### THERMODYNAMIC AND KINETIC STABILITY: LIGAND EXCHANGE KINETICS

The difference between kinetic and thermodynamic stability can be demonstrated by using  $[Ni(en)_3]^{2+}$  and  $[Co(en)_3]^{3+}$ .

- EQUIPMENT
  - 2 x 1 L beakers
  - stirring rod
  - light box

REAGENTS

- St.
- 1,2-ethanediamine,  $NH_2CH_2CH_2NH_2$  (30 g)
  - ("en" represents ethylenediamine, 1,2-diaminoethane or 1,2-ethanediamine)
- nickel(II) chloride-6-water, NiCl<sub>2</sub>·6H<sub>2</sub>O (59.5 g)
- activated charcoal (2 g)
- cobalt(II) sulfate-7-water, CoSO<sub>4</sub>·7H<sub>2</sub>O (14 g)
- hydrochloric acid, HCl (10 M, 5 mL)
- sulfuric acid,  $H_2SO_4$  (2 M, 300 mL)

### **PREPARATION** Preparation of [Ni(en)<sub>3</sub>]<sup>2+</sup>.

- Prepare a 0.5 M solution of nickel(II) chloride by dissolving 59.5 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 500 mL distilled water.
- Prepare a 0.5 M 1,2-ethanediamine solution by diluting 30 g 1,2-ethanediamine to 500 mL.
- Prepare a fresh solution of [Ni(en)<sub>3</sub>]<sup>2+</sup> by mixing 500 mL of 0.5 M 1,2ethanediamine and 170 mL nickel(II) chloride solution.

Preparation of racemic  $[Co(en)_3]^{3+}$  (in solution).

This step requires air to be drawn through the solution for 4 hours.

- Mix 13 mL of 1,2-ethanediamine and 25 mL of distilled water in a 250 mL conical flask.
- Cool the solution in an ice bath, then add 5 mL of 10 M hydrochloric acid, a solution of 14 g of cobalt(II) sulfate-7-water in 25 mL water and 2 g of activated charcoal.
- Bubble air through the mixture for 4 hours.
- Carefully adjust the pH of the solution to 7.0–7.5 with either 1,2-ethanediamine or 3 M hydrochloric acid, added dropwise.
- Heat the mixture on a steam bath (in a fume cupboard) for 15 minutes, cool and filter off the charcoal under suction in a Büchner funnel.
- Wash the charcoal with 10 mL of water and retain the filtrate and washings.

## **PROCEDURE** • Transfer the $[Ni(en)_3]^{2+}$ to one beaker and the $[Co(en)_3]^{3+}$ solution to the second beaker.

- Whilst stirring, add 150 mL of the sulfuric acid to the [Ni(en)<sub>3</sub>]<sup>2+</sup>.
- Add 150 mL of the acid to the  $[Co(en)_3]^{3+}$  solution.

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**RESULTS** The violet tris(1,2-ethanediamine)nickel(II) chloride solution will change to a green  $[Ni(OH_2)_6]^{2+}$  solution instantly.

The orange tris(1,2-ethanediamine)cobalt(III) solution will remain unchanged. This demonstration demonstrates that  $[Ni(en)_3]^{2+}$  is a *labile* complex–there is rapid exchange of the en ligands by aqua ligands and hence the colour change.

 $[Ni(en)_3]^{2+}(aq) + 6H_2O(I) \ 1 \ [Ni(OH_2)_6]^{2+}(aq) + 3en(aq)$ 

The tris(1,2-ethanediamine)cobalt(III) is an example of an *inert* complex in that it takes part in ligand exchange reactions very slowly, if at all. Hence the lack of a noticeable colour change.

Both of these complexes are thermodynamically unstable; they both have enormously large K values for dissociation indicating that in reactions, such as the one above, the equilibrium lies overwhelmingly to the right hand side. Thus the distinction between the two reactions is a kinetic one.

Tip: as the Co complex doesn't change colour and takes a long time to produce, a 'fake' solution can be used, ie weak Potassium dichromate solution.

