CAVE CHEMISTRY

A senior student's guide to the caves in the Margaret River Region

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Overview

This package is designed to provide information and content for high school teachers to use in the classroom before or after a visit to the caves of the Margaret River Region. It focuses on the CO_2 equilibrium and the chemical processes involved in the formation of limestone, caves and speleothems, which mirrors those associated with ocean acidification.

Curriculum Links

- Understand the characteristics of equilibrium systems, and explain and predict how they are affected by changes to temperature, concentration and pressure.
- Understand the difference between the strength and concentration of acids, and relate this to the principles of chemical equilibrium.

Teacher Notes

- Similar to the chemical processes that result in ocean acidification, the equilibrium of carbon dioxide dissolved in water affects the production and precipitation of limestone caves and cave formations.
- When water moves through the atmosphere picking up carbon dioxide it forms a weak carbonic acid solution. This is not a one way chemical process, it is reversible, and the solution continually dissolves and dissociates attempting to maintain an equilibrium between reactants and products. In the atmosphere, CO_2 gas is usually present at around 0.035%, however, in the soil environment these levels can be much higher. This is due to plant root respiration, and the breakdown of decomposing organic materials. With higher soil CO_2, the chemical process is weighted towards the product, increasing the acidity of the solution.
- When carbonic acid comes into contact with calcium carbonate (limestone), it dissolves the carbonate and forms a new solution, calcium bicarbonate. Essentially, the more carbon dioxide, the stronger the carbonic acid and the more calcium carbonate it can carry. Typically, the soil-rock interface is a site of aggressive corrosion and where acidic solution starts to break down the limestone, eventually leading to collapses and cave systems.
- When the calcium bicarbonate solution passes into the cave environment, where the CO_2 levels are lower, the equilibrium shifts and becomes weighted towards the reactants. The solution releases CO_2, becomes less acidic and is no longer able to hold the $CaCO_3$ (calcium carbonate) molecules, depositing them in the cave and forming stalactites, stalagmites and other cave decorations.
- Climate can also have an effect on the process, such as in warmer areas like the tropics. Here, higher temperatures mean the aqueous solution is less able to hold gas resulting in a weaker acidic solution. This would indicate less caves in warmer areas. However, areas of higher temperatures such as the tropics often have well developed soil structures with healthy soil microbes excreting more CO_2. Add to this a higher rainfall, often experienced in tropical areas and the fact that chemical reactions occur more quickly under heat, and it becomes evident why many of our best cave and karst systems occur in cool and temperate or warm and moist climates.

Equilibrium Basics

CO2 gas dissolves in water to create carbonic acid, a weak acidic solution. This is a chemical reaction which can go both ways, forwards and backwards. When we talk about these processes we might say the reaction moves forward to create carbonic acid or backward to release water and carbon dioxide.

This reaction would be written like this (note the arrow points both ways);

$$CO_{2\,(aq)} + H_2O \longleftrightarrow H_2CO_{3\,(aq)}$$

In the above equation, CO2 and H2O are called reactants and carbonic acid is the product. So the chemical process may be described as moving forwards to create the product(s) or backward towards the reactants.

These processes are somewhat arbitrary, meaning, as molecules of CO2 and H2O bounce around in a system, they are continually combining as carbonic acid and dissociating to water and CO2.

This arbitrary process is always trying to find an equilibrium, a balance between the reactants and products, hence the term chemical equilibrium.

As you can imagine, if you change the concentration of reactants or products, or the environment the process occurs in, the equilibrium will shift. For example, if you increase the amount of CO2 in a system and change the balance, the solution will attempt to correct itself and create a new equilibrium. In this case, the process is weighted forwards, toward the product and creates more carbonic acid. If you remove CO2 from the system, it will work backwards and move towards the reactants, meaning more water and less carbonic acid.

According to Le Chatelier, when any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to counteract (partially) the effect of the applied change and a new equilibrium is established.

A great way to visualise this, is with a bottle of fizzy soda water from the fridge. This is simply CO2 mixed with water, so a weak carbonic acid. When it remains unopened the contents are at equilibrium, CO2 gas is trapped (pressurised) in the top of the bottle and a percentage of CO2 is dissolved in the water. When you open the bottle, you change the pressure of the gas, and CO2 is released into the atmosphere. The solution immediately starts to degas in an attempt to establish a new equilibrium, as you will see with the bubbles rising in the solution.

