

ChemE 2200 - Physical Chemistry II for Engineers  
Solutions to Exercises for Calculation Session 13

1. The reaction is elementary as written; the reaction breaks one bond and makes one bond.
2. One method is to devise a mechanism of elementary reactions consistent with the rate equation, reverse the directions of the reactions, and derive the rate equation of the reverse reaction. This method is viable, but unnecessarily long.

Instead, we use the fact that equilibrium is a dynamic balance of rates. At equilibrium, the rates of the forward and reverse reactions are equal.

$$r_{\text{reverse}} = r_{\text{forward}} = k_{\text{forward}}[\text{Cl}_2\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}^{1/2} \quad (1)$$

The equilibrium constant is the ratio of the forward and reverse rate constants.

$$K_{\text{eq}} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}{[\text{Cl}_2\text{CO}]_{\text{eq}}}$$

Solve for  $k_{\text{forward}}$ ,

$$k_{\text{forward}} = \frac{[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}{[\text{Cl}_2\text{CO}]_{\text{eq}}} k_{\text{reverse}}$$

and substitute into eqn (1).

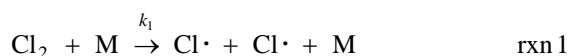
$$r_{\text{reverse}} = k_{\text{forward}}[\text{Cl}_2\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}^{1/2} = \frac{[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}{[\text{Cl}_2\text{CO}]_{\text{eq}}} k_{\text{reverse}}[\text{Cl}_2\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}^{1/2}$$

$$r_{\text{reverse}} = k_{\text{reverse}}[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}^{3/2}$$

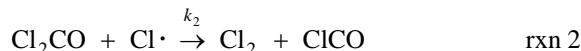
Therefore the rate equation for the formation of phosgene is

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$$

If you wish to verify this by devising a mechanism of elementary reactions, start with the clues given by the rate equation for the forward reaction. The fractional reaction order for  $[\text{Cl}_2]$  suggests the mechanism begins with the dissociation of  $\text{Cl}_2$



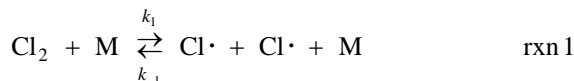
The next reaction is likely the reaction of intermediate  $\text{Cl}\cdot$  and reactant  $\text{Cl}_2\text{CO}$  to form product  $\text{Cl}_2$  and the other possible intermediate,  $\text{ClCO}$ .



The intermediate then decomposes into the other product.



This has the makings of a chain reaction. Reaction 1 is initiation and reactions 2 and 3 propagate by radicals  $\text{Cl}\cdot$  and  $\text{ClCO}$ . But we are given the hint this is not the case. We need the equivalent of a termination reaction to eliminate the  $\text{Cl}\cdot$  or the  $\text{ClCO}$ . Assume reaction 1 is reversible. Furthermore, the half-order in the rate equation suggests reaction 1 is in pre-equilibrium.



Use reaction 2 to write a rate equation.

$$-\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_2[\text{Cl}_2\text{CO}][\text{Cl}\cdot] \quad (2)$$

We need an expression for  $[\text{Cl}\cdot]$ . Apply pre-equilibrium to reaction 1.

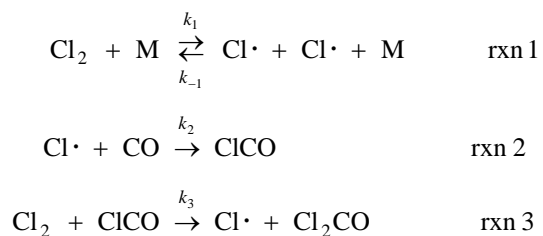
$$k_1[\text{Cl}_2][\text{M}] = k_{-1}[\text{Cl}\cdot]^2[\text{M}]$$

$$[\text{Cl}\cdot] = \sqrt{\frac{k_1}{k_{-1}}}[\text{Cl}_2]^{1/2} \quad (3)$$

Substitute equation (3) into equation (2) and the observed rate equation obtains.

$$-\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_2[\text{Cl}_2\text{CO}][\text{Cl}\cdot] = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Cl}_2\text{CO}][\text{Cl}_2]^{1/2}$$

Now reverse the mechanism and derive the rate equation.



