

## JCC CEM 142 Phase I Problem Set

### IM forces

- List the three states of matter in order of (a) increasing molecular disorder and (b) increasing intermolecular attractions.
- How does the average kinetic energy of molecules compare with the average energy of attraction between molecules in solids, liquids, and gasses?
  - Why does increasing the temperature cause a substance to change in succession from a solid to a liquid to a gas?
  - Why does compressing a gas at constant temperature cause it to liquefy?
- Why are gases more compressible than liquids?
  - Why are liquid and solid forms of a substance referred to as condensed phases?
  - Why do liquids have a greater ability to flow than solids?
- Benzoic acid,  $C_6H_5COOH$ , melts at  $122^\circ C$ . The density in the liquid state at  $130^\circ C$  is  $1.08 g/mL$ . The density of solid benzoic acid at  $15^\circ C$  is  $1.266 g/mL$ .
  - In which of these two states is the average distance between molecules the greater?
  - Explain the difference in densities at the two temperatures in terms of the kinetic-molecular theory.
- Which type of intermolecular attractive force operates between
  - all molecules
  - polar molecules
  - the hydrogen atom of a polar bond and a nearby small electronegative atom
- Describe the intermolecular forces that must be overcome to convert each of the following from a liquid to a gas:
  - $Br_2$ , b.  $CH_3OH$ , c.  $H_2S$ .
- What type of intermolecular force accounts for the following differences in each case?
  - $CH_3OH$  boils at  $65^\circ C$ ,  $CH_3SH$  boils at  $6^\circ C$ .
  - Xe is liquid at atmospheric pressure and 120 K, whereas Ar is a gas.
  - Kr, atomic weight 84, boils at 120.9 K, whereas  $Cl_2$ , molecular weight about 71, boils at 238 K.
- Which member of the following pairs has the larger London dispersion forces:
  - $H_2O$  or  $H_2S$ , (b)  $CO_2$  or  $CO$ , (c)  $CH_4$  or  $SiH_4$ ?
- Rationalize the difference in boiling points between the members of the following pairs of substances: (a) HF ( $20^\circ C$ ) and HCl ( $-85^\circ C$ ), (b)  $CHCl_3$  ( $61^\circ C$ ) and  $CHBr_3$  ( $150^\circ C$ ) (c)  $Br_2$  ( $59^\circ$ ) and ICl ( $97^\circ C$ ).
- State the principal reasons why  $CH_4$  is a gas at room temperature, whereas  $H_2O$  is a liquid.
- Of the following substances, \_\_\_\_\_ has London dispersion forces as its only intermolecular force.  
 $CH_3OH$   $NH_3$   $H_2S$   $CH_4$   $HCl$
- Which one of the following should have the lowest boiling point? Why?  
 $PH_3$   $H_2S$   $HCl$   $SiH_4$   $H_2O$
- The strongest interparticle attractions exist between particles of a \_\_\_\_\_ and the weakest interparticle attractions exist between particles of a \_\_\_\_\_.
  - solid, liquid
  - solid, gas
  - liquid, gas
  - liquid, solid
  - gas, solid
- Large intermolecular forces in a substance are manifested by \_\_\_\_\_.
  - low vapor pressure
  - high boiling point
  - high heats of fusion and vaporization
  - high critical temperatures and pressures
  - all of the above
- London Dispersion Forces tend to \_\_\_\_\_ in strength with increasing molecular weight.
- Which of the following exhibits dipole-dipole attraction between molecules?  
 $XeF_4$   $AsH_3$   $CO_2$   $BCl_3$   $Cl_2$   $OCS$
- \_\_\_\_\_ are particularly polarizable.
  - Small nonpolar molecules
  - Small polar molecules
  - Large nonpolar molecules
  - Large polar molecules
  - Large molecules, regardless of their polarity,
- What is the predominant intermolecular force in  $CBr_4$ ?

13. In which of the following molecules is hydrogen bonding a component of the total intermolecular forces?

CH<sub>4</sub> C<sub>5</sub>H<sub>11</sub>OH C<sub>6</sub>H<sub>13</sub>NH<sub>2</sub> CH<sub>3</sub>OH CO<sub>2</sub>

18. The substance with the largest heat of vaporization is \_\_\_\_\_. Why?

I<sub>2</sub> Br<sub>2</sub> Cl<sub>2</sub> F<sub>2</sub> O<sub>2</sub>

19. Which one of these substances would you expect to be a gas at STP: NI<sub>3</sub>, BF<sub>3</sub>, PCI<sub>3</sub>, CH<sub>3</sub>CHOOH? Why?

21. Arrange the following substances in the expected order of increasing boiling point: H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, CH<sub>3</sub>CH<sub>3</sub>. Give the reasons for your ranking.

22. What is the most important intermolecular force involved at the freezing point of each of the following substances? What other intermolecular force(s) is are involved?

(a) CH<sub>3</sub>CH<sub>2</sub>OH (b) CH<sub>3</sub>CH<sub>2</sub>Cl (c) HCOONa

23. The boiling points of pure HCl, HBr, and HI (Not the aqueous solutions) are -85 °C, -67 °C, and -35 °C, and -35 °C, respectively. How do the relative strengths of the different types of intermolecular forces in these three gases compare? Explain.

24. As the intermolecular attractive forces between molecules increase in magnitude, do you expect each of the following to increase in magnitude, do you expect each of the following to increase or decrease in magnitude?

(a) vapor pressure, (b) heat of vaporization, (c) viscosity, (d) freezing point ; (f) surface tension (g) critical temperature

### Viscosity/adhesion/cohesion

25. What determines the shape of a meniscus and whether it is convex or concave?

26. Explain the following observations: (a) the surface tension of CHBr<sub>3</sub> is greater than that of CHCl<sub>3</sub> (b) As temperature increases, oil flows faster through a narrow tube. (c) Raindrops that collect on a waxed automobile hood take on a nearly spherical shape.

### Phase Changes

27. Which phase changes are exothermic?

28. The heat of fusion of water is 6.01 kJ/mol. The heat capacity of liquid water is 75.3 J/mol · K. The conversion of 50.0 g of ice at 0.00°C to liquid water at 22.0°C requires \_\_\_\_\_ kJ of heat.

29. Explain why the heat of fusion of any substance is generally lower than its heat of vaporization.

31. For many years drinking water has been in hot climates by evaporating it from the surface of canvas bags or porous clay pots how many grams of water can be cooled from 35°C to 22°C by the evaporation of 50g of water? (The heat of vaporization of water in this temperature range is 2.4 kJ/g. The specific heat of water is 4.18 J/g-K.)

32. Ethanol (C<sub>2</sub>H<sub>5</sub>OH) melts at -114°C and boils at 78°C. The enthalpy of fusion of ethanol is 5.02 kJ/ mol, and its enthalpy of vaporization is 38.56 kJ/ mol. The specific heats of solid and liquid ethanol are 0.97 J/g-K, respectively. How much heat is required to convert 75.0 g of ethanol at -120°C to the vapor phase at 78°C?

