) is a constant at each temperature if (35) is obeyed. Expressing the data in this way yields:

<table>
<thead>
<tr>
<th>[M]</th>
<th>(\frac{r_p}{[M]}(50^\circ))</th>
<th>(\frac{r_p}{[M]}(70^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.944</td>
<td>1.62 \times 10^{-5}</td>
<td>8.69 \times 10^{-5}</td>
</tr>
<tr>
<td>1.89</td>
<td>1.77 \times 10^{-5}</td>
<td>9.84 \times 10^{-5}</td>
</tr>
<tr>
<td>3.78</td>
<td>1.78 \times 10^{-5}</td>
<td>10.16 \times 10^{-5}</td>
</tr>
<tr>
<td>5.66</td>
<td>1.72 \times 10^{-5}</td>
<td>10.00 \times 10^{-5}</td>
</tr>
</tbody>
</table>

Both columns of \(r_p / [M]\) appear sensibly constant and we conclude that (35) is obeyed. The average values, with standard deviations are:

\[
\left( \frac{r_p}{[M]} \right)_{50^\circ} = 1.72 \times 0.06 \times 10^{-5} \text{ sec}^{-1}
\]

\[
\left( \frac{r_p}{[M]} \right)_{70^\circ} = 9.67 \times 0.58 \times 10^{-5} \text{ sec}^{-1}
\]

(b) According to (35)
\[
\frac{r_p}{[M]} = (2fk_i[I])^{1/2} \left( \frac{k_p^{1/2}}{2k_i} \right) = (f[I])^{1/2} \left( \frac{k_p^{1/2}k_i}{k_i} \right)
\]

\[
\ln \frac{r_p}{[M]} = \ln (f[I])^{1/2} + \ln \left( \frac{k_p^{1/2}k_i}{k_i} \right)
\]

\[
\ln (f[I])^{1/2} + \ln \frac{A_pA_i^{1/2}}{A_i^{1/2}} \cdot \left( \frac{E_p - \frac{1}{2}E_i + \frac{1}{2}E_i}{RT} \right)
\]

So

\[
\ln \left( \frac{r_p/[M]_{60^\circ}}{r_p/[M]_{90^\circ}} \right) = \left( \frac{E_p - \frac{1}{2}E_i + \frac{1}{2}E_i}{R} \right) \left[ \frac{1}{323} - \frac{1}{343} \right]
\]

or

\[E_p \cdot \frac{1}{2}E_i + \frac{1}{2}E_i = 19,000 \text{ cal/mole}\]

(c) From Table 12.2 in the text: \[E_p - \frac{1}{2}E_i = 4900 \text{ cal/mole}\]

Therefore, \(E_i = 28,200 \text{ cal/mole}\)

(d) \[\overline{DP} = 2v \left( \frac{1 + \frac{k_m}{k_i}}{1 + \frac{2k_m}{k_i}} \right) \text{ and } v = \frac{r_z}{r_i} = \left( \frac{k_p^{1/2}}{2k_i} \right)^{1/2} \frac{[M]}{r_i^{1/2}}\]
so $\overline{\text{DP}} = \left( \frac{k_p^2}{k_i k_i} \right)^{1/2} \left( 1 + \frac{k_m}{k_{ic}} \right) \left( \frac{1}{1 + \frac{2}{k_{ic}}} \right) \left( \frac{1}{f[I]} \right)^{1/2} [M]$.

The above expression predicts that $\overline{\text{DP}}$ should increase linearly with [M]. As shown in Figure 12.3, a plot of $\overline{\text{DP}}$ versus [M] is not quite linear in [M]. $\overline{\text{DP}}$ appears to increase with [M] to a positive power less than unity. The reason is most likely that f depends weakly on [M]. We may write the expression for $\overline{\text{DP}}$ as

$$\ln \overline{\text{DP}} = \ln \text{Constant} - \frac{E_p - \frac{1}{2} E_i - \frac{1}{2} E_i}{RT} = \ln \text{Constant} + \frac{9200}{RT}$$

Differentiating,

$$\frac{d \ln \overline{\text{DP}}}{dT} = -\frac{9200}{RT^2}$$

Since T and R are always positive numbers, the derivative is negative, which means that $\overline{\text{DP}}$ decreases as T increases.

Figure 12.3
4. The distribution function for propagating radicals is

\[ f_n = \frac{1}{v} \left( 1 + \frac{1}{v} \right)^n = \frac{[R_n]}{[R]} \]

The mole fraction of polymer molecules of \( \overline{DP} = n \) is

\[ X_{n,d} = \frac{\frac{d[P_n]}{dt}}{\sum_n \frac{d[P_n]}{dt}} = \frac{\frac{d[P_n]}{dt}}{\frac{d[P]}{dt}} \]

where

\[ \frac{d[P_n]}{dt} = 2k_{id} [R]^2 \]

to evaluate \( \frac{d[P_n]}{dt} \) we write down and sum the rates of all the ways that \( P_n \) can be formed.

Thus

\[ R_1 + R_n \rightarrow P_1 + P_n \]
\[ R_1 + R_n \rightarrow P_1 + P_n \]

\[ . . . . . . . \]
\[ R_m + R_n \rightarrow P_m + P_n \]

\[ \frac{d[P_n]}{dt} = \sum_{m=1}^{n} 2k_{id} [R_n][R_m] = 2k_{id} [R_n][R] = 2k_{id} f_n [R]^2 \]

\[ X_{n,d} = \frac{2k_{id} f_n [R]^2}{2k_{id} [R]^2} \]
and hence,

\[ X_{n,d} = f_n = \frac{1}{v} \left( 1 + \frac{1}{v} \right)^n \]

5. It was shown in this chapter, Eq. 67 and 69, that the number distributions corresponding to termination by combination \((k_{td} = 0)\) and to termination by disproportionation \((k_{tc} = 0)\) are:

\[ X_{n,c} = \frac{n-1}{v^2} \left( 1 + \frac{1}{v} \right)^n \]

\[ X_{n,ad} = \frac{1}{v} \left( 1 + \frac{1}{v} \right)^n \]

As discussed in the text and in Problem 8, the weight fraction is related to the number fraction or mole fraction by

\[ W_n = \frac{n}{DP} X_n \]

With \(k_{td} = 0\), \(DP = 2v\) and with \(k_{tc} = 0\), \(DP = v\). Hence,

\[ W_{nc} = \frac{n(n-1)}{2v^3} \left( 1 + \frac{1}{v} \right)^n \]

\[ W_{nad} = \frac{n}{v^2} \left( 1 + \frac{1}{v} \right)^n \]

Plots of these functions are shown in Figures 12.4 and 12.5 for \(v = 500\).
6. The chain transfer steps

\[ R_2 + X \xrightarrow{k_t} P_n + X^* \]

\[ X^* + M \xrightarrow{} R_1 \]

are added to the mechanism of free radical polymerization given early in the chapter (p. 272) and the derivation proceeds analogously to that leading to eq. 67. Thus

\[
\frac{d[R_n]}{dt} = k_p [M][R_{n-1}] - k_p [M][R_n] - k_{s} [X][R_n] - 2k_s [R_n][R] = 0
\]
From which,

\[
\frac{[R_{n}]}{[R_{n-1}]} = \frac{k_p [M]}{k_p [M] + k_s [X] + 2k_i [R]} = \frac{1}{1 + \frac{k_s [X]}{k_p [M]} + \frac{2k_i [R]}{k_p [M]}}
\]

Let the chain transfer term be represented by \( \gamma \), i.e.,

\[
k_s [X] \frac{k_M}{k_p [M]} + k_s [Y] \frac{1}{k_p [M]} + \ldots = \gamma
\]

and as before,

\[
\frac{1}{v} = \frac{2k_i [R]}{k_p [M]}
\]

Then by the same procedure as shown in the text for derivation of (67)

\[
\frac{[R_{n}]}{[R_1]} = \left( 1 + \frac{1}{\gamma} + \gamma \right)^{1-a}
\]

and \( f_s = \frac{[R_{n}]}{[R]} = \frac{[R_1]}{[R]} \left( 1 + \frac{1}{\gamma} + \gamma \right)^{1-a} \)

Writing the steady state expressions for \( R_1 \) and \( R \)

\[
\frac{d[R_1]}{dt} = r_i - 2k_i [R]^2 = 0
\]
\[
\frac{d[R_i]}{dt} = r_i + k_x [X] [R] - k_p [M] [R_i] - k_s [X] [R_i] - 2k_i [R_i] [R] = 0
\]

Elimination of \( r_i \) from these expressions gives

\[
\frac{[R_i]}{[R]} = \frac{2k_i [R] + k_x [X]}{k_p [M] + k_x [X] + 2k_i [R]} = \frac{2k_i [R] + k_x [X]}{k_p [M] + k_x [X] + 2k_i [R]}
\]

or

\[
\frac{[R_i]}{[R]} = \frac{1 + \gamma}{1 + \frac{1}{v} + \gamma} = \left(1 + \frac{1}{v} + \gamma\right)^{-1}
\]

Substitution of this expression into \( f_n \) gives the distribution function for \([R_n]\) as

\[
f_n = \left(\frac{1 + \gamma v}{v}\right)^n \left(1 + \frac{1}{v} + \gamma\right)^{-1}
\]

The rate of formation of polymer of DP = \( n \) is

\[
\frac{d[P_n]}{dt} = k_x [X] [R_n] + k_x \sum_{m=1}^{n-1} [R_{n-m}] [R_m]
\]

\[
= k_x [X] f_n [R] + k_x [R] \sum_{m=1}^{n-1} f_{n-m} f_m
\]

\[
\frac{d[P_n]}{dt} = k_x [R]^n \left(1 + \frac{1}{v}\right)^n \left(\frac{1 + \gamma v}{v}\right)^n + k_x [X] [R] \left(1 + \frac{1}{v} + \gamma\right)^{-1}
\]

48
\[
\left(\frac{1+\gamma v}{v}\right)\left(1+\frac{1}{v}+\gamma\right)^n \left[\left(n-1\right)\left(1+\gamma v\right)\frac{k_i}{v} [R]^2 + k_i [X][R]\right]
\]

\[X_n = \text{fraction of polymer with } DP = n \quad \text{or} \]

\[
X_n = \frac{\frac{d[P_i]}{dt}}{\frac{d[P]}{dt}}
\]

and

\[
\frac{DP}{d[P]} \frac{r_p}{d[P]} = \frac{k_p [M][R]}{k_s [X] + k_i [R]}
\]

so that in view of eq. (73), namely,

\[
\frac{DP}{d[P]} = \frac{k_p [M]}{k_s [X] + k_i [R]} = \frac{1}{k_s [X] + k_i [R]} \left(\frac{1}{\frac{1}{\gamma} + \frac{1}{2v}}\right)
\]

we find

\[
\frac{d[P]}{dt} = \frac{k_p [M][R]}{DP} = k_p [M][R] \left(\frac{1+2\gamma v}{2v}\right)
\]

substituting

\[
X_n = \left(\frac{1+\gamma v}{v}\right)\left(1+\frac{1}{v}+\gamma\right)^n \left[\left(n-1\right)\left(1+\gamma v\right)\frac{k_i}{v} [R]^2 + k_i [X][R]\right]
\]

which upon rearrangement gives
\[ X_n = \left( \frac{1+\gamma u}{1+2\gamma u} \right)^n \left( \frac{1+\gamma u}{1+\gamma u} \right)^n \left[ \frac{(n-1)(1+\gamma u)}{u^2} + 2\gamma \right] \]

