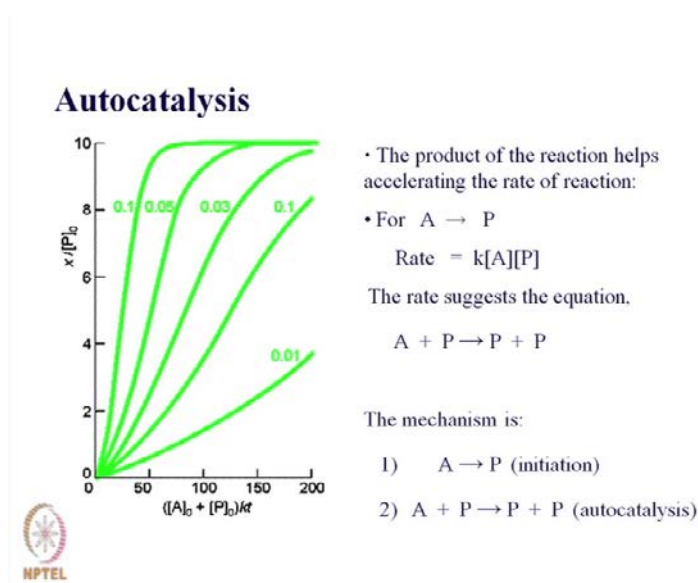


**Rate Processes**  
**Prof. M. Halder**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Module No. # 01**  
**Lecture No. # 17**  
**Oscillatory Reactions**

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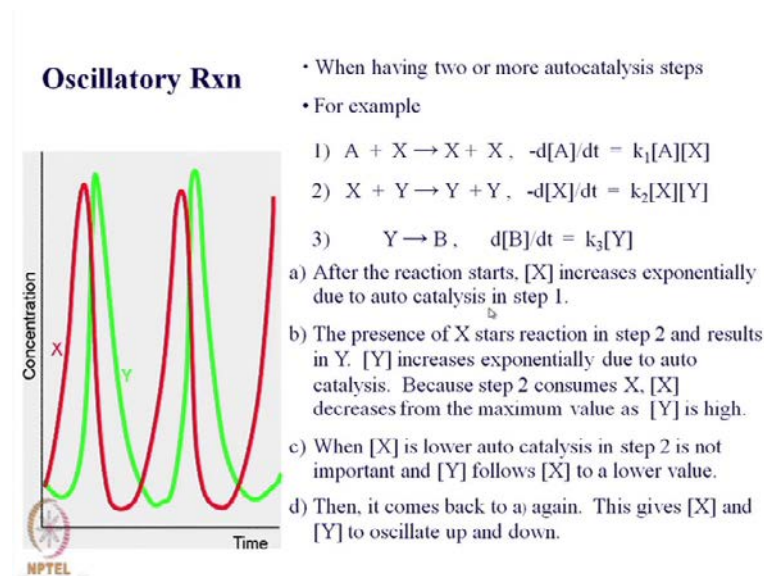
Good morning everybody so today we will start with oscillatory reactions so before going in to the details of it let us talk about what is autocatalysis again we just like to recapitulate now in case of autocatalytic reactions if you know commonly observed cases you know reaction of permanganate with oxalic acid. So, initially the color of permanganate does not decolorize fast what is happening under one condition.

If you add permanganate in oxalic acid solution it persists for some time and then after some time means may be after 30 seconds or so, the moment what is happening that the moment you add more of permanganate the color disappears fast. So this happens, because of the formation of your manganese ion the initially there was no manganese ion but, the moment it is generated it catalyzes it acts as the auto catalyst for the reaction.

So, the product of reaction helps accelerating the rate of reaction for your auto catalysis so what is happening that A giving rise to product and this product again along with A is involved in the rate expression. So, that is your A giving rise to product this product A is again used up so, rate is equal to  $k[A][P]$ .

So, initially since product is very small. So, the rate is smaller is lower rate and the moment this is build up so, its concentration is appreciable and as a result of which the rate is increased the rate suggests the equation that  $A + P \rightarrow P + P$  the mechanism is  $A \rightarrow P$  is an initiation step and then  $A + P \rightarrow P + P$  is the auto catalytic step that is if this one is again used up over here used up over here.

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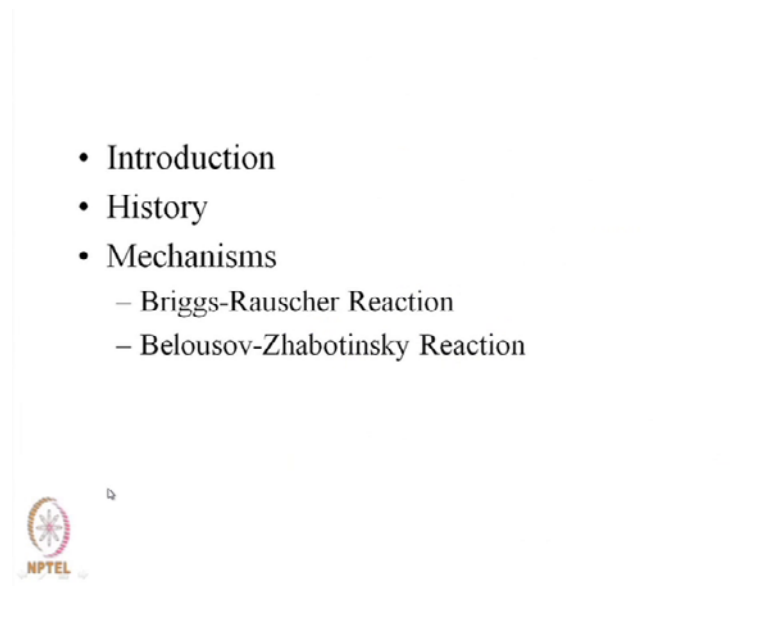


Oscillatory reaction when having two or more auto catalysis steps then we can get oscillatory reaction that is  $A + X \rightarrow X + X$   $X + Y \rightarrow Y + Y$   $Y \rightarrow B$ .

