Appendices

Encore

From Smoothing to Fuguing

Skinner's Constant:

That quantity which, when multiplied by, divided by,
added to, or subtracted from the answer you got,
gives you the answer you should have gotten.

A.1 Dilatometry: Experiment and Theory

A.1.1 Experimental Procedures for Dilatometry

A seed latex is prepared by conventional emulsion polymerization. It must be designed to have a well-defined particle size (*i.e.* a narrow particle size distribution) and is generally dialyzed to remove residual initiator and excess surfactant. Alternatively, if the surfactant level is sufficiently low, the reaction temperature may be maintained such that residual initiator decomposes.

The seed may then be diluted to the desired concentration, additional surfactant added (if required) and then the latex is transferred to the dilatometer. This mixture is then warmed and stirred under reduced pressure, backfilling with high-purity nitrogen. To ensure that bubbles do not form on heating to reaction temperature (especially with an azo-initiator that will lead to an increase in the N_2 concentration over time), care must be taken to reduce the gas concentration in the reaction mixture.

Monomer (inhibitor removed) is added to the dilatometer and degassing is continued. If the monomer is degassed prior to loading into the dilatometer and transferred by means of a glass syringe to minimize entraining of air, little degassing is required following addition; as an additional benefit, the mass of monomer used may be measured by the difference in weight of the syringe assembly.

Additional degassed water is then added to the system and the mixture brought up to reaction temperature using a circulating water-bath. Initiator is dissolved in degassed water to a predetermined concentration and further degassed before being loaded into a syringe. The syringe may be placed into the top of the water-bath to bring the initiator solution to temperature.

Once the reaction mixture has reached the desired temperature, the mixture may protrude into the capillary. Additional degassed water should be added so that, when the initiator solution is added, the meniscus will be at a height suitable for dilatometric monitoring of the reaction. This degassed water and the initiator solution are delivered to the dilatometer by means of a thin polyethylene tube attached to a needle and syringe.

After the initiator solution is added, a small amount of a light oil (*e.g.* dodecane or hexadecane) is added to the top of the meniscus. Approximately 1 cm of the oil is sufficient to ensure that the meniscus descends evenly; a water meniscus tends to be quite uneven in its movement down the capillary, rather than remaining level throughout the reaction.

The autodilatometer may then be engaged, tracking the last of the thermal expansion due the addition of the initiator and then the commencement of polymerization. The autodilatometer may follow the meniscus by measuring the intensity of the light that passes through the capillary. The greater refractive index of the oil compared to the air means that the light intensity is greater below the meniscus than above.

Care needs to be taken to protect the dilatometer from draughts, such as those from air conditioners or due to fumehoods, as well as temperature fluctuations caused by air conditioner cycling. Uniform lighting conditions will also improve the data collected, as stray light will cause the autodilatometer to register a change in the meniscus height; indeed, it is possible to estimate when sunrise occurred in the dilatometry data from some overnight reactions. Wrapping the assembly in cloth (*e.g.* using a lab-coat) is sufficient to ameliorate many of these problems.

A.1.2 Obtaining Data from Dilatometry

A.1.2.1 Volume Changes

The volume change in the dilatometer provides a way of monitoring the progress of the reaction. It must be realized that the only experimental measurement made is the height of the meniscus in the dilatometer: every quantity beyond that is *calculated* based on various assumptions.

The height of the meniscus is measured as a function of time giving a discrete function h_t. It is assumed that the inside of the capillary is uniform in cross-section with cross-sectional area πr_c^2, giving an equivalent internal radius for the capillary of r_c. If the size and shape (*i.e.* volume) of the glassware stays the same (and small temperature fluctuations may invalidate this), the volume of the reaction, V_t, is given by:

$$V_t = V_0 - \pi r_c^2 h_t \tag{A.1}$$

where the initial height in the capillary, h_0, is taken to be the zero of height, with a drop in the meniscus being an increase in h_t.

If the temperature of the reaction mixture is constant *and* no bubbles form during the course of the reaction *and* no leaks occur from the capillary/dilatometer joint, then only the chemical reactions being undertaken inside the dilatometer lead to a change in the volume of the reaction mixture. These are perhaps the most difficult conditions to meet; while the emergence of bubbles or leaks from the capillary may be prevented through good experimental procedures, slight temperature variations may lead to a significant change in the reaction volume.

Assuming further that the density change from monomer to polymer is a step function (*i.e.* that aqueous and non-aqueous oligomeric species have the density of polymer), the fractional conversion, x, is given by:

$$x_t = \frac{h_t}{h_{100}} \tag{A.2}$$

where h_{100} is the height drop for 100% conversion. Note that the above assumption about the density of oligomeric species is likely to be inconsequential for most systems, where the number concentration of oligomers is quite small compared to the number of long, dead chains. In living systems, however, there is a tendency to form a very large number of living oligomers at the start of the reaction, which may make this assumption more problematic. Moreover, with only dilatometry data, it is not possible to break the cyclic dependency between chain-length, density and conversion to obviate this problem, even if data for the densities of the oligomeric species were available.

The maximum height drop for the reaction, h_{100}, may be calculated from the mass of monomer added to the system, m_0, and the densities of monomer and polymer, ρ_m and ρ_p respectively. It is also convenient to introduce the contraction factor c_F for the system.[1]

$$c_\mathrm{F} = \frac{1}{\rho_\mathrm{m}} - \frac{1}{\rho_\mathrm{p}} \tag{A.3}$$

$$h_{100} = \frac{m_\mathrm{m} c_\mathrm{F}}{\pi r_\mathrm{c}^2} \tag{A.4}$$

A.1.2.2 Rate of Polymerization

The rate of polymerization may be determined from conversion *vs* time data, without any mechanistic assumptions. The rate of change in conversion is simply dx/dt. Similarly the rate of polymerization, R_p, is given by:

$$R_\mathrm{p} = \frac{\mathrm{d}x}{\mathrm{d}t} n_\mathrm{m}^0 \tag{A.5}$$

where n_m^0 is the initial amount of monomer per unit volume of aqueous phase in the system:

$$n_\mathrm{m}^0 = \frac{n_\mathrm{m}}{V_\mathrm{aq}} \tag{A.6}$$

In many emulsion polymerization systems, the only parameter that removes the experiment-to-experiment variation in particle number and mass of monomer added is $\bar{n}$, the average number of radicals per particle.

The general relationship for the rate of conversion is:[1]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_\mathrm{p} C_\mathrm{p} \bar{n} N_\mathrm{c}}{n_\mathrm{m}^0 N_\mathrm{A}} \tag{A.7}$$

where k_p is the second-order rate coefficient for the propagation of the polymeric radical, C_p is the concentration of monomer in the particles and N_A is Avogadro's constant.

It should be noted that this relationship is true for systems in Intervals I, II and III. However, in each of these intervals, some of the parameters on the right-hand side may not be constant. For example, during Intervals I and II, C_p is equal to the saturation concentration of monomer in polymer, C_p^{sat}; during Interval I, N_c will vary due to micellar (and possibly homogeneous) nucleation.

A.1.2.3 General Analysis of Data

With a simple model for the behavior of C_p as a function of conversion, it is possible to directly extract $\bar{n}$ from dx/dt data (assuming that the gel-effect does not begin to alter k_p, of course). For a sparingly water soluble monomer (such as styrene), the amount of monomer in the aqueous phase is negligible; thus, once Interval III is entered, C_p may be assumed to be linearly dependent on conversion. Taking $x^{II/III}$ to be the critical conversion at which the system changes from Interval II to Interval III (which may be a theoretical, negative conversion), C_p may be calculated to be:[1,2]

$$C_p = \min\left(C_p^{sat}, \frac{C_p^{sat}}{1 - x^{II/III}}\right) \tag{A.8}$$

Using the above general expression for dx/dt, the calculated value of C_p at each conversion and literature values for all other variables, it is possible to estimate $\bar{n}$.

A.1.2.4 Interval II Analysis of Data

This method only works for the system in Interval II, but is still useful. In Interval II, the rate of conversion may be rewritten as:

$$\frac{dx}{dt} = \frac{k_p C_p^{sat} \bar{n} N_c}{n_m^0 N_A} = A\bar{n} \tag{A.9}$$

where A is a constant calculable from the experimental conditions and literature values:

$$A = \frac{k_p C_p^{\mathrm{sat}} N_c}{n_m^0 N_A} \tag{A.10}$$

The linear dependence of $\bar{n}$ on dx/dt allows this value to be quite easily calculated and, indeed, the veracity of this model to be quickly tested. A plot of x vs t should have a significant linear region (the steady state region of Interval II), the slope of which may be used to calculate $\bar{n}$. Alternatively, numerical differentiation may be employed.

A.1.2.5 Interval III Analysis of Data

Similar to the Interval II method, this approach only works for the system in Interval III, but is still useful. In Interval III, using the model for C_p with a sparingly water soluble monomer outlined above, the dependence of dx/dt on $\bar{n}$ is no longer linear. Instead, the relationship should be written as:[2]

$$\frac{\mathrm{d}\left[-\ln(1-x)\right]}{\mathrm{d}t} = \frac{k_p C_p^{\mathrm{init}} \bar{n} N_c}{n_m^0 N_A} = A\bar{n} \tag{A.11}$$

$$\frac{\mathrm{d}\left[-\ln(1-x)\right]}{\mathrm{d}t} = \frac{k_p \bar{n}}{V_s N_A} = A\bar{n} \tag{A.12}$$

where C_p^{init} is the initial value of C_p if the experiment began in Interval III and A is a constant calculable from the experimental conditions and literature values:

$$A = \frac{k_p C_p^{\mathrm{init}} N_c}{n_m^0 N_A} \tag{A.13}$$

$$A = \frac{k_p}{V_s N_A} \tag{A.14}$$

If the experiment did not begin in Interval III, then one of two approaches must be taken in order to use this analysis method for the Interval III section of the data: either a new conversion parameter, x_3, must be used that corresponds to the fractional conversion within Interval III, or the value of C_p^{init} must be scaled up.

If the new conversion parameter is to be used, $x_3 = 0$ should be either within Interval III or at $x^{\mathrm{II/III}}$, the critical conversion for the transition from Interval II to Interval III. The above equations should then be used replacing x with x_3. Of course values of $x_3 < 0$ have no physical meaning as do any data calculated using those values.

The alternative method of analysis is to scale up value of $C_{\mathrm{p}}^{\mathrm{init}}$ to physically unreasonable values. This is effectively the same as the previous method, but is computationally easier as it does not require the recalculation of conversion coordinates. In this case, $C_{\mathrm{p}}^{\mathrm{init}}$ is taken to be the value of C_{p} at $x = 0$ that would have been in the experiment, if there were no saturation limit $\mathrm{C}_{\mathrm{p}}^{\mathrm{sat}}$:

$$C_{\mathrm{p}}^{\mathrm{init}} = \frac{C_{\mathrm{p}}^{\mathrm{sat}}}{1 - x^{\mathrm{II/III}}} \tag{A.15}$$

As for the Interval II analysis described above, a plot of $-\ln(1-x)$ should produce a significant linear region in the Interval III area.

A.1.2.6 Rates of Entry and Exit: Approach to Steady State

The rates of entry and exit may be determined from the approach to the steady state of polymerization. For a zero-one system in Interval II, the entry and exit rate coefficients may be determined by looking at the slope and intercept of the extrapolation of the straight-line section of the x vs t plot.

If the line-of-fit through the straight-line section of the x vs t plot has the form:

$$y = a + bx \tag{A.16}$$

then the pseudo-first-order entry rate coefficient, ρ, is given by:

$$\rho = \frac{b}{a}\left(\bar{n}_0 - \frac{b}{a}\right) \tag{A.17}$$

where $\bar{n}_0$ is the initial value of $\bar{n}$. From this value, the first-order exit rate coefficient, k, may be calculated from:

$$k = \frac{A}{b}\rho - 2\rho \tag{A.18}$$

where A is the Interval II constant as above.

A.1.3 Obtaining Kinetic Parameters from Relaxations

In a polymerization obeying Limit 3 or pseudo-bulk kinetics, termination occurs predominantly between two polymeric radicals within the same particle. This is in contrast to Limit 1 and Limit 2 kinetics in which termination is predominantly as a result of transfer to monomer followed by exit of the monomeric radical. This radical may then terminate in the aqueous phase (Limit 1) or in another particle following subsequent re-entry of the monomeric radical (Limit 2).