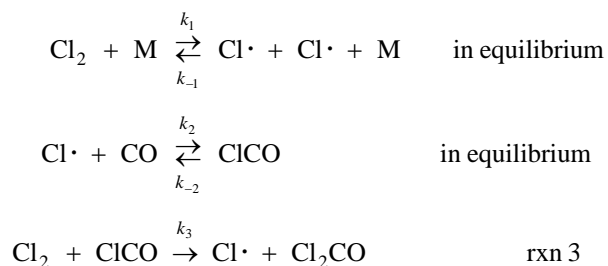
Use reaction 2 to write a rate equation.

$$-\frac{d[\text{CO}]}{dt} = k_2[\text{CO}][\text{Cl}\cdot] \quad (4)$$

Here we encounter problem. If we use the assumption from the forward reaction - that reaction 1 is reversible and in equilibrium - we obtain eqn (3) and a one-half reaction order with respect to  $[\text{Cl}_2]$ . Reversible thermodynamics demands that the reaction order with respect to  $[\text{Cl}_2]$  is 3/2. Which is wrong - thermodynamics or kinetics?

The problem is our mechanism; it has features unimportant to the forward reaction. Because ClCO is unstable, reaction 2 is reversible. Indeed ClCO is so unstable that it is more likely to decompose than encounter a  $\text{Cl}_2$  molecule and react. Reaction 2 is reversible and in equilibrium.

The mechanism is now:



With this model, reaction 3 is the rate-limiting step. Use reaction 3 to write a rate equation.

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{Cl}_2][\text{ClCO}] \quad (5)$$

Use equilibrium of reaction 2 to obtain an expression for  $[\text{ClCO}]$ .

$$k_2[\text{Cl}\cdot][\text{CO}] = k_{-2}[\text{ClCO}]$$

$$[\text{ClCO}] = \frac{k_2}{k_{-2}}[\text{Cl}\cdot][\text{CO}] \quad (6)$$

Substitute into rate equation (5).

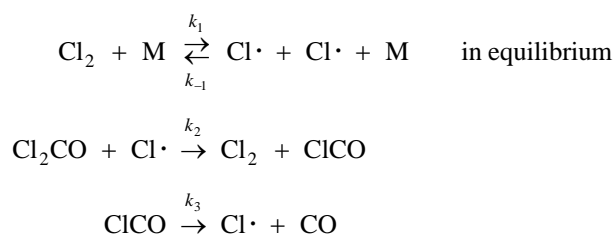
$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{Cl}_2][\text{ClCO}] = k_3[\text{Cl}_2]\frac{k_2}{k_{-2}}[\text{Cl}\cdot][\text{CO}] \quad (7)$$

Now use the result of pre-equilibrium on reaction (1) for the expression for  $[\text{Cl}\cdot]$ ; use eqn (3).

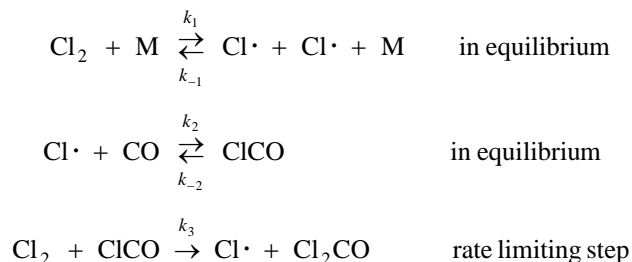
$$\begin{aligned} \frac{d[\text{Cl}_2\text{CO}]}{dt} &= k_3[\text{Cl}_2]\frac{k_2}{k_{-2}}\left(\sqrt{\frac{k_1}{k_{-1}}}[\text{Cl}_2]^{1/2}\right)[\text{CO}] \\ \frac{d[\text{Cl}_2\text{CO}]}{dt} &= \frac{k_2k_3}{k_{-2}}\sqrt{\frac{k_1}{k_{-1}}}[\text{CO}][\text{Cl}_2]^{3/2} \end{aligned} \quad (8)$$

The rate equation from the mechanism of elementary reactions is now consistent with the result from equilibrium thermodynamics.