7. As shown in Problem 6

\[ f_n = \frac{[R_n]}{[R]} = \left( \frac{1+\gamma u}{u} \right)^n \left( \frac{1+\gamma u}{u} + \gamma \right)^n \]

The rate of formation of \( P_n \) when only disproportionation occurs, i.e. \( k_c = 0 \), is

\[ \frac{d[P_n]}{dt} = 2k_i [R_n][T] + k_x [X][R_n] \]

\[ = f_n \left( 2k_i [R]^2 + k_x [X][R] \right) \]

The number fraction with DP = n is

\[ X_n = \frac{d[P_n]}{dt} \quad \text{and} \quad \frac{d[P]}{dt} = \frac{r_p}{DP} = \frac{k_p [M][R]}{DP} \]

According to eqn (73) when \( k_c = 0 \),

\[ \frac{1}{k_i [X] + 2k_i [R]} = \frac{k_i [X] + 2k_i [R]}{k_p [M] + k_p [M]} \]

or

\[ \frac{1}{\gamma + 1/\nu} = \frac{\nu}{1+\gamma u} \]
and \[ \frac{d[P]}{dt} = k_p [M][R]\left(\frac{1+\gamma v}{v}\right) \]

Substituting into \( X_n \)

\[ X_n = f_n \left( \frac{2k_i [R]}{k_p [M]} \frac{v}{1+\gamma v} + \frac{k_s [X]}{k_p [M]} \cdot \frac{v}{1+\gamma v} \right) \]

\[ X_n = f_n \left( \frac{1}{v} \cdot \frac{v}{1+\gamma v} + \frac{\gamma v}{1+\gamma v} \right) = f_n \left( \frac{1}{1+\gamma v} + \frac{\gamma v}{1+\gamma v} \right) \]

\[ X_n = f_n = \left( \frac{1+\gamma v}{v} \right) \left( 1+\frac{1}{v} + \gamma \right)^n \]

8. According to the definition of weight fraction, \( W_n \),

\[ W_n = \frac{w_n}{\sum w_n} \]

where \( w_n \) is the weight of polymer molecules which contain \( n \)-monomer molecules. Thus

\[ w_n = N_n M_n \]

where \( N_n \) is the number of polymer molecules containing \( n \) monomers and \( M_n \) is the molecular weight of the polymer containing \( n \) monomers. If \( M_o \) is the molecular weight of the monomer

\[ M_n = nM_o \]
and, hence,

\[ W_n = \frac{N_n nM_o}{\sum_n N_n nM_o} = \frac{nN_n}{\sum_n nN_n} \]

The mole fraction \( X_n \) is defined by

\[ X_n = \frac{N_n}{\sum_n N_n} \]

so that \( N_n = X_n \sum_n N_n \)

Substituting,

\[ W_n = \frac{n \sum_n N_n}{\sum_n nN_n} X_n \]

by the definition of an arithmetic average, \( \bar{n} = \frac{\sum nN_n}{\sum N_n} \) and therefore

\[ W_n = \frac{n}{\bar{n}} X_n = \frac{n}{DP} X_n \]

9. The solution of vinyl acetate in benzene contains 4 moles of vinyl acetate per liter of solution. If we assume the volumes are additive

\[ n_{VA} \overline{V_{VA}} + n_B \overline{V_B} = 1000 \text{ cm}^3 \]
where \( n_{VA} = 4 \) and \( \bar{V}^o \) is the molar volume of a pure component. From the Handbook of Chemistry, the densities of benzene and vinyl acetate may be taken as 0.87 and 0.93 g/cm\(^3\), respectively and the molecular weights are 78 and 86 g/mole, respectively. Then from the above expression

\[
n_B = \frac{1000 - 4 \left( \frac{86}{0.93} \right)}{\left( \frac{78}{0.87} \right)} = 7.0 \text{ moles/liter of solution} = [B]
\]

\[
\tau_i = 2f k_d [I] = (2)(0.75) \left( 3.0 \times 10^{13} e^{-\frac{29,600}{RT}} \right)(0.05)
\]

\( \tau_i = 8.39 \times 10^4 \text{ moles/liter-sec} \)

(a) \( \tau_p = \left( \frac{k_p^2}{2k_i} \right)^{1/2} [M]^n = (0.13)(4.0)(8.39 \times 10^4)^{1/2} \)

\[= 1.5 \times 10^{-4} \text{ moles/liter-sec} \]

(b) \( \nu = \tau_p / \tau_i = 1.5 \times 10^{-4} / 8.39 \times 10^4 = 1.8 \times 10^3 \)

(c) \( \left( \overline{DP} \right)^{-1} = \left( \overline{DP} \right)_o^{-1} + C \frac{[S]}{[VA]} \) where \([S] = \text{solvent concentration}\)

\[
\left( \overline{DP} \right)_o^{-1} = C_m + \frac{1}{\nu} = 2.5 \times 10^4 + (1.80 \times 10^{-3})^{-1} = 8.1 \times 10^4
\]
\[
(DP)^{1} = 8.1 \times 10^{4} + 2.2 \times 10^{4} \frac{(7.0)}{(4.0)} = 1.2 \times 10^{3}
\]

\[
DP = 8.4 \times 10^{2}
\]

(d) \[
X_n = f_n = \left( \frac{1 + \gamma u}{u} \right)^{\alpha} \left( 1 + \frac{1}{u} + \gamma \right)^{\gamma} = C_M + C_S \frac{[B]}{[VA]} = 2.5 \times 10^{4} + 2.2 \times 10^{-7} \frac{(7)}{(4)}
\]

\[
\gamma = 6.4 \times 10^{-4} \text{ and } u = 1.8 \times 10^{3}
\]

so

\[
X_n = 1.2 \times 10^{3} (1.0012)^{\gamma}
\]

A plot of this function is shown in Figure 12.6

![Figure 12.6](image_url)

(e) The mean lifetime of a species R, namely \( \bar{\tau}(R) \), at a steady state concentration \([R]\) is
\[ \tau(R) = \frac{[R]}{2k_i[R]^2} = \frac{1}{2k_i[R]} \]

\[ = \frac{1}{2k_i \left( \frac{t_i}{2k_i} \right)^{1/2}} = \left( \frac{1}{2k_i t_i} \right)^{1/2} \]

From table 12.4, \( k_i = 3.2 \times 10^7 \) liter/mole-sec, so

\[ \tau(R) = \left( \frac{1}{6.4 \times 10^7 \times 8.39 \times 10^{-8}} \right)^{1/2} = 0.43 \text{ sec} \]

\[ (f) \quad \tau(R_{15}) = \frac{[R_{15}]}{k_p [M][R_{15}] + k_m [M][R_{15}] + k_s [S][R_{15}] + 2k_i[R][R][R_{15}]} \]

Inspection of relative values of rate constants in Tables 12.3 and 12.4 shows that \( k_p [M] >> k_m [M] + k_s [S] + 2k_i [R] \)

Hence, \( \tau(R_{15}) = \frac{1}{k_p [M]} = \frac{1}{1.0 \times 10^3 \times 4.0} = 2.5 \times 10^4 \text{ sec} \)

10. (a) \( u = \left( \frac{k_p^2}{2k_i} \right)^{1/2} [M]^{1/2} \)

From data in Table 12.2, \( \left( \frac{k_p^2}{2k_i} \right)^{1/2} = 3.22 \times 10^{-3} \text{ (l/mole-sec)}^{1/2} \) at 0°C.
So

\[ t^I = 2.77 \times 10^3 \]

\[ t_i = 7.7 \times 10^{10} \text{ moles/liter-sec} \]

(b) From Chapter 3, Problem 6, \( \frac{k_{id}}{k_{ic}} = 2.39 \times 10^3 \exp \left( \frac{5847}{RT} \right) \)

\[
\left( \frac{k_{id}}{k_{ic}} \right)_{0^\circ C} = 0.0498
\]

Also \( C(T_2) = C(T_1) \exp \left( \frac{(E_v - E_x)}{RT} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right) \) and from the data in Table 12.3

\[ C_M(0^\circ C) = 4.4 \times 10^6 \]

\[ C_V(0^\circ C) = 1.75 \times 10^3 \]

Then

\[
\overline{DP}^{-1} = C_M + C_V \frac{[Y]}{[M]} + \frac{1}{2v} \left( \frac{1 + 2 \frac{k_{id}}{k_{ic}}}{1 + \frac{k_{id}}{k_{ic}}} \right) = 4.4 \times 10^4 + 1.75 \times 10^3 \left( \frac{0.1}{8.6} \right) + \frac{1}{1910}
\]

and \( \overline{DP} = 1.8 \times 10^1 \) If we had assumed 100% combination we would have obtained \( \overline{DP} = 1.9 \times 10^1 \).

(c) At 100°C,
\[ C_M = 2.2 \times 10^{-4} \]

\[ \left( \frac{k_p^2}{2k_1} \right)^{1/2} = 8.41 \times 10^{-2} \text{ (l/mole-sec)}^{1/2} \]

\[ C_Y = 7.46 \times 10^{-3} \]

\[ n = 2.61 \times 10^4 \]

and \[ DP = 3.1 \times 10^3 \]

If we assumed 100% combination, we would have obtained \[ DP = 3.0 \times 10^3 \]

11. A direct plot of the data results in an experimental differential distribution in which the data is much too scattered to be instructive. This may be smoothed out by plotting the integral distribution, drawing the best smooth curve between the points, and then differentiating the curve to obtain the differential distribution.

(a) First calculate the weight fractions and mole fractions for each value of DP. The integral distribution curves are then plotted as shown in figure 12.7. The derivatives are obtained by the relationships

\[ \frac{dy}{dx} = \frac{y_{i+1} - y_i}{x_{i+1} - x_i} \]
where the slope \( \frac{dy}{dx} \) is the slope at \( x = \frac{x_{i+1} + x_i}{2} \).

The values obtained are shown as points in figures 12.8 and 12.9.

(b) For the number distribution eq. (67) states

\[
x_s = \frac{n-1}{v^3} \left(1 + \frac{1}{v}\right)^s
\]

Integral Distribution Curves

\[
W_s = X_s \frac{n}{DP}
\]

If combination predominates \( DP = 2v \), so that

\[
W_s = \frac{n(n-1)}{2v^3} \left(1 + \frac{1}{v}\right)^s
\]
These theoretical distributions are superimposed on the experimental points in figures 12.8 and 12.9.

