

## CHAPTER 4 SOLUTIONS

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1. Determine  $[\text{Cl}^-]$  for each sample:

$$\text{NH}_4\text{Cl}: \frac{0.30 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol solute}} = 0.30 \quad [\text{Cl}^-] = 0.30$$

$$\text{NaCl}: \frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol solute}} = 0.10 \quad [\text{Cl}^-] = 0.10$$

$$\text{KCl}: \frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol solute}} = 0.20 \quad [\text{Cl}^-] = 0.20$$

$$\text{MgCl}_2: \frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol solute}} = 0.40 \quad [\text{Cl}^-] = 0.40$$

$$\text{FeCl}_3: \frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{3 \text{ mol Cl}^-}{1 \text{ mol solute}} = 0.30 \quad [\text{Cl}^-] = 0.30$$

The highest concentration of  $\text{Cl}^-$  ions is found in solution D, 0.20 *M*  $\text{MgCl}_2$ .

The correct choice is (D).

2. Osmotic pressure, a colligative property, is lowered by the presence of particles in solution. The correct choice identifies the solution with the smallest total molarity of all ions.

The correct choice is (B).

3. The solution with the highest vapor pressure is the solution that has the lowest concentration of all ions. See solution to question (2) above.

The correct choice is (B).

4. Of the samples listed, the solution with the greatest mass is 500 mL of 0.10 *M*  $\text{NaCl}$ , choice (B). At 500 mL of solution, the mass of the system includes nearly 500 g  $\text{H}_2\text{O}$  plus 2.9 grams (0.05 mol) of solute. The next closest value is 400 mL of 0.030 *M*  $\text{NH}_4\text{Cl}$ , with nearly 400 g  $\text{H}_2\text{O}$ .

The correct choice is (B).

5. Estimate mass of solute for each solution:

$$(A) \text{ NH}_4\text{Cl: } 0.400 \text{ L} \times \frac{0.30 \text{ mol solute}}{1 \text{ L solution}} \times \frac{53.5 \text{ g}}{1 \text{ mol solute}} \approx 0.12 \times 54 \approx 6 \text{ g}$$

$$(B) \text{ NaCl: } 0.500 \text{ L} \times \frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{58.5 \text{ g}}{1 \text{ mol solute}} \approx 0.05 \times 59 \approx 3 \text{ g}$$

$$(C) \text{ KCl: } 0.200 \text{ L} \times \frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{74.5 \text{ g}}{1 \text{ mol solute}} \approx 0.04 \times 75 \approx 3 \text{ g}$$

$$(D) \text{ MgCl}_2: 0.100 \text{ L} \times \frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{95.3 \text{ g}}{1 \text{ mol solute}} \approx 0.02 \times 95 \approx 2 \text{ g}$$

$$(E) \text{ FeCl}_3: 0.200 \text{ L} \times \frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{162 \text{ g}}{1 \text{ mol solute}} \approx 0.02 \times 160 \approx 3 \text{ g}$$

The question appears to call for calculations. However, a satisfactory answer can be obtained by estimating values. Estimation is also a valuable timesaver when precise calculation is not required.

The correct choice is (A).

6.  $\text{Cl}^-$  ions come from both sources:

$$0.250 \text{ L} \times \frac{0.20 \text{ mol CaCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^- \text{ ion}}{1 \text{ mol CaCl}_2} = 0.10 \text{ mol Cl}^- \text{ ions}$$

$$0.250 \text{ L} \times \frac{0.40 \text{ mol KCl}}{1 \text{ L solution}} \times \frac{1 \text{ mol Cl}^- \text{ ion}}{1 \text{ mol KCl}} = 0.10 \text{ mol Cl}^- \text{ ions}$$

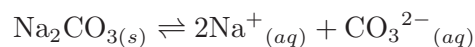
Mixing together in 0.50 liter solution

$$\frac{0.20 \text{ mol Cl}^- \text{ ions}}{0.50 \text{ L of solution}} = 0.40 \text{ M}$$

Other answers are results of calculations when the values provided are used incorrectly.

