CHAPTER 7

Kinetics

Questions 270–273 refer to the following choices:

(A) Rate = k [M]
(B) Rate = k [M][N]
(C) Rate = k [M][N]^2
(D) Rate = k [M]^2[N]^2
(E) Rate = k [N]^2

270. Doubling the concentration of M has no effect on the reaction rate.

271. Doubling the concentration of M and N increases reaction rate by 2.

272. Doubling the concentration of M only quadruples the reaction rate.

273. Doubling the concentration of M and N increases the reaction rate by eight fold. Halving the concentration of N decreases the reaction rate four fold.

274. The production of iron (II) sulfide occurs at a significantly higher rate when iron filings are used instead of blocks (volume = 0.1 mL). Which of the following best explains this observation?

(A) The iron filings are partially oxidized due to their greater exposure to oxygen.
(B) The iron in the block is $Fe_{(s)}$ and the iron in the filings is Fe^{2+}.
(C) The iron block is too concentrated to chemically react.
(D) The iron filings have a much greater area in contact with sulfur.
(E) The reactant order of iron in the rate law is 1 for $Fe_{(s)}$ and 2 for Fe^{2+}.

275. A chemistry student sitting around a campfire observes that the large pieces of wood burn slowly, but a mixture of small scraps of wood and sawdust added to the flame combusts explosively. The correct explanation for the difference in the combustion between these two forms of wood is that, compared with the wood scraps and sawdust, the large pieces of wood

(A) have a greater surface area-to-volume ratio.
(B) have a smaller surface area per kilogram.
(C) have a higher percent carbon.
(D) contain compounds with a lower heat of combustion.
(E) contain more carbon dioxide and water.

276. All of the following result in an increased rate of reaction in an aqueous solution *except*:

(A) Increasing the temperature of an endothermic reaction.
(B) Increasing the temperature of an exothermic reaction.
(C) Increasing the surface area of a solid reactant.
(D) Increasing the pressure on the solution.
(E) Mixing or stirring the solution.

277. Factors that affect the rate at which a chemical reaction proceeds include which of the following?

I. The orientation of the reactants at time of collision
II. The kinetic energy of the collisions between reactants
III. The frequency of collisions between reactants

(A) I only
(B) II only
(C) III only
(D) I and II only
(E) I, II, and III

278. Which of the following correctly explain(s) the effect of increased temperature on the rate of a chemical reaction?

I. Increases the reaction rate of endothermic reactions
II. Increases the reaction rate of exothermic reactions
III. Decreases the reaction rate of reactions with a $-\Delta H$

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I and III only

279. All of the following statements regarding the kinetics of radioactive decay are true *except*:

(A) The length of time of a half-life is specific to a particular element.
(B) All radioactive decay displays first-order kinetics.
(C) In a sample of a pure, radioactive isotope, one-half the number of radioactive atoms and one-half the mass of the radioactive substance remains after one half-life.
(D) The half-life of an atom does not change when the atom is incorporated into a compound.
(E) The half-life of a particular substance does not change with time or temperature.

Questions 280–285 refer to the reaction of nitrogen monoxide (nitric oxide) and oxygen and the following data.

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

	[NO] (mol L^{-1})	[O$_2$] (mol L^{-1})	RATE (M s^{-1})
Trial 1	2.4×10^{-2}	3.5×10^{-2}	1.43×10^{-1}
Trial 2	1.5×10^{-2}	3.5×10^{-2}	5.6×10^{-2}
Trial 3	2.4×10^{-2}	4.5×10^{-2}	1.84×10^{-1}

280. The rate law for this reaction is:

(A) Rate = k $[NO][O_2]$
(B) Rate = k $[NO][O_2]^2$
(C) Rate = k $[NO]^2[O_2]$
(D) Rate = k $[NO]^2[O_2]^2$
(E) Rate = k $[NO][O_2]^{1.25}$