Figure 12.8
12. (a) $\gamma = \frac{1 + r_1 \left[ \text{vinyl acetate} \right]}{1 + r_2 \left[ \text{vinyl chloride} \right]}$ with $r_1$ and $r_2$ given in Table 12.5

$$\gamma = \frac{1 + 0.23 \frac{3.5}{1.5}}{1 + 1.68 \frac{1.5}{3.5}} = 0.893 = \frac{f_1}{1-f_1}$$

where $f_1 = \text{mole fraction of vinyl acetate in the copolymer.}$

Hence, $f_1 = 0.47$

$f_2 = 0.53$
(b) \[ m_{VA} = 1 + r_1 \frac{[VA]}{[VC]} = 1 + 0.23 \left( \frac{3.5}{1.5} \right) = 1.54 \]

\[ m_{VC} = 1 + r_2 \frac{[VC]}{[VA]} = 1 + 1.68 \left( \frac{1.5}{3.5} \right) = 1.72 \]

(c) \[ R = \frac{200}{m_1 + m_2} = 61 \]

(d) \[ P_{\text{M}_1} (8) = P_{11}^{m-1} P_{12} = P_{11}^{m-1} (1 - P_{11}) \]

\[ P_{11} = \frac{r_1 [M_1]}{r_1 [M_1] + [M_2]} = \frac{(0.23)(3.5)}{(0.23)(3.5) + 1.5} = 0.349 \]

\[ P_{\text{M}_1} (8) = (0.347)^7 (0.651) = 4.1 \times 10^{-4} \]

13. \[ r_1 = \frac{Q_1}{Q_2} e^{-\sigma_1 (e_1 - e_2)} \]

\[ r_2 = \frac{Q_2}{Q_1} e^{-\sigma_2 (e_2 - e_1)} \]

where the Q's and e's are given in Table 12.6.

<table>
<thead>
<tr>
<th></th>
<th>M_1</th>
<th>M_2</th>
<th>r_1</th>
<th>r_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Acrylonitrile</td>
<td>Butadiene</td>
<td></td>
<td>0.017</td>
<td>0.38</td>
</tr>
<tr>
<td>(b) Methyl Acrylate</td>
<td>Vinyl Chloride</td>
<td>7.5</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>
(c) Methyl Vinyl Ketone    p-Methoxystyrene    0.21    0.18
(d) Styrene                p-Methoxystyrene    0.94    0.96

14. Because of Coulombic attractions, it is much harder to separate two species of opposite charge than two uncharged species.

15. It is present in large amounts in typical polymerizations.

16. It is present in very small amounts in typical polymerizations.

17. No; see equation 80a.
1. (a) \[ [M] = [M]_0 e^{-\frac{1}{2} k_p [GA] t} \] since \([\text{anion}]_{\text{total}} = \frac{1}{2} [GA]_0\)

\[ k_p = \frac{2}{[GA]_0 t} \ln \frac{[M]}{[M]_0} = \frac{2}{(10^{-3})(3)} \ln \frac{0.2}{1.73 \times 10^{-3}} \]

\[ k_p = 1900 \text{ liter/mole-sec.} \]

(b) \( (r_p)_0 = \frac{1}{2} k_p [GA]_0 [M]_0 = \frac{1}{2} (1900)(10^{-3})(0.2) = 0.190 \text{ moles/liter-sec.} \)

(c) \[ [M] = [M]_0 e^{-\frac{1}{2} k_p [GA] t} \]

\[ -\frac{d[M]}{dt} = \frac{1}{2} k_p [GA]_0 [M]_0 e^{-\frac{1}{2} k_p [GA] t} \]

\[ = \frac{1}{2} (1900)(10^{-3})(0.2) e^{-\frac{1}{2} (1900)(10^{-3})(0.2)} \]

\[ -\frac{d[M]}{dt} = 1.42 \times 10^{-5} \text{ moles/liter-sec} \]

(d) For sodium naphthylene and styrene

\[ \overline{DP} = \frac{\text{no. of monomers reacted}}{\text{no. of dianions}} \]
\[ = 2 \frac{[M]_0}{[GA]_0} (1 - e^{-\frac{1}{2} \ln([GA])_0}) \]

\[
\overline{DP} = \frac{(2)(0.2)}{(10^3)} \left(1 - e^{-4.75}\right) = 4.0 \times 10^2
\]

\[ M_s = M_{styrene} \overline{DP} = (104)(4.0 \times 10^2) = 4.2 \times 10^4 \]

(e) For this reason, which proceeds from dianions (cf. p. 313), reaction (1b) on p. 311 is followed immediately by dimerization, i.e.

\[ 2\text{AM}^- \rightarrow (\text{AM}^-)_2 \]

so that \([\text{dianion}]_{\text{total}} = [\left((\text{AM}^-)_2\right)_0 = \frac{1}{2} [\text{GA}]_0 \]

The propagation reactions are

\[
(\text{AM}^-)_2 + M \rightarrow (\text{AM}^-)_2 M
\]

\[
(\text{AM}^-)_2 M + M \rightarrow (\text{AM}^-)_2 M_2
\]

etc.

If now the treatment on pp. 314-316 is applied to this mechanism, one obtains for the concentration and mole fraction of n-mers

\[
\left[ (\text{AM}^-)_2 M_{n-2} \right] = \frac{1}{2} [\text{GA}]_0 \frac{\nu n^2 e^{-\nu}}{(n-2)!}
\]

\[ X_n = \frac{\nu n^2 e^{-\nu}}{(n-2)!} \]
In these expressions the term n-2 arises because the first initiating dianion contains two monomer molecules. Defining the kinetic chain length in terms of the monomer reacted per dianion.

\[ v^- = 2 \frac{[M]_0}{[GA]_0} = 4.0 \times 10^2 \]

\[ X_n = \frac{400^{n-2} e^{-400}}{(n-2)!} = \frac{400^m e^{-400}}{m!} \quad \text{where } m = n-2 \]

According to Stirling's approximation for factorials:

\[ m! = (2\pi m)^{1/2} m^m e^{-m} \]

Substituting, taking logarithms and differentiating

\[ \frac{d\ln X_n}{dm} = \ln 400 - \frac{1}{2m} \ln m \]

At the maximum \( \frac{d\ln X_n}{dm} = 0 \) which gives

\[ m_{\text{max}} e^{2m_{\text{max}}} = 400 \]

Since: \( m_{\text{max}} \) is a large number, i.e. \( -400, e^{2m_{\text{max}}} \equiv 1 \).

Hence with very little error we may write
\[ m_{\text{max}} = 400 = n_{\text{max}} - 2 \]

\[ n_{\text{max}} = 402 \]

Therefore, we may plot \( X_n \) versus \( n \) in the regions \( n=400 \) to obtain the width of the peak at half-maximum as shown in Figure 13.1.

![Graph showing the peak width at half-maximum](image)

\[ \Delta n = 47 \]

Fig. 13.1

2. For p-methoxystyrene added to the mixture of Problem (1) [p:methyl-styrene is a typographical error] \( k_p \) from Table 13.1 is: \( k_p = 52 \) liter/mole-sec.

(a) \[ (r_p)_i = k_p [GA]_o [M]_o = (52)(10^{-3})(0.15) = 7.8 \times 10^{-3} \text{ moles/liter-sec} \]

(b) \[ [M]_t = [M]_o e^{-k_p t[GAL]} \]

After 10 seconds
\[ r_p = [GA]_0 [M]_0 e^{k_p [GA]_1 t} = (52) \left( 10^{-3} \right) (0.15) e^{\left( \frac{52}{10^{-3}} \right) t} \]

\[ r_p = 4.6 \times 10^{-3} \text{ moles/liter-sec.} \]

(a) For this polymerization \( \overline{DP} = 2\nu = 2 \frac{[M]_0}{[GA]_0} (1 - e^{-k_p [GA]_1 t}) \)

1st Polymerization: \( \overline{DP} = 2\nu = 2 \left( \frac{0.2}{10^{-3}} \right) = 4 \times 10^2 \) (Styrene)

2nd Polymerization: \( \overline{DP} = 2\nu = 2 \left( \frac{0.15}{10^{-3}} \right) (1 - e^{-k_p [GA]_1 t}) \)

\[ = \left( \frac{0.3}{10^{-3}} \right) \left( 1 - e^{-\left( \frac{52}{10^{-3}} \right) (100)} \right) \]

\[ = 298 \text{ (p-methoxystyrene)} \]

\( \overline{DP} \) for copolymer = 698

3. (a) \[ \gamma = \left( \frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = \frac{1 + r_1 \frac{[M_1]}{[M_2]}}{1 + r_2 \frac{[M_1]}{[M_2]}} \]

where \( M_1 = \text{styrene} \) and \( M_2 = \text{p-methoxystyrene} \)

Assuming that \( r_1 \) and \( r_2 \) for \( \text{C}_4\text{H}_9\text{Li} \) initiation at 25°C are the same as for Li initiation at 0°C. (Table 13.2).
\[
\begin{align*}
\left( \frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} &= \frac{1 + 2.9 \left( \frac{0.5}{1} \right)}{1 + 0.23 \left( \frac{1}{0.5} \right)} = 1.67 = \left( \frac{X_1}{X_2} \right)_{\text{copolymer}}
\end{align*}
\]

Since \( X_1 + X_2 = 1 \), the composition is:

- styrene = 62.5%
- \( p \)-methoxystyrene = 37.5%

(b) \( \bar{m}_1 = 1 + r_1 \frac{[M_1]}{[M_2]} = 1 + 2.9 \left( \frac{0.5}{1} \right) = 2.45 \)

(c) \( P_{M_1}(5) = P_{11}^{-1} P_{12} = (1 - P_{12})^{-1} P_{12} \)

\[
\begin{align*}
P_{12} &= \frac{[M_2]}{r_1 [M_1] + [M_2]} = \frac{1}{(2.9)(0.5) + 1} = 0.408
\end{align*}
\]

\[
P_{M_1}(5) = (0.592)^5 (0.408) = 0.050
\]
4. \[ \frac{-d[M_1]}{dt} = [M_1]\left\{k_{11}\left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] + k_{21}\left[\begin{array}{c} M_1 \\ M_2 \end{array}\right]\right\} \]

\[ \frac{-d[M_2]}{dt} = [M_2]\left\{k_{12}\left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] + k_{22}\left[\begin{array}{c} M_1 \\ M_2 \end{array}\right]\right\} \]

where \( M_1 = \) styrene and \( M_2 = \) p-methoxystyrene

The assumptions mean:

\[ \left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] = \left[\begin{array}{c} M_1 \circ \o \\ M_2 \circ \o \end{array}\right] \]

at all times

and also we have

\[ \left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] = \left[\begin{array}{c} [C_4H_8Li] \circ \o \end{array}\right] \]

so that

\[ \left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] = \frac{1}{3}[C_4H_8Li]_o \]

\[ \left[\begin{array}{c} M_1 \\ M_2 \end{array}\right] = \frac{2}{3}[C_4H_8Li]_o \]

From Tables 13.1 and 13.2 and the assumption that the reactivity ratios are the same for Li initiator as for \( C_4H_8Li \) in tetrahydrofuran, one obtains

\[ k_{11} = 950 \text{ liter/mole-sec.} \quad k_{12} = 328 \text{ liter/mole-sec.} \]
\[ k_{21} = 52 \text{ liter/mole-sec.} \quad k_{22} = 226 \text{ liter/mole-sec.} \]

Integration of the rate equations and substitution of these rate constants yields

\[ [M_1] = [M_1]_o e^{-467[C_4H_8Li]_o t} \]
\[ [M_2] = [M_2]_0 e^{-144[C_4H_9Li]_0 t} \]

These cannot be plotted unless a value for \([C_4H_9Li]_0\) is assumed. Using the value \([C_4H_9Li]_0 = 10^{-3}\) moles/liter, the monomer concentrations are plotted as follows as shown in Figure 13.2.

