Today

Kinetics Rate Laws

Finding the order of a reaction

Integrated Rate Laws

What is the concentration as a function of time?

The grand overview of all of the kinetics

$$aA + bB \longleftrightarrow cC + dD$$

measure in experiment

figure out from data

$$\frac{-\Delta[A]}{a\Delta t} = \frac{\Delta[C]}{c\Delta t} = \text{rate} = k[A]^x[B]^y$$

we are looking only at the rate of the "forward" reaction
This depends only on the concentration of the reactants

Method of Initial Rates

$$A + 2B \longrightarrow C$$

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

The reaction is what order in A? - work out on doc cam

Method of Initial Rates

$$A + 2B \longrightarrow C$$

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

the reaction is what order in B?

A. 0

B. 1

C. 1.5

D. 2

Method of Initial Rates

$$A + 2B \longrightarrow C$$

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

what is k?

A. 273 $M^{-1}\ s^{-1}$

B. 27.3 s^{-1}

C. 61.4 s^{-1}

D. 614 $M^{-1}\ s^{-1}$

E. 6.14 $M\ s^{-1}$

Integrated rate laws
(the concentration as a function of time)

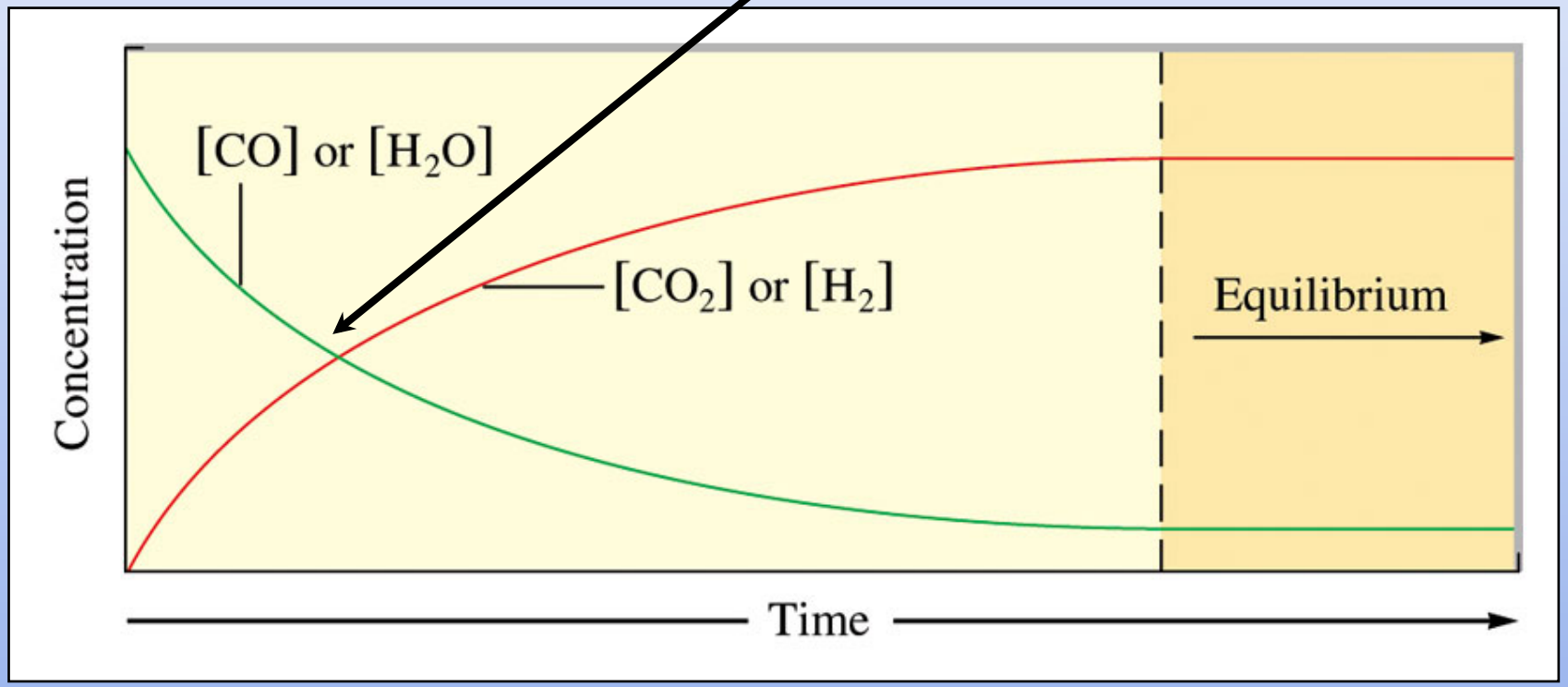
We need a situation in which either

I. The rate law depends on only one reactant

II. Only one reactant is changing much in concentrations, so effectively only one concentration is changing

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$$

Both CO and H_2O changing at the same time!