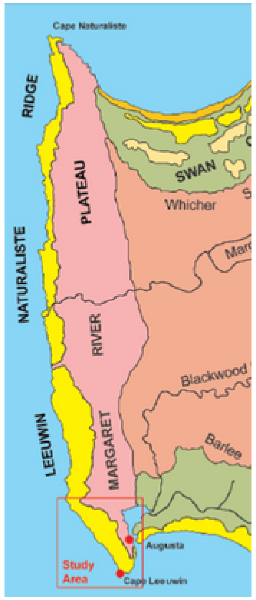
Continuing the example with the bottle of soda. As the temperature of the water rises, even to room temperature, even more CO2 is released. This is because solutions that are heated are able to dissolve less gas. A similar example is when you heat water, you'll see gas bubbling out of the water long before it actually comes to the boil.

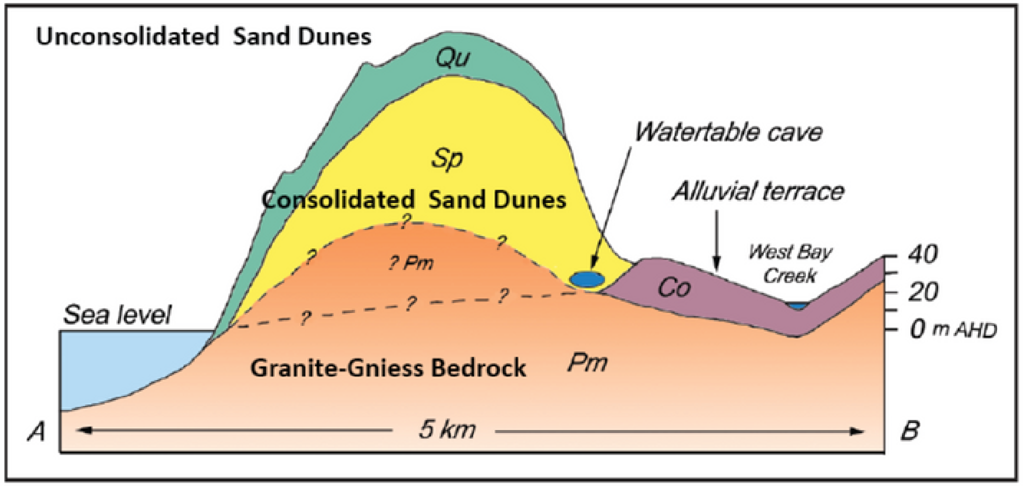
CO_2 Equilibrium in the Karst Environment

The Leeuwin Naturaliste Ridge, is the name for the geological formation which extends approximately 100km from Cape Naturaliste in the north to Cape Leeuwin in the south. It is primarily comprised of a 600 million year old granite-gniess bedrock supporting a young and porous layer of limestone believed to be less than two million years old. The limestone is mainly formed by consolidated sand dunes, consisting of a high level of calcium carbonate. Within this lie many cave systems created by the action of water moving through underground drainage systems. A landscape formed by the erosion and corrosion of water is commonly known as Karst.

The yellow band on the left hand side of this diagram indicates the Leeuwin Naturaliste Ridge.

Images sourced and adapted from: S. Eberhard, Jewel Cave Karst System, Western Australia: Environmental Hydrogeology and Groundwater Ecology, 2002. Pages 6 & 24.