In summary, the mechanism for the forward reaction  $\text{Cl}_2\text{CO} \rightarrow \text{Cl}_2 + \text{CO}$  is

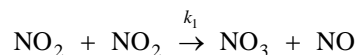


and the mechanism for the reverse reaction  $\text{Cl}_2 + \text{CO} \rightarrow \text{Cl}_2\text{CO}$  is

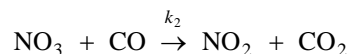


The rate equations derived from the forward and reverse mechanisms agree with equilibrium thermodynamics. And the two mechanisms are mutually consistent - microscopic reversibility. That is, the third reaction in the forward mechanism can be assumed to be reversible and in equilibrium with no affect on the forward rate equation.

- 3.(A) The rate equation suggests the rate-limiting step involves the reaction of two  $\text{NO}_2$  molecules. The product of this reaction is the intermediate  $\text{NO}_3$  and the product  $\text{NO}$ .



The intermediate  $\text{NO}_3$  reacts with the other reactant, as follows.



Use the second reaction to write a rate equation for  $[\text{CO}_2]$ .

$$\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}] \quad (1)$$

Assume the first reaction is rate-limiting and the second reaction is fast. Apply the steady-state approximation to  $\text{NO}_3$ .

$$\frac{d[\text{NO}_3]}{dt} = 0 = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}]$$

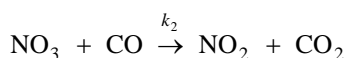
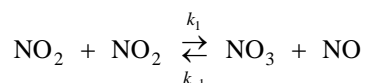
$$k_1[\text{NO}_2]^2 = k_2[\text{NO}_3][\text{CO}] \quad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\text{CO}_2]}{dt} = k_1[\text{NO}_2]^2$$

Thus  $k = k_1$ .

- (B) The rate equation from part (A) has the correct reaction order with respect to  $\text{NO}_2$  but lacks the terms in the denominator. The  $[\text{NO}]$  in the denominator suggests  $\text{NO}$  opposes the overall progress of the reaction. This feature can be added to the mechanism by making the first reaction reversible, as follows.



Again apply the steady-state approximation to  $\text{NO}_3$ .

$$\frac{d[\text{NO}_3]}{dt} = 0 = k_1[\text{NO}_2]^2 - k_{-1}[\text{NO}_3][\text{NO}] - k_2[\text{NO}_3][\text{CO}]$$

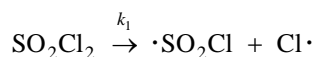
$$[\text{NO}_3] = \frac{k_1[\text{NO}_2]^2}{k_{-1}[\text{NO}] + k_2[\text{CO}]} \quad (3)$$

Substitute eqn (3) into eqn (1).

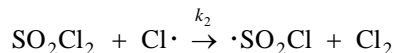
$$\frac{d[\text{CO}_2]}{dt} = k_2 \frac{k_1[\text{NO}_2]^2}{k_{-1}[\text{NO}] + k_2[\text{CO}]} [\text{CO}] = \frac{k_1 k_2 [\text{NO}_2]^2 [\text{CO}]}{k_{-1}[\text{NO}] + k_2[\text{CO}]}$$

This is the correct mechanism. The rate constants are thus  $\alpha = k_1 k_2$ ,  $\beta = k_{-1}$ , and  $\gamma = k_2$ .

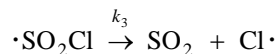
4. Start with the hint. A likely source of the chlorine atom is the unimolecular decomposition of  $\text{SO}_2\text{Cl}_2$ , which we will represent by the following elementary step, with due respect to Lindemann.



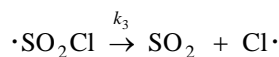
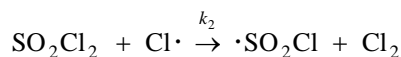
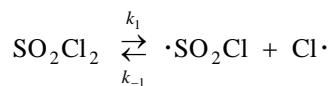
With what does  $\text{Cl}\cdot$  react? Keep the mechanism simple; react with the reactant and form a product.



