

# Chapter 1

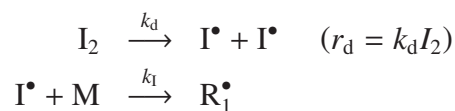
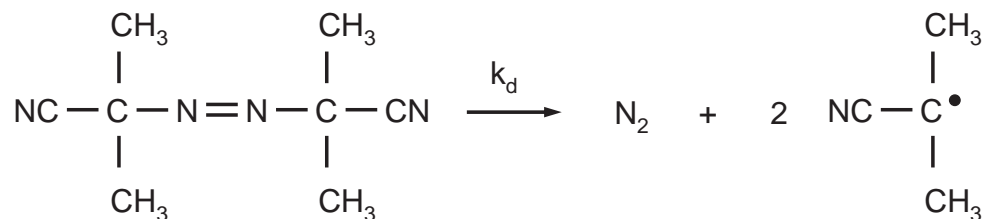
## Free-Radical Polymerization

### 1.1 Chemical Reactions

#### 1.1.1 Initiation

The initiation reaction produces free radicals. There are several ways to do this:

- Chemical initiation The decomposition of the initiator (e.g. AIBN) forms free radicals:



$$\frac{d\text{I}^\bullet}{dt} = 2fk_d I_2 - k_1 \text{I}^\bullet \text{M} \approx 0 \quad (1.1)$$

$$\Rightarrow k_1 \text{I}^\bullet \text{M} = 2fk_d I_2 \equiv R_1 \quad (1.2)$$

where  $f$  is the initiator efficiency, typically  $f = [0.5, 1]$ . Note that in order to ensure a continuous production of radicals all over the process,  $1/k_d$  should be larger than the characteristic time of the polymerization reaction. Examples of the decomposition characteristic time,  $\tau_d$  for some commercial initiators are:

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	$\tau_d$	$T$
Acetyl peroxide	2 h	80 °C
Cumyl peroxide	12 h	110 °C
<i>t</i> -Butyl hydroperoxide	45 h	150 °C

Since this is a first order process,  $\tau_d = 1/k_d$ .

- Thermal initiation: thermal decomposition of the monomer (e.g. styrene).

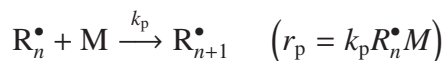
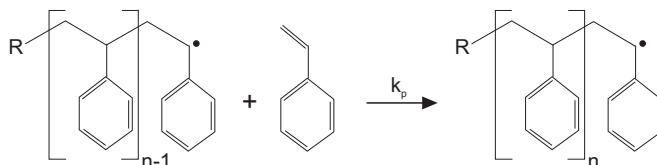
This represents a danger, for example during monomer transportation, since it may lead to undesired polymerization of the monomer. For this reason, inhibitors (scavengers of radicals) are usually added to the monomers before storage. This causes the occurrence of a non reproducible induction period when such monomers are polymerized.

- Initiation by radiation

The decomposition of the initiator is caused by light or another source of radiation. Since this method is quite expensive, it is only applied to polymerization systems operating at very low temperatures.

### 1.1.2 Propagation

Propagation is the addition of a monomer molecule to a radical chain.



### 1.1.3 Chain Transfer

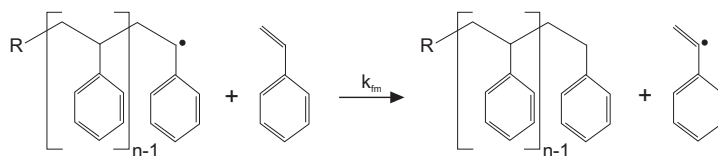
- Chain transfer to monomer



The reactants are the same as for the propagation reaction, but the activation energy is much larger. Accordingly,  $k_{fm}$  is usually at least  $10^3$  times smaller than  $k_p$ . This reaction

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leads to the formation of a polymer chain with a terminal double bond. This can induce chain branching through the terminal double bond propagation reaction.

- Chain transfer to chain transfer agent



A chain transfer agent, S is a molecule containing a weak bond that can be broken to lead to radical transfer, similarly as in the case of monomer above (e.g.  $\text{CCl}_4$ ,  $\text{CBr}_4$ , mercaptans).

