

## Chapter 2

### Theories on the Liesegang Phenomena

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*Theoretical models of Liesegang rhythmic precipitation pattern formation are reviewed and presented. Even though many scientists speculated on this subject for a century and different theories have been tailored, so far, no single theory of periodic precipitation seems to be able to account for all the observed features of the phenomenon. There is still disagreement as to the mechanisms underlying the patterning. In view of the variety and complexity of the phenomenon, the mechanisms responsible for these structures are still under discussion.*

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#### 2.1 Introduction

The kinetics of Liesegang banding is generally very complex, involving the coupling of diffusion and precipitation processes in non-equilibrium regime. Many researchers have developed several theoretical models for explaining the mechanism of this self-organized phenomenon [1-13]. All the theories share the assumption that the precipitate appears as the system passes through some nucleation or coagulation thresholds. However, the theories differ on pre or post nucleation assumptions. The main unresolved task in all the theories is that how the diffusive reagents  $A$  and  $B$  turn into immobile precipitate  $P$ ,



where  $Q$  is an intermediate reaction product, which is generally not well known. The uncertainty about the intermediate compound and its dynamics

is the basis for the existence of the number of competing theories and the continuance of theoretical investigations on the kinetics of the process.

Most of the theories are based on Ostwald's supersaturation model [14], which considers band formation as a spatially discontinuous nucleation process. According to the promoters of this theory, the outer electrolyte  $A$  and the inner reactant  $B$  turn directly into precipitate  $P$  and there is no intermediate compound formation in between  $A$ ,  $B$  and  $P$ . Nucleation of the precipitate  $P$  occurs when the local product of the ion concentration  $C_A C_B$  reaches some threshold  $C^*$ , the so called solubility product which is a thermodynamic parameter of the reactive system. Since the process is diffusion limited (reaction time is negligibly small in comparison with the diffusion time), precipitation results in the depletion of the local level of supersaturation to the extent that no further nucleation becomes possible. As the reaction front proceeds further into the medium, the concentration product eventually attains the threshold level and the nucleation of the precipitate is triggered again. Repetition of this sequence results in the formation of periodic precipitate patterns. Morse and Pierce [1], Wagner [2], Prager [5] and others developed mathematical models based on this concept of supersaturation of ion-product.

In another scenario [9,15], the two species  $A$  and  $B$  react to produce a new intermediate compound  $Q$  and the mechanism of band formation is based on the supersaturation of the intermediate compound. It is assumed that  $Q$  also diffuses in the gel. The nature of  $Q$  is not clearly specified; it may be a molecule or a colloid particle. When the local concentration of  $Q$  reaches some threshold value, nucleation occurs and the nucleated particles  $P$  act as aggregation seeds. The  $Q$  particles near  $P$  aggregate to the existing

droplet (hence become  $P$ ), provided their local concentration is larger than a given aggregation threshold. Two thresholds, one for nucleation and one for droplet growth characterize these models. The depletion mechanism is similar to the one described for the ion product theory and it leads to band formation. This theory is generally referred as the theory of nucleation and droplet growth [13].

The other often-applied theory is the induced sol-coagulation theory [6]. According to this model, the intermediate compound  $Q$  is assumed to be a sol and this sol coagulates if the following two conditions are satisfied. First, the concentration of  $Q$  exceeds a supersaturation threshold and second, the local concentration of the outer electrolyte  $C_A$  is above a critical coagulation threshold  $C_A^*$ . When the concentration of the outer electrolyte reaches the critical coagulation concentration, stability of the sol vanishes and the sol particles will aggregate. Because of their large size they will not be able to move in the network any more. The band formation, according to this theory, is a consequence of the nucleation and growth of the precipitate combined with the motion of the front where  $C_A = C_A^*$ . At the place of the coagulation, a visible precipitation zone will appear. Around the zone, concentration of the sol particles decrease, which causes slow diffusion of the sol towards the precipitated zone. This leads to the formation of a depleted zone around the precipitate band where the formation of the sol particles can continue but the sol concentration will be too low for coagulation. This means that an alternating pattern of stable and coagulated precipitate will form.

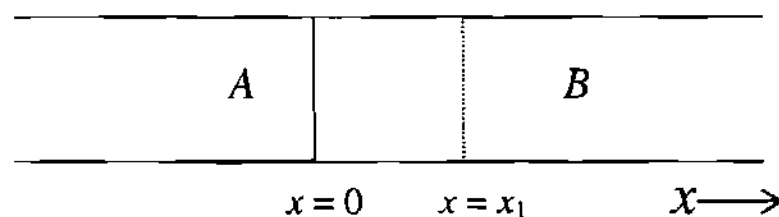
From an experimental point of view the main difference between the supersaturation theory and sol coagulation theory is the distribution of

the precipitate. According to the supersaturation theory, areas between precipitate zones are really empty or they do not contain precipitate at all. Against this, the sol-coagulation model leads to a continuous precipitate distribution. The zones between bands contain a very dilute stable sol.

Many researchers have dedicated much effort in developing a comprehensive unified model to explain all the observed spatial and temporal arrangements of Liesegang patterns. However the complexity and sometimes chaotic nature of this phenomenon have somehow obstructed it [16].