33. A 0.506-kg chunk of ice at 0.0 °C is added to an insulated container holding 315 mL of water at 20.2 °C. Will any ice remain after thermal equilibrium is established?

34. The fluorocarbon C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> has a normal boiling point of 47.6°C. The specific heats of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> (l) and C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> (g) are 0.91 J/g-K and 0.67 J/g-K, respectively. The heat of vaporization of the compound is 27.49 kJ/mol. The heat required to convert 50.0 g of the compound from the liquid at 5.0°C to the gas at 80.0°C is \_\_\_\_\_ kJ.

35. Ethanol (C<sub>2</sub>H<sub>5</sub>OH) melts at -114°C. The enthalpy of fusion is 5.02 kJ/mol. The specific heats of solid and liquid ethanol are 0.97 J/g-K and 2.3 J/g-K, respectively. How much heat (kJ) is needed to convert 25.0 g of solid ethanol at -135°C to liquid ethanol at -50°C? 34.

36. Heat of sublimation can be approximated by adding together \_\_\_\_\_ and \_\_\_\_\_.

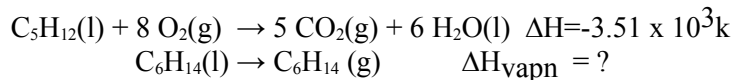
37. As a solid element melts, the atoms become \_\_\_\_\_ and they have \_\_\_\_\_ attraction for one another.

A) more separated, more B) more separated, less C) closer together, more D) closer together, less E) larger, greater

38. The fluorocarbon compound C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> has a normal boiling point of 47.6 °C. The specific heats of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>(l) and C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>(g) are 0.91 J/g-k and 0.67 J/g-K, respectively the heat of vaporization for the compound is 27.49 kJ/ mol. Calculate the heat required to convert 25.0 g of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> from a liquid at 5.00°C to a gas at 82.00°C.

39. How many grams of propane must be burned to supply the heat required to vaporize 6.75 L of water at 298 K?

41. The combustion of 1.25 g of pentane produces just enough heat to vaporize 165 g of hexane. What is the molar enthalpy of vaporization of hexane?



42. The table shown here lists the molar heats of vaporization for several organic compounds. Use specific examples from this list to illustrate how the heat of vaporization varies with (a) molar mass, (b) molecular shape, (c) molecular polarity, (d) hydrogen-bonding interactions. Explain these comparisons in terms of the nature of the intermolecular forces at work. (You may find it helpful to draw out the structural formula for each compound.)

Compound	Heat of Vaporization (kJ/mol)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	19.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	27.6
CH <sub>3</sub> CHBrCH <sub>3</sub>	31.8
CH <sub>3</sub> COCH <sub>3</sub>	32.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	33.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	47.3

43. You can hold your hand in an oven at 100°C for some time without feeling great discomfort. However, you can hold your hand a centimeter or two above rapidly boiling water in a kettle for only a second or less. Explain why the effects are different.

44. The following data are for CCl<sub>4</sub>: normal melting point, -23°C; normal boiling point, 77 °C; density of liquid, 1.59 g/mL; heat of fusion, 3.28 kJ/mol; vapor pressure at 25.0 °C, 110 mmHg. (a) How much heat must be absorbed to convert 10.0 g of solid CCl<sub>4</sub> to liquid at -23 °C? (b) What volume is occupied by 1.00 mol of the saturated vapor at 77 °C? (c) What phases (solid, liquid, and/or vapor) are present if 3.5 g CCl<sub>4</sub> is kept in an 8.21 – L volume at 25.0 °C?

45. An ice cube with a mass of 25.5 g at a temperature of 0.0 °C is added to 125 mL of water at 26.5 °C in an insulated container. What will be the final temperature after the ice has melted?

### Vapor Pressure

40. Explain how each of the following affects the vapor pressure of a liquid: (a) volume of a liquid, (b) surface area, (c) intermolecular attractive forces, (d) temperature.

46. a. Place the following substances in order of increasing volatility:

CH<sub>4</sub>, CBr<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, CHBr<sub>3</sub>, and CH<sub>2</sub>Br<sub>2</sub>. Explain.

b. How do the boiling points vary through this series?

47. a. Two pans of water are on different burners of a stove. One pan of water is boiling vigorously, while the other is boiling gently. What can be said about the temperature of the water in the two pan areas?

b. A large container of water and a small one are at the same temperature. What can be said about the relative vapor pressures of the water in the two containers?

48. Suppose you have two colorless molecular liquids, one boiling at -84°C, the other at 34°C, and both at atmospheric pressure. Which of the following statements is correct for those that are not correct, modify the statements is correct? For those that are not correct, modify the statement so that it is correct.

a. The higher-boiling liquid has greater total intermolecular forces than the other.

b. The lower boiling liquid must consist of no polar molecules.

c. The lower-boiling liquid has a lower molecular weight than the higher-boiling liquid

d. the two liquids have identical vapor pressures at their normal boiling points

e. at 34°C both liquids have vapor pressures of 760 mm Hg.

49. Equilibrium is established between a small quantity of Cl<sub>4</sub>(l) and its vapor at 40.0°C in a flask having a volume of 285mL. The total mass of vapor present is 0.480 g. What is the vapor pressure of CCl<sub>4</sub>, in mmHg, at 40.0°C?

51. A 0.625-g sample of methanol is injected into a 8.77-L flask at 0°C. At equilibrium, what phase(s) of methanol will be present, that is, solid and/or liquid and/or vapor? Explain.

52. Suppose the vapor pressure of a substance is measured at two different temperatures.

a. By using the Clausius-Clapeyron equation, derive the following relationship between the vapor pressures, P<sub>1</sub> and P<sub>2</sub>, and the

absolute temperatures at which they were measured,  $T_1$  and  $T_2$ :

b. The melting point of potassium is  $63.2^\circ\text{C}$ . Molten potassium has a vapor pressure of 10.00 torr at  $443^\circ\text{C}$  and a vapor pressure of 400.0 torr at  $708^\circ\text{C}$ . Use these data and the equation in part (a) to calculate the heat of vaporization of liquid potassium.

c. By using the equation in part (a) and the data given in part (b), calculate the boiling point of potassium.

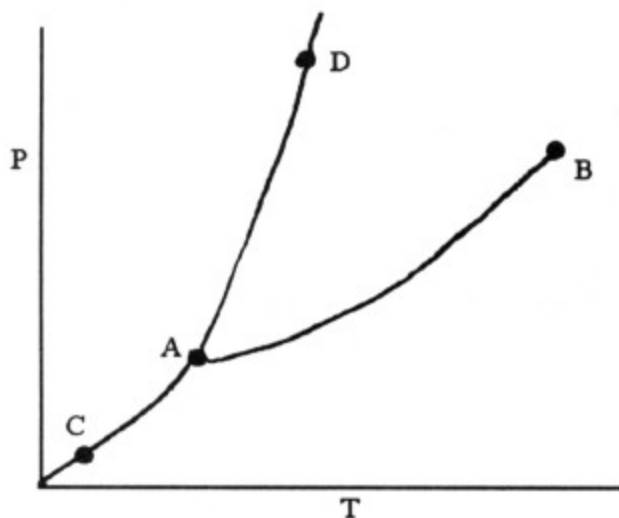
d. Calculate the vapor pressure of liquid potassium at  $100^\circ\text{C}$ .