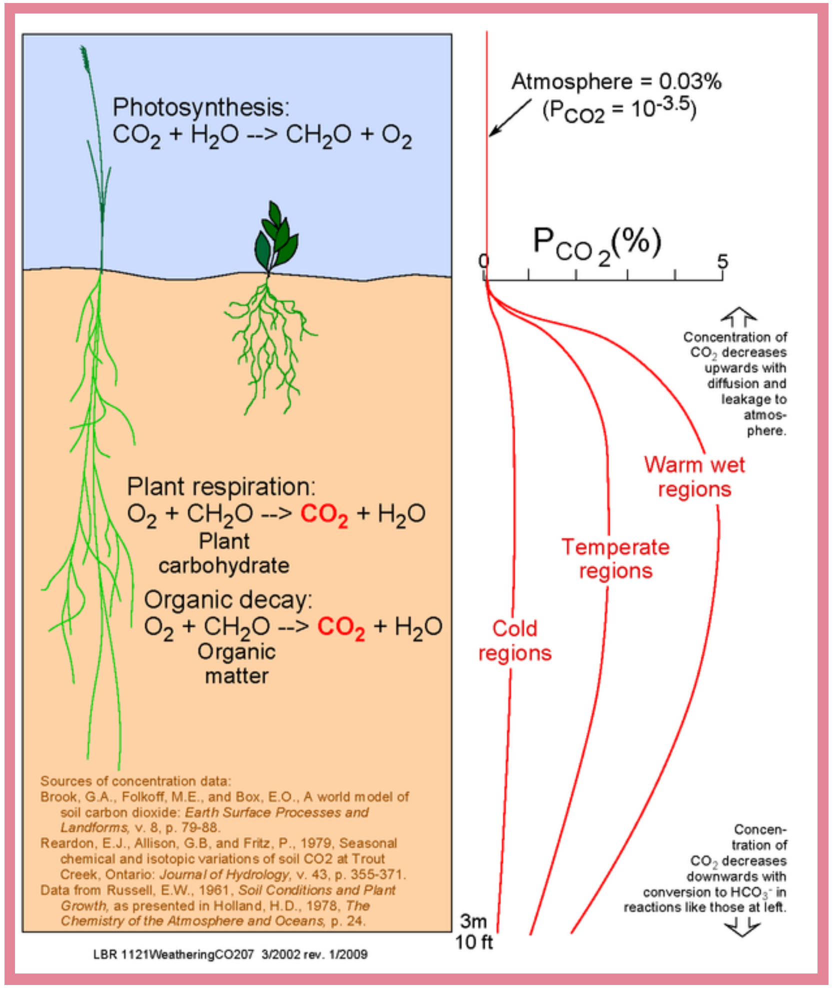
Cross-section of sample of Leeuwin-Naturaliste dune ridge with a simplified and exagerrated interpretation of the geomorphic structure.

The processes that result in cave systems and cave decorations (speleothems) are complicated, but can be generalised as occurring through the action of acidic, carbonated water, dissolving and precipitating calcium carbonate (limestone). The equilibrium system that plays a part of this formation commences in the atmosphere as water molecules (H_2O) mix with CO_2 molecules suspended in the air. An equilibrium is established between the reactants CO_2 and H_2O, and the product H_2CO_3 (carbonic acid). When carbonic acid (H_2CO_3) comes into contact with calcium carbonate ($CaCO_3$), it dissolves the $CaCO_3$, creating a new solution called calcium bicarbonate, $Ca(HCO_3)_2$.

CO2 Equilibrium in the Soil Environment

When water moves from the atmosphere into and through healthy soil, there is a dramatic increase in the concentration of CO2. Soil microbes, plant roots and decomposing organic material release CO2 which, trapped by the labyrinth of soil particles, becomes sequestered in the ground. Consequently the partial pressure of CO2 increases in the soil atmosphere and becomes much higher than the outside atmosphere (see figure a). With an increase in reactants, the equilibrium shifts and becomes weighted towards the product, resulting in an increased concentration of carbonic acid. This is important in geochemistry as carbonic acid is able to dissolve limestone.