Each of these limits has a different kinetic scheme; hence, the mathematical description of the number of radicals in each particle is rather different.

While systems that obey Limit 1 or Limit 2 kinetics are zero-one in nature,[1] systems that are in Limit 3 are not. Rather, they are pseudo-bulk systems; there are no effects due to the compartmentalization of radicals. Limit 3 systems may have a low value for $\bar{n}$, the average number of radicals per particle, but will not display a limiting value of $\bar{n} = ½$ for increasing initiator concentration, as is seen in zero-one systems.[1]

A.1.3.1 Limit 3: Intra-particle Termination is Rate-Determining

The kinetics of a Limit 3 reaction are described by the pseudo-bulk equation:[3,4]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho - 2c\bar{n}^2 \tag{A.19}$$

where ρ is the pseudo-first-order rate coefficient for radical entry into the particles and c is the pseudo-first-order rate coefficient for radical termination. Here, c is given by the average second-order rate coefficient for termination, $\langle k_t \rangle$, and the swollen volume of the particles, V_s:

$$c = \frac{\langle k_t \rangle}{N_A V_s} \tag{A.20}$$

The pseudo-bulk equation (Eq. A.19) may be solved for the situation where a system is moving from an initial steady state (denoted by subscripts "i" in the following expressions) to a final steady state (denoted "f").

Firstly taking the reciprocal of Eq. A.19:

$$\frac{\mathrm{d}t}{\mathrm{d}\bar{n}} = \frac{1}{\rho_f - 2c\bar{n}^2} \tag{A.21}$$

and then integrating by the method of partial fractions, the following expression is obtained:

$$t = \frac{1}{2\bar{n}_f c} \left\{ \frac{1}{2} \ln\left(\frac{|\,\bar{n}_f + \bar{n}\,|}{|\,\bar{n}_f - \bar{n}\,|} \right) \right\} + D \tag{A.22}$$

where $\bar{n}_f$ is the value of $\bar{n}$ in the new steady state and D is a constant of integration to be determined later.

There are two different mathematical possibilities that may arise from Eq. A.22, corresponding to two different experimental situations:

- **Case 1:** $\bar{n}_f < \bar{n} < \bar{n}_i$

  This corresponds to a stepwise reduction in initiation (*e.g.* due to removal from a γ-source)

- **Case 2:** $\bar{n}_f > \bar{n} > \bar{n}_i$

  This corresponds to a stepwise increase in initiation (*e.g.* due to insertion into a γ-source)

These two cases will be dealt with in turn.

A.1.3.2 Relaxations

In the case where $\bar{n}_\mathrm{f} < \bar{n} < \bar{n}_\mathrm{i}$, such as during the approach to steady state in a relaxation following removal from a γ-source, the following relation holds:

$$\frac{|\bar{n}_\mathrm{f} + \bar{n}|}{|\bar{n}_\mathrm{f} - \bar{n}|} = -\frac{\bar{n}_\mathrm{f} + \bar{n}}{\bar{n}_\mathrm{f} - \bar{n}} \tag{A.23}$$

Additionally, $\bar{n}_\mathrm{f} = \bar{n}_\mathrm{sp} = (\rho_\mathrm{sp}/2c)^{1/2}$ is the value of $\bar{n}$ that may be attributed to spontaneous (thermal) polymerization (*i.e.* the steady-state solution of Eq. A.19 taking the special case where $\rho_\mathrm{f} = \rho_\mathrm{sp}$). The following final relation is found by further simplification:

$$\bar{n} = \frac{\bar{n}_\mathrm{sp}}{\tanh\left(2\bar{n}_\mathrm{sp}ct + D_1\right)} \tag{A.24}$$

The constant of integration, D_1, may be determined from Eq. A.24 using the initial condition that $\bar{n}(t{=}0) = \bar{n}_\mathrm{i}$, giving:

$$D_1 = \tanh^{-1}\left(\frac{\bar{n}_\mathrm{sp}}{\bar{n}_\mathrm{i}}\right) \tag{A.25}$$

A.1.3.3 Insertions

In the case where $\bar{n}_\mathrm{f} > \bar{n} > \bar{n}_\mathrm{i}$, which occurs during the approach to steady state following an insertion into a γ-source, the following relation holds:

$$\frac{|\bar{n}_\mathrm{f} + \bar{n}|}{|\bar{n}_\mathrm{f} - \bar{n}|} = \frac{\bar{n}_\mathrm{f} + \bar{n}}{\bar{n}_\mathrm{f} - \bar{n}} \tag{A.26}$$

The following final relation is found by further simplification, using $\bar{n}_\mathrm{f} = (\rho_\mathrm{f}/2c)^{1/2}$, giving the general steady-state solution of Eq. A.19:

$$\bar{n} = \bar{n}_\mathrm{f}\tanh\left(2\bar{n}_\mathrm{f}ct + D_2\right) \tag{A.27}$$

where the constant of integration, D_2, may once again be determined from the initial condition that $\bar{n}(t=0) = \bar{n}_\mathrm{i}$:

$$D_2 = \tanh^{-1}\left(\frac{\bar{n}_\mathrm{i}}{\bar{n}_\mathrm{f}}\right) \tag{A.28}$$

A.1.4 Data Processing for Dilatometry

A.1.4.1 Data Smoothing

The algorithm presented here was designed to smooth a set of irregularly spaced data points. Note that most other smoothing algorithms do not allow for data points to be at irregular spacing.[5]

Given a set of points (x_i, y_i) and a normal distribution function $n(x)$, with mean $\mu = 0$ and standard deviation σ, the smoothed set ($x_{\mathrm{s},i}$, $y_{\mathrm{s},i}$) may be determined by an algorithm using the addition-assignment operator "+=", as shown in Scheme A.1.

```
$\forall x_i$
        $\forall x_j$:  $x_i - 3\sigma \le x_j \le x_i + 3\sigma$
                $y_\mathrm{s}$ += $n(x_j - x_i)y_j$
                $w$ += $n(x_j - x_i)$
        $y_{\mathrm{s},i} = y_\mathrm{s}/w$
```

Scheme A.1: The Gaussian data-smoothing algorithm for irregularly spaced data.

In Scheme A.1, y_s is a temporary variable and w is the sum of the weightings given to each of the points which is used to normalize the smoothed value (which also means that the normal function $n(x)$ needs only to be Gaussian in shape and not necessarily normalized to unit area).

This algorithm may be expressed mathematically as:

$$y_{\mathrm{s},i} = \sum_{x_j \in [x_i \pm 3\sigma]} \frac{n(x_j - x_i)y_j}{n(x_j - x_i)} \tag{A.29}$$

In practice, the use of smoothed data in the fitting of relaxation curves is usually not advisable, as the smoothing process will tend to obscure interesting features of the data, such as the beginning of a relaxation. However, data smoothing is useful in the case where visual inspection of the derivative is to be performed, such as the $\overline{n}$ *vs* t plots presented in Chapter 7.

A.1.4.2 Numerical Differentiation

The numerical derivative of the height *vs* time data obtained from dilatometry experiments is used in the determination of the rate of polymerization and $\overline{n}$.

Given a stream of points (x_i, y_i), the numerical derivative function (x_i', y_i') may be approximated by the following three-point derivative:

$$x_i' = x_i \tag{A.30}$$

$$y_i' = \frac{3s_{\mathrm{xy}} - s_{\mathrm{x}}s_{\mathrm{y}}}{3s_{\mathrm{xx}} - s_{\mathrm{x}}^2} \tag{A.31}$$

where:

$$s_{\mathrm{x}} = x_{i-1} + x_i + x_{i+1} \tag{A.32}$$

$$s_{\mathrm{y}} = y_{i-1} + y_i + y_{i+1} \tag{A.33}$$

$$s_{\mathrm{xx}} = x_{i-1}^2 + x_i^2 + x_{i+1}^2 \tag{A.34}$$

$$s_{\mathrm{xy}} = x_{i-1}y_{i-1} + x_iy_i + x_{i+1}y_{i+1} \tag{A.35}$$

Note that this numerical derivative is undefined when $3s_{\mathrm{xx}} - s_{\mathrm{x}}^2 = 0$.

A.2 Particle Growth Kinetics & Dilatometry

Various different limits to the general Smith–Ewart equations[6] may be derived. While these limits have formal mathematical bases, they also have distinct physical meanings. Historically, they have been classified in terms of the physical processes that may be attached to the events involved.[1] While such classification is highly instructive in conventional emulsion polymerization systems, its meaning is unclear in the context of RAFT-mediated systems.

The three groups of limits are those for: complete aqueous-phase termination of exited monomeric radicals (Limit 1), negligible aqueous-phase termination of exited monomeric radicals (Limit 2) and rapid radical exchange between particles such that compartmentalization is no longer evident (Limit 3). Historically, Limits 1 and 2 have been compactly described in terms of a fate parameter α.[1,7]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho + \alpha k\bar{n})(1 - 2\bar{n}) - k\bar{n} \tag{A.36}$$

Importantly, the value of α is often a function of $\bar{n}$ (since the aqueous-phase kinetics are dependent on the rate of radical exit), making this treatment unsuitable for situations in which the fate of the exited radicals is not in one of the limiting cases (*i.e.* the use of α is only valid for $\alpha \in \{-1, 0, 1\}$). In cases where α is a function of $\bar{n}$, a full treatment of the aqueous-phase kinetics is also required. The use of α is thus only a convenient notational tool for the cases where $\alpha \in \{-1, 0, 1\}$, such as in the limits described below. Note that, in Eq. A.36, the various values of α include at least a first-order dependence on $\bar{n}$ and optionally a second-order dependence.

A.2.1 Limit 1: Complete Aqueous-Phase Termination

The simplest of the limits are the ones where all desorbing monomeric radicals undergo aqueous-phase termination. Three limits have been identified within this category:[1]

A.2.1.1 Limit 1a & Limit 1c

These limits are mathematically equivalent, although they have completely different physical interpretations. In Limit 1a, the monomeric radicals undergo homotermination in the aqueous phase. In Limit 1c, however, the initiator has such a low efficiency that the effect of heterotermination between desorbed radicals and initiator-derived radicals on the concentration of the initiator-derived radicals is negligible.

In both cases, the time evolution may be described by:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{spon}})(1 - 2\bar{n}) - k_{\mathrm{ct}}\bar{n} \qquad \text{(A.37)}$$

which gives $\alpha = 0$ and $k = k_{\mathrm{ct}}$ in Eq. A.36; $k_{\mathrm{ct}} = k_{\mathrm{tr}}C_{\mathrm{p}}P(\mathrm{exit})$, where $P(\mathrm{exit})$ is the probability of exit, given by $P(\mathrm{exit}) = k_{\mathrm{dM}} / (k_{\mathrm{p}}^{1}C_{\mathrm{p}} + k_{\mathrm{dM}})$.

A.2.1.2 Limit 1b

In this limit, it is assumed that the initiator efficiency in the absence of desorbed radials is 100% and all termination of exiting radicals occurs by heterotermination with initiator-derived species. This gives a second-order dependence on $\bar{n}$:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{spon}})(1 - 2\bar{n}) - 2k_{\mathrm{ct}}\bar{n} + 2k_{\mathrm{ct}}\bar{n}^{2} \qquad \text{(A.38)}$$

which gives $\alpha = -1$ and $k = k_{\mathrm{ct}}$ in Eq. A.36.

A.2.2 Limit 2: Negligible Aqueous-Phase Termination

In the case where desorbing monomeric radicals undergo negligible aqueous-phase termination, it may be expected that these radicals will eventually enter a different particle. Once a radical has re-entered, it may or may not re-escape. The two limits within this category make use of this behavior.