- Refer to HIRAC
- Set up in Red Tray

### VARIATION OF REACTION RATES WITH TEMPERATURE

This demonstration uses a chemiluminescent reaction to illustrate the effect of temperature on rates of reaction.

- **EQUIPMENT** 2 Cyalume sticks
  - 2 beakers
- **PREPARATION** Place one Cyalume stick into a beaker of hot water and the other stick into a beaker of iced water.
- **RESULTS** The Cyalume stick in the hot water glows more brightly than the one in cold water. At higher temperatures the reaction rate is faster and produces more light.

### A SLOW IODINE REACTION

#### 2 L beaker EQUIPMENT

- 3 x 500 mL volumetric flasks
- 500 mL measuring cylinder
- 250 mL measuring cylinder
- 50 mL measuring cylinder
- stirring rod •
- nickel spoon •
- light box

REAGENTS

- potassium iodide, KI (8.3 g)

- sulfuric acid,  $H_2SO_4$  (0.02 M, 175 mL)
- hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (30 w/v% fresh)
- Vitex
- deionised water

#### **PREPARATION** . Prepare the following fresh aqueous solutions.

- Make up 175 mL of 0.02 M sulfuric acid.
- Prepare 500 mL of 0.02 M hydrogen peroxide by dissolving 1.26 mL of 30 w/v% solution in 500 mL of deionised water; [ measure out 50 mL after dilution ]
- Prepare 500 mL of 0.1 M potassium iodide solution by dissolving 8.3 g of KI in 500 mL of deionised water.
- Place the 2 L beaker and the three solutions on the light box.
- Supply Vitex, nickel spoon and stirring rod.

#### PROCEDURE Pour the iodide solution into the beaker. •

- Add a full nickel spoon of Vitex and stir. (Vitex may also be omitted; see below.)
- Now add the acid and the peroxide solutions simultaneously. .
- Stir briefly.
- Depending on the ambient temperature, the deep-blue colour will develop RESULTS gradually over the period of a minute or longer. Without Vitex a gradually deepening yellow appears.

The reaction below indicates that in acidic solution, iodide ions are oxidized by hydrogen peroxide to triiodide ions:

 $3I^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \zeta I_3^{-}(aq) + 2H_2O(I)$ 

- Refer to HIRAC
- Set up in Red Tray

### THE "IODINE CLOCK"

This "Clock" reaction illustrates that the rate of reaction is dependent on the concentration of the reactants.

- **EQUIPMENT** 3 x 500 mL beakers
  - 3 x 250 mL beakers
  - 2 x 250 mL volumetric flasks
  - 2 x 250 mL measuring cylinders
  - 2 x 25 mL measuring cylinder
  - 3 stirring rods
  - light box
  - stop watch(es)
  - nickel spoon
- REAGENTS
- iodic acid,  $HIO_3$  (5 g)
  - sodium sulfite, Na<sub>2</sub>SO<sub>3</sub> (2.1 g)
- Vitex
- distilled water
- **PREPARATION** The success of the demonstration depends on the purity of the water and the freshness of the solutions; preparation should occur within 24 hours of the demonstration.

Using volumetric flasks, prepare the following two solutions:

- **Solution A**: dissolve 5 g of iodic acid in distilled water and make up to 100 mL.
- **Solution B**: dissolve 2.1 g of sodium sulfite in distilled water and make up to 100 mL.
- Arrange the beakers in three pairs of one large and one small beaker.
- Label the pairs "I", "II" and "III". Distribute the solutions as follows:

Pair I	large beaker	20 mL of Solution A	
		200 mL of distilled water	
		1 heaped nickel spoon Vitex	
	small beaker	20 mL of Solution B	
		200 mL of water	
Pair II	large beaker	15 mL of Solution A	
	large beaker	200 mL of distilled water	
		1 heaped nickel spoon vitex	
	small beaker	15 mL of Solution B	
		200 mL of water	
Pair III	large beaker	12 mL of Solution A	
		200 mL of distilled water	
		1 heaped nickel spoon Vitex	
	small beaker	12 mL of Solution B	
		200 mL of water	

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- Set up the beakers on the light box in pairs.
- Provide stirring rods and stop watch(es).
- **PROCEDURE** For each of the pairs, pour the contents of the small beaker into the associated large beaker.
  - Note the time taken for reaction to occur in each case.
- **RESULTS** After mixing, the solutions will be clear but after some time they will sequentially (and suddenly) change to deep blue.