## 2.2 Morse and Pierce model

Shortly after the discovery of Liesegang rings, Morse and Pierce [1] discussed their formation by studying the diffusive behavior of silver ions into a gel containing uniformly mixed chromate ions to form silver chromate precipitate. They obtained the physical conditions of the process by the straightforward analysis of Fick's diffusion equations for the outer ions ( $A$ ) and the inner ions ( $B$ ). Their model assumes an inexhaustible reservoir of  $A$  ions and a diffusion process undisturbed by the band formation. In the problem of formation of precipitate bands, for simplicity, the two ions are considered to be diffusing from opposite sides and forming the precipitation band at  $x = x_1$  (Figure 2.1).



**Figure 2.1:** One-dimensional diffusion of  $A$  ions into a gel impregnated with  $B$  ions.

Fick's second law for outer and inner ions, respectively, is

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (2.2)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad (2.3)$$

where  $C_A(x, t)$  and  $C_B(x, t)$  are the outer and inner ion concentrations.  $D_A$  and  $D_B$  are the diffusion coefficients of the outer and inner ions in the gel medium. Since the reservoir ion concentration is large enough,  $C_A(x, t) = C_{A0}$  for  $x < 0$  at all times will be a good approximation. Also at  $t = 0$ ,  $C_B(x, t) = C_{B0}$  for all positive values of  $x$  and  $C_B(x, t) = 0$  for all negative values. With these boundary conditions, the solutions of the differential equations 2.2 and 2.3 are

$$C_A(x, t) = \frac{2C_{A0}}{\sqrt{\pi}} \int_{x/2\sqrt{D_A t}}^{\infty} e^{-\beta^2} d\beta \quad (2.4)$$

$$C_B(x, t) = \frac{C_{B0}}{\sqrt{\pi}} \int_{x/2\sqrt{D_B t}}^{\infty} e^{-\beta^2} d\beta \quad (2.5)$$

where  $\beta$  is a variable of integration. For the formation of precipitate at  $x = x_1$ , the supersaturation product shall exceed a critical limit. Morse and Pierce stated this condition as

$$C^* = C_A^2 C_B = \frac{4C_{A0}^2 C_{B0}}{\sqrt{\pi^3}} \left[ \int_{x/2\sqrt{D_A t}}^{\infty} e^{-\beta^2} d\beta \right]^2 \left[ \int_{x/2\sqrt{D_B t}}^{\infty} e^{-\beta^2} d\beta \right] \quad (2.6)$$

If  $C^*$ ,  $D_A$  and  $D_B$  are constants, from equation 2.6 it follows that

$$\frac{x}{\sqrt{t}} = \text{Constant} \quad (2.7)$$

and is found to be independent of  $C_{A0}$  and  $C_{B0}$ . This conclusion, as we discussed earlier, is the time law, which is confirmed experimentally by many investigators [1,17-20]. Other characteristic equations of Liesegang phenomenon can also be derived [3] from this condition or directly from the diffusion equations [2].

Morse & Pierce model could not explain the successive ring formation. Since the number of ions incorporated in the gel is limited, immediately after the formation of the first ring, the concentration level of the  $B$  type ions is reduced to a low value. The model also does not give any explanation for the concentration contour distortion by ring formation. The time of formation of a ring has been interpreted as the time by which a critical supersaturation is reached in the region. Hence the critical supersaturation is a necessary and sufficient condition for the formation of the ring. Though this model has all these shortcomings, many of the researchers after Morse and Pierce followed the same path in dealing with the problem.

### 2.3 The Wagner model

In spite of contrary opinions of some authors, Wagner [2] considered the Ostwald's supersaturation theory as an ideal tool for explaining the periodic precipitate band formation. According to Wagner the supersaturation condition and the existence of a meta stable concentration limit for the formation of nuclei play an important role. He carefully studied the situation keeping in mind all the above concepts and solved the problem by a straightforward mathematical analysis of the diffusion processes and by considering the concentrations as functions of time and distance. The whole space is divided into two regions in which either  $A$  type ions or  $B$  type ions are prevalent and accordingly the concentration of the other component is

negligible. The precipitation is expected at  $x = x_1$ , where the two types of ions diffusing in opposite directions encounter each other. Moreover Wagner suggested that at  $x = x_1$  the diffusion rates are equivalent with opposite signs. To avoid lengthy expressions he also assumed that the diffusion coefficients of the two ions are equal and thus may be designated by the common symbol  $D$ . Hence at  $x = x_1$ ,

$$-D \frac{\partial C_A}{\partial x} = +D \frac{\partial C_B}{\partial x} \quad (2.8)$$

In the region  $x < x_1$ , A type ions are prevalent and their consumption by the precipitation reaction can be practically disregarded. The second Fick's equation for the A ions can be written in the usual form for  $x < x_1$  as

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} \quad (2.9)$$

and likewise for B ions for  $x > x_1$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial x^2} \quad (2.10)$$

The initial conditions for concentrations, as referred to above are

$$\begin{aligned} C_A &= C_{A0} \quad \text{at } x < 0 \text{ and } t = 0 \\ C_B &= C_{B0} \quad \text{at } x > 0 \text{ and } t = 0 \end{aligned} \quad (2.11)$$

With these initial conditions and the additional condition in equation 2.8, the solutions of Fick's differential equations 2.9 and 2.10 can be obtained. For  $x < x_1$ ,

$$C_A = \frac{1}{2}(C_{A0} - C_{B0}) - \frac{1}{2}(C_{A0} + C_{B0})\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2.12)$$

