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Computational models of chemical systems inspired by Braess' paradox

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Abstract

Systems chemistry is a new discipline which investigates the interactions within a network of chemical reactions. We have studied several computational models of chemical systems inspired by mathematical paradoxes and have found that even simple systems may behave in a counterintuitive, non-linear manner depending upon various conditions. In the present study, we modeled a set of reactions inspired by one such paradox, Braess' paradox, an interesting phenomenon whereby the introduction of additional capacity (e.g. pathways) in some simple network systems can lead to an unexpected reduction in the overall flow rate of "traffic" through the system. We devised several chemical systems that behaved in this counterintuitive manner; the overall rate of product formation was diminished when an additional pathway was introduced and, conversely, there was an enhancement of product formation when the same interconnecting pathway was removed. We found that, unlike a traffic model, the chemical model needed to include reversible pathways in order to mimic "congestion" – a condition necessary to produce Braess-like behavior. The model was investigated numerically, but a full analytical solution is also included. We propose that this intriguing situation may have interesting implications in chemistry, biochemistry and chemical engineering.

Key Words: Kinetic models Chemical networks Systems chemistry

1 Introduction

Systems chemistry is a fairly new and unconventional chemical niche discipline that investigates interactions of reactions in a chemical network, rather than single, independent chemical reactions [1]. One typical feature of systems in chemistry, biology, engineering and physics is the presence of outcomes that are difficult to predict solely by observing the individual components; given enough time, asymmetries may arise in seemingly simple networks. An important challenge in systems chemistry is that of understanding how the various reactions interact with each other, especially in the fields of prebiotic synthesis and chemical evolution [2].

Mathematical paradoxes have inspired chemical systems that yield counterintuitive results, which may be exploited for novel applications. One such example is Parrondo's paradox, which inspired an investigation of the effect of oscillating thermal conditions in simple chemical reaction systems; in these systems, thermal cycling counterintuitively produced a greater yield of product than any fixed temperature in the range of cycled temperatures [3].

Might other mathematical paradoxes also suggest novel chemical models? To answer this question, we investigated a paradox attributed to Dietrich Braess. Braess' paradox is an interesting relationship whereby the introduction of additional capacity (i.e. pathways) into some simple networks can lead to an unexpected reduction in the overall rate of flux through the system. Conversely, in some systems, eliminating pathways can indeed result in an overall increase in flow through the systems. Braess' paradox is typically applicable to traffic flow [4]. Notable examples include the improvement of travel time in New York City when 42nd Street was closed, and in Stuttgart, Germany when construction of a new road led to an increase in travel time [5,6]. Variations of the paradox have been demonstrated with electrical, hydraulic, mechanical and thermal networks [7]. Further examples of Braess' paradox can be found at the following references [8, 9].

Fig.1 shows a schematic of a simple network of pathways displaying Braess' paradox. In traveling from Start to Finish, there is more than one possible route. In the absence of the extra pathway (green), there are two possible routes from Start to Finish -- blue – red or red – blue. In the

presence of the extra pathway, there is a third possible route, red – green – red. The constant rate of travel on the blue pathway is slow, and on the green pathway, it is fast. The hash marks on the red pathways denote that the rate of travel on the red road is not constant but rather is capacity dependent, i.e. subject to congestion. The emergence of Braess' paradox is dependent upon the total traffic through the system, rates of flow through the individual pathways, the magnitude of the capacity-dependent congestion and the presence or absence of the extra connecting pathway. Additional constraints necessary for a Braess' paradox-like effect in the traffic model are first that the travelers moving through the system act selfishly in finding the most expedient route and second that significant congestion increases the travel time of the red pathways, but not the blue pathways [4].

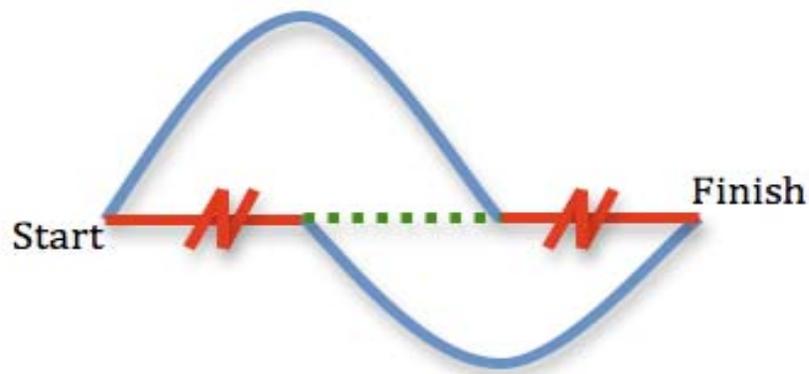


Fig. 1 Illustration of a network that can demonstrate Braess' paradox. In the absence of the extra pathway (green), there are two possible routes from Start to Finish: blue – red or red – blue. In the presence of the extra pathway, there is a third possible route, red – green – red.

Simple observation of the network of Fig.1 would suggest that the addition of the extra pathway might increase the overall transit rate at which travelers could move from Start to Finish. However, depending on the rates of each road, it turns out that the addition of the extra pathway can result in an overall *reduction* of the efficiency of system and *increase* the average travel time through the system because further congestion (reduced flow) develops on the red pathways (“fast”). With

the addition of the extra path (green), it is assumed that most of the travelers will take the red-green-red pathway; this increases the use of the red pathways, thus slowing down the rate of travel on these pathways and reducing the efficiency of the system.

But is there a chemical analog to Braess' paradox? We have found a model of such a system of chemical reactions such that, under certain kinetic circumstances, the overall rate of the process can indeed be reduced by the addition of an interconnecting pathway. Conversely, inhibition of an intermediate connecting reaction can result in an increase in the overall rate of reaction.