281. The numerical value for the rate constant (k) is closest to:

(A) 5.9×10^{-2}
(B) 170
(C) 3×10^3
(D) 7×10^3
(E) 1.2×10^5

282. The unit of the rate constant (k) is:

(A) sec^{-1}
(B) $L\ mol^{-1}\ sec^{-1}$
(C) $L^2mol^{-2}\ sec^{-1}$
(D) $L^3mol^{-3}\ sec^{-1}$
(E) $L^4mol^{-4}\ sec^{-1}$

283. Increasing the initial concentration of NO fivefold would increase the reaction rate by:

(A) 5 X
(B) 10 X
(C) 25 X
(D) 3,125 X
(E) No substantial margin

284. What would be the reaction rate if the initial concentration of NO was 2×10^{-2} M and the initial concentration of O_2 was 4×10^{-2} M?

(A) 3.2×10^{-5}
(B) 8×10^{-4}
(C) 2.3×10^{-2}
(D) 1.1×10^{-1}
(E) 5.7

285. Which of the following is a correct statement about reaction order?

(A) Reaction order must be a whole number.
(B) Reaction order can be determined mathematically using only coefficients of the balanced reaction equation.
(C) Reaction order can change with increasing temperature.
(D) A second-order reaction must involve at least two reactants.
(E) Reaction order can only be determined experimentally.

286. Properties of a catalyst include all of the following *except:*

(A) A catalyst that works for one chemical reaction may not work for a different reaction.
(B) A catalyst is not consumed by the reaction it catalyzes.
(C) Catalysts can be solids or gases.
(D) A catalyst will only speed up a chemical reaction in *either* the forward *or* reverse direction.
(E) Catalysts speed up chemical reactions by providing an alternate pathway for reaction in which the activated complex is of lower energy.

287. Which of the following can be used to calculate or measure the rate of a chemical reaction?

I. The appearance of product over time
II. The disappearance of one or more substrates over time
III. The rate law
IV. The K_{eq} (equilibrium constant) and Q (reaction quotient) of the reaction

(A) I and II only
(B) I and III only
(C) I, II, and III only
(D) I, II, and IV only
(E) I, II, III, and IV

288. The reaction of nitric oxide with hydrogen gas at 25°C and 1 atm is represented below. The rate law for this reaction is: rate = $k\ [H_2][NO]^2$.

$$2\ NO_{(g)} + 2\ H_{2\ (g)} \rightarrow N_{2\ (g)} + 2\ H_2O_{\ (g)}$$

According to the rate law, which of the following is the best prediction of the rate of this reaction?

(A) The rate of disappearance of NO is always twice as great as the disappearance of H_2.
(B) The rate of disappearance of NO is always four times as great as the disappearance of H_2.
(C) The rate of disappearance of NO is twice as great as the disappearance of H_2 if the concentration of NO is initially twice that of H_2.
(D) The rate of disappearance of NO is four times as fast as that of H_2, but only if the initial concentration of NO is initially twice that of H_2.
(E) The relative disappearances of NO and H_2 cannot be deduced without the value of the rate constant (k).

289. The reaction between nitrogen dioxide and carbon monoxide is represented above. The proposed reaction mechanism is as follows:

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Which of the following reaction mechanisms is consistent with the proposed mechanism?

(A) Rate = k $[NO_2]$
(B) Rate = k $[NO_2]^2$
(C) Rate = k $[NO][CO]$
(D) Rate = k $[NO]^2[CO]$
(E) Rate = k $[CO]$

$$2\ NO_{(g)} + Br_{2(g)} \rightarrow 2\ NOBr_{(g)}$$

290. The reaction between nitrogen monoxide (commonly called nitric oxide) and bromine is represented above. The proposed reaction mechanism is as follows:

$NO + Br_2 \Leftrightarrow NOBr_2$ (fast)

$NOBr_2 + NO \rightarrow 2\ NOBr$ (slow)

Which of the following reaction mechanisms is consistent with the proposed mechanism?