53. When an atom or group of atoms is substituted for an H atom in benzene ( $\text{C}_6\text{H}_6$ ), the boiling points:  $\text{C}_6\text{H}_5\text{Cl}$  ( $132^\circ\text{C}$ ),  $\text{C}_6\text{H}_5\text{Br}$  ( $156^\circ$ ),  $\text{C}_6\text{H}_5\text{OH}$  ( $182^\circ$ ).

54. a. When you exercise vigorously, you sweat. How does this help your body cool?

b. A flask of water is connected to a vacuum pump. A few moments after the pump is turned on, the water begins to boil. After a few minutes, the water begins to freeze. Explain why these processes occur.

### Phase Diagrams



55. On the phase diagram above, segment \_\_\_\_\_ corresponds to the conditions of temperature and pressure under which the solid and the gas of the substance are in equilibrium.

AB AC AD CD BC

56. On the phase diagram shown, the coordinates of point \_\_\_\_\_ correspond to the critical temperature and pressure.

57. If the triple-point pressure of a substance is greater than 1 atm, we expect which of the following?

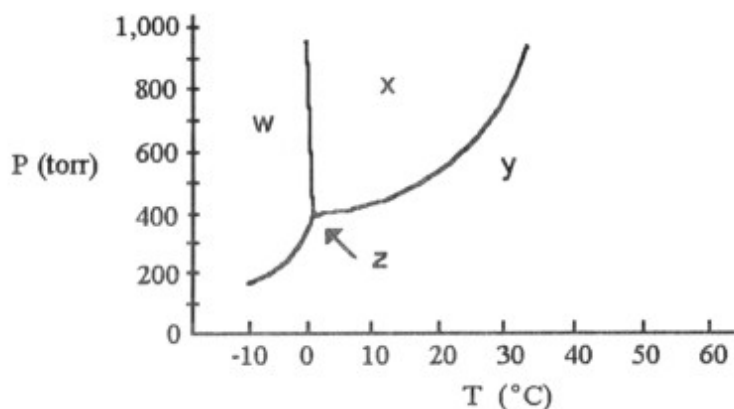
(a) the solid to sublime without melting

(b) the boiling-point temperature to be lower than triple-point temperature

(c) the melting point of the solid to come at a lower temperature than the triple point

(d) that the substance cannot exist as a liquid

58. Using the phase diagrams in your text as a guide, sketch a phase diagram and label four points, W, X, Y, and Z, so that (a) the transition from W to X is from liquid to solid at constant temperature; (b) the transition from X to Y is from solid to gas at constant pressure; (c) the transition from Y to Z involves no phase change, although both temperature and pressure change.



59. The phase diagram of a substance is given above. The region that corresponds to the solid phase is \_\_\_\_\_.

61. The phase diagram of a substance is shown above. The area labeled \_\_\_\_\_ indicates the gas phase for the substance.
62. According to the phase diagram shown above, the normal boiling point of this substance is \_\_\_\_\_ °C.
63. What is significant about point z?
64. Refer to a phase diagram for water, and describe all the phase changes that would occur in each of the following cases:
- Water vapor originally at  $1.0 \times 10^{-3}$  atm and  $-0.10^\circ\text{C}$  is slowly compressed at constant T until the final pressure is 10 atm.
  - Water originally at  $100.0^\circ\text{C}$  and 0.50 atm is cooled at constant pressure until the temperature is  $-10^\circ\text{C}$ .
65. Refer to a phase diagram for carbon dioxide, and describe the phase changes (and the temperatures at which they occur) when  $\text{CO}_2$  is heated from  $-80^\circ\text{C}$  to  $-20^\circ\text{C}$  at
- a constant pressure of 3 atm,
  - a constant pressure of 6 atm.
66. The normal melting and boiling points of  $\text{O}_2$  are  $-218^\circ\text{C}$  and  $-183^\circ\text{C}$ , respectively. Its triple point is at  $-219^\circ\text{C}$  and 1.14 torr, and its critical point is at  $-119^\circ\text{C}$  and 49.8 atm.
- Sketch the phase diagram for  $\text{O}_2$ , showing the four points given and indicating the area in which each phase is stable.
  - Will  $\text{O}_2(\text{s})$  float on  $\text{O}_2(\text{l})$ ? Explain.
  - As it is heated, will solid  $\text{O}_2$  sublime or melt under a pressure of 1 atm?

### Bonding in Solids

67. Which type (or types) of crystalline solid is characterized by each of the following :
- high mobility of electrons throughout the solid;
  - softness, relatively low melting point;
  - high melting point and poor electrical conductivity;
  - network of covalent bonds;
  - charged particles throughout the solid.
68. A white substance melt with some decomposition at  $730^\circ$ . As a solid, it is a nonconductor of electricity, but it dissolves in water to form a conducting solution. Which type of solid might the substance be?
69. For each of the following pairs of substances, predict which will have the higher melting point and indicate why:
- Ar, Xe;
  - $\text{SiO}_2$ ,  $\text{CO}_2$ ;
  - KBr,  $\text{Br}_2$ ;
  - $\text{C}_6\text{Cl}_6$
71. For each of the following pairs of substances, predict which will have the higher melting point, and indicate why; (a) HF, HCl; (b) C (graphite),  $\text{CH}_4$ ; (c) KBr,  $\text{Br}_2$ ; (d) LiF,  $\text{MgF}_2$

### Solutions/Solvation Processes

72. Indicate the type of solute –solvent interaction that should be most important in each of the following solutions:
- $\text{CCl}_4$  in benzene ( $\text{C}_6\text{H}_6$ ),
  - methanol ( $\text{CH}_3\text{OH}$ ) in water,
  - KBr in water,
  - HCl in acetonitrile ( $\text{CH}_3\text{CN}$ )
73. The solubility of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in water is 208 g per 100 g of water at  $15^\circ\text{C}$ . A solution of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in water at  $35^\circ$  is formed by dissolving 324 g in 100 water. When this solution is slowly cooled to  $15^\circ\text{C}$ , no precipitate forms (a) What term describes this solution? (b) What action might you take to initiate crystallization? Use molecular-level processes to explain how your suggested procedure works.
74. The solubility of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in water at  $20^\circ\text{C}$  is 70 g per 100 mL of water
- is a 1.22 M solution of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in water at  $20^\circ\text{C}$  saturated supersaturated or unsaturated?
  - Given a solution of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  of unknown concentration, what experiment could you perform to determine whether the new solution is saturated, supersaturated or unsaturated?
75. Which one of the following substances is more likely to dissolve in  $\text{CCl}_4$  ?
- A)  $\text{CBr}_4$     B) HBr    C) HCl    D)  $\text{CH}_3\text{CH}_2\text{OH}$     E) NaCl
76. Which of the following in each pair is likely to be more soluble in hexane  $\text{C}_6\text{H}_{14}$ :
- $\text{CCl}_4$  or  $\text{CaCl}_2$ ;
  - benzene ( $\text{C}_6\text{H}_6$ ) or glycerol,  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ;
  - octanoic acid,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ , or acetic acid,  $\text{CH}_3\text{COOH}$ . Explain your answer in each case.

