SWITCHING CHEMICAL REACTION DYNAMICS AND KINETIC VS. THERMODYNAMIC CONTROL IN REFERENCE TO POLYMORPHIC PRECIPITATION OF HgI₂ CRYSTALS

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Resumen

Las características experimentales observadas en la precipitación polimórfica de iodo de mercurio en una solución acuosa indicaron una biestabilidad del sistema de la reacción con vías bimodales dependientes de la concentración inicial $n_{R_0}$ del reactante y la temperatura del baño $T$. Cada vía funciona cuando el estado del sistema es cinéticamente favorable lo cual es determinado por $n_{R_0}$ y $T$ después de los respectivos límites críticos $n_{c_0}$ y $T_c$ para que la reacción cambie de un lado a otro dinámicamente entre las regiones bistables siempre que el estado cruce por encima de los límites críticos. Este fenómeno es interpretado en términos de una dinámica de reacción hipotética llamada Mecanismo de Histerésis de Reacción Química (MHRQ). Una unión entre la biestabilidad y el modelo de formación bicolor espacial periódico de Liesegang en gel del sistema se discute y se sugiere la posibilidad de una oscilación química no-periodica sostenida de este sistema en un flujo continuo por agitación en un reactor.

Palabras Clave: Precipitación Polimórfica de HgI₂, Sistema de reacción bistable, Mecanismo de Histéresis de Reacción Química, Banda de Liesegang

Abstract

Experimental characteristics observed in the polymorphic precipitation of mercuric iodide in aqueous solution implied a bistability of the reaction system with bimodal pathways contingent upon initial concentration of reactant $n_{R_0}$ and bath temperature $T$. Each pathway functions when the state of the system is in the kinetically favorable region that is determined by the $n_{R_0}$ and $T$ beyond the respective critical limits $n_{c_0}$ and $T_c$ so that the reaction switches back and forth dynamically between the bistable regions whenever the state crosses over the critical limits. This phenomenon is interpreted in terms of a hypothetical reaction dynamics called Switching Chemical Reaction Mechanism (SCRM). A linkage between the bistability and the periodic bicolor spatial Liesegang pattern formation in gel of the system is discussed and possibility of a sustained aperiodic chemical oscillation of this system in a continuos-flow stirred tank reactor is suggested.

Keywords: Polymorphic precipitation of HgI₂, Bistable reaction system, Chemical switching mechanism, Liesegang band
1. Introduction

Numerous papers have been published on kinetic vs. thermodynamic control of products formation in both organic and inorganic reactions [1-7]. In discussing relative yield of two different products A and B from reactant R by a parallel reaction under rather restrictive conditions that for the specific reaction rate coefficients \( k_1 > k_2 \) and for the equilibrium constants \( K_1 (= k_1 / k_1) < K_2 (= k_2 / k_2) \), more rapidly formed product A is called the kinetically controlled product and the stable product B formed after a certain time is designated the thermodynamically controlled product [1].

In spite of recent criticisms on this title phrase and concept [6,7], the precipitation of polymorphic mercuric iodide crystals, red tetragonal \( \alpha \)-HgI\(_2\) and yellow orthorhombic \( \beta \)-HgI\(_2\), in aqueous solution at room temperature

\[
\text{HgCl}_2(\text{aq}) + 2\text{KI}(\text{aq}) = \text{HgI}_2(\text{s}) + 2\text{KCl}(\text{aq})
\]

has incorrectly been interpreted [5] as

\[
\text{HgCl}_2(\text{aq}) + 2\text{KI}(\text{aq}) = (\beta \rightarrow \alpha)\text{HgI}_2(\text{s}) + 2\text{KCl}(\text{aq})
\]

These two reaction processes switch or flop over between them across the critical condition as the system condition changes. This reaction dynamics is proposed as the Switching Chemical Reaction Mechanism (SCRM). The proposed mechanism is analyzed in detail in the present paper and suggested a possible chemical oscillation process, i.e. [9-11], based on our mechanism.