![Graph showing concentration over time for M2 (p-methoxystyrene) and M1 (Styrene)]

Figure 13.2

5. (a) \( \overline{DP} = \frac{[M]}{[GA]_0} (1 - e^{-v_{GA} t}) \)

At completion of reaction: \( \overline{DP} = v_{m} = \frac{[M]_0}{[GA]_0} = \frac{0.75}{5 \times 10^{-3}} \)
\[
\overline{DP} = v = 150
\]

(b) \( X_n = \frac{v^{n-1}e^{-v}}{(n-1)!} = \frac{(150)^{n-1}e^{-150}}{(n-1)!} \)

\[
W_n = \frac{n}{DP} X_n = \frac{n}{v} X_n = \frac{n}{150} X_n
\]

To evaluate, it is convenient to let \( m = n - 1 \) and use the Stirling Formula form!, namely

\[
m! = (2\pi m)^{\frac{1}{2}} m^m e^{-m}
\]

Substituting \( X_n = \left( \frac{v}{m} \right)^m e^{m} (2\pi m)^{\frac{1}{2}} \)

The distribution are plotted in Figure 13.3.
(6) Plot \( \frac{1}{DP} \) versus \( \frac{1}{[C_4H_6]} \) and draw the best straight line through the data. From the slope and intercept of the line in Figure 13.4, one obtains

\[
\frac{k_{r}}{k_{p}} = 9.8 \pm 3.1 \times 10^{-5}
\]

\[
\frac{k_{l}}{k_{p}} = 5.14 \pm 0.37 \times 10^{-5}
\]
Figure 13.4

7. The intercept of a plot of \( \frac{1}{(DP)^1} \) versus \([M]^{-1}\) is equal to the ratio \( \frac{k_{\text{r}}}{k_p} \). Hence, plot

\[
\ln \frac{k_{\text{r}}}{k_p} \text{ versus } \frac{1}{T},
\]
as in Figure 13.5. The slope is \( \frac{(E_p - E_{\text{r}})}{R} \). Hence

(a) \( E_p - E_{\text{r}} = -10.0 \pm 0.1 \text{ kcal/mole} \)

(b) Since \( \ln \frac{k_{\text{r}}}{k_p} = \ln \frac{A_{\text{r}}}{A_p} + \frac{E_p - E_{\text{r}}}{R} \left( \frac{1}{T} \right) \) the intercept is equal to \( \ln \frac{A_{\text{r}}}{A_p} \). Thus

\[
\frac{A_{\text{r}}}{A_p} = 1.6 \pm 0.4 \times 10^4
\]
Figure 13.5

(c) If chain transfer is more important than termination

\[ \frac{\overline{DP}}{k_{tr}} = \frac{k_p}{k_{tr}} = \frac{A_p}{A_{tr}} e^{(E_p-E_r)/RT} \]

and from the results of part (a) and (b)

\[ \ln \overline{DP} = -11.98 + \frac{5033}{T} \]
This function is shown in Figure 13.6

Figure 13.6

8. At least approximately, all chains start at the same time, have the same reactivity, and run out of monomer at the same time.
CHAPTER 14

1. \[
\delta^2 = \frac{\Delta E_{\text{vap}}}{V_{\text{molar}}} = \frac{\Delta H_{\text{vap}} - RT}{M/\rho}
\]

where \( M \) is the molecular weight and \( \rho \) is the density. Then

(a) Toluene: \( \delta^2 = 79.5 \text{ cal/cm}^3 \)

(b) Carbon Disulfide: \( \delta^2 = 100.3 \text{ cal/cm}^3 \)

(c) Water: \( \delta^2 = 552 \text{ cal/cm}^3 \)

2. Specific volume of PMMA = \( \frac{1}{\rho} = 0.847 \text{ cm}^3/\text{gram} \).

Assuming additivity of volumes, the volume fractions in the solution are:

\[
\phi_{\text{Chem}} = \phi_1 = \frac{50.000}{50.847} = 0.9833
\]

\[
\phi_{\text{PMMA}} = \phi_2 = 1 - \phi_1 = 1.67 \times 10^{-2}
\]

\[
\Delta H_{\text{dissolution}} = \phi_2 (\delta_1 - \delta_2)^2 \text{ in cal/cm}^3
\]
For the solution on hand

\[
\Delta H = \phi \phi_2 (\delta_1 - \delta_2)^2 (50.847) = (0.9833)(1.67 \times 10^{-2})
\]

\[
(\sqrt{82.8} - \sqrt{83.7})^2 (50.847)
\]

\[
\Delta H = 2.0 \times 10^{-3} \text{ calories}
\]

3. (a) \(M_n = 1.00 \times 10^4, M_W = 1.05 \times 10^4, M_Z = 1.09 \times 10^4, M_v = 1.04 \times 10^4;\)

\[
M_W/M_n = 1.05, M_V/M_n = 1.04, M_v/M_W = 0.990.
\]

(b) \(M_n = 1.00 \times 10^4, M_W = 1.32 \times 10^4, M_Z = 1.48 \times 10^4, M_v = 1.30 \times 10^4;\)

\[
M_W/M_n = 1.32, M_V/M_n = 1.30, M_v/M_W = 0.985.
\]

Note that the second distribution covers a wider range of \(M\), and this is reflected by a larger value of the polydispersity index \(M_W/M_n\). Also note that \(M_V\) is closer to \(M_W\) than it is to \(M_n\).

4. \(14.2 \times 10^3 \text{ g/mol.}\)

5. \(2.9 \times 10^3 \text{ g/mol.}\)

6. \(10.1 \times 10^3 \text{ g/mol.}\)
7. \[ \frac{\pi}{c} = \frac{RT}{M_n} \left( 1 + \Gamma c + g \Gamma^2 c^2 + \ldots \right) \]

\[ m = \frac{1000 w_p / M_n}{\rho_s V_s} = \frac{1000}{\rho_s M_n} c \]

so \[ c = \rho_s M_n m \times 10^3 = (1.11)(4.28 \times 10^3)(7.0 \times 10^{-6})(10^{-3}) = 3.33 \times 10^{-3} \text{ g/cm}^3 \]

From Figures 14.4 and 14.5, in the text, \( g = \frac{1}{4} \)

Then

\[ \pi = \frac{(8.31 \times 10^7)(298)(3.33 \times 10^{-3})}{4.28 \times 10^3} \left( 1 + (94.5)(3.33 \times 10^{-3}) + \frac{(94.5 \times 3.33 \times 10^{-3})^2}{4} \right) \]

\[ \pi = 258 \text{ dynes/cm}^2 = \frac{258 \text{ dynes/cm}^2}{981 \text{ cm/sec}^2} = 0.236 \text{ g/cm}^3 \]

Ideal osmotic pressure = \( \pi_{\text{ideal}} = \frac{(8.31 \times 10^7)(298)(3.33 \times 10^{-3})}{4.28 \times 10^3} \)

\[ \pi_{\text{ideal}} = 193 \text{ dynes/cm}^2 = 0.197 \text{ g/cm}^2 \]

\[ \frac{\pi}{\pi_{\text{ideal}}} = 1.34 \]
8. According to Eqn. 14.21

\[
\frac{\pi}{c} = \frac{RT}{M_n} \left(1 + \Gamma c + g c^2 + \ldots\right)
\]

A plot of \( \frac{\pi}{c} \) versus \( c \) is shown in Figure 14.1 and is seen to be linear with an intercept of 2.01 \times 10^5 \text{ (ergs/gram)} and a slope of 1.97 \times 10^7 \text{ (ergs/gram-concn.).}

(a) From the intercept \( M_n = \frac{RT}{2.01 \times 10^5} = 1.25 \times 10^5 \text{ g/mole.} \)

(b) \( \Gamma = \text{slope/intercept} = 98.0 \text{ conc.}^{-1} = 98.0 \text{ cm}^3/\text{gram.} \)

(c) \( \Gamma = \frac{M_n \rho_s}{M_s \rho_p^2} \left(\frac{1}{2} X_1\right) \) Taking \( \rho_s \) from Lange's Handbook of Chemistry to be 0.867, one obtains \( X_1 = 0.370 \)

![Figure 14.1](image)
9. \[ \frac{\pi}{c} = \frac{RT}{M_n} \left( 1 + \Gamma c + g \Gamma^2 c^2 + \ldots \right) \]

and from the intercepts and slopes of Figure 14.6 in the text one obtains values of \( \overline{M_n} \) and \( \Gamma \) in the two solvents. Insertion of these values into Eqn. 14.22, along with the densities of toluene and methylethyl-ketone of 0.867 and 0.805 g/cm\(^3\), respectively (Lange’s Handbook of Chemistry), gives:

\[ X_1 \text{ (Toluene)} = 0.444 \]
\[ X_1 \text{ (MEK)} = 0.488 \]

10. From eqn. 14.24, \( \pi = \rho_{\text{solute}} \gamma' \Delta h \)

(a) \( \pi = \rho_{\text{solvent}} \gamma' \Delta h = (0.867)(981)(0.467) = 397 \text{ dynes/cm}^2 \)

(b) \[ \frac{\pi}{c} = \frac{RT}{M_n} \left( 1 + \Gamma c + g \Gamma^2 c^2 \right) \]

\[ \frac{397}{1.5 \times 10^3} = \left( \frac{8.31 \times 10^7}{M_n} \right) \left( 298 \right) \left[ 1 + (200)(1.5 \times 10^{-3}) + \frac{(200)(1.5 \times 10^{-3})^3}{4} \right] \]

From which \( \overline{M_n} = 1.24 \times 10^5 \text{ g/mole} \)

11. \( M_n = 2.17 \times 10^5 \text{ g/mol} \) and \( A_2 = 1.81 \times 10^{-4} \text{ cm}^3 \text{mol/g}^2 \).
12. \( \frac{H_c}{\tau} = \frac{1}{M_w} (1+2\Gamma_c + \ldots) = \frac{1}{M_w} \) at \( c \) as low as \( 2.0 \times 10^4 \) g/cm\(^3\)

\[
\tau = H_c M_w = \frac{32\pi^3}{3\lambda^4 N_o} n_o^2 \left( \frac{n-n_o}{c} \right)^2 \]