The correct choice is (D).

7. This system illustrates solubility equilibrium established according to the equation



Statement I is correct.

Molality is defined as moles solute per kilogram solvent; molarity is defined as moles solute per liter of solution. For most aqueous solutions, the numerical value for molality is generally greater than the corresponding value for molarity. This is especially true at high concentrations where the solute may form an appreciable fraction of the volume of the solution. Statement II is not correct.

The dissolving process is represented in the equation above. Note that two moles of the cation dissolve for every one mole of anions. Statement III is correct.

The correct choice is (D).

8. The vapor pressure of the solution varies directly with the mole fraction,  $\chi$ , of the volatile solvent ( $23.8 \text{ mm Hg} \times 0.90 = 21.4 \text{ mm Hg}$ ). Exact calculation is not required since estimation allows determination of the answer.

The correct choice is (D).

9. Density is defined as mass per unit volume. When molality is known, moles of solute per kilogram of solvent is specified.

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

To obtain mol solute per kilogram of **solution**, add mass of solute present to 1.00 kg solvent as shown below.

$$\frac{6.0 \text{ mol sucrose}}{\left(6.0 \text{ mol sucrose} \times \frac{0.342 \text{ kg sucrose}}{1 \text{ mol sucrose}}\right) + 1 \text{ kg solvent}}$$

The denominator gives the mass of the solute + mass of the solvent (the solution). In order to calculate density, a connection to volume of solution must be known. Molarity, moles of solute per liter of solution, provides such a connection. The expression below shows how to use the known information to obtain density.

$$\frac{\text{kg solution}}{\text{mol solute}} \times \frac{\text{mol solute}}{\text{L solution}}$$

The correct choice is (B).

10. Quick mental arithmetic shows that one mole of acetic acid is mixed with five moles of water. The mole fraction of  $\text{HC}_2\text{H}_3\text{O}_2$  becomes  $\frac{1}{6}$ , one mole of the acid to six moles total.

The correct choice is (B).

11. Molarity is defined as moles of solute per liter of solution. The number of moles of solute determined by calculation is generally measured by weighing. However, the quantity of solution is specified as a volume. Of those listed, the device for measuring volume with the greatest precision is the volumetric flask.

The correct choice is (B).

12. For mass percent, solute (component) is compared to solution (total mixture). Thus 25 g solute compared to 125 g total in the solution gives 20%.

The correct choice is (B).

13. If the final rinsing of a buret in a titration experiment is taken with water rather than the standard solution, the standard solution becomes slightly diluted by residual water in the buret as its initial volume reading is taken. Thus, an apparently slightly larger volume of the standard solution will have been added to the reaction mixture when the endpoint is reached. This causes the number of moles of base used to be reported too large and therefore the number of moles of acid reacting is also reported too large. The mistake does not affect the volume of solute used for the solid acid. (That volume is not used in any calculation for the assigned result.) Only statement III is correct.

The correct choice is (C).

14. Parts per million refers to mass of solute per million units of mass of solvent. Drinking water with 0.050 ppm arsenic contains 0.050 g arsenic per  $10^6$  (million) grams of water. One way to respond to this question is to change each answer to the same units as given, i.e., ..?.. g arsenic per  $10^6$  (million) grams of water

$$(A) \frac{0.050 \text{ mg As}}{1 \text{ mL water}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mL water}}{1 \text{ g water}} \times \frac{10^6}{\text{million}} = \frac{50 \text{ g As}}{\text{million g water}}$$

$$(B) \frac{0.050 \text{ mg As}}{1 \text{ liter water}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ liter water}}{1000 \text{ g water}} \times \frac{10^6}{\text{million}} = \frac{0.050 \text{ g As}}{\text{million g water}}$$