(A) Rate = k $[NO]^2$
(B) Rate = k $[NO][Br_2]$
(C) Rate = k $[NO][Br_2]^2$
(D) Rate = k $[NO]^2[Br_2]$
(E) Rate = k $[NO]^2[Br_2]^2$

291. The rate constant for a certain chemical reaction at 25°C is 9.0×10^5 $L^2mol^{-2}sec^{-1}$. Which of the following must be true regarding this reaction?

(A) This reaction is slower than a reaction that has a rate constant of $9.0\ L^2mol^{-2}sec^{-1}$.
(B) This reaction is exothermic.
(C) The rate of this reaction will decrease with increasing temperature.
(D) The reaction order is 3.
(E) Doubling the concentration of reactants will increase the reaction rate by a factor of 8.1×10^{10}.

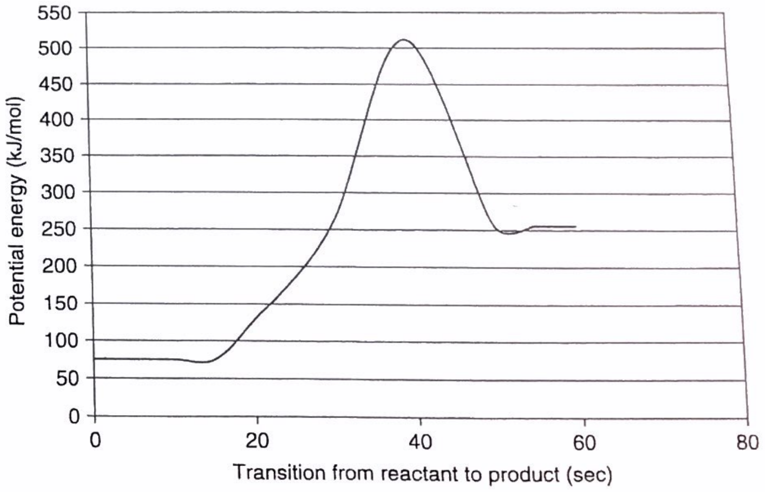
of the breakdown of ozone (O_3) into molecular oxygen (O_2)?

(A) The catalyst that converts ozone to oxygen is inhibited by oxygen.
(B) The rate at which ozone is converted to oxygen increases as the concentration of oxygen decreases.
(C) There is an inverse square relationship between ozone and oxygen concentrations.
(D) The conversion of oxygen to ozone is faster than the conversion of ozone to oxygen.
(E) The negative reactant order of oxygen indicates that the reaction is a equilibrium and the forward reaction is more favorable.

293. All of the following statements regarding the activated complex are true *exce*

(A) The energy of the activated complex determines the activation ener of the reaction.
(B) The activated complex represents the highest energy state along the transition path of a chemical reaction.
(C) The activated complex of a chemical reaction is specific to that reaction.
(D) The configuration of atoms in the activated complex of an uncatalyzed reaction is the same as that of a catalyzed reaction, exc for the presence of the catalyst.
(E) A reaction in which the energy of the activated complex is very la indicates that the reactants are very thermodynamically stable (as opposed to chemically stable).

Questions 294 and 295 refer to the following graph of a chemical reaction over



294. Which of the following is true concerning the reaction at 25°C?

I. The reaction is endothermic.
II. The activation energy (E_a) is approximately 510 kJ mol^{-1}.
III. The magnitude of the difference between energy of the reactants and products is approximately 175 kJ mol^{-1}.

(A) I only
(B) II only
(C) III only
(D) II and III only
(E) I and III only

295. Which of the following is true concerning the effect of adding a catalyst?

(A) The activated complex would form in less than 40 seconds.
(B) It lowers the energy of the products.
(C) It increases the energy of the reactants.
(D) More reactions would occur per second.
(E) The equilibrium would shift to favor the products.

Time (minutes)	0	5	10	15	20	25	30
Reactant Remaining (*g*)	100	75	56	42	32	24	18

296. A reaction was observed for 30 minutes. Every 5 minutes, the percent of reactant remaining was measured. According to the data in the table above, which of the following most accurately describes the reaction order and half-life of this reaction?