$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$$

The rate law for this reaction is

$$\text{rate} = k[H_2O][CO]$$

it is first order in H_2O and
first order in CO

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$$

What if we started with a whole lot of H_2O compared to CO?

The $[H_2O]$ ~ constant (since there is so much of it)

Now we can combine the $[H_2O]$ with k (since both are constant)

and write the rate law as

$$\text{rate} = k[H_2O][CO] = k'[CO]$$

we now say the reaction is pseudo-first order in CO

Integrated rate laws
(the concentration as a function of time)

We need a situation in which either

I. The rate law depends on only one reactant

for example it is first order with respect to A

II. Only one reactant is changing much in concentrations, so effectively only one concentration is changing

for example it is pseudo first order with respect to A

Integrated Rate Law

First Order

The rate is proportional to the concentration of only one reactant. We'll call it A

$$\text{rate} = \frac{-d[A]}{a\,dt} = k[A]$$

then some calculus

stoichiometric coeficient

time

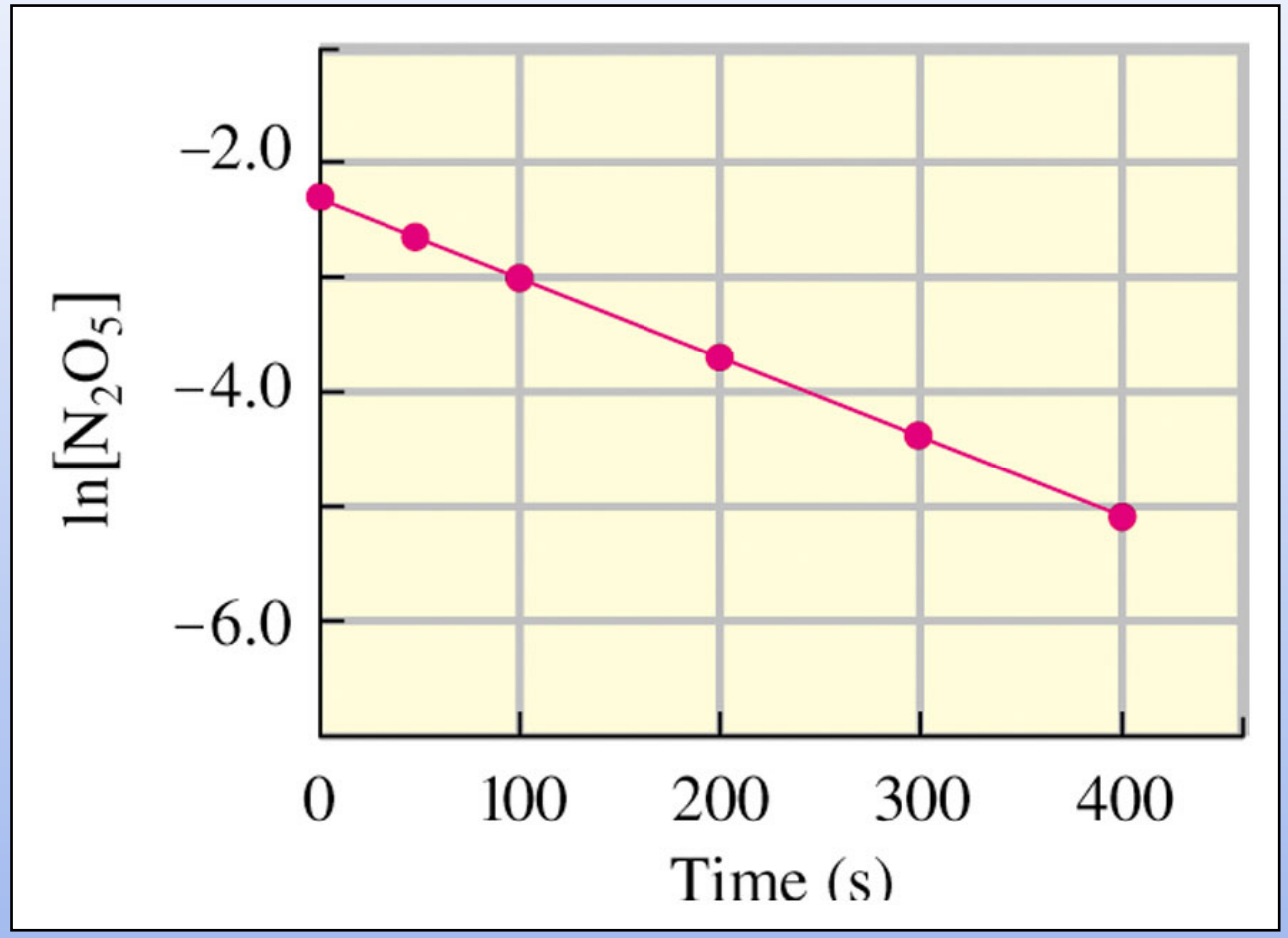
Integrated Rate Law

First Order

$$[A] = [A]_o e^{-akt}$$

$$\ln[A] = -akt + \ln[A]_o$$

So if you plot ln[A] vs time you get
a straight line with a slope of -ak



Half life

TABLE 15.3 Concentration/Time Data for the Reaction $2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g)$ (at 45°C)

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

The half-life is the time at which half the initial concentration remains.

What is the approximate half-life for the reaction at the left?