So, say the so, basically one I mean two or more catalytic step if it is there then we can get oscillatory situation so, the corresponding rate expressions are like this the after the reaction starts  $x$  increases exponentially due to auto catalysis step that is step 1 then in presence of  $X$  you know the second reaction starts and results in  $Y$   $Y$  again increases exponential due to auto catalysis, and because of step 2 which consumes  $X$ .

So, decrease so, X decreases from maximum value as Y is high when X is lowered auto catalysis step X is lower auto catalysis in step 2 is not important and Y follows X to A lower value. So, you see X initially builds up then it decreases and Y after some time it is going up that is Y is following X you see X is oscillating Y is oscillating but, there is a phase difference.

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So, this why is it is happening now here we will talk about this history, and also the mechanism one is Briggs-Rauscher reaction another is Belousov-Zhabotinsky reaction one is BR reaction another is BZ reaction.

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- The Briggs-Rauscher (BR) and the Belousov-Zhabotinsky (BZ) reactions are two of the most commonly demonstrated oscillating reactions.



BR and BZ reactions are two of the most commonly demonstrated oscillating reactions. BR reaction it is a reaction is a colorless liquids are mixed to form an amber solution.

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- Briggs-Rauscher reaction - colorless liquids are mixed to form an amber solution which turns to blue-black color, and periodically goes back and forth between the two colours.
- BZ reaction - the reaction mixture revolves through green, blue, purple, and red colours.



That is the basic description which turns to blue-black color and periodically goes back and forth between two colors and BZ reaction you know the reaction mixture revolves through green blue purple and red colors. So, color wise there are four colors over here, and here you know amber to blue-black.

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## The Chemists

- B.P. Belousov - Russian Chemist
  - 1950s - attempting to study Krebs cycle
  - Discovered oscillatory reaction
  - His manuscript was rejected on the grounds that "it's impossible"
  - Conventional opinion of the time - all reactions should proceed to thermodynamic equilibrium



Now the chemists involved in such studies B P Belousov is a was a Russian chemist in 1950s attempting to study krebs cycle and this covered the oscillatory reaction, and he sent his manuscript to a journal, and it was eventually rejected his manuscript was rejected the grounds on the grounds that it is impossible it cannot happen, because conventional opinion of the time that is within understanding was that all reactions should proceed to thermodynamic equilibrium. So, there is no way that the reaction can you know revert back.

So, this oscillation is not in harmony with the (( )) thermodynamic understanding I mean people never thought of such reaction I mean never can imagine so, conventional idea is that to that why the reaction will be you know get back to another you know I mean color should get back to the initial and then initial will again go to the final and final again back to initial why should it happen.

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- Belousov was so offended by the rejection that left science forever!
- Biochemistry Professor S.E. Schnoll took up Belousov's reaction
- Under Schnoll, A.M. Zhabotinsky investigated the mechanism and spatial distribution patterns of the reaction



So, that is why his manuscript was rejected and, Belousov was so, offended by such rejection actually he was quite sure that this is real observation there is nothing wrong in it so, he was so, frustrated due to this rejection and he left science forever he never tried anything, because he will think that I mean he was so, frustrated now biochemistry professor Schnoll, and took up Belousov's reaction under Schnoll and Zhabotinsky investigated the mechanism and special distribution patterns of the reaction.

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## The Chemists

- W.C. Bray and H. Leibhafsky, U.C. Berkeley
  - Described first homogeneous isothermal chemical oscillator in 1921, that was ignored by scientific journals for many years
- T.S. Briggs and W.C. Rauscher – Galileo High School in San Francisco
  - Investigated Bray reaction at U.C. Berkeley
  - Combined parts of the Bray reaction with parts of the BZ reaction to have their BR reaction



So it is the Zhabotinsky who under the guidance of Schnoll did I mean they studied this reaction later on Bray and others in U C Berkeley described first homogenous isothermal chemical oscillation you know in 1921 and later on means not you know in the in 1950 before 1950 in 1921, and this was ignored by scientific journals for many years means before you know Belousov the first description of you know homogenous isothermal chemical oscillation was in 1921 by Bray and others Leibhafskey Bray and Leibhafskey then a later on I mean later time Briggs and Rauscher in Galileo high school in San Francisco investigated Bray reaction at U C Berkeley combine parts of Bray reaction with parts of BZ reaction to have their own BR reaction that is Briggs Rauscher reaction.

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## Briggs-Rauscher Reaction

- Three solutions are mixed:
  - A: 4.0M  $\text{H}_2\text{O}_2$
  - B: 0.20M  $\text{KIO}_3$  and 0.077M  $\text{H}_2\text{SO}_4$
  - C: 0.15M malonic acid and 0.020M  $\text{MnSO}_4$
  - Spiked with 1% starch solution



So, Briggs-Rauscher reaction that is BR reaction three solutions are mixed solution one that is A is four molar  $\text{H}_2\text{O}_2$  B is point two molar potassium iodide  $\text{KIO}_3$  and 0 point 77 molar  $\text{H}_2\text{SO}_4$  that is solution B and A third one is point 15 molar Malonic acid and point 02 molar  $\text{MnSO}_4$  these are the three solutions and spiked with one percent starch solution that is an indicator very little amount of you know starch solution has been added there starch as an indicator.