In the case of pair I, this will take about 3 seconds, pair II will take about 10 and pair III some 20 seconds.

**Note:** The reaction rate depends on ambient temperature, freshness of solution and the purity of reagents and water.

## THE OSCILLATING IODINE REACTION

Three solutions are added together quickly. The resultant solution then oscillates between golden brown, blue and colourless, finally stopping at a deep blue colour.

The phenomenon of the oscillating iodine clock reaction was reported by Briggs and Rauscher, J. Chem. Educ. <u>50</u>, 496 (1973).

- **EQUIPMENT** 2 x 500 mL conical flasks + stoppers
  - 1 x 2 L conical flask
  - magnetic heater/stirrer and spin bar
  - long stirring rod
  - light box
- **REAGENTS** potassium iodate, KIO<sub>3</sub> (29 g)

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- perchloric acid, HClO $_4$  [ or 10 ml of 6M sulfuric acid ]
- malonic acid,  $CH_2(CO_2H)_2$  (10.5 g)
- manganese sulfate,  $MnSO_4H_2O(1.68 g)$
- hydrogen peroxide,  $H_2O_2$  (25%)( 500mL)
- Vitex (starch solution)
- distilled water

**PREPARATION** All the following solutions must be freshly prepared:

#### Solution A

- Label the flask 2 L as "A".
- Put 700 mL of distilled water into the flask.
- Place it on the warm hot plate.
- Add the stirring bar.
- Add potassium iodate (29 g). Stir to dissolution.
- Remove from heat.
- Add 10ml of 6M sulfuric acid to prevent reprecipitation.
- This is essential to prevent the potassium iodate from coming out of solution as it will not readily re-dissolve under these acidic conditions.
- Make up to the 1 L mark.
- Stopper lightly.
- Allow to cool.

#### Solution B

- Calibrate a 500 mL conical flask by placing a mark at the 500 mL level.
- Label the flask "B" and put in 400 mL of distilled water.
- Add the following: manganese sulfate (1.68 g), malonic acid (10.5 g) and one nickel spoon full of Vitex.
- Stir well.
- Make up to the 500 mL mark and stopper lightly.

Solution C



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- Add 420mL of 30% hydrogen peroxide to a 500mL flask. Make up the solution to 500mL using deionised water. Transfer the solution to a labelled bottle. If preparing the hydrogen peroxide solution a day before store the solution in the fridge.
- **PROCEDURE** Transfer the contents of flask B and C as quickly as possible to flask A.

**RESULTS** The frequency and number of oscillations of this reaction sequence cannot be accurately predicted. Among the determining parameters are ambient temperature, purity of reagents and the time elapsed between preparation and demonstration. Should the demonstration fail to work altogether, the most likely cause will be the quality of the peroxide used. If possible, use a previously unopened bottle.

Initially, the solution will be clear and colourless. After several seconds a rapid colour change to golden brown will occur. After several further seconds the solution will change to deep-blue, then colourless again. The above sequence should repeat itself up to 15 times before the solution settles to a permanent, deep blue.

The overall reaction is:

 $IO_{3}^{-} + 2H_{2}O_{2} + CH_{2}(CO_{2}H)_{2} + H^{+} \Phi ICH(CO_{2}H)_{2} + 2O_{2} + 3H_{2}O$ 

- Refer to HIRAC
- Set up in Red Tray

### AN OSCILLATING REACTION TRAVELLING WAVES OF COLOUR

A blue dot spontaneously appears in a red solution, as the spot grows larger, red spots appear inside the blue spot, forming blue rings.

