

Practice Exercises

Multiple-Choice

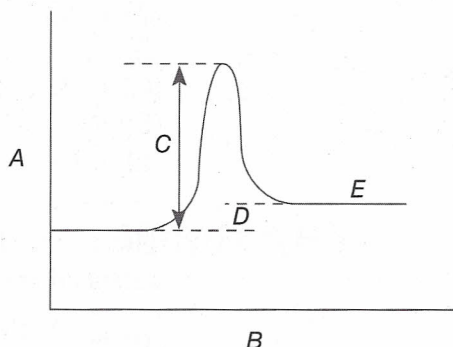
For the first four problems below, one or more of the following responses applies; each response may be used more than once or not at all in these questions.

- I. activation energy
- II. orientation
- III. potential energy curve
- IV. frequency
- V. activated complex

1. The heat of a reaction is best deduced from the
 - (A) I
 - (B) II
 - (C) III
 - (D) IV
 - (E) V
2. The collision theory involves
 - (A) I and III
 - (B) II
 - (C) II and IV
 - (D) IV
 - (E) I, III, and V
3. The transition-state theory involves
 - (A) I and III
 - (B) III
 - (C) III and V
 - (D) IV
 - (E) I, III, and V
4. The rate of a chemical reaction is related to
 - (A) I and III
 - (B) II
 - (C) I, II, and IV
 - (D) IV
 - (E) I, III, and V
5. The activated complex may be described as
 - (A) an elementary reaction in a mechanism
 - (B) the shape of the molecules at the top of the potential energy diagram
 - (C) the shape of the reaction product
 - (D) the phase—liquid, solid, or gas—in which a reaction takes place
 - (E) a coordination state

6. A reaction in which the rate and the rate constant have the same units is
- (A) a radioactive decay
 - (B) a second-order reaction
 - (C) a reaction with a one-step mechanism
 - (D) a first-order reaction
 - (E) a zero-order reaction

Questions 7–9 refer to the following diagram:



7. In the reaction profile, *A*, *B*, and *C* should be labeled as shown in

<i>A</i>	<i>B</i>	<i>C</i>
(A) potential energy	reaction coordinate	activation energy
(B) heat of reaction	reaction coordinate	potential energy
(C) potential energy	reaction coordinate	heat of reaction
(D) heat of reaction	potential energy	activation energy
(E) activation energy	extent of reaction	heat of reaction

8. In the reaction described by the reaction profile,
- (A) forward $E_a >$ reverse E_a and ΔH is exothermic
 - (B) reverse $E_a >$ forward E_a and ΔH is endothermic
 - (C) forward $E_a <$ reverse E_a and ΔH is exothermic
 - (D) reverse $E_a <$ forward E_a and ΔH is endothermic
 - (E) reverse $E_a =$ forward E_a and ΔH is zero
9. Addition of a catalyst to the reaction mixture will affect only
- (A) *A*
 - (B) *B*
 - (C) *C*
 - (D) *D*
 - (E) *E*

10. A fast reaction should have
 (A) a high activation energy
 (B) a catalyst present
 (C) a large equilibrium constant
 (D) a low activation energy
 (E) an exothermic heat of reaction
11. Which of the following rate laws has a rate constant with units of $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$?
 (A) $\text{Rate} = k [\text{A}]$
 (B) $\text{Rate} = k [\text{A}]^2$
 (C) $\text{Rate} = k [\text{A}] [\text{B}]$
 (D) $\text{Rate} = k [\text{A}] [\text{B}]^2$
 (E) $\text{Rate} = k [\text{A}]^0$
12. Which of the following is LEAST effective in increasing the rate of a reaction?
 (A) increasing the pressure by adding an inert gas
 (B) grinding a solid reactant into small particles
 (C) increasing the temperature
 (D) eliminating reverse reactions
 (E) adding a catalyst
13. A first-order reaction has a half-life of 36 min. What is the value of the rate constant?
 (A) $3.2 \times 10^{-4} \text{s}^{-1}$
 (B) $1.9 \times 10^{-3} \text{L mol}^{-1} \text{s}^{-1}$
 (C) 1.2s^{-1}
 (D) 0.028s^{-1}
 (E) $9.3 \times 10^{-4} \text{L mol}^{-1} \text{s}^{-1}$
14. If a reactant's concentration is doubled and the reaction rate increases by a factor of 8, the exponent for that reactant in the rate law should be
 (A) 0
 (B) 1
 (C) 2
 (D) 3
 (E) $\frac{1}{2}$
15. In general, if the temperature of a reaction is raised from 300 K to 320 K, the reaction rate will increase by a factor of approximately
 (A) $\frac{320 \text{ K}}{300 \text{ K}}$
 (B) $\frac{22^\circ \text{C}}{2^\circ \text{C}}$
 (C) 4
 (D) 2
 (E) 20
16. A graph of the reciprocal of reactant concentration versus time will give a straight line for
 (A) a zero-order reaction
 (B) a first-order reaction
 (C) a second-order reaction
 (D) both (A) and (C)
 (E) (A), (B), and (C)
17. The rate at which CO_2 is produced in the following reaction:

$$2\text{C}_6\text{H}_6(g) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$$
 is $2.2 \times 10^{-2} \text{mol L}^{-1} \text{s}^{-1}$. What is the rate at which O_2 is consumed?
 (A) $2.2 \times 10^{-2} \text{mol L}^{-1} \text{s}^{-1}$
 (B) $1.3 \times 10^{-1} \text{mol L}^{-1} \text{s}^{-1}$
 (C) $2.8 \times 10^{-2} \text{mol L}^{-1} \text{s}^{-1}$
 (D) $1.8 \times 10^{-3} \text{mol L}^{-1} \text{s}^{-1}$
 (E) $-2.2 \times 10^{-2} \text{mol L}^{-1} \text{s}^{-1}$

CHALLENGE

18. Which of the following will be most helpful in determining the stability or shelf life of a new drug?
 (A) the reaction mechanism for its decomposition
 (B) the rate law for its decomposition
 (C) the Arrhenius plot of the decomposition reaction
 (D) the integrated rate law plot
 (E) the overall chemical reaction

19. An Arrhenius plot is a graph of

- (A) the rate constant versus concentration
- (B) the natural logarithm ($\ln$) of the rate constant versus concentration
- (C) the reciprocal of the rate constant versus $\ln T$
- (D) the rate constant versus $\ln (1/T)$
- (E) the natural logarithm ($\ln$) of the rate constant versus $1/T$

20. A first-order reaction has a half-life of 85 s. What fraction of the reactant is left after 255 s?

- (A) $\frac{1}{2}$
- (B) $\frac{1}{4}$
- (C) $\frac{1}{8}$
- (D) $\frac{1}{3}$
- (E) $\frac{7}{8}$

CHALLENGE

21. A rate law is found to be

$$\text{Rate} = k[A]^2[B]$$

The order of the reaction is

- (A) first order
- (B) second order
- (C) third order
- (D) fourth order
- (E) The order of the reaction cannot be determined.

CHALLENGE

22. A rate law is found to be

$$\text{Rate} = k[A]^2[B]$$

Which of the following actions will NOT change the initial reaction rate?

- (A) doubling the concentrations of both A and B
- (B) doubling the concentration of A and halving the concentration of B
- (C) halving the concentration of A and doubling the concentration of B
- (D) halving the concentration of A and quadrupling the concentration of B
- (E) doubling the concentration of A and quadrupling the concentration of B

23. What is the half-life of a reaction that has a first-order rate constant of $2.6 \times 10^{-4} \text{ s}^{-1}$?

- (A) $2.7 \times 10^3 \text{ s}$
- (B) $1.3 \times 10^{-4} \text{ s}$
- (C) $1.2 \times 10^3 \text{ s}$
- (D) $7.7 \times 10^3 \text{ s}$
- (E) $1.3 \times 10^{-4} \text{ s}$

24. Modern automobiles use a catalytic converter to

- (A) increase horsepower by burning more gasoline
- (B) absorb pollutants from the exhaust
- (C) complete the combustion of unburned gases
- (D) cool the exhaust gases
- (E) convert pollutants into water

25. A catalyst will NOT

- (A) increase the forward reaction rate
- (B) shift the equilibrium to favor the products
- (C) alter the reaction pathway
- (D) increase the speed at which equilibrium will be achieved
- (E) increase the reverse reaction rate

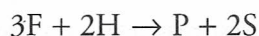
ANSWER KEY

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|------|-------|-------|-------|-------|
| 1. C | 6. E | 11. D | 16. C | 21. C |
| 2. C | 7. A | 12. A | 17. C | 22. D |
| 3. E | 8. D | 13. A | 18. C | 23. A |
| 4. C | 9. C | 14. D | 19. E | 24. C |
| 5. B | 10. D | 15. C | 20. C | 25. B |

See Appendix 1 for explanations of answers.

Free-Response

- (a) Sketch and label a potential energy diagram (reaction profile) and discuss its implications for chemical reactions. How does the addition of a catalyst alter the diagram? What effect will a change in temperature have?
- (b) Describe the collision theory.
- (c) Describe the transition-state theory.
- (d) How are rate laws and reaction mechanisms related?
- (e) Use the table of data below to determine the rate law for the reaction



Experiment Number	Concentration F (mol/L)	Concentration H (mol/L)	Initial Reaction Rate (mol/L s)
1	0.000345	0.000765	3.24×10^{-8}
2	0.000690	0.000765	3.24×10^{-8}
3	0.000537	0.00765	3.24×10^{-7}

- (f) Calculate the rate constant and give its units.