2 The Model

To study Braess-like behavior in a chemical system, we designed a model that is a general chemical network with alternate pathways from the starting reactant (A) to the product (F) with the possibility of an additional pathway (green) linking intermediates (B and C) where all reaction steps are assumed to be first order (Fig. 2). Unlike the traffic model described above where commuters are motivated to choose pathways to potentially optimize their speed through the network, molecules react by alternate pathways based on relative reaction rates, which reflect differences in energies of activation as determined by the Arrhenius equation. The overall rate of formation of product in a complex system is analyzed by solving the governing equations using the individual reaction steps. The reversible pathways are represented by the reactions $A \rightleftharpoons C$ and $B \rightleftharpoons D$ and provide a means of introducing "congestion" in this reaction system; we define "congestion" in a chemical system as an obstruction to a forward reaction ($A \rightarrow C$ or $B \rightarrow D$) resulting from a reverse reaction ($C \rightarrow A$ or $D \rightarrow B$). The pathway $D \rightarrow F$ was added to provide insight into the overall system dynamics. This pathway also controls the degree of "congestion" of the system. The formation of the final product F was compared in the system when the intermediate pathway was active ($k_6, k_{-6} > 0$) to the system when the alternate pathway was absent ($k_6 = k_{-6} = 0$).

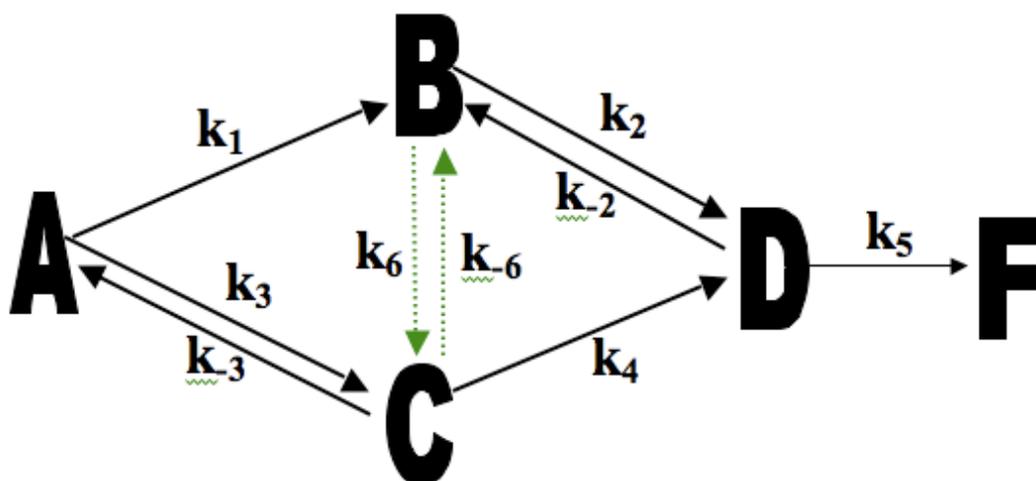


Fig. 2 A chemical reaction system inspired by Braess' paradox.

3 Preliminary Studies

The model shown in Fig.2 was initially explored using the chemical kinetic program, Kintecus. Kintecus 3.96 is a deterministic, Arrhenius-based program developed by James Ianni and is free for academic use [10]. Various values of the rate constants were tested, and the concentrations of F were determined for $0 < t < 1000$ sec. A network of chemical reactions that behaved analogous to Braess' paradox is shown in Fig.3; note the inhibitory effect of the extra interconnecting pathway on the rate of production of the F.

Rate Constants	k values	Reaction
k_1	0.03	$A \rightarrow B$
k_2	0.10	$B \rightarrow D$
k_{-2}	0.12	$D \rightarrow B$
k_3	0.10	$A \rightarrow C$
k_{-3}	0.12	$C \rightarrow A$
k_4	0.03	$C \rightarrow D$
k_5	0.001	$D \rightarrow F$
k_6	2.00/0	$B \rightarrow C$
k_{-6}	2.00/0	$C \rightarrow B$

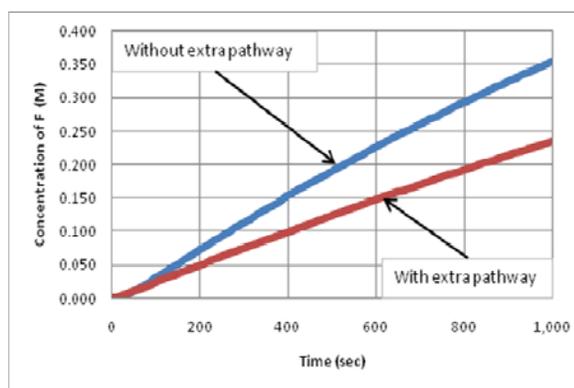


Fig. 3 Plot of the concentration of F vs. reaction time of the system with ($k_6 = k_{-6} = 2.00$) and without ($k_6 = k_{-6} = 0.0$) the extra pathway, $B \rightleftharpoons C$ (Fig. 2) (Note: $A_0 = 1.0M$ and depleting)

The effect of the rate constant k_5 on “congestion” and hence, the Braess-like behavior, was explored by varying k_5 , allowing A to deplete, and determining the concentration of reaction product F after 100sec. (Fig. 4a). We note that $k_5 < 0.22$ promotes sufficient congestion in the system to cause Braess-like behavior, which was lost when $k_5 > 0.22$. A similar trend was found if we fix A at 1M, Fig.4b. In this case, the concentration of F was determined at 1000 secs, and Fig.4b indicates that the cross-over from Braess to non-Braess occurs for $k_5 = 0.16$.