For  $x > x_1$ ,

$$C_B = -\frac{1}{2}(C_{A0} - C_{B0}) + \frac{1}{2}(C_{A0} + C_{B0})\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2.13)$$

Setting  $C_A = 0$  in equation 2.12 and  $C_B = 0$  in equation 2.13 at  $x = x_1$

$$\frac{C_{B0}}{C_{A0}} = \frac{1 - \operatorname{erf}\left(\frac{x_1}{2\sqrt{Dt}}\right)}{1 + \operatorname{erf}\left(\frac{x_1}{2\sqrt{Dt}}\right)} \quad (2.14)$$

Introducing a new variable

$$\frac{x_1}{2\sqrt{Dt}} = \gamma \quad (2.15)$$

$$\frac{C_{B0}}{C_{A0}} = \frac{1 - \operatorname{erf}(\gamma)}{1 + \operatorname{erf}(\gamma)} \quad (2.16)$$

Thus the distance of formation of the bands can be set as a function of  $(C_{B0} / C_{A0})$ . For  $C_{B0} \ll C_{A0}$ , which is the situation in the actual Liesegang experiment, the following approximations can be made for  $\gamma > 1.5$

$$1 - \operatorname{erf}(\gamma) \cong \frac{1}{\sqrt{\pi}\gamma} \exp(-\gamma^2) \quad (2.17)$$

$$1 + \operatorname{erf}(\gamma) \cong 2 \quad (2.18)$$

Upon introduction of equations 2.17 and 2.18 in equation 2.16

$$\frac{C_{B0}}{C_{A0}} \cong \frac{1}{2\sqrt{\pi}\gamma} \exp(-\gamma^2) \quad (2.19)$$

which yields  $C_{B0} / C_{A0} < 0.02$  if  $\gamma > 1.5$



The concentration of both the ions as functions of distance  $x$  from the boundary of the original solutions are shown in Figure 2.2. Since  $C_{A0} \gg C_{B0}$ , the A type ions diffuse into the region  $x > 0$ , initially occupied by B type ions. After a given time the precipitation zone extends from  $x = 0$  to  $x = x_1$ , and the characteristic distance  $x_1$  varies as the square root of time according to the relation

$$x_1 = 2\gamma\sqrt{Dt} \quad (2.20)$$

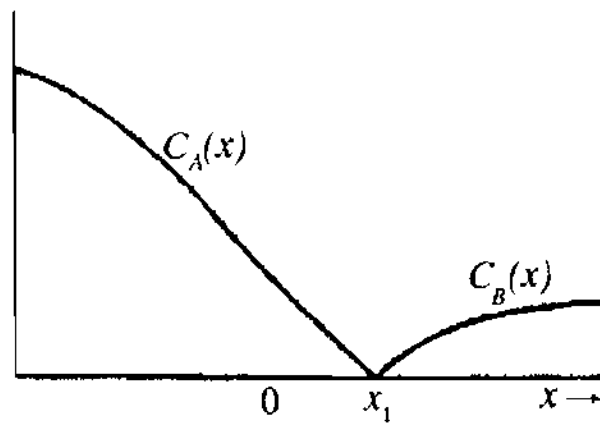


Figure 2.2: Concentration distribution of A and B type ions as functions of the distance  $x$  from the gel - solution interface according to equations 2.12 and 2.13.

Even though a continuously advancing precipitation zone is assumed, Wagner suggested that equation 2.15 also applies approximately to periodic precipitations as first shown by Morse and Pierce [1]. Wagner considered periodic interruptions as small perturbations in the general diffusion processes. If the concentration of a solution is only slightly greater than the saturation concentration, the rate of formation of the nuclei is very small but rises considerably with increasing supersaturation. The formation of the nuclei takes place only if the supersaturation exceeds a certain 'meta stable limit'. Once this limit is achieved, the precipitation zone or the nuclei of the crystal can

grow into the medium in the direction of  $x$  - axis with a rate corresponding to the increase in  $x$  according to the equation 2.15. No attempt will be made here to reproduce fully the Wagner's mathematical derivation, but his qualitative description of the process is given.

As shown above we have  $C_A = C_B = 0$  at the end of the precipitation zone at  $x = x_1$  [Figure 2.3(a)] and according to equation 2.8 the diffusion rate of  $A$  ions in the positive direction of the  $x$ -axis equals that of  $B$  ions in the negative direction. If nuclei are missing in the region  $x > x_1$ , the precipitation no longer can advance for reasons indicated above. Since the curve  $C_A(x)$  is concave upward, the concentration  $C_A(x)$  increases in the course of time; conversely, the curve  $C_B(x)$  is concave downward, and accordingly the concentration  $C_B(x)$  decreases. Thus more  $A$  ions than  $B$  ions arrive at  $x = x_1$  and consequently,  $A$  ions enter the region  $x > x_1$  as shown in Figure 2.3(b). According to the continuing precipitation and consumption of  $A$  ions at  $x = x_1$ , there is a discontinuity for the curve  $C_A(x)$  at  $x = x_1$ .

