

Solutions

Answers and Explanations

1. A

A solution is a homogeneous mixture. Foggy air, milk, and cytoplasm are all heterogeneous. Within the mixture, at the molecular level, there are a variety of different phase spaces. Foggy air includes a suspended mist of water droplets. Both milk and cytoplasm are heterogeneous emulsions. They are colloidal suspensions. 14 carat gold, though, is a solution. It's a homogeneous alloy of gold, silver, copper and zinc. It is a true solution.

2. D

Molarity is the concentration of a solution expressed as the number of moles of solute per liter of solution, the concentration in terms of the spatial density of the molecules of solute. As such, molarity is the concentration expression that is directly proportional to the thermodynamic or kinetic activity of