	Reaction Order	**Half-Life (minutes)**
(A)	Zero	10
(B)	First	12
(C)	First	8
(D)	Second	12
(E)	Second	8

297. The rate laws for the reaction between O_2 and NO is $k = [O_2][NO]^2$. If the reaction rate is first measured with O_2 and NO of 2.5×10^{-4} M each, by what factor will the rate increase if the concentration of O_2 and NO are both increased to 5.0×10^{-4} each?

(A) 2
(B) 3
(C) 4
(D) 6
(E) 8

Questions 298 and 299 refer to the data below.

Trial	[X]	[Y]	Formation of Product Z
1	0.5	0.1	R
2	0.25	0.2	?

298. Consider the data shown above. If the data were obtained from a reaction whose rate law is $k = [X][Y]^2$, what would be the expected rate of reaction for Trial 2?

(A) R
(B) 2R
(C) 4R
(D) $\frac{R}{2}$
(E) $\frac{R}{4}$

299. Suppose the data were obtained for a reaction whose rate law is $k = [X]^2[Y]$. What would be the expected rate of reaction for Trial 2?

(A) R
(B) 2R
(C) 4R
(D) $\frac{R}{2}$
(E) $\frac{R}{4}$

300. The units of the rate constant (k) for a reaction that occurs between two second-order reactants is:

(A) sec^{-1}
(B) L mol^{-1} sec^{-1}
(C) L^2 mol^{-2} sec^{-1}
(D) L^3 mol^{-3} sec^{-1}
(E) L^4 mol^{-4} sec^{-1}

reactant order of NO is 2, and the concentration of NO was doubled, we'd expect the rate would increase by fourfold. If the concentration was increased by 1.6, $1.6^2 = 2.56$, or 2.6.

We can apply the same methodology to the reactant order of O_2. The two trials in which *only* the concentration of O_2 changes are Trials 1 and 3. The O_2 concentration increases from 0.035 to 0.045, an increase of about 1.3 times. The rate increases from 0.143 to 0.184. If we recognize that 0.143 is about two-thirds of 0.184, we can determine that the reaction rate increased by one-third. Therefore, with regard to O_2, increasing the concentration by one-third increases the reaction rate by one-third. (Please see the important note from the author at the beginning of the book.)

281. (D) All we need to do here is substitute the data from one of the trials into the rate law. Use the trial that has the easiest numbers to crunch. Using the data from Trial 1:

$\text{Rate} = k[NO]^2[O_2]$

$k = \text{rate}/[NO]^2[O_2]$

$k = 0.143/[0.024]^2[0.035]$

$k = 7{,}093 \text{ or } 7.0 \times 10^3$

Remember, the numerical value of the rate constant, k, always increases with increasing temperature. So the value of k calculated for a particular reaction occurring at one temperature will not be the same in the same reaction performed at a different temperature. (Please see the important note from the author at the beginning of the book.)

282. (C) We can memorize the units of the rate constant or calculate them. Notice that the absolute value of the exponent for L and mol are always one less than the reaction order.

Reaction Order	Units of k
1	sec^{-1}
2	$L\ mol^{-1}\ sec^{-1}$
3	$L^2\ mol^{-2}\ sec^{-1}$
4	$L^3\ mol^{-3}\ sec^{-1}$

To calculate k, just substitute the units into the rate law.

$\text{Rate} = k[NO]^2[O_2]$

$M\ s^{-1} = k\ (mol\ L^{-1})^2\ (mol\ L^{-1})$

Remember that the units of M are $mol\ L^{-1}$

$mol\ L^{-1}\ s^{-1} = k\ mol^3\ L^3$

$k = L^2\ mol^{-2}\ sec^{-1}$

(Please see the important note from the author at the beginning of the book.)

283. (C) The reaction order for NO is 2, so increasing its concentration would increase the reaction rate by $25 \times ([5x]^2 = 25$-fold increase in rate). (Please see the important note from the author at the beginning of the book.)

284. (D) All we need to do is plug the numbers into the rate law, using the value of k determined in **Question 281**.

