# Le Chatelier’s Principle

## Introduction

Le Chatelier's principle states that if a system in equilibrium is put under stress so that it is no longer in equilibrium, then it will change in such a way to minimize the stress. A simpler way of putting it is whatever you do to a system, the system tries to undo.

There are generally three types of stresses studied in general chemistry: change in concentration, change in temperature, and change in other external conditions such as pressure. We will consider these one at a time.

The ***concentration*** of a reactant or product may be either increased or decreased. If a reactant or product is removed, then equilibrium will shift to make more of it; if a reactant or product is added, then equilibrium will shift to remove it. The only way for a system to do this is to change the relative concentrations of *all* reactants and products.

Changing the ***temperature*** of a system in equilibrium is equivalent to adding or removing heat. Temperature affects equilibrium because reaction rate constants are temperature dependent, and the forward and reverse rate constants are affected to different degrees. A simple conceptual picture of temperature effects is to treat the enthalpy, ∆H, as a reactant or product and follow the rules for concentration. If a reaction is endothermic, enthalpy is a reactant; if it is exothermic, enthalpy is a product. If heat is added to an endothermic reaction (a temperature increase) then the reaction shifts to the right and more products are formed to store the excess heat. The opposite shift occurs if heat is removed (a temperature decrease), and the shifts are exactly opposite for exothermic reactions.

The only other common external condition that typically affects equilibrium is changes in ***pressure*** for gas phase chemical species. Here, the principle is that if the external pressure on the system increases, equilibrium will shift to decrease the total number of gas particles present (if possible). The opposite condition prevails if the external pressure is decreased.

***The common ion effect*** is a name given to systems that have more than one equilibrium present and at least one chemical species common to both.

Consider the system,

(a) A + B ⬄ C + D

(b) D + E ⬄ F

where species D is the common ion. Suppose the amount of E was increased. Based on le Chatelier’s Principle, F would increase, and D would decrease. But a decrease in D because of the second equilibrium will also decrease D in the first equilibrium. So, when E is added, A and B are also decreased and the amount of C is increased, *even though E is not a reactant in the first equilibrium*. This occurs because D is a common ion of both equilibria.

In this activity, Le Chatelier's principle will be applied to several chemical equilibria. In each case, the reversible reaction will be written, and the distinguishing characteristics of the products or reactants will be noted. A prediction should be recorded of what will be observed, which will be compared with the actual experimental observations.

*Instructions*

All of the equilibria may be observed in small test tubes. Solutions will be provided. Around 0.5-1.0 ml will be sufficient for these observations.

Add test reagents drop-wise until an effect is seen or until you are confident that there will be no effect.

For some of these tests, it may be useful to remember the following equilibrium must exist in all aqueous solutions:

(1) OH- + H3O+ ⬄ 2 H2O

PART I: The chromate - dichromate system

The chromate ion, CrO42-, is yellow in color; the dichromate ion, Cr2O72-, is orange. The equilibrium reaction is

(2) 2 CrO42- + 2 H3O+ ⬄ Cr2O72- + 3 H2O

In pH neutral solutions, the yellow chromate ion predominates.

Obtain two samples of the yellow chromate solution in separate test tubes. Based on equation (2), predict the color change (if any) of adding an acid such as 1.0 M HCl to the yellow solution.

Also predict the effect of adding a base such as 1.0 M NaOH to the yellow solution. Although the hydroxide ion, OH-, is not a reactant or product in equation (2), consider equation (1) and the common ion effect.

Next, obtain two samples of the orange dichromate solution in separate test tubes. Based on equation (2), predict the color change (if any) of adding acid and base (separately) to the orange solutions.

If any of the four solutions changed color – yellow to orange, or orange to yellow – how could they be changed back to their original colors? Make a prediction then test it.

PART II: The solubility of barium chromate

The equilibrium reaction for the precipitation of barium chromate is

(3) Ba2+ + CrO42- ⬄ BaCrO4(s)

Use one of the yellow chromate solutions from Part I for these tests. Add one or two drops of 0.1 M aqueous barium chloride (the source of barium ions) to a yellow chromate solution. Explain your observations based on equations (3) and le Chatelier’s principle.

Predict, and test whether adding an acid or a base to the mixture will re-dissolve the barium chromate formed. Explain the results using le Chatelier’s principle and equations 1, 2, and 3. Were any other effects observed besides the dissolution of the solid barium chromate? Can they be explained using le Chatelier’s principle?

PART III: Cobalt ion complexes

Cobalt cations are able to form different ionic complexes. An example of an equilibrium that may exist between two of them is

(4) [CoCl4]2- + 6 H2O ⬄ [Co(H2O)6]2+ + 4 Cl-

The cobalt chloride ion is blue, and the hydrated complex is pink. Tests will be made on a sample of the chloride complex dissolved in ethanol. Temperature effects will also be tested.

Obtain two samples of cobalt chloride dissolved in ethanol. Predict and test the effect of adding water to cobalt chloride solution. Do this dropwise using a wash bottle.

Predict and test the effect of adding concentrated HCl to the second cobalt chloride solution. CAREFUL! Concentrated hydrochloric acid is very corrosive!

How can you undo what you did to each solution? Test your prediction.

PART IV: Temperature Effects

Add water and hydrochloric acid, as needed, to create samples of cobalt chloride in each of the two test tubes that are violet-colored: somewhere between the blue and pink colors. Place one solution in warm water and the other in an ice water bath. From your observations, decide whether the reaction as written is exothermic or endothermic. Explain your reasoning based on le Chatelier’s principle applied to temperature effects.

PART V: An indicator

Acid-base indicators are just acids and bases that have distinct colors depending on whether the hydrogen ion is attached or not:

(5) HIn + H2O ⬄ H3O+ + In-

“In” in this equation is a general label for the portion of the molecule that changes color.

Choose an indicator such as methyl red or bromothymol blue. Add a drop of the indicator to a sample of 0.1 M hydrochloric acid, and also to a sample of 0.1 M sodium hydroxide. From your observations, deduce the colors of the protonated form (HIn) and unprotonated form (In-) of the indicator.

Confirm that the indicator is in equilibrium and follows le Chatelier’s principle by adding a few drops of acid to the base solution, and a few drops of base to the acid solution, and noting the effects.