Important Concepts

Forms of energy
 Law of conservation of energy
 Hess's law
 Standard state
 Gibbs free energy, entropy, and enthalpy
 Spontaneous and nonspontaneous reactions

Important Equations

$$q = (\text{SPECIFIC HEAT}) (\text{MASS}) (\text{TEMPERATURE CHANGE})$$

$$q = (\text{HEAT CAPACITY}) (\text{TEMPERATURE CHANGE})$$

$$\Delta E = q - P\Delta V = q_v$$

$$\Delta H = q_p$$

$$S = k \ln w = q_{\text{rev}}/T$$

$$\Delta E = q + w$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G = \Delta G^\circ - RT \ln Q$$

$$\Delta G^\circ = -RT \ln K$$

Practice Exercises

Multiple-Choice

For the first four problems below, one or more of the following responses will apply; each response may be used more than once or not at all in these questions.

- I. ΔG°
- II. ΔS°
- III. ΔH°
- IV. ΔG
- V. H

1. Which of these must be negative for a reaction to be spontaneous?

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

2. Which of these cannot be determined?

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

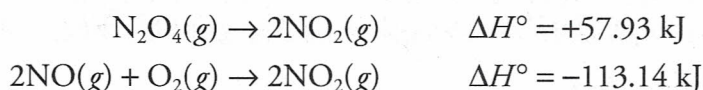
3. Which of these are extensive values?

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

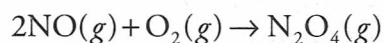
4. If _____ is negative and _____ is positive, a reaction will never be spontaneous.
- (A) II, III
(B) III, IV
(C) I, II
(D) IV, III
(E) I, V
-
5. When 0.400 g of CH_4 is burned in excess oxygen in a bomb calorimeter that has a heat capacity of $3245 \text{ J } ^\circ\text{C}^{-1}$, a temperature increase of $6.795 \text{ }^\circ\text{C}$ is observed. What is the value of q_v ?
- (A) 220 kJ mol^{-1}
(B) -882 kJ
(C) 477 kJ
(D) -22.05 kJ
(E) 8.820 kJ g^{-1}
6. Using the data in question 5, determine ΔH° for the combustion of methane.
- (A) $-22.05 \text{ kJ mol}^{-1}$
(B) -882 kJ
(C) $+22.05 \text{ kJ}$
(D) -8.820 kJ g^{-1}
(E) This value cannot be determined because w is not known.
7. Which of the following describes a system that CANNOT be spontaneous?
- (A) ΔH° is positive, and ΔS° is negative.
(B) ΔH° is positive, and ΔS° is positive.
(C) ΔH° is negative, and ΔS° is negative.
(D) ΔH° is negative, and ΔS° is positive.
(E) ΔH° is 0.00, and ΔS° is positive.
8. Which of the following explains the fact that, when KCl is dissolved, water condenses on the outside of the beaker?
- (A) ΔH° is positive, and ΔS° is negative.
(B) ΔH° is positive, and ΔS° is positive.
(C) ΔH° is negative, and ΔS° is negative.
(D) ΔH° is negative, and ΔS° is positive.
(E) ΔH° is 0.00, and ΔS° is negative.
9. The reaction with the greatest expected entropy decrease is
- (A) $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
(B) $\text{CH}_4(l) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
(C) $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
(D) $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(s) + 2\text{H}_2\text{O}(g)$
(E) $\text{CH}_4(l) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
10. Water boils at $100 \text{ }^\circ\text{C}$ with a molar heat of vaporization of $+43.9 \text{ kJ}$. At $100 \text{ }^\circ\text{C}$ what is the entropy change when water condenses?
- $$\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$$
- (A) Problem cannot be solved; ΔG° must also be known.
(B) Problem cannot be solved; this is not a chemical reaction.
(C) -439 J K^{-1}
(D) $+0.439 \text{ J K}^{-1}$
(E) -118 J K^{-1}