In the region  $x > x_1$ , a new precipitation zone is formed only if the supersaturation product is reached. The position of the beginning of the new precipitation zone can be obtained by determining the position at which the product of the concentrations as a function of time is maximum and then by finding the position  $x_1 + \delta x_1$  at which the maximum of the concentration product equals the supersaturation product. Immediately after the formation of new nuclei,  $B$  ions are prevalent and thus the concentration of  $A$  ions decrease practically to zero as indicated in Figure 2.3(c). Later on, the diffusion rate of  $A$  ions arriving at  $x_1 + \delta x_1$  increases and conversely that of  $B$  ions decreases until the diffusion rates of  $A$  and  $B$  ions are equivalent. Thus conditions similar to the initial conditions are reached, as indicated by

Figure 2.3(d). In this manner a large number of distinctly separate precipitation zones can be formed. In contrast to Figure 2.3(a), 2.3(d) shows a small concentration of A ions in the region beyond the new precipitation zone at  $x > x_1 + \delta x_1$ , but this difference may be disregarded.

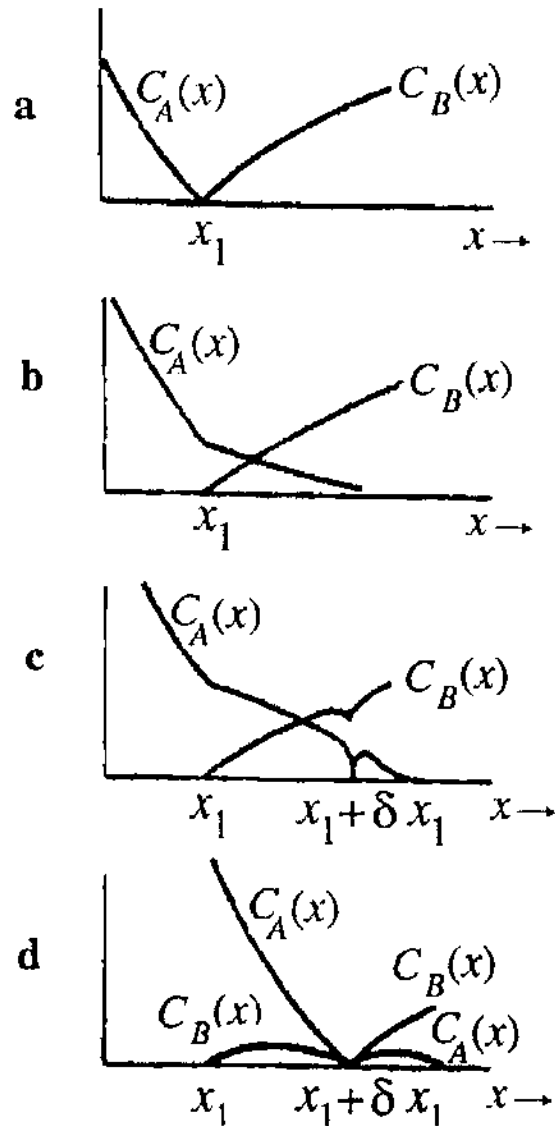


Figure 2.3: Concentrations of A and B type ions as functions of the distance at different times after the formation of a quasi-continuous precipitation zone.

Wagner also calculated the expression for the distance between consecutive precipitation zones. The distance  $\delta x_n$  between consecutive precipitation zones is found to be proportional to the distance  $x_n$  from the

boundary of the original solutions and has been verified empirically by several investigators [21-23]. One important aspect reflected in this theory is the dependence of ring spacing on the concentration of the outer and inner electrolytes. The ratio  $\delta x_n / x_n$  is found to be inversely proportional to the  $[(\nu_A + \nu_B) / (2\nu_A + \nu_B)]^{\text{th}}$  power of the initial concentration  $C_{A0}$  or  $C_{B0}$  if the ratio of the concentrations  $C_{A0} / C_{B0}$  is kept constant. Here  $\nu_A$  and  $\nu_B$  are the number of ions of *A* and *B* contained in the virtually insoluble precipitate. The distance between two consecutive precipitation zones is greater when the solutions are more dilute. If  $C_{A0} \gg C_{B0}$ , the characteristic ratio  $\delta x_n / x_n$  depends slightly on the concentration  $C_{A0}$  provided the concentration  $C_{B0}$  is kept constant. In such a situation the ratio  $\delta x_n / x_n$  is found to be almost inversely proportional to the  $[(\nu_A + \nu_B) / (2\nu_A + \nu_B)]^{\text{th}}$  power of the initial concentration  $C_{B0}$ .

The relations 2.8, 2.9, and 2.10 are found to be in accordance with many experiments reported in the literature. In view of the multiplicity of the approximations made in this theory and complexity of the experimental set up, Wagner himself admitted that this model was not suitable to all systems.