(a)



Le Chatelier's Principle

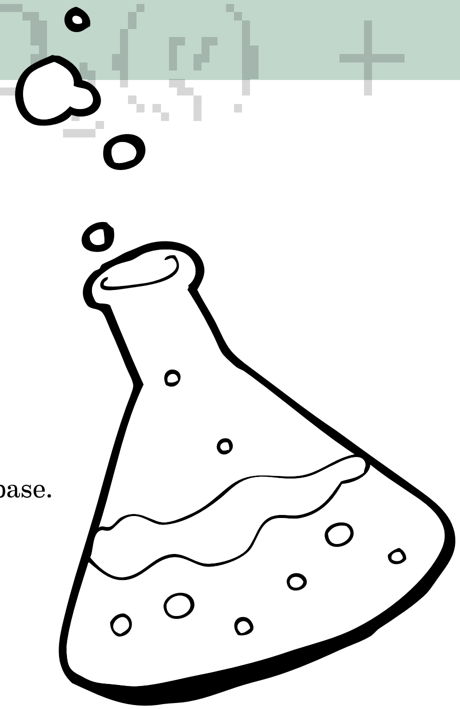
"Changes in the temperature, pressure, volume, or concentration of a system will result in predictable and opposing changes in the system in order to achieve a new equilibrium state." The above case illustrates how an increase in the concentration of the reactants results in opposing changes and an increase in product to create a new equilibrium.

Cave Equations

Only about 1% of dissolved CO2 exists as H2CO3. Carbonic acid is a weak acid which dissociates in two steps.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_{a2} = 4.8 \times 10^{-11}$$



Although 'insoluble' in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as Bronsted base.

$$CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2CO_3(aq)$$

The aqueous carbonic acid dissociates, producing carbon dioxide gas.

$$H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g)$$

In nature, water becomes acidic when it comes into contact with CO2 in the atmosphere or soil. This acidic water can dissolve limestone (CaCO3).

$$CO_2(aq) + H_2O(l) + CaCO_3(s) \longrightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq)$$

The reaction occurs in three steps.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + CO_3^{2-}(aq) \rightleftharpoons 2\,HCO_3^-(aq)$$

In the third step, carbonate ions accept hydrogen ions from carbonic acid. This reaction often occurs underground when rainwater saturated with CO2 seeps through a layer of limestone. As the solution dissolves calcium carbonate, it forms openings in the limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of CaCO3. If the solution containing dissolved Ca(HCO3)2 reaches the ceiling of a cavern, it will degas releasing the carbon dioxide and depositing the calcium carbonate on the ceiling, walls or floor.

$$Ca^{2+}(aq) + 2\,HCO_3^-(aq) \longrightarrow H_2O(g) + CO_2(g) + CaCO_3(s)$$

Source; Learn about Carbon Dioxide. http://scifun.chem.wisc.edu/chemweek/CarbonDioxide2017.pdf

Partial Pressure and Concentration

Here are two figures illustrating the effects of an increased partial pressure of CO2 on a solution, and the changing concentrations of CaCO3 in a solution at a temperature of 10°C.

Figure (b) shows the normal chemical pathway leading to the development of cave formations. At point A, we have high carbon dioxide partial pressure (pCO2) as found in soil. When percolating water with a high pCO2 reaches carbonate materials (limestone), they will be dissolved, increasing the calcium concentration in the solution.

In a closed system where no new CO2 is introduced the solution reaches saturation at point B. However, if CO2 is replenished, to maintain a constant pCO2 then saturation will be reached at point C.

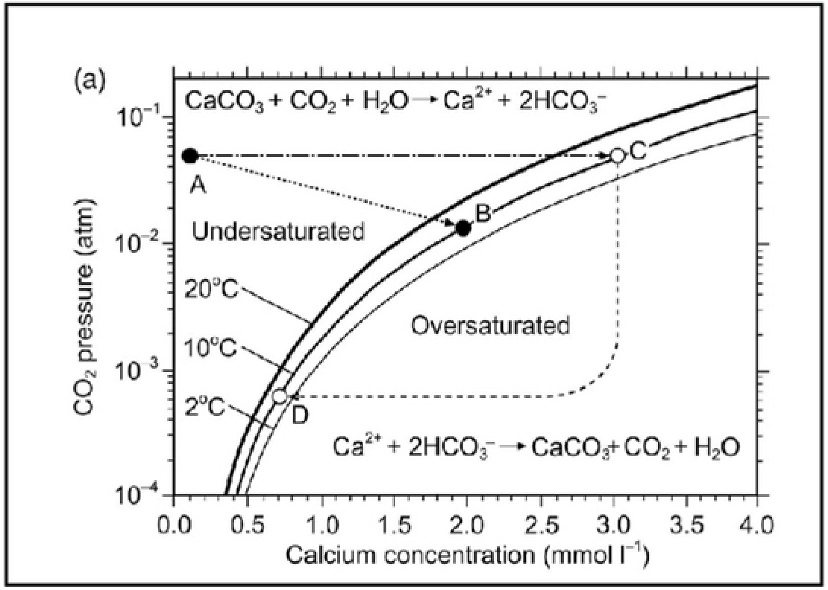
As the water descends into the karst system, at some point it may enter an air space with a lower pCO2 than the soil, i.e. a cave. As the water degasses it enters the over-saturated field and precipitates or deposits CaCO3 (as per the dashed line Point C to Point D.)