$$(C) \frac{0.050 \text{ As}}{10^6 \text{ L water}} \times \frac{1 \text{ liter water}}{1000 \text{ g water}} \times \frac{10^6}{\text{million}} = \frac{0.000050 \text{ g As}}{\text{million g water}}$$

$$(D) \frac{0.050 \text{ mg As}}{10^6 \text{ L water}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ liter water}}{1000 \text{ g water}} \times \frac{10^6}{\text{million}} = \frac{0.000000050 \text{ g As}}{\text{million g water}}$$

$$(E) \frac{0.050 \text{ mg As}}{10^6 \text{ g water}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{10^6}{\text{million}} = \frac{50 \text{ g As}}{\text{million g water}}$$

The value, 0.050 mg As per liter of water, choice (B), is another way to express 0.050 ppm.

The correct choice is (B).

15. Since the denominator of molality is kg of solvent and there is 0.1 kg (100 g) of water, you must find a temperature where approximately 0.3 moles (about 22 g) of KCl will dissolve.

The correct choice is (A).

16. Mass percentage of the solution is given by  $\frac{(100 \text{ g water})}{(100 \text{ g water} + 50 \text{ g KCl})}$  which is equivalent to 67%.

The correct choice is (D).

17. The amount of solute dissolved is temporarily above the solubility curve, hence supersaturated.

The correct choice is (E).

18. The quantity of solute precipitated is represented by the difference between 40 g and the solute value represented on the solubility curve at 40°C, about 2 g.

The correct choice is (B).

19. The Tyndall effect is the glow observed along the path of a beam of light shining through a colloid. This effect is not observed in a solution because the dispersed particles are too small to affect light. Since the particles of a suspension are much larger, that type of dispersion is opaque to visible light.

The correct choice is (A).

20. The stearate ion,  $\text{C}_{17}\text{H}_{35}\text{COO}^-$ , is large enough to have a charged part that is attracted to water and an uncharged part that is attracted to nonpolar molecules. Hydrophobic molecules are likely to be nonpolar molecules that form strong intermolecular attractions with each other and thus “repel” water. In the presence of the stearate ion, those molecules are attracted to stearate ions and repulsion to water decreases. This accounts for the cleaning action of ordinary soap.

The correct choice is (E).

21. Adding water to a solution of potassium nitrate will cause the solution to become more dilute in potassium nitrate. In addition, the volume of the solution will increase. At lower concentration, the solution will have higher vapor pressure and higher freezing point (options I and II). Its mass per unit volume (density) will decrease (option III). Its properties become more like pure water.

The correct choice is (E).

22. In this solution, the addition of NaCl to water causes density to increase, vapor pressure to decrease, freezing point to decrease, and osmotic pressure to increase. The lower vapor pressure accounts for the increase in the boiling point as the solute is added to the solution, not lower boiling point as in choice (C).

The correct choice is (C).

23. In a spontaneous, exothermic dissolving process,  $\Delta G_{soln}$  is negative (spontaneous process),  $\Delta H_{soln}$  is negative (exothermic process), and  $\Delta T$  is positive because the energy given off causes the temperature of the system to increase. Only options I and II are correct.

The correct choice is (C).

24. Increasing the temperature while maintaining contact with excess solute causes more solute to dissolve. Both molality and density of the solution increase (options I and III). The solution remains saturated because it remains in contact with excess solute (option II).

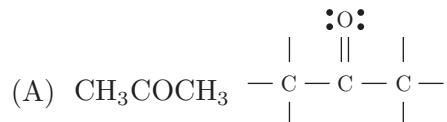
The correct choice is (E).

25. Increasing the temperature of any aqueous NaCl solution causes the vapor pressure to increase because the vapor pressure of the solvent increases (option I). The number of ion pairs in solution remains the same because in a dilute solution of an ionic solid such as NaCl, the solute is fully dissociated. The difference between the boiling point and the freezing point remains the same because the concentration of the solution remains the same. Options II and III are not correct.

The correct choice is (A).

## Free Response Questions

26. **Strategy:** Recognize that propanone is a ketone, a hydrocarbon derivative with the general formula R-CO-R'.