#### 2.4 The Prager model

The mathematical formulation of the problem of periodic precipitation developed by Prager [5] essentially follows Wagner's theory with two important exceptions. The first simplification is that the precipitation removes only a negligibly small amount of *A*, so that the concentration  $C_A$  remains virtually unaffected. A sufficient condition for this to be true is that

$$C_{B0} \ll C^*/(v_A + v_B) \quad (2.21)$$

It is easily seen that if the inequality 2.21 is satisfied, then  $C_A \gg C_B$  wherever precipitation is occurring or about to occur. Prager solved the usual diffusion equation 2.2 subject to the conditions

$$C_A(0, t) = C_{A0} \quad (2.22a)$$

$$C_A(x, 0) = 0 \quad (2.22b)$$

and the result is the familiar equation

$$C_A(x, t) = C_{A0} \operatorname{erfc} \frac{x}{(4D_A t)^{1/2}} \quad (2.23)$$

The boundary conditions for the diffusion of  $B$  ions are

$$C_B(x, t) = 0 \quad (2.24a)$$

$$C_B(x, 0) = C_{B0} \quad (2.24b)$$

Prager introduced a zone extending from  $x = 0$  to  $x = x_0$  which initially contains neither  $A$  or  $B$ . Thus, while the initial distribution of  $A$  given by equation 2.22b is still valid, equation 2.24b must be replaced by

$$\begin{aligned} C_B(x, 0) &= 0 && \text{for } x < x_0 \\ C_B(x, 0) &= C_{B0} && \text{for } x > x_0 \end{aligned} \quad (2.24c)$$

To further simplify the matter it is supposed that  $B$  is prevented from entering the region  $x < x_0$  say by a semi permeable membrane, although  $A$  is assumed to diffuse freely. This means that the distribution of  $B$  will not change at all until  $t = t_0$ . When  $A$  reaches the critical concentration at  $x = x_0$  at time  $t_0$ , the concentration of  $B$  at  $x_0$  drops abruptly from  $C_{B0}$  to 0, and is maintained there for all  $t > t_0$ . Accordingly  $C_B(x, t)$  is obtained by solving 2.3 and is given by

$$C_B(x, t) = C_{B0} \operatorname{erf} \frac{x - x_0}{[4D_B(t - t_0)]^{1/2}} \quad (2.25)$$

until precipitation occurs at some point other than  $x = x_0$ . Combining 2.23 and 2.25 Prager obtained the solubility product as

$$K(x, t) = C_{A0}^{\nu_A} C_{B0}^{\nu_B} \left[ \operatorname{erfc} \frac{x}{(4D_A t)^{1/2}} \right]^{\nu_A} \left[ \operatorname{erf} \frac{x - x_0}{\{4D_B(t - t_0)\}^{1/2}} \right]^{\nu_B} \quad (2.26)$$

Introducing the conditions  $\nu_A = \nu_B = 1$  and  $D_A = D_B$ , Prager showed that precipitation will occur again at the point  $x = x_n$  and time  $t = t_n$  where the solubility product reaches  $C^*$  for the second time. By solving the following equations,  $x_n$  and  $t_n$  can be found out.

$$K(x, t) = C^* \quad (2.27)$$

$$\frac{\partial K}{\partial x} = 0 \quad (2.28)$$

This procedure can be extended to give the positions of the subsequent bands as well, for which the new boundary conditions on equation 2.3 are given by

$$C_{B_n}(x_{n-1}, t) = 0 \quad (2.29)$$

$$C_{B_n}(x, t_{n-1}) = C_{B_{n-1}}(x, t_{n-1}) \quad (2.30)$$

These relations represent the  $x - t$  dependence of  $C_B$  for  $t_{n-1} \leq t < t_n$  and  $x \geq x_{n-1}$ . Replacing equation 2.26 by the more general relation and solving, Prager obtained the values of  $x_n / x_{n-1}$  and  $t_n / t_{n-1}$ . These values

were found to be in agreement with the data of Morse and Pierce on silver chromate bands.

## 2.5 The Keller and Rubinow model

Keller and Rubinow [7] have proposed a model, which includes a sink term in the diffusion equations for the ion concentrations. As discussed earlier, the reactants  $A$  and  $B$  can react to form a product  $Q$  that can form a precipitate  $P$ . The reaction rate  $R(C_A, C_B, C_Q)$  is a function of the molar concentrations  $C_A(x, t)$ ,  $C_B(x, t)$ ,  $C_Q(x, t)$  of  $A$ ,  $B$  and  $Q$  respectively. If the reaction is of orders  $\nu_A$  in  $A$ ,  $\nu_B$  in  $B$  and  $\nu_Q$  in  $Q$ , then the law of mass action yields

$$R = k_+ C_A^{\nu_A} C_B^{\nu_B} - k_- C_Q^{\nu_Q} \quad (2.31)$$

Here  $k_+$  and  $k_-$  are the rate constants for the forward and backward reactions respectively. Precipitation of  $Q$  is assumed to begin only when its concentration exceeds a certain supersaturation concentration. Once the precipitation has begun it can continue as long as the concentration is above the saturation concentration.

In addition to reacting,  $A$ ,  $B$ , and  $Q$  can diffuse, while  $Q$  can also precipitate. Thus  $C_A(x, t)$ ,  $C_B(x, t)$ ,  $C_Q(x, t)$  satisfy the reaction-diffusion-precipitation equations:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - \nu_A R \quad (2.32)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - \nu_B R \quad (2.33)$$

$$\frac{\partial C_Q}{\partial t} = D_Q \frac{\partial^2 C_Q}{\partial x^2} + v_Q R - P_r \quad (2.34)$$

