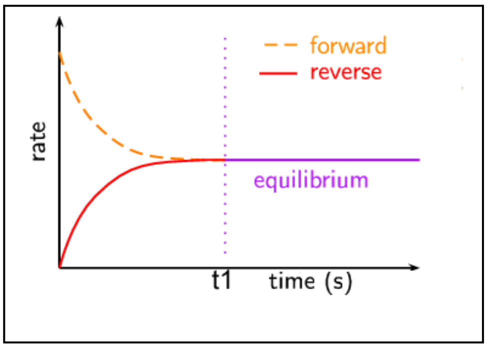
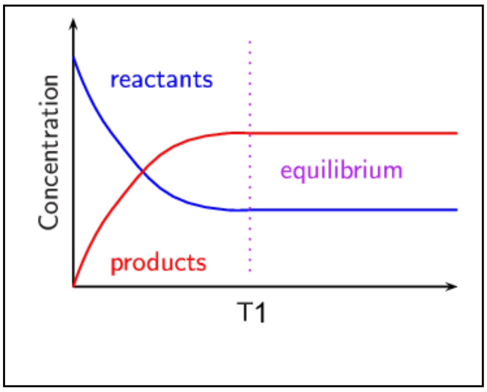
Lesson 4 equilibrium - interpreting equilibrium graphs

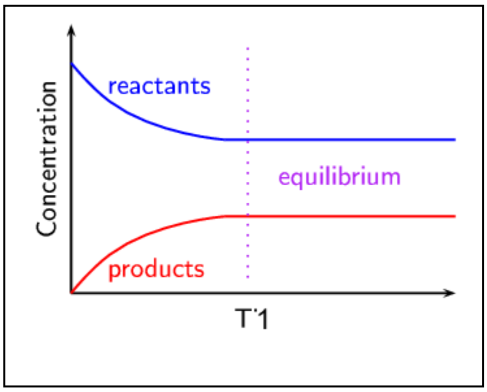
Equilibrium systems are often depicted using concentration-time graphs and rates graphs. It is handy to know how changes to a chemical system, at equilibrium, influences the concentration-time and rate graphs of that system.

1) At equilibrium the rates of the forward and backward reactions are equal. Remember, it is a dynamic equilibrium. Hence the rates graph should indicate that both the forward and backward rates are equal. A typical reaction rates graph when a system is at equilibrium is shown on the right at t1.
   For concentration-time graphs equilibrium is depicted when there is no change in the reactants or products.
   Notice how the concentrations of products and reactants do not have to be the same, as is the case for rates graphs.

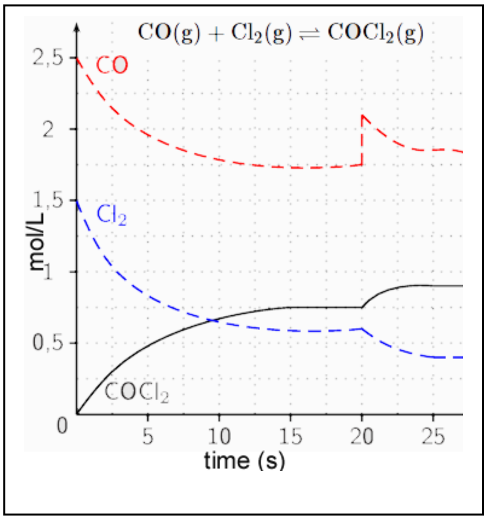
   Hence, when looking at a concentration-time graph we can tell when a system has reached equilibrium by the flat line of the concentration graphs. Here at T1 equilibrium has been reached.