A.
200 s

B.
400 s

C.
1100 s

D.
1600 s

Integrated Rate Law

Zero Order

The rate is independent of the concentration of our reactant A

$$\text{rate} = \frac{-d[A]}{a\,dt} = k$$

then some calculus

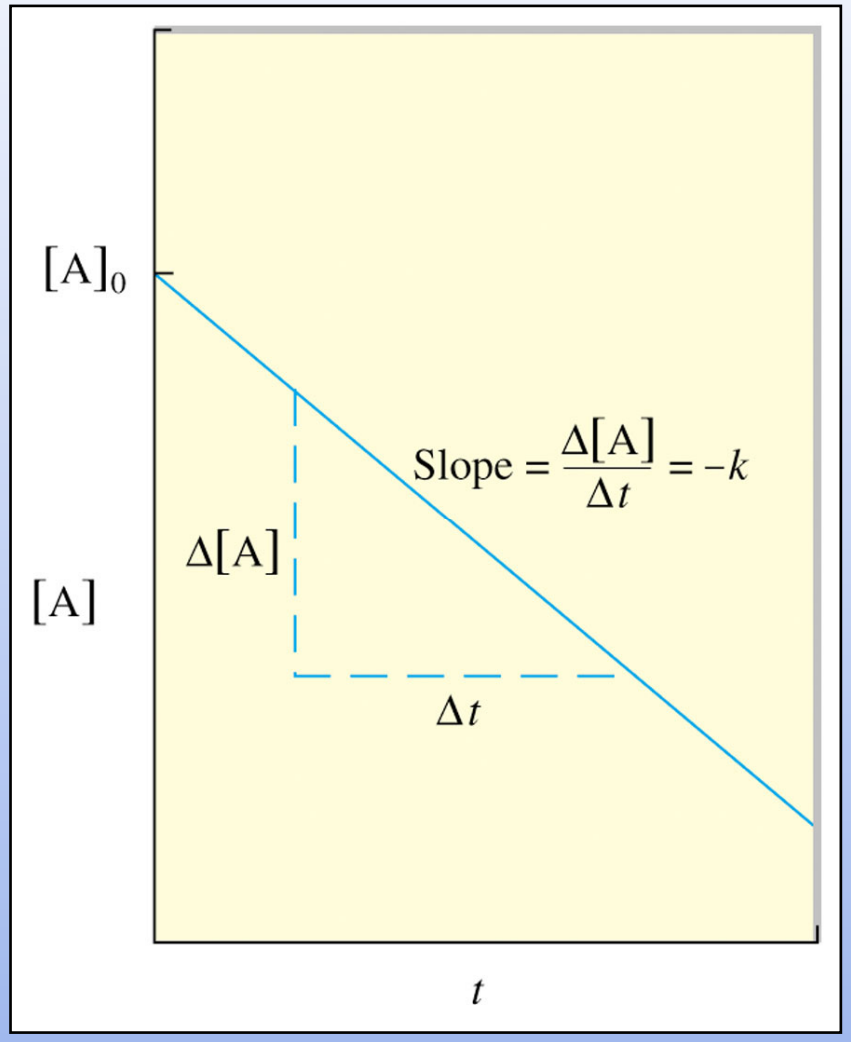
stoichiometric coeficient

time

Zeroth Order

$$[A] = -akt + [A]_o$$

Plot of [A] vs time yields a straight line with a slope of -ak



Integrated Rate Law

Second Order

The rate is dependent of the concentration of our reactant A squared