According to Keller and Rubinow  $P$  does not diffuse, so its concentration  $C_P(x,t)$  will be connected to the precipitation rate  $P_r$  by the equation:

$$\frac{\partial C_P}{\partial t} = P_r \quad (2.35)$$

The boundary conditions are

$$C_A = 0, \quad C_B = C_{B0}, \quad C_Q = 0, \quad C_P = 0 \quad \text{at } t = 0, \quad x > 0 \quad (2.36)$$

$$C_A = C_{A0}, \quad \frac{\partial C_B}{\partial x} = 0, \quad \frac{\partial C_Q}{\partial x} = 0 \quad \text{at } t > 0, \quad x = 0 \quad (2.37)$$

This is equivalent to a tube initially containing  $B$  but not containing  $A$ ,  $Q$  or  $P$ , with a supply of  $A$  located at  $x = 0$ . The problem is to solve equations 2.32 to 2.37 for  $C_A$ ,  $C_B$ ,  $C_Q$  and  $C_P$  in  $x > 0$ ,  $t > 0$ . Then, the regions in which  $C_P > 0$  when  $t$  is large will be the zones or bands, which we wish to find.

To make a heuristic simplification of the problem, Keller and Rubinow incorporated four approximations viz.,

- (i) The reaction process is fast compared to both diffusion and precipitation. As the reaction is assumed to be fast they set  $R = 0$ .
- (ii)  $C_{A0}$ , the concentration of  $A$  at the end  $x = 0$ , is very large compared to the concentration of  $Q$ .
- (iii) The diffusion coefficient  $D_Q = D_B$
- (iv)  $v_Q = v_B$



and the conditions under which recurrent precipitation resulting in rings or bands were determined. The location and time of formation of the  $n^{\text{th}}$  band was calculated analyzing the two conditions formulated:

$$C_Q(x_n, t_n) = C^* \quad (2.38)$$

$$\left. \frac{\partial C_Q}{\partial x} \right|_{x_n, t_n} = 0 \quad (2.39)$$

Keller and Rubinow obtained the conditions as:

$$\operatorname{erf} \left[ \frac{x_n - x_{n-1}}{2\sqrt{D(t_n - t_{n-1})}} \right] \left[ \frac{1}{k^{-\nu} \operatorname{erfc}^{-\nu} \left( \frac{x_n}{2\sqrt{t_n}} \right) + 1} \right] = C^* \quad (2.40)$$

$$\begin{aligned} & \sqrt{\frac{t_n}{D(t_n - t_{n-1})}} \exp \left[ \frac{-(x_n - x_{n-1})^2}{4D(t_n - t_{n-1})} \right] \left[ k^{\nu} \operatorname{erfc}^{\nu} \frac{x_n}{2\sqrt{t_n}} + 1 \right] \operatorname{erfc} \left( \frac{x_n}{2\sqrt{t_n}} \right) \\ & - \nu \exp \left( \frac{-x_n^2}{4t_n} \right) \operatorname{erf} \left[ \frac{x_n - x_{n-1}}{2\sqrt{D(t_n - t_{n-1})}} \right] = 0 \end{aligned} \quad (2.41)$$

where

$$k^{\nu} = k_+ C_{A0}^{\nu_A} C_{B0}^{\nu_B - \nu} / k_- \quad , \quad \nu = \nu_A / \nu_B \quad \text{and} \quad D = D_B / D_A$$

Equations 2.40 and 2.41 have a solution of the form [7]:

$$x_n = \mu^{n-1} x_1 \quad (2.42)$$

$$t_n = \mu^{2(n-1)} t_1 \quad (2.43)$$

The result 2.42 shows that

$$x_{n+1} / x_n = \mu \quad (2.44)$$

which is just the experimentally well-known spacing law [21] of Liesegang bands. From equation 2.43 if  $\rho = x_1 / 2t_1^{1/2}$  it follows that

$$x_n / t_n^{1/2} = 2\rho \quad (2.45)$$

and this is the time law discovered experimentally by Morse and Pierce [1].

Thus incorporating the processes of reaction, diffusion and precipitation Keller and Rubinow successfully deduced the space and time laws of Liesegang bands. They showed that the ratios  $x_{n+1} / x_n$  and  $x_n / t_n^{1/2}$  are constants for sufficiently large  $n$  values.

The difficulty with the pure diffusion theories is their inability to explain why a precipitation zone stops growing. Wagner recognized that a band of precipitation, once started, would continue growing as a single band without stopping. To make it stop, he assumed that the nuclei necessary for precipitation were confined to a zone of finite width. Then he had to assume that there were other finite width zones of nuclei at the locations of the other bands. In Keller- Rubinow theory, it is taken that the first band automatically grows at a decreasing rate and finally stops growing. The qualitative explanation of this is that diffusion of the reactant  $B$  and the product  $Q$  into the band depletes their concentration in the neighborhood of the band. Consequently, the concentration of  $Q$  cannot reach the supersaturation value there, so the precipitation band cannot grow further. A new band can start to form when the reactant  $A$  has diffused out into the region where  $B$  has not been appreciably depleted.

## 2.6 Dee, LeVan & Ross models

In the scenario suggested independently by Dee [9] and LeVan and Ross [24], the two species  $A$  and  $B$  react to produce a new species  $Q$  that

also diffuses. When the local concentration of this new species reaches some threshold value, nucleation occurs. The nucleated particles  $P$  at the reaction front deplete their surroundings of the reaction product. As a result, the level of supersaturation drops dramatically and the nucleation process stops. After some time, the reaction front has moved away and the concentration of product at the moving front reaches a large enough value, allowing the nucleation to occur again, and separated bands will appear.