We have now identified  $\cdot\text{SO}_2\text{Cl}$  as the second propagating radical in the chain reaction. What becomes of  $\cdot\text{SO}_2\text{Cl}$ ? We need another propagating reaction that forms the other product,  $\text{SO}_2$ , and reforms the first propagating radical,  $\cdot\text{Cl}$ . Assume  $\cdot\text{SO}_2\text{Cl}$  discards a chlorine atom,



The propagation cycle is complete. We now need a termination reaction. The combination of two chlorine atoms requires a termolecular collision. A collision of two  $\cdot\text{SO}_2\text{Cl}$  radicals is complicated; it is likely to break bonds rather than form bonds. Try the collision of the two propagating radicals; try the reverse of the initiation reaction. Our proposed mechanism is three elementary reactions:



The rate of formation of  $\text{SO}_2$  is given by step 3.

$$\frac{d[\text{SO}_2]}{dt} = k_3[\cdot\text{SO}_2\text{Cl}] \quad (1)$$

We need an expression for  $[\cdot\text{SO}_2\text{Cl}]$ . Assume the rate of initiation of radicals in reaction 1 forward equals the rate of termination of radicals in reaction 1 reverse; assume equilibrium of this reaction.

$$\begin{aligned} k_1[\text{SO}_2\text{Cl}_2] &= k_{-1}[\cdot\text{SO}_2\text{Cl}][\text{Cl}\cdot] \\ [\cdot\text{SO}_2\text{Cl}] &= \frac{k_1[\text{SO}_2\text{Cl}_2]}{k_{-1}[\text{Cl}\cdot]} \end{aligned} \quad (2)$$

We need an expression for  $[\text{Cl}\cdot]$ . Assume the rate of propagation in reaction 2 equals the rate of propagation in reaction 3.

$$\begin{aligned} k_2[\text{SO}_2\text{Cl}_2][\text{Cl}\cdot] &= k_3[\cdot\text{SO}_2\text{Cl}] \\ [\text{Cl}\cdot] &= \frac{k_3[\cdot\text{SO}_2\text{Cl}]}{k_2[\text{SO}_2\text{Cl}_2]} \end{aligned} \quad (3)$$

Use equation (3) to substitute for  $[\text{Cl}\cdot]$  in equation (2) and solve for  $[\cdot\text{SO}_2\text{Cl}]$ .

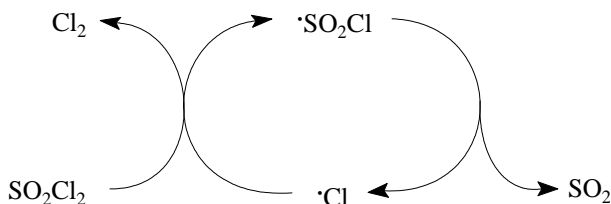
$$\begin{aligned} [\cdot\text{SO}_2\text{Cl}] &= \frac{k_1[\text{SO}_2\text{Cl}_2]}{k_{-1} \frac{k_3[\cdot\text{SO}_2\text{Cl}]}{k_2[\text{SO}_2\text{Cl}_2]}} \\ [\cdot\text{SO}_2\text{Cl}]^2 &= \frac{k_1 k_2 [\text{SO}_2\text{Cl}_2]^2}{k_{-1} k_3} \\ [\cdot\text{SO}_2\text{Cl}] &= \left( \frac{k_1 k_2}{k_{-1} k_3} \right)^{1/2} [\text{SO}_2\text{Cl}_2] \end{aligned} \quad (4)$$

Finally, use equation (4) to substitute for  $[\cdot\text{SO}_2\text{Cl}]$  in equation (1).

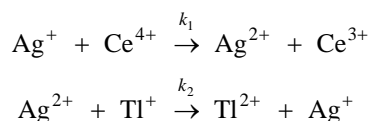
$$\begin{aligned} \frac{d[\text{SO}_2]}{dt} &= k_3 \left( \frac{k_1 k_2}{k_{-1} k_3} \right)^{1/2} [\text{SO}_2\text{Cl}_2] \\ \frac{d[\text{SO}_2]}{dt} &= \left( \frac{k_1 k_2 k_3}{k_{-1}} \right)^{1/2} [\text{SO}_2\text{Cl}_2] \end{aligned}$$

Check the result. The overall rate is first-order in  $\text{SO}_2\text{Cl}_2$  and the rate-limiting step (initiation) is first-order in  $\text{SO}_2\text{Cl}_2$ , so this is reasonable. If the values of  $k_1$ ,  $k_2$ , or  $k_3$  increase, the rate of reaction increases, which is reasonable. If the rate constant for the termination reaction,  $k_{-1}$ , increases, the rate of reaction decreases, which is reasonable.