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## Briggs-Rauscher Reaction

- **Non-radical reduction of iodate to hypoiodous acid:**
- If there is an abundance of  $I^-$  ions:
  - $IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI$  (1)
  - $HIO_2 + I^- + H^+ \rightarrow 2 HOI$  (2)
  - $HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O$  (3)
- The net result is:
  - $IO_3^- + 2 H_2O_2 + H^+ \rightarrow HOI + 2 O_2 + 2 H_2O$  (4)
- Hypoiodous acid reacts with malonic acid:
  - $HOI + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H_2O$  (5)
- As HOI is consumed in rxn (5), the  $[I^-]$  from rxn (3) decreases, and rxns (1) and (2) slow down greatly



So, start reaction indicator if iodine is liberated so it becomes blue or blue-black so, reaction scheme is like this non radical reduction of iodate to hypoiodous acid so, if there is an abundance of iodate ion the following reactions will take place there are three steps like this  $IO_3^- + I^-$  in presence of an acid giving rise to  $HIO_2 + HOI$  then  $HIO_2 + I^- + H^+$  giving rise to hypoiodous acid then  $HOI + H_2O_2$  giving rise to  $I^- + O_2 + H^+ + H_2O$ .

So, net reaction is iodate plus  $H_2O_2 + H^+$  giving rise to  $HOI + 2 O_2 + 2 H_2O$  then this hypoiodous acid HOI reacts with malonic acid malonic acid is  $CH_2(CO_2H)_2$  that means it is the dicarboxylic acid. So, it is iodination of this on this carbon that is  $CH_2$  carbon and then as HOI is consumed in the reaction five you see here it is consumed the  $I^-$  from reaction three this one decreases and reaction 1 2 slows down greatly this one these two are slow down greatly.



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## Briggs-Rauscher Reaction

- When  $[I^-]$  is low, the radical reduction of iodate takes over, but has the same end product as the non-radical reduction
  - $IO_3^- + HIO_2 + H^+ \rightarrow 2 IO_2\cdot + H_2O$  (6)
  - $IO_2\cdot + Mn^{2+} + H_2O \rightarrow HIO_2 + Mn(OH)^{2+}$  (7)
- Since  $HIO_2$  is produced more than consumed, the rate of the above two steps increase as they occur, and therefore much more  $HOI$  is formed from rxn (8):
  - $2 HIO_2 \rightarrow IO_3^- + HOI + H^+$  (8)
- $Mn^{2+}$  is oxidized in rxn (7), providing a means for the reduction of  $IO_2\cdot$  to  $HIO_2$ , and  $Mn^{4+}$  is reduced in rxn (9):
  - $Mn(OH)^{2+} + H_2O_2 \rightarrow Mn^{2+} + H_2O + HOO\cdot$  (9)
  - $2 HOO\cdot \rightarrow H_2O_2 + O_2$  (10)



So when  $I^-$  is low the radical reduction of iodate takes over that is it becomes predominant and but, as the same in product as non radical reduction so this is the non radical scheme this is the non radical scheme and this is your radical scheme. So, when  $I^-$  is low. So, the radical reaction is like this  $IO_3^- + HIO_2 + H^+$  plus giving rise to  $IO_2\cdot + H_2O$  then  $IO_2\cdot + Mn^{2+} + H_2O$  plus giving rise to this, and since  $HIO_2$  is produced more than it is consumed that rate of the above two steps increase as they occur and therefore, much more  $HOI$  is formed from reaction 8.

So, more of this is formed, because when this is low this radical reaction is predominating and  $Mn^{2+}$  is oxidized in reaction 7 you see it is two and this is plus four state providing a means for the reduction of  $IO_2\cdot$  to  $HIO_2$  and  $Mn^{4+}$  plus is reduced in reaction 9 here  $Mn^{4+}$  plus is then reduced to  $Mn^{2+}$  plus giving rise to  $HOO\cdot$  then this  $HOO\cdot$  gives rise to  $H_2O_2 + O_2$  so, this is this is your radical scheme this is your radical scheme.

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## Briggs-Rauscher Reaction

- The HOI produced in the radical process reacts with malonic acid, as in rxn (5) of the non-radical process.
- The production of HOI from the radical process is faster than its rxn with malonic acid, and an excess of HOI builds up
- This excess HOI reacts with  $H_2O_2$  as in rxn (3) to produce  $I^-$
- The buildup of  $I^-$  shuts off the radical process and returns the system to the slow, nonradical process we saw initially



So this for the this BR reaction the HOI produced in the radical process reacts with Malonic acid as in reaction 5 this one reaction 5 then the production of HOI from the radical process is faster than its reaction with Malonic acid and an excess of HOI builds up from this radical process this excess HOI reacts with  $H_2O_2$  in this particular step HOI plus  $H_2O_2$  because it is it is excess because it is less consumed.

You see here this HOI generated here it is less consumed so, concentration of HOI is increasing since it is increasing the thoughts that is third step is again promoted and iodide is produced. So, build up of  $I^-$  shifts of the radical process and returns the system to slow non radical process as we have seen initially so, as  $I^-$  is more, because you see in step 3 this  $I^-$  is again generated when abundance of  $I^-$  is there these steps are predominating when  $I^-$  is less then radical steps are predominating.

