Learning Objectives and Worksheet XII

Chemistry 1B-AL Fall 2016

Sessions ~~Lectures~~ (21-23) Chemical Kinetics

To date CHEM1B-AL has focused on the structure and chemical properties of atoms and molecules. Chemical kinetics, the final topic of the course, shifts attention to chemical reactions. In particular we will study how measuring the factors affecting the rate of a chemical reaction gives clues to the series of individual steps, i.e. the mechanism, by which the reaction proceeds.

I. Basic Concepts and Definitions

1. For a chemical reaction, what are the differences between the information that is provided by **thermodynamics** *[equilibrium]* (CHEM-1A, CHEM-1C) and **kinetics** ?

HW#10: 64, S20
Related videos:
https://youtu.be/wyQEPWTGHao

2. In a kinetics experiment one measures decreases in _____ or increases in _____ vs _____.

II. Differential rate laws

1. The rate at which a reaction occurs is written in terms of the _____ of the

_____ reactants (raised to powers) since for higher

_____ there are a greater number of molecular

_____ allowing the possibility that the reaction will proceed more

rapidly.

2. In the differential rate expression:

$$-\frac{d[X]}{dt} = +n\frac{d[Y]}{dt} = k_f[A]^m[B]^n - k_r[C]^k[D]^l$$

    i. $-\frac{d[X]}{dt}$ represents the _____ of a _____ X.

ii. $\dfrac{d[Y]}{dt}$ represents the _____ of a _____ Y.

iii. k_f and k_r are the _____ and _____

_____ respectively.

iv. the order of the above reaction in reactant A is _____.

3. The expression

$$-\dfrac{d[A]_0}{dt} = k_f[A]_0^m[B]_0^n$$

describes the rate of reaction when _____ and thus is called the

_____ rate law. Here the total rate order is _____.

4. If $-\dfrac{d[A]}{dt} = k_f[A]^m$, the instantaneous rate of reaction is given by the _____

of a plot of [A] vs t.

III. Determining order of a reaction

i. If The initial rate increases 9-fold when $[A]_0$ is tripled (i.e. $[A]_0$ increased 3-fold), the
order of the reaction in [A] is _____.

ii. If the reaction was third-order in [A] and the concentration of $[A]_0$ is doubled, the
initial rate of reaction increases by a factor of _____ .

iii. If the rate of reaction doesn't change when $[A]_0$ is doubled, the order of the reaction
in reactant A is _____ .

2. A reaction has an initial reaction rate (loss of [A]) that is first-order in $[A]_0$ and second-order
in $[B]_0$. For the initial concentrations of $[A]_0$=1 M and $[B]_0$=2 M the initial rate is $-\dfrac{20\,mol}{L\,sec}$.

The rate constant for the reaction is _____ .

IV. Integrated rate expressions

1. While the **differential** rate expression gives the _____ of the concentration
of a reactant or product with _____, the **integrated** rate expression gives the
total _____ of the reactant or product as a function of

_____.

i. Since integral calculus is not a prerequisite for CHEM1B (however you better take
this important class!!), you will be given the formulas for the integrated rate

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WHAT HOMEWORK!?

HW#10: **66**

Related videos:
https://youtu.be/wYqQCojggyM

expressions will be supplied on your exams. However you should recognize:

For the reaction where effectively only reactant [A] varies:

for $ln[A] = -kt + ln[A]_0$ the order x= _____

ii. for $\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$ the order x= _____

iii. for $[A] = -kt + [A]_0$ the order x= _____

2. For the integrated rate expression:

   i. for $ln[A] = -kt + ln[A]_0$ a plot of _____ vs _____ would be a straight line with slope _____ .

   ii. for $\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$ a plot of _____ vs _____ would be a straight line with slope _____ .

   iii. for $[A] = -kt + [A]_0$ a plot of _____ vs _____ would be a straight line with slope _____ .

V. Kinetics and the mechanism of a chemical reaction

In O-Chem and beyond you will be studying how different kinetic analyses are used to determine a variety of reaction mechanisms. In CHEM1B we will get a 'taste' of the process of kinetics → mechanism for a multi-step reaction but limit the playing field to one type of process- a slow initial step followed by a fast reaction.

VI. Elementary reactions

1. An elementary reaction is one that corresponds to _____

   _____ .

2. When the measured rate law for a chemical reaction does not correspond to the reaction stoichiometry the reaction is _____ an elementary reaction. When the measured rate law for a chemical reaction corresponds to the reaction stoichiometry the reaction _____ an elementary reaction.

WHAT HOMEWORK!?

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An elementary reaction involving only the interaction (collision) between two reactants is _____ and has a _____ order overall rate.

An elementary reaction involving only decomposition of a single reactant _____ and has a _____ order overall rate.

5. An elementary reaction that requires the improbable collision of three molecular species is a

   _____ and is a __   nentary reaction.

VII. Temperature dependence of the rate constant

1. The Arrhenius equation is $k = zpe^{-E_a/RT}$

2. The factor z is related to the _____ of the molecules

   participating in the reaction.

3. The magnitude of factor p depends on how the reaction depends on the _____

   The term $e^{-E_a/RT}$ enters into the rate giving the relative _____

   _____ .

4. At a given temperature a larger activation energy E_a will result in _____ collisions

   having _____ .

5. For a given activation energy E_a a higher temperature T will result in _____

   collisions having _____ .

6. A maxima in the reaction profile (energy vs extent of reaction, reactants → products),

   corresponds to the _____ for the reaction.

7. The energy difference between the reactants and the maximum is the _____

   _____ .

8. The energy difference between the products and the maximum is the _____

   _____ .

9. A relative minimum in the reaction profile is a _____ .

VIII. Catalysis

1. In general, a catalyst increases the rate of reaction by allowing a reaction pathway that

   _____ .

2. What are three types of catalysis

   i.
   ii.
   iii.