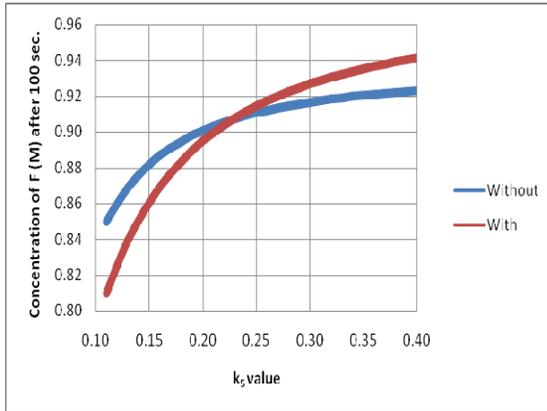


Fig. 4a (left) The production of F after 100 sec. vs. the value of k_5 . Note: $A_0 = 1.0M$ and A is depleting.

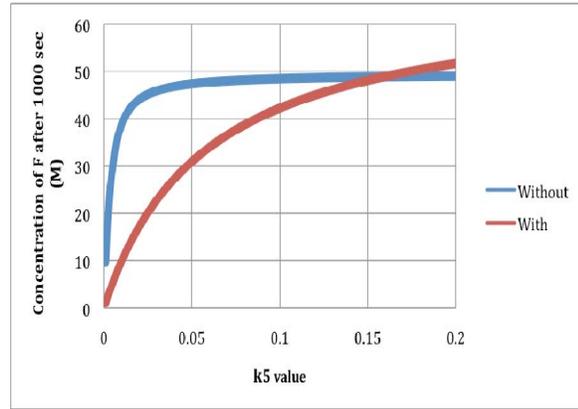


Fig. 4b (right) The production of F after 1000 sec. vs. the value of k_5 Note A =1.0M and is held constant.

4 Model Analysis

By way of investigating the possible Braess-like behavior in chemical systems, an analysis of the model of Fig.2 is here presented. Denoting the various concentrations by A,B,C,D,F, the governing equations read:

$$\begin{aligned}\frac{d}{dt}A &= -(k_1 + k_3)A + k_{-3}C \\ \frac{d}{dt}B &= -(k_2 + k_6)B + k_{-6}C + k_{-2}D + k_1A \\ \frac{d}{dt}C &= k_6B - (k_{-3} + k_4 + k_{-6})C + k_3A \\ \frac{d}{dt}D &= k_2B + k_4C - (k_{-2} + k_5)D \\ \frac{d}{dt}F &= k_5D\end{aligned}$$

We investigated the four following cases:

Case 1: $A=A(t)$, $k_6>0$

Case 2: $A=A(t)$, $k_6=0$

Case 3: $A= \text{constant}$, $k_6>0$

Case 4: $A= \text{constant}$, $k_6=0$

(Note: The $k_6 = 0$ and $k_6 > 0$ cases are analyzed separately because for $k_6 = 0$ the A,C equations decouple from the B, D equations and the eigenvalue-eigenvector approach used for $k_6 > 0$ is not so conveniently used when $k_6 = 0$. Furthermore, the analysis is carried out for the most general case of $k_{-6} \neq k_6$, though in most applications we will restricted ourselves to the special case of $k_{-6} = k_6$.)

Case 1: $A=A(t)$, $k_6>0$

For $k_6 > 0$, the governing equations are fully coupled, and it is convenient to treat the problem as standard eigenvalue-eigenvector problem. The equations are cast into matrix form:

$$\frac{d}{dt} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = -[M] \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix},$$

in which the matrix of coefficients, M, is given by

$$[M] = \begin{pmatrix} k_1 + k_3 & 0 & -k_{-3} & 0 \\ -k_1 & k_2 + k_6 & -k_{-6} & -k_{-2} \\ -k_3 & -k_6 & k_{-3} + k_4 + k_{-6} & 0 \\ 0 & -k_2 & -k_4 & k_{-2} + k_5 \end{pmatrix}.$$

Now substitute $A, B, C, D \sim e^{-\lambda t}$ and solve the determinantal equation (i.e. “frequency eqn.”) $|M - \lambda I|=0$ for the four eigenvalues $\lambda = \lambda_1, \lambda_2, \lambda_3, \lambda_4$. For each λ there corresponds a non-normalized eigenvector satisfying the equation

$$([M] - \lambda_i [I]) \begin{pmatrix} 1 \\ \beta_i \\ \gamma_i \\ \delta_i \end{pmatrix} = 0.$$

The general solution to the governing equations follows:

$$\begin{aligned} A &= \xi_1 e^{-\lambda_1 t} + \xi_2 e^{-\lambda_2 t} + \xi_3 e^{-\lambda_3 t} + \xi_4 e^{-\lambda_4 t} \\ B &= \beta_1 \xi_1 e^{-\lambda_1 t} + \beta_2 \xi_2 e^{-\lambda_2 t} + \beta_3 \xi_3 e^{-\lambda_3 t} + \beta_4 \xi_4 e^{-\lambda_4 t} \\ C &= \gamma_1 \xi_1 e^{-\lambda_1 t} + \gamma_2 \xi_2 e^{-\lambda_2 t} + \gamma_3 \xi_3 e^{-\lambda_3 t} + \gamma_4 \xi_4 e^{-\lambda_4 t} \\ D &= \delta_1 \xi_1 e^{-\lambda_1 t} + \delta_2 \xi_2 e^{-\lambda_2 t} + \delta_3 \xi_3 e^{-\lambda_3 t} + \delta_4 \xi_4 e^{-\lambda_4 t} \end{aligned}$$

where the coefficients ξ_1, \dots, ξ_4 are found from the “initial- condition” matrix equation (for $A_0=1$):

$$\begin{pmatrix} 1 & 1 & 1 & 1 \\ \beta_1 & \beta_2 & \beta_3 & \beta_4 \\ \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4 \\ \delta_1 & \delta_2 & \delta_3 & \delta_4 \end{pmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \\ \xi_4 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