From Table 14.3, \( \left( \frac{n-n_o}{c} \right) = 0.120 \text{ cm}^3/\text{gram} \)

\[
\tau = \frac{32\pi^3 (1.3688)^2 (0.120)^2 (5.20 \times 10^4)(2.9 \times 10^4)}{(3)(5.46 \times 10^{-5})^4 (6.023 \times 10^{23})} = 1.73 \times 10^{-5}
\]

\[
\frac{I}{I_o} = 1 - e^{-\tau} = 1 - e^{-1.73 \times 10^{-5}} = 1.73 \times 10^{-5}
\]

13. \( \tau = \frac{I}{I_o} = \int_0^\pi \int_0^{2\pi} R(\theta) \sin \theta d\theta d\phi \)

\[R(\theta) = \frac{2\pi^2 (n-1)^3 M}{\lambda^4 N_o c} (1+\cos^2 \theta) \text{ for a dilute gas [Eqn. 14.25]}\]

\[
\tau = \frac{2\pi^2 (n-1)^3 M}{\lambda^4 N_o c} \int_0^\pi (1+\cos^2 \theta) \sin \theta d\theta \int_0^{2\pi} d\phi
\]

\[
= \frac{2\pi^2 (n-1)^3 M}{\lambda^4 N_o c} \left[ -\cos \theta \right]_0^\pi \cos^3 \theta \left|_0^\pi \right] (2\pi) = \frac{2\pi^2 (n-1)^3 M}{\lambda^4 N_o c} \left( \frac{16\pi}{3} \right)
\]
Hence, for a dilute gas, \( \tau = \frac{32\pi^2}{3\lambda^4N_o} \left( \frac{n-1}{c} \right)^2 M \)

For an ideal gas at 1 atm and 298°K, \( \frac{n}{V} = \frac{P}{RT} = \frac{1}{(82.06)(298)} \)

\( = 4.09 \times 10^{-3} \text{ moles/cm}^3 \)

For \( \text{SO}_2 \), \( c = (4.09 \times 10^{-5} \text{ moles/cm}^3)(64.0 \text{ g/mol}) = 2.62 \times 10^{-3} \text{ g/cm}^3 \)

\( \tau = \frac{32\pi^2 (0.000665)^2 (64.0)}{3(5.46 \times 10^{-5})^4 (6.02 \times 10^{23}) (2.62 \times 10^{-3})} = 6.67 \times 10^{-7} \)

\( I_0 = I - e^{-\tau} = 1 - e^{-6.67 \times 10^{-7}} = 6.67 \times 10^{-7} \)

14. Prepare a Zimm plot by plotting \( \frac{Kc(1+\cos^2 \theta)}{R(\theta)} \) versus \( (1000c+\sin^2 \frac{\theta}{2}) \) as shown in Figure 14.2, where

\( K = \frac{2\pi^2}{\lambda^4N_o} \left( n-n_o \right)^2 \left( \frac{n-n_o}{c} \right)^2 \)

(a) The limit of the double extrapolation from Figure 14.2, and Eqn. 51 is,
\[
\lim_{\theta \to 0} \frac{Kc(1+\cos^2 \theta)}{R(\theta)} = \frac{1}{M_w} = 0.165 \times 10^6
\]

or \( M_w = 6.06 \times 10^6 \) g/mole

(b) In the limit of \( \theta = 0 \), we have

\[
\lim_{\theta \to 0} \frac{Kc(1+\cos^2 \theta)}{R(\theta)} = \frac{1}{M_w} + \frac{2\Gamma}{M_w} + \ldots
\]

so that the limit of the \( \theta = 0 \) line is \( \frac{2\tau}{M_w} \). Thus

\[
\frac{2\tau}{M_w} = 1.23 \times 10^4
\]

\( \tau = 373 \) cm\(^3\)/gram
NOTE! The data in the table are actually \( R(\theta) \times 10^4 \) and not \( (R(\theta)/(1+\cos^2\theta)) \times 10^4 \) as indicated. Therefore, the result of plotting \( Kc(1+\cos^2\theta)/R(\theta) \) as ordinate is to yield a value of \( M_w \) too high by a factor of 2 and a value of \( \tau \) too high by a factor of 2 as compared with the result in the cited reference.

15. From Eqn. (14.50)

\[
R(\theta) = \frac{Kc(1+\cos^2\theta)}{1 + \frac{2\Gamma c}{M_w} + \frac{3\Gamma^2 c^2}{M_w} + \ldots}
\]

where \( K = \frac{2\pi^2 n_o^2}{\lambda^4 N_o} \left( \frac{n-n_o}{c} \right)^2 \)

According to eqn. 14.52
\[ P(\theta) = \frac{2}{v^2} \left[ e^{-v} (1-v) \right] \]

and

\[ v = \frac{8\pi^2}{3} \frac{r^2}{n_e^2} \left( \frac{r^2}{\lambda^2} \right) \sin^3 \frac{\theta}{2} \]

One must assume a wavelength of the incident light, so assuming the typical value of \( \lambda = 4358 \) Å, we may calculate values of \( R(\theta) \) and \( P(\theta) \) which are given in the table in (a).

(a) The value of \( R(\theta) \) and \( P(\theta) \) in range 15°-180° are:

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( P(\theta) )</th>
<th>( R(\theta) \times 10^4 (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.9628</td>
<td>2.56</td>
</tr>
<tr>
<td>30</td>
<td>0.8652</td>
<td>2.11</td>
</tr>
<tr>
<td>45</td>
<td>0.7386</td>
<td>1.57</td>
</tr>
<tr>
<td>60</td>
<td>0.6134</td>
<td>1.10</td>
</tr>
<tr>
<td>75</td>
<td>0.5068</td>
<td>0.790</td>
</tr>
<tr>
<td>90</td>
<td>0.4273</td>
<td>0.626</td>
</tr>
<tr>
<td>105</td>
<td>0.3621</td>
<td>0.576</td>
</tr>
<tr>
<td>120</td>
<td>0.3181</td>
<td>0.596</td>
</tr>
<tr>
<td>135</td>
<td>0.2876</td>
<td>0.649</td>
</tr>
<tr>
<td>150</td>
<td>0.2678</td>
<td>0.707</td>
</tr>
<tr>
<td>165</td>
<td>0.2566</td>
<td>0.750</td>
</tr>
<tr>
<td>180</td>
<td>0.2529</td>
<td>0.765</td>
</tr>
</tbody>
</table>
(b) \[ Z = \frac{i_x(45^\circ)}{i_x(135^\circ)} = \frac{R(45^\circ)}{R(135^\circ)} = \frac{1.57}{0.649} = 2.42 \]

(at the concentration of the experiment, namely \(1.0 \times 10^{-4}\) g/cm\(^3\))

In the limit as \(c \to 0\), \[ Z_c = \left[ \frac{i_x(45^\circ)}{i_x(135^\circ)} \right]_{c \to 0} = \frac{P(45^\circ)}{P(135^\circ)} = 2.57 \]
16. \[ \frac{Kc}{R(\theta)} (1+\cos^2\theta) = \frac{1}{M_w P(\theta)} + \frac{2\Gamma c}{M_w} + \ldots \]

where \[ K = \frac{2\pi^2 \hbar n_o^2 \left( \frac{n-n_o}{c} \right)^2}{\lambda^4 N_o} = 3.245 \times 10^{-7} \text{ mole-cm}^{-2} \text{ g}^{-2} \]

Plot \[ \frac{Kc}{R(\theta)} (1+\cos^2\theta) \] versus \[ 2000c + \sin^2 \frac{\theta}{2} \] as shown in Figure 14.4 and extrapolate to \( c = 0 \) and \( \theta = 0 \). In this limit, the intercept is

(a) \[ \frac{1}{M_w} = 2.88 \times 10^{-7} \]

or \[ M_w = 3.47 \times 10^6 \text{ g/mol} \]

(b) \[ Z_{45} = \frac{R(45^\circ)}{R(135^\circ)} \]

\[ Z_{45}^o = \lim_{c \to 0} \frac{R(45^\circ)}{R(135^\circ)} \]

A plot of \( Z_{45} \) versus \( c \) is linear with \( Z_{45}^o = 2.63 \) as shown in Figure 14.5.
Figure 14.5

From Figure 14.10 in the text, assuming a random coil model,

\[
\left( \frac{n_2 s}{\lambda^2} \right)^{1/2} = 0.515
\]

or \( (\frac{s^2}{\lambda})^{1/2} = (0.515)(436)/(1.4976) = 150 \) nanometers

(c) Slope \( \theta = 0 \) line \( \frac{2\Gamma}{M_w} = 2.134 \times 10^4 \frac{\text{mole-cm}^3}{\text{gram}^2} \)

Hence \( \Gamma = 370 \ cm^3/\text{gram} \)

88
(d) \[ \tau = \frac{16\pi}{3} \frac{R(\theta)}{1+\cos^2 \theta} \]

To calculate \( \tau \) for \( c = 0.2 \) we must use \( R(0) \) in order to eliminate intraparticle interference, since \( P(\theta) \to 1 \) as \( \theta \to 0 \)

\[ \tau = \frac{16\pi}{3} \frac{R(0)}{2} \]

From Zimm plot: \[ \lim_{\theta \to 0} \frac{(0.2 \times 10^{-3})K(1+\cos^2 \theta)}{R(\theta)} = \frac{0.2 \times 10^{-3}K(2)}{R(0)} = 3.20 \times 10^{-7} \]

Hence \[ \frac{R(0)}{2} = \frac{0.2 \times 10^{-3}K}{3.20 \times 10^{-7}} = \frac{(0.2 \times 10^{-3})(3.245 \times 10^{-7})}{3.20 \times 10^{-7}} = 2.03 \times 10^{-4} \]

and \[ \tau = \frac{16\pi}{3} (2.03 \times 10^{-4}) = 3.40 \times 10^{-3} \]

NOTE! The data in the table (text) are actually \( R(\theta) \times 10^4 \) and not \( (R(\theta)/(1+\cos^2 \theta)) \times 10^4 \) as indicated. Therefore, the result of plotting \( Kc(1+\cos^2 \theta)/R(\theta) \) as ordinate is to obtain values of \( M_w \) and \( \Gamma \) that are too high by a factor of 2 as compared with the reference cited.