#### **EQUIPMENT** • 4 conical flasks

- petri dish
- 10 mL measuring cylinder
- 50 mL beaker
- 5 mL graduated pipette
- stirring rod
- **REAGENTS** potassium bromate, KBrO<sub>3</sub> (0.5 M, 6.0 mL)
  - potassium bromide, KBr (0.5 M, 1.0 mL)
  - sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (6 M, 0.60 mL)
  - malonic acid,  $CH_2(CO_2H)_2$  (2.5 mL)
  - ferroin solution (0.025 M, 1.0 mL)

### CAUTION

Bromates are strong oxidising agents. Mixtures of bromates with finely divided organic materials, metals, or other combustible
materials are easily ignited or explosive. Malonic acid is a strong irritant to the skin, eyes and mucous membranes.

**PREPARATION** These solutions should be prepared 10 minutes before the demonstration.

- Potassium bromate solution: Dissolve 0.84 g of KBrO<sub>3</sub> in 10 mL of distilled water.
- Sulfuric acid solution: Pour 3.3 mL of 18 M H<sub>2</sub>SO<sub>4</sub> into 10 mL distilled water.
- Malonic acid stock solution: dissolve 0.52 g CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in 10 mL.
- Ferroin stock solution: dissolve 0.069 g iron(II) sulfate-6-water and 0.135 g 1,10-phenanthroline in 10 mL of distilled water.
- Potassium bromide stock solution: dissolve 0.59 g KBr in 10 mL of distilled water.
- **PROCEDURE** Pour 6.0 mL of potassium bromate into the 50 mL beaker.
  - To the above solution add 0.60 mL of sulfuric acid, 1.0 mL of potassium bromide solution and 2.5 mL malonic acid.
  - Stir the solution until the amber colour disappears.
  - Add 1.0 mL of ferroin solution. The solution will turn blue, then redorange.
  - Pour the solution into the petri dish and swirl the dish to coat the bottom of it uniformly.
  - Place the petri dish on the overhead projector and adjust the projector so that the solution is in focus on the screen.



RESULTS The induction time for this demonstration is five-ten minutes after which one or more blue dots will appear in the solution. These dots will grow slowly, and after a time, the centre of the blue dot will turn red-orange, forming a blue ring. The blue ring will expand, its red-orange interior will grow, and another blue dot will appear at the centre. By alternately turning blue, then red-orange, the centre will produce a series of concentric rings which gradually advance through the solution. When several sets of rings develop at different centres in the dish, they will eventually interact to form complex pattern of blue and orange bands. The dish may be swirled to mix the solution, to allow for the formation of new rings. The blue dots will reappear and generate a new pattern. After some time, bubbles of carbon dioxide will appear in the solution, making it difficult to observe the pattern. Eventually the solution will become completely blue, and no more patterns will develop. Traces of chloride ions in the solution will interfere with the mechanism of the reaction.

See - Showalter, Noyes & Turner, J. Am. Chem. Soc. 101, 7463 (1979).

Unlike the previous oscillating reactions, which are temporal in nature, this reaction involves spatial oscillations – rings of high [Fe(III)] moving through regions of high [Fe(II)].

The overall chemical change involves bromate oxidation of malonic acid which is catalysed by ferroin.

 $BrO_{3}^{-}(aq) + 2Br^{-}(aq) + 3H^{+}(aq) + 3CH_{2}(CO_{2}H)_{2}(aq) \zeta \ 3BrCH(CO_{2}H)_{2}(aq) + 3H_{2}O(I)$ 

- Refer to HIRAC
- Set up in Red Tray

### OXIDATION OF METHANOL CATALYSED BY PLATINUM

A heated piece of platinum gauze is brought near warmed methanol. The gauze then begins to glow.