F(t) follows from $F = k_5 \int_0^t D dt$, viz:

$$F / A_0 = k_5 \left[\frac{\delta_1 \xi_1}{\lambda_1} (1 - e^{-\lambda_1 t}) + \dots + \frac{\delta_4 \xi_4}{\lambda_4} (1 - e^{-\lambda_4 t}) \right].$$

$$\text{As } t \rightarrow \infty, \text{ this yields } F/A_0 \rightarrow k_5 \left[\frac{\delta_1 \xi_1}{\lambda_1} + \dots + \frac{\delta_4 \xi_4}{\lambda_4} \right] = 1.$$

This result is to be expected of course since it represents the fact that “what goes in one end”, namely $A=A_0$, has to “come out the other end”, together with the observation that A,B,C,D, all deplete to zero as $t \rightarrow \infty$. It is also easy to see this result using the governing equations which, when summed, yield $d/dt (A+B+C+D+F) = 0$, i.e. $A+B+C+D+F = A_0$ yielding $F \rightarrow A_0$ as $t \rightarrow \infty$, since $A,B,C,D \rightarrow 0$ in the same limit.

Using the k values in Fig.3, with $k_6 = k_{-6} = 2$, we obtain eigenvalues: $\lambda_1 = 0.250235$, $\lambda_2 = 4.127255$, $\lambda_3 = 0.0002714$, $\lambda_4 = 0.123239$ corresponding (resp.) to eigenvectors (for $A_0 = 1.0M$)

$$\begin{pmatrix} 1 \\ -1.00174 \\ -1.00195 \\ 1.00772 \end{pmatrix}, \begin{pmatrix} 1 \\ 32.88164 \\ -33.3105 \\ -0.57132 \end{pmatrix}, \begin{pmatrix} 1 \\ 1.11201 \\ 1.08107 \\ 1.18972 \end{pmatrix}, \begin{pmatrix} 1 \\ 0.00710 \\ 0.05634 \\ -1.07214 \end{pmatrix}.$$

The corresponding values of ξ are: $\xi_1 = 0.26647$, $\xi_2 = 0.0002674$, $\xi_3 = 0.22892$, $\xi_4 = 0.50434$.

It is clear that the transient contributions to $F(t)$ corresponding to λ_1 , λ_2 , and λ_4 become vanishingly

small after a few seconds ($t \sim 20s$) after which time $F(t)/A_0 \sim 1 - k_5 \frac{\delta_3 \xi_3}{\lambda_3} e^{-\lambda_3 t}$, dominated by the

“slow” eigenvalue $\lambda_3 = 0.000271$. For $k_5 = 0.001$, this reads $F(t)/A_0 = 1 - 1.0033e^{-\lambda_3 t}$.

Case 2: $A=A(t)$, $k_6=0$

For $k_6 = 0$, the A and C equations decouple from the B and D equations, viz:

$dA/dt = -(k_1 + k_3)A + k_3C$, $dC/dt = k_3A - (k_3 + k_4 + k_{-6})C$, which are easily solved to yield

$$A = A_0 (\eta_+ e^{-\xi_- t} - \eta_- e^{-\xi_+ t}) / (\eta_+ - \eta_-)$$

$$C = A_0 (e^{-\xi_+ t} - e^{-\xi_- t}) / (\eta_+ - \eta_-),$$

where η_{\pm} are the solutions of $k_3 \eta^2 + (k_3 + k_4 + k_{-6} - k_3 - k_1)\eta - k_3 = 0$ and $\xi_{\pm} = k_1 + k_3(1 - \eta_{\pm})$.

These solutions are then substituted into the B and D equations,

$dB/dt = -k_2B + k_2D + k_{-6}C + k_1A$, $dD/dt = k_2B - (k_2 + k_5)D + k_4C$,

and these equations are combined by introducing σ , as follows:

$$\frac{d}{dt}(B + \sigma D) = -k_2(1 - \sigma)B + (k_{-2} - (k_{-2} + k_5)\sigma)D + k_1A + (k_{-6} + k_4\sigma)C$$

Choosing σ_{\pm} to be the solutions of the quadratic $k_2(1 - \sigma)\sigma + k_2(1 - \sigma) - k_5\sigma = 0$, we have

$$\frac{d}{dt} \{(B + \sigma_{\pm} D) e^{k_2(1-\sigma_{\pm})t}\} = e^{k_2(1-\sigma_{\pm})t} \{k_1 A + (k_{-6} + k_4 \sigma_{\pm}) C\}$$

Integrating and applying the initial conditions, $B(0)=0=D(0)$, the solutions for $B(t)$ and $D(t)$, follow.

Then $F(t)$ follows from $F = k_5 \int_0^t D dt$.

For the k values in Fig.3, and $k_6 = k_{-6} = 0$, the transient behavior of F/A_0 is determined by exponentials $e^{-0.03t}$, $e^{-0.25t}$, $e^{-0.22t}$, and $e^{-0.0004534t}$, so that for $t \geq 50s$, the transient behavior is dominated by the last exponential and we find that $F(t)/A_0 \sim 1 - 1.016 e^{-0.00045t}$. Comparing this with the $k_6=k_{-6}=2$ form of $F(t)$ (Case 1, above), it is clear that the behavior of $F(t)$ is Braess-like, i.e. $F(t)$ is greater for $k_6=k_{-6}=0$ (no pathway) than for $k_6 = k_{-6} = 2$ (pathway), with both of them converging to A_0 as $t \rightarrow \infty$.