A.2.2.1 Limit 2a

In Limit 2a, there is minimal re-escape of a radical. Once a monomeric radical has re-entered, it will either propagate (hence be so water insoluble so as to not escape) or terminate with another radical in the particle. The nature of this complete re-entry gives a condition on this limit of $\mathrm{k}_{\mathrm{dM}}\bar{n} \ll k_{\mathrm{p}}^{1}C_{\mathrm{p}}$:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{spon}})(1 - 2\bar{n}) - k_{\mathrm{cr}}\bar{n}^{2} \tag{A.39}$$

which gives $\alpha = 1$ and $k = k_{\mathrm{cr}}$ in Eq. A.36. Note that $k_{\mathrm{cr}} = k_{\mathrm{tr}}C_{\mathrm{p}}P(\mathrm{exit})$, where $P(\mathrm{exit})$ is the probability of exit, given by $P(\mathrm{exit}) = k_{\mathrm{dM}} / (k_{\mathrm{p}}^{1}C_{\mathrm{p}} + k_{\mathrm{dM}})$. Using the previous relation $\mathrm{k}_{\mathrm{dM}}\bar{n} \ll k_{\mathrm{p}}^{1}C_{\mathrm{p}}$, the expression for k_{cr} may be further simplified to $k_{\mathrm{cr}} = k_{\mathrm{tr}}k_{\mathrm{dM}} / k_{\mathrm{p}}^{1}$.

A.2.2.2 Limit 2b

If a re-entering radical will always re-escape rather than propagate (*i.e.* $\mathrm{k}_{\mathrm{dM}}\bar{n} \gg k_{\mathrm{p}}^{1}C_{\mathrm{p}}$), the desorbed radical will continually re-escape/re-enter until it enters a particle already containing a radical (*i.e.* $P(\mathrm{exit}) = 1$ in the absence of a second radical). Thus, radical loss in the system has only a first-order dependence on $\bar{n}$:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{spon}})(1 - 2\bar{n}) - 2k_{\mathrm{tr}}C_{\mathrm{p}}\bar{n} \tag{A.40}$$

which gives $\alpha = 0$ and $k = 2k_{\mathrm{tr}}C_{\mathrm{p}}$ in Eq. A.36.

A.2.3 Limit 3: Rapid Exchange of Radicals

As opposed to the previous two sets of limits, Limit 3 systems do not obey zero-one kinetics. The requirements for a Limit 3 system are that the desorbed radical is able to undergo rapid re-entry and re-escape but that termination is not pseudo-instantaneous (as was assumed in the zero-one systems described above). Indeed, it is assumed that termination is slow enough that the radicals are able to grow to beyond the entanglement length before termination occurs. The loss of compartmentalization in the system and the long length of the radicals involved leads to the overall kinetics being that of a bulk system. Thus, the pseudo-bulk equation may be applied to such systems:[4]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho - 2c\bar{n}^2 \tag{A.41}$$

This kinetic scheme is purely second-order on $\bar{n}$, hence it cannot be described in terms of the fate parameter in Eq. A.36.

A.2.4 Pseudo-bulk Systems with Few Radicals

In pseudo-bulk systems where $\bar{n}$ is low ($\bar{n} \ll 1$), the population of particles with two radicals in the particle is quite small, although it is not required to be zero by the zero-one assumption. In the evaluation of the kinetics of the system studied by Maeder and Gilbert[8] (Chapter 5), it became necessary to estimate how much polymer was produced in a two-radical environment (such that termination would be the primary chain-stopping reaction) and how much was produced in a single radical environment (such that transfer to monomer was the primary chain-stopping reaction). What follows is an approximate treatment of the Smith–Ewart theory for radical population balance,[6] within the pseudo-bulk regime.

Consider a pseudo-bulk system with the number of particles containing i radicals denoted N_i. The processes of entry, ρ, and termination, c, occur, giving the pseudo-bulk equation:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho - 2c\bar{n}^2 \tag{A.42}$$

which in a steady-state, gives:

$$\bar{n} = \left(\frac{\rho}{2c}\right)^{½} \tag{A.43}$$

It must be recognized that, in the low-$\bar{n}$ limit of pseudo-bulk kinetics, this relation will be somewhat in error due to the closure relation used its derivation (see Chapter 6 or the work of Ballard *et al.*[4]); however, for the purposes of this approximation it is sufficiently precise.

Taking the population balance for the N_0 particles gives:

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = cN_2 - \rho N_0 + kN_1 \tag{A.44}$$

Taking the usual approximation[4,9] of $\rho = \rho_1 + \alpha k\bar{n}$ with $\alpha = 1$ and noting that if $\bar{n} \ll 1$ then $\bar{n} \approx N_1$ (with the population of N_i normalized to $N_c = 1$) gives a steady state:

$$\frac{N_0}{N_2} = \frac{c}{\rho_1} \tag{A.45}$$

or simply:

$$\frac{N_0}{N_2} \approx \frac{2}{\bar{n}^2} \tag{A.46}$$

Consider further the actual calculation of $\bar{n}$ in terms of the populations of N_i particles:

$$\bar{n} = \frac{N_1 + 2N_2 + \sum_{i=3}^{\infty} iN_i}{N_0 + N_1 + N_2 + \sum_{i=3}^{\infty} N_i} \tag{A.47}$$

In the low-$\bar{n}$ limit, the number of particles containing a large number of radicals is much less than the population of particles containing no radicals, and $N_1 \gg N_2$ (as used above), hence:

$$\bar{n} \approx \frac{N_1}{N_0} \tag{A.48}$$

Combining Eq. A.46 and A.48, the following approximate relation is obtained (neglecting the factor of two in Eq. A.46 for the purposes of this approximate argument):

$$N_0{:}N_1{:}N_2 \approx 1{:}\bar{n}{:}\bar{n}^2 \tag{A.49}$$

which is, at least, a reasonable approximation to estimate that the number of particles containing two radicals. As reported in Chapter 5, in the system studied by Maeder and Gilbert,{Maeder, 1998 #1428} the number of particles containing two radicals is vanishingly small in the low-$\overline{n}$ case.

A.3 Aqueous-Phase Kinetics

A.3.1 Maxwell–Morrison Model for Entry of Oligomeric Radicals

The Maxwell–Morrison model for the entry of oligomeric radicals into particles[10] provides a useful model for estimating frequency of the entry of radicals. It has been experimentally verified for a number of different systems.[10-15] Useful parameters that may be obtained from this model include the pseudo-first-order rate coefficient for radical entry into particles, ρ, and the initiator efficiency, f. For both these parameters, it is computationally simplest to assume that the aqueous-phase radical concentrations are in steady state.

A.3.1.1 Aqueous-Phase Radical Reactions

The decomposition of initiator forms radicals that may react with aqueous monomer. For many common initiators (such as potassium persulfate) the decomposition process forms two identical radicals. Since decomposition is slow and the species under consideration are quite reactive, their concentrations are typically quite low and, thus, the steady state approximation may be used in determining the concentration of the initiator fragments.[1,10]

In the description of these reactions, it is assumed that the decomposed initiator radicals, $\mathrm{I}^\bullet$, will have propagated before they are able to undertake termination reactions with other radical species. Thus, the reactions involved at this stage are:

decomposition $$\mathrm{I{-}I} \xrightarrow{k_\mathrm{d}} 2\,\mathrm{I}^\bullet \qquad \text{(A.50)}$$

addition $$\mathrm{I}^\bullet + \mathrm{M} \xrightarrow{k_\mathrm{pI}} \mathrm{IM}^\bullet \qquad \text{(A.51)}$$

Previous studies have shown that the termination and propagation rate coefficients for $\mathrm{I}^\bullet$ are quite similar in magnitude;[1,10] however, the concentration of monomer in the aqueous phase is typically orders of magnitude greater than the concentration of radicals.

Thus, termination of the $I^\bullet$ species is thus considered to be negligible. Eq. A.50 and A.51 may be reduced to:

$$\text{I–I} \xrightarrow[\text{M}]{k_\text{d}} 2\ \text{IM}^\bullet \tag{A.52}$$

The remaining reactions for the oligomeric radicals of degree of polymerization from 1 to $z - 1$ (*i.e.* non-surface active species) are:

$$\text{propagation} \qquad \text{IM}_i^\bullet + \text{M} \xrightarrow{k_\text{p,aq}^i} \text{IM}_{i+1}^\bullet \tag{A.53}$$

$$\text{termination} \qquad \text{IM}_i^\bullet + \text{R}^\bullet \xrightarrow{k_\text{t,aq}^\text{R}} \text{unreactive products} \tag{A.54}$$

$$\text{termination} \qquad \text{IM}_i^\bullet + \text{IM}_i^\bullet \xrightarrow{k_\text{t,aq}} \text{unreactive products} \tag{A.55}$$

where Eq. A.54 and A.55 describe radical recombination or disproportionation reactions resulting in the termination of the radical. Note that, since the change in $[\text{IM}_i^\bullet]$ is different for each of these reactions, they must be treated separately, with different rate coefficients. In line with previous work,[10] it is assumed that these termination rate coefficients are not dependent on the length of the chains involved and may thus be interpreted as an "average" rate coefficient. Importantly, $R^\bullet$ in Eq. A.54 is not the RAFT re-initiating radical $R^\bullet$, rather it is a generic radical species; moreover, different for each i, as it does not include $\text{IM}_i^\bullet$; $R^\bullet$ is any $\text{IM}_j^\bullet$ $(i \neq j)$, since $I^\bullet$ adds to M quite fast, it may be neglected in the calculations, giving:

$$[\text{R}^\bullet] = T_\text{R} - [\text{IM}_j^\bullet] \tag{A.56}$$

for each i in Eq. A.54, where T_R is the total concentration of all aqueous phase radicals (once again ignoring the rapidly reacting $I^\bullet$ and rapidly entering $\text{IM}_z^\bullet$):

$$T_\text{R} = \sum_{i=1}^{z-1} [\text{IM}_i^\bullet] \tag{A.57}$$

Finally, there is the entry process itself. Here, it is assumed that entry is so fast that the z-mer does not undergo the termination reactions shown in Eq. A.54 and A.55.

$$\text{entry} \qquad \mathrm{IM}_z^{\bullet} + (\text{particle}) \xrightarrow{k_\mathrm{e}^{z}} (\mathrm{IM}_z^{\bullet} + \text{particle}) \qquad (\mathrm{A.58})$$

A.3.1.2 Termination Rate Coefficients

The presence of two different termination reactions (Eq. A.54 and A.55) poses a problem in obtaining (approximate) analytic solutions for the kinetic scheme presented above, so it is useful to review the nature of these termination reactions with a view to finding a relation between the rate coefficients. Importantly, the rate coefficients for the "hetero-termination" (Eq. A.54) and "homo-termination" (Eq. A.55) reactions are defined differently according to IUPAC convention, with the expressions in Eq. A.61 and A.66 being the appropriate rate laws.

Consider first the diffusion-controlled collision rate for the "hetero-termination" reaction (Eq. A.54), $R_\mathrm{coll}^\mathrm{I+R}$, in terms of the Smoluchowski equation:

$$R_\mathrm{coll}^\mathrm{I+R} = 4\pi D_\mathrm{IR}(r_\mathrm{I} + r_\mathrm{R})n_\mathrm{I}n_\mathrm{R} \qquad (\mathrm{A.59})$$

where D_IR is the mutual diffusion coefficient of the two species ($\mathrm{IM}_i^{\bullet}$ and $\mathrm{R}^{\bullet}$), r_I and r_R are the interaction radii and n_I and n_R are the number concentrations of each species.