- EQUIPMENT 250 mL beaker
  - bunsen burner
  - tripod and wire mat
  - retort stand
  - 2 boss heads and clamps
  - watch glass and/or damp cloth
  - fine copper wire

REAGENTS

- piece of platinum gauze (ideally, a platinum cathode such as those used in the teaching laboratories)
- methanol, CH<sub>3</sub>OH (25 mL fresh)
- hydrochloric acid, HCl

**PREPARATION** There are three things which frequently prevent this demonstration from working satisfactorily:

- the platinum has not been cleaned before use.
- old (partially oxidised) methanol has been used.
- the methanol and/or platinum had either not been pre-warmed sufficiently or it is being over-heated.
- Clean the gauze in the following way: Place some concentrated hydrochloric acid in a 100 mL beaker. Light a bunsen burner and heat the platinum gauze until it is red-hot. Plunge the gauze into the hydrochloric acid and hold the gauze over the flame until it is red-hot. Repeat three times. Rinse in alcohol.
- Set up retort stand and clamp, bunsen burner, tripod and wire mat.
- Suspend the gauze from the clamp by a thin piece of wire.
- Place some methanol (25 mL) in the beaker and set it on the wire mat over the tripod so that it is directly below the gauze.
- Provide matches and watch glass or damp cloth.

## • Light the bunsen and gently warm the methanol just enough to generate some vapour in the upper portion of the beaker.

- Remove the flame and use it to quickly warm the platinum gauze.
- Without delay lower the gauze into the flask to within a centimetre of the surface of the methanol.
- **RESULTS** Within a few seconds the gauze will begin to glow: exothermic oxidation of methanol is taking place.

 $2CH_{3}OH(I) + 3O_{2}(g) \zeta 2CO_{2}(g) + 4H_{2}O(g)$ 

### CAUTION

If the glowing platinum is allowed to come too close to the methanol surface, the methanol itself will ignite. The flame can be easily
extinguished by placing the watch glass or damp cloth over the mouth of the flask.

### CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

Manganese dioxide is used to catalyse the decomposition of hydrogen peroxide.

This demonstration may be performed on a small or large scale. In the instructions below, the amounts needed for the large-scale demonstration are given in square brackets [].

- **EQUIPMENT** 1 L measuring cylinder [specially made cylinder, 1.5 m high, 6 cm diameter]
  - 2 x 25 mL [2 x 100 mL] measuring cylinders
  - 100 mL [500 mL] measuring cylinder
  - plastic tray
  - glass stirring rod, length depending on the cylinder used [retort stand and clamp]
- **REAGENTS** manganese dioxide, MnO<sub>2</sub>, one nickel spoonful
  - sodium hydroxide, NaOH (1 M, 20 mL [60 mL])
  - hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (30%), 100 mL [300 mL] fresh)
  - Teepol (20 mL [60 mL])
- **PREPARATION** Prepare a 1 M solution of sodium hydroxide by dissolving 4.0 g of solid sodium hydroxide in 100 mL of distilled water.
  - Place 1 [3] heaped nickel spoonful of manganese dioxide into the cylinder.
  - Set the 1 L cylinder in the plastic tray [support the tall cylinder with retort stand and clamp].
  - Provide reagents in the appropriate measuring cylinders, as well as the stirring rod.
- **PROCEDURE** Make a slurry of manganese dioxide with the sodium hydroxide solution and Teepol.
  - Add the hydrogen peroxide and stir briefly.
- **RESULTS** The mixture will undergo rapid decomposition and oxygen will be given off. A thick grey foam will form which should fill the cylinder to over-flowing.

**Note:** The volume of foam depends on the strength of the peroxide and the effectiveness with which Teepol traps the oxygen.

 $2H_2O_2(aq) \stackrel{MnO_2(s)}{\zeta} 2H_2O(I) + O_2(g)$ 

### **COMPARISON OF CATALYSTS**

The following catalysts are used to decompose hydrogen peroxide: manganese dioxide, liquid bromine, sodium bromide, ground and unground liver, and platinum gauze. A comparison is made of the rates of reaction with each catalyst.