17. \( M_w = 1.1 \times 10^6 \) g/mole, \( A_2 = 3.3 \times 10^{-4} \) cm\(^3\) mol/g\(^2\), and \( <s^2>^{1/2} = 1.550 \) Å.
18. $v_p = \text{volume of displaced solvent per gram of polymer} \equiv \frac{1}{\rho_p}$

$$V_p = \frac{4}{3} \pi R^3 = \frac{4}{3} \pi (7.0 \times 10^{-7})^3 = 1.436 \times 10^{-18} \text{ cm}^3/\text{particle}$$

$$\rho_p = \frac{M_p}{N_a V_p} = \frac{10^6}{(6.02 \times 10^{23})(1.436 \times 10^{-18})} = 1.156 \text{ g/cm}^3$$

$$v_p = \frac{1}{\rho_p} = 0.8649 \text{ cm}^3/\text{gram}$$

According to Eqn. 14.61,
\[ u_s = \frac{M(1 - v_p \rho_s)g}{6N_0 \pi \eta R} \]

so

\[ u_s = \frac{(10^6)(1 - [0.8649][0.805])(980)}{(6)(6.02 \times 10^{23})\pi(4.284 \times 10^{-3})(7.0 \times 10^{-7})} \]

\[ u_s = 8.75 \times 10^{-9} \text{ cm/sec} \]

19. Angular velocity \( \omega = (65,000 \text{ rev/min}) \left(2\pi \frac{\text{radians}}{\text{rev}} \right) \left(\frac{1 \text{ min}}{60 \text{ sec}} \right) \)

\[ \omega = 6807 \text{ radians/sec.} \]

(a) \[
\frac{\text{Centrifugal Acceleration}}{\text{Gravitational Acceleration}} = \frac{\omega^2 x}{g} = \frac{(6807)^2(5.0)}{980} = 2.36 \times 10^5
\]

(b) For the spherical polymer in problem 12, the sedimentation velocity in the centrifuge is

\[ u_s = 8.75 \times 10^{-9} \times 2.36 \times 10^5 = 2.07 \times 10^{-3} \text{ cm/sec.} \]

20. According to eqn. (14.67)

\[
\overline{M_w} = \frac{s_o RT}{D_v(1 - v_p \rho_s)}
\]

where the partial specific volume of polymer, \( v_p \), is given by
\[
\bar{v}_p = \frac{1}{\rho_s} \left( 1 - \frac{\rho_p - \rho_s}{c} \right)
\]

(a) Using data given in the problem we find

\[
\bar{v}_p = 0.985
\]

\[
M_w = 9.17 \times 10^5
\]

(b) According to Eqn. (14.65)

\[
u_r = s\omega^2 x
\]

and for the centrifuge in prob. 13, \(\omega = 6807\) radians/sec.

Therefore,

\[
u_s = (17.9 \times 10^{-13})(6807)^2(5.0) = 4.15 \times 10^{-4}\ \text{cm/sec.}
\]

Is the sedimentation velocity at infinite dilution. If the 2nd Virial coefficient \(\Gamma\) was known, we could calculate \(u_s\) for the actual solution using eqn. (14.68).

21. \(D = \frac{RT}{N_o F}\)

and for spherical particles \(F = 6\pi\eta r\). Hence, from the data given

\[
r = \frac{RT}{6\pi\eta N_o F} = 3.1 \times 10^{-7}\ \text{cm}
\]

Volume of the particle is: \(V_p = \frac{4}{3}\pi r^3 = 1.2 \times 10^{-19}\ \text{cm}^3/\text{particle}\). The volume of the polymer particles per gram is 0.749 cm\(^3\)/g. Hence the mass of a particle is

\[
m = \frac{1.2 \times 10^{-19}}{0.749} = 1.6 \times 10^{-19}
\]
and the molecular weight is
\[ M = N_a m = 9.9 \times 10^4 \]

22. (a) We may plot \( \frac{1}{s} \) and \( D \) versus \( c \) to obtain, from the intercepts, \( s_o \) and \( D_o \) and, in addition, to have \( s \) and \( D \) as a function of \( c \). From the values of \( s_o \) and \( D_o \) obtained (see Figure 14.6), the value of \( v_p \) given, and the value of \( \rho_{\text{solvent}} \) from problem #14 we have

\[
\overline{M_w} = \frac{s_o RT}{D_o (1-v_p \rho_s)} = \frac{(8.62 \times 10^{-13})(8.314 \times 10^7)(293)}{(1.91 \times 10^7)(1-0.8788 \times 0.91)} = 5.5 \times 10^9 \text{ g/mole}
\]

(b) Using the plots of \( D \) and \( 1/s \) versus \( c \), we may plot the function \( \frac{D_o (1-v_p \rho_s)}{s_o RT} \) versus \( c \) as suggested by the virial equation

\[
\frac{D_o (1-v_p \rho_s)}{s_o RT} = \frac{1}{M_w} (1+2\Gamma c+3g\Gamma^2 c^2+\ldots.)
\]

Such a plot of the data is shown in figure 14.7. The slope from the figure is \( 5.18 \times 10^{-4} \text{ cm}^3 \cdot \text{mole/g}^2 \). Then

\[
\text{slope} = \frac{2\Gamma}{M_w} = 5.18 \times 10^{-4} \quad \text{so} \quad \Gamma = 142 \text{ cm}^3/\text{g}
\]
Fig. 14.6

Figure 14.7
23. $T = 35^\circ C$

<table>
<thead>
<tr>
<th>$c \times 10^3$ g/cm$^3$</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s \times 10^{12}$ sec</td>
<td>14.8</td>
<td>13.9</td>
<td>13.1</td>
<td>12.4</td>
<td>11.8</td>
<td>11.2</td>
</tr>
<tr>
<td>$1/s \times 10^{-11}$</td>
<td>6.76</td>
<td>7.19</td>
<td>7.63</td>
<td>8.06</td>
<td>8.47</td>
<td>8.93</td>
</tr>
</tbody>
</table>

$\rho_s = 0.765$ g/cm$^3$

$\overline{v_p} = 0.93$ cm$^3$/gram

$D_o = 1.3 \times 10^{-4} (M_w)^{-0.497}$ cm$^2$/sec.

(a) Plot $\frac{1}{s}$ versus $c$ to get $s_o$. This is shown in Figure 14.8. From plot

$s_o = 16.9 \times 10^{-13}$ sec.

(b) The Svedberg equation is:

$$\overline{M_w} = \frac{s_o RT}{D_o(1 - \overline{v_p} \rho_s)}$$

In view of the value of $D_o$ given this becomes

$$\overline{M_w} = \frac{s_o RT}{1.3 \times 10^{-4} (M_w)^{-0.497}(1 - \overline{v_p} \rho_s)}$$
\[
(M_w)^{0.503} = \frac{s_nRT}{1.3 \times 10^4(1 - v_p\rho_s)} = \frac{(16.9 \times 10^{-13})(8.314 \times 10^7)(308)}{(1.3 \times 10^4)(1 - v_p\rho_s)}
\]

\[
(M_w)^{0.503} = 1.15 \times 10^3
\]

\[
M_w = 1.22 \times 10^6 \text{ g/mole}
\]

\[
\frac{1}{S_0} = 5.90 \times 10^{11} \text{ sec}^{-1}
\]

\[
S_0 = 16.9 \times 10^{-13} \text{ sec} = 16.9 \text{ Svedbergs}
\]

Fig. 14.8
CHAPTER 15

1. According to the general expression for an average molecular weight, given by eqn. 15.23 (not 15.15 as stated in the text).

\[ \overline{M}_p = \frac{\sum w_i M_i^\beta}{\sum w_i M_i^{\beta-1}} \]

since \( w_i = N_i M_i \)

\[ \overline{M}_\alpha = \frac{\sum N_i M_i^{1+\beta}}{\sum N_i M_i^\beta} \]

the definition of \( \overline{M}_\alpha \) is

\[ \overline{M}_\alpha = \frac{\sum N_i M_i}{\sum N_i} \]

hence, \( \overline{M}_{p-0} = \overline{M}_\alpha \), since \( 1+\beta = 1 \) or \( \beta = 0 \) for the two to agree

the definition of \( \overline{M}_\alpha \) = \[ \frac{\sum N_i M_i^2}{\sum N_i M_i} \]

hence \( \overline{M}_{p-1} = \overline{M}_\alpha \) since for agreement \( 1+\beta = 2 \) or \( \beta = 1 \)

2. Plot \( \log [\eta] \) versus \( \log \overline{M}_\alpha \), as in figure 15.1. The slope of the line is \( a \), i.e.,
\[ a = \frac{2.32 - 0.28}{4.00 - 3.00} = 0.68 \]

From the graph below, we see that \([\eta] = 10^{1.63} = 42.7\) at \(M_w = 10^5\), hence

\[
K = \frac{[\eta]}{M_w} = \frac{42.7}{(10^5)^{0.68}} = 1.70 \times 10^{-2}
\]

\[ \text{Figure 15.1} \]

3. With kinetic energy correction: \(\frac{\eta}{\rho} = at^{\frac{\beta}{t}}\), without kinetic energy correction: \(\frac{\eta}{\rho} = at\)

where \(a = \frac{\pi R^4 h g}{8L V} = 2.24 \times 10^{-3} \text{ (cm/sec)}^2\)

\(\beta = \frac{V}{8\pi L} = 1.45 \times 10^{-2} \text{ cm}^2\)

(a) Pure CHCl₃: \(t = 170\) sec.
\[ \frac{\eta}{\rho} = 3.81 \times 10^{-3} \text{ cm}^2/\text{sec} \text{ without kinetic energy correction} \]

\[ \frac{\eta}{\rho} = 3.72 \times 10^{-3} \text{ cm}^2/\text{sec} \text{ with the correction} \]

\[ \% \text{ Error in omitting correction} = \frac{0.09 \times 100}{3.72} = -2.4\% \]

(b) Solution of polymethylmethacrylate: \( t = 230 \text{ sec.} \)

\[ \left( \frac{\eta}{\rho} \right) = 5.09 \times 10^{-3} \text{ cm}^2/\text{sec} \text{ for solution with the correction} \]

\[ \eta_{\text{relative}} = \frac{\eta}{\eta_o} = \frac{5.09 \times 10^{-3}}{3.72 \times 10^{-3}} = 1.368 \text{ with correction} \]

\[ \eta_{\text{relative}} = \frac{\alpha t}{\alpha t_o} = \frac{t}{t_o} = \frac{230}{170} = 1.353 \text{ without correction} \]

\[ \% \text{ Error in omission} = \frac{1.353 - 1.368}{1.368} \times 100 = -1.1\% \]

4. \[ \frac{\eta}{\rho} = \alpha t \frac{\beta}{\tau} = 5.13 \times 10^{-3} \text{ cm}^2/\text{sec}. \]

Assuming densities of solvent and solution are the same

\[ \eta_{\text{rel}} = \left( \frac{\eta}{\rho} \right)_{\text{solute}} = \frac{5.13 \times 10^{-3}}{3.72 \times 10^{-3}} = 1.379 \]

\[ \eta_{sp} = \eta_{\text{rel}} - 1 = 0.379 \]

\[ \frac{\eta_{sp}}{c} = \frac{0.379}{0.0865} = 4.38 \]

Huggins eqn. states \[ \frac{\eta_{sp}}{c} = [\eta] + 0.4[\eta]^2 c \]

Which for the values of this problem yields the quadratic

99
\[ [\eta]^2 + 28.9[\eta] - 127 = 0 \]

from which \[ [\eta] = \frac{-28.9 + \sqrt{(28.9)^2 + 4(127)}}{2} = 3.87 \]

Mark-Houwink eqm. States \[ [\eta] = K\overline{M}_w \] or \[ \overline{M}_w = \left( \frac{[\eta]}{K} \right)^\lambda \]