The rate of reaction may be obtained from the collision rate using the proportion of collisions that result in reaction, p:

$$R_\mathrm{rxn}^\mathrm{I+R} = 4\pi p D_\mathrm{IR}(r_\mathrm{I} + r_\mathrm{R})n_\mathrm{I}n_\mathrm{R} \qquad (\mathrm{A.60})$$

From Eq. A.54, this rate is also given by:

$$R_\mathrm{rxn}^\mathrm{I+R} = k_\mathrm{t,aq}^\mathrm{R}[\mathrm{IM}_i^{\bullet}][\mathrm{R}^{\bullet}] \qquad (\mathrm{A.61})$$

Consider next the diffusion-controlled collision rate for the "homo-termination" reaction (Eq. A.55), $R_{\text{coll}}^{\text{I+I}}$, where care must be taken to count the number of interactions correctly because the two reactants are identical:

$$R_{\text{coll}}^{\text{I+I}} = 4\pi D_{\text{II}}(r_{\text{I}} + r_{\text{I}})\binom{n_{\text{I}}}{2} \tag{A.62}$$

$$R_{\text{coll}}^{\text{I+I}} = 4\pi D_{\text{II}}(r_{\text{I}} + r_{\text{I}})\frac{n_{\text{I}}(n_{\text{I}} - 1)}{2} \tag{A.63}$$

The rate of reaction may be similarly obtained from the collision rate, noting that two $\text{IM}_i^{\bullet}$ are involved in the reaction:

$$R_{\text{rxn}}^{\text{I+I}} = 2 \times \left(4\pi p D_{\text{II}}(r_{\text{I}} + r_{\text{I}})\frac{n_{\text{I}}(n_{\text{I}} - 1)}{2}\right) \tag{A.64}$$

where p should be the same as in Eq. A.60 (in practice, p may be estimated from the probability that the two radicals are of correct spin to react,[1,16] giving $p = \frac{1}{4}$). Eq. A.64 may be further simplified by recognizing that $n_{\text{I}} - 1 \approx n_{\text{I}}$, as $n_{\text{I}} \gg 1$:

$$R_{\text{rxn}}^{\text{I+I}} \approx 4\pi p D_{\text{II}}(r_{\text{I}} + r_{\text{I}})n_{\text{I}}^2 \tag{A.65}$$

From Eq. A.55, this rate is also given by:

$$R_{\text{rxn}}^{\text{I+I}} = 2k_{\text{t,aq}}[\text{IM}_i^{\bullet}]^2 \tag{A.66}$$

Taking a ratio between the reaction rates for the hetero- and homo-termination reactions gives:

$$\frac{R_{\text{rxn}}^{\text{I+R}}}{R_{\text{rxn}}^{\text{I+I}}} = \frac{k_{\text{t,aq}}^{\text{R}}[\text{IM}_i^{\bullet}][\text{R}^{\bullet}]}{2k_{\text{t,aq}}[\text{IM}_i^{\bullet}]^2} \approx \frac{4\pi p D_{\text{IR}}(r_{\text{I}} + r_{\text{R}})n_{\text{I}}n_{\text{R}}}{4\pi p D_{\text{II}}(r_{\text{I}} + r_{\text{I}})n_{\text{I}}^2} \tag{A.67}$$

Here, the diffusion coefficients D_{IR} and D_{II} are approximately equal, as are the interaction radii r_{I} and r_{R}. Moreover, the concentrations and number concentrations will be in identical ratio (*i.e.* $n_{\text{I}}n_{\text{R}}/n_{\text{I}}^2 = [\text{IM}_i^{\bullet}][\text{R}^{\bullet}]/[\text{IM}_i^{\bullet}]^2$), giving:

$$\frac{k_{\text{t,aq}}^{\text{R}}}{2k_{\text{t,aq}}} \approx 1 \tag{A.68}$$

or, as used in the subsequent section to simplify the kinetic equations:

$$k_{\mathrm{t,aq}}^{\mathrm{R}} \approx 2k_{\mathrm{t,aq}} \tag{A.69}$$

A.3.1.3 Kinetic Scheme for Radical Concentrations

The aqueous phase kinetics are thus described by the following equations:

$$\frac{\mathrm{d}[\mathrm{IM}^\bullet]}{\mathrm{d}t} = 2k_\mathrm{d}[\mathrm{I{-}I}] - k_\mathrm{p}[\mathrm{IM}^\bullet]C_\mathrm{w} - k_{\mathrm{t,aq}}^{\mathrm{R}}[\mathrm{IM}^\bullet]\big(T_\mathrm{R} - [\mathrm{IM}^\bullet]\big) - 2k_{\mathrm{t,aq}}[\mathrm{IM}^\bullet]^2 \tag{A.70}$$

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{IM}_i^\bullet]}{\mathrm{d}t} &= k_\mathrm{p}C_\mathrm{w}[\mathrm{IM}_{i-1}^\bullet] - k_\mathrm{p}C_\mathrm{w}[\mathrm{IM}_i^\bullet] \\ &\quad - k_{\mathrm{t,aq}}^{\mathrm{R}}[\mathrm{IM}_i^\bullet]\big(T_\mathrm{R} - [\mathrm{IM}_i^\bullet]\big) - 2k_{\mathrm{t,aq}}[\mathrm{IM}_i^\bullet]^2 \qquad (2 \le i \le z{-}1)\end{aligned} \tag{A.71}$$

If it is assumed that the entry process described by Eq. A.58 is quite rapid, then $[\mathrm{IM}_z^\bullet] = 0$ and $\mathrm{d}[\mathrm{IM}_z^\bullet]/\mathrm{d}t = 0$. Moreover, an expression for the total concentration of radicals in the aqueous phase, T_R, may be obtained by neglecting radical loss due to entry (hence the only processes changing the radial concentration are initiator decomposition and termination), giving:

$$\begin{aligned}\frac{\mathrm{d}T_\mathrm{R}}{\mathrm{d}t} &= 2k_\mathrm{d}[\mathrm{I{-}I}] - \sum_{i=1}^{z-1} k_{\mathrm{t,aq}}^{\mathrm{R}}[\mathrm{IM}_i^\bullet]\big(T_\mathrm{R} - [\mathrm{IM}_i^\bullet]\big) - \sum_{i=1}^{z-1} k_{\mathrm{t,aq}}[\mathrm{IM}_i^\bullet]^2 \\ &= 2k_\mathrm{d}[\mathrm{I{-}I}] - (2k_{\mathrm{t,aq}} - k_{\mathrm{t,aq}}^{\mathrm{R}})\sum_{i=1}^{z-1}[\mathrm{IM}_i^\bullet]^2 - k_{\mathrm{t,aq}}^{\mathrm{R}}T_\mathrm{R}\sum_{i=1}^{z-1}[\mathrm{IM}_i^\bullet] \\ &= 2k_\mathrm{d}[\mathrm{I{-}I}] - (2k_{\mathrm{t,aq}} - k_{\mathrm{t,aq}}^{\mathrm{R}})\sum_{i=1}^{z-1}[\mathrm{IM}_i^\bullet]^2 - k_{\mathrm{t,aq}}^{\mathrm{R}}T_\mathrm{R}^2\end{aligned} \tag{A.72}$$

Now, the termination rate coefficients are linked using the diffusion-based arguments presented above, culminating in Eq. A.69. This gives a simplified expression for the rate of change of T_R:

$$\frac{\mathrm{d}T_\mathrm{R}}{\mathrm{d}t} = 2k_\mathrm{d}[\mathrm{I{-}I}] - 2k_{\mathrm{t,aq}}T_\mathrm{R}^2 \tag{A.73}$$

The steady-state value for T_R is thus:

$$T_R \approx \left(\frac{k_d[\text{I–I}]}{k_{t,aq}}\right)^{1/2} \tag{A.74}$$

Continuing the steady-state approximation for each of the $IM_i^\bullet$, the following expressions are obtained (once again using $k_{t,aq}^{R} = 2k_{t,aq}$ to simplify the expressions):

$$[IM^\bullet] = \frac{2k_d[\text{I–I}]}{k_pC_W + 2k_{t,aq}T_R} \tag{A.75}$$

$$[IM_i^\bullet] = \frac{k_pC_W[IM_{i-1}^\bullet]}{k_pC_W + 2k_{t,aq}T_R} \qquad (2 \le i \le z-1) \tag{A.76}$$

These expressions may be combined, allowing a closed expression for each $[IM_i^\bullet]$ to be written:

$$\begin{aligned}[IM_i^\bullet] &= \frac{2k_d[\text{I–I}]}{k_pC_W + 2k_{t,aq}T_R} \times \prod_{j=2}^{z-1} \frac{k_pC_W}{k_pC_W + 2k_{t,aq}T_R} \\ &= \frac{2k_d[\text{I–I}]}{k_pC_W}\left(\frac{k_pC_W}{k_pC_W + 2k_{t,aq}T_R}\right)^{z-1} \qquad (2 \le i \le z-1)\end{aligned} \tag{A.77}$$

A.3.1.4 Estimating the Initiator Efficiency

Defining the initiator efficiency, *f*, as being the proportion of initiator-derived radicals that enter a particle (*i.e.* those that do not undergo aqueous phase termination) within an infinitesimal time-slice δt, gives:

$$f = \frac{\displaystyle\int_t^{t+\delta t} \frac{d[IM_z^\bullet]}{dt}dt}{\displaystyle\int_t^{t+\delta t} \frac{d[IM_z^\bullet]}{dt}dt + \int_t^{t+\delta t} \frac{d[\text{R–R}]}{dt}dt} \tag{A.78}$$

where R–R is the termination product and the time-derivatives of $[IM_z^\bullet]$ are the rate of formation of *z*-mer species. Each of these integral expressions may be further simplified using the definition of the primitive function, yielding:

$$f = \frac{[\mathrm{IM}_z^\bullet]|_{t+\delta t} - [\mathrm{IM}_z^\bullet]|_t}{[\mathrm{IM}_z^\bullet]|_{t+\delta t} - [\mathrm{IM}_z^\bullet]|_t + [\mathrm{R{-}R}]|_{t+\delta t} - [\mathrm{R{-}R}]|_t} \tag{A.79}$$

which, in the limit that $\delta t \to 0$, may be further simplified using the definition of the derivative function:

$$f = \frac{\dfrac{\mathrm{d}[\mathrm{IM}_z^\bullet]}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{IM}_z^\bullet]}{\mathrm{d}t} + \dfrac{\mathrm{d}[\mathrm{R{-}R}]}{\mathrm{d}t}} \tag{A.80}$$

As the radical species must either propagate to become a z-mer or terminate to form the R–R species above, the denominator of this expression is equal to the rate of $\mathrm{I}^\bullet$ formation:

$$f = \frac{\dfrac{\mathrm{d}[\mathrm{IM}_z^\bullet]}{\mathrm{d}t}}{-2\dfrac{\mathrm{d}[\mathrm{I{-}I}]}{\mathrm{d}t}} \tag{A.81}$$

Now, the rate of decomposition of initiator is given by Eq. A.50 to be:

$$\frac{\mathrm{d}[\mathrm{I{-}I}]}{\mathrm{d}t} = -k_\mathrm{d}[\mathrm{I{-}I}] \tag{A.82}$$

and the rate of formation of z-mer species is:

$$\frac{\mathrm{d}[\mathrm{IM}_z^\bullet]}{\mathrm{d}t} = k_\mathrm{p} C_\mathrm{W}[\mathrm{IM}_{z-1}^\bullet] \tag{A.83}$$

Eq. A.77 provides a suitable expression for $[\mathrm{IM}_{z-1}^\bullet]$ and Eq. A.74 for T_R, which, by substitution into Eq. A.81, gives:

$$\begin{aligned} f &= \frac{k_\mathrm{p} C_\mathrm{W} \dfrac{2k_\mathrm{d}[\mathrm{I{-}I}]}{k_\mathrm{p} C_\mathrm{W}} \left(\dfrac{k_\mathrm{p} C_\mathrm{W}}{k_\mathrm{p} C_\mathrm{W} + 2k_\mathrm{t,aq} T_\mathrm{R}}\right)^{z-1}}{2k_\mathrm{d}[\mathrm{I{-}I}]} \\ &= \left(\frac{k_\mathrm{p} C_\mathrm{W}}{k_\mathrm{p} C_\mathrm{W} + 2k_\mathrm{t,aq} T_\mathrm{R}}\right)^{z-1} \\ &= \left(\frac{k_\mathrm{p} C_\mathrm{W} + 2k_\mathrm{t,aq}\left(\dfrac{k_\mathrm{d}[\mathrm{I{-}I}]}{k_\mathrm{t,aq}}\right)^{1/2}}{k_\mathrm{p} C_\mathrm{W}}\right)^{1-z} \end{aligned} \tag{A.84}$$

This is readily simplified, yielding:

$$f = \left(1 + \frac{2\sqrt{k_{\mathrm{t,aq}} k_{\mathrm{d}} [\mathrm{I{-}I}]}}{k_{\mathrm{p}} C_{\mathrm{w}}}\right)^{1-z} \tag{A.85}$$

A.3.1.5 Estimating the Entry Rate Coefficient

From the expression for the entry efficiency, *f*, in Eq. A.85, the pseudo-first-order rate coefficient for the entry of radicals into a particle, ρ, may be estimated.

If the aqueous-phase processes were 100% efficient, ρ would be given simply by the number of initiator fragments formed, normalized by the number of particles present in the system:

$$\rho_{100} = \frac{2k_{\mathrm{d}}[\mathrm{I{-}I}]N_{\mathrm{A}}}{N_{\mathrm{c}}} \tag{A.86}$$

where N_{A} is Avogadro's constant and N_{c} is the number concentration of particles in the system.