This process is described in terms of rate equations for the local densities of  $A$ ,  $B$  and  $Q$ . In appropriate units, they are written as

$$\frac{\partial C_A}{\partial t} = \frac{\partial^2 C_A}{\partial x^2} - k C_A C_B \quad (2.46)$$

$$\frac{\partial C_B}{\partial t} = \frac{D_B}{D_A} \frac{\partial^2 C_B}{\partial x^2} - k C_A C_B \quad (2.47)$$

$$\frac{\partial C_Q}{\partial t} = \frac{D_Q}{D_A} \frac{\partial^2 C_Q}{\partial x^2} + k C_A C_B - u \quad (2.48)$$

where  $D_A$ ,  $D_B$  and  $D_Q$  are the diffusion constants for the species  $A$ ,  $B$  and  $Q$  respectively,  $k$  is the reaction constant and  $u$  the nucleation and aggregation term. Because of diffusion, the reaction front position  $x_f(t)$  obeys the relation

$$x_f(t) \sim \sqrt{t} \quad (2.49)$$

with an amplitude depending on the difference of the concentrations  $C_A$  and  $C_B$  [25].

In both the studies it was assumed that the nucleated particles are spherical and remain so as they grow. The growth rate is proportional to the supersaturation [24]. It is also assumed that the particles are immobile in the

gel medium and their growth is interface controlled. Thus, the growth of the droplets by coagulation is not included. Dee [9] and LeVan and Ross [24] used different expressions for  $u$ , obtained from the theory of homogeneous nucleation and droplet growth. LeVan and Ross investigated the problem using two assumed nucleation rates; one they labeled as 'discontinuous' for which the nucleation rate is zero up to a critical supersaturation and then rises. The second nucleation law labeled 'continuous' is similar to the classical nucleation theory. Dee used the second nucleation law. The system of coupled non-linear partial differential equations obtained by the inclusion of  $u$  when solved numerically, exhibit oscillatory solutions for the density of precipitate, and are interpreted as bands. The solutions obtained are found to be consistent with experimental observations.

According to the investigators [9,24] Ostwald ripening only affects the intra-band morphology at later stages of the evolution and hence plays no role in the initial formation of the pattern. The characteristics of the reaction zone influence the details of the patterns formed. In particular, the width of the reaction zone affects both the band spacing and the bandwidth. It is seen that for higher values of  $k$ , a larger number of narrower bands are obtained. They also observed precipitate material between the bands and in front of the leading band.

## **2.7 Dhar, Shinohara models**

The 'coagulation theory' presented by Dhar [26], though qualitative, seems to be effective in explaining many unresolved facts of periodic pattern formation. According to Dhar, the substance to be precipitated is produced first as a colloidal solution and the precipitation is due to the flocculation of the sol by the addition of electrolytes. Later,

proceeding along the same line, Shinohara [6] divided the mechanism of the phenomena into three stages viz., the sol-forming stage, the flocculation stage and the stoppage of flocculation. According to him, three stages proceed one after the other, in turn, forming the rhythmic pattern of precipitates.

When the outer electrolyte diffuses into the gel impregnated with the inner electrolyte, the inner one diffuses in the opposite direction. The reaction occurs only on the boundary and there remain reaction product as a sol and the parasitic substance. The movement of the boundary is assumed to be along the positive direction of  $x$ . The concentration of the two electrolytes is also taken to be zero at the boundary. The movement of the boundary is assumed to be along the forward direction, leaving a sol region behind. Shinohara named the boundary as the 'sol front'. The concentration of the outer electrolyte varies with  $x$  from the largest value  $C_{A0}$  at the origin to zero at the front. Flocculation occurs suddenly when the total ionic concentration at the end of the sol region exceeds a characteristic value, the flocculation value of the sol. The flocculation causes the liberation of charges from sol particles. A sudden ionic change due to flocculation at the end of the sol region stimulates the adjacent layer of sol and induces a new flocculation, and the latter stimulates another layer of sol, and so on. The advancing speed of flocculation front is very large compared to that of the sol front. At the moment when the flocculation front arrives at the sol front, flocculation stops because there is no more sol particles to flocculate. A new sol region spreads from the point where the preceding flocculation stopped. After a lapse of time a new flocculation front will start from this point. There must be clear intervals between adjoining flocculation regions,

for the sol substance in these places are carried off by diffusion. This is why striped pattern of precipitate is observed. Shinohara deduced and fully explained the time and spacing laws from the assumption of the constancy of the speed of flocculation.

