Chemical Kinetics Mastery of Fundamentals Answers
CH353 – Prof. Wu

Here are some questions to test your mastery of the fundamentals of chemical kinetics. Once you’ve mastered the material, you should be able to answer these questions without reference to your notes or textbook.

For Chemical Kinetics I (Rate Laws):

1. Given the stoichiometric equation for a chemical reaction, e.g.,
   \[ \nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z, \]
   write down the rate of reaction, \( v(t) \), in terms of the time derivatives of the concentrations.

   \[
   v(t) = \frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Y} \frac{d[Y]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt}
   \]

2. What is a rate law? What is a rate constant? What is the order of a reaction? Do all rate laws have a reaction order?

   A rate law is an equation relating the rate of reaction to the concentrations of various reactants, products or other species. The rate constant is a constant that appears in the rate law. When the rate law is a product of the concentrations of species taken to different powers, those powers are called the order of reaction in each species, and the multiplicative constant in front is the rate constant. The sum of the orders is the overall order of reaction. Not all rate laws have this form, and so do not all have a reaction order.

3. Can one determine the rate law only from knowledge of the stoichiometry of a reaction?

   No! (Only if the reaction is an elementary reaction….see below.)

4. How does one determine a rate law from experimental data? Specifically, how does one use initial rates (i.e., method of initial rates and method of isolation)?

   One can first of all try to hold all but one of the species at constant concentration. Then by varying the concentration of one species alone, it is possible to determine the functional dependence of the rate law on that species. This is the method of isolation. We can also look at short times, before reactants have had a chance to change much from their initial concentrations, and then look at the rate dependence on a species whose concentration we vary. This is called the method of initial rates.

5. What are characteristic features associated with a first-order reaction? A second-order reaction? How would you plot data in order to determine the order of a reaction?

   A first-order reaction has a time-dependence of the concentration of reactants which is an exponential decay to zero. Because of this, the half-life is a constant independent of the concentration of reactant. A second-order reaction such as
A + B \rightarrow \text{products} with equal initial concentrations \([A]_0 = [B]_0\) shows a time-dependence of the concentration that is a power law: \(\frac{1}{[A]} = \frac{1}{[A]_0} + kt\). This has a half-life that does depend on concentration. When \([A]_0 \neq [B]_0\), the time-dependence is more complicated.

6. What is a reversible first-order reaction? A reversible first-order reaction also shows an exponential behavior in the time-dependence of concentrations—how does it differ from a first-order reaction that is irreversible (i.e., forward reaction with no reverse reaction)?

A reversible first-order reaction is a first-order reaction such as \(A \rightarrow k_1 B\) occurring simultaneously with the reverse (also first-order) reaction \(B \rightarrow k_{-1} A\). The exponential behavior of the concentration of A (or B) is a decay to its equilibrium value, which is normally not zero.

7. What is the relaxation time in a reversible first-order reaction? Together with the equilibrium constant, how is it used to determine the rate constants?

The relaxation time, \(\tau\), is the coefficient in the exponential decay of a reversible first-order reaction:
\[
[A] - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k_1 + k_{-1})t} = ([A]_0 - [A]_{eq})e^{-t/\tau}
\]
and so \(\tau = \frac{1}{k_1 + k_{-1}}\). Since the equilibrium constant is \(K_{eq} = \frac{k_1}{k_{-1}}\), we have two equations in the two unknowns \(k_1\) and \(k_{-1}\) to determine both.

8. What is the Arrhenius equation for the temperature-dependence of the rate constant? What is the activation energy and pre-exponential factor? Sketch a diagram illustrating the idea behind the Arrhenius equation. Can the pre-exponential factor be predicted from quantum mechanics?

The Arrhenius equation is \(k = Ae^{-E_a/k_B T}\), where \(A\) is the pre-exponential factor, and \(E_a\) is the activation energy. This equation is approximate. The pre-exponential factor can be calculated from quantum mechanics and transition-state theory.

For Chemical Kinetics II (Reaction Mechanisms):

9. What is an elementary reaction? How does one determine the rate law of an elementary reaction? Is it related to the stoichiometry? Of the reactants? Of the products?