However, it is well known that initiators in emulsion polymerization are frequently quite inefficient.{Gilbert, 1995 #894} Using the above definition of *f*, it is possible to write an expression for ρ that includes inefficiencies in initiation due to aqueous-phase termination reactions:

$$\begin{aligned} \rho &= \rho_{100} \times f \\ &= \frac{2k_{\mathrm{d}}[\mathrm{I{-}I}]N_{\mathrm{A}}}{N_{\mathrm{c}}}\left(1 + \frac{2\sqrt{k_{\mathrm{t,aq}} k_{\mathrm{d}} [\mathrm{I{-}I}]}}{k_{\mathrm{p}} C_{\mathrm{w}}}\right)^{1-z} \end{aligned} \tag{A.87}$$

A.3.2 Acknowledgements

Mr Kim van Berkel (Canterbury University) is thanked for his assistance in preparing this appendix, in particular for his help in getting the "2" in the right place in Eq. A.85.

A.4 Exit of Radicals from Particles

Molecules are continually entering into and exiting from particles. In modeling the kinetics of emulsion polymerization, it becomes necessary to describe the kinetics of molecular entry and exit. In the first instance, it is simplest to consider the entry and exit of a monomer unit from a particle, and then draw analogy to this situation for other molecules. Finally, it is necessary to develop a more general approach to take account of non-monomer-like molecules.

A.4.1 Monomer and Monomer-Like Molecules

A.4.1.1 Monomer Adsorption and Desorption

To model the way in which a monomeric radical (or some other small molecule) may enter and leave a particle, consider first the following equilibrium between a monomer unit in the aqueous phase and one bound to a particle:[1,9]

$$\mathrm{M} + \text{particle} \underset{k_{\mathrm{dM}}}{\overset{k_{\mathrm{ads}}}{\rightleftharpoons}} (\mathrm{M{-}particle}) \tag{A.88}$$

In this way, it is possible to consider the adsorption (“ads”) and desorption (“dM”) processes in this equilibrium. Indirect experimental evidence to support this approach has been reported.[15,17] The adsorption of the monomer onto the surface of the particle may be expressed in terms of Smoluchowski diffusion with a rate coefficient, k_{ads}:

$$k_{\mathrm{ads}} = 4\pi D_{\mathrm{w}}\, r_{\mathrm{s}} N_{\mathrm{A}} \tag{A.89}$$

where D_{w} is the diffusion coefficient of the monomer unit in water and r_{s} is the swollen radius of the particle.

The first-order rate coefficient for the desorption of monomer, k_{dM}, may be found by looking at the particle–monomer equilibrium in Eq. A.88. The rate of change of the monomer concentration in the aqueous phase is given by:

$$\frac{\mathrm{d}[\mathrm{M(aq)}]}{\mathrm{d}t} = -k_{\mathrm{ads}} C_{\mathrm{w}} \frac{N_{\mathrm{c}}}{N_{\mathrm{A}}} + k_{\mathrm{dM}} V_{\mathrm{s}} N_{\mathrm{c}} C_{\mathrm{p}} \tag{A.90}$$

where $V_{\mathrm{s}} = \frac{4}{3}\pi r_{\mathrm{s}}^3$ is the swollen volume of each particle and C_{w}, C_{p} are the equilibrium concentrations of the monomer in the water and particle phases respectively.

At equilibrium, this derivative (Eq.A.90) is equal to zero, giving the expression for k_{dM}:

$$k_{\mathrm{dM}} = \frac{3 D_{\mathrm{w}} C_{\mathrm{w}}}{r_{\mathrm{s}}^2 C_{\mathrm{p}}} \tag{A.91}$$

Of course, C_{w} and C_{p} may be estimated from the empirical relation:[1,10]

$$\left(\frac{C_{\mathrm{w}}}{C_{\mathrm{w}}^{\mathrm{sat}}}\right) = \left(\frac{C_{\mathrm{p}}}{C_{\mathrm{p}}^{\mathrm{sat}}}\right)^{0.6} \tag{A.92}$$

where "sat" indicates the saturation concentration of the monomer in the relevant phase.

A.4.1.2 Extension to Labeled Monomer

To begin generalizing this formula for other small molecules in the system, first consider the addition of some deuterium labeled monomer (D) to the system above. If the mole fraction of D is χ_{D} then the equilibrium concentrations of D in the water and particle phases, $C_{\mathrm{w}}^{\mathrm{D}}$ and $C_{\mathrm{p}}^{\mathrm{D}}$, may be given by:

$$C_{\mathrm{w}}^{\mathrm{D}} = \chi_{\mathrm{D}} C_{\mathrm{w}} \tag{A.93}$$

$$C_{\mathrm{p}}^{\mathrm{D}} = \chi_{\mathrm{D}} C_{\mathrm{p}} \tag{A.94}$$

The derivation outlined above may then be recast in terms of $C_{\mathrm{w}}^{\mathrm{D}}$ and $C_{\mathrm{p}}^{\mathrm{D}}$; the final value for the rate coefficient for the desorption of D from a particle, k_{dD}, is identical to Eq. A.91, as the ratio $C_{\mathrm{w}}^{\mathrm{D}}/C_{\mathrm{p}}^{\mathrm{D}} = C_{\mathrm{w}}/C_{\mathrm{p}}$.

A.4.1.3 Extension to Monomeric Radicals

In the case of a monomeric radical, the deuterated monomer example (above) may be further extended by arguing that the monomeric radical (E, differing from the monomer unit by only a hydrogen radical) will be chemically identical to the monomer unit in terms of solubility. It must be stressed that this approach disregards any radical reactions E can undergo. Once again the relationship described by Eq. A.91 may be derived, where $C_{\mathrm{w}}^{\mathrm{E}}/C_{\mathrm{p}}^{\mathrm{E}} = C_{\mathrm{w}}/C_{\mathrm{p}}$ and C_{w}, C_{p} still refer to the concentration of monomer in the water and particle phases.

A.4.1.4 Extension to Other Small Molecules

Recently, attempts have been made to estimate the exit rate coefficients of other small molecules (R) from latex particles.[18] In the calculations reported elsewhere,[18] the same approach as for the monomeric radical was used, where it was argued that $C_{\mathrm{w}}^{\mathrm{R}}/C_{\mathrm{p}}^{\mathrm{R}} = C_{\mathrm{w}}/C_{\mathrm{p}}$. The validity of this assumption certainly is dependent on the nature of the small molecule (or radical) R. In the case of a cumyl radical in a styrene emulsion polymerization, the solubility of the cumyl radical and the styrene monomer are quite similar (the cumyl group has an extra methyl group over styrene and would actually be more analogous to α-methyl styrene). However, the analogy is a little more forced than that between E and M presented above. This will change the ratio $C_{\mathrm{w}}^{\mathrm{R}}/C_{\mathrm{p}}^{\mathrm{R}}$ somewhat.

At this stage, the validity of the assumptions for small styrene-like radicals (such as the cumyl radical) is unclear. It can, however, be said that these assumptions are likely to be quite poor for other, more water-soluble species. Specifically, the values of C_{w} and C_{p} for methyl methacrylate in a poly(methyl methacrylate) matrix have been used for the ethyl methacrylate radical, $^{\bullet}C(CH_3)_2CO_2Et$, desorbing from a poly(styrene)/poly(methyl methacrylate) matrix.[18] One may suggest that such a calculation would be somewhat flawed.

A.4.2 Other Molecules – More General Treatment

In light of the difficulties outlined in transferring the arguments for monomeric radicals over to other molecules that are not monomer-like, it is necessary to formulate a new approach. It is possible to take an approach similar to that outlined above for the monomeric radical.

A.4.2.1 Molecular Adsorption and Desorption

As before, consider the following equilibrium between a molecule in the aqueous phase and one bound to a particle. In this way, it is possible to consider the adsorption ("ads") and desorption ("dR") processes in this equilibrium:

$$\mathrm{R} + \text{particle} \underset{k_{\mathrm{dR}}}{\overset{k_{\mathrm{ads}}^{\mathrm{R}}}{\rightleftharpoons}} (\mathrm{R}\text{–particle}) \tag{A.95}$$

If R and the particle are non-interacting, the adsorption onto the surface of the particle may be expressed in terms of Smoluchowski diffusion with a rate coefficient, $k_{\mathrm{ads}}^{\mathrm{R}}$:

$$k_{\mathrm{ads}}^{\mathrm{R}} = 4\pi D_{\mathrm{w}}^{\mathrm{R}}\, r_{\mathrm{s}} N_{\mathrm{A}} \tag{A.96}$$

where $D_{\mathrm{w}}^{\mathrm{R}}$ is the diffusion coefficient of R in water and r_{s} is the swollen radius of the particle.

The first-order rate coefficient for the desorption of R, k_{dR}, may be found by looking at the particle–R equilibrium in Eq. A.95. The rate of change of the concentration or R in the aqueous phase is given by:

$$\frac{\mathrm{d}[\mathrm{R(aq)}]}{\mathrm{d}t} = -k_{\mathrm{ads}}^{\mathrm{R}} C_{\mathrm{w}}^{\mathrm{R}} \frac{N_{\mathrm{c}}}{N_{\mathrm{A}}} + k_{\mathrm{dR}} V_{\mathrm{s}} N_{\mathrm{c}} C_{\mathrm{p}}^{\mathrm{R}} \tag{A.97}$$

where $V_\mathrm{s} = \frac{4}{3}\pi r_\mathrm{s}^3$ is the swollen volume of each particle and C_w^R, C_p^R are the equilibrium concentrations of R in the water and particle phases respectively, *in the presence of monomer*.

Once again, at equilibrium, this derivative (Eq.A.90) is equal to zero, giving the expression for k_dR:

$$k_\mathrm{dR} = \frac{3D_\mathrm{w}^\mathrm{R} C_\mathrm{w}^\mathrm{R}}{r_\mathrm{s}^2 C_\mathrm{p}^\mathrm{R}} \tag{A.98}$$

Of course, C_w^R and C_p^R may be empirically determined as described below.

A.4.2.2 Extension to Other Radicals

In the case of R being a radical, the relation in Eq. A.98 may be used, following the same arguments as for extension from the monomer to the monomeric radical. In this case, it is necessary to use the values of C_w^R and C_p^R for a R-like non-radical (e.g. α-methyl styrene for the cumyl radical) *in the presence of monomer*.

A.4.2.3 Determining Radical Concentrations in the Presence of Monomer

An experimental technique for determining C_w^R and C_p^R in the presence of monomer is required to allow the calculation of k_dR following the method just described, analogous to the method used to determine C_w and C_p for monomers.[19,20] It is simplest to contemplate a concrete example; consider the emulsion polymerization of styrene in which the kinetics of the ethyl methacrylate radical $^\bullet C(CH_3)_2CO_2Et$ (described elsewhere[18]) is of interest.

Initially, a non-radical species that will have almost identical solubility behavior to the radical must be selected. In the case of the ethyl methacrylate radical, ethyl methacrylate would appear to be an appropriate choice.

A series of seeds then need to be swollen with monomer; however, monomer droplets must not exist. Measured amounts of ethyl methacrylate may then be added, looking for evidence of creaming (to indicate that the system is saturated). Centrifugation coupled with gas chromatography on the aqueous phase would allow $C_{\mathrm{w}}^{\mathrm{R}}$ to be determined, yielding $C_{\mathrm{p}}^{\mathrm{R}}$ by subtraction.

In practice, this technique may be a little problematic. While detecting a small amount of ethyl methacrylate in the water phase may be possible, the analogous molecule to the cumyl radical is even more water insoluble. Detecting an even smaller amount of α-methyl styrene in a water phase saturated by styrene would be quite difficult.

A.5 Initiation Using a γ-Source

The use of γ-sources to initiate the polymerization of various monomers has been reported for a variety of systems. Examples of the use of γ-initiation, in particular relating to γ-relaxations, are presented in Chapters 6 and 7.