2. Experimental

Experimental details and materials used are presented in our previous paper [8], in which we demonstrated a precipitation reaction scheme of polymorphic \( \alpha \) and \( \beta \) mercuric iodide crystals represented by their color as a function of starting or initial molar concentration \([R^e]\) or \(n_{R^e}\) of reactant \(R(Hg_2^{2+}+2I^-)\) in terms of \(\text{HgCl}_2\) and of reaction time \(R^e-t\) scheme) at room temperature as shown in Fig. 1.

The detailed studies on the precipitation reaction characteristics based on complete reaction field explored in terms of a set of reaction system variables; initial concentrations of reactants [8] and temperature (present work) including reaction time, showed a bistability nature in the chemical reaction system. The operative reaction mechanism consists of two independent competing parallel chemical processes or pathways across the critical conditions, namely the critical initial concentration of reactants \([R^e]\) and the critical temperature \(T_c\) of the reaction system: a one-step path-II process is operative above the critical condition and a two-step consecutive path-I process is operative below the critical condition as

\[
\text{HgCl}_2(\text{aq}) + 2\text{KI}(\text{aq}) = \alpha \text{-HgI}_2(\text{s}) + 2\text{KCl}(\text{aq})
\]

at \([R^e] > [R^e_c]\) and \(T > T_c\)

\[
\text{HgCl}_2(\text{aq}) + 2\text{KI}(\text{aq}) = (\beta \rightarrow \alpha)\text{HgI}_2(\text{s}) + 2\text{KCl}(\text{aq})
\]

at \([R^e] < [R^e_c]\) and \(T < T_c\)

The initial lemon yellow suspension of metastable \(\beta\)-HgI\(_2\) crystallites was only observed for \([R^e]\) below about 0.06M \(\text{HgCl}_2\). Its color rapidly changed to rose which in turn gradually converted into the bright red color of thermodynamically stable \(\alpha\)-HgI\(_2\) crystallites. At \([R^e]\) above about 0.17M \(\text{HgCl}_2\) the red crystallites formed immediately. This limit 0.17M \(\text{HgCl}_2\) is termed the critical initial reactant concentration \([R^e_c]\) or \(n_{R^e_c}\). As the metastable yellow precipitate transforms so rapidly into
the stable red crystallite, the X-ray powder diffractogram of the final crystallite obtained from 0.01M Hg\textsuperscript{2+} starting solution after a reaction period of 30 min. revealed the only red modification of tetragonal $\alpha$-HgI\textsubscript{2} crystal (SG N° 137, file N° 21-1157 [12] as shown in Fig. 2. We thus, for the first time, identified the initial yellow suspension formed in the ionic aqueous Hg\textsuperscript{2+}+2H\textsuperscript{+} solution by powder XRD method [8] as the metastable yellow orthorhombic $\beta$-HgI\textsubscript{2} crystal (SG N°36) by employing the colloidal protection technique [13].

![Figure 2](image1.png)

**Fig. 2.** The powder XRD pattern of red $\alpha$-HgI\textsubscript{2} precipitates.

The color photo (Fig. 3) represents our gelatinized X-ray powder sample plate of the yellow suspension captured by the colloidal protection method. The pressure exerted by the scribbling steel pencil on the gelatinized yellow spread caused immediate color change (the red chinese character in Fig.3) due to the solid state phase transformation, $\beta$(yellow)-HgI\textsubscript{2} $\rightarrow$ $\alpha$(red)-HgI\textsubscript{2}, and the colors remained as they were for weeks after the photo was taken[8]. In fact, because of its rapid conversion to $\alpha$ form in the solution in addition to its physicochemical vulnerability [8] the powder XRD work on the yellow $\beta$-HgI\textsubscript{2} formed in the aqueous solution has been left for more than a century.