$\text{Rate} = k[NO]^2[O_2]$

$\text{Rate} = 7.3 \times 10^3\ [2 \times 10^{-2}]^2\ [4 \times 10^{-2}]$

$\text{Rate} = \mathbf{1.1 \times 10^{-1}}$

(Please see the important note from the author at the beginning of the book.)

285. (E) The effect that the concentration of a particular reactant has on a reaction cannot be determined until the actual experiment of changing the concentration of that reaction and measuring the rate change that results is performed. In writing the equilibrium expression, the exponents that accompany reactions are taken from the balanced equation, but the equilibrium concentrations must be measured to actually determine the K_{eq} for the reaction. (Please see the important note from the author at the beginning of the book.)

286. (D) We should certainly remember the statements in choices (A), (B), (C), and (E) as important facts about catalysts. Choice (D) is the opposite of what is true, and this is also important to remember: A catalyst ***does not differentiate*** between the forward and reverse reactions. The activated complex is the same whether a reaction occurs in the forward or reverse reaction, so decreasing the energy of the activated complex will decrease the activation energy in both directions by an equal amount. Because a catalyst increases the rates of both forward and reverse reactions equally, the presence of a catalyst *does not change* the K_{eq} for a reaction. It doesn't change the ΔH_{rxn}, either (yet another important thing to remember about catalysts). (See **Answer 11** for an *except* question strategy.)

287. (E) Statements I and II are standard ways of measuring reaction rates. The rate law (III) can be used to predict the rate of a chemical reaction. The reaction quotient (Q) can be used in conjunction with the equilibrium constant (K_{eq}) to calculate how far a reaction is from equilibrium.

288. (A) Reaction rates are typically measured in one of two ways, the appearance of product over time, and/or the disappearance of one or more substrates over time. When using reaction data, it is vital to consider the stoichiometric coefficients when to compare relative rates of appearance or disappearance. For example, for each mole NO consumed by this reaction, one mole of H_2 will be consumed as well and one mole of H_2O will form, as well. However, only half of a mole of N_2 will form. Related to time, N_2 will be formed at half the rate as H_2O formation, and half the rate at which NO and H_2 are consumed.

289. (B) The slowest (rate determining) step in a multistep reaction governs the rate law of the reaction. CO is not involved in the rate determining step, so it is not included in the rate law. Because two NO_2 molecules are necessary for collision (it is bimolecular), the reactant order for NO_2 is two.

290. **(D)** It is more difficult to determine the rate law from a reaction mechanism in which an intermediate (NOBr, in this case) is involved in the slow (rate determining) step. Notice that the first, fast step is at equilibrium, so that the forward *and* reverse reactions are occurring at the same rate. We can write and equate a rate law for these reactions, then solve for [NOBr], which allows us to use the intermediate that we normally don't include in the rate law, but need when it is part of the rate determining step.

$k_{forward}\,[NO][Br_2] = k_{reverse}\,[NOBr]$

$\mathbf{[NOBr] = k_{forward}/k_{reverse}\,[NO][Br_2]}$

The rate law for the slow step, if NOBr was not an intermediate, would look like this:

$Rate = k\,[NOBr][NO]$

but now we substitute for [NOBr]

$Rate = k_2\,\mathbf{(k_f/k_r)[NO][Br_2]}[NO]$

and simplify to get rate $= k_{rxn}\,[NO]^2[Br_2]$.

The value of $k_{rxn} = k_2k_f / k_r$.

291. **(D)** The numerical value of the rate constant, k, is irrelevant to answering this question. It is the *unit* of the rate constant that gives us the most information (at first). From the unit, we can deduce that this is a third-order reaction. Remember, the absolute value of the exponent for L and mol is 1 less than the reaction order. (For reaction order *n*, the units of the rate law will be $L^{(n-1)}\ mol^{-(n-1)}\ sec^{-1}$.) (See **Answer 282** for a table of the rate constant units and how to determine them.)