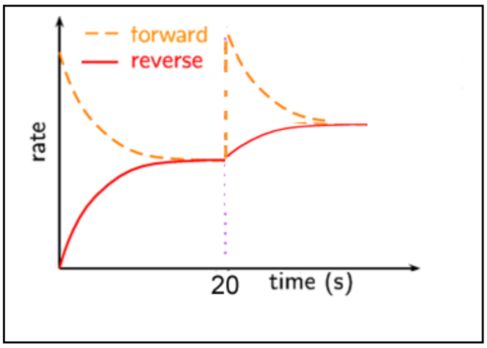




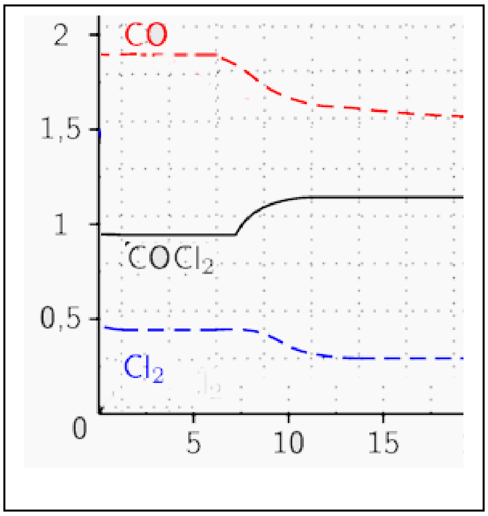
2) A spike in the concentration of one of reactants or products indicates the addition of substance to the system and so the system responds to remove it.
   Take the system shown on the right
   $CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)$ ΔH = *negative*
   At the 15 s mark equilibrium is reached at 20 s CO is added and the system responds by moving in a net forward direction in order to ***partially*** remove the added CO.



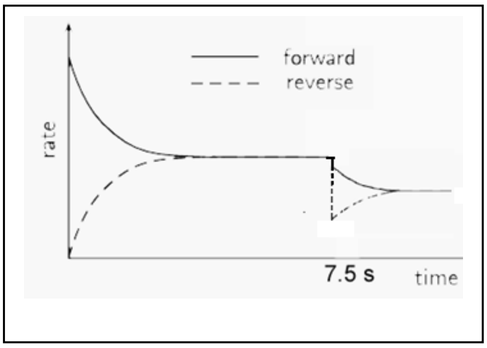
The rate graph should show a sudden spike in the forward reaction, as the system moves in a net forward direction, followed by a slow increase in the backward direction until both rates are equal once more.



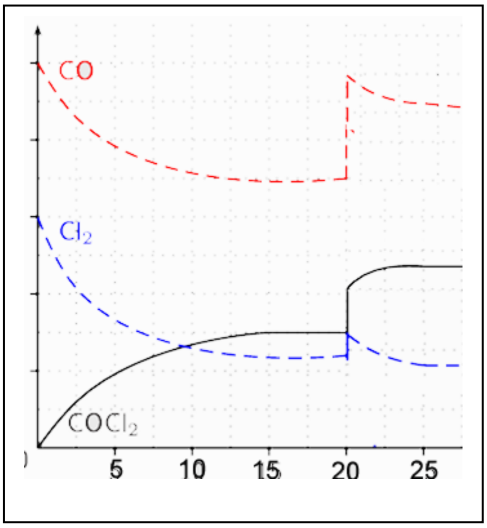
3) A slow change of the concentrations of all species present, as shown at 7.5 s, indicates a temperature change. Since the reaction is moving in a net forward direction we can say that temperature has decreased and the system is moving in a net forward direction to partially undo the removal of energy from the system. At 15s a new equilibrium has been reached.



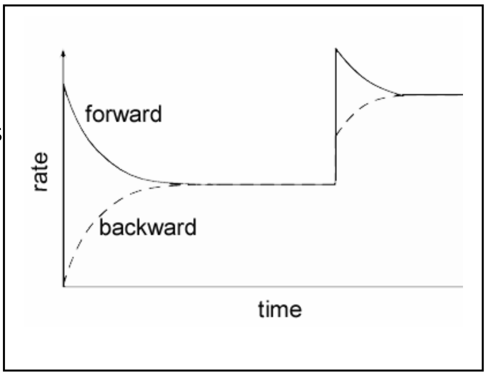
The rates graph for a temperature decrease looks like the one on the right. Both the forward and backward rates should decrease instantly with temperature decrease but since there is a net forward movement the forward rate should drop less than the backward rate. The rates then change, forward rate declines as reactants are being used up and the backward rate should increase steadily as the product concentration increases. This will continue until equilibrium is reached where the rates of both reverse and forward reactions are equal, albeit at a lower rate than before.



4) A sudden change of the concentration or pressure of all the species indicates a volume change. A sharp rise, as shown on the right at 20s, indicates a volume decrease. Notice how the system moves in a net forward direction, direction of least particles, to partially undo the increase in pressure or concentration.