We extended experiment to prove if the rosy transient zone in between the initial yellow and the final red in Fig. 1 were represented supposingly by a mixture of $\alpha$ and $\beta$ crystallites resulted from the phase transformation $\beta$$\rightarrow$$\alpha$ in the solution through the reaction processs (4b). The two sediments obtained after five days resulted from the reactions of a set of starting solutions, (0.02M HgCl\textsubscript{2} + 0.04M KI) and (0.04M HgCl\textsubscript{2} + 0.08M KI) of 50 ml each, in the lightly magnetically stirred 200ml of 1% gelatine solutions, were yellow for the former as before [8] and rose for the latter. The powder XRD spectra taken next day on the dried sample plates exhibited $\beta$-HgI\textsubscript{2} for the yellow and mixture of $\alpha$ and $\beta$ phases for the rosy plate as shown in Fig. 4.

![Figure 3](image2.png)

**Fig. 3.** Color photo of the X-ray powder diffraction sample plate of the transient initial metastable yellow $\beta$-HgI\textsubscript{2} precipitates that were captured by protective colloid technique. The red chinese character on the dry gelatinized spread was substantiated by the phase transformation, $\beta$(yellow)-HgI\textsubscript{2} $\rightarrow$ $\alpha$(red)-HgI\textsubscript{2}, caused by the pressure exerted by the scribbling steel pencil [8].

![Figure 4](image3.png)

**Fig. 4.** The powder XRD spectra of red $\alpha$-HgI\textsubscript{2} and yellow $\beta$-HgI\textsubscript{2}, and their rosy mixture $(\alpha + \beta)$. The outcome proves that the metastable initial yellow $\beta$ form transforms into the stable final red $\alpha$ form through the $\beta$$\rightarrow$$\alpha$ phase transformation in the solution. For details see the text.

The outcome proves that the metastable initial yellow $\beta$ indeed transforms into the stable final red $\alpha$ through the $\beta$$\rightarrow$$\alpha$ phase transformation in the solution, which in fact represents the transient rosy zone in Fig. 1. The characteristics of rapid and transient nature of initial yellow precipitation process manifests that the yellow $\beta$-HgI\textsubscript{2} crystal is the true intermediate reaction product and is indeed the metastable phase.

The previously observed temperature effect on the behavior of the same precipitation reaction [8] is fully extended here and obtained a new reaction phase field as a function of reaction bath temperature versus reaction...
time (T-t scheme) as demonstrated in Fig. 5, which appears similar to R涛-t scheme of Fig. 1.

The reaction phenomenon (5) suggests a chemical dynamics with bistability nature; an existence of bistable reaction regimes, having the relevant reaction pathways I and II, separated by a limit of instability at a critical condition of the reaction system defined either by the \([R_c^o]\) or \(n_c^o\) at a given temperature or by the \(T_c\) at a fixed initial concentration.

The two chemical processes, path-I and path-II, with distinctive overall forward velocities, \(v_I\) and \(v_{II}\), both leading to the thermodynamically stable ultimate same product \(\alpha\)-phase, can be independent but are competitive across the critical conditions, \([R_c^o]\) and \(T_c\). Above the critical condition, \([R_c^o] > [R_c^o]\) and \(T > T_c\), the path-II is active and red \(\alpha\)-phase directly precipitates out from solution while below the critical conditions, \([R_c^o] < [R_c^o]\) and \(T < T_c\), the two-step series path-I reaction becomes active. The first \(R \rightarrow \beta\) step must be faster as precipitation of yellow metastable \(\beta\)-phase involves nucleation through liquid-liquid reaction as in the case of path-II reaction compared to the second step at where a sluggish phase transition, \(\beta \rightarrow \alpha\), reaction takes place in the solid state within the solution bath. The operative mechanism flips or switches when the conditions change into either region of the reaction fields the state of the system resides. The two paths can dynamically flip-flap or switch back and forth between them whenever the state of the system changes across the instability point either \([R_c^o] \rightarrow [R_c^o]\) at a fixed \(T\) or \(T \rightarrow T_c\) at a fixed \([R_c^o]\). The mechanism responsible for the proposed reaction dynamics is termed here the Switching Chemical Reaction Mechanism (SCRM).