Plots of the concentrations A, B, C, D , and F vs t are shown in Fig.5 (open pathway) and Fig.6 (closed pathway) In both cases, the transient behavior is “slow” (c.f. the inverse time constants 0.000271 and 0.00045). However, an extension of t beyond 1000s would confirm that indeed $A \dots D$ deplete to zero. Likewise, although the $F(t)/A_0$ vs. t plots look linear, one does find that in both cases they do indeed approach 1 as $t \rightarrow \infty$. The most important point made by Figs. 5 and 6 is that the presence of the pathway $B \rightarrow C$ (i.e. $k_6=k_{-6} > 0$) inhibits rather than enhances the production rate of F .

While Cases 1 and 2 are interesting from a chemical point of view and certainly suggestive of the possibility of a Braess-like phenomenon occurring in chemical systems, the relationship to the Braess paradox itself should not be taken too literally, primarily because the processes in the above cases are at best quasi-equilibrium; the input A depletes in a finite time before full equilibrium can be established. Thus, we now investigate the effect of keeping the input A constant, that is replenishing it as it is used up, as our best hope of achieving dynamical equilibrium. Again, we consider separately $k_6 > 0$ and $k_6 = 0$.

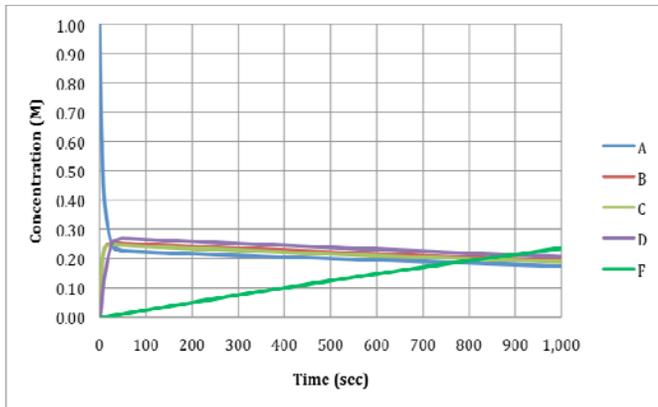


Fig. 5 Concentrations of A, B, C, D, and F after 1000 seconds with $k_6 = k_{-6} = 2.00$, using the nominal k values and the initial concentration 1.0M. (Case 1)

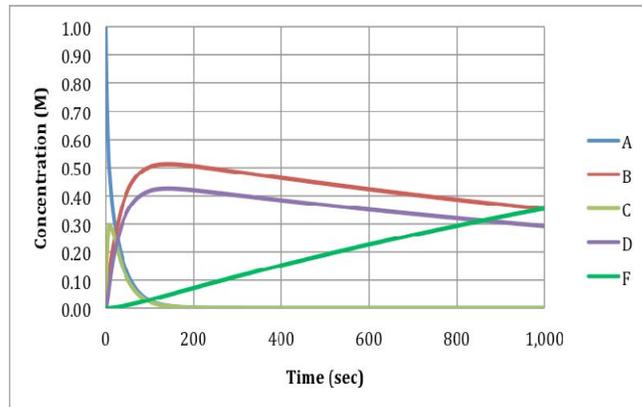


Fig. 6 Concentrations of A, B, C, D, and F after 1000 seconds with $k_6 = k_{-6} = 0$, using nominal k values and the initial of A being concentration of A being 1.0M. (Case 2)

Case 3: A= constant, $k_6 > 0$

Writing the equations for B, C, and D in matrix form:

$$\frac{d}{dt} \begin{pmatrix} B \\ C \\ D \end{pmatrix} = -[M] \begin{pmatrix} B \\ C \\ D \end{pmatrix} + \begin{pmatrix} k_1 A \\ k_3 A \\ 0 \end{pmatrix},$$

with $A = A_0$, and separating B, C, D, into their transient and steady-state pieces,

$B \rightarrow B_t + B_{ss}$, $C \rightarrow C_t + C_{ss}$, $D \rightarrow D_t + D_{ss}$, the steady-state values of B, C, D, follow from

$$\begin{pmatrix} B_{ss} \\ C_{ss} \\ D_{ss} \end{pmatrix} = [M]^{-1} \begin{pmatrix} k_1 A_0 \\ k_3 A_0 \\ 0 \end{pmatrix}$$

and the transient parts of B, C, D satisfy

$$\frac{d}{dt} \begin{pmatrix} B_t \\ C_t \\ D_t \end{pmatrix} = -[M] \begin{pmatrix} B_t \\ C_t \\ D_t \end{pmatrix}.$$

The problem again becomes an eigenvalue-eigenvector problem: Substituting

$$B \sim e^{-\lambda t}, C \sim e^{-\lambda t}, D \sim e^{-\lambda t}$$

yields the determinant $|M - \lambda(I)| = 0$. The resulting cubic equation for λ yields three solutions: $\lambda_1, \lambda_2, \lambda_3$ and for each eigenvalue, λ_i , there corresponds an eigenvector (non-normalized), the solution of

$$([M] - \lambda_i [I]) \begin{pmatrix} 1 \\ \beta_i \\ \gamma_i \end{pmatrix} = 0.$$

The general solution of the system equations now follow:

$$\begin{aligned} B &= \xi_1 e^{-\lambda_1 t} + \xi_2 e^{-\lambda_2 t} + \xi_3 e^{-\lambda_3 t} + B_{ss} \\ C &= \beta_1 \xi_1 e^{-\lambda_1 t} + \beta_2 \xi_2 e^{-\lambda_2 t} + \beta_3 \xi_3 e^{-\lambda_3 t} + C_{ss} \\ D &= \gamma_1 \xi_1 e^{-\lambda_1 t} + \gamma_2 \xi_2 e^{-\lambda_2 t} + \gamma_3 \xi_3 e^{-\lambda_3 t} + D_{ss} \end{aligned}$$

and the coefficients ξ_1, ξ_2, ξ_3 follow from the initial conditions $B(0) = 0, C(0) = 0, D(0) = 0$.