### Solubility

77. The solubility of a nonreactive gas in water increases with which of the following?
- an increase in temperature
  - an increase in gas pressure

(c) increase both in temperature and gas pressure (d) an increase in the V of gas in equilibrium with available water.

78. The solubility of oxygen gas in water at 25 °C and 1.0 atm pressure of oxygen is 0.041 g/L The solubility of oxygen in water at 3.0 atm and 25 °C is \_\_\_\_\_ g/L.

79. In a saturated solution of a salt in water, \_\_\_\_\_.

- A) the rate of crystallization > the rate of dissolution
- B) the rate of dissolution > the rate of crystallization
- C) seed crystal addition may cause massive crystallization
- D) the rate of crystallization = the rate of dissolution
- E) addition of more water causes massive crystallization

81. The principal reason for the extremely low solubility of NaCl in benzene (C<sub>6</sub>H<sub>6</sub>) is the \_\_\_\_\_.

- A) strong solvent-solvent interactions
- B) hydrogen bonding in C<sub>6</sub>H<sub>6</sub>
- C) strength of the covalent bond in NaCl
- D) weak solvation of Na<sup>+</sup> and Cl<sup>-</sup> by C<sub>6</sub>H<sub>6</sub>
- E) increased disorder due to mixing of solute and solvent

82. Pressure has an appreciable effect on the solubility of \_\_\_\_\_ in liquids.

- A) gases B) solids C) liquids D) salts E) solids and liquids

83. The solubility of CO<sub>2</sub> (g) pressure is maintained at 1 atm. What id the concentration of CO<sub>2</sub>(g) pressure id maintained at 1atm. What is the concentration of CO<sub>2</sub> in water that is saturated with air at 20<sup>0</sup>C? Express this concentration as mL CO<sub>2</sub> (STP)/100 g water. Use the fact that the mole percent of CO<sub>2</sub> in air is 0.037%.

### Henry's Law

84. The solubility of O<sub>2</sub>(g) in water is 4.43 mg O<sub>2</sub>/100g H<sub>2</sub>o at 20<sup>0</sup>C and a gas pressure of 1 atm.

- a. What id the molarities of the saturated solution?
- b. What pressure of O<sub>2</sub> (g) would be required to produce a saturated solution that is 0.010 M O<sub>2</sub>?

85. The Henry's law constant for helium gas in water at 30 °C is  $3.70 \times 10^{-4}$  M/atm. When the partial pressure of helium above a sample of water is 0.650 atm, the concentration of helium in the water is \_\_\_\_\_ M.

### Units of Concentration

86. Explain why morality is temperature dependent, whereas morality is not. Is mole fraction temperature- dependent? Is volume percent? Is mass percent?

87. Describe how you would prepare 2.30 kg of an aqueous solution that is 4.85 % NaNO<sub>3</sub>by mass.

88. A solution is prepared by dissolving 23.7 g of CaCl<sub>2</sub> in 375 g of water. The density of the resulting solution is 1.05 g/mL. The concentration of CaCl<sub>2</sub> is \_\_\_\_\_% by mass.

89. The concentration of urea in a solution prepared by dissolving 16 g of urea in 39 g of H<sub>2</sub>O is \_\_\_\_\_% by mass. The molar mass of urea is 60.0 g/mol.

91. A solution is prepared by dissolving calcium chloride in water and diluting to 500.0 mL. If this solution contains 44 ppm chloride ions, the concentration of calcium ions is \_\_\_\_\_ ppm.

92. The concentration of KBr in a solution prepared by dissolving 2.21 g of KBr in 897 g of water is \_\_\_\_\_ m.

93. The concentration of lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) in a 0.726 M solution is \_\_\_\_\_ molal. The density of the solution is 1.202 g/mL.

94. A solution is prepared by dissolving 16.2 g of benzene (C<sub>6</sub>H<sub>6</sub>) in 282 g of carbon tetrachloride (CCl<sub>4</sub>)  
The concentration of benzene in this solution is \_\_\_\_\_ molal. The molar masses of C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub> are 78.1 g/mol and 154 g/mol, respectively.

95. At 20°C, a 3.54 M aqueous solution of ammonium chloride has a density of 1.0512 g/mL. What is the mass % of ammonium chloride in the solution? The formula weight of  $\text{NH}_4\text{Cl}$  is 53.50 g/mol.
96. The mole fraction of He in a gaseous solution prepared from 4.0 g of He, 6.5 g of Ar, and 10.0 g of Ne is \_\_\_\_\_.
97. What is the molarity of sodium chloride in solution that is 13.0% by mass NaCl and that has a density of 1.10 g/mL?
98. What is the mass percent of solution in each of the following solutions?
- 175 mg NaCl/g solution
  - 4.5 L ethylene glycol ( $d=1.114$  g/mL) in 6.5 L propylene glycol ( $d=1.036$  g/mL)
  - 4.12 g NaOH/100.0 g  $\text{H}_2\text{O}$
  - 5.00 mL ethanol ( $d=0.789$  g/mL) in 50.0 g  $\text{H}_2\text{O}$
99. What is the volume percent of the first named component in each of the following solutions?
- 58.0 mL water in 625 mL of an ethanol- water solution
  - 10.00 g methanol ( $d=0.791$  g/mL) in 75.00 g ethanol ( $d=0.789$  g/mL). Assume V is additive
  - 24.0 % by mass ethanol ( $d=0.789$  g/mL) in an aqueous solution with  $d=0.963$  g/mL
101. Express the following aqueous concentrations in the unit indicated.
- 1  $\mu\text{g}$  benzene/ L water; as ppb benzene
  - 0.0035% NaCl, by mass, as ppm of NaCl
  - 2.4 ppm  $\text{F}^-$ , as molarity of fluoride ion,  $[\text{F}^-]$
102. A solution of KCl in water has a concentration of 260 ppm KCl. What is the concentration in (a) ppm (b) molality . What further information would you need to determine the molarity of the solution?
103. An aqueous solution is prepared by diluting 3.30 mL acetone,  $\text{CH}_3\text{COCH}_3$  ( $d=0.789$  g/mL) with water to a final volume of 75.0 mL. The density of the solution is 0.993 g/mL. What are the molarity and molality of acetone in this solution?
104. What mass sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , must be dissolved per liter of water ( $d=0.995$  g/mL) to obtain a solution with 2.50 mole percent  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ?
105. How many moles of ethylene glycol are present in 2.30 L of 6.27 m  $\text{HOCH}_2\text{CH}_2\text{OH}$  ( $d=1.035$  g/mL)?
106. Commercial (aq) nitric acid has a density of 1.42 g/mL and is 16 M. Calculate the %  $\text{HNO}_3$  by mass in the solution.
107. Commercial concentrated (aq) ammonia is 28%  $\text{NH}_3$  by mass and has a  $d=0.90$  g/mL. What is the molarity of this solution?
108. A dilute sulfuric acid solution that is 3.39 m  $\text{H}_2\text{SO}_4$  has a density of 1.18 g/mL. How many moles of  $\text{H}_2\text{SO}_4$  are there in 375 mL of this solution?
- 109.. What is the molarity of each of the following solutions:
- 25.0 g  $\text{Al}_2(\text{SO}_4)_3$  in 0.350 L solution
  - 5.25 g  $\text{Mn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 175 mL of solution
  - 35.0 mL of 9.00M  $\text{H}_2\text{SO}_4$  diluted to 0.500 L
111. Ascorbic acid (vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) is a water soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g water has a density of 1.22 g/mL at 55°C. Calculate. (a) The mass percentage, (b) the molarity of ascorbic acid in this solution.
112. Calculate the molarity of each of the following solutions:
- 8.66 g benzene ( $\text{C}_6\text{H}_6$ ) dissolved in 23.6 g carbon tetrachloride ( $\text{CCl}_4$ ),
  - 4.80 g NaCl dissolved in 0.350 L of water.
113. What is the mole fraction of naphthalene,  $\text{C}_{10}\text{H}_8$ , in
- a solution prepared by dissolving 23.5 g  $\text{C}_{10}\text{H}_8(\text{s})$  in 375 g benzene  $\text{C}_6\text{H}_6(\text{l})$
  - a 0.250 m solution of  $\text{C}_{10}\text{H}_8$  in  $\text{C}_6\text{H}_6$ ?
114. Without doing detailed calculations, which of the following aqueous solutions has the greatest mole fraction of solute:
- (a) 1.00 m  $\text{CH}_3\text{OH}$       (b) 5.0%  $\text{CH}_3\text{CH}_2\text{OH}$ , by mass      (c) 10.0%  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , by mass. Explain.