So, as a result of which at one time low  $I^-$  radical process high  $I^-$  your non radical process. So, these are you know changing from one situation one mechanism to another depending on the concentration of  $I^-$ .

So, as a result of which at one time low  $I^-$  radical process high  $I^-$  your non radical process so, these are you know changing from one situation one mechanism to another depending on the concentration of  $I^-$ .

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## Briggs-Rauscher Reaction

- The colour change.....
  - The reaction of HOI and malonic acid is a sequential one...
  - $I^- + HOI + H^+ \rightarrow I_2 + H_2O$  (11)
  - $I_2 + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H^+ + I^-$  (12)
- The amber color is the  $I_2$  produced in rxn (11)
  - $[HOI] > [I^-]$  from radical process
- The dark blue color is from an  $I_3^-$  complex with starch
  - When  $[I^-] > [HOI]$  from rxn (3) with  $H_2O_2$  causes slower non-radical process to take over
  - Color fades as  $I_2$  is consumed by rxn (12)
  - Cycle repeats once radical process starts over again



And what about the color change color change is like this the reaction of HOI, and Malonic acid is a sequential one  $I^- + HOI$  you are this step eleven step it is giving  $I_2 + H_2O$  in presence of an acid.

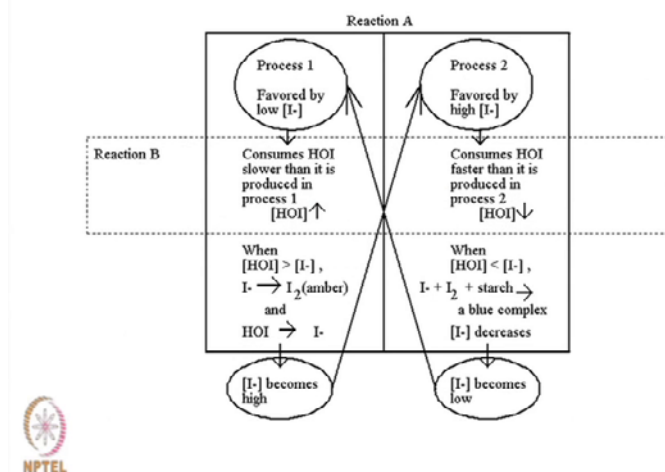
So, this  $I^-$  is an amber colored one this  $I_2$  is amber color this  $I_2$  reacts with Malonic acid producing iodo two iodo Malonic acid and giving rise to  $I_3^-$  amber color is the  $I_2$  produced in reaction element now the dark blue color is from  $I_3^-$  complex with starch so, when  $I^-$  is greater than HOI from reaction 3 with  $H_2O_2$  causes a slower non radical processes to take over.

And the color fades as  $I_2$  is consumed by reaction 12 you see  $I_2$  is again consumed so amber colored initial solution is as a result of  $I_2$  formation of  $I_2$ , and this dark blue color in presence of starch is because of the of the formation of  $I_3^-$  complex. Now, this  $I_3^-$  complex will be more if  $I^-$  is more because  $I_3^-$  is formed as a result of reaction between  $I_2$  plus  $I^-$ .

So, when  $I^-$  concentration is less then  $I_3^-$  complex that is the color of the starch color is diminished starch I mean in presence of starch there is blue-black color is blue dark blue color is diminished. So, depending on the concentration of  $I^-$  and the depending and depending on how much iodine is produced you know the color will switch from you know amber to dark blue and again dark blue to amber.

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## Briggs-Rauscher Reaction



So, if we look into the reaction scheme. If you look into the reaction scheme you see they act there are two processes one is favored by  $I^-$  when it is process one is favored you see favored by low  $I^-$  so, low  $I^-$  means when low  $I^-$  then radical step  $I^-$  mean radical steps are prevalent compared to non radical one and when there is an abundance of  $I^-$  then your these steps are prevalent so, process one low  $I^-$  that means radical one and process two favored by high  $I^-$ .

So, for this BR reaction we can you know we can classify the situation in terms of the concentration of  $I^-$  we that  $I^-$  concentration is high or  $I^-$  concentration is low. So, process one is prevalent when  $I^-$  is low. So,  $I^-$  is low that means it consumes HOI slower than it is produced. So, HOI is built up when HOI is greater than  $I^-$  because you see low  $I^-$  then  $I^- + I_2$  is produced that is amber colored and HOI  $\rightarrow I^-$ .

So, the moment it is amber colored and this is producing  $I^-$  so, it slowly increases the concentration of  $I^-$  so, let us again go back to radical steps that in radical step you see that when  $I^-$  is low so HOI is generated so HOI is generated means more HOI means this one this step this step will take place more HOI means more you know this one and more HOI means again you see in presence of  $H_2O_2$  more  $I^-$  is generated.

So, HOI more means this step is again prevalent even though for your radical process. So, that is why you have written over here  $I^-$  to  $I_2$ , and also  $HOI + I^-$  and then as a result of which as a result of this particular step  $I^-$  tends to increase the concentration of  $I^-$  increases the moment it is increasing what is happening that this process is taking over this process so, then non radical process is prevalent because, concentration of  $I^-$  has become high so, in presence of high iodate concentration non radical process.

That is these steps are prevalent  $IO_3^- + I^- + 2H^+$  giving rise to  $HOI + I_2$  plus  $HOI$  hypiodous acid  $IO_2^- + I^-$  giving rise to  $2HOI$  so these steps are prevalent so when high because you see these two steps are requiring iodides that is why so high iodide these steps are you know promoted more  $I^-$  recommend all though here one iodide is released but, you see consumption is more than the release.