The rate constant represents an "adaptor" between the concentration of reactants and the reaction rate (at a particular temperature), it doesn't tell us anything about the enthalpy changes that occur in the reaction, nor can it be used for comparing reaction rates with other reactions for which nothing but the rate constant is known. The units of the rate constant *do* provide a quantitative relationship between concentration changes and reaction rates. In this third-order reaction, doubling the concentrations of all the reactions will result in an eightfold increase in reaction rate ($[2x]^3 = 8 \times$ rate), *not* an 8.1×10^{10}-fold rate increase.

292. **(B)** Reactant orders can be positive, negative, or fractional. A negative reactant order indicates that the reaction rate increases as the reactant with the decreased concentration of that reactant.

293. **(D)** The activated complex formed during a chemical reaction without a catalyst *must* be different from the one formed by the same reaction *with* a catalyst. First, the potential energies are different. Second, the presence of a catalyst provides an alternative pathway for reaction, which means a different set of intermediates are formed. (See **Answer 11** for an *except* question strategy.)

294. **(E)** The reaction is endothermic because the products have more potential energy than the reactants. The E_a is calculated by subtracting the energy of the reactants from the energy of the activated complex ∴ 510 − 75 = 435 kJ mol^{-1}. The potential energy of the products is approximately 250 kJ mol^{-1} and the energy of the reactants is about 75 kJ mol^{-1} ∴ $\Delta H = 250 - 75 = 175$ kJ mol^{-1}.

295. **(D)** Reaction rate is measured by product formation (or substrate consumption) over time and is a function of the number of effective collisions that occur in a given period of time.

296. **(B)** It takes between 10 and 15 minutes to decrease the amount of reactant by 50 percent. It takes another 10 to 15 minutes to decrease the amount of reactant by another 50 percent, therefore the reaction order is 1, and the half-life is between 10 and 15 minutes ∴ 12 minutes.

297. **(E)** The total reaction order is 3, so doubling *both* reactants will increase the reaction rate eightfold ($[2x]^3$) = 8-fold increase in rate).

298. **(B)** In Trial 2, the concentration of X is cut by half, so we expect the rate to decrease by half since X is a first-order reactant (∴ $^R/_2$). The concentration of Y is doubled, however, and Y is a second-order reactant, so the change in reaction rate due to doubling [Y] = 4R. $(^R/_2) \times (4R) = 2R$.

299. **(D)** In Trial 2, the concentration of X is cut by half so we expect the rate to decrease by one-fourth since X is a second-order reactant in this situation (∴ $^R/_4$). The concentration of Y is doubled, however, and since Y is a first-order reactant in this case, the change in reaction rate due to doubling is [Y] = 2R. $(^R/_4) \times (2R) = {}^R/_2$.

300. **(D)** The units of the rate constant for a fourth-order reaction is $L^3\ mol^{-3}\ sec^{-1}$ Remember that the absolute value of the exponents of L and mol is 1 less than the reactior order. (See the table under **Answer 282** for a summary of the units of k.)

Chapter 8: Equilibrium

301. **(D)** *Le Chatelier's principle*: If a chemical system at equilibrium experiences a change ir concentration, volume, temperature, or partial pressure, the equilibrium shifts to counterac the change and a new equilibrium will be established. To increase the amount of MgC produced, a disturbance to the equilibrium must be applied that will be counteractec by the production of *more* MgO. Removing $Mg_{(s)}$ (or adding it) will not cause any chang in the equilibrium because it is a solid. Solids don't have a concentration and they are no represented in the equilibrium expression. *Increasing* the pressure on a gaseous system a equilibrium will cause the equilibrium to shift to favor the side of the reaction with th fewest moles of gas. *Decreasing* the pressure shifts the equilibrium to favor the side of th reaction with the most moles of gas. Changing the pressure of a gaseous system *does nc change* the value of K_p, however. The ratio of partial pressures *after* the pressure change wi equal the same value of K_p. Adding more $O_{2(g)}$ will increase MgO formation because th system will consume the O_2 in an effort to counteract the increase in O_2 pressure. (See tabl in **Answer 307**.)