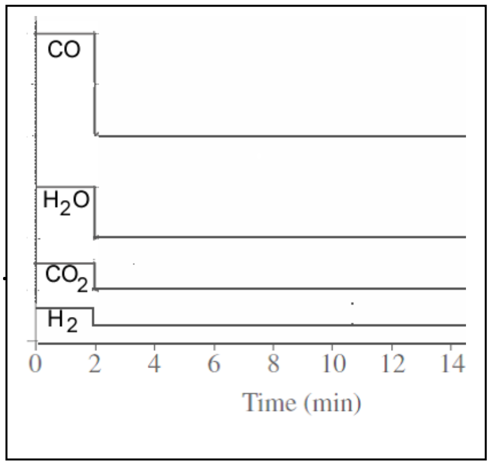
The rate graph for a volume decrease should resemble the graph on the right.



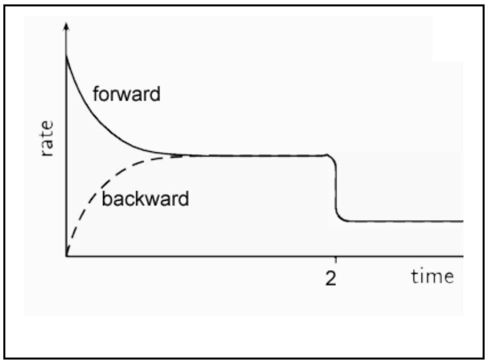
Since a volume decrease increases concentrations of both reactants and products the forward and backward reaction should increase. Since the a net forward direction is favoured the rate of the forward reaction should increase more than the backward. Notice how both rates adjust to be equal, at this point equilibrium is reached once more.

* Note that a change in volume only disrupts the system at equilibrium if the reaction is able to respond. What is meant by this statement is that if equal moles of reactants and products appear on either side of the reaction as shown in the equation below, then the system cannot respond.

$CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g)$

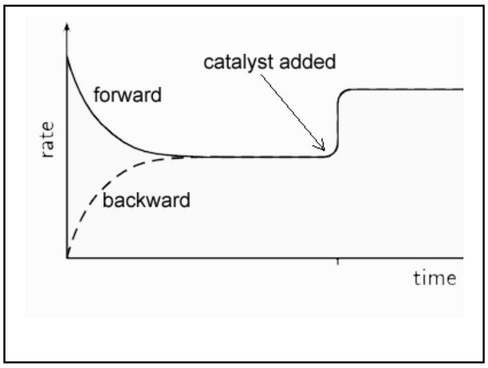


So the graph may look like the one on the right where the volume was increased with a subsequent decrease in concentration of all species, however, the system is not responding by moving in a net forward or backward direction.



The rate graph looks like the one on the right. Since the all the concentrations are diluted the rate of the forward and backward reactions will decrease accordingly, but still remain equal as the system is not shifted out of equilibrium.

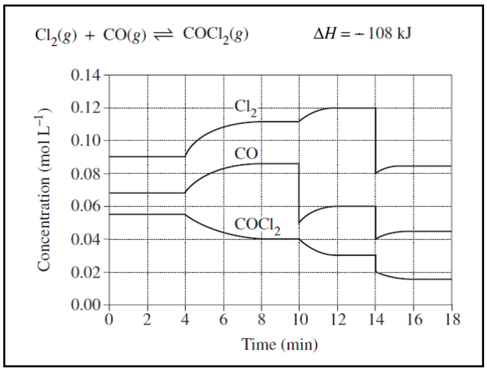
5) If a catalyst is used when a system is already at equilibrium the equilibrium position of the system is unaffected. The rate, however, of the backward and forward reactions will increase equally so as not to push the system in a net forward or backward direction.



1) Consider the changes made to the system represented by the reaction

$Cl_2(g) + CO(g) \leftrightarrows COCl_2(g)$.

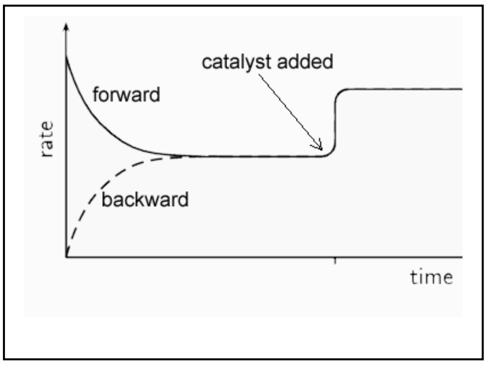
The graph on the right shows how the system responded to certain changes.



a) A change was made at the 2 minute mark. What could this change have been if nor gas was added to the system? Explain.