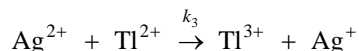
It was not requested, but who can resist sketching a propagation cycle? Not me.



5. Because this overall reaction is catalyzed by  $\text{Ag}^+/\text{Ag}^{2+}$  assume  $\text{Ag}^+$  donates an electron to  $\text{Ce}^{4+}$  and  $\text{Ag}^{2+}$  extracts an electron from  $\text{Tl}^+$ . Two possible reactions are as follows:



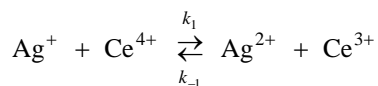
We expect either reaction may be reversible. To complete the overall reaction, another  $\text{Ag}^{2+}$  could extract an electron from  $\text{Tl}^{2+}$ .



We are told  $\text{Tl}^{2+}$  is short lived. Thus step 3 is probably faster than step 2. Assume step 2 is rate-limiting. The overall rate is thus given by the rate of step 2.

$$\frac{d[\text{Tl}^{3+}]}{dt} = -\frac{d[\text{Tl}^+]}{dt} = k_2[\text{Ag}^{2+}][\text{Tl}^+] \quad (1)$$

We need to express  $[\text{Ag}^{2+}]$  in terms of  $[\text{Ce}^{4+}]$  and  $[\text{Ag}^+]$ . The simplest solution is to assume the first reaction is reversible and in equilibrium.



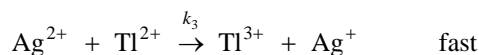
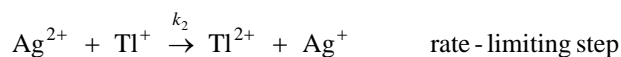
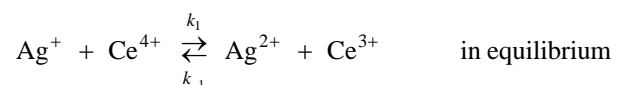
$$k_1[\text{Ag}^+][\text{Ce}^{4+}] = k_{-1}[\text{Ag}^{2+}][\text{Ce}^{3+}]$$

$$[\text{Ag}^{2+}] = \frac{k_1[\text{Ag}^+][\text{Ce}^{4+}]}{k_{-1}[\text{Ce}^{3+}]} \quad (2)$$

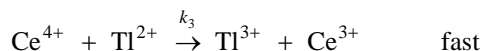
Substitute eqn (2) into eqn (1).

$$\frac{d[\text{Tl}^{3+}]}{dt} = k_2[\text{Ag}^{2+}][\text{Tl}^+] = k_2 \frac{k_1[\text{Ag}^+][\text{Ce}^{4+}]}{k_{-1}[\text{Ce}^{3+}]}[\text{Tl}^+] = \frac{k_1 k_2}{k_{-1}} \frac{[\text{Ag}^+][\text{Ce}^{4+}][\text{Tl}^+]}{[\text{Ce}^{3+}]}$$

This is the observed rate equation, such that  $k = k_1 k_2 / k_{-1}$ . The sequence of elementary steps is as follows:



The reaction that follows the rate-limiting step need only transform  $\text{Tl}^+$  into  $\text{Tl}^{2+}$ . The exact mechanism cannot be determined from the rate equation. It would be equally valid to transfer the electron directly to  $\text{Ce}^{4+}$  to form  $\text{Ce}^{3+}$ , as follows.



6. For complete condensation, the number of acid groups ( $-\text{COOH}$ ) must equal the number of alcohol groups ( $-\text{CH}_2\text{OH}$ ). Because 6-hydroxyhexandioic acid has one acid group and one alcohol group per molecule, it is balanced. One can add an arbitrary fraction of 6-hydroxyhexandioic acid: 0% to 100%. Because 1,6-hexanediol has two alcohol groups per molecule, we must add an equal number of moles of terephthalic acid, which has two acid groups per molecule.

Add 23 mol of terephthalic acid.

7. As with all chain reactions, it is useful to begin by classifying the elementary steps. Step 1 is initiation and step 2 is propagation. Step 3 is either termination (because it terminates the living polymer) or inhibition (because it also creates an initiation anion.) The distinction is not important - either name means it quenches the propagating radical.

