

5.20: Problems

1. A dimeric molecule, A_2 , dissociates in aqueous solution according to $A_2 \rightarrow 2A$. One millimole of A_2 is dissolved rapidly in one liter of pure water. After 100 seconds, the concentration of A_2 is 8.0×10^{-4} M.

- What is the concentration of A ?
- What is the average rate at which A has been formed, in moles per liter per second?
- What is the average rate at which A_2 has reacted?
- What is the average reaction rate?

2. The initial concentration of A in a solution is 10^{-2} M. The initial concentrations of B and C are both 10^{-3} M. The volume of the solution is 2 L. Reaction occurs according to the stoichiometry: $A + 2B \rightarrow 3C$. After 50 seconds, the concentration of C is 1.3×10^{-3} M.

- What is the concentration of A ?
- What is the concentration of B ?
- What is the change in the extent of this reaction during this 50 s period?
- What is the average reaction rate?

3. When A_2 dissociates according to $A_2 \rightarrow 2A$, the observed rate law is

$$\frac{1}{V} \frac{dn_A}{dt} = \left(\frac{k}{2} \right) [A_2]^{3/2}$$

- What is the order of the reaction in $[A_2]$?
- What is the order of the reaction overall?

4. For the reaction $A + 2B \rightarrow 3C$, the observed rate law is

$$\frac{1}{V} \frac{d\xi}{dt} = \frac{k[A][B]^2}{[C]}$$

- What is the order of the reaction in $[A]$?
- $\ln[B]$?
- $\ln[C]$?
- What is the order of the reaction overall?

5. You deposit \$1000 in a bank that pays interest at a 5% annual rate. How much will your account be worth after one year if the bank compounds interest annually? How much if it compounds interest monthly? Daily? Continuously?

6. We deduced that $\exp(rt) = \lim_{m \rightarrow \infty} \left(1 + \frac{r}{m}\right)^{mt}$.

Take $r = 0.2$ and $t = 10$. Calculate $\exp(rt)$. Calculate $\left(1 + \frac{r}{m}\right)^{mt}$ for $m = 1, 10, 100, 10^3, 10^4$. Do the same for $r = -0.2$ and $t = 10$.

7. Suppose that you invest \$10,000 in the stock market and that your nest egg grows at the rate of 11% per year. (This number, or something close to it, is often cited as the historical long-term average performance of equities traded on the New York Stock Exchange.) Assuming continuous compounding, what will be the value of your nest egg at the end of 30 years?

8. Suppose instead that you “invest” your \$10,000 in an automobile. The value of the automobile will most likely decrease with time, by, say, roughly 20% per year. Assuming continuous decay at this rate, what will be the value of the automobile at the end of 5 years? 30 years?

9. At particular reaction conditions, a compound C decays in a first-order reaction with rate constant 10^{-3} s^{-1} . If the initial concentration of C , is $[C]_0 = 10^{-2} \text{ mol L}^{-1}$, how much does $[C]$ change in the first second? What is $[C]$ after 100 seconds? 1000 seconds? 2000 seconds? 4000 seconds?

10. In problem 9, how long does it take for one-half of the original concentration of C to disappear? How does the half-life depend on the initial concentration of C ?

11. C^{14} is produced continuously in the upper atmosphere. It decays with a half-life of 5715 years. Since this has been going on for a long time, the concentration of C^{14} in the atmosphere has reached a steady-state value. Living things continuously exchange carbon with the atmosphere, so the concentration of C^{14} (i.e., the fraction of the C that is C^{14}) in the biosphere is the same as it is in the atmosphere. When an organism dies, it ceases to exchange carbon with the biosphere, and the concentration of C^{14} in its remains begins to decrease. Charcoal found at an ancient campsite during an archeological dig has a C^{14} content that is 22% of the atmospheric value.

(a) What is the rate constant, in y^{-1} , for C^{14} decay?

(b) How old is the charcoal?

(c) Reverend Smith tells his parishioners that God created the universe about 4000 B.C. If Smith accepts that the atmospheric concentration and the decay rate of C^{14} have been constant since the time of creation, what would he conclude about the C^{14} content of the charcoal when God created it?