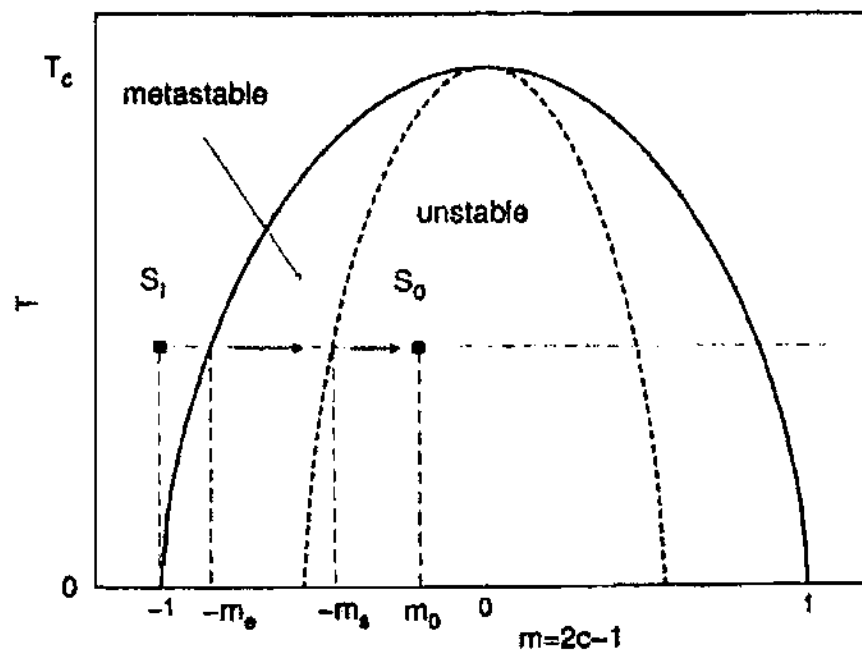
## 2.8 The Spinodal decomposition scenario

In Liesegang experiments, once the patterns are formed they appear to be in quasi-steady states or said to be frozen [27-30]. (There are reports, which suggest that the pattern does not change even for a 30-year period [31]). This fact suggests that a phase separation occurs during the formation of bands. The picture of the bands can also be taken as an evidence of phase separation [28].

In the discussion of the mechanism of spinodal decomposition for the formation of Liesegang patterns, the interpreters of the theory restricted themselves to the intermediate compound theories. According to them, as a result of the  $A+B \rightarrow Q$  reaction-diffusion process, a moving reaction-diffusion front is present and an intermediate compound  $Q$  of constant concentration  $c_0$  is formed. The intermediate particles  $Q$  can move only by diffusion due to the presence of the gel. Small clusters of particles nucleate at and aggregate behind the front. The characteristic time scale for nucleation is much larger than the time needed by the front to put out the local concentration  $c_0$ , then the system reaches the unstable state, and phase separation or Liesegang band formation takes place on a short time scale. This band acts as a sink for the particles and, in the vicinity of the band the local concentration of the particles decreases and the front is no longer in the unstable region of the phase space. When the front moves far enough, the depleting effect of the band diminishes. Thus the concentration of the

particles grows and the process repeats. The repetition of the process leads to the formation of regular Liesegang patterns.

A more familiar and easily understandable description of the problem was formulated in terms of a spin-half kinetic Ising model with competing spin flip and spin-exchange dynamics [32]. Empty and occupied lattice sites are associated with down and up spins respectively. One starts from the empty state where all the spins are in the down state (no  $Q$  particles present). The moving front flips the down spins at a given rate producing a local magnetization (thus producing the  $Q$  particles). This process can be described by Glauber dynamics [33] while a spin exchange processes or Kawasaki dynamics [34] describes diffusion.



**Figure 2.4:** Qualitative phase diagram for the Ising model. The magnetization  $m$  is related to the density  $c$  of the intermediate particles through the relation  $m = 2c - 1$ . The solid line is the coexistence curve and the dotted line is the spinodal line.  $S_1$  is the initial state with  $m = -1$ ,  $\pm m_e$  are the equilibrium magnetizations at a given temperature  $T$  while  $\pm m_s$  are the magnetizations at the spinodal line.

To explain qualitatively how bands emerge, Antal et. al. [27] considered the phase diagram of an Ising model depicted in Figure 2.4. One starts from a state with all the spins down ( $S_l$  in Figure 2.4). The  $A+B \rightarrow Q$  reaction front leaves behind a constant density  $c_0$  of  $Q$  particles, thus correspondingly the spin-flipping front produces a local magnetization  $m_0 = 2c_0 - 1$ . Since the front should bring the system into the unstable state, it is assumed that  $m_0 > -m_s$ . As time evolves, the local state moves from  $S_l$  towards  $S_0$ . The system crosses successively the coexistence line ( $m = -m_c$ ) and the spinodal line ( $m = -m_s$ ) and end up into the unstable states domain where phase separation takes place. Thus a spin-up domain or a band is rapidly formed at or behind the front. This mechanism is possible because the time scale for nucleation is much larger than the time needed by the front to put the system in the unstable states domain. The new band formed acts as a sink for the up-spins in its vicinity. Thus the local magnetization decreases and the front is no longer in the unstable domain. However, when the front has moved far enough, the depleting effect of the band disappears. The front can bring again the system into the unstable domain and a new band is formed. In short, the new feature of this scenario is the assumption that the state of the front is quasi periodically driven into the unstable states domain. Droz studied the properties of this model at a microscopic level and explained the experimental patterns obtained in long test tubes. This model also yields Matalon-Packter law and allows the calculation of the spacing coefficient.

## 2.9 Conclusions

Even though important theoretical progress has been made towards the understanding of Liesegang phenomena, one has to recognize that the



suggested scenarios cannot explain all the experimental observations and conditions related to the formation of patterns. There is still disagreement among researchers with regard to the mechanisms underlying this phenomenon. Also several challenging problems remain open in this fascinating field of pattern formation in non-equilibrium systems. Hence the mechanisms responsible for these structures still stimulate research [35-60].

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