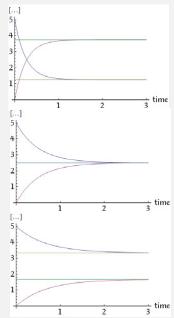
 

[TP] Consider three different chemical reactions,
reactants ⇄ products
For each reaction, initially [reactant] = 5 and [product] = 0, and yet reactant is consumed at different rates.
This means that …

33% 1. Rate depends only on […]
33% 2. Rate is constant but different for each reaction.
33% 3. Rate depends on […] and something else.



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# Lecture 34 CH102 A1 (MWF 9:05 am)
Friday, April 26, 2019

Ch18: How long does a reaction take to reach equilibrium?
- The goal of kinetics
- Concentration versus time → $K = k_{\text{for}}/k_{\text{rev}}$
- Definition of "rate"
- Rate vs concentration from experiment

Next lecture: Complete: Rate vs concentration from experiment. Making sense of rate vs concentration: Reaction mechanism. Making sense of rate constants: The Arrhenius relation.

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## The goal of kinetics: How long?

What direction are we going?

$$-T\Delta S_{\text{tot}} = \Delta G = RT\ln(Q/K)$$

How far will we go?

$$-T\Delta S°_{\text{tot}} = \Delta G° = -RT\ln(K) = \Delta H° - \Delta S°$$

How long to get there?

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## The goal of kinetics: How long?

What direction are we going?

$$-T\Delta S_{\text{tot}} = \Delta G = RT\ln(Q/K)$$

How far will we go?

$$-T\Delta S°_{\text{tot}} = \Delta G° = -RT\ln(K) = \Delta H° - \Delta S°$$

How long to get there?

Chemical Kinetics!

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## Concentration vs time → $K = k_{for}/k_{rev}$

Consider the reaction A ⇄ B. Assume initially [A] = 1 M but [B] = 0.

How do you expect [A] to change with time?



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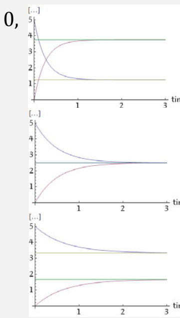




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## What does concentration vs time depend on?

The initial rate of a reaction like X → Y is …

$$rate_{\text{for}} \propto [\text{X}] = k_{\text{for}}[\text{X}]$$

The initial rate of its reverse reaction Y → X is …

$$rate_{\text{rev}} \propto [\text{Y}] = k_{\text{rev}}[\text{Y}]$$



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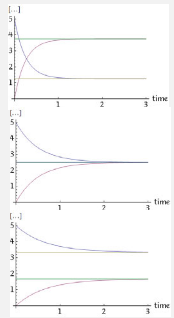
## What does […] versus time depend on?

Concentrations stop changing when the rate of the forward and rate of the reverse reaction balance each other …

$$rate_{\text{for}} = rate_{\text{rev}}$$

[TP] For X → Y, eventually concentrations stop changing.
This means that $rate_{\text{for}} = rate_{\text{rev}}$ and so that always …

0% 1. $k_{\text{for}} = k_{\text{rev}}$
0% 2. $[X] = [Y]$
0% 3. $k_{\text{for}}[X] = k_{\text{rev}}[Y]$
0% 4. $k_{\text{for}}[X]_e = k_{\text{rev}}[Y]_e$
0% 5. None of these



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## What does [...] versus time depend on?

Concentrations stop changing when the rate of the forward and rate of the reverse reaction balance each other …

$$rate_{\text{for}} = rate_{\text{rev}}$$

Rates match at equilibrium, where concentrations have their equilibrium values.

So rates match when …

$$k_{\text{for}}[X]_e = k_{\text{rev}}[Y]_e$$

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## What does [...] versus time depend on?