Figure (c) shows the amount of CaCO3 that can be dissolved in water containing CO2 at 10°C. You will note that it is not a straight line.

At normal atmospheric levels of CO2 (0.03%), only about 70 milligrams (mg) per litre (often referred to as parts per million - ppm) of CaCO3 will be held in solution. Soil air at 10% CO2, (a very high level) when in equilibrium with water, can produce a solution containing about 500 ppm of calcium carbonate.

The two arrows on Figure (c) labelled "L" and "M" are the next points for consideration (L = less; M = more). As discussed above, when the water moves from equilibrium in the soil atmosphere to a cave atmosphere, it degases and becomes less acidic. Less acid means less calcium carbonate is able to be held in solution. This carbonate must go somewhere and precipitates or deposits forming cave decorations, such as stalactites.

(b)



(c)

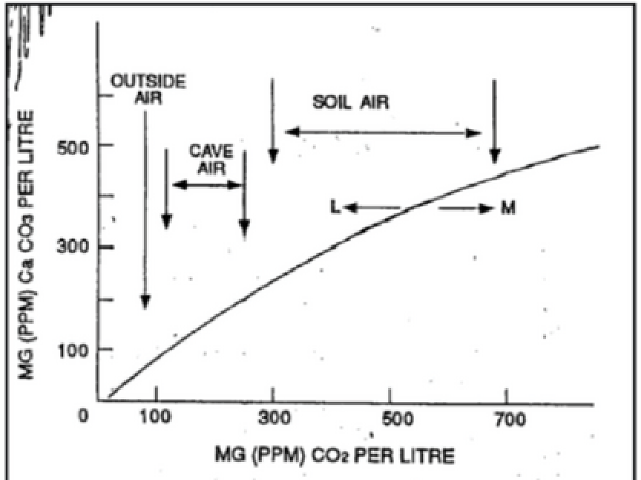


FIGURE 1: The amount of CaCo} which can dissolve in water at 10°C at vrious concentrations of CO{. See text for additional details.

Temperature

For all our explorations thus far we have chosen 10°C as the norm, but what happens if it is hotter or cooler?

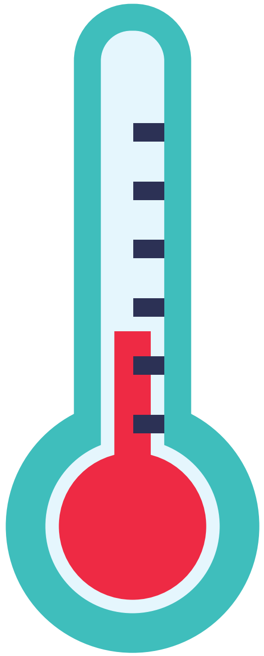
Firstly, 10°C is near enough to the sorts of temperature at which solution takes place - at least in southern Australasia. You will have noted that when you heat water, small bubbles come out of the solution long before the water boils. Hot liquids dissolve less gas, and thus in more tropic climes, water contains less carbon dioxide, and should be less aggressive than in temperate latitudes - this is in fact so. Conversely, in cooler climates there should be more CO2, and thus more solution - this is also true.

Why then, do we get extensive caves and karst features in warm places?