Finally, the concentration F follows from $F = k_5 \int_0^t D dt$. Note that D_{ss} is the slope of the asymptotic

straight-line solution for F , i.e. $F = k_5 D_{ss} t$ as t becomes large.

In anticipation of investigating the effect of k_5 ($D \rightarrow F$ rate constant) the above system was solved using the nominal values in Fig. 3 with $k_6 = k_{-6} = 2$, to yield the following eigenvalue, eigenvector, and steady-state-concentration data:

$k_5 = 0.001$

$\lambda_1 = 0.03364$	$\lambda_2 = 0.21117$	$\lambda_3 = 4.126187$	
$\xi_1 = -0.9564$	$\xi_2 = -0.15616$	$\xi_3 = 0.008516$	$B_{ss} = 1.10402$
$\beta_1 = 0.94502$	$\beta_2 = 1.03155$	$\beta_3 = -1.01205$	$C_{ss} = 1.0735$
$\gamma_1 = 1.4693$	$\gamma_2 = -1.45223$	$\gamma_3 = -0.01739$	$D_{ss} = 1.17858$

$k_5 = 0.01$

$\lambda_1 = 0.038153$	$\lambda_2 = 0.21566$	$\lambda_3 = 4.126189$	
$\xi_1 = -0.8867$	$\xi_2 = -0.14524$	$\xi_3 = 0.00852$	$B_{ss} = 1.02342$
$\beta_1 = 0.94704$	$\beta_2 = 1.03394$	$\beta_3 = -1.012049$	$C_{ss} = 0.99853$
$\gamma_1 = 1.39809$	$\gamma_2 = -1.52954$	$\gamma_3 = -0.01743$	$D_{ss} = 1.01767$

$k_5 = 0.03$

$$\begin{array}{lll} \lambda_1 = 0.047358 & \lambda_2 = 0.226447 & \lambda_3 = 4.126194 \\ \xi_1 = -0.79097 & \xi_2 = -0.12229 & \xi_3 = 0.008519 \\ \beta_1 = 0.95118 & \beta_2 = 1.03974 & \beta_3 = -1.012046 \\ \gamma_1 = 1.25227 & \gamma_2 = -1.71611 & \gamma_3 = -0.017514 \end{array} \quad \begin{array}{l} B_{ss}=0.90475 \\ C_{ss}=0.88814 \\ D_{ss}=0.78079 \end{array}$$

$k_5 = 0.05$

$$\begin{array}{lll} \lambda_1 = 0.055471 & \lambda_2 = 0.23833 & \lambda_3 = 4.126199 \\ \xi_1 = -0.73775 & \xi_2 = -0.10166 & \xi_3 = 0.008519 \\ \beta_1 = 0.95487 & \beta_2 = 1.04620 & \beta_3 = -1.01204 \\ \gamma_1 = 1.12326 & \gamma_2 = -1.92282 & \gamma_3 = -0.017602 \end{array} \quad \begin{array}{l} B_{ss}=0.83089 \\ C_{ss}=0.81943 \\ D_{ss}=0.63336 \end{array}$$

$k_5 = 0.1$

$$\begin{array}{lll} \lambda_1 = 0.071462 & \lambda_2 = 0.272325 & \lambda_3 = 4.126213 \\ \xi_1 = -0.67574 & \xi_2 = -0.06192 & \xi_3 = 0.008519 \\ \beta_1 = 0.962215 & \beta_2 = 1.065147 & \beta_3 = -1.012037 \\ \gamma_1 = 0.86757 & \gamma_2 = -2.52182 & \gamma_3 = -0.017828 \end{array} \quad \begin{array}{l} B_{ss}=0.72914 \\ C_{ss}=0.72478 \\ D_{ss}=0.43026 \end{array}$$

For $k_5 = 0.001$, the eigenvalues $\lambda_1 = 0.03364$, $\lambda_2 = 0.21117$, $\lambda_3 = 4.126187$ indicate that the transient behavior of $F(t)$ is dominated by the $e^{-0.03364t}$ contribution for $t > 20s$ at which time the other two transient pieces are vanishingly small. Substituting the above data into the expression for $D(t)$ and

evaluating $F = k_5 \int_0^t D dt$ subject to $F(0)=0$, we obtain for $t > 20s$

$$F(t)/A_o \sim k_5 \left[\left(\frac{\gamma_1 \xi_1}{\lambda_1} + \frac{\gamma_2 \xi_2}{\lambda_2} + \frac{\gamma_3 \xi_3}{\lambda_3} \right) - \frac{\gamma_1 \xi_1}{\lambda_1} e^{-\lambda_1 t} + D_{ss} t \right]$$

i.e. $F(t)/A_o \sim 0.001 [1.1786t + 41.773 e^{-0.03364t} - 40.7]$

From the above data we note that as k_5 is increased, the resulting value of D_{ss} decreases. However the asymptotic production rate of F , namely $dF/dt = k_5 D_{ss}$ increases. This is consistent with Fig. 4b: Increasing k_5 reduces congestion in the system, so promoting the production rate of F (and subsequent value of F at time t) and pushing the system towards the non-Braess part of parameter space. As indicated in Fig. 4b the cross-over from Braess to non-Braess behavior occurs at $k_5=0.16$.