- Chain transfer to polymer



In this reaction the growing radical chain,  $R_n^\bullet$  extracts a hydrogen from the dead chain,  $P_m$ . Since this extraction can occur on any of the  $m$  monomer units along the chain, the rate of this reaction is proportional to the length of  $P_m$ .

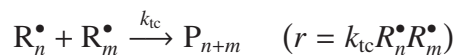
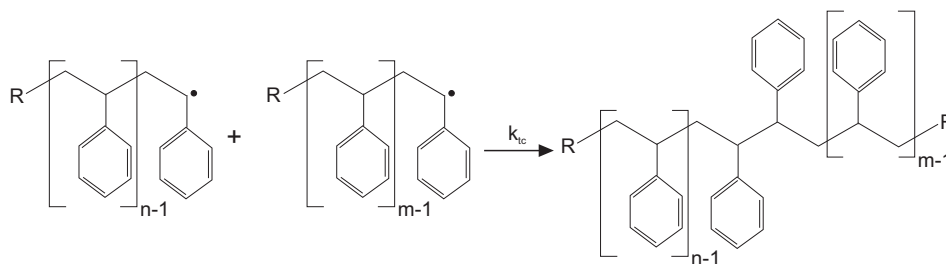
General observations on the role of chain transfer reactions:

- The concentration of radicals is not affected and therefore the rate of monomer consumption is also unchanged.
- The growth of polymer chains is stopped and therefore shorter chains are produced.
- Each transfer event leaves a different end-group on the chain that can be detected (NMR, titration) so as to identify and quantify the corresponding chain transfer reaction.
- Nonlinear (branched) polymer chains are produced: directly by chain transfer to polymer or indirectly through the propagation of the terminal double bond left by a chain transfer to monomer event.

### 1.1.4 Bimolecular Termination

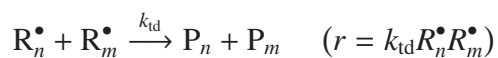
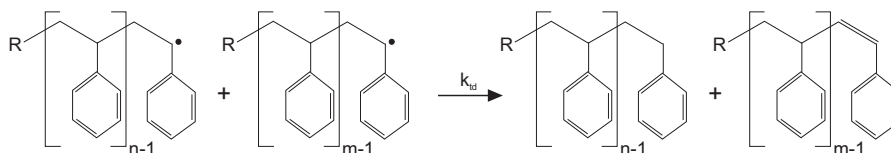
Bimolecular termination occurs according to two different mechanisms: termination by combination and termination by disproportionation. Their relative importance depends upon the specific polymerization system.

- Termination by combination



This reaction results in an increase of the chain length.

- Termination by disproportionation



The chain length remains constant during the termination reaction. Note that also in this case chains with terminal double bond are produced, which can therefore lead to the occurrence of branching.

## 1.2 Diffusion Control of Chemical Reactions

When dealing with macromolecules we can regard the reaction event as constituted by two steps in series:

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- a relative motion or diffusion of the two molecules in order to overlap their active centers (note that the centers of gravity of the two macromolecules already overlap, i.e., we have no mass transport involved)
- the reaction event per se, i.e., breakage and formation of chemical bonds.

Since the two steps are in series, the slowest one defines the rate of the overall process, that is the reaction rate.

In the case of termination by combination, the reaction step is very fast, while the diffusion step is slow due to the difficulty of the two macromolecules to find their respective active centers (the two chains exhibit strong entanglements). The result is that diffusion is the rate determining step. Accordingly the rate constant of termination by combination,  $k_{tc}$  has the following characteristics:

- decreases with viscosity (and therefore with conversion)
- increases very mildly with temperature
- is substantially independent of the chemical nature of the radicals.

This effect is usually referred to as *Trommsdorf* or *gel effect*. This is responsible for the accumulation of radicals during the reaction which can also lead to thermal runaway of the reactor.

Let us now consider the other involved reactions. It is found that in most cases they are not diffusion controlled for the following reasons:

- termination by disproportionation: the reaction step is slower (can still be diffusion controlled)
- chain transfer to polymer: reaction is slower and diffusion is faster since we have many reactive points along the chain.
- propagation: reaction is slower and diffusion much faster due to the small dimension of the monomer (this reaction stops below the glass transition temperature)

## **1.3 Polymerization Processes**

### **1.3.1 Bulk Polymerization**

- ingredients: monomer and initiator only
- products: high purity
- disadvantage: poor temperature control at high conversion (thermal runaway!)

