Pseudo order reactions

Reactions which appear to be proceeding with lower order than what actually is are called pseudo order reactions.

It happens when any reactant appearing in rate law expression is in large excess or catalyst appears in rate law expression.

Examples:

i) When one reactant is present in large excess:

Consider the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t=0$) and completion ($t=\infty$) of the reaction are given below:

	$CH_3COOC_2H_5$	+ H_2O	→ CH_3COOH	+ C_2H_5OH
$t=0$	0.01 mol	10 mol	0	0
$t=\infty$	0	9.99	0.01	0.01

It is a second order reaction with rate law as follows:

$$\text{Rate} = k'[H_2O][CH_3COOC_2H_5]$$

Here as water is present in large excess, the concentration of water does not get altered much during the course of the reaction. The term $[H_2O]$ can be taken as constant.

The equation thus becomes:

$$\text{Rate} = k[CH_3COOC_2H_5], \quad k = k'[H_2O]$$

The reaction which actually is second order behaves as first order reaction. This is pseudo first order reaction

ii) When rate law expression involves catalyst:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

cane sugar — glucose — fructose

This is a second order reaction with rate law expression:

$$\text{Rate} = k'[H^+][C_{12}H_{22}O_{11}]$$

As H^+ is catalyst, its concentration remains constant throughout the reaction. Thus $k'[H^+]$ is a constant, let it be k. So rate raw expression becomes:

$$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

This is pseudo first order reaction.