Case 4: A= constant, k₆=0

For k₆=0, the dC/dt equation decouples from the B and D eqns., viz:

dC/dt = -(k₋₃ + k₄ + k₋₆)C + k₃A₀, with solution

$$C = \frac{k_3}{k_4 + k_{-6} + k_{-3}} A_0 (1 - e^{-(k_{-3} + k_4 + k_{-6})t})$$

The B and D equations, dB/dt = -k₂B + k₋₆C + k₂D + k₁A₀ and dD/dt = k₂B - (k₋₂+k₅)D + k₄C may now be combined by introducing σ, as follows:

$$\frac{d}{dt}(B + \sigma D) = -k_2(1 - \sigma)B + (k_{-2} - (k_{-2} + k_5)\sigma)D + k_1A_0 + (k_{-6} + k_4\sigma)C]$$

Choosing σ_± to be the solutions of the quadratic k₂(1-σ)σ + k₋₂(1-σ) - k₅σ = 0, we have

$$\frac{d}{dt} \{(B + \sigma_{\pm} D)e^{k_2(1-\sigma_{\pm})t}\} = e^{k_2(1-\sigma_{\pm})t} \{k_1A_0 + (k_{-6} + k_4\sigma_{\pm})C\}$$

Integrating and applying the initial conditions, B(0)=0=D(0), the solutions for B(t) and D(t), follow.

Then F(t) follows from $F = k_5 \int_0^t D dt$.

Again, k₅ was varied to yield the following data:

k ₅	σ ₊	σ ₋	k ₂ (σ ₊ -1)	k ₂ (σ ₋ -1)
0.001	0.99546	-1.2055	-0.000454	-0.22055
0.01	0.95567	-1.2557	-0.00443	-0.36057
0.03	0.87361	-1.3736	-0.01264	-0.2374
0.05	0.8	-1.5	-0.02	-0.25
0.1	0.649	-1.849	-0.0351	-0.2849

For the k values of Fig.3, with k₆=k₋₆=0 and k₅=0.001, the transient behavior of F/A₀ is now determined by exponentials e^{-0.15t}, e^{-0.22t}, and e^{-0.00045t}, so that at “large” t, the transient behavior is

dominated by the last exponential. Evaluating $F = k_5 \int_0^t D dt$ using $F(0)=0$ as usual, we find that for $t > 20s$, $F(t)/A_0 \sim [0.05t - 110.29 + 110.23 e^{-0.00045t}]$.

We should here note that the coefficient of t in the expression for F/A_0 is actually *independent* of k_5 , deriving from a steady state ($t \rightarrow \infty$) component of $D(t)/A_0$ of the form α/k_5 where α depends on the remaining rate constants but is independent of k_5 . This fact is also evident from Fig.4b where the plot of $F(1000)/A_0$ vs k_5 flatlines for $k_5 \geq 0.05$. (At lower values of k_5 the parts of $F(t)$ that are not linear in t and which depend on k_5 are such that the piece that is linear in t and independent of k_5 has yet, at $t=1000s$, to dominate the solution for F .) Recalling the data for Case 3 above, it is clear that for an open $B \rightarrow C$ pathway, $k_5 D_{ss} \neq \text{constant}$ and thus the asymptotic ($t \rightarrow \infty$) rate of production of F is strongly dependent on the $D \rightarrow F$ rate constant k_5 .

We further note that as k_5 increases, the value of the slower “eigenvalue” $k_2(1 - \sigma_+)$ increases (to 0.0351 at $k_5=0.1$) meaning the corresponding transient term in $F(t)$ decreases quicker, which in turn means the rate $dF/dt = k_5 D$ reaches its asymptotic value of 0.05 quicker, meaning $F(1000)$ approaches its flatline value of 50 as k_5 increases, again as indicated again in Fig.4b.

The predictions of our model for Cases 3 and 4, $A = \text{constant}$ (i.e. A being continually replenished), for $k_5 = 0.001$, are shown in Fig. 7 and 8, which make clear the fact that chemicals B , C , and D asymptote to steady values and, since $dF/dt = k_5 D_{ss}$, this leads directly to a constant rate of formation of F . Also obvious from Figs. 7 and 8 is the significant (order of magnitude) inhibitory effect of opening the $B \rightarrow C$ pathway ($k_6 = k_{-6} > 0$) analogous to the classical Braess paradox in transportation systems.

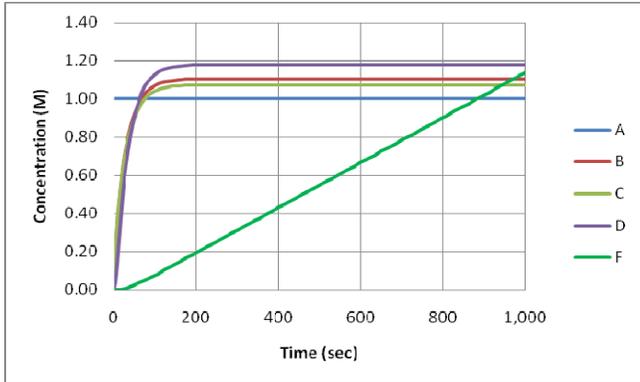


Fig. 7 Concentrations of A, B, C, D, and F after 1000 seconds with $k_6 = k_{-6} = 2.00$, using the nominal k values and the concentration of A being a constant 1.0 M. (Case 3)