Using values of \( K \) and \( a \) from table 15.3

\[
\overline{M}_w = \left( \frac{3.87}{0.48 \times 10^{-2}} \right)^{0.8} \\
\overline{M}_w = 4.3 \times 10^3
\]

5. See p. 403

6. See p. 404

The values of \([\eta]\) are the intercepts of figure 15.2. These are:

Fraction 1: \([\eta]_{f1} = 128 \text{ cm}^3/\text{gram} \]

Fraction 2: \([\eta]_{f2} = 276 \text{ cm}^3/\text{gram} \]

\[
\overline{M}_{w(f1)} = \left( \frac{[\eta]_{f1}}{K} \right)^\lambda \\
\overline{M}_{w(f2)} = \left( \frac{[\eta]_{f2}}{K} \right)^\lambda
\]

From table 15.3, \( K = 0.48 \times 10^{-2}, a = 0.80 \)

\[
\overline{M}_{w(f1)} = \left( \frac{128}{4.8 \times 10^{-3}} \right)^{0.8} = 3.41 \times 10^4 \text{ g/mole} \\
\overline{M}_{w(f2)} = \left( \frac{276}{4.8 \times 10^{-3}} \right)^{0.8} = 8.90 \times 10^4 \text{ g/mole}
\]

8. See p. 404

9. See p. 405

10. See p. 406
11. For each elution volume the quantity \([\eta]\text{M}_x\) is equal to the corresponding product \([\eta]\text{M}_x\) of the unknown. Since for the unknown (polyvinylbromide), \([\eta]\text{M}_x=1.59\times10^{-2}\text{ M}_x^{0.64}\), the molecular weight of the polyvinylbromide corresponding to each \(V_e\) is

\[
\text{M}_x = \left(\frac{[\eta]\text{M}_x}{K_x}\right)^{\frac{1}{[\eta]}} = \left(\frac{\eta_b\text{M}_x}{1.59\times10^{-2}}\right)^{0.610}
\]

thus for polyvinylbromide we obtain the following calibration

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
V_e \times (1/5) \text{ cm}^3 & 29.8 & 31.4 & 35.4 & 37.3 & 39.9 & 43.8 & 46.8 & 50.7 \\
\hline
\text{M}_x \times 10^{-5} & 13.5 & 6.29 & 2.54 & 1.38 & 0.701 & 0.261 & 0.132 & 0.062 \\
\hline
\end{array}
\]

These data are plotted as \(\log \text{M} \) versus \(V_e\) in figure 15.2

---

**Figure 15.2**
12. The elution volume at the peak maximum is

\[ V_e = 2 \text{ cm}^3/\text{min} \times 90 \text{ min} = 180 \text{ cm}^3. \]

according to the calibration curve of problem 6

\[ \log \bar{M} = 5.29 \]

\[ \bar{M} = 1.95 \times 10^{-5} \text{ g/mole} \]

If a calibration curve for vinylbromide is not available from problem 6, one may use the calibration data of problem 6 as follows. At an elution volume of 180 cm\(^3\) (that corresponding to the sample of this problem) the product \(\eta_v M_s\) for the polystyrene standard is found by linear interpolation to be

\[ \eta_v M_s = 8.46 \times 10^6 \]

according to the universal calibration procedure, at a given \(V_e\)

\[ \eta_s \bar{M}_x = \eta_v M_s \]

hence at \(V_e = 180\)

\[ \eta_s \bar{M}_x = 8.460 \times 10^6 = K_s \bar{M}_x^{1.86} \]

the Mark-Houwink constants for vinylbromide are given in problem 6, so

\[ \bar{M}_x = \left( \frac{8.460 \times 10^6}{K_s} \right)^{\frac{1}{1.86}} = 2.10 \times 10^5 \text{ g/mole} \]

13. For each elution volume we may calculate \([\eta]_s M_s\), where the subscript \(s\) indicates standard polystyrene samples, and for this fixed elution volume \(V_e\),

\[ \eta_s M_s = \eta_i M_i \]

where the subscript \(i\) indicates unknown, poly(dimethylsiloxane). Then using the Mark-Houwink equation
\[ K_x M_i^{+} M_s = K_x M_s^{+} M_s \]
solving for \( M_x \), we obtain

\[
M_x = \left( \frac{K_x}{K_s} \right)^{1/a_s} M_{s}^{1+a_s}
\]

thus for each \( V_e \) we obtain \( M_x \). The calibration data in this case are:

<table>
<thead>
<tr>
<th>( V_e \times 1/5 \text{ cm}^3 )</th>
<th>23.75</th>
<th>24.55</th>
<th>25.20</th>
<th>25.80</th>
<th>27.30</th>
<th>28.20</th>
<th>29.40</th>
<th>31.30</th>
<th>32.50</th>
<th>34.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_x \times 10^{-3} )</td>
<td>1950</td>
<td>884</td>
<td>681</td>
<td>415</td>
<td>160</td>
<td>97.7</td>
<td>50.4</td>
<td>19.4</td>
<td>10.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

A plot of \( \log M_x \) versus \( V_e \) is shown in figure 15.3.

Figure 15.3
14. Using the calibration curve of problem 8, the distribution in the table below is calculated.

<table>
<thead>
<tr>
<th>Δη</th>
<th>Relative concentration</th>
<th>% of molecules</th>
<th>M x 10^-4 g/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6</td>
<td>1.2</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>7.1</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>12.4</td>
<td>25.7</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>31.1</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>11.7</td>
<td>24.3</td>
<td>6.84</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>8.5</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.1</td>
<td>16.6</td>
</tr>
</tbody>
</table>

A plot of this distribution is shown in figure 15.4.

Figure 15.4
1. For 100 cm\(^3\) of solution: \(n(\text{styrene}) = 10^{-3}\) moles = \(n_2\)

\[n(\text{xylene}) = (100 \times 0.861)/106.1 = 0.8117 \text{ mole} = n_1\]

\(X_{\text{styrene}} = 1.230 \times 10^{-3}\)

\(X_{\text{xylene}} = 0.9988\)

\(N_{\text{styrene}} = 6.023 \times 10^{20} = N_2\)

\(N_0 = N_1 + N_2 = 4.895 \times 10^{23}\)

\(N_{\text{xylene}} = 4.889 \times 10^{23} = N_1\)

\[\Omega(\alpha) = \frac{N_0!}{N_1!N_2!} \text{ and } \ln \Omega = \ln N_0! - \ln N_1! - \ln N_2!\]

Use Stirling's approximation for \(\ln N!\) which states

\[N! = N^{(N+1/2)}e^{-N}(2\pi)^{1/2}\]

or \(\ln N! = (N+1/2) \ln N - N + 1/2 \ln 2\pi = N \ln N - N\) since \(N \sim 10^{20}\)

then

\[\ln \Omega = N_0 \ln N_0 - N_0 - N_0 \ln N_1 + N_1 - N_2 \ln N_2 + N_2\]

\[= N_0 \ln N_0 - N_0 \ln N_1 - N_1 \ln N_2\]

Inserting numbers for \(N_0, N_1\) and \(N_2\)

\[\ln \Omega = 4.5 \times 10^{21} = 2.303 \log \Omega\]

\[\ln \Omega = 2.0 \times 10^{21}\]

\[\Omega = 10^{(2.0 \times 10^{21})}\]

(b) \(\Delta S_{\text{mix}} = -R[n_1 \ln X_1 + n_2 \ln X_2]\)

\[= -1.987[0.8117 \ln 0.9988 + (1 \times 10^{-3}) \ln 1.23 \times 10^{-3}] = 1.52 \times 10^{-2} \text{ cal/deg}]

105
2. In this case (as compared to problem 1)

\[ n(\text{polystyrene}) = 10^{-6} = n_2 \]
\[ n(\text{xylene}) = 0.8117 = n_1 \]
\[ X_2 = 1.23 \times 10^6 \quad X_1 = 0.9999988 \]
\[ N_2 = 6.023 \times 10^{17} \quad N_1 = 4.889 \times 10^{23} \]
\[ N_0 = N_1 + xN_2 = 4.895 \times 10^{23} \]

(a) \[ \Omega = \frac{N_0!}{N_1!N_2!} \left( \frac{z-1}{N_0} \right)^{N_2(x-1)} \]

Using Stirling’s approximation, as shown in problem 1

\[ \ln \Omega = N_0 \ln N_0 - N_1 \ln N_1 - N_2 \ln N_2 + N_2(x-1) \ln \frac{z-1}{N_0} \]

and inserting the data above (with \( x = 1000 \) and \( z = 12 \)) one obtains

\[ \ln \Omega = 1.9 \times 10^{21} \quad \log \Omega = 8.3 \times 10^{20} \quad \Omega = 10^{83 \times 10^{20}} \]

comparing with problem 1, we see

\[ \frac{\Omega_{\text{polystyrene soln}}}{\Omega_{\text{xylene soln}}} = 10^{-12 \times 10^6} \]

(b) \[ \Delta S_{\text{max}} = -R \left[ n_1 \ln \frac{N_1}{N_1 + xN_2} + n_2 \ln \frac{xN_2}{N_1 + xN_2} \right] - R \left[ n_1 \ln \frac{N_1}{N_0} + n_2 \ln \frac{xN_2}{N_0} \right] \]

substituting the numerical values given above

\[ \Delta S_{\text{max}} = -1.987[0.8117 \ln 0.9988 + 1 \times 10^{-6} \ln 1.23 \times 10^{-3}] = 1.95 \times 10^{-3} \text{ cal/deg} \]

3. \[ \Delta S_0 = R \left[ n_2 \ln x + n_2(x-1) \ln \frac{z-1}{e} \right] \text{ where} \]

\[ n_2 = 10^{-6} \text{ moles} \quad x = \text{DP} \quad z = 12 \]
substituting the numerical values

\[ \Delta S_{\text{dis}} = 1.40 \times 10^{-3} \text{ cal/deg} \]

4. From the data given

\[ n_{\text{CHCl}_3} = n_1 = \frac{150}{119.5} = 1.26 \text{ moles} \]

\[ \phi_{\text{PMMA}} = \phi_2 = \frac{m_2}{\rho_2} = \frac{n_2 M_2}{\rho_2} = 8.21 \times 10^{-3} \]

from table 16.1 \( \chi_i = 0.377 \) and

\[ \Delta H_{\text{mix}} = R T \chi_i n_i \phi_2 = (1.987)(293)(0.377)(1.26)(8.21 \times 10^{-3}) \]

\[ \Delta H_{\text{mix}} = 2.27 \text{ cal} \]