- (B) Propanone forms a solution with water because both are polar molecules (“like dissolves like”). Polar solutes dissolve readily in polar solvents. The greater the attractive forces between the solvent and solute molecules, the greater the solubility.

- (C) It is helpful to set up a table to organize the information.

	propanone	2-propanol	solution
<b>volume</b>	30.0 mL	50.0 mL	80.0 mL
<b>density</b>	0.792 g mL <sup>-1</sup>	0.785 g mL <sup>-1</sup>	N/A
<b>mass</b>	23.8 g	39.3 g	63.1 g
<b>moles*</b>	0.410 mol	0.654 mol	N/A

\* Calculated using molar mass. Because the solution is a mixture with no molar mass, it is not correct to calculate “moles of solution”. The solution is a mixture of 0.410 mol solute and 0.654 mol solvent. The total number of moles of particles in the mixture is 1.064 mol.

- (i)  $\frac{39.3 \text{ g 2-propanol}}{63.1 \text{ g solution}} = 0.623 \times 100\% = 62.3\%$  2-propanol by mass
- (ii)  $\frac{30.0 \text{ mL propanone}}{80.0 \text{ mL solution}} = 0.375 \times 100\% = 37.5\%$  propanone by volume
- (iii)  $\frac{0.410 \text{ mol propanone}}{1.064 \text{ mol total}} = 0.385$  mole fraction propanone
- (D) The freezing point of the solution is expected to be lower than that of the pure solvent, an example of one colligative property of the solution. The presence of propanone particles in the 2-propanol interferes with the arrangement of solvent particles as they change from the disorder of a liquid into an orderly solid lattice, thus requiring more energy to be removed from the system. A lower freezing point is established.

27. **Strategy:** Dissolving of a solid solute in a liquid solvent requires separation of solute particles, attraction of solute particles to solvent and separation of solvent particles to provide space for the dissolving solute. As these components of the dissolving process occur, the solute becomes dispersed into the solvent to form the solution, a mixture of molecule and ion size particles.
- (A) The two major energy changes related to dissolving are **lattice energy** and **hydration energy**.
- Lattice energy is the energy required to overcome attraction between solute particles in the solid phase and separate the solute into particles small enough to be dispersed in the solvent. Those particles are generally ions or molecules.
  - Hydration energy is the energy released when the solute particles are attracted to the water molecules.
- (B) As an ionic solid dissolves in water, entropy increases. The ionic solid is a highly ordered system. When dissolved in water, the extent of disorder (randomness) increases. Hydrated ions become randomly dispersed throughout the mixture. The entropy change,  $\Delta S$ , is given by  $\Delta S = S_{\text{prod}} - S_{\text{react}}$ . In the dissolving process for an ionic solid,  $S_{\text{prod}}$  is generally greater than  $S_{\text{react}}$ ; therefore  $\Delta S$  is positive.
- (C) Providing the lattice energy requires input of energy. Hydration of solute particles releases energy. The balance struck between these changes helps determine the solubility of the ionic solid. When the hydration energy is greater than the lattice energy, (that is, when the algebraic sum of these energy changes is negative),  $\Delta H$  is negative and solubility tends to be greater. (See also part D below.)
- (D) In order for an ionic solid to be soluble, the value for  $\Delta G$  for the dissolving process must be negative. In the relationship,  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta S$  is nearly always positive because the system becomes more disordered as dissolving occurs. The  $\Delta H$  term is the algebraic sum of the hydration energy (exothermic, negative) and the lattice energy (endothermic, positive). When  $\Delta H$  is negative and  $\Delta S$  is positive as above,  $\Delta G$  is negative at all values of  $T$  and the dissolving process occurs at any temperature. However, when  $\Delta H$  is positive, it is the magnitude of the  $T\Delta S$  term that determines whether or not  $\Delta G$  is negative, that is, whether or not the dissolving process does occur. At higher temperatures, increasing entropy plays a greater role in determining solubility.
- (E) The dissolving process for ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , in water is endothermic.
- (1) **The temperature of the mixture decreases.** In an endothermic dissolving process, heat is absorbed from the surroundings. The vessel and the system become colder; that is, temperature of the system and its container decreases.
  - (2) **If the amount of solute to be dissolved is doubled, the amount of decrease in temperature,  $\Delta T$ , is expected to be doubled.** In the dissolving process, twice as much energy is absorbed from the surroundings in order to overcome the attractive forces between twice as many particles of solute.