To substantiate the proposed SCRM in terms of the familiar transition state activated-complex-theory (ACT), the required thermophysical quantities of the polymorphic phases are presented in Table 1.
Table 1. Structure and Thermophysical Quantities of the $\alpha$-HgI$_2$ and $\beta$-HgI$_2$ Crystals

<table>
<thead>
<tr>
<th>Structure</th>
<th>Color</th>
<th>$\rho$ (kg.m$^{-3}$)</th>
<th>$C_p$ (J.mole$^{-1}$.K$^{-1}$)</th>
<th>$\Delta H^0_{298}$ (kJ.mole$^{-1}$)</th>
<th>$\Delta S^0_{298}$ (kJ.mole$^{-1}$.K$^{-1}$)</th>
<th>$T_1$ (K)</th>
<th>$\Delta H_f$ (kJ.mole$^{-1}$)</th>
<th>$T_f$ (K)</th>
<th>$\Delta H_f$ (kJ.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-HgI$_2$</td>
<td>yellow</td>
<td>6094.4*</td>
<td>84.52*</td>
<td>-102.72*</td>
<td>(178.2)$^a$</td>
<td>-96.7*</td>
<td>400.15*</td>
<td>532.15*</td>
<td>18.8*</td>
</tr>
<tr>
<td>orthorhombic$^c$</td>
<td>Cmc2$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-HgI$_2$</td>
<td>red</td>
<td>6364*</td>
<td>77.4*</td>
<td>-105.4*</td>
<td>(178.2)$^d$</td>
<td>-100.71*</td>
<td>2.72*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetragonal$^a$</td>
<td>P4/nmc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
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(*) Ref.14, (+) Ref.15, (#) Ref.16, ($)$ Ref.17, (a) Ref. 18

Fig. 6. The proposed representative free energy potential profile of the polymorphic precipitation reaction of $\alpha$-HgI$_2$ and $\beta$-HgI$_2$ phases from ionic aqueous solution. For details see the text.

The thermodynamic stability of $\alpha$ over $\beta$ is well reflected by the densities, especially by the standard free energy of formation by the relation

$$\Delta G^0_{298}(\alpha) = -100.71 \text{ kJ/mole} < \Delta G^0_{298}(\beta) = -96.7 \text{ kJ/mole}$$

with a relatively small difference between them as

$$\Delta G^0_{298}(\beta-\alpha) = \Delta G^0_{298}(\alpha) - \Delta G^0_{298}(\beta) = -4.06 \text{ kJ/mole} \quad (6)$$

An appropriate and plausible free energy potential profile is devised in Fig.6 in relation to thermodynamic stabilities of the phases. The profile is depicted based approximately on the data of free energies of formation, $\Delta G^0_1(\alpha)$ and $\Delta G^0_2(\alpha)$ and of transition $\Delta G^0_1(\alpha) = \Delta G^0_2(\alpha) - \Delta G^0_1(\beta)$. The respective activation free energies, $\Delta G^*_1(\beta)$, $\Delta G^*_2(\alpha)$ and $\Delta G^*_{1-2}(\alpha) = G^*_{\beta}(\alpha) - G^*_{\beta}$, are reasonably scaled for favorable explanation of the chemical dynamics by also taking into account the interrelations among k, K and $G^*$. Application of the sequences, $\Delta G^*_{1-2}(\alpha) < \Delta G^*_{1}(\alpha) < \Delta G^*_{2}(\alpha)$, $\Delta G^*_{1}(\beta) < \Delta G^*_{2}(\alpha) < \Delta G^*_{2}(\beta)$ and $\Delta G^*_{1}(\beta) > \Delta G^*_{2}(\alpha)$ for equilibrium between normal and activated complex, $n$ and $n^*$, in our particular experimental ranges in concentration and temperature.

$$\Delta G^* = (G^* - G) = -RT \ln K^* \quad (9)$$

$$K^* = \frac{n^*}{n} = \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (8)$$

results in the following relevant relations among $k$ and $K$

$$k_1 > k_2 > k_1^* \text{ or } k_1 > k_2, k_1 >> k_1^* \text{ and } k_2 > k_1^* \quad (10)$$

$$K_2 > K_1 >> K_1^* \text{ or } K_1 >> K_1^* \text{ and } K_2 > K_1 \quad (11)$$