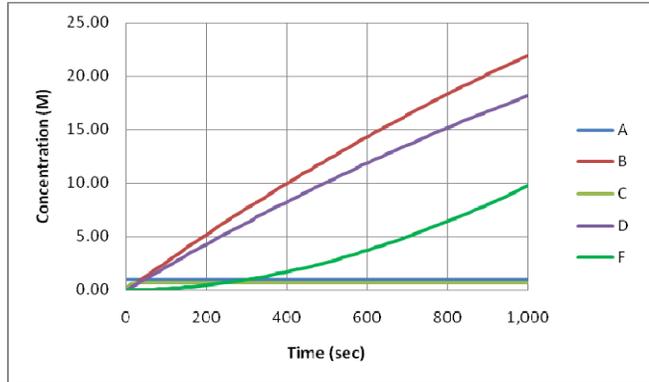


Fig. 8 Concentrations of A, B, C, D, and F after 1000 seconds with $k_6 = k_{-6} = 0$, using nominal k values and the concentration of A being a constant 1.0 M. Note differences in y-axis values compared to Fig. 7. (Case 4)

5. Further Investigation of System Dynamics

In order to explore the behavior of the model, the actual rates of each reaction (e.g. rate $A \rightarrow B$ is k_1A , rate $B \rightarrow D$ is k_2B ...) were calculated at 1000 seconds using the solutions for Cases 3 to 4 for various values of rate constants k_1 and k_5 and using a fixed concentration of $A = 1M$; the resulting rates are shown in Table 1, which clearly reflects a Braess-like effect for certain ranges of k_1 and k_5 , in that the $D \rightarrow F$ rate (bolded) decreases when the interconnecting pathway is active ($k_6 = k_{-6} = 2$). Also, when the extra pathway is present in the system, the “congestion” of the system (i.e. the obstruction to the forward reaction by the reverse reaction) increases. For example if $k_4 = k_1 = 0.03$ and $k_5 = 0.001$, when the pathway is absent, the $B \rightarrow D$ reaction rate (2.19M/sec) is greater than the $D \rightarrow B$ reaction rate (2.18M/sec), whereas when the pathway is present, the reverse reaction rate $D \rightarrow B$ (0.14 M/sec) now exceeds the forward reaction rate $B \rightarrow D$ (0.11 M/sec). This trend continues as k_1 increases as long as k_5 remains sufficiently low. At the same time, for low k_1 , even a relatively high k_5 , results in non-Braess behavior, e.g. for $k_1 = 0.03$ and $k_5 = 0.20$, with the presence of the pathway, the reaction rate $D \rightarrow B$ (0.031 M/sec) no longer exceeds the reaction rate of $B \rightarrow D$ (0.064 M/sec), i.e. the presence of the pathway does not cause congestion. Note the value $dF/dt = 0.052$ when the pathway is present compared with 0.05 when closed (non-Braess behavior). These observations on

reaction rates are yet again consistent with the production of final product shown in Fig. 4b., which, again, confirms the $k_1 = 0.16$ transition from Braess to non-Braess behavior.

It is also evident in Table 1 that introducing the extra pathway causes congestion independent of whether or not the reversible reactions have the higher rate constant than the irreversible reactions. This is significant because in a traffic Braess paradox, the “fast” pathway is subject to congestion, and thus longer travel time, because the extra pathway causes all cars prefer to travel on these “fast” pathways. We have found that for a chemical system, the “fast” pathways (highest rate constant) do not have to be subject to “congestion” (i.e. reversible reaction) in order for a Braess-like effect to emerge; the reversible reactions need only be present in the system.

		Table 1. Rates of reaction (M/sec) at 1000 seconds					
		$k_1 = 0.03$		$k_1 = 2.0$		$k_1 = 0.03$	
		$k_6 = k_{-6}$					
		k_5					
Rate Constants	Reaction						
k_1	A --> B	0.03	0.03	2.00	2.00	0.03	0.03
$k_2 = 0.10$	B --> D	2.19	0.11	92.6	3.12	0.06	0.064
$k_{-2} = 0.12$	D --> B	2.18	0.14	91.3	33.17	0.03	0.031
$k_3 = 0.10$	A --> C	0.10	0.10	0.10	0.10	0.10	0.10
$k_{-3} = 0.12$	C --> A	0.08	0.13	0.006	1.82	0.08	0.077
$k_4 = k_1$	C --> D	0.02	0.03	0.094	30.33	0.02	0.02
k_5	D --> F	0.017	0.001	0.761	0.276	0.050	0.052
k_6	B --> C	0.00	2.21	0.00	62.38	0.00	1.29
k_{-6}	C --> B	0.00	2.15	0.00	30.33	0.00	1.30

6 Conclusions

When dealing with chemical networks, complex behavior may arise unexpectedly and it is imperative to examine interactions of reactions in the system and not simply independent reactions [1]. In the present study, we modeled a set of reactions inspired by Braess' paradox and we

concluded that the introduction of additional capacity (e.g. pathways) in some chemical systems led to an unexpected reduction in the overall formation of product. Conversely, inhibition of specific intermediate pathways can result in increased product formation.

Novel chemical systems can be inspired by mathematical paradoxes [3,11]. Here, we have explored the kinetic relationships of a system of reactions that mimic the counterintuitive activity described in Braess' paradox. The model provided in the present investigation is a general chemical system so as to explore scenarios leading to Braess-like behavior. This model may thus lead to the creation of novel chemical systems and to the understanding of biochemical pathways that naturally behave in a Braess-like manner. Another possible extension of this model might be to improve the understanding of some chemical inhibitors, which may act paradoxically. Drugs are often designed to inhibit the production of an intermediate in a reaction pathway in order to reduce the formation of a final product. However, our present investigation suggests that in some cases the opposite effect might occur, i.e. there may be circumstances when an inhibitor actually increases the efficiency of the overall chemical system. Braess' paradox might be just as relevant to chemical and biochemical systems as to everyday traffic networks [6,7], and thus worthy of further investigation.

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