28. Strategy: Preparation of any solution calls for the determination of measurable amounts of any two of the following:
- solute, most often a solid or liquid
  - solvent, usually a liquid
  - solution, usually a liquid

Measurable amounts could be expressed as mass or volume. The mass and volume of the resulting mixture are determined by the amounts of solute and solvent that are mixed together. Note that masses of solute and solvent must add up to give the mass of the solution. However, the volumes of the solute plus solvent do not necessarily add up to the volume of the solution formed. Thorough mixing of the solute and solvent generally produces a mixture with less volume than the sum of its components. In addition, the volume of a given mass of solid solute to be dissolved is easily affected by the degree of subdivision of that solid.

- (A) Measure, precisely to two significant figures, 0.50 mol, that is, 49 grams, of  $\text{H}_2\text{SO}_4$ . A balance may be used for weighing the assigned quantity. Alternatively, to use volumetric equipment such as graduated cylinder, pipet or buret, the volume that contains the specific mass can be calculated from the specific gravity information supplied with the concentrated sulfuric acid. The assigned quantity of solute is 0.50 mol and the concentration of the solution to be 1.0  $M$ ; therefore, the volume of the solution to be prepared is 0.50 liter. Obtain a heat-resistant (borosilicate) volumetric flask with volume specified as 500 mL. Add enough distilled water so that the flask is at least half-filled. Then carefully add the measured 0.50 mole of liquid  $\text{H}_2\text{SO}_4$  to the water. (A very noticeable exothermic reaction will occur.) Swirl gently to mix. When the mixture has cooled to room temperature, add distilled water until the meniscus is at the 500 mL mark on the neck of the flask. (Note: it is **not** correct, and actually unsafe, to add any amount of water to the measured amount of acid.)
- (B) Again, the assigned amount of solute,  $\text{H}_2\text{SO}_4$ , is 0.050 mol (49 grams), obtained either by weighing or taking a measured volume. To use all of this solute, the amount of solvent needed is precisely 500 g (500 mL). The solution must be prepared in a heat-resistant vessel that holds more than 500 mL of solution because the volume of the assigned amount of  $\text{H}_2\text{SO}_4$  is added to the 500 g (500 mL) of water.
- (C) **The percent by mass of  $\text{H}_2\text{SO}_4$  is greater in the 1.0  $M$  solution.** The mass of  $\text{H}_2\text{SO}_4$  used for each solution is the same. For the 1.0  $M$  solution, the mass of water used is some amount less than 500 g (500 mL). The mass of water used for the 1.0 m solution is precisely 500 g. Therefore, the solution with the lesser amount of water has a greater percent by mass of  $\text{H}_2\text{SO}_4$ .
- (D) As with any laboratory activity, use of safety goggles and protective clothing is necessary. When working with any acid, it is a general rule to always add acid to water. Concentrated  $\text{H}_2\text{SO}_4$  is very corrosive to the skin. In addition, as it is mixed with water, much energy is evolved. To avoid boiling and spattering, sulfuric acid should always be added to water slowly and with constant mixing. Mixing should always be done in heat-resistant glassware and in a sink or other space where dilution of any spills can be carried out safely.
- (E) **For this process, crystal lattice energy is greater than hydration energy.** In an endothermic dissolving process, more energy is taken on (stored) than given off (released). In this process, more energy is taken on as crystal lattice energy (bonds broken) than is given off as hydration energy (bonds formed).