

- $c < \min\{c_{\text{sol,I}}(T), c_{\text{sol,II}}(T)\}$  the system is undersaturated for both populations. All crystals are dissolving,
- $c > \max\{c_{\text{sol,I}}(T), c_{\text{sol,II}}(T)\}$  the system is supersaturated for both populations. All crystals are growing and nucleation might occur for both forms,
- $\min\{c_{\text{sol,I}}(T), c_{\text{sol,II}}(T)\} < c < \max\{c_{\text{sol,I}}(T), c_{\text{sol,II}}(T)\}$  the more soluble crystals are dissolving whereas the less soluble are growing.

It should be highlighted under the concentration conditions described by the last bullet-point the more soluble crystals will fully be transformed to the less soluble crystals. This process is called solvent mediated polymorphic transformation. The mathematical model of such a system consists of the PBEs of form I and form II crystals, which are coupled through the mass balance.

The form I crystal PBE takes the form:

$$\frac{\partial n_i(L,t)}{\partial t} + \frac{\partial [G_i n_i(L,t)]}{\partial L} = B_i \delta(L - L_n) + \frac{n_{i,f}(L,t) - n_i(L,t)}{\tau}, \text{ if } c > c_{\text{sol},i}(T), i = \text{I, II} \quad (2.67)$$

$$\frac{\partial n_i(L,t)}{\partial t} - \frac{\partial [D_i n_i(L,t)]}{\partial L} = \frac{n_{i,f}(L,t) - n_i(L,t)}{\tau}, \text{ if } c < c_{\text{sol},i}(T), i = \text{I, II} \quad (2.68)$$

with the corresponding initial and boundary conditions. Here  $B_i$ ,  $G_i$  and  $D_i$  denote the nucleation, growth and dissolution rate of form  $i$  under the given thermodynamic conditions.

The mass balance equation takes into consideration the impact of crystallization or dissolution of both polymorphs:

$$\frac{dc}{dt} = -\sum_i \rho_{c,i} k_{v,i} R_{v,i} + \frac{c_f - c}{\tau} \quad (2.69)$$

with the corresponding initial condition, where  $R_{v,i}$  denotes the impact of crystallization on the liquid concentration. Depending on the solubility conditions, these functions have the forms listed in Table 2.10.

The four PB eqn (2.67) and (2.68) are solved simultaneously with the mass balance eqn (2.69) with a suitable solution method. Since during the solvent

**Table 2.10** Impact of crystallization of the two polymorphs on the liquid concentration as a function of concentration conditions.

	$c < \min\{c_{\text{sol,I}}, c_{\text{sol,II}}\}$	$c > \max\{c_{\text{sol,I}}, c_{\text{sol,II}}\}$	Otherwise
$R_{v,\text{I}}$	$-3D_{\text{I}} \int_0^{L_{\text{max}}} L^2 n_{\text{I}}(L,t) dL$	$B_{\text{I}} L_n^3 + 3G_{\text{I}} \int_0^{L_{\text{max}}} L^2 n_{\text{I}}(L,t) dL$	$B_{\text{I}} L_n^3 + 3G_{\text{I}} \int_0^{L_{\text{max}}} L^2 n_{\text{I}}(L,t) dL$
$R_{v,\text{II}}$	$-3D_{\text{II}} \int_0^{L_{\text{max}}} L^2 n_{\text{II}}(L,t) dL$	$B_{\text{II}} L_n^3 + 3G_{\text{II}} \int_0^{L_{\text{max}}} L^2 n_{\text{II}}(L,t) dL$	$-3D_{\text{II}} \int_0^{L_{\text{max}}} L^2 n_{\text{II}}(L,t) dL$