12. Mordred has introduced an exotic fungus that is growing on the surface of King Arthur's favorite pond at Camelot. Merlin has calculated that the area covered by the fungus increases by 10% per day. That is,

$$d(\text{area})/dt = (0.10/\text{day}) \times \text{area}$$

Fortunately, a trained Knight of the Round Table can clear 100 m^2 of fungus per day. Arthur has six trained knights who would cheerfully perform this remediation work, but all six are committed to out-of-town dragonslaying activities for the next 10 days. Merlin says that the fungus covers 2874 m^2 at 8:00 a.m. this morning. (The total area of the pond is about $11,200 \text{ m}^2$.) Can Arthur wait for the dragon slayers to return, or does he need to develop an alternative effective management action plan?

13. What happens to the balance in a bank account, $P(t)$, if $P(0) < 0$? What do bankers call this sort of account?

14. Suppose that you have an account whose initial balance is $-\$1000$. The bank will continuously compound interest on this account at the annual rate of 11%. You make continuous payments to this account at a rate of q dollars/year. What must q be if you want to increase the value of the account to exactly zero at the end of 10 years?

For problems 15 – 18, prove that your conclusion is correct by making an appropriate plot. In each case, the reaction occurs at constant volume.

15. The reaction $A + B \rightarrow C$ is studied with a large excess of B. ($[A]_0 = 10^{-2} \text{ M}$. $[B]_0 = 10^{-1} \text{ M}$. $[C]_0 = 0.0 \text{ M}$.) Concentration versus time data are given in the table below. What is the order of the reaction in the concentration of A, and what is the rate constant?

Time, s	$[A]$, M
100	9.1×10^{-3}
300	7.4×10^{-3}
500	6.1×10^{-3}
800	4.6×10^{-3}
1000	3.6×10^{-3}
1500	2.3×10^{-3}
2000	1.3×10^{-3}
2500	8.3×10^{-4}

16. The following data are collected for a reaction in which A dimerizes: $2A \rightarrow A_2$. What is the order of the reaction in $[A]$, and what is the rate constant?

Time, hr	$[A], \text{M}$
0.0	1.0×10^{-2}
0.28	9.1×10^{-3}
0.56	8.3×10^{-3}
1.39	6.7×10^{-3}
2.78	5.0×10^{-3}
5.56	3.3×10^{-3}
11.10	2.0×10^{-3}
16.70	1.4×10^{-3}

17. In the reaction $A + B \rightarrow C$, the rate at which B is consumed is first-order in $[B]$. In a series of experiments whose results are tabulated below, the observed first-order rate constant, k_{obs} is measured for the disappearance of B in the presence of large excesses of A . What is the order of the reaction in $[A]$? The rate law? The rate constant? ($[B]_0 = 10^{-4} \text{ M}$ in all experiments.)

$[A]_0, \text{M}$	k_{obs}, s^{-1}
2.0×10^{-1}	2.6×10^{-5}
1.1×10^{-1}	1.4×10^{-5}
6.3×10^{-2}	8.2×10^{-6}
2.5×10^{-2}	3.3×10^{-6}
9.1×10^{-3}	1.2×10^{-6}

18. In the reaction $A + B \rightarrow C$, the rate at which B is consumed is first-order in $[B]$. The table below presents first-order rate constants for the disappearance of B in the presence of large excesses of A . Plot these data to test the hypothesis that

$$k_{obs} = \frac{k_1[A]_0}{1 + k_2[A]_0}$$

What are the values of k_1 and k_2 ?

$[A]_0, \text{M}$	k_{obs}, s^{-1}
5.0×10^{-1}	8.3×10^{-5}
2.0×10^{-1}	6.7×10^{-5}
1.0×10^{-1}	5.0×10^{-5}
5.0×10^{-2}	3.3×10^{-5}
1.4×10^{-2}	1.2×10^{-5}
7.6×10^{-3}	7.1×10^{-6}
3.0×10^{-3}	3.0×10^{-6}

19. For the reaction $A + 2B \rightarrow C + D$, the rate law is

$$\frac{d[C]}{dt} = k[A][B]^2$$

The volume is constant. Suggest a mechanism for this reaction that **does not** include a termolecular elementary process. Show that this mechanism is consistent with the rate law.

20. For the reaction $X + 2Y \rightarrow W + Z$, the rate law is

$$d[W]dt = k[X]$$

The volume is constant. Suggest a mechanism for this reaction. Show that this mechanism is consistent with the rate law.