A.5.1 Initiating Radicals

In a γ-initiated emulsion polymerization, the γ-source creates most of its radicals in the aqueous-phase through ionization of water molecules, generating the initiating radicals $HO^{\bullet}(aq)$, $H^{\bullet}(aq)$ and $e^{-}(aq)$.[21] The first reaction in the process is the γ-induced ionization of the water molecule:

γ-ionization $$H_2O \xrightarrow[\gamma]{} H_2O^{+\bullet} + e^{-} \qquad \text{(A.99)}$$

The products from this reaction are extremely reactive, with the $H_2O^{+\bullet}$ surviving for around 10^{-14} s and the free e^{-} species for around 10^{-9} s. The electron acquires an inner solvation sphere of between 4 and 6 water molecules and a second sphere of the order of 12 water molecules.

decomposition of $H_2O^{+\bullet}$ $$H_2O^{+\bullet} \longrightarrow HO^{\bullet} + H^{+}(aq) \qquad \text{(A.100)}$$

solvation of e^{-} $$e^{-} \longrightarrow e^{-}(aq) \qquad \text{(A.101)}$$

In terms of generating the initiating radicals, the $e^{-}(aq)$ may join with a proton to make $H^{\bullet}$:

protonation of $e^{-}(aq)$ $$e^{-}(aq) \longrightarrow H^{\bullet} \qquad \text{(A.102)}$$

The radiation chemical yield of radicals (per 100 eV of irradiation energy) for the ^{60}Co γ-source is given in Table A.1.

Table A.1: The radiation chemical yield of radical species for the γ-irradiation of water using a ^{60}Co γ-source, from O'Donnell and Sangster.[21]

species	radiation chemical yield [a]
$HO^{\bullet}$	2.8
$H^{\bullet}$	0.55
$e^{-}(aq)$	2.7

[a] Values for *G* summarized here are expressed in terms of the number of radicals produced per 100 eV of energy absorbed.[21-23]

The radicals so formed by the γ-irradiation of water may then go on to react with monomer in the system via two important reaction pathways: addition across the vinyl double bond and abstraction of a proton from the monomer.

The addition of the $HO^{\bullet}$, $H^{\bullet}$ and $e^{-}(aq)$ species to vinyl groups is believed to be diffusion controlled,[24] with rate coefficients around 10^{9} dm^{3} mol^{-1} s^{-1} (the $HO^{\bullet}$ species adds to styrene monomer with a rate coefficient of[24] 6×10^{9} M^{-1} s^{-1}). The resulting species are shown below and are capable of adding to vinyl monomers, thus initiating polymerization:

$$HO^{\bullet} + CH_2{=}CRR' \longrightarrow HOCH_2{-}C^{\bullet}RR' \qquad (A.103)$$

$$H^{\bullet} + CH_2{=}CRR' \longrightarrow HCH_2{-}C^{\bullet}RR' \qquad (A.104)$$

$$e^{-} + CH_2{=}CRR' \longrightarrow {}^{-}CH_2{-}C^{\bullet}RR' \xrightarrow{H^{+}} CH_3{-}C^{\bullet}RR' \qquad (A.105)$$

The abstraction reactions are significantly slower than the addition reactions (best estimates being that the abstraction reactions have rate coefficients up to approximately 1/10 that for the addition reactions). The species formed as the primary product of the abstraction reaction with styrene monomer is thought to be able to initiate chain growth, although this has not been confirmed.[24]

In the case of an aromatic monomer such as styrene, a third class of reactions is also able to occur – the addition of the $HO^{\bullet}$, $H^{\bullet}$ or $e^{-}(aq)$ species to the ring structure. This reaction is believed to take place first by coordination of the radical with the π-system of the ring such that the radical species is held above the plane of the ring. This intermediate adduct then rearranges to form a cyclohexadiene species. In the case of the reaction with $e^{-}(aq)$, this species would be rapidly protonated. It should be noted that only $HO^{\bullet}$ is believed to proceed by this reaction pathway to any significant extent, with addition across the vinylic group and attack of the ring being equally likely to occur for this species. Moreover, it is believed that the cyclohexadienyl radical ($CH_2{=}CH(C^{\bullet}C_5H_5)$) is unable to initiate the polymerization of styrene.[24]

For convenience, the radical species $CH_3{-}C^{\bullet}R$ and $CH_2{=}C^{\bullet}R$ will henceforth be referred to as $M^{\bullet}$ as their chemical and phase transfer behavior are indistinguishable within the accuracy of present kinetic experiments. The $HOCH_2{-}C^{\bullet}HR$ species will be represented by $HOM^{\bullet}$. The distribution of species formed for the γ-irradiation of a styrene/water system (in terms of the radiation chemical yield) is shown in Table A.2.

Table A.2: The radiation chemical yield of monomer-containing radical species for the electron-beam irradiation of water, from McAskill and Sangster.[24]

species	radiation chemical yield [a]	proportion of radicals
$HOM^{\bullet}$	1.4	23%
$M^{\bullet}$	3.3	54%
$CH_2{=}CH(C_6H_4OH)^{\bullet}$ [b]	1.4	23%

[a] Values for *G* are expressed here in terms of the number of radicals produced per 100 eV of energy absorbed.[21-23]

[b] Note that this species is thought to be unable to initiate polymerization; the radical is within the π-system of the aromatic ring.

Each of these radical species can terminate with any one of the other radical species, $R^{\bullet}$, present. It may be argued that termination in this situation would be purely diffusion controlled.

$$\text{termination} \qquad \mathrm{HO}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{t}}^{\mathrm{HO}}} \text{unreactive products} \tag{A.106}$$

$$\text{termination} \qquad \mathrm{HOM}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{t}}^{\mathrm{HOM}}} \text{unreactive products} \tag{A.107}$$

$$\text{termination} \qquad \mathrm{M}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{t}}^{\mathrm{M}}} \text{unreactive products} \tag{A.108}$$

The $\mathrm{HOM}^{\bullet}$ and $\mathrm{M}^{\bullet}$ species may also undergo entry into a latex particle (it is also plausible that the $\mathrm{HO}^{\bullet}$ species is able to enter):

$$\text{entry} \qquad \mathrm{HO}^{\bullet} + (\text{particle}) \xrightarrow{k_{\mathrm{e}}^{\mathrm{HO}}} (\mathrm{HO}^{\bullet} + \text{particle}) \tag{A.109}$$

$$\text{entry} \qquad \mathrm{HOM}^{\bullet} + (\text{particle}) \xrightarrow{k_{\mathrm{e}}^{\mathrm{HOM}}} (\mathrm{HOM}^{\bullet} + \text{particle}) \tag{A.110}$$

$$\text{entry} \qquad \mathrm{M}^{\bullet} + (\text{particle}) \xrightarrow{k_{\mathrm{e}}^{\mathrm{M}}} (\mathrm{M}^{\bullet} + \text{particle}) \tag{A.111}$$

Comparison of the pseudo-first-order rate coefficients for termination, entry and addition (using a typical particle, say $r_{\mathrm{s}} = 50$ nm) reveals that the most likely reaction sequence is as follows:

$$\gamma\text{-radiolysis} \qquad \mathrm{H_2O} \xRightarrow[\gamma]{} \left\{ \begin{array}{l} \mathrm{H}^{\bullet}(\mathrm{aq}) \\ \mathrm{HO}^{\bullet} \\ \mathrm{e}^{-}(\mathrm{aq}) \end{array} \right. \tag{A.112}$$

$$\text{addition} \qquad \left. \begin{array}{r} \mathrm{HO}^{\bullet} \\ \mathrm{H}^{\bullet}(\mathrm{aq}) \\ \mathrm{e}^{-}(\mathrm{aq}) \end{array} \right\} + \mathrm{M}(\mathrm{aq}) \Longrightarrow \left\{ \begin{array}{l} \mathrm{HOM}^{\bullet}(\mathrm{aq}) \\ \mathrm{M}^{\bullet}(\mathrm{aq}) \end{array} \right. \tag{A.113}$$

$$\text{entry} \qquad \mathrm{R}^{\bullet} + (\text{particle}) \longrightarrow (\mathrm{R}^{\bullet} + \text{particle}) \tag{A.114}$$

The flux of radicals entering the particles may thus be represented by $\mathrm{M}^{\bullet}$ and $\mathrm{HOM}^{\bullet}$.

A.5.2 Estimating the Radical Flux from a γ-Source

Initiating polymerization reactions using a γ-source offers a number of advantages, including being able to cease initiation simply by removing the reaction vessel from the source. However, the mathematical tools required to estimate the radical flux from the γ-source are completely different from those required for calculating the radical flux for a chemically initiated experiment.

The dose rate of the gamma source, D, is a measure of the energy imparted per unit mass per unit time.[23] The SI units for this quantity are Gy s^{-1} (although Gy h^{-1} are also used), which is equivalent to J kg^{-1} s^{-1}. The radiation chemical yield (often simply called the G-value), G, measures the number of radicals produced for a given energy input. Values for G are commonly expressed in terms of the number of radicals produced per 100 eV of energy absorbed.[22,23]

The radical flux, ϕ_{radical}, may thus be estimated by combining the D (in Gy s^{-1}) and G (in radicals per 100 eV) values for the system:

$$\phi_{\text{radical}} = \frac{D\,G}{100\,e\,N_{\text{A}}} \tag{A.115}$$

where e is the charge on an electron ($\approx 1.602 \times 10^{-19}$ C) and N_{A} is Avogadro's constant. This may be rewritten in terms of the Faraday constant ($\approx 9.649 \times 10^{4}$ C mol^{-1}):

$$\phi_{\text{radical}} = \frac{D\,G}{100\,F} \tag{A.116}$$

yielding a radical flux measured in mol kg^{-1} s^{-1}.

A.5.3 Acknowledgements

Many thanks to Mr David Sangster for the patient hours of explanations about γ-irradiation, γ-relaxations and dilatometry in general.

A.6 Mass-Balance in Emulsion Polymerization

There are a number of simple relations used throughout the course of this work that rely on little more than mass-balance. Most rely purely on mass-balance[1] and are recorded here for completeness.

A.6.1 Monomer Concentrations

A.6.1.1 Basic Equations

The empirical relationship between the concentration of monomer in the water phase, C_w, and the concentration of monomer in the polymer phase, C_p, provides the basic relationship required for this calculation:[1,10]

$$\left(\frac{C_\mathrm{w}}{C_\mathrm{w}^\mathrm{sat}}\right) = \left(\frac{C_\mathrm{p}}{C_\mathrm{p}^\mathrm{sat}}\right)^{0.6} \tag{A.117}$$

where $C_\mathrm{w}^\mathrm{sat}$ is the saturation concentration of monomer in the water phase and $C_\mathrm{p}^\mathrm{sat}$ is the saturation concentration of monomer in the polymer phase.

By definition, C_p and C_w may be expressed in terms of the amount of monomer in the particle and water phases, respectively, n_m^p and n_m^w:

$$C_\mathrm{p} = \frac{n_\mathrm{m}^\mathrm{p}}{V_\mathrm{s}} \tag{A.118}$$

$$C_\mathrm{w} = \frac{n_\mathrm{m}^\mathrm{w}}{V_\mathrm{aq}} \tag{A.119}$$

where V_s is the swollen volume of the particles and V_aq is the volume of the aqueous phase.

$$n_\mathrm{m} = n_\mathrm{m}^\mathrm{p} + n_\mathrm{m}^\mathrm{w} \tag{A.120}$$

Finally, V_s is given by:

$$V_s = \frac{m_p}{\rho_p} + \frac{n_m^p M_m}{\rho_m} \tag{A.121}$$

where M_m is the molecular weight of the monomer, m_p is the mass of polymer in the system and ρ_p and ρ_m are the densities of the polymer and monomer respectively.

A.6.1.2 Iterative Process

The above equations may be combined into an iterative process by simple rearrangement. This iterative process is suitable for implementation in a spreadsheet or other programmatic data analysis tools.

$$C_w = C_w^{sat} \left(\frac{C_p}{C_p^{sat}} \right)^{0.6} \tag{A.122}$$

$$n_m^w = C_w V_{aq} \tag{A.123}$$

$$n_m^p = n_m - n_m^w \tag{A.124}$$

$$V_s = \frac{m_p}{\rho_p} + \frac{n_m^p M_m}{\rho_m} \tag{A.125}$$

$$C_p = \frac{n_m^p}{V_s} \tag{A.126}$$

A.6.2 Decomposition of Persulfate Initiator

The kinetics of decomposition of persulfate normally follow a simple, unimolecular reaction scheme,[1] notwithstanding the monomer-assisted decomposition of persulfate reported by De Bruyn *et al.* for the emulsion polymerization of vinyl acetate.[25]

Under simple unimolecular kinetics, the following relation has been reported:[1]

$$k_d = 8 \times 10^{15}\ \text{s}^{-1} \exp\left(\frac{-135\ \text{kJ mol}^{-1}}{RT} \right) \tag{A.127}$$

where k_d is the (first-order) unimolecular rate coefficient for the dissociation of initiator.