### **1.3.2 Solution Polymerization**

- ingredients: solvent, monomer and initiator
- guarantees an efficient heat transfer
- disadvantage: low productivity because of low solubility of the produced polymer

### **1.3.3 Suspension Polymerization**

- ingredients: water, monomer, initiator and stabilizer
- size of formed polymer particles approx. 0.01 – 0.5 cm
- initiator is solubilized in monomer phase
- polymerization occurs within the monomer droplets
- high productivity (> 40 % solid)
- heat production is under control

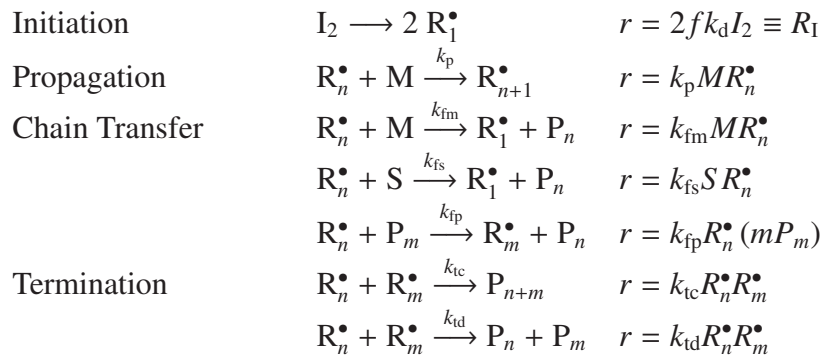
### **1.3.4 Emulsion Polymerization**

- ingredients: water, monomer, initiator and stabilizer
- size of formed polymer particles approx. 0.05 – 1  $\mu\text{m}$
- initiator is solubilized in water phase
- polymerization occurs mainly within the polymer particles

- high productivity (> 40 % solid)
- heat production is under control
- advantage: high molecular weight as well as high polymerization rate can be achieved simultaneously

## 1.4 Kinetics of Free-Radical Polymerization

### 1.4.1 Involved Chemical Reactions



where  $n, m = [1 \dots \infty]$

Note that all reaction rate constants are assumed to be chain length independent, i.e., we use the Terminal Kinetic Model.

### 1.4.2 Population Balance Equations in a Batch Reactor

- $n=1$ :

$$\begin{aligned}
 \frac{dR_1^\bullet}{dt} = & R_I - k_p M R_1^\bullet \\
 & + (k_{fm} M + k_{fs} S) \sum_{n=2}^{\infty} R_n^\bullet \\
 & + k_{fp} (1P_1) \sum_{n=1}^{\infty} R_n^\bullet - \left[ k_{fp} \sum_{n=1}^{\infty} (nP_n) \right] R_1^\bullet \\
 & - (k_{tc} + k_{td}) \left[ \sum_{n=1}^{\infty} R_n^\bullet \right] R_1^\bullet
 \end{aligned} \tag{1.3}$$

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- $n \geq 2$ :

$$\begin{aligned}
 \frac{dR_n^\bullet}{dt} &= k_p MR_{n-1}^\bullet - k_p MR_n^\bullet \\
 &\quad - (k_{fm}M + k_{fs}S) R_n^\bullet \\
 &\quad + k_{fp} (nP_n) \sum_{m=1}^{\infty} R_m^\bullet - k_{fp} \sum_{m=1}^{\infty} (mP_m) R_n^\bullet \\
 &\quad - (k_{tc} + k_{td}) \left[ \sum_{m=1}^{\infty} R_m^\bullet \right] R_n^\bullet
 \end{aligned} \tag{1.4}$$