### **Raoult's Law/V.P.**

115. A solution has 1:4 mole ratio of pentane of hexane. The vapor pressures of the pure hydrocarbons of 20°C are 441 mmHg from pentane and 121 mmHg for hexane (a) what are the partial pressures of the two hydrocarbons above the solution? (b) What is the mole fraction composition of the vapor?

116. The vapor pressure of pure ethanol at 60 °C is 0.459 atm. Raoult's Law predicts that a solution prepared by dissolving 10.0 mmol naphthalene (nonvolatile) in 90.0 mmol ethanol will have a vapor pressure of \_\_\_\_\_ atm.

117. The vapor pressure of pure water at 25 °C is 23.8 torr. What is the vapor pressure (torr) of water above a solution prepared by dissolving 18.0 g of glucose (a nonelectrolyte, MW = 180.0 g/mol) in 95.0 g of water?

118. A 0.100 m solution of which one of the following solutes will have the lowest vapor pressure?

A)  $\text{KClO}_4$  B)  $\text{Ca}(\text{ClO}_4)_2$  C)  $\text{Al}(\text{ClO}_4)_3$  D) sucrose E) NaCl

119. A solution has a 2:3 mass ratio of toluene ( $\text{C}_7\text{H}_8$ ) to benzene ( $\text{C}_6\text{H}_6$ ). The vapor pressures to toluene and benzene at 25°C are 28.4 mmHg and 95.1 mmHg, respectively, (a) What are the partial pressures of the two hydrocarbons above the solution? (b) What is the mole fraction composition of the vapor?

121. A solution contains 150.8 grams of NaCl in 678.3 grams of water. Calculate the vapor pressure lowering (in torr) of the solution at 25.0 °C. (Note: the vapor pressure of pure water at 25.0 °C is 23.76 torr.)

122. Explain why carbonated beverages must be stored in sealed containers. (b) Once the beverage has been opened, why does it maintain more carbonation when refrigerated than at room temperature?

### Colligative Properties (BP↑, FP↓)

123. What is colligative property? Name two properties of a solution that are not colligative. What are the chief colligative properties discussed in this chapter? Is the density of a solution a colligative property? Explain.

124. The freezing point of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is -114.6 °C. The molal freezing point depression constant for ethanol is 2.00 °C/m. What is the freezing point (°C) of a solution prepared by dissolving 50.0 g of glycerin ( $\text{C}_3\text{H}_8\text{O}_3$  a nonelectrolyte) in 200 g of ethanol?

125. Calculate the freezing point (0°C) of a 0.05500 m aqueous solution of  $\text{NaNO}_3$ . The molal freezing-point-depression constant of water is 1.86 °C/m.

126. George is making spaghetti for dinner. He places 4.01 kg of water in a pan and brings it to a boil. Before adding the pasta, he adds 58 g of table salt to the water and again brings it to a boil. The temperature of the salty, boiling water is \_\_\_\_\_ °C. It is a nice day at sea level so that pressure is 1.00 atm. Assume negligible evaporation of water.  $K_b$  for water is 0.52°C/m.

127. The freezing point will be depressed most by dissolving which of the following in 250.0 grams of water?  
(a) 25.0 g  $\text{CH}_3\text{OH}$  (b) 30.0 g  $\text{CH}_3\text{CH}_2\text{OH}$  (c) 35.0 g  $\text{C}_6\text{H}_{12}\text{O}_6$

128. As the concentration of a solute in a solution increases, the freezing point of the solution \_\_\_\_\_ and the vapor pressure of the solution \_\_\_\_\_.

A) increases, increases B) increases, decreases C) decreases, increases  
D) decreases, decreases E) decreases, is unaffected

129. Which of the following liquids will have the lowest freezing point?

A) pure  $\text{H}_2\text{O}$  B) aqueous glucose (0.60 m) C) aqueous sucrose (0.60 m)  
D) aqueous  $\text{FeI}_3$  (0.24 m) E) aqueous KF (0.50 m)

131. Arrange the following aqueous solutions in order of decreasing freezing point, and state your reasons:

(a) 0.15 m  $\text{CH}_3\text{COOH}$ , (b) 0.15 m  $\text{CO}(\text{NH}_2)_2$  (urea), (c) 0.10 m  $\text{H}_2\text{SO}_4$  (d) 0.10 m  $\text{Mg}(\text{NO}_3)_2$ , (e) 0.15 m  $\text{H}_2\text{SO}_4(\text{aq})$

132. Coniferin, a sugar derivative found in conifers such as fir trees, has a composition of 56.13% C, 6.48% H, and 37.39% O, by mass. A 2.216-g sample is dissolved in 48.68 g of  $\text{H}_2\text{O}$ , and the solution is found to have a boiling point of 100.068 °C. What is the molecular formula of coniferin?

133. Physical properties of a solution that depend on the quantity of the solute particles present, but not the kind or identity of the particles, are termed \_\_\_\_\_ properties.

134. A 1.684-g sample of an unknown oxygen derivative of a hydrocarbon yields 3.364 g CO<sub>2</sub> and 1.377 g H<sub>2</sub>O upon complete combustion. A 0.0605-g sample of the same compound dissolved in 34.89 g water lowers the freezing point of the water to -0.244 °C. What is molecular formula of the compound?