11. Which of the following will indicate if a given mixture of chemicals will react in the forward or in the reverse direction?
- (A) ΔG
 - (B) ΔG°
 - (C) ΔS°
 - (D) ΔH°
 - (E) ΔH
12. A gas is allowed to expand from an initial volume of 5.00 L and pressure of 3.00 atm to a volume of 15.0 L and pressure of 1.00 atm. What is the value of w ?
- (A) +30.0 L atm
 - (B) +10.0 L atm
 - (C) -45.0 L atm
 - (D) +15.0 L atm
 - (E) -10.0 L atm
13. In question 12 the units of work are given as L atm. To convert L atm to the metric unit of joules, we need to know
- (A) Avogadro's constant and Planck's constant
 - (B) the universal gas law constant in units of L atm mol⁻¹ K⁻¹
 - (C) the universal gas law constant in units of J mol⁻¹ K⁻¹
 - (D) both B and C
 - (E) A, B, and C
14. Which of the following is the LEAST probable for a combustion reaction?
- (A) ΔG° is a large negative number.
 - (B) ΔS° is a large negative number.
 - (C) ΔH° is a large negative number.
 - (D) K_{eq} is a large positive number.
 - (E) Q , the reaction quotient, is a small number.
15. Of the following, which can be precisely determined for a chemical substance?
- (A) entropy, S
 - (B) enthalpy, H
 - (C) free energy, G
 - (D) internal energy, E
 - (E) all of these
16. The heat of formation of $\text{CH}_3\text{OH}(l) = -238.6 \text{ kJ mol}^{-1}$, of $\text{CO}_2(g) = -393.5 \text{ kJ mol}^{-1}$, and of $\text{H}_2\text{O}(g) = -241.8 \text{ kJ mol}^{-1}$. What is ΔH° for the heat of combustion of methanol to gaseous products?
- (A) -396.7 kJ
 - (B) -1277 kJ
 - (C) -638.5 kJ
 - (D) +396.7 kJ
 - (E) This value cannot be calculated without the heat of formation for $\text{O}_2(g)$.
17. The rate of reaction will be large if
- (A) ΔG° is a large negative number
 - (B) ΔS° is a large negative number
 - (C) ΔH° is a large negative number
 - (D) K_{eq} is a large positive number
 - (E) None of the above can be used to estimate reaction rates

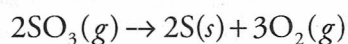
18. Given the following thermochemical data:



determine the heat of the reaction



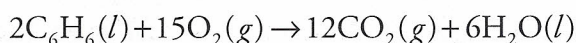
- (A) 171.07 kJ
 (B) -55.21 kJ
 (C) -171.07 kJ
 (D) +55.21 kJ
 (E) -85.54 kJ
19. Which of the following can change the value of ΔG° for a chemical reaction?
- (A) changes in the total pressure
 (B) changes in the pressures of the reactants
 (C) changes in the concentrations of the reactants
 (D) changes in the temperature in $^\circ\text{C}$
 (E) the presence of a catalyst
20. At what temperature is $K_{\text{eq}} = 1.00$ if $\Delta S^\circ = 22.6 \text{ J K}^{-1}$ and $\Delta H^\circ = 15.3 \text{ kJ}$ for a chemical reaction?
- (A) 404°C
 (B) 677°C
 (C) 0.67°C
 (D) 1477°C
 (E) 1204°C
21. The standard heat of formation of $\text{SO}_3(g)$ is -396 kJ mol^{-1} . The standard entropies of $\text{S}(s)$, $\text{O}_2(g)$, and $\text{SO}_3(g)$ are 31.8, 205.0, and $256 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Calculate the free energy for the decomposition of SO_3 in the reaction



at 25°C .

- (A) +396 kJ
 (B) -446 kJ
 (C) +346 kJ
 (D) -346 kJ
 (E) +742 kJ

22. The reaction



is expected to have

- (A) a positive ΔH and a negative ΔS
- (B) a negative ΔH and a negative ΔS
- (C) a positive ΔH and a positive ΔS
- (D) a negative ΔH and a negative ΔS
- (E) These predictions cannot be made.

CHALLENGE

23. The evaporation of any liquid is expected to have

- (A) a positive ΔH and a negative ΔS
- (B) a negative ΔH and a negative ΔS
- (C) a positive ΔH and a positive ΔS
- (D) a positive ΔH and a negative ΔS
- (E) These predictions cannot be made.

24. Which of the following is most likely to be true?

- (A) No products are formed in a nonspontaneous reaction.
- (B) A positive ΔG° indicates a spontaneous reaction.
- (C) A positive ΔS° always means that the reaction is spontaneous.
- (D) A spontaneous reaction always goes to completion.
- (E) Combustion of organic compounds has a negative ΔH° .

ANSWER KEY

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|------|-------|-------|-------|-------|
| 1. A | 6. B | 11. A | 16. B | 21. E |
| 2. E | 7. A | 12. E | 17. E | 22. B |
| 3. D | 8. B | 13. D | 18. C | 23. C |
| 4. A | 9. C | 14. B | 19. D | 24. E |
| 5. D | 10. E | 15. A | 20. A | |

See Appendix 1 for explanations of answers.

Free-Response

Answer the following questions using the concepts of thermodynamics and equilibrium and the methods for solving problems.

- (a) What parameters define whether or not a given reaction is spontaneous? Based on those parameters, what does it mean to say a reaction is spontaneous? What indicates if a mixture of chemicals will proceed in the forward direction or in the reverse direction?
- (b) What is the difference between E , ΔE , and ΔE° ?