Autocatalysis and Oscillatory Reactions:

Important notes:

✓✓ autocatalysis and oscillations are non-linear in nature.

* Belousov-Zhabotinski (B–Z) reaction is one type of autocatalysis reaction.

✓✓ Autocatalysis: Consider the reaction

$$A \longrightarrow P$$

where P is the product.

If the rate law is given by

$$v = k[A][P]$$

then the P is said to catalyse the reaction.

* In the B–Z reaction, described in steps (a) and (b) below,

(a) $BrO_3^{\ominus} + HBrO_2 + H_3O^+ \longrightarrow 2BrO_2 + H_2O$

(b) $2BrO_2 + 2Ce(III) + 2H_3O^+ \longrightarrow 2HBrO_2 + 2Ce(IV) + 2H_2O$

The product $HBrO_2$ is a reactant in step (a). The rate of the reaction (2-step) directly depends on $HBrO_2$. So $HBrO_2$ acts as a catalysis.

✓✓ In autocatalysis, several intermediates cause oscillations.

✓✓ → tells to write in the examination

The Oregonator: The following reaction mechanism has been suggested for the oregonator:

(a) $A + Y \longrightarrow X$

(b) $X + Y \longrightarrow C$

(c) $B + X \longrightarrow 2X + Z$

(d) $2X \longrightarrow D$

(e) $Z \longrightarrow Y$

A stands for $HBrO_2$,

B for Br^-,

Z for Ce^{4+}.

A, B, C, D are kept constant by supplying or removing from the reactor.

* Step (c) is autocatalytic.

The following three conditions should be fulfilled by oscillatory reactions:

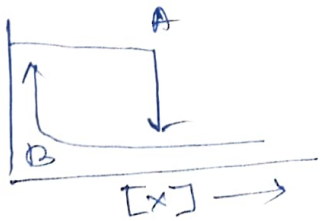
(a) The reactions must be far from equilibrium.

(b) The reactions must involve autocatalytic steps.

(c) The system must exist in two steady-states, i.e., it must have bistability.

* In this reaction mechanism, the concept of bistability is explained considering two intermediates X and Y.

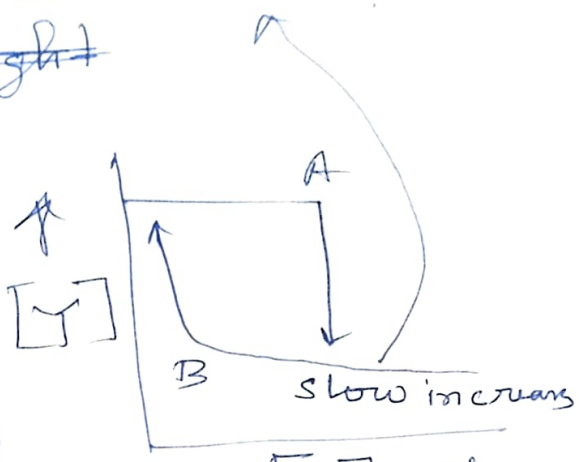
Suppose the concentration of Y is at some high value in a reactor (Fig. a) and the addition of X decreases the concentration of Y, as shown by the upper line.



(Fig. a)

Concentration of Y is decreased as the intermediate X transforms Y into C according to the step (b).

If X is at some high value, the the addition of Y ~~right~~ increases its concentration [Y] slowly. See the lower line.

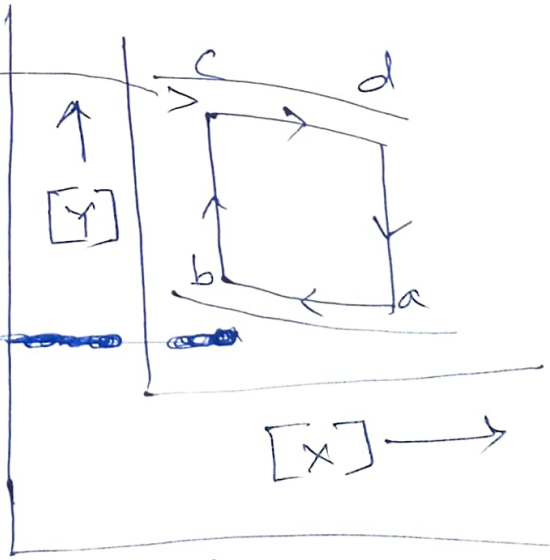


The two curves represent the two stable states of a bistable system.

At each stage a concentration [X] or [Y] may be reached at which the concentration will jump from one curve to the ~~ove~~ other one.

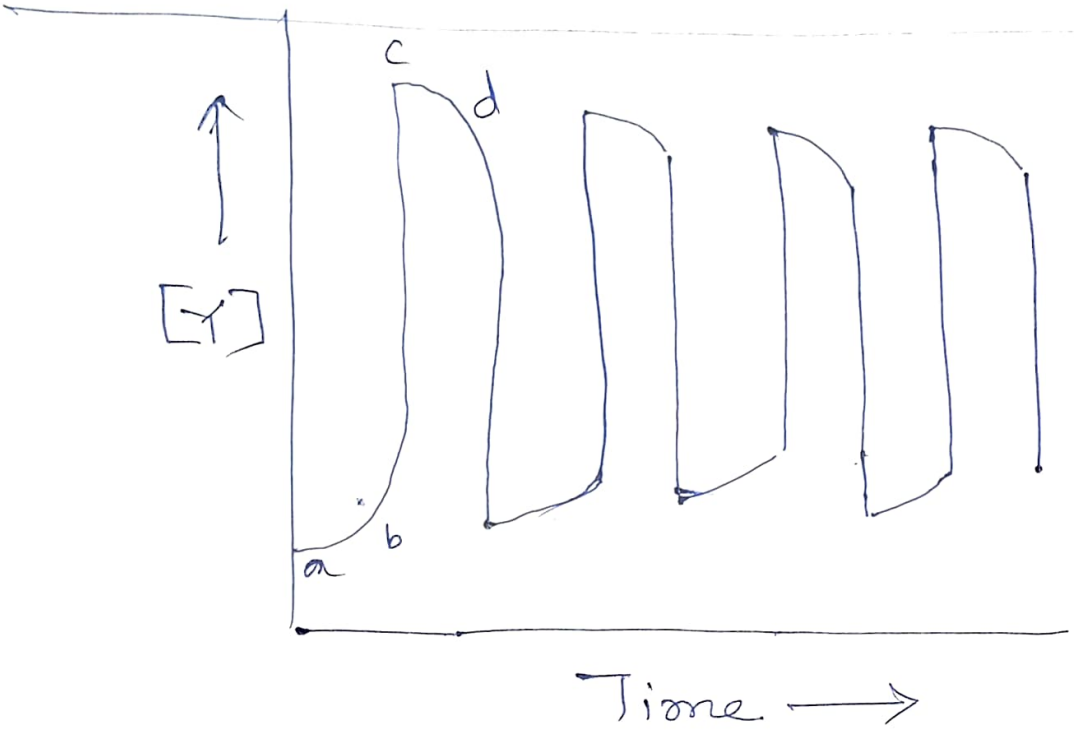
Effect of the third intermediate Z:

When Z reacts with Y to produce X, Y decreases and X increases so that the state of the system move towards the right along the curve until a sudden transition occurs to the lower curve.



Therfore, if Z reacts with X ~~producing~~ to produce Y, Y will increases and X will decreses.

Then the state of the system moves towards the left along the lower curve until another sudden transition occurs to the upper curve when the process starts again.



Oscillation of [Y] as a function of time is presented in the above figure.