So, the process two is favored so it consumes HOI faster than it is produced in process too all though in other case what is happening that HOI is consumed slower than it is produced but, here HOI is consumed faster than it is produced so, a so what is happening HOI is reduced. So, when HOI is all though in other case you see HOI is building up here HOI becomes deficient I mean HOI concentration is reduced as a result of high iodide concentration.

So, that means when HOI is less than  $I^-$  that is high iodide concentration then  $I^- + I_2 + \text{starch}$  giving a dark blue complex, and again by this  $I^-$  is decreased. So, the  $I^-$  is decreased means again we are now switching over from high  $I^-$  zone to a low  $I^-$  zone so what is happening the system is transferred from here to here.

So, in this region to this region back to back to process one so, again your radical steps are favored see you see that reaction goes this way giving rise to amber colored when  $I^-$  becomes high is transferred to process two giving rise to your starch blue complex. So, amber to blue transition the moment blue is you know at again it is transferred to here again amber colored so this way it is oscillating like this.

So, this way you know you can  $I^-$  means you can explain why this color is a changing next we move on to the other case that is Belousov-Zhabotinsky reaction so BR reaction this is one this is one oscillatory reaction where we are having two color stages one is

amber another is blue but, in case of Belousov-Zhabotinsky reaction it is a multi color I mean four color situations now in this case like your Br there are three solutions required 1 is 1 is point 2 3 molar  $\text{KBrO}_3$ .

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## B-Z Reaction

- Three Solutions are mixed
  - A: 0.23M  $\text{KBrO}_3$
  - B: 0.31M malonic acid and 0.059M KBr
  - C: 0.019M cerium(IV) ammonium nitrate and 2.7M  $\text{H}_2\text{SO}_4$
  - Spiked with ferroin solution
    - 1,10-phenanthroline, ferrous sulfate



These numbers are best optimized mixtures B is point 31 molar Malonic acid and point 59 molar KBr at the c the solution is 0 point 0 1 9 molar ceric ammonium nitrate and 2 point 7 molar sulfuric acid and spiked with ferroin solution as indicator ferroin is nothing but, 110 phenanthroline ferrous sulfate complex it is a blood red color ferroin indicator.

So like Br let us go back to Br again what was the there were also three solutions it was spiked with one percent starch solution there are three solutions, and here we are also having three solutions. Now Belousov originally used citric acid as instead of malonic acid it was later found that a number of different carboxylic acids could be used and you know in place of citric acid.

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## B-Z Reaction

- Belousov originally used citric acid instead of malonic acid
- It was later found that a number of different carboxylic acids could be used
- Also, manganese ions could be used instead of cerium ions
- This overall rxn is cerium-catalyzed oxidation of malonic acid by bromate ions in dilute sulfuric acid



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## B-Z Reaction

- The overall rxn is represented by this eqn:
  - $3 \text{CH}_2(\text{CO}_2\text{H})_2 + 4 \text{BrO}_3^- \rightarrow 4 \text{Br}^- + 9 \text{CO}_2 + 6 \text{H}_2\text{O}$  (1)
  - But, this equation does not account for the color changes seen in the reaction, the catalytic effect of cerium, or the role of bromide ions
- Again, the mechanism involves 2 different processes
  - Process A: ions and 2-electron transfers
  - Process B: radicals and 1-electron transfers
- Concentration of  $\text{Br}^-$  ions determines which process is dominant.
  - Process A: High  $\text{Br}^-$  concentration
  - Process B: Low  $\text{Br}^-$  concentration



You can use other carbolic I mean carboxylic acids as well also manganese ions could be used instead of cerium ions and the overall reaction is cerium-catalyzed oxidation of Malonic acid by bromate ions in dilute sulfuric acid. So, over all reaction is this so what is the overall reaction the overall reaction is represented here your Malonic acid bromate giving rise to bromate carbon dioxide and water but, looking at this equation we cannot say anything about this colored change scheme.

So, this gives you the overall you know mass balance but, this equation cannot explain why the color is changing that is the details of this reaction you know details of this reaction is not understandable from this you know scheme. So, this equation does not account for the color changes seen in the reaction the catalytic effect of cerium ion and the role of bromide ions.

So, this is a gross equation which cannot explain all this again the mechanism involves two different processes process A ions and two electron transfer process B is radicals and one electron transfer like BR reaction in one case it is it is promoted by non radical another case it is promoted by radical processes so in the same way here process a ions, and two electron transfer process B radicals.

And one electron transfer and concentration of b r ions b r minus ions determines which process is dominant like you know in other case your like here I iodide concentration when low process one is favored when high process two is favored in the same way here when high Br concentration process A that is two electron transfer, and ions ion process and one electron transfer radical process with low Br concentration.

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## B-Z Reaction

- Process A net reaction:
  - $\text{BrO}_3^- + 5 \text{Br}^- + 6 \text{H}^+ \rightarrow 3 \text{Br}_2 + 3 \text{H}_2\text{O}$  (2)
  - This is a reduction of bromate ions by bromide ions in 2 electron transfers
  - This occurs when solutions A and B are mixed
- This process occurs through these three steps:
  - $\text{BrO}_3^- + \text{Br}^- + 2 \text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr}$  (3)
  - $\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2 \text{HOBr}$  (4)
  - $\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$  (5)



Now process a net reaction  $\text{BrO}_3^-$  plus process A means ions so,  $\text{BrO}_3^-$  plus 5  $\text{Br}^-$  plus in presence of acid giving rise to  $\text{Br}_2$ . So, this is the reduction of bromate ions by bromide ions in two electron transfer process so is a bromate bromide reaction giving rise to bromate it is a typical happening also in case of iodate iodide




reaction and this reaction occurs when A and A are mixed A and A are mixed this bromate bromide this process occurs through this the following three steps bromate bromide H plus HBrO 2 plus HOBr then HBrO 2 plus Br minus giving rise to HOBr plus Br minus giving rise to Br 2 and H 2 O all in presence of acid so it this happens to a through three steps as written over here and what about malonic acid.

