

Chemical Kinetics - Formulas

All rates written as $\frac{\Delta \text{conc}}{\Delta \text{time}}$ or $\frac{\Delta [A]}{\Delta t}$. Instantaneous rate is the slope of a concentration vs time plot and is shown by the differential equation: $\frac{d[A]}{dt}$. Overall rates for forward reactions are shown as POSITIVE rates, therefore, all reactants (which have negative rate of change) must have their rates negated $-\frac{d[A]}{dt}$.

In general for the overall reaction:



Note that each individual rate is divided by it's coefficient in the balanced chemical equation.

Half-life ($t_{1/2}$): The time it takes for the concentration to drop to one half its current value during the course of the reaction. Note that the "current value" is typically the initial starting value - but not always.

Rate Laws for: $a A \rightarrow \text{products}$ (all the following equations assume that k is for the overall reaction)

Zero Order	First Order	Second Order
rate = ak	rate = $ak[A]$	rate = $ak[A]^2$
$[A]_0 - [A]_t = akt$	$\ln[A]_0 - \ln[A]_t = akt$ $\ln\left(\frac{[A]_0}{[A]_t}\right) = akt$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt$
$[A]_t = -akt + [A]_0$	$\ln[A]_t = -akt + \ln[A]_0$	$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$
$t_{1/2} = \frac{[A]_0}{2ak}$	$t_{1/2} = \frac{\ln 2}{ak}$	$t_{1/2} = \frac{1}{ak[A]_0}$

Watch out for this! Make sure you know HOW k is defined for a reaction. It must be known WHICH component that the rate is being expressed. Is it A? B? C? D? Many times k is given for the *overall reaction*. If that is the case then you must remember to scale k by the coefficients (a , b , c , or d) given in order to get the right rates for each component. That is: $k = ak'$, etc... (this is discussed in section 15.2 in your textbook)

Temperature dependence of rate (Arrhenius Equation) $k = Ae^{-E_a/RT}$

Here's the straight line plot ($y = mx + b$) version:

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

When finding the new k at a new T ...

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Note this is the typical Arrhenius Equation where you have 2 specific rate constants at 2 specific temperatures. Remember they come in pairs. Also note how the Arrhenius factor A , has factored OUT of the equation.

Here is the version using half-lives instead of k 's

$$\ln \left(\frac{t_1}{t_2} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This is still the Arrhenius Equation, EXCEPT we now show TIME in place of rate constant. Time is inversely proportional to rate so the positions are switched. Any common timed event will work - half-life is the most common.

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AW Chickering



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Table of Contents Chemistry Kinetics Cheat Sheet

1. Understanding the eBook Chemistry Kinetics Cheat Sheet
 - The Rise of Digital Reading Chemistry Kinetics Cheat Sheet
 - Advantages of eBooks Over Traditional Books
2. Identifying Chemistry Kinetics Cheat Sheet
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Chemistry Kinetics Cheat Sheet
 - User-Friendly Interface
4. Exploring eBook Recommendations from Chemistry Kinetics Cheat Sheet
 - Personalized Recommendations
 - Chemistry Kinetics Cheat Sheet User Reviews and Ratings
 - Chemistry Kinetics Cheat Sheet and Bestseller Lists
5. Accessing Chemistry Kinetics Cheat Sheet Free and Paid eBooks
 - Chemistry Kinetics Cheat Sheet Public Domain eBooks
 - Chemistry Kinetics Cheat Sheet eBook Subscription Services
 - Chemistry Kinetics Cheat Sheet Budget-Friendly Options

6. Navigating Chemistry Kinetics Cheat Sheet eBook Formats
 - ePub, PDF, MOBI, and More
 - Chemistry Kinetics Cheat Sheet Compatibility with Devices
 - Chemistry Kinetics Cheat Sheet Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Chemistry Kinetics Cheat Sheet
 - Highlighting and Note-Taking Chemistry Kinetics Cheat Sheet
 - Interactive Elements Chemistry Kinetics Cheat Sheet
8. Staying Engaged with Chemistry Kinetics Cheat Sheet
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Chemistry Kinetics Cheat Sheet
9. Balancing eBooks and Physical Books Chemistry Kinetics Cheat Sheet
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Chemistry Kinetics Cheat Sheet
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Chemistry Kinetics Cheat Sheet
 - Setting Reading Goals Chemistry Kinetics Cheat Sheet
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Chemistry Kinetics Cheat Sheet
 - Fact-Checking eBook Content of Chemistry Kinetics Cheat Sheet
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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