$$\text{rate} = \frac{-d[A]}{a\,dt} = k[A]^2$$

then some calculus

stoichiometric coeficient

time

Integrated Rate Law

Second Order

$$1/[A] = akt + 1/[A]_o$$

So if you plot 1/[A] vs time you get
a straight line with a slope of ak

Graphically determining the overall order of a reaction

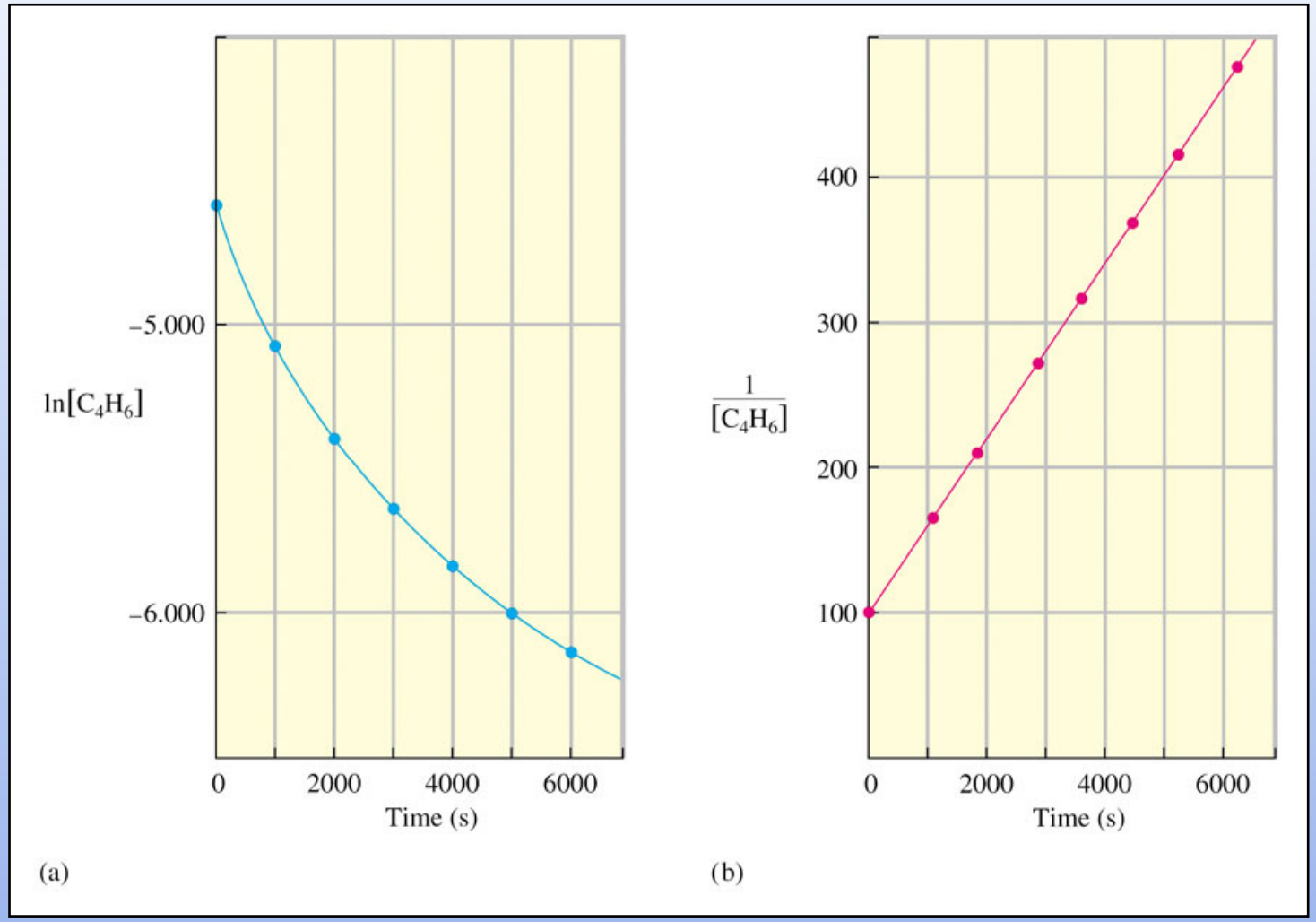


TABLE 15.6 Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate law	Rate $= k$	Rate $= k[A]$	Rate $= k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