Subsequent kinetics are as follows:

$$\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = -k_\mathrm{d}[\mathrm{S_2O_8}^{2-}] \tag{A.128}$$

$$[\mathrm{S_2O_8}^{2-}] = [\mathrm{S_2O_8}^{2-}]_0\exp(-k_\mathrm{d}t) \tag{A.129}$$

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{d}} \tag{A.130}$$

where $t_{1/2}$ is the half-life of the initiator species.

A.6.3 Interval II/III Transition

The transition from Interval II to Interval III is when monomer droplets disappear from the system. The conversion at which this transition occurs may be estimated by looking at the mass of monomer that can be held by the particles in the reaction, $m_\mathrm{mon}^\mathrm{p}$, and the mass of monomer that can be dissolved in the aqueous phase, $m_\mathrm{mon}^\mathrm{w}$. The total mass of monomer that the system can hold without having any monomer droplets present, $m_\mathrm{mon}^\mathrm{III}$, is thus given by:

$$m_\mathrm{mon}^\mathrm{III} = m_\mathrm{mon}^\mathrm{p} + m_\mathrm{mon}^\mathrm{w} \tag{A.131}$$

Moreover, these quantities are given by:

$$m_\mathrm{mon}^\mathrm{p} = \frac{M_0 C_\mathrm{p}^\mathrm{sat} d_\mathrm{m} m_\mathrm{p}}{d_\mathrm{p}(d_\mathrm{m} - M_0 C_\mathrm{p}^\mathrm{sat})} \tag{A.132}$$

$$m_\mathrm{mon}^\mathrm{w} = M_0 C_\mathrm{w}^\mathrm{sat} V_\mathrm{aq} \tag{A.133}$$

where M_0 is the molecular weight of the monomer, $C_\mathrm{p}^\mathrm{sat}$ is the saturation concentration of monomer in the polymer, d_p and d_m are the densities of polymer and monomer respectively, m_p is the mass of polymer in the system and $C_\mathrm{w}^\mathrm{sat}$ is the saturation concentration of monomer in the water phase.

To avoid monomer droplets in the system, a mass of monomer less than $m_{\mathrm{mon}}^{\mathrm{III}}$ should be used; if a mass of monomer, m_{mon}, in excess of $m_{\mathrm{mon}}^{\mathrm{III}}$ is added to the system, monomer droplets will be present in the system, and the conversion at which the Interval II/III transition occurs, $x^{\mathrm{II/III}}$ will be:

$$x^{\mathrm{II/III}} = \frac{m_{\mathrm{mon}} - m_{\mathrm{mon}}^{\mathrm{III}}}{m_{\mathrm{mon}}} \tag{A.134}$$

A.6.4 Particle Number, Particle Size and Percentage Solids

The number concentration of particles (per volume of aqueous phase), N_{c}, is given by:

$$N_{\mathrm{c}} = \frac{m_{\mathrm{p}}}{\frac{4}{3}\pi r_{\mathrm{u}}^{3} \rho_{\mathrm{p}} V_{\mathrm{aq}}} \tag{A.135}$$

where m_{p} is the mass of polymer in the system, r_{u} is the unswollen radius of the particles, ρ_{p} is the density of polymer and V_{aq} is the volume of the aqueous phase.

It should be noted that m_{p} may be obtained as:

$$m_{\mathrm{p}} = \tfrac{4}{3}\pi r_{\mathrm{u}}^{3} N_{\mathrm{c}} \rho_{\mathrm{p}} V_{\mathrm{aq}} \tag{A.136}$$

and the volume of polymer, V_{p}, may be given by:

$$V_{\mathrm{p}} = \tfrac{4}{3}\pi r_{\mathrm{u}}^{3} N_{\mathrm{c}} V_{\mathrm{aq}} \tag{A.137}$$

The fractional polymeric solids, s, in the system is thus:

$$s = \frac{\frac{4}{3}\pi r_{\mathrm{u}}^{3} N_{\mathrm{c}} \rho_{\mathrm{p}}}{\frac{4}{3}\pi r_{\mathrm{u}}^{3} N_{\mathrm{c}} \rho_{\mathrm{p}} - \rho_{\mathrm{aq}}} \tag{A.138}$$

Naturally, this relationship may be inverted to give N_{c} as a function of s:

$$N_{\mathrm{c}} = \frac{s \rho_{\mathrm{aq}}}{\frac{4}{3}\pi r_{\mathrm{u}}^{3} \rho_{\mathrm{p}} (1 - s)} \tag{A.139}$$

A.6.5 Initial and Final Particle Sizes

The initial, unswollen particle radius, r_i, may be related to the final particle radius, r_f, through the initial mass of polymer in the system, m_pi, and the mass of monomer added $m_\mathrm{m.}$

The final mass of polymer, m_pf, (assuming 100% conversion) is:

$$m_\mathrm{pf} = m_\mathrm{pi} + m_\mathrm{m} \tag{A.140}$$

Using the relationship between particle radius, N_c, and m_p, the final particle radius may be determined from the relationship:

$$r_\mathrm{f}^3 = \frac{m_\mathrm{pi} + m_\mathrm{m}}{m_\mathrm{pi}} r_\mathrm{i}^3 \tag{A.141}$$

A.6.6 Relating Swollen and Unswollen Radii

The swollen and unswollen radii, r_s and r_u respectively, are trivially related by mass balance, using the density of the polymer, d_p, and the density of monomer, d_m.

The volume of the swollen particle is the sum of the polymer volume, V_p, and monomer volume, V_m, which may in turn be related to r_s.

$$V_\mathrm{p} + V_\mathrm{m} = \tfrac{4}{3}\pi r_\mathrm{s}^3 \tag{A.142}$$

The concentration of monomer in the particles, C_p, is given by:

$$C_\mathrm{p} = \frac{m_\mathrm{m}}{M_0(V_p + V_\mathrm{m})} \tag{A.143}$$

where M_0 is the molecular weight of the monomer.

This may be rearranged to give:

$$V_\mathrm{m} = \frac{m_\mathrm{m}}{C_\mathrm{p} M_0} - V_\mathrm{p} \tag{A.144}$$

which, combined with Eq. A.142, gives:

$$\frac{m_\mathrm{m}}{C_\mathrm{p}M_0} = \tfrac{4}{3}\pi r_\mathrm{s}^3 \tag{A.145}$$

Now, V_m is given by the difference between the swollen and unswollen volumes of the particle (assuming that the monomer/polymer mixing is perfect):

$$V_\mathrm{m} = \tfrac{4}{3}\pi(r_\mathrm{s}^3 - r_\mathrm{u}^3) \tag{A.146}$$

which may be related to m_m using d_m, giving:

$$\tfrac{4}{3}\pi(r_\mathrm{s}^3 - r_\mathrm{u}^3)\,\frac{d_\mathrm{m}}{C_\mathrm{p}M_0} = \tfrac{4}{3}\pi r_\mathrm{s}^3 \tag{A.147}$$

$$r_\mathrm{s}^3 = r_\mathrm{u}^3\,\frac{d_\mathrm{m}}{d_\mathrm{m} - C_\mathrm{p}M_0} \tag{A.148}$$

A.6.7 Calculating the Weight-Fraction of Polymer

The weight fraction of polymer, w_p, in a polymer/monomer mixture is defined as:

$$w_\mathrm{p} = \frac{m_\mathrm{p}}{m_\mathrm{p} + m_\mathrm{m}} \tag{A.149}$$

Using $d_\mathrm{m} = m_\mathrm{m}/V_\mathrm{m}$, the following expression is obtained for m_m from Eq. A.143:

$$m_\mathrm{m} = \frac{C_\mathrm{p}M_0V_\mathrm{p}}{1 - C_\mathrm{p}M_0/d_\mathrm{m}} \tag{A.150}$$

Eq. A.150 and the density relation for polymer, $m_\mathrm{p} = d_\mathrm{p}V_\mathrm{p}$, gives:

$$w_\mathrm{p} = \frac{d_\mathrm{p}V_\mathrm{p}}{d_\mathrm{p}V_\mathrm{p} + \dfrac{C_\mathrm{p}M_0V_\mathrm{p}}{1 - C_\mathrm{p}M_0/d_\mathrm{m}}} \tag{A.151}$$

which is readily simplified to:

$$w_\mathrm{p} = \frac{d_\mathrm{p}}{d_\mathrm{p} + \dfrac{C_\mathrm{p}M_0}{1 - C_\mathrm{p}M_0/d_\mathrm{m}}} \tag{A.152}$$

A.7 Notes of Fugal Form and Research

As briefly described in Chapter 1, the fugue is a musical form in which different themes are simultaneously performed by different voices. The fugue is based on imitation with the different voices "chasing" each other through the music.

The fugue grew from the simple canon (or round) in the 17th century and the early Baroque period. Various Germanic composers embellished the simple canon with polyphonic (many-voiced) writing, with the toccata leading to the "Prelude and Fugue" combination.[26] In 1722 and 1747, J.S. Bach published in two volumes *Das wohltemperirte Clavier* (*The Well-tempered Clavier)*, a collection of 48 preludes and fugues, two in each of the major and minor keys.

In *Die Kunst der Fugue* (*The Art of Fugue*), Bach wrote a cycle of 14 fugues, all based upon the same theme. *Die Kunst der Fugue* was never finished, as Bach died before he could complete his masterpiece. The last of the fugues made use of the countersubject "B–A–C–H" (in Germanic music notation, B is B♭ and H is B♮). One of his sons, Carl Philipp Emanuel Bach wrote in the margin on the original manuscript for *Die Kunst der Fugue*, "N.B. In the course of this fugue, at the point where B.A.C.H. was brought in as countersubject, the composer died".[27]

While a detailed analysis of fugal form is somewhat beyond the scope of this Appendix, a simple overview is as follows. A single theme (the *subject*) is presented by one voice (in the context of a fugue, a voice may be a singer, an instrument such as a violin or simply one part played by an organist amongst the other parts). Subsequently, it is imitated by the other voices, the first imitation being called the *answer*. The answer may commence before the initial subject has been completed (*stretto fugue*). Throughout the fugue, the material of the subject appears in slightly modified form, using *modulation* to different keys, *augmentation* (slower), *diminution* (faster), *inversion* (upside-down) or even in *retrograde* (backwards). Against the subject, the *countersubject* is presented, being a second theme designed to complement the subject. These aspects of the fugal form are illustrated in Harold Owen's *Fuguing by Doing* reproduced in Appendix A.8.

The greater structure of a fugue includes the presentation of the subject and countersubject in the *exposition*, followed by sections of fugal writing based on these themes. A *codetta* and several *episodes* may appear throughout the fugue and frequently make use of entirely new material, which is often only alluded to in other parts of the work at most. Finally, the fugue may come to a conclusion in a *cadenza*. Of course, not all fugues follow this structure; indeed, the masters of fugal form, Bach and Handel, were the best at both writing and breaking the rules.

The similarities between a musical fugue and scientific research have been described in great detail by Hofstadter.[27] The idea of parts chasing each other through the music is seen in the way experiment leads to the development of new theory, then theoretical predictions are tested with new experiments. Themes are seen to return to a scientific investigation with modulation, approaches to a problem may be inverted (top-down instead of bottom-up) and the pace of work may be seen to be faster or slower (in augmentation or diminution).