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### B-Z Reaction

- Malonic acid exists mainly in the diacid form but slowly enolizes..

- The bromine reacts with the enol form of malonic acid:
  - $\text{Br}_2 + \text{CH}_2(\text{CO}_2\text{H})_2 \rightarrow \text{BrCH}(\text{CO}_2\text{H})_2 + \text{Br}^- + \text{H}^+$  (6)
- These reactions together reduce the concentration of Br<sup>-</sup> in the solution



Now, this malonic acid exist mainly in diacid form but, its slowly enolizes to this all though predominantly it is in acid form but, a little fraction of it of it may be in this form. So, enol form and this enol form reacts with bromine to produce bromo two bromo Malonic acid and this reactions together reduced the concentration of Br minus in the solution.

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## B-Z Reaction

- Once process A has consumed most of the Br<sup>-</sup>, process B takes over
- The overall reaction of process B is represented by:  
$$- 2 \text{BrO}_3^- + 12 \text{H}^+ + 10 \text{Ce}^{3+} \rightarrow \text{Br}_2 + 6 \text{H}_2\text{O} + 10 \text{Ce}^{4+} \quad (7)$$
- This process is composed the following rxns:
  - $\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2 \text{BrO}_2\cdot + \text{H}_2\text{O} \quad (8)$
  - $\text{BrO}_2\cdot + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{4+} \quad (9)$
  - $2 \text{HBrO}_2 \rightarrow \text{HOBr} + \text{BrO}_3^- + \text{H}^+ \quad (10)$
  - $2 \text{HOBr} \rightarrow \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \quad (11)$
  - $\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$



So this is one reaction and this one another reaction so that tends to reduce the bromide concentration and solution so, once process A has consumed most of the bromide ions process B takes over process B means what process B means low bromide concentration radical reaction, and one electron transfer process so the overall reaction again is like this  $\text{BrO}_3^- + 12 \text{H}^+ + 10 \text{Ce}^{3+} \rightarrow \text{Br}_2 + 6 \text{H}_2\text{O} + 10 \text{Ce}^{4+}$ .

This process is composed of the following steps 1 2 3 4 5 so one is like  $\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2 \text{BrO}_2\cdot + \text{H}_2\text{O}$  giving rise to  $\text{BrO}_2\cdot$  then  $\text{BrO}_2\cdot + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{4+}$  giving rise to ceric then  $2 \text{HBrO}_2 \rightarrow \text{HOBr} + \text{BrO}_3^- + \text{H}^+$  plus  $\text{HBrO}_2$  giving rise to  $\text{HOBr}$  plus  $\text{BrO}_3^-$  there is  $\text{BrO}_3^-$  again comes back then  $2 \text{HOBr} \rightarrow \text{HBrO}_2 + \text{Br}^- + \text{H}^+$  giving rise to  $\text{HBrO}_2$  plus  $\text{Br}^-$  and  $\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$  giving rise to  $\text{Br}_2$  so, this is a complicated scheme and of these first two steps involves radicals.

So, when bromide concentration is less so, the process B predominates that is you know when most of the bromide is consumed so, three steps can no longer take place or even if it happens it happens with a very you know slow kinetics. So, the net result is means if we combine equations we get  $2 \text{Ce}^{3+} + \text{BrO}_3^- + \text{HBrO}_2 + 3 \text{H}^+ \rightarrow 2 \text{Ce}^{4+} + \text{H}_2\text{O} + \text{HBrO}_2$ .

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## B-Z Reaction

- The net result of eqn (8) + (2) (eqn 9) is:  
–  $2 \text{Ce}^{3+} + \text{BrO}_3^- + \text{HBrO}_2 + 3 \text{H}^+ \rightarrow 2 \text{Ce}^{4+} + \text{H}_2\text{O} + 2\text{HBrO}_2$  (13)
- This sequence produces  $\text{HBrO}_2$  autocatalytically
- Autocatalysis is an essential feature of this reaction, but does not continue until the reactants are depleted, because there is a second-order destruction of  $\text{HBrO}_2$  (rxn 10)
- Rxns (11) and (12) represent the disproportionation of hyperbromous acid ( $\text{HOBr}$ ) to bromous acid ( $\text{HBrO}_2$ ) and  $\text{Br}_2$



So, this sequence produces  $\text{HBrO}_2$  autocatalytically so autocatalysis is an essential feature of this reaction but, does not continue until the reactants are depleted because there is a second order destruction of  $\text{HBrO}_2$  in reaction chain is this destruction so reaction 11 12 represent the disproportionation of hyperbromous acid to bromous acid and  $\text{Br}_2$  reaction 11 and 12 this is number 11, and this is number 12.

So, these two represent your disproportionation of hyperbromous acid to bromous acid and  $\text{Br}_2$  so it is basically a very complicated situation as you look into the expressions that is whether it is a catalytic I mean it is a radical reaction or it is an elect I means non radical reaction ion reactions but, it is a very complicated situations, and one is connected to the other by some feedback mechanism that is I means in one case when bromine is I mean bromide is less than the other step is promoted I mean the other radical step is promoted I mean the other radical step is promoted.