The single energy profile of Fig. 6 is remodeled into a double energy profile in Fig. 7 to facilitate argument of the author's concept on the chemical switch as flip-flap between two independent pathways, path-I (left) and path-II (right), across the instability limit, $n_c^0$ or $T_c$, of our proposed bistable reaction system. The fact $k_1 > k_2$ manifests path-I kinetically prevails over path-II when the state is below critical condition, where the formation of $\beta$ predominates over $\alpha$ both kinetically and thermodynamically even though the $\alpha$ is the thermodynamically stable ultimate phase because simultaneously $k_1 >> k_1^*$ and $K_1 >> K_1^*$ since $\Delta G^*_{1}(\beta) < \Delta G^*_{1}(\alpha) < \Delta G^*_{1}(\beta)$ and $\Delta G^*_{1}(\alpha) > \Delta G^*_{1}(\beta)$, to equations (7) and (8) [19]
Whenever the state crosses over into the region above critical condition, a new situation, $k_2 > k_1'$ and $K_2 > K_1$, arises, which makes it now possible to trigger path-II reaction so that the path-I switches into path-II since not only the kinetics favors path-II over path-I by the fact $k_2 > k_1'$ but also the equilibrium constant $K_2$ for direct $\alpha$ formation predominates over the rest, $K_1$ and $K_1'$ at the same time.

The above phenomenological interpretation of the SCRM can be much elegantly explained in terms of $n^*$ and $V$ in conjunction with Fig. 7 and Fig. 8 since the both of them are simultaneous functions of $n$ and $T$ as well as of activation free energies as

$$n^*(n,T) = K^*n = n \exp\left(-\frac{\Delta G^*}{RT}\right)$$

Equation (12) leads to the following two overall velocities if one pays attention only to the same ultimate product $\alpha$

$$V_I(R \to \beta \to \alpha) = k_1' = n_1(\frac{k_B T}{h})\exp\left(-\frac{\Delta G_1^*(\alpha)}{RT}\right)$$

$$V_{II}(R \to \alpha) = k_2 = n_2(\frac{k_2'}{h})\exp\left(-\frac{\Delta G_2^*(\alpha)}{RT}\right)$$

When the state of the system is in the regime below the critical condition, the path-I reaction is effective because the $n_R^*(\beta)$ in the free energy level $G_R^*(\beta)$ for $\beta$ formation is already reached to trigger this reaction $R \to \beta(k_1)$ since $\Delta G_1^*(\beta) < \Delta G_2^*(\alpha)$. Once it starts, it produces $\beta$ very rapidly by

$$V_I(R \to \beta) = k_1n_R = n_R \left(\frac{k_B T}{h}\right)\exp\left(-\frac{\Delta G_1^*(\beta)}{RT}\right)$$

which makes the $\beta$ accumulates fast enough to decompose slowly into the product $\alpha$ by sluggishly passing over the following second high energy barrier $\Delta G_2^*(\alpha)$ for phase transformation $\beta \to \alpha$ as the thermodynamic stability of $\alpha$, $\Delta G_2^*(\beta) + \Delta G_2^*(\alpha) < 0$, favors the $\alpha$ over $\beta$. The overall rate of this reaction path, $v_I (R \to \beta \to \alpha)$ of (14), is slow because this second step for $\beta \to \alpha(k_1')$ acts as the rate-limiting-step since $\Delta G_2^*(\alpha) > \Delta G_2^*(\beta)$ and $k_1' << k_1$.

When the state is above the critical condition, the $n_R^*(\alpha)$ beyond the level $G_R^*(\alpha)$ required for direct pass over activation peak $\Delta G_2^*(\alpha)$ of path-II reaction $R \to \alpha(k_2)$

$$n_R^*(\alpha) = n_R \exp\left(-\frac{\Delta G_2^*(\alpha)}{RT}\right)$$

becomes sufficient enough that the reactants directly form the end product $\alpha$ with velocity $v_{II}(R \to \alpha)$ of (15) without having recourse to path-I since $k_2 > k_1'$ and $K_2 > K_1$ favor path-II in this state so that, by now, the existence of the first small barrier $\Delta G_1^*(\beta)$ of path-I is irrelevant.