As with previous chain polymerizations, we define  $[\text{NH}_2\text{-M}^-]$  to represent all living polymer chains, regardless of length,

$$[\text{NH}_2\text{-M}^-] \equiv \sum_{n=1} [\text{NH}_2\text{-M}_n^-]$$

The rate of chain propagation is the sum of the rates of all propagation reactions for  $n \geq 2$ .

$$\begin{aligned} \text{rate of chain propagation} &= \sum_{n=2} k_2 [\text{M}] [\text{NH}_2\text{-M}_{n-1}^-] \\ &= k_2 [\text{M}] [\text{NH}_2\text{-M}^-] \end{aligned} \quad (1)$$

Apply the steady-state approximation to  $[\text{NH}_2\text{-M}^-]$ .

$$\begin{aligned} \frac{d[\text{NH}_2\text{-M}^-]}{dt} &= 0 = k_1 [\text{NH}_2^-] [\text{M}] - k_3 [\text{NH}_2\text{-M}^-] [\text{NH}_3] \\ [\text{NH}_2\text{-M}^-] &= \frac{k_1 [\text{NH}_2^-] [\text{M}]}{k_3 [\text{NH}_3]} \end{aligned} \quad (2)$$

Substitute eqn (2) into eqn (1).

$$r = k_2 [\text{M}] \frac{k_1 [\text{NH}_2^-] [\text{M}]}{k_3 [\text{NH}_3]} = \frac{k_1 k_2}{k_3} \frac{[\text{NH}_2^-] [\text{M}]^2}{[\text{NH}_3]}$$

The Team Competition Champions for Calculation Session 13

Team String Cheese

Gee Tam & Demir Muhtaroglu



The only team submission with 6 out of 6 correct!



*Team Competition Solution:*

The end point is a key feature of a reaction trajectory plot. Does every trajectory end at the same point, or does the end point depend on the starting point? If the end point is a pure substance (A, B, or C), this indicates an irreversible reaction sequence that terminates in that substance. If the end point terminates on a triangle border, this indicates these two substances are in equilibrium.

The shape of the trajectory is another key feature. If the path is straight, this is probably a single reaction. If the path is curved, this is probably multiple reactions in series.

Diagram 1. Pure A terminates at a 1:1 mixture of B and C. The end point depends on the starting point, so the reaction does not involve  $B \rightleftharpoons C$ ; all  $B \rightleftharpoons C$  reactions would terminate at the same point on the B-C border. The only choices with B products are reaction 9:  $A \rightarrow B$ ,  $A \rightarrow C$  (parallel reactions) and reaction 7:  $2A \rightarrow B + C$ . Only reaction 7 guarantees a 1:1 B:C product from pure A. Diagram 1 is reaction 7:  $2A \rightarrow B + C$ .

Diagram 2. Pure A terminates as a mixture of B and C. But the ratio of B:C is not 1:1, so this is not reaction 7,  $2A \rightarrow B + C$ . Moreover, the end point depends on the initial mixture: more C initially results in more C at the end and more B initially results in more B at the end. Diagram 2 is reaction 9,  $A \rightarrow B$ ,  $A \rightarrow C$  (parallel reactions).

Diagram 3. All starting points terminate at a line with a constant ratio of A:B. Also, the trajectories are parallel to the A-B border, so the amount of C does not change. Diagram 3 is reaction 11:  $A \rightleftharpoons B$ , C is inert.

Diagram 4. All trajectories terminate at a mixture of A, B, and C, so all reactions must be reversible. Diagram 4 is reaction 4:  $A \rightleftharpoons B \rightleftharpoons C$ .

Diagram 5. A 1:1 mixture of A and B terminates at pure C. If A is initially in excess, the end point is a mixture of A and C. If B is initially in excess, the end point is a mixture of B and C. Diagram 5 is reaction 5,  $A + B \rightarrow 2C$ .

Diagram 6. All trajectories terminate at pure B, so the reaction is either reaction 11 “ $A \rightarrow B$ , C is inert” or reaction 12 “ $A \rightarrow B$ ,  $A \rightleftharpoons C$ .” There is evidence of a pre-equilibrium mixture of A and C and there is no residual C even when the initial mixture contains C. So Diagram 6 is reaction 12,  $A \rightarrow B$ ,  $A \rightleftharpoons C$ .