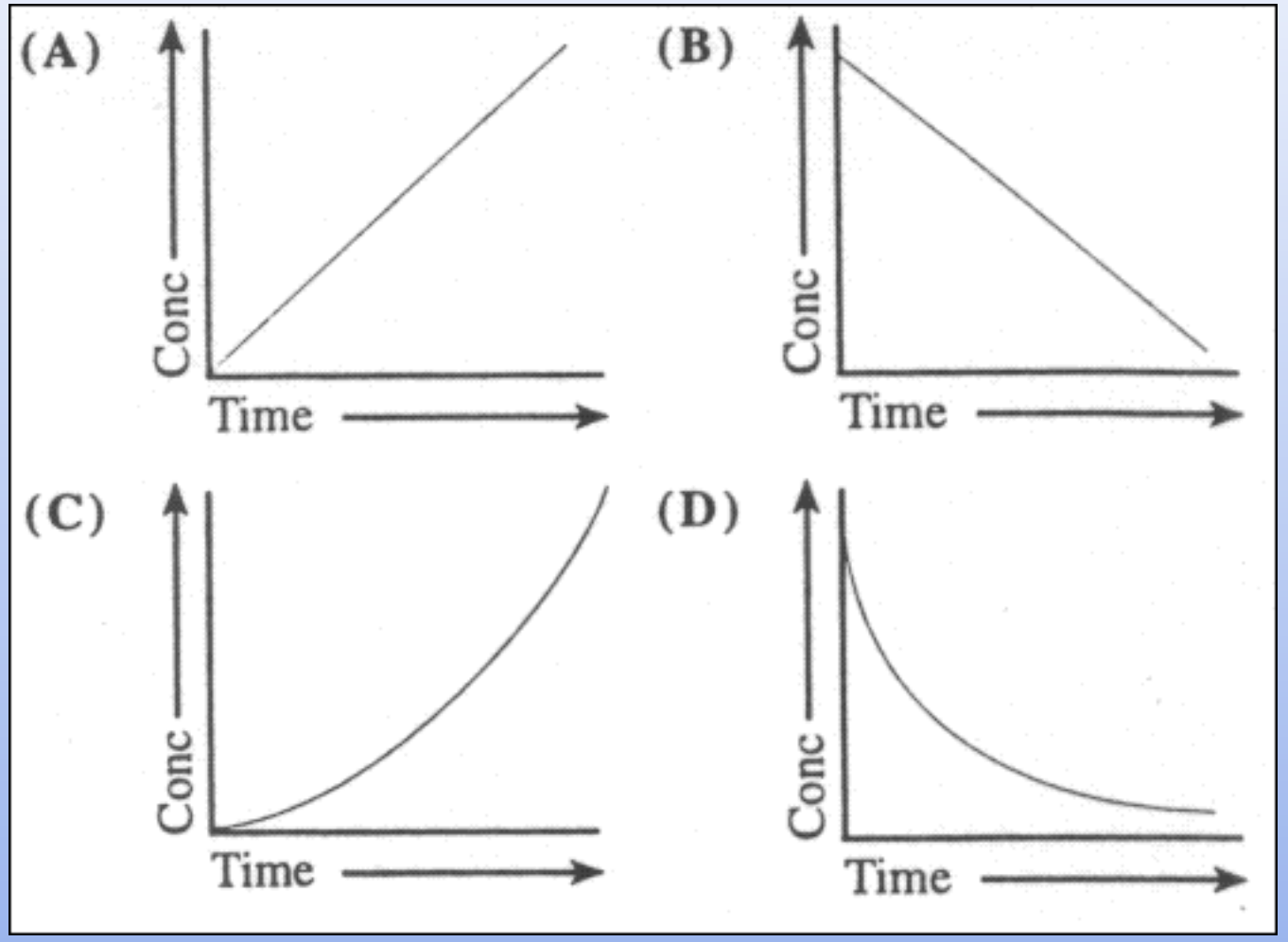
Half Life

Time after which half the material has reacted

Important for first order reactions
as it is independent of the concentration

$$t_{1/2} = \ln 2/k = 0.693/k$$

Which of the following is a plot of the concentration of a reactant that is first order?



Which of the following is a plot of the concentration of a reactant that is zeroth order?