Fig. 8. An overall view of dynamic switching mode of our bimodal reaction system contingent upon $n_R^*$ and $T$, which function as the control elements (regulators) and the activated complex $n_R^*$ acts as a control agent inducing switch between the bistable pathways. When the condition $n_R^*$ or $T$ crosses over the respective instability threshold, $n_c$ or $T_c$, the reaction switches over. See the text for more details.
4. Discussion

An overall view of the dynamic switching mode of our reaction system with bimodal pathways contingent upon \( n_{R}^{0} \) and \( T \) in a closed stirred reactor (CSR) is presented graphically in Fig. 9. The \( n_{R}^{0} \) and \( T \) function as the control elements (regulators) and \( n_{R}^{*} \) acts as a control agent inducing switch between the bistable pathways when the \( n_{R}^{0} \) or \( T \) crosses over the respective critical point or threshold of instability, \( n_{c}^{0} \) or \( T_{c} \). This phenomenon is analogous to tilting process of a beam by crossing a person over a fulcrum point so that the \( n_{c}^{0} \) or \( T_{c} \) corresponds to the fulcrum of the beam. The arguments favor the kinetics view on the dominant factor because the \( n_{R}^{*} (n,T) \) in relation to \( \Delta G_{R}^{*} \) plays the determinant agent in our reaction system.

![Fig. 9. The proposed chemical reaction switching dynamic scheme operative between two independent reaction pathways, path-I and path-II, having respective overall reaction velocities, \( V_{I} \) and \( V_{II} \), in the polymorphic precipitation reactions of HgI2 crystals leading to the stable ultimate \( \alpha \)-HgI2 form in the aqueous solution. See the text for more details.](image)

Fig. 9. The proposed chemical reaction switching dynamic scheme operative between two independent reaction pathways, path-I and path-II, having respective overall reaction velocities, \( V_{I} \) and \( V_{II} \), in the polymorphic precipitation reactions of HgI2 crystals leading to the stable ultimate \( \alpha \)-HgI2 form in the aqueous solution. See the text for more details.

The proposed physical cause on bistability quite predicts a chemical oscillation in our system when the reaction is carried out in a continuous-flow stirred tank reactor (CSTR) [9,10] even our system is not a transient and self-oscillating type of Belousov-Zhabotinsky (B-Z) reaction observed either in a closed reactor (CR; a beaker) or in a CSR [20]. Our oscillation mechanism is expected to be simpler than those numerous variety of oscillation behaviors [9-11, 21-23] as discussed in the following.

It is, in principle, possible to imagine that the two independent reaction paths could result in a genuine concurrent or parallel reaction provided that the CSTR was designed to maintain the state of the system exactly at the critical condition as purely idealized situation, \( n_{R}^{0} = n_{c}^{0} \) and \( T = T_{c} \), at where the two overall rates in terms of \( n_{R}^{0} \) must become equal, \( V_{I} = V_{II} \), so that the two reactions become interdependent and will interfere each other in the fashion

\[
\frac{k_{1} k_{2}^{*}}{(k_{1} - k_{1}^{*}) k_{2}} = \frac{e^{-k_{2}^{*}t}}{e^{-k_{1}^{*}t} - e^{-k_{1}^{*}t}}
\]

This ideal situation is represented by the horizontal dotted arrows in Fig. 10. In practice, however, it is expected to be impossible experimentally to maintain the ideal operational condition of a CSTR. The resulting external variation of either \( n_{R}^{0} \) or \( T \) or both around instability point, \( n_{c}^{0} \) or \( T_{c} \), shall trigger a fluctuation between the bistable pathways. Even if the operation of the CSTR were in the ideal condition, an additional fluctuation may be inevitable because of perturbation of state variables, \( p, V, T \) and \( n \), of reaction system caused by their internal natural fluctuations. Wave form of the resulting sustained chemical oscillation should be dictated by the dominant one between the external and internal fluctuations. A mixed fluctuation of the two may give rise to a complex aperiodic behaviors or chemical chaos. A hypothetical oscillation is also presented in Fig. 10. The proposed chemical oscillation may be observed if one employs a sophisticated experimental setup attached with appropriate rapid and sensitive opto-chemical sensors coupled with detectors.