5. The problem is really to show \( x N_2 \phi_i = N_1 \phi_2 \) where

\[ x = \frac{V_2}{V_1}, \text{ i.e. the ratio of molar volumes} \]

the volume fraction \( \phi_i \) is defined as

\[ \phi_i = \frac{N_i \overline{V}_i}{N_i \overline{V}_1 + N_2 \overline{V}_2} \]

and hence

\[ x N_2 \phi_i = \left( \frac{V_2}{V_1} \right) \left( \frac{N_i \overline{V}_i}{N_i \overline{V}_1 + N_2 \overline{V}_2} \right) = N_1 \left( \frac{N_i \overline{V}_2}{N_i \overline{V}_1 + N_2 \overline{V}_2} \right) = N_1 \phi_2 \]

since \( \phi_2 = \frac{N_2 \overline{V}_2}{N_1 \overline{V}_1 + N_2 \overline{V}_2} \)
6. \( \Delta G_{\text{mix}} = RT(\chi, n_1 \phi_2 + n_2 \ln \phi_1 + n_2 \ln \phi_2) \)

from problem 4

\[ n_1 = 1.26 \text{ moles} \quad n_2 = 10^{-5} \text{ moles} \]

\[ \phi_2 = 8.21 \times 10^{-3} \quad \phi_1 = 1 - \phi_2 = 0.9918 \]

from table 16.1, \( \chi_1 = 0.377 \)

Substituting: \( \Delta G_{\text{mix}} = (1.987)(293)[(0.377)(1.26)(8.21 \times 10^{-3}) + 1.26 \ln 0.9918 + 10^{-5} \ln 8.21 \times 10^{-3}] \)

\[ \Delta G_{\text{mix}} = -3.80 \text{ cal} \]

7. As shown by eqns. 16.44 and 16.45,

\[ \mu_1 - \mu_1^0 = RT \left[ \frac{n_1}{\phi_1} \left( \frac{\partial \phi_1}{\partial n_1} \right)_{n_2} + \ln \phi_1 + \frac{n_2}{\phi_2} \left( \frac{\partial \phi_2}{\partial n_1} \right)_{n_2} \right] + \chi_1 \phi_2 + \chi_1 n_1 \left( \frac{\partial \phi_2}{\partial n_1} \right)_{n_2} \]

\[ \phi_1 = \frac{n_1 \bar{V}_1}{n_1 \bar{V}_1 + n_2 \bar{V}_2} \]

\[ \phi_2 = \frac{n_2 \bar{V}_2}{n_1 \bar{V}_1 + n_2 \bar{V}_2} \]

\[ \left( \frac{\partial \phi_1}{\partial n_1} \right)_{n_2} = \frac{n_2 \bar{V}_2 \bar{V}_1}{(n_1 \bar{V}_1 + n_2 \bar{V}_2)^2} \]

\[ \left( \frac{\partial \phi_2}{\partial n_1} \right)_{n_2} = \frac{n_2 \bar{V}_2 \bar{V}_1}{(n_1 \bar{V}_1 + n_2 \bar{V}_2)^2} \]

Substitution into the expression for \( \mu_1 - \mu_1^0 \) gives

\[ \mu_1 - \mu_1^0 = RT \left[ \phi_1 + \ln \phi_1 - \frac{n_2}{n_1} \phi_1 + \chi_1 \phi_2 - \chi_1 \phi \phi_2 \right] \]

From the definitions of volume fractions we may write
\[
\frac{n_2}{n_1} = \phi_2 \frac{n_1 \bar{V}_1 + n_2 \bar{V}_2}{\bar{V}_2} = \phi_2 \frac{\bar{V}_1}{\bar{V}_2} = \frac{\phi_2}{\phi_1} \frac{1}{x}
\]

Substituting this value of \(\frac{n_2}{n_1}\) into expression for \(\mu_1 - \mu_1^0\) and writing \(\phi_1 = 1 - \phi_2\) we obtain

\[
\mu_1 - \mu_1^0 = RT \left[ \phi_2 \left( 1 - \frac{1}{x} \right) + \ln(1 - \phi_2) + \chi_1 \phi_2^2 \right]
\]

8. According to eqn. 16.55, the osmotic pressure of a solution is:

\[
\pi = \frac{RT}{\bar{V}_1} \left[ \frac{\phi_2}{x} + \left( \frac{1}{2} - \chi_1 \right) \phi_2^2 + \frac{1}{3} \phi_2^4 + \ldots \right]
\]

where \(\bar{V}_1\) and \(\bar{V}_2\) are partial molar volumes, \(\phi_2\) is the volume fraction of solute, \(x\) is the molar volume ratio \(\left( \frac{\bar{V}_2}{\bar{V}_1} \right)\) and \(\chi_1\) is a dimensionless interaction constant.

\[
\phi_2 = \frac{n_2 \bar{V}_2}{V_{\text{solution}}} = \frac{m_2 \bar{V}_2}{M_2 V_{\text{solution}}} = \frac{\bar{V}_2}{M_2}
\]

Substituting and rearranging

\[
\pi = \frac{RT}{c M_2} \left[ \frac{1}{x} \bar{V}_2 \bar{V}_2 \bar{V}_1 M_2 + \frac{1}{3} \bar{V}_1 \bar{V}_1 M_1 c^2 + \ldots \right]
\]

Now \(x = \left( \frac{n_2}{n_1} \right) = \left( \frac{\bar{V}_2}{\bar{V}_1} \right)\) and the partial specific volume \(\bar{V}_2\) is related to the partial molar volume \(\bar{V}_2\) by \(\bar{v}_2 = \frac{\bar{V}_2}{M_2}\). Substituting and rearranging gives

\[
\pi = \frac{RT}{c M_2} \left[ 1 + \left( \frac{1}{2} - \chi_1 \right) \frac{\bar{V}_2^2 M_2}{\bar{V}_1} c^2 + \frac{1}{3} \frac{\bar{V}_2^3 M_2}{\bar{V}_1} c^2 + \ldots \right]
\]
which is eqn. 16.57.

9. Assuming that toluene is a "good" solvent for polystyrene, eqns. 16.59 and 16.60 can be written

\[
\frac{g\Gamma^2}{\Gamma} = \frac{\Gamma}{4} = \frac{\bar{v}_2 M_2}{3 V_1} \frac{\bar{V}_1}{\bar{v}_2 M_2} \left( \frac{1}{2} \chi_i \right) \quad \text{or} \quad \left( \frac{1}{2} - \chi_i \right) = \frac{4 \bar{v}_2^3}{3 \Gamma}
\]

\( \bar{v}_2 \), the partial specific volume of polystyrene in toluene is (inadvertently) not specified in this problem. According to problem 16 in chapter 14, \( \bar{v}_2 \) for polystyrene in toluene is: \( \bar{v}_2 = 0.91 \) cm\(^3\)/gram.

Then, \( \chi_i = \frac{1}{2} - \frac{(4)(0.91)}{(3)(219)} = 0.494 \)

10. See p. 424

11. According to eqn. 16.55

\[
\pi = \frac{RT}{V_1} \left[ \frac{\phi_2}{x} + \left( \frac{1}{2} - \chi_i \right) \phi_1^2 + \frac{1}{3} \phi_1^3 + \ldots \right]
\]

assume \( T = 298 \) K

\[
\phi_2 = \frac{m_2 \bar{v}_2}{m_1 \bar{v}_1 + m_2 \bar{v}_2} = \frac{\left( 50 \times 10^{-3} \right)}{\left( 1.20 \right)} = 0.0413
\]

\[
\chi = \frac{V_{2,\text{molar}}}{V_{1,\text{molar}}} = \frac{M_2 \rho_2}{M_1 \rho_1} = \frac{(3.52 \times 10^3)(1.49)}{(119.5)(1.20)} = 3.66 \times 10^3
\]
$$\overline{V}_i = \frac{M_i}{\rho_i} = \frac{119.5}{1.49} = 80.2 \text{ cm}^3/\text{mole}, \text{ and from table 16.1, } \chi_i = 0.377$$

so

$$\pi = \frac{(82.05)(298)}{(80,2)} \left[ \frac{0.0413}{3.66 \times 10^3} + (0.5-0.377)(0.0413)^2 + \frac{(0.0413)^3}{3} + ... \right] \text{ atm}$$

$$\pi = 7.46 \times 10^{-2} \text{ atm} = 77.1 \text{ g/cm}^2$$

12. In the athermal case, the heat of mixing is zero, which makes $\chi_i$ as well. This low value of $\chi_i$ increases the second virial coefficient $A_2 = (1/2 - \chi_i)$, which increases $\pi$.

13. $\Theta = 178.3^\circ\text{C}$ and $\Psi_i = 0.67$.

14. $\Delta H_u = 2,580 \text{ cal/mol}, \chi_i = 1.5$, and $B = -7.4 \text{ cal/cm}^3$.

15. 6.28.

16. $\alpha = 0.264$ and $CR = 5.80$.

17. $-1.06 \times 10^{-1} \text{ deg}^{-1}$.

18. $0.90 \times 10^{-3} \text{ deg}^{-1}$.
CHAPTER 17

5. As examples, the first two entries in the Table give $T_g/T_m=0.73$ and 0.70, respectively.

6. 50%.

7. -17°C, in good agreement with the observed value of -20°C.

CHAPTER 18

3. Eight atoms gives seven skeletal bonds, five of which affect the spatial configurations: $2^5=32$.

6. Unity; note that 90° is the average of the permitted range 0-180°, so obtaining the same value as for the freely-jointed chain could have been expected.

7. CR = 3.32.

8. CR = 4.66.

9. States are equally spread over the range 0-360°, and are of equal energy, so $<\cos\phi> = 0$ and the stiffening ratio = 1.0.

10. Diverges to infinity: $r^2 \propto n^2$ and $m^2 \propto n$, so CR ratio $\propto n$, and diverges as n increases.

11. Differentiate the function with respect to $r$, set the result to zero, and choose the non-trivial root.

112
12. Helical regions would be of low energy and high spatial extension, so raising the temperature would introduce non-helical sequences of lower spatial extension, and the dimensions would decrease.

13. \( Z = 20. \)

14. Only non-zero element would be a unity in the 2,2 position.

15. Dipole vectors are more likely to be in subtractive orientations than are skeletal bond vectors.

16. It would increase, since this is a revision toward the highly extended trans states.

17. Chains are either all gauche\(^+\) or gauche\(^-\).

CHAPTER 20

3. 17.9°C.

CHAPTER 21

7. A. \( 2C_1 = 0.0736 \text{ N mm}^{-2} \), and \( 2C_2 = 0.0495 \text{ N mm}^{-2} \).
   B. \( \mu/V = 2.96 \times 10^3 \text{ mols cm}^{-3} \).
   C. \( M_e = 15.5 \times 10^3 \text{ g mol}^{-1} \).

8. \( f^* = (2kT/V)(\alpha - \alpha^3) \).
9. $f_e/f = 0.035$, and $d\ln<r^2>_0/dT = 0.10 \times 10^{-3} \text{deg}^{-1}$.

10. $u/2V^* = 3.7 \times 10^{-5} \text{ mols cm}^{-3}$.

11. $f = 1.33 f_5$.

CHAPTER 22

6. The propylene "irregularities" suppress the crystallinity that would otherwise prevent high deformability with recoverability.

7. 4950 and 450 g/mol.

CHAPTER 23

9. The conductivity would be both intramolecular (along the chains) and intermolecular (hopping between chains), and the balance between the two mechanisms would likely depend significantly on the lengths of the chains.

10. Ease of processibility and robustness.

11. Changing the output of a laser to a frequency more appropriate for a particular application.