135. How does increasing the concentration of a nonvolatile solute in water affect the following properties (a) vapor pressure (b) freezing point (c) boiling point; (d) osmotic pressure?

136. Consider two solution one formed by adding 10 g of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) to 1 L of water and the other formed by adding 10 g of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>12</sub>) to 1 L of water. Are the vapor pressures over the two solutions the same? Why or why not?

137. A solution is prepared by dissolving 7.00 g of glycerin (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) in 201 g of ethanol (C<sub>2</sub>H<sub>5</sub>OH). The freezing point of the solution is \_\_\_\_\_ °C. The freezing point of pure ethanol is -114.6 °C at 1 atm. The molal-freezing-point-depression constant (K<sub>f</sub>) for ethanol is 1.99 °C/m. The molar masses of glycerin and of ethanol are 92.1 g/mol and 46.1 g/mol, respectively.

139. a. Why does a 0.10 m aqueous solution of NaCl have higher boiling point than a 0.10 m aqueous solution of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>?  
b. Calculate the boiling point of each solution  
c. The experimental boiling point of the NaCl solution is lower than that calculated, assuming that NaCl is completely dissociated in solution. Why is this the case?

141. The osmotic pressure of 0.010 M aqueous solution of CaCl<sub>2</sub> is found to be 0.674 atm at 25°C

a. Calculate the van't Hoff factor *i* for the solution.  
b. How would you expect the value of *i* to change as the solution becomes more concentrated? Explain.

### Osmotic Pressure

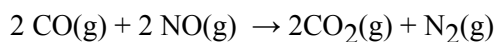
142. For each pair of solution at 25°C, indicate which member has the higher osmotic pressure. (a) 0.1 M NaHCO<sub>3</sub>, 0.05 M NaHCO<sub>3</sub> (b) 1 M NaCl, 1 M glucose (c) 1 M NaCl, 1 M glucose (c) 1 M CaCl<sub>2</sub> (d) 1 M NaCl, 3 M glucose

143. Osmotic pressure exerted by a 0.325-g sample of the polymer polystyrene in 50.00 mL of benzene at 25°C is capable of supporting a column of the solution (d=0.88g/mL) 5.3 mm in height. What is the molar mass of the polystyrene? (Hint: What is the height of mercury [d=13.6 g/mL] equivalent to that of the polymer solution?)

144. What is the osmotic pressure (in atm) of a 0.040 M solution of a non-electrolyte at 30.0 °C?

### Rxn Rates

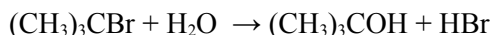
145. Explain why the rate of disappearance of NO and the rate of formation of N<sub>2</sub> are not the same in the reaction:



146. a. What is meant by the term reaction rate?  
b. Name three factors that can affect the rate of a chemical reaction.  
c. What information is necessary to relate the rate of disappearance of reactants to the rate of appearance of products?

147. a. What are the units usually used to express the rates of reactions occurring in solution?  
b. From your everyday experience, give two examples of the effects of temperature on the rates of reactions.  
c. What is the difference between average rate and instantaneous rate?

148. The conversion of tert-butyl bromide to tert-butyl alcohol is achieved in the first-order reaction



The half-life of this reaction is 14.1 h at 25°C and 48.8 min at 50°C. How long will it take for this conversion to go to 90% completion at 65°C?

149. You perform a series of experiments for the reaction A → B + C and find the rate law has the form of rate = k[A]<sup>x</sup>. Determine the value of *x* in the following cases:

a. There is no rate change when [A] is tripled  
b. The rate increases by a factor of 9 when [A] is tripled  
c. When [A] is double, the rate increases by a factor of 8.

151. Consider the following hypothetical aqueous reaction: A(aq) → B(aq). A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected:

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	.031

- a. Calculate the number of moles of B at each time in the table, assuming that there are no molecules of B at time zero. b. Calculate the average rate of disappearance of A for each 10-min interval, in units of M/s. c. Between  $t = 10$  min and  $t = 30$  min, what is the average rate of appearance of B in units of M/s? Assume that the volume of the solution is constant.

152. For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product of disappearance of each reactant:

- (a)  $2 \text{HBr(g)} \rightarrow \text{H}_2\text{(g)} + \text{Br}_2\text{(g)}$   
 (b)  $2 \text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{SO}_3\text{(g)}$   
 (c)  $2 \text{NO(g)} + 2 \text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$

153. Consider the combustion of ethylene,  $\text{C}_2\text{H}_4\text{(g)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$ . If the concentration of  $\text{C}_2\text{H}_4$  is decreasing at the rate of 0.37 M/s, what are the rates of change in the concentrations of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ?

154. That rate of decrease in  $\text{N}_2\text{H}_4$  partial pressure in a closed reaction vessel from the reaction  $\text{N}_2\text{H}_4\text{(g)} + \text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$  is 63 torr/h. What are the rates of change of  $\text{NH}_3$  partial pressure and total pressure in the vessel?

### Rate Laws/ Orders of Rxn

155. For the second  $\text{A} \rightarrow$  products, a plot of  $[\text{A}]$  versus time is found to be a straight line. The order of this rxn is

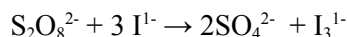
- (a) first (b) second (c) zero (d) impossible to determine from this graph

156. The reaction  $2 \text{A} + \text{B} \rightarrow \text{C} + 2 \text{D}$  is first order in A and first order in B. For this reaction

- (a) rate of reaction =  $k[\text{A}]^2[\text{B}]$  (b) rate of reaction =  $k[\text{A}]^2$   
 (c) rate of disappearance of A = rate of disappearance of B (d) rate of formation of C = -(rate of disappearance of B)

157. In the reaction  $\text{A} + 2\text{B} \rightarrow \text{C} + 3 \text{D}$ , the rate of disappearance of B is  $-6.2 \times 10^{-4} \text{ M s}^{-1}$ . What is (a) the rate of disappearance of A? (b) The rate of formation of D?

158. The rate of the following reaction in aqueous solution is monitored by measuring the rate of formation of  $\text{I}_3^-$ . Data obtained are listed in the table.



Experiment	$[\text{S}_2\text{O}_8^{2-}], \text{M}$	$[\text{I}^-]$	Initial Rate, $\text{M s}^{-1}$
1	0.038	0.060	$1.4 \cdot 10^{-5}$
2	0.076	0.060	$2.8 \cdot 10^{-5}$
3	0.076	0.120	$5.6 \cdot 10^{-5}$

(a) Determine the order of the reaction with respect to  $\text{S}_2\text{O}_8^{2-}$ , with respect to  $\text{I}^-$ , and the overall.

(b) What is the value of the rate of constant K?

(c) What would be the initial rate of reaction if  $[\text{S}_2\text{O}_8^{2-}] = 0.083 \text{ M}$  and  $[\text{I}^-] = 0.115 \text{ M}$ ?

159. In the reaction  $\text{A} \rightarrow$  products, we find that when  $[\text{A}]$  has fallen to half its initial value, the reaction proceeds at the same rate as its initial rate. Is the reaction zero order, first order, or second order? Explain.