21. For the reaction $A_2 + 2B \rightarrow 2C$, the rate law is

$$\frac{d[C]}{dt} = k[A_2]^{1/2}[B]$$

The volume is constant. Suggest a mechanism for this reaction. Show that this mechanism is consistent with the rate law.

22. For the reaction $AB + C \rightarrow A + D$, the rate law is

$$-d[D]/dt = \frac{k_u [AB][C]}{k_v [A] + k_w [C]}$$

The volume is constant. Suggest a mechanism for this reaction. Show that this mechanism is consistent with the rate law.

23. When we use the flooding technique to study a reaction rate, we often say that the concentrations of species present in great stoichiometric excess are essentially constant. This is a convenient but rather imprecise way to describe a useful approximation. Consider the reaction $A + B \rightarrow C$. Over any time interval, Δt , we have $\Delta[B] = \Delta[A]$. In absolute terms, $[B]$ is no more constant than $[A]$. Suppose that the reaction rate is described by $R = k[A][B]$ and that $[B]_0 = 100[A]_0$. Define the extent of reaction by $\xi = [A]_0 - [A] = [B]_0 - [B]$. Find

$$\frac{\partial R / \partial [B]}{\partial R / \partial [A]}$$

and evaluate this relative concentration dependence at 0% conversion, $\xi = 0$ (where $[A] = [A]_0$), and at 90% conversion, $\xi = 0.9[A]_0$ (where $[A] = 0.9[A]_0$). Give a more precise statement of what we mean when we say that “the concentration of B is essentially constant” in such circumstances.

24. For the reaction $aA + bB \rightleftharpoons cC + dD$, we define the extent of reaction $\xi = -(n_A - n_A^0)/a$. When the reaction reaches equilibrium (at $t = \infty$), the extent of reaction becomes $\xi = -(n_A^\infty - n_A^0)/a$. If A is the limiting reagent and the reaction goes to completion, the theoretical extent of reaction is $\xi_{\text{theoretical}} = n_A^0/a$. Why? It is often useful to describe the amount of reaction that has occurred as a dimensionless fraction. If the reaction does not go to completion, $n_A^\infty > 0$. Use ξ and ξ_∞ to express the “extent of equilibration,” $f_{\text{equilibrium}}$, as a dimensionless fraction. Use ξ and $\xi_{\text{theoretical}}$ to express the “conversion,” $f_{\text{conversion}}$, as a dimensionless fraction. How would you define the “equilibrium conversion”?

25. We often exercise a degree of poetic license in talking about “fast” and “slow” steps in reaction mechanisms. In [Section 5.12](#), Case I, for example, we say that the step that consumes A to produce intermediate C is “slow” but the step that consumes C to produce D is “fast.” We then write $-d[A]/dt \approx d[D]/dt$. Discuss.

26. Find the rate law for the simplest-case Michaelis-Menten mechanism by applying the steady-state approximation to the concentration of the enzyme– substrate complex. Under what conditions do this treatment and the result developed in the text converge to the same rate law?

27. What is the half-life of a constant-volume secondorder reaction, $2A \rightarrow C$, for which

$$\frac{d[A]}{dt} = -\frac{2}{V} \frac{d\xi}{dt} = -2k[A]^2$$

28. For the reaction between oxygen and nitric oxide, $2NO + O_2 \rightarrow 2NO_2$, the observed rate law, at constant volume, is

$$\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$$

Show that this rate law is consistent with either of the following mechanisms:

- (i) $NO \rightleftharpoons N_2O_2$ (fast equilibrium)
 $N_2O_2 + O_2 \rightarrow 2NO_2$ (rate-determining step)
- (ii) $O + O_2 \rightleftharpoons NO_3$ (fast equilibrium)
 $NO_3 + NO \rightarrow 2NO_2$ (rate-determining step)

29. For the reaction between gaseous chlorine and nitric oxide, $2NO + Cl_2 \rightarrow 2NOCl$, doubling the nitric oxide concentration quadruples the rate, and doubling the chlorine concentration doubles the rate.

(a) Deduce the rate law for this reaction.

(b) Keeping mind the mechanisms in problem 28, write down two possible mechanisms that are consistent with the rate law you deduced in part (a). Show that each of these mechanisms is consistent with the rate law in part (a).