No change occurs to an system at equilibrium if an inert gas or a catalyst are added. A catalyst may have been added. Since there is no change to the equilibrium position of the system and no gas added.

b) Indicate how the rates of the forward and backward reactions changed at the 2 minute mark on the set of axes shown on the right.

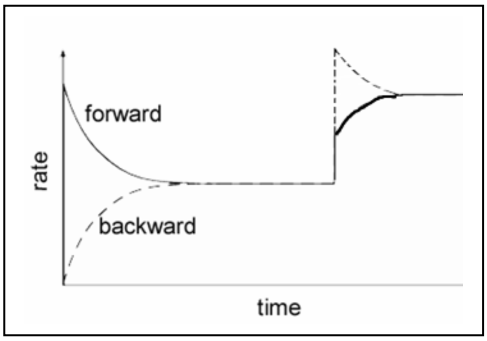


Both the forward and backward reactions have increase by the same amount and remain equal.

c) What happened at the 4 minute mark? Explain

Most likely temperature was increased and the system moves in a net backward direction to partially remove the energy.

d)) Indicate how the rates of the forward and backward reactions changed at the 4 minute mark on the set of axes shown on the right.

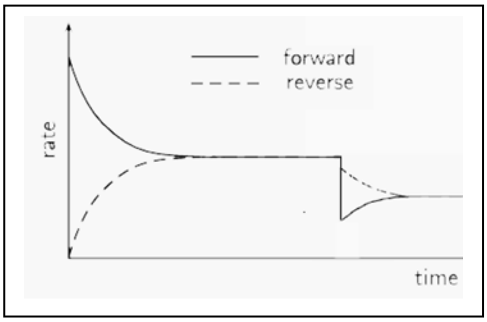


e) Suggest what happened at the 10 minute mark.

Some CO was suddenly removed hence the forward rate of reaction decreases.

The system moved in a net backward direction to partially compensate for the change.

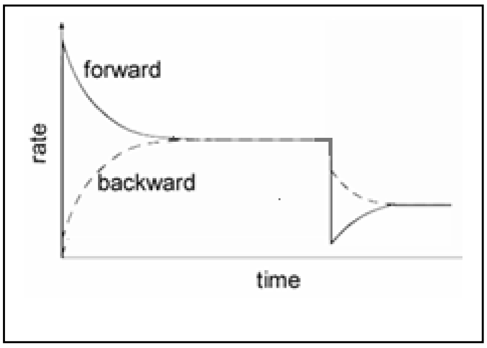
f) Indicate how the rates of the forward and backward reactions changed at the 10 minute mark on the set of axes shown on the right.



g) Suggest what happened at the 14 minute mark.

Most likely the volume of the reaction vessel was increased. All concentrations have been reduced.

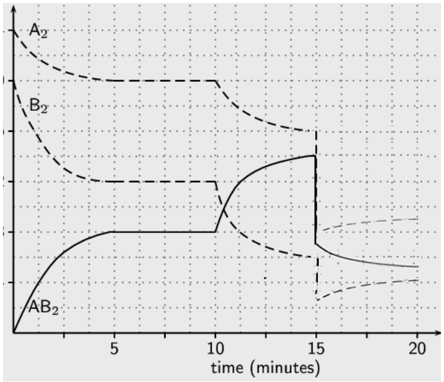
h) Indicate how the rates of the forward and backward reactions changed at the 14 minute mark on the set of axes shown on the right.



Since all concentrations are reduced both the forward and backward rates will reduce, however, since the reaction is moving in a net backward direction the backward rate will reduce less.

2) The graph on the right shows the system
$A_2(g) + 2B_2(g) \leftrightarrows 2AB_2(g)$ ΔH = *negative*
A mixture of gases A_2 and B_2 is placed in a sealed vessel and allowed to react according to the equation above.
Draw on the graph on the right how the system responds if:

For all the changes notice how the system is shown to respond in the correct stoichiometric ratio.



a) The system reached equilibrium within 5 minutes.
b) At the 10 minute mark the temperature was reduced in the reaction vessel.
c) At the 15 minute mark the system had reached equilibrium.
d) Just after 15 minutes the volume of the reaction vessel was doubled the system responded and reached equilibrium again in 5 minutes