A.7.1 Acknowledgements

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A.8 “Fuguing by Doing” – Harold Owen

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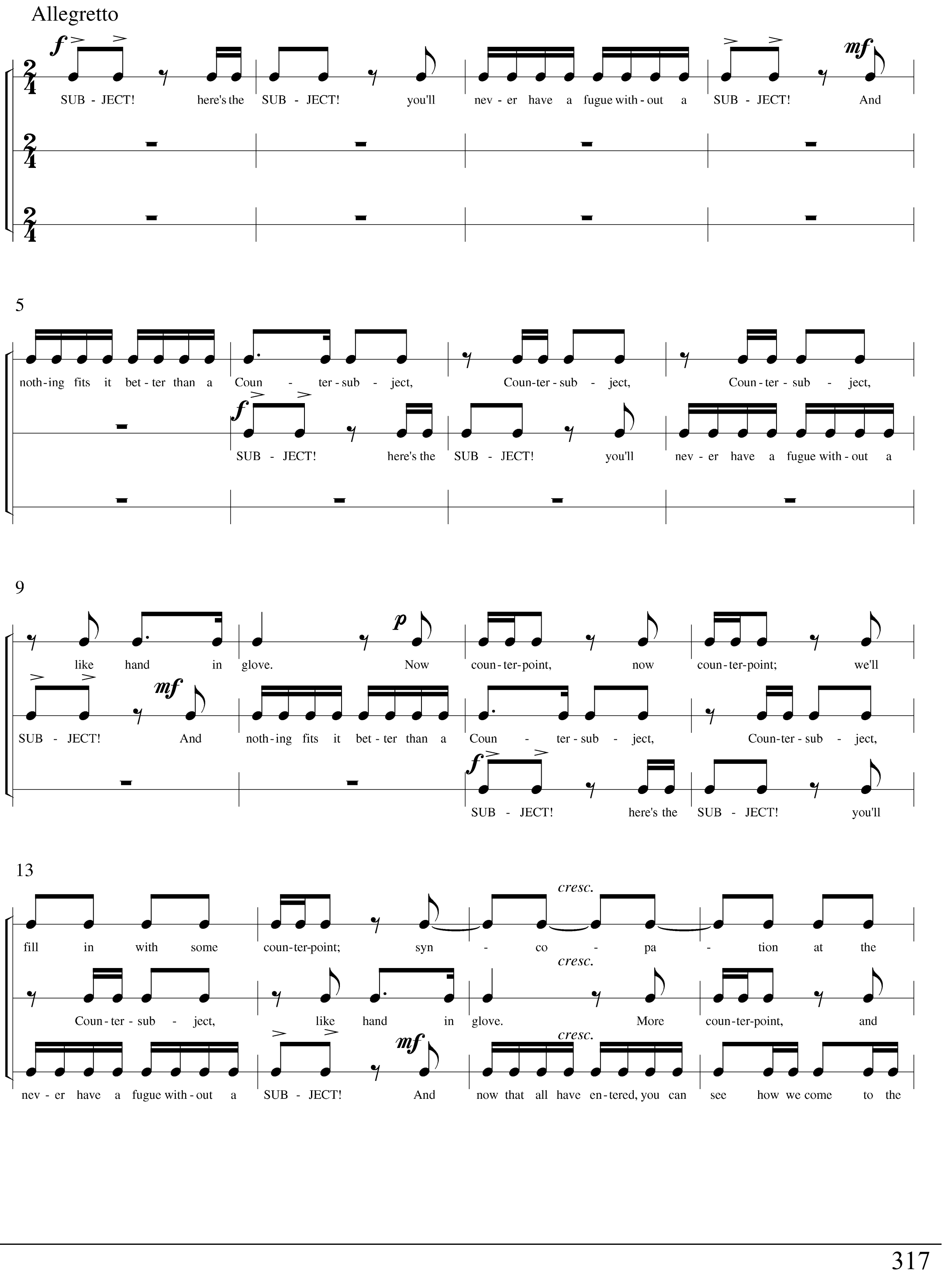
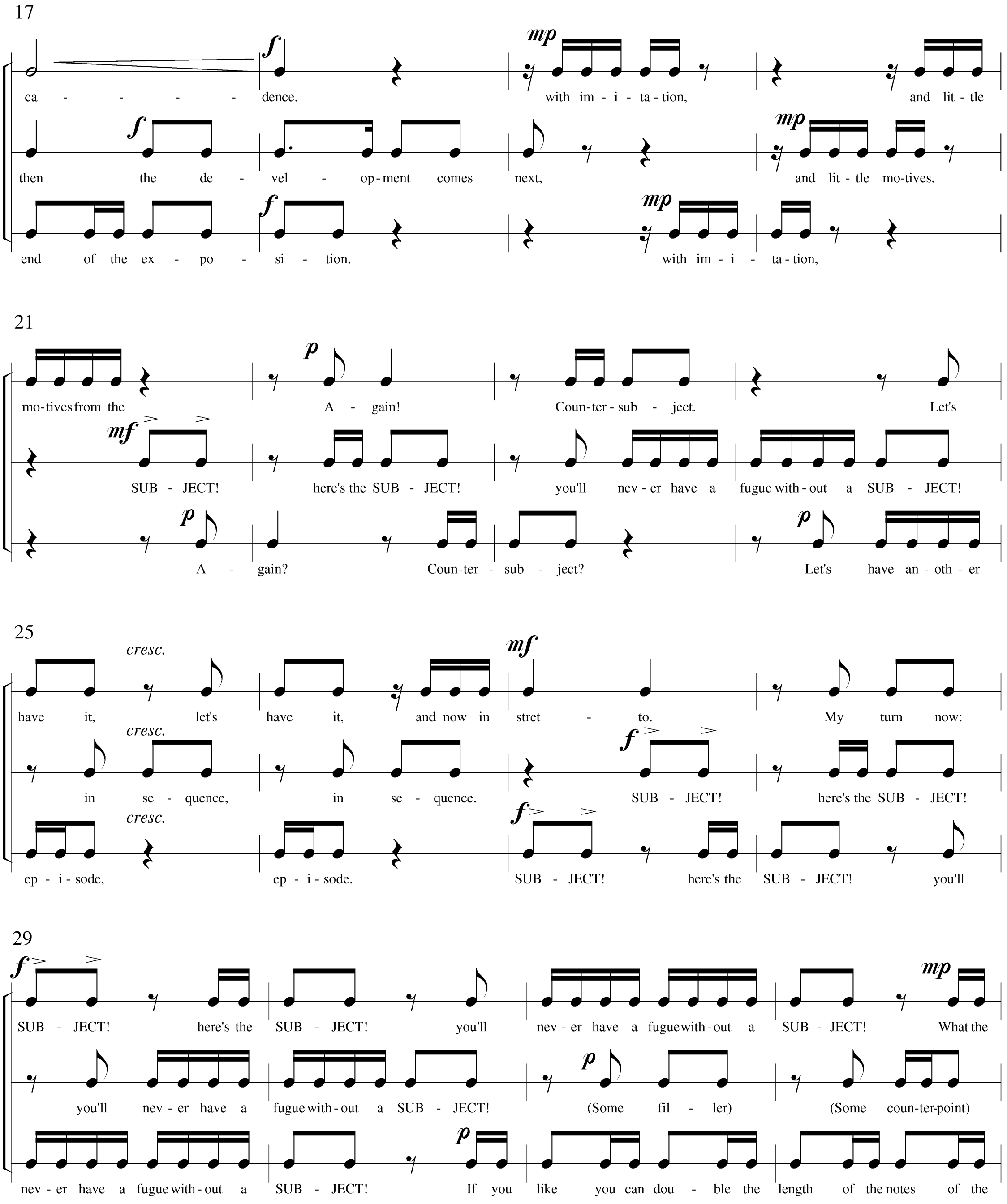
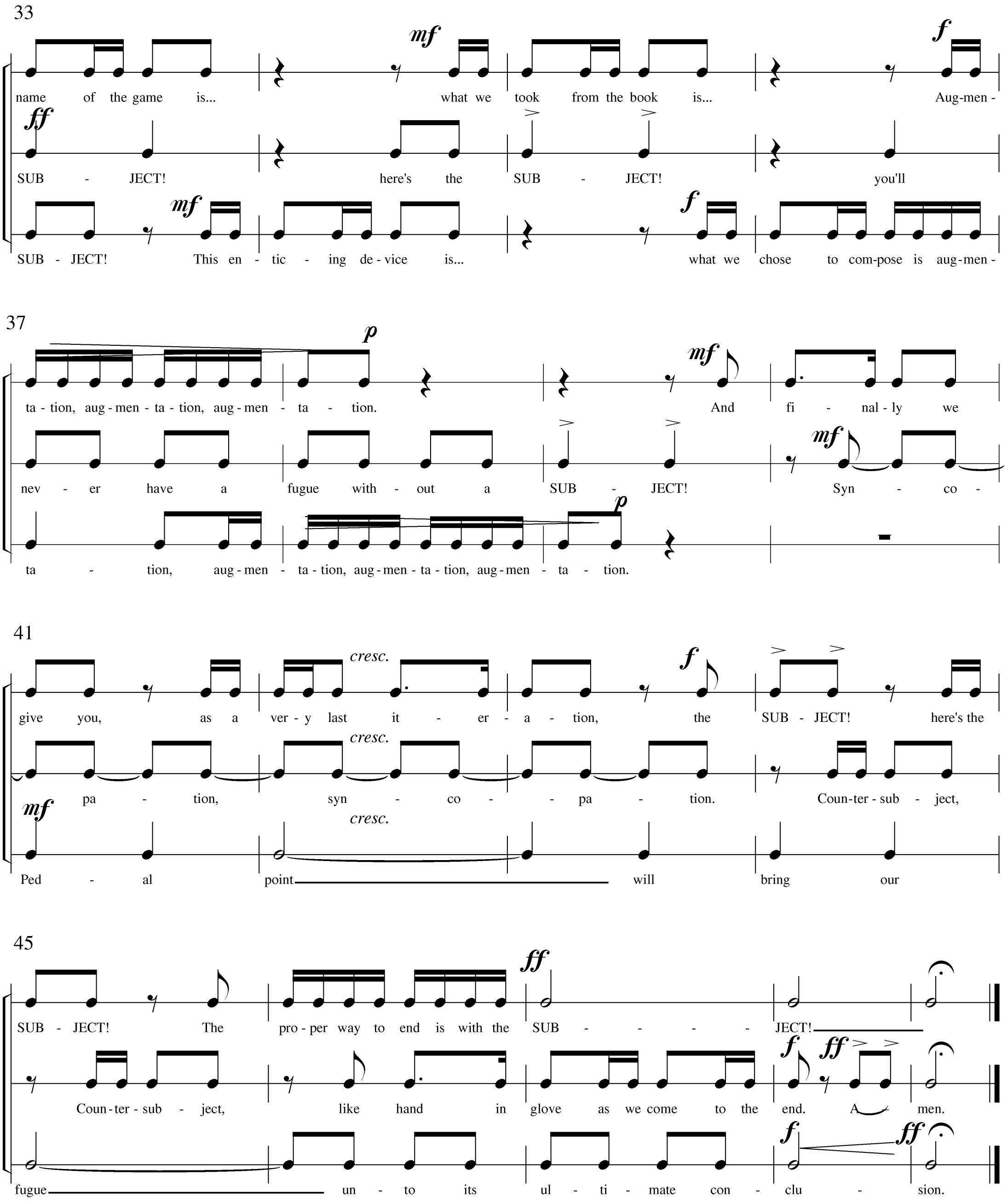



17
f
mp
ca - - - - - dence. with im - i - ta - tion, and lit - tle
f
mp
then the de - vel - op - ment comes next, and lit - tle mo-tives.
f
mp
end of the ex - po - si - tion. with im - i - ta - tion,
21
p
mo - tives from the A - gain! Coun - ter - sub - ject. Let's
mf
SUB - JECT! here's the SUB - JECT! you'll nev - er have a fugue with - out a SUB - JECT!
p
p
A - gain? Coun - ter - sub - ject? Let's have an - oth - er
25
cresc.
mf
have it, let's have it, and now in stret - to. My turn now:
cresc.
f
in se - quence, in se - quence. SUB - JECT! here's the SUB - JECT!
cresc.
f
ep - i - sode, ep - i - sode. SUB - JECT! here's the SUB - JECT! you'll
29
f
mp
SUB - JECT! here's the SUB - JECT! you'll nev - er have a fugue with - out a SUB - JECT! What the
p
you'll nev - er have a fugue with - out a SUB - JECT! (Some fil - ler) (Some coun - ter - point)
p
nev - er have a fugue with - out a SUB - JECT! If you like you can dou - ble the length of the notes of the

A.8.1 Acknowledgements

Thomson Learning is thanked for permission to reproduce *Fuguing by Doing* in the print edition of this thesis (Request #B2482). Thanks also to the composer, Emeritus Professor Harold Owen (University of Oregon), for providing a clean copy of the manuscript.

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