30. Nitric oxide reacts with hydrogen according to the equation, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$. At constant volume, the following kinetic data have been obtained for this reaction at 1099 K. [1 mm = 1 torr = (1/760) atm.] C. N. Hinshelwood and T. Green, *J.*

$P^0 (H_2)$, mm	$P^0 (NO)$, mm	Initial reaction rate, mm s ⁻¹
289	400	0.162
205	400	0.110
147	400	0.079
400	359	0.150
400	300	0.103
400	152	0.025

(a) What is the rate law for this reaction?

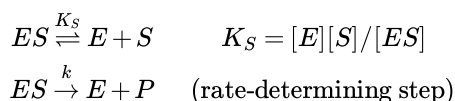
(b) Suggest two mechanisms for this reaction that are consistent with the rate law you deduce in part (a).

31. Review the reactions, rate laws, and mechanisms that you considered in problems 28, 29, and 30.

(a) Does comparing these three reactions and their rate laws provide any basis for preferring one set of mechanisms to the other?

(b) Which set of mechanisms do you prefer; that is, which mechanism in each of problems 29, 30, and 31 seems more likely to you? Why?

32. The rate of an enzyme-catalyzed reaction, commonly called the velocity, v , is measured directly as $v = d[P] / dt \approx \Delta[P] / \Delta t = -\Delta[S] / \Delta t$. For small S_0 , a plot of v versus the initial substrate concentration, S_0 , increases with increasing S_0 . For large values of S_0 , v reaches a constant value, v_{max} . The substrate concentration at which the reaction rate is equal to $v_{max} / 2$ is defined to be the Michaelis constant, K_M . It is customary to express the equilibrium constant as the dissociation constant for the enzyme-substrate complex. Let the total enzyme concentration be E_0 . For the mechanism



(a) Show that the velocity is given by

$$v = kE_0 \left(1 + \frac{KS}{S_0} \right)$$

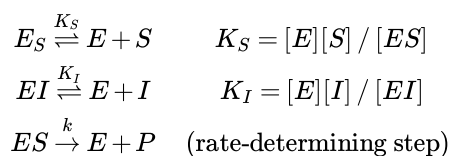
(b) What is v_{max} ?

(c) What is the Michaelis constant, K_M ?

(d) Does a larger value of K_M correspond to stronger or weaker complexation of the substrate by the enzyme?

(e) Sketch the curve of v versus S_0 for the reaction rate described in (a). On this sketch, identify v_{max} , $v_{max} / 2$, and K_M .

(f) If a second substrate, I , can form a complex with the enzyme, the reaction rate for substrate S decreases in the presence of I . Such substrates, I , are called inhibitors. Many kinds of inhibition are observed. One common distinction is between inhibitors that are competitive and inhibitors that are not competitive. Competitive inhibition can be explained in terms of a mechanism in which the enzyme equilibrates with both substrates.



Show that the velocity is given by

$$v = kE_0 / \left[1 + \frac{K_S}{S_0} \left(1 + \frac{I_0}{K_I} \right) \right]$$

(g) A series of experiments is done in which S_0 is varied, while I_0 is maintained constant. The results are described by the equation in (f). What is v_{max} in this series of experiments?

(h) For the series of experiments done in (g), what is the Michaelis constant, K_M ?

33. Consider a bimolecular reaction between molecules of substances A and B . If there are no forces of attraction or repulsion between A molecules and B molecules, we expect their collision rate to be $k[A][B]$, where k is a constant whose value is independent of the values of $[A]$ and $[B]$. Now suppose that molecules of A and B experience a strong attractive force whenever their intermolecular separation becomes comparable to, say, twice the diameter of an A molecule. Will the value of k be different when there is a strong force of attraction than when there is no such force?

Notes

¹ See Fred Basolo and Ralph G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd Ed., John Wiley & Sons, Inc., New York, 1967, pp 177-193.

² R.C. Tolman, *The Principles of Statistical Thermodynamics*, Dover Publications, 1979, (published originally in 1938 by Oxford University Press), p 163.

³ R. L. Burwell and R. G. Pearson, *J. Phys. Chem.*, **79**, 300, (1966).

⁴ George M. Fleck, *Chemical Reaction Mechanisms*, Holt, Rinehard, and Winston, Inc., New York, NY, 1971, pp 104-112.

⁵ G. N. Lewis, *Proc. Nat. Acad. Sci. U. S.*, **11**, 179 (1925).

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