- **EQUIPMENT** 6 x 100 mL measuring cylinders
  - platinum gauze
  - 6 drip trays

#### **REAGENTS** • manganese dioxide, MnO<sub>2</sub>/NaOH saturated solution

- sodium bromide, NaBr
- bromine water, Br<sub>2</sub>
- liver (ground and unground)
- hydrogen peroxide,  $H_2O_2(10\% \text{ w/w})$
- Teepol
- **PROCEDURE** Place each measuring cylinder in a drip tray.
  - In each cylinder place 10 mL of  $H_2O_2$  and 6 mL of Teepol.
  - Add the following catalysts to each cylinder in turn:
    - 1. MnO<sub>2</sub>/NaOH
    - 2. platinum gauze
    - 3. NaBr(aq)
    - 4.  $Br_2(aq)$
    - 5. unground liver
    - 6. ground liver
  - Note the rate at which the foam reaches the top of each cylinder.
- **RESULTS** The general reaction is:

 $2H_2O_2(aq) \xrightarrow{catalyst} 2H_2O(l) + O_2(g)$ 

For  $MnO_2$  as the catalyst, see Demonstration 7.8. The platinum gauze catalyses the reaction at a slower rate because it proceeds by way of adsorption of the peroxide on to the surface of the catalyst. The rates of reaction when using either bromine water or sodium bromide are the same. But the latter has a lead time as the concentration of Br<sub>2</sub> must build up first.

The ground liver has a larger surface area than the unground liver and hence more sites of catalysis; the rate of decomposition is faster. The catalyst in the case of liver is catalase.

After a series of reactions on the surface of the catalyst, water and oxygen are liberated.

### THE PRODUCTION OF AN ACTIVATED COMPLEX

A pink cobalt catalyst is added to a solution of sodium potassium tartrate and hydrogen peroxide. A green activated complex is formed and the reaction proceeds. When the green complex disappears, the reaction ceases.

- EQUIPMENT 600 mL beaker
  - 2 x 250 mL beakers
  - 100 mL measuring cylinder
  - hot plate
  - spatula
  - scales
  - thermometer



- hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (5%, 80 mL)
- cobalt(II) chloride-6-water, CoCl<sub>2</sub>·6H<sub>2</sub>O (9–13 g)
- distilled water (300 mL)

**PREPARATION** .

Prepare a solution of sodium potassium tartrate (200 mL) by dissolving 12 g of NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O in distilled water (200 mL) in a 250 mL beaker.

sodium potassium tartrate-4-water, NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O (12 g)

- Prepare a solution of 5% hydrogen peroxide by adding 20 mL of 30% hydrogen peroxide to 100 mL of distilled water in the other 250 mL beaker.
- Pour 80 mL of the 5% hydrogen peroxide into the measuring cylinder.
- Heat the hot plate to 70°C.
- Pour the sodium potassium tartrate (200 mL) solution into the 600 mL beaker and place it on the hot plate. Checking with the thermometer heat the solution to 70°C.
  - Add the hydrogen peroxide and the cobalt(II) chloride-6-water.

**RESULTS** This reaction involves the oxidation of tartaric acid  $HO_2CCH(OH)CH(OH)CO_2H$  by hydrogen peroxide in the presence of a cobalt(II) chloride catalyst. It is a complex set of reactions involving the production of carbon dioxide, carbon monoxide and oxygen. The green colour is due to the formation of a cobalt-tartrate activated complex. Note that the original catalyst, cobalt(II) chloride, is pink in aqueous solution. As the tartrate is oxidized, the activated complex is broken down to the original catalyst, and the pink colour returns. Oxygen and carbon dioxide gases are also produced. Oxalic acid,  $HO_2CCO_2H$ , is probably produced also.

This demonstration can also be used to show the relationship between temperature and the reaction rate. Typically, initial temperatures of 50, 60 or 70°C produce a reaction times of 200, 90 or 40 seconds, respectively. Thus as a general rule, increasing the temperature of reaction by 10°C will double the reaction rate.



### AUTOCATALYSIS

When a small amount of sulfuric acid is added to the blue solution of potassium chlorate, sodium sulfite and bromophenol blue indicator in a measuring cylinder, a yellow colour forms at the top of the cylinder and gradually moves downwards.