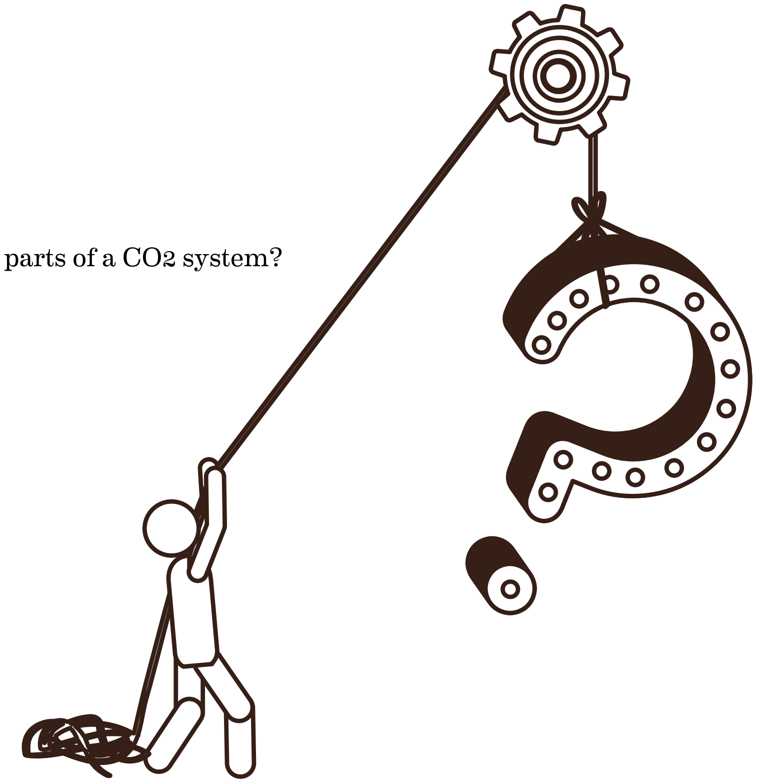
Amongst many other variables warm, moist climates enhance biological activity (e.g. rainforests). Thus more CO2 is available to make waters more aggressive. Added to this, warmer temperatures make chemical reactions, and this is one, proceed more quickly. Thus we get our best caves and karst in cool and temperate or warm and moist climates.

Characteristics of an Equilibrium System

1. Equilibrium may only be obtained in a closed system.
2. The rate of the forward reaction is equal to the rate of the reverse reaction.
3. Catalysts have no effect on the equilibrium point. However, changes in the concentrations of either the products or reactants, temperature, volume, or pressure can offset the equilibrium point. This point is illustrated in Le Chatelier's Principle.
4. The consistency of observable or physical properties such as concentration, colour, pressure, and density can indicate a reaction has reached equilibrium.



Question Time



Equilibrium Basics
1. What are the reactant(s) and product(s) in the CO_2 equilibrium system?
2. What chemical equation demonstrates the reactions in this system?
3. What happens when you change the concentration, temperature, volume, or pressure of parts of a CO_2 system? Give an example and draw a diagram to help explain your answer.

CO_2 Equilibrium in the Karst Environment
4. What are the primary geological components of the Leeuwin Naturaliste Ridge?
5. What is a Karst landscape?
6. What are the reactant(s) and product(s) in this equilibrium system?

CO_2 Equilibrium in the Soil Environment
7. Why is the concentration of CO_2 often higher in healthy soil?
8. What is Le Chatelier's Principle of equilibrium?

Cave Equations
9. Write out the three steps in which carbonic acid dissolves calcium carbonate

Partial Pressure and Concentration
10. What happens when percolating water with a high pCO_2 reaches carbonate materials?
11. What happens when the calcium/water solution moves from equilibrium in the soil atmosphere to a cave atmosphere?

Temperature and Characteristics
12. Why do we get our best cave systems in areas of cool, temperate and warm, moist climates?
13. Below are the characteristics of an equilibrium system. Circle the sentence(s) that are written incorrectly. Write the correct statement(s) on your answer page.

- Equilibrium may only be obtained in a closed system.
- The rate of the forward reaction is almost always equal to the rate of the reverse reaction.
- Catalysts have no effect on the equilibrium point. However, changes in the concentrations of either the products or reactants, temperature, volume, or pressure can offset the equilibrium point.
- The consistency of observable or physical properties such as concentration, colour, pressure, temperature and density can indicate a reaction has not reached equilibrium.

References

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