Let us define

$$R^\bullet \equiv \sum_{n=1}^{\infty} R_n^\bullet \tag{1.5}$$

and sum up equations (1.3) and (1.4) from  $n = 1$  to  $\infty$ . In this way we obtain:

$$\begin{aligned}
 \frac{dR^\bullet}{dt} &= \frac{dR_1^\bullet}{dt} + \sum_{n=2}^{\infty} \frac{dR_n^\bullet}{dt} \\
 &= R_I - k_p MR_1^\bullet + k_p M \sum_{n=2}^{\infty} R_{n-1}^\bullet - k_p M \sum_{n=2}^{\infty} R_n^\bullet \\
 &\quad + (k_{fm}M + k_{fs}S) \sum_{n=2}^{\infty} R_n^\bullet - (k_{fm}M + k_{fs}S) \sum_{n=2}^{\infty} R_n^\bullet \\
 &\quad + k_{fp} (1P_1) \sum_{n=1}^{\infty} R_n^\bullet - k_{fp} \left[ \sum_{n=1}^{\infty} (nP_n) \right] R_1^\bullet \\
 &\quad + k_{fp} \sum_{n=2}^{\infty} [nP_n] \sum_{m=1}^{\infty} R_m^\bullet - k_{fp} \left[ \sum_{n=2}^{\infty} R_n^\bullet \right] \left[ \sum_{m=1}^{\infty} (mP_m) \right] \\
 &\quad - (k_{tc} + k_{td}) R_1^\bullet \sum_{n=1}^{\infty} R_n^\bullet - (k_{tc} + k_{td}) \left[ \sum_{n=2}^{\infty} R_n^\bullet \right] \left[ \sum_{m=1}^{\infty} R_m^\bullet \right]
 \end{aligned} \tag{1.6}$$

$$\begin{aligned}
 \frac{dR^\bullet}{dt} &= R_I - k_p MR^\bullet + k_p M \sum_{n=1}^{\infty} R_n^\bullet \\
 &\quad + k_{fp} R^\bullet \left[ P_1 + \sum_{n=2}^{\infty} (nP_n) \right] - k_{fp} \left[ \sum_{n=1}^{\infty} (nP_n) \right] \left[ R_1^\bullet + \sum_{n=2}^{\infty} R_n^\bullet \right] \\
 &\quad - (k_{tc} + k_{td}) R^\bullet \left[ R_1^\bullet + \sum_{n=2}^{\infty} R_n^\bullet \right]
 \end{aligned} \tag{1.7}$$

$$\Rightarrow \frac{dR^\bullet}{dt} = R_I - (k_{tc} + k_{td}) R^{\bullet 2} \tag{1.8}$$



### 1.4.3 Rate of Monomer Consumption

Under the assumption of pseudo steady state for the concentration of active chains (see 1.5) we can write:

$$\frac{dR^\bullet}{dt} = R_I - (k_{tc} + k_{td}) R^{\bullet 2} = 0 \quad (1.9)$$

and obtain:

$$R^\bullet = \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} \quad (1.10)$$

Let us now consider the rate of monomer consumption,  $R_p$ . Neglecting the chain transfer to monomer reaction we have:

$$R_p = k_p M \sum_{n=1}^{\infty} R_n^\bullet = k_p M \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} \quad (1.11)$$

The mass balance for the monomer can be written as follows (still in the case of a batch reactor):

$$\frac{dM}{dt} = -R_p = -k_p M R^\bullet \quad (1.12)$$

Considering  $k_p R^\bullet$  as the pseudo-first order reaction rate constant for monomer consumption, we can conclude that the characteristic time for the process of monomer consumption is  $\tau_M = \frac{1}{k_p R^\bullet}$ . Using the conversion instead of the concentration,  $X = (M_0 - M) / M_0$ , and combining equation (1.11) and (1.12) we get:

$$\frac{dX}{dt} = -\frac{1}{M_0} \frac{dM}{dt} = \frac{R_p}{M_0} = (1 - X) k_p \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} \quad (1.13)$$

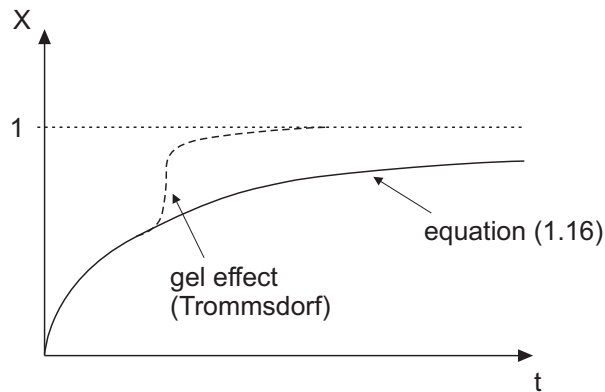
$$\frac{dX}{(1 - X)} = k_p \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} dt \quad (1.14)$$

where the initial condition is  $X(t = 0) = 0$ . Therefore we can write:

$$X = 1 - \exp \left[ - \int_0^t k_p \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} \cdot dt \right] \quad (1.15)$$