Rates match at equilibrium, so then concentrations have their equilibrium values, and so at equilibrium

$$k_{\text{for}}[X]_e = k_{\text{rev}}[Y]_e$$

Express the equilibrium constant for X → Y in terms of its equilibrium concentrations …

$$K = [Y]_e / [X]_e$$

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## What does [...] versus time depend on?

Rates match at equilibrium, so then concentrations have their equilibrium values, and so at equilibrium

$$k_{\text{for}}[X]_e = k_{\text{rev}}[Y]_e$$

Express the equilibrium constant for X → Y in terms of its forward and reverse rate constants …

$$K = k_{\text{for}} / k_{\text{rev}}$$

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[TP] A ⇄ B has $k_{for} = 10k_{rev}$,
C ⇄ D has $k_{for} = 100k_{rev}$, and
E ⇄ F has $k_{for} = 0.01k_{rev}$.
Which reaction will produce the greatest amount of products relative to reactants?

0% 1. A ⇄ B
0% 2. C ⇄ D
0% 3. E ⇄ F

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## Definition of rate of reaction

a A + b B → c C ...

rate ...

= −(1/a) d[A] / d$t$

= −(1/b) d[B] / d$t$

= +(1/c) d[C] / d$t$

Rate of reaction = always positive

Rate always has units M/s

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[Quiz] In the chemical reaction
2 A + 3 B → C
the initial rate of consumption of B is 0.15 M/s.
This means that the rate of the reaction is ...

0% 1. −0.15 M/s
0% 2. +0.15 M/s
0% 3. −0.10 M/s
0% 4. +0.050 M/s
0% 5. None of these

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Rate versus concentration from experiment

We know how to define rate.

We also know that rate = $k$ × concentration

So, we need to learn (1) how rate depends on concentration and (2) what determines the rate constant, $k$.

We'll use data to learn how rate depends on concentration, the so-called differential rate law.

We'll see that each reaction will have it own particular dependence.

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## Differential rate laws: rate vs concentration

In liquid methanol, $CH_3OH$, the following reaction occurs:

$(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

Write a rate law for this reaction.

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## Differential rate laws: rate vs concentration

In liquid methanol, $CH_3OH$, the following reaction occurs:

$(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

How can we know whether the predicted rate law is correct?

Measure rate for different combinations of reactant concentrations.

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## $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | 2.8 x $10^{-5}$ |
| 0.0002 | 0.0001 | 5.6 x $10^{-5}$ |
| 0.0001 | 0.0002 | 2.8 x $10^{-5}$ |

$rate_{for} \approx [(CH_3)_3CBr]^a$, $rate_{for} \approx [{}^{-}OCH_3]^b$

1. What is the order, $a$, in $(CH_3)_3CBr$?
2. What is the order, $b$, in ${}^{-}OCH_3$?
3. What is the full differential rate law?
4. What is the value of the forward rate constant $k_{for}$?

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[TP] For $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the order in $(CH_3)_3CBr$ ?

1. 1
2. 2
3. Neither of the above
4. More info needed

| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
|---|---|---|
| 0.0001 | 0.0001 | 2.8 x $10^{-5}$ |
| 0.0002 | 0.0001 | 5.6 x $10^{-5}$ |
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1. 1
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| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
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[TP] For $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the full differential rate law?

1. rate = $k_{for}\ [(CH_3)_3CBr]\ [{}^{-}OCH_3]$
2. rate = $k_{for}\ [(CH_3)_3CBr]$
3. rate = $k_{for}\ [{}^{-}OCH_3]$
4. Neither of the above

| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
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[Quiz] For $(CH_3)_3CBr + {}^{-}OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the value of $k_{for}$?

1. $2.8 \times 10^{-5}$ M s$^{-1}$
2. $2.8 \times 10^{-1}$ s$^{-1}$
3. $2.8 \times 10^{-1}$ M s$^{-1}$
4. None of the above

| $[(CH_3)_3CBr]$ | $[{}^{-}OCH_3]$ | Rate (M/s) |
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| 0.0001 | 0.0001 | $2.8 \times 10^{-5}$ |
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