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## B-Z Reaction

- $\text{Ce}^{4+}$  and  $\text{Br}_2$  oxidize malonic acid to form bromide ions
- Once this concentration of  $\text{Br}^-$  becomes high enough, process A is reactivated



So, basically they are connected these steps are connected by nice feedback mode feedback mechanism now  $\text{Ce}^{4+}$  and  $\text{Br}_2$  oxidize Malonic acid to form bromide ions once this concentration of  $\text{Br}^-$  becomes high end of the process A is reactivated so I means in place of process B when we started to talk to about process B. We told that when  $\text{Br}^-$  is less but, now if we go back to here you see here  $\text{Br}^-$  is generated. So, that means  $\text{Ce}^{4+}$  and  $\text{Br}_2$  when oxidizes this Malonic acid then again  $\text{Br}^-$  is generated.

So, this way so basically what is happening that you see that  $\text{Ce}^{4+}$  is generated ceric ion is generated this ceric ion along with bromine oxidizes your Malonic acid, and there by generating  $\text{Br}^-$  so, when  $\text{Br}^-$  is generated so slowly  $\text{Br}^-$  builds up and when  $\text{Br}^-$  is built up then again process a is reactivated so automatically with  $\text{Br}^-$  concentration process A is reactivated so, again go back to process A you see here this is a process A.

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## B-Z Reaction

- Ferriin provides two of the colors seen in this reaction
  - As  $[\text{Ce(IV)}]$  increases, it oxidizes the iron in ferriin from iron(II) (red) to iron(III) (blue)
- Cerium(III) is colorless, and Ce (IV) is yellow
  - The combination of Ce(IV) and Fe(III) make the green color
- The oscillating concentrations and oxidation states of Fe and Ce account for the color changes



So, it recovers  $\text{Br}^-$  so, these steps are again prevalent so, this way at one time process A is prevalent in other time process B is prevalent like we talked about I know with  $\text{Br}^-$  reaction process one process two depending on whether high iodide concentration or low iodide concentration the similar is the situation you see that that you know here  $\text{Br}^-$  is the determining factor and in this step  $\text{Br}_2$  oxidizing Malonic acid to you know the corresponding bromo derivative you know and  $\text{Br}^-$  is generated that is brominating your Malonic acid and they are by generating  $\text{Br}^-$  they once  $\text{Br}^-$  is generated then process A is reactivated.

So, this way back and forth hence one time process B another time process A. So, it is switching from B to A B to A and the correspondingly color will also change so we will come to that we will come to that so, what is the role of ferriin is the indicator ferrous ortho phenanthroline complex. So, how these colors are coming as cerium four that is ceric ion increases it oxidizes iron 2 of ferriin two iron three of ferriin I mean oxidizes iron 2 to iron 3 in phenanthroline complex.

So, iron 2 in phenanthroline is red, and iron three in phenanthroline is blue. So, basically there is a change over from red to blue and may be blue to red and ceric ion is I mean and correspondingly ceric ion is reduced to cerous that is cerium three it is the colorless and cerium 4 is yellow so the combination of yellow and blue.

So, cerium four yellow and iron three blue this combination mix the green color so the oscillating concentrations and oxidation states of iron and cerium accounts for the color change so, now we can explain the color change in both BR reaction, and in BZ reaction all though for BR case all though for BR case it is I know it is a simpler situation but, for cerius ceric and I mean BZ reaction it is a combination of you know you see red blue then yellow, and depending on how much of red how much of blue and how much of yellow is present.


So, accordingly the color will change accordingly the color will change so, this the oscillating concentrations of you know here the deciding factor is bromide and the various oxidation states so, one is iron 2 iron 3 another is cerous ceric then the various oxidation states of bromo bromine also these are responsible for you know switching of color from one to another.

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Oscillating reactions are much more than a laboratory curiosity: they are known to occur in some industrial processes, and there are many examples in biochemical systems where a cell plays the role of a chemical reactor.

Oscillating reactions, for example, maintain the rhythm of the heartbeat. They are also known to occur in the glycolytic cycle, in which one molecule of glucose is used to produce (through enzyme catalysed reactions involving ATP) two molecules of ATP.

All the metabolites in the chain oscillate under some conditions, and do so with the same period but with different phases.



Now, why do we need to study such things is it just a just you know for laboratory curiosity or just for you know having fun with chemistry or it has got some you know extra significance. Now oscillating reactions are much more than laboratory curiosity they are known to occur in some industrial processes and there are many examples in biochemical systems where a cell plays the role of a chemical reactor.

So, cells are nothing but, small chemical reactors basically a biochemical reactors now oscillating reactions for example, maintain the rhythm of heart beat they are also known

to occur in the glycolytic cycle in which one molecule of glucose is used to produce through enzyme catalyzed reaction involving at P 2 moles of at P 2 moles of at P so it is important there all the all the metabolites in the in the chain oscillate under the same condition, and do so with same period but, with different phases.

So, this oscillatory reactions all though and BZ reaction and BR reaction this demonstrate you know the apparent you know anomaly all though it is not an anomalous thing apparent anomaly means if you look into these colors it looks something anomalous that why chemical reaction this color will come back it looks like as if your reactant is you know regenerated but, chemical reaction should not case of chemical reaction that should not happen.

So, it is contrary to our you know general understanding, and you know simple minded understanding but, it happens so basically if you can design the reaction or may be a number of reacting reactions steps in such a way that they are inter connected and if you optimize the concentrations of the reactants in such a way that one reaction acts as the feedback for the other reaction.