As long as the temperature in the reactor remains constant, i.e., before the onset of the so-called gel effect,  $k_{tc}$  and  $k_{td}$  are independent of the conversion  $X$ . Moreover, if the half-life of the initiator is much larger than the characteristic time of the monomer consumption process,  $\tau_M, \tau_d \gg \tau_M$ , the solution to equation (1.15) is:

$$X = 1 - \exp \left[ -k_p \sqrt{\frac{R_I}{(k_{tc} + k_{td})}} \cdot t \right] \quad (1.16)$$



- Which kinetic parameter(s) can be estimated from the plot of the monomer conversion vs. time?

## 1.5 Pseudo Steady State Approximation

In this section we introduce an important concept often used in chemical reaction engineering, the so-called pseudo steady state approximation (PSSA). Therefore, let us consider two consecutive first-order reactions occurring in a batch reactor:



with initial conditions  $I(0) = I_0$ ,  $R(0) = R_0$  and  $P(0) = 0$ . The mass balances are:

$$\frac{dI}{dt} = -k_1 I \quad (1.17)$$

$$\frac{dR}{dt} = k_1 I - k_2 R \quad (1.18)$$

The solution of equation (1.17) is:

$$I = I_0 \exp(-k_1 t) \quad (1.19)$$

which substituted in equation (1.18) leads to a linear non-homogeneous ODE. We consider the solution of the homogeneous associated equation:

$$R^H = A \exp(-k_2 t) \quad (1.20)$$

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and then the particular solution having the form:

$$R^P = K \exp(-k_1 t) \quad (1.21)$$

Substituting in equation (1.18) we get:

$$-k_1 K \exp(-k_1 t) = k_1 I_0 \exp(-k_1 t) - k_2 K \exp(-k_1 t) \quad (1.22)$$

$$\Rightarrow k_1 K + k_1 I_0 - k_2 K = 0 \quad (1.23)$$

$$\Rightarrow K = \frac{k_1 I_0}{k_2 - k_1} \quad (1.24)$$

Thus the general solution is:

$$R = R^H + R^P = A \exp(-k_2 t) + \frac{k_1 I_0}{k_2 - k_1} \exp(-k_1 t) \quad (1.25)$$

which using the initial condition to compute  $A$  reduces to:

$$R = \left( R_0 - \frac{k_1 I_0}{k_2 - k_1} \right) \exp(-k_2 t) + \frac{k_1 I_0}{k_2 - k_1} \exp(-k_1 t) \quad (1.26)$$

Let us now consider the case where  $R$  is a very reactive species, that is  $k_2 \gg k_1$ , then equation (1.26) reduces to:

$$R = \frac{k_1 I_0}{k_2} \exp(-k_1 t) = \frac{k_1}{k_2} I \quad (1.27)$$

This means that  $R$  starts at  $R_0$  and after a short time of the order of  $1/k_2$  the term  $\exp(-k_2 t)$  vanishes and  $R = k_1 I/k_2$  as shown in the figure.

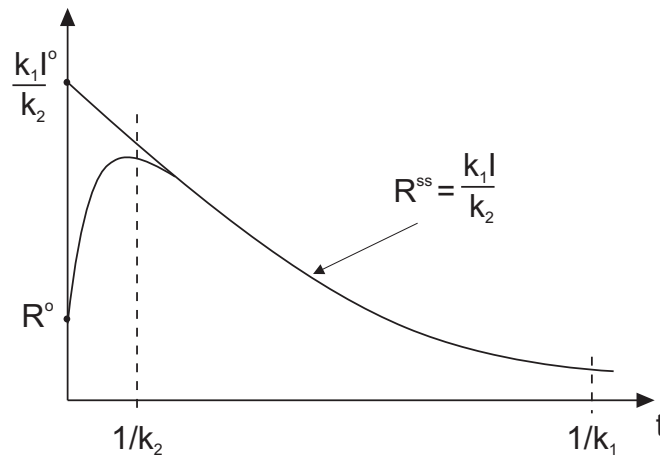
We see two time scales in the process:

- $1/k_2$ : characteristic time of disappearance for  $R \Rightarrow$  fast
- $1/k_1$ : characteristic time of disappearance for  $I \Rightarrow$  slow

Since the dynamics of  $R$  is faster than that of  $I$ , we can assume that  $R$  is at any given time at steady state with respect to  $I$ , i.e.,  $R$  is so fast to reach steady state before  $I$  can change significantly. This is the PSSA, which means that we can assume  $dR/dt = 0$  in equation (1.18), and compute the PSSA value of  $R$ :

$$R^{ss} = \frac{k_1}{k_2} I \quad (1.28)$$

which is the same value given by equation (1.27).



### Note

In the PSSA we do not mean that  $dR/dt = 0$ , and in fact in the case above we see that:

$$\frac{dR^{ss}}{dt} = -\frac{k_1^2 I_0}{k_2} \exp(-k_1 t) = -\frac{k_1^2}{k_2} I \quad (1.29)$$

Actually we simply mean that

$$\frac{dR^{ss}}{dt} \ll k_1 I \quad \text{and} \quad \frac{dR^{ss}}{dt} \ll k_2 R^{ss} \quad (1.30)$$

as it is readily seen by comparison noting that  $k_1/k_2 \ll 1$ .

### Another Point of View

Let us rewrite equation (1.18) as follows:

$$\frac{dR}{dt} = k_2 \left( \frac{k_1}{k_2} I - R \right) = k_2 (R^{ss} - R) \quad (1.31)$$

We can observe that:

$$\begin{aligned} \text{if } R > R^{ss} &\Rightarrow dR/dt < 0 \Rightarrow R \text{ decreases} \\ \text{if } R < R^{ss} &\Rightarrow dR/dt > 0 \Rightarrow R \text{ increases} \end{aligned}$$

which means that  $R$  remains always “around”  $R^{ss}$ . Note that this is not true in general, but only in the case where  $k_2$  is very large we have that the “force” attracting  $R$  to  $R^{ss}$  increases up to the point where  $R$  cannot differ significantly from  $R^{ss}$ .

### Conclusion

The PSSA can be applied when we have very different characteristic times, typically when the intermediate species is very reactive, i.e.,  $k_2 \gg k_1$ . The obtained solution is valid for most of the process time, with the exception of a short initial transient. We have two characteristic times:

- the fast one ( $1/k_2$ ) which belongs to  $R$  and where  $I$  does not change significantly
- the slow one ( $1/k_1$ ) which belongs to  $I$  and determines the process time, that is the time needed by the slowest species to complete its dynamics.

With respect to numerical integration this has important implications:

- the integration time is given by the process time, i.e.,  $\tau_p \approx 1/k_1$
- the integration step is proportional to the characteristic time of the fastest dynamics that we want to follow, i.e.,  $\Delta\tau \approx 1/k_2$
- the number of integration steps is proportional to  $\tau_p/\Delta\tau \approx k_2/k_1$  which means that the larger is  $k_2/k_1$  the more we are entitled to use PSSA ... and the more integration steps we have to compute if we fail to use it.

### 1.5.1 Stiffness Ratio

In general, for a system of ODEs the ratio between the largest and the smallest eigenvalue is referred to as the stiffness ratio of the system. This gives a measure of the difficulty in integrating a system of ODEs numerically. The coefficient matrix of the system of ODEs, defined as:

$$\frac{dx}{dt} = \underline{\underline{A}} x \quad (1.32)$$

in our case is given by:

$$\underline{\underline{A}} = \begin{vmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{vmatrix} \quad \text{with } \underline{x} = \begin{vmatrix} I \\ R \end{vmatrix} \quad (1.33)$$

The eigenvalues of  $\underline{\underline{A}}$  are given by:

$$\begin{aligned} (-k_1 - \lambda)(-k_2 - \lambda) &= 0 \\ \Rightarrow \lambda_1 &= -k_1, \quad \lambda_2 = -k_2 \end{aligned}$$

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and the stiffness ratio is then given by:

$$\frac{\lambda_2}{\lambda_1} = \frac{k_2}{k_1} \quad (1.34)$$

which, as discussed above, is proportional to the integration steps to be used in the numerical integration of the system of ODEs.