An elementary reaction is one that does not involve any intermediates and occurs in a single step. For a unimolecular reaction, this would be a molecule undergoing a
transformation without interactions with other molecules, and for bimolecular or termolecular reaction, the reaction occurs because of collisions. As a result, the rate of reaction for elementary reactions are simply proportional to the concentration of the reactants only. An elementary reaction is denoted by an arrow with double lines, e.g.  \[ A + B \rightarrow C + D. \] For this example, the rate law would be \( v = k[A][B] \). Note that if more than one molecule of a given reactant is involved in an elementary reaction, its concentration appears to that power in the rate law, e.g. for \( A + 2B \rightarrow C + D \), the rate law is \( v = k[A][B]^2 \).

10. What is a reaction mechanism? Is it always a sequence of consecutive steps?

A reaction mechanism is the set of elementary reactions that allow an overall reaction to occur between reactants to form products. It is not always in the form a of a sequence of consecutive steps.

11. Does an observed rate law uniquely determine the mechanism of a reaction?

Yes. See question 9 above.

12. What is the relationship between the equilibrium constant and the rate constants (principle of detailed balance)?

The equilibrium constant is the ratio of the forward rate constant to the reverse rate constant, but only for elementary reactions.

13. What is an intermediate? How can we tell if there is an intermediate? When can or can’t we tell from the apparent rate of reaction?

An intermediate is a species other than the reactants or the products that occur in the course of a reaction (and thus appears in the mechanism). An intermediate can be detected directly (e.g. spectroscopically, or by reaction with a compound sensitive to that intermediate), or by the effect it has on the rate of reaction. However, sometimes the overall rate of reaction is unaffected by the fact that an intermediate exists. (For instance in the reaction \( A \Rightarrow I \Rightarrow P \), if the intermediate is quickly converted to product \( P \).

14. What is a rate-determining step? Is there always one in a mechanism?

Sometimes in a mechanism, the overall rate of reaction is determined by one step (elementary reaction) in a mechanism. The typical example is when the mechanism is a sequence of consecutive steps; in this case the slowest step is the rate-determining (or rate-limiting) step. But not all mechanisms have a rate-determining step.

15. What is the steady-state approximation? Under which conditions is it justified?
In many instances, when an intermediate, \( I \), is short-lived, one can approximate the reaction as proceeding as if the intermediate were present with a fixed, steady-state concentration (typically much smaller than the concentration of products or reactants). In this case, we can often set \( \frac{d[I]}{dt} = 0 \) as a way to simplify the equations determining the rate of reaction.

16. What is a chain reaction? What are the initiation, propagation, inhibition, and termination steps?

A chain reaction is a reaction whose mechanism has steps where the product of one step is the reactant in another step, in such a way that the reaction can occur by cycling through a chain of such steps in the mechanism. The steps that participate in the cycling are propagation steps, if they move the extent of reaction forward, and inhibition steps, if they move the extent of reaction backward (typically the reverse of the propagation steps). The initiation step creates an intermediate that enters into the propagation steps, and a termination step removes the intermediates that allow the chain reaction to proceed.

17. What is the Michaelis-Menten mechanism? What is the behavior in the limit of low and high substrate concentration?

The Michaelis-Menten mechanism explains the kinetics of many enzymes as proceeding via two stages: the reversible binding of substrate to enzyme followed by the reversible (or sometimes irreversible if the reverse rate, \( k_2 \), is negligible)

\[
E + S \rightleftharpoons ES \rightleftharpoons E + P
\]

unbinding to form enzyme and product: \( E + S \rightleftharpoons ES \rightleftharpoons E + P \). The rate law for Michaelis-Menten kinetics simplifies in the limit of \( k_2 [P] \to 0 \) (i.e. irreversible formation of product, or very low product concentration such as occurs at the start of a reaction) to

\[
v = \frac{k_2[S]_0[E]_0}{K_m + [S]_0}
\]

where \( K_m \) is the Michaelis-Menten constant

\[
K_m = \frac{(k_{-1} + k_2)}{k_1}
\]

At low substrate concentration, the rate law takes the limit \( v = \frac{k_2[S]_0[E]_0}{K_m} \) and is first-order in substrate and in enzyme. At high substrate concentration, the rate law takes the limit \( v = k_2[E]_0 \) and thus shows a plateau in the maximum achievable rate. The turnover number for an enzyme with a single active site is defined as the maximum number of substrate molecules that can be converted to product per enzyme molecule per unit time, and is given by \( k_2 \).

In addition, you should feel comfortable doing problems like those that have been assigned in homework. Here are some additional problems you should feel comfortable doing once you’ve mastered the material.
1. Given the half-life for either a first or second order reaction, calculate the time-
   dependence of the concentration of a reactant for all times.
2. Apply the steady-state approximation to a given mechanism to derive an 
   expression for the rate law.