161. The half-life circle for the first-order decomposition of sulfuryl chloride at 320. C is 8.75 h.



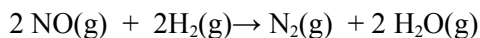
162.a) A reaction  $\text{A} + \text{B} \rightarrow \text{C}$  obeys the following rate law:  $\text{Rate} = k[\text{B}]^2$ . (a) If  $[\text{A}]$  is doubled, how will the rate change? Will the rate constant change? Explain. (b) What are the reaction orders for A and B? What is the overall reaction order? (c) What are the units of the rate constant?

163. For the reaction  $\text{A} \rightarrow 2\text{B} + \text{C}$ , the following data are obtained for  $[\text{A}]$  as a function of time:  $t = 0$  min,  $[\text{A}] = 0.80 \text{ M}$ ; 8 min,  $[\text{A}] = 0.60 \text{ M}$ ; 24 min,  $[\text{A}] = 0.35 \text{ M}$ ; 40 min,  $[\text{A}] = 0.20 \text{ M}$ .

- (a) Establish the order of the reaction.  
 (b) What is the value of the rate constant, K?  
 (c) Calculate the rate of formation of B at 22 min.

164. A reaction  $A + B \rightarrow C$  obeys the following rate law:  $\text{Rate} = k[B]^2$ . (a) if  $[A]$  is doubled, how will the rate change? Will the rate constant change? Explain. (b) What are the reaction orders for A and B? What is the overall reaction order? (c) What are the units of rate constant?

165. Consider the following reaction:



(a) The rate for this reaction is first order in  $\text{H}_2$  and second order in  $\text{NO}$ . Write the rate law. (b) If the rate constant for this reaction at 1000 K is  $6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$ , what is the reaction rate when  $[\text{NO}] = 0.025 \text{ M}$  and  $[\text{H}_2] = 0.015 \text{ M}$ ? (c) What is the reaction rate at 1000 K when the concentration of  $\text{NO}$  is increased to 0.10 M, while the concentration of  $\text{H}_2$  is 0.010 M?

166. The iodide reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way:  $\text{OCI}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^-$ . This rapid reaction gives the following rate data:

$[\text{OCI}^-], \text{M}$	$[\text{I}^-], \text{M}$	Rate, M/s
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	$1.36 \times 10^{-4}$
$3.0 \times 10^{-3}$	$1.5 \times 10^{-3}$	$2.72 \times 10^{-4}$
$1.5 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.72 \times 10^{-4}$

(a) Write the rate law for this reaction (b) Calculate the rate constant. (c) Calculate the rate when  $[\text{OCI}^-] = 2.0 \times 10^{-3} \text{ M}$  and  $[\text{I}^-] = 5.0 \times 10^{-4} \text{ M}$ .

167. The following data were measured for the reaction  $\text{BF}_3(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{F}_3\text{BNH}_3(\text{g})$ :

Experiment	$[\text{BF}_3] (\text{M})$	$[\text{NH}_3] (\text{M})$	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

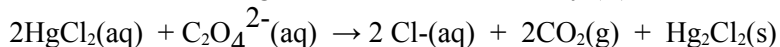
(a) What is the rate law for the reaction? (b) What is the overall order of the reaction? (c) What is the value of the rate constant for the reaction? (d) What is the rate when  $[\text{BF}_3] = 0.100 \text{ M}$  and  $[\text{NH}_3] = 0.500 \text{ M}$ ?

168. Consider the gas-phase reaction between nitric oxide and bromine at 273°C:  $2 \text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{NOBr}(\text{g})$ . The following data for the initial rate of appearance of  $\text{NOBr}$  were obtained:

Experiment	$[\text{NO}] (\text{M})$	$[\text{Br}_2] (\text{M})$	Initial Rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(a) Determine the rate law. (b) Calculate the average value of the rate constant for the appearance of  $\text{NOBr}$  from the four data sets. (c) How is the rate of appearance of  $\text{NOBr}$  related to the rate of disappearance of  $\text{Br}_2$ ? (d) What is the rate of disappearance of  $\text{Br}_2$  when  $[\text{NO}] = 0.075 \text{ M}$  and  $[\text{Br}_2] = 0.25 \text{ M}$ ?

169. Consider the following reaction between mercury (II) chloride and oxalate ion:



The initial rate of this reaction was determined for several concentrations of  $\text{HgCl}_2$  and  $\text{C}_2\text{O}_4^{2-}$ , and the following rate data were

obtained for the rate of disappearance of  $\text{C}_2\text{O}_4^{2-}$ :

Experiment	$[\text{HgCl}_2]$ (M)	$[\text{C}_2\text{O}_4^{2-}]$ (M)	Rate (M/s)
1	0.164	0.15	$3.2 \times 10^{-5}$
2	0.164	0.45	$2.9 \times 10^{-4}$
3	0.082	0.45	$1.4 \times 10^{-4}$
4	0.246	0.15	$4.8 \times 10^{-5}$

(a) What is the rate law for this reaction? (b) What is the value of the rate constant? (c) What is the reaction rate when the concentration of  $\text{HgCl}_2$  is 0.050 M and that of  $\text{C}_2\text{O}_4^{2-}$  is 0.10 M, if the temperature is the same as that used to obtain the data shown?

### Concentration vs. Time

171. (a) Define the following symbols that re encountered in rate equations:  $[A]_0$ ,  $t_{1/2}$ ,  $[A]_t$ ,  $k$ . (b) What quantity, when graphed versus time, will yield a straight line for the first-order reaction?

172. (a) For a second-order reaction, what quantity, when graphed versus time, will yield a straight line? (b) How do the half-lives of first-order and second-order reactions differ?

173. (a) The gas-phase decomposition of  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ , is first order in  $\text{SO}_2\text{Cl}_2$ . At 600 K the half-life for this process is  $2.3 \times 10^5$  s. What is the rate constant at this temperature? (b) At 320°C the rate constant is  $2.2 \times 10^{-5} \text{ s}^{-1}$ . What is the half-life at this temperature?

174. The first-order rate constant for the decomposition of  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  at 70°C is  $6.82 \times 10^{-3} \text{ s}^{-1}$ . Suppose we start with 0.0250 mol of  $\text{N}_2\text{O}_5(\text{g})$  in a volume of 2.0 L. (a) How many moles of  $\text{N}_2\text{O}_5$  will remain after 2.5 min? (b) How many minutes will it take for the quantity of  $\text{N}_2\text{O}_5$  to drop to 0.010 mol? (c) What is the half-life of  $\text{N}_2\text{O}_5$  at 70°C?

175. The gas-phase decomposition of  $\text{NO}_2$ ,  $\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{O}_2(\text{g})$ , is studied at 282°C, giving the following data:

Time (min)	$[\text{NO}_2]$ (M)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

(a) Is the reaction first order or second order with respect to the concentration of  $\text{NO}_2$ ?  
 (b) What is the value of the rate constant?