- EQUIPMENT 2 x 500 mL beakers
  - 500 ml measuring cylinder
  - magnetic stirrer
  - dropper

REAGENTS



- potassium chlorate,  $KCIO_3$  (20 g)
  - sodium sulfite, Na<sub>2</sub>SO<sub>3</sub> (62.5 g)
  - bromophenol blue indicator
  - sulfuric acid,  $H_2SO_4$  (3 M, 20 mL)
  - distilled water (500 mL)
- **PREPARATION** Dissolve 20 g potassium chlorate and 62.5 g sodium sulfite in 250 mL of water.
  - Do not mix the solids first.
  - Add some bromophenol blue indicator.
  - In another beaker, add 20 mL sulfuric acid to 250 mL of water.
  - Slowly, with stirring, add the diluted acid to the contents of the first beaker.
  - Stir until everything dissolves.
  - This solution should be blue-violet.
  - Fill the measuring cylinder with this solution.
- **PROCEDURE** Add two droppers-full of  $3 \text{ MH}_2\text{SO}_4$  to the top of the liquid in the measuring cylinder.
- **RESULTS** A yellow colour will appear at the top of the solution, and a yellow-blue interface will form. This interface will gradually move down the cylinder.

The overall reaction is:

 $ClO_{3^{-}}(aq) + 3SO_{3^{2^{-}}}(aq) \zeta Cl^{-}(aq) + 3SO_{4^{2^{-}}}(aq)$ 

When sulfuric acid is dropped on the surface,  $H^+$  and other acidic products form. These acidic products catalyse further reactions to produce more acidic products, thus the autocatalytic nature of the reaction. Bromophenol blue is yellow in highly acidic conditions. Thus, as autocatalysis proceeds, the indicator changes from blue to yellow.

### Belousov-Zhabotinsky Reaction (Cerium –Catalysed)

Three solutions are combined with ferroin indicator to produce a reaction which oscillates between green, blue,violet and red, in intervals of approximately 1 minute. Oscillations can last for up to 1 hour.

- **EQUIPMENT** Conical flask, 1X 1L
  - Conical flask, 2X 250mL
  - Measuring Cylinder, 1X 5mL
  - Stirring Rod
  - Measuring Cylinder, 1X 5mL
  - Light Box
- **REAGENTS** Potassium bromate, KBrO<sub>3</sub> (8 g)
  - Malonic acid, CH<sub>2</sub>(COOH)<sub>2</sub> (6.4g)
  - Potassium Bromide, KBr (1.4g)
  - sulfuric acid,  $H_2SO_4$  (2.7 M, 200 mL)
  - Cerium ammonium nitrate, ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (4.24g)
  - Ferroin Indicator (12mL) (0.5%)
  - distilled water (500 mL)
- **PREPARATION** Prepare the following solutions. Distilled water is essential:small amounts of chloride can interfere with the reaction. Solutions can be made 2 days in advance.
  - **Solution A-**Dissolve 7.6g of Potassium Bromate in 200mL of distilled water and provide it in a 250mL flask. Stir and warm the solution to dissolve the solids
  - **Solution B-**Dissolve 6.4g of Malonic acid and 1.14g of Potassium bromide in 200mL of distilled water and provide in a 250mL flask.
  - **Solution C** Dissolve 4.24g of Cerium Ammonium nitrate in 200mL of 2.7M sulphuric acid and allow the solid to dissolve and provide the cooled solution in a 250mL flask.
  - **Ferroin solution** To prepare 100mL of 0.5% Ferroin solution dissolve 0.23g of Iron (II) sulphate 7H<sub>2</sub>0 and 0.62g of 1,10-phenanthroline monohydrate in distilled water. Use 12 mL for the demonstration.
- PROCEDURE Transfer Solution A into a 1L flask. To this add solution B and stir the solution for approximately 1 minute. Add solution C and 12mL ferroin to the above solution resulting in a green turbid solution. Continue stirring until cloudiness dissolves, then let stand on light box (continued stirring is optional)
- **RESULTS** After about a minute , the oscillation begins and continues in approximately 1-minute intervals: the green solution turns blue, violet and then red, before finally returning t green.
- **DISPOSAL** Neutralise the solution with NaHCO3 and dispose as heavy metal waste