![Fig. 10. Two additional imaginary reaction modes over the pathways I and II; a purely idealized genuine parallel reaction represented by the horizontal dotted arrows and a probable aperiodic chemical oscillation when the reaction is carried out in a continuous-flow stirred tank reactor. See the text for more details.](image)

Fig. 10. Two additional imaginary reaction modes over the pathways I and II; a purely idealized genuine parallel reaction represented by the horizontal dotted arrows and a probable aperiodic chemical oscillation when the reaction is carried out in a continuous-flow stirred tank reactor. See the text for more details.

Our chemical switching mechanism is phenomenologically equivalent to that of recent molecular switch [24] and of those popular electrical threshold switching of gas
(i.e. neon-lamp) [25] and solid (i.e. VO₂ [26] provided that our switching regulator (n_R° or T) and control agent (n_e*) are properly identified with regulators and agents in other systems. In case of molecular switch an acidity (pH) functions as a regulator and a hydronium ion (H₃O⁺) acts as an agent in the translocation between the two ligation states. In case of electrical switches of the mentioned gas and solid a voltage (V) functions as a regulator and electrons act as an agent in the transition between the two states with different resistances; normal and ionized in gas, and OFF (insulator or semiconductor) and ON (metallic) in solid in the language of Mott [27]. The molecular switch may also oscillate in accord with our hypothesis as those gas and solid demonstrate experimental evidence that a bistable system actuates either switching or oscillation depending on imposed condition on the system [25, 26, 28, 29]. We have extensively studied this phenomenon on many inorganics and semiconductors including VO₂ [29].

Figures 11 and 12 demonstrate our previous experimental results on the precipitation of HgI₂ crystallites from HgCl₂ and 2KI in two different set of concentrations [8], that were obtained by gel technique [30]. The test tube containing a low concentration solutions, 0.02M HgCl₂ in silica gel and 0.04M KI as supernatant, formed a spatial and rhythmic two color Liesegang pattern or bands (Fig. 11) while the other tube containing a high concentration solutions, 0.24M HgCl₂ in gel with 0.48M KI supernatant, produced a mass of red crystallites (Fig. 12).

The outcome, formation of interleaved bicolor, yellow (β)/red (α), periodic bands at below the critical concentration (0.02M < n_R° = 0.17 M HgCl₂) and production of mass of red crystals at above the critical condition (0.24M > n_R° = 0.17 M HgCl₂), tempts us to think of a probable linkage between the precipitation behavior in gel and the proposed chemical switch mechanism of Eq. (5), which may in turn shed light on those hitherto controversial theory of the Liesegang phenomenon [9, 31-34]. In accord with our switching mechanism, the single step path-II reaction must be active at the condition n_R° > n_e° so that the precipitation of red α-HgI₂ should continue until the opposing gradients can not maintain the required level of concentration for the nucleation of red phase at the reaction front, at where metastable yellow β-HgI₂ starts to precipitate. Figure 12 indicates that the reaction system is probably reached in this stage of process. However, when the starting condition of the reaction system is at n_R° < n_e°, the two step path-I reaction prevails so that a repetitive precipitation process of two different color phases, R → β(yellow) → α(red), continues until the reservoir reactants become depleted. Figure 11 explicitly demonstrates the proposed process; the mixed bicolor yellow/red bands reside near the reaction front and those red bands consist of ultimate α-phase are accumulated behind them.

Fig. 11. Formation of interleaved bicolor, yellow (β)/red (α), periodic bands in silica gel when the two step path-I reaction takes place below the critical concentration n_R° < n_e°. See the text for details.

Fig. 12. Precipitation of a mass of red α-HgI₂ crystallites when the single step path-II reaction takes place above the critical concentration n_R° > n_e°. See the text for details.
5. References