

## Zero order reaction

In zero order reaction, rate is independent of the concentration of the reactants.

$A \rightarrow \text{Products}$

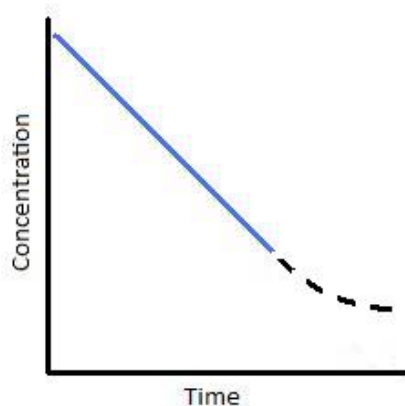
$$\text{Rate} = -dC/dt = k_0 [A]^0$$

$$-dC = k_0 dt$$

Upon integrating the equation from concentration from initial concentration  $C_0$  to concentration after time  $t$ ,  $C_t$  from time zero to time  $t$ , results

$$C_t = -kt + C_0$$

This is an equation of straight line

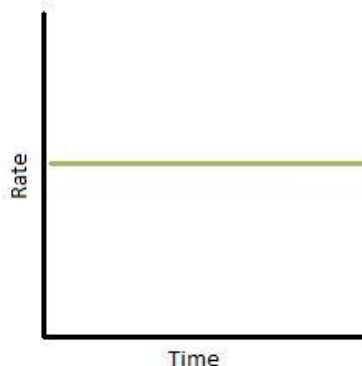
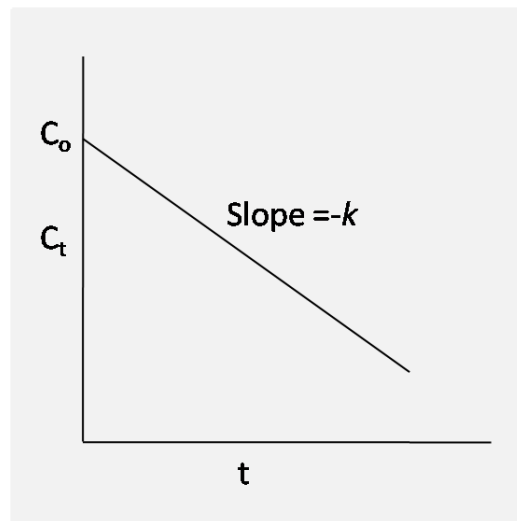


The integrated form of the rate law allows us to find the population of reactant at any time after the start of the reaction. Zero-order reactions are *only* applicable for a very narrow region of time. Therefore, the linear graph shown below is only realistic over a limited time range. If we were to extrapolate the line of this graph downward to represent all values of time for a given reaction, it would tell us that as time progresses,

the concentration of our reactant becomes negative. We know from general chemistry that concentrations can never be negative.

To understand where the above graph comes from, let us consider a catalyzed reaction. At the beginning of the reaction, and for small values of time, the rate of the reaction is constant. This is indicated by the blue line in graph below. This situation typically happens when a catalyst is saturated with reactants. As a reaction progresses through time, however, it is possible that less and less substrate will bind to the catalyst. As this occurs, the reaction slows and we see a tailing off of the graph. This portion of the reaction is represented by the dashed black line. In looking at this particular reaction, we can see that reactions are *not* zero-order under all conditions. They are only zero-order for a limited amount of time.

If we plot rate as a function of time, we obtain the graph below. Again, this only describes a narrow region of time. The slope of the graph is equal to  $k$ , the rate constant. Therefore,  $k$  is constant with time. In addition, we can see that the reaction rate is completely independent of how much reactant you put in.



## Relationship between Half-life and Zero-order Reactions

The half-life is a timescale in which each half-life represents the reduction of the initial population to 50% of its original state. We can represent the relationship by the following equation.

$$dx/dt = k$$

$$dx = k dt$$

$$x = kt \quad t = x/k$$

at time  $t_{1/2}$ , concentration  $x = a/2$

$$t_{1/2} = a/2k$$

Notice that, for zero-order reactions, the half-life depends on the initial concentration of reactant and the rate constant.

The catalytic decomposition of nitrogen and hydrogen in presence of platinum catalyst is the example of zero order reaction.



## Collision theory

The collision theory of reaction rate attempts to account for the observed kinetics of reactions in terms of molecular behavior of reacting system. In collision theory, in order to a reaction to happens, the reactant molecules must

- Collide
- Possess or collide with sufficient energy for them to be activated
- Collide with proper orientation

Thus according to the theory, the rate constant for a reaction is given by the product of three factors

- The collision frequency ( $z$ ): It can be defined by the number of molecules colliding per area per time in a reacting system containing 1 mole of reactant in 1 liter.
- The fraction of collision having energy equal to or greater than the energy of activation. It can be expressed by  $f$
- The fraction of collision that occur with reactant molecules properly oriented, sometimes called steric factor and can be expressed as  $p$

Thus rate constant  $k = zfp$

Collision frequency can be calculated by kinetic theory of gases and for a gas containing one kind of molecules, the number of colliding molecules per cubic centimeter per second is

$$Z = \sqrt{2} \pi \sigma^2 v n^2$$

Where,  $\sigma$  is the molecular diameter,  $v$  is the average molecular velocity and  $n$  is the number of molecules.

The fraction of molecular collision having energy equal to or greater than the energy of activation, changes rapidly in most reactions with even small temperature changes. It can be shown that  $f$  is related to the activation energy,  $E_a$ , by

$$f = e^{-\frac{E_a}{RT}}$$

The reaction rate also depends on the steric factor,  $p$ , and the proper orientation of the reactant molecules when they collide. This factor is independent on temperature change.

Thus considering the three factors, the rate constant of the reaction according to the collision theory is given by

$$k = pze^{-\frac{E_a}{RT}}$$

Limitations of collision theory

1. It can be applied only in simple molecules and usually in gas phase
2. Collision theory does not provide any prediction of the steric factor,  $p$ .
3. It consider only the kinetic energies, however there are some other energies associated with molecular motion viz. rotational, vibrational.
4. It does not consider the bond breaking or bond making and the measured activation energies are lower than the energies of the bonds that have to be broken in reactions