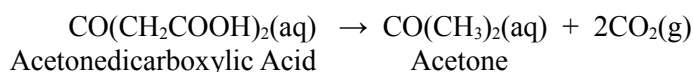
176. The reaction  $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$  has the rate constant  $k = 0.63 \text{ M}^{-1}\text{s}^{-1}$ . Based on the units for  $k$ , is the reaction first or second order in  $\text{NO}_2$ ? If the initial concentration of  $\text{NO}_2$  is 0.100 M, how would you determine how long it would take for the concentration to decrease to 0.025 M?

### Kinetic Molecular Theory

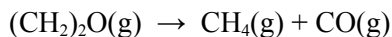
177. Why is the orientation of the colliding molecules an important factor in determining the rate of a reaction in some reactions but not in all reactions?

178. A mixture of hydrogen and oxygen gases is indefinitely stable at room temperature, but if struck by a spark, the mixture immediately explodes. What explanation can you offer for this observation?

179. Rate constants for the 1<sup>st</sup> order decomp. of acetonedicarboxylic acid are  $k = 4.75 \times 10^{-4} \text{ s}^{-1}$  at 293 K and  $k = 10^{-3} \text{ s}^{-1}$  at 303 K. What is the activation energy,  $E_a$ , of this reaction?



181. The decomposition of ethylene oxide at 652 K is the first-order reaction with  $k = 0.0120 \text{ min}^{-1}$  and an activation energy of 218 kJ/mol.



182. A rule of thumb in chemical kinetics states that for many reactions, the rate approximately doubles for a temperature rise of  $10^\circ\text{C}$ . What must be the activation energy of a reaction if the rate is indeed found to double between  $25^\circ\text{C}$  and  $35^\circ\text{C}$ ?

183. (a) Two reactions have identical values of  $E_a$ . Does this ensure that they will have the same rate constant if run at the same temperature? Explain. (b) Two similar reactions have the same rate constant at  $25^\circ\text{C}$ , but at  $35^\circ\text{C}$  one of the reactions has a higher rate constant than the other. Account for these observations.

184. The first-order rate constant for reactions of a particular organic compound with  $\text{H}_2\text{O}$  varies with T as follows:

Temperature (K)	Rate Constants ( $\text{s}^{-1}$ )
300	$3.2 \times 10^{-11}$
320	$1.0 \times 10^{-9}$
340	$3.0 \times 10^{-8}$
355	$2.4 \times 10^{-7}$

From these data, calculate the activation energy in units of kJ/mol.

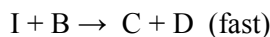
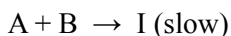
### Temp and Rate

185. (a) What factors determine whether a collision between two molecules will lead to a chemical reaction? (b) According to the collision model, why does temperature affect the value of the rate constant?

186. Understanding the high-temperature behavior of nitrogen oxides is essential for controlling pollution generated in automobile engines. The decomposition of nitric oxide (NO) to  $\text{N}_2$  and  $\text{O}_2$  is second order with a rate constant of  $0.0796 \text{ M}^{-1} \text{ s}^{-1}$  at  $737^\circ\text{C}$  and  $0.0815 \text{ M}^{-1} \text{ s}^{-1}$  at  $947^\circ\text{C}$ . Calculate the activation energy for the reaction.

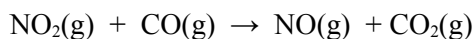
### Mechanisms

187. The following is proposed as a plausible reaction mechanism:



What is (a) the net reaction described by this mechanism, and (b) a plausible rate law for the reaction?

188. At temperatures below 600 K, the following reaction exhibits the rate law:  $\text{Rate} = k[\text{NO}_2]^2$ .



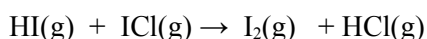
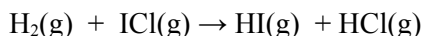
Propose a two-step mechanism involving one fast step and one slow step that is consistent with the net equation and the observed rate law.

189. (a) What is meant by the term elementary reaction? (b) What is the difference between a unimolecular and a bimolecular elementary reaction (c) What is a reaction mechanism?

191. (a) What is meant by the term molecularity? (b) Why are termolecular elementary reactions so rare? (c) What is a reaction mechanism?

192. (a) Based on the following reaction profile, how many intermediates are formed in the reaction A. D? (b) How many transition states are there? (c) Which step is the fastest? (d) Is the reaction A. D exothermic or endothermic?

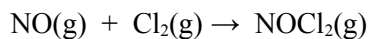
193. The following mechanism has been proposed for the gas-phase reaction of  $\text{H}_2$  with  $\text{ICl}$ :



(a) Write the balanced equation for the overall reaction. (b) Identify any intermediates in the mechanism. (c) Write rate laws for each elementary reaction in the mechanism. (d) If the first step is slow and the second one is fast, what rate law do you expect to be observed for the overall reaction?

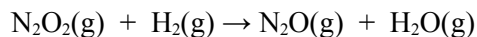
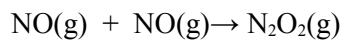
194. The reaction  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{NOCl}(\text{g})$  obeys the rate law,  $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$ . The following mechanism has been

proposed for this reaction:



(a) What would the rate law be if the first step were rate determining? (b) Based on the observed rate law, what can we conclude about the relative rates of the two steps?

195. The following mechanism has been proposed for the reaction of NO with H<sub>2</sub> to form N<sub>2</sub>O and H<sub>2</sub>O:



(a) Show that elementary reactions of the proposed mechanism add to provide a balanced equation for the reaction. (b) Write a rate law for each elementary reaction in the mechanism. (c) Identify any intermediates in the mechanism. (d) The observed rate law is  $\text{rate} = k[\text{NO}]^2[\text{H}_2]$ . If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second reactions?

### Catalysis

196. The activation energy of an uncatalyzed reaction is 95 kJ/mol. The addition of a catalyst lowers the activation energy to 55 kJ/mol. Assuming that the collision factor remains the same, by what factor will the catalyst increase the rate of the reaction at (a) 25°C, (b) 125°C?

IA

# The Periodic Table of the Elements

VIIA

1 <b>H</b> 1.008	IIA																17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95																											
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012	IIIB										VIII		IB		IIB		13 <b>B</b> 10.81	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95																						
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95																						
19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3	19 <b>Sc</b> 44.96	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80										
37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	72 <b>Hf</b> 178.5	73 <b>Ta</b> 180.9	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)	37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3											
55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	89 <b>Ac</b> (227)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (266)	107 <b>Bh</b> (264)	108 <b>Hs</b> (269)	109 <b>Mt</b> (268)	110 <b>Uun</b> (271)	111 <b>Uuu</b> (272)	112 <b>Uub</b> (277)	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La</b> 138.9	58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La</b> 138.9	58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (266)	107 <b>Bh</b> (264)	108 <b>Hs</b> (269)	109 <b>Mt</b> (268)	110 <b>Uun</b> (271)	111 <b>Uuu</b> (272)	112 <b>Uub</b> (277)	87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	90 <b>Th</b> 232.0	91 <b>Pa</b> (231)	92 <b>U</b> 238.0	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)	87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	90 <b>Th</b> 232.0	91 <b>Pa</b> (231)	92 <b>U</b> 238.0	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)