That is I mean when some concentration in reached I mean concentration of one reactant is has reached certain you know limit then may be second reaction starts and the second reaction again what it does us is that again reduces or increases the concentration of that particular component like say in case of BR it is iodide or in case of BZ it is bromide. So, if they are inter connected then you can simply play with different colors.

So, basically you know the importance of starting is that of such reaction is that it is apparently something you know you know we do not we cannot may be it looks like that as if it is contrary to our general understanding that is why you see that Belousov's paper was rejected because people did not have the idea at the then time that such situation may be may be possibly reached otherwise may be may be Belousov might not have left science and who knows that he could have given us more interesting things.

So, you know and also the important point is that as I told you at the very beginning that that two or more auto catalytic steps if these steps are involved in some reactions then we may get oscillatory reaction and if we look into the concentration of species different species you see that they are oscillating in time and there is phase lack you see its

maxima is here and the green maxima is here because may be the green substance is generated out of red substance.

So, when red substance is maximum than green is may be minimum and then when as with time green I mean red is depleted green is generated. So, they are inter connected so that is why when we think of auto catalysis reaction and two or more auto catalytic steps are involved in a particular reaction in a particular reaction we can get such nice you know oscillation of colors it is basically a chemically oscillation but, the thing is that these reactions will not will not to occur you know for in finite period of time at some point of time it will it'll stop oscillating and a true equilibrium will be reached true equilibrium means I know when there is no further you know color change.

So, if I mean no further color change and it is basically it will be showing some damping pattern and I mean initially the color change you know will be varied distinct and later on with time this color change will be will be damp like a damped oscillation because ultimately you know for your say as I told you for your BZ reaction Malonic acid when gets oxidize by bromo bromine produce bromide.

So, bromide when high bromide is there then the process a is produce I mean process A means this one that is non radical reaction is promoted so, Malonic acid you have got Malonic concentration of Malonic acid to a fixed value. So, during the course of reaction the concentration of Malonic acid is reduced so reduced and ultimately it is may be exhausted so when it is exhausted then what will happen that further reaction to produce bromide ions will not be there.

So, that is why thing is that ultimately the reaction will stop at some point of time so so what have we learnt out of this before that I must say one thing that that students are encouraged to try this try these reactions may be a proper if proper safety precautions are there then you can try because sometimes sulfuric acids may be dangerous so I recommend that you get in touch with a your teachers or may be some you know chemical laboratory or may be some research laboratory where these reactions can be carried out with a maintaining the proper safety issues.

So like a for BR reaction you know you can get  $\text{H}_2\text{O}_2$   $\text{KIO}_3$   $\text{H}_2\text{SO}_4$  Malonic acid and  $\text{MnSO}_4$  and three solutions if these two are mixed and if you put a little amount of starch then you will you will be getting this color change from amber to dark blue and



then dark blue to amber and so and it will oscillate with time in the same way for your Belousov-Zhabotinsky if you use this you can get you know nice colorations.

So, basically the color for your BZ reaction there are four colors because depending on as I discussed the depending on the pop I mean concentration of various colored substances you will be getting different colors so, what have we learnt out of this out of but, of this discussion that auto catalysis is a key point and more than one auto catalytic steps are very important for such oscillatory reaction to be absorbed auto catalysis means your product once yours your product is used up as a reactant.

So, the more product more you know reactant so reaction is a is enormously with high rate so, when there are more than I mean two or more auto catalytic steps you can get such oscillation of concentration and correspondingly oscillation of color if you have a typical indicator means corresponding indicator like ferroin or may be like your starch as I discusses with your BR or BZ reaction and history is like a Belousov-Zhabotinsky they are reaction.

So, these are I know commonly demonstrated or oscillatory reaction and Belousov in 1950 this I know discover this particular reaction but, unfortunately people or scientific community did not accept it later on it was a established by Zhabotinsky that is why it is Belousov-Zhabotinsky reaction, and there is another reaction which is BR reaction Belousov I mean Briggs-Rauscher reaction.

So, that is also a an oscillatory reaction and we have discussed in both the cases like in BR well as you know BZ reaction it has got non radical and I mean one is free radical step another is non free radical step I mean free radical step it is a free radical non free radical one another is radical one so, both reactions are going through radical as well as non radical path is depending on the concentration of iodide for your BR reaction when abundance of I minus is there.

Then your non radical channel is opened up and for your radical step when the concentration of iodide is low then radical step is prevalent next is and we have we have tried to explain why this color is shifting from one to another why the color is shifting from one to another and it depends on the concentration of I minus and when concentration of I minus is low then this amber color is produced when concentration is

high then is a blue color is produced so with this diagram we have been able to you know we have explained it nicely.

Then we came to BZ reaction and like BR reaction it has got you know this process A and process B process A is a non radical ion reaction with two electron transfer and process one is a radical reaction with one electron transfer and here malonic acid is a very important ingredient and this color is a because of this cerous ceric and ferrous ferric system as I explained over here and ferrous ferric ferroin form ferroin form of ferrous ferric gives you different colors like red to blue and cerous ceric ceric is yellow cerus is colorless.

So, depending on the concentration of iron 3 and iron 2 and also cerium 3 and cerium 4 the color is you know visible different colors are visible so this oscillatory reaction are very important not only in laboratory perspective but, also in your biochemical cases may be living system and these are very important. So, with this today we would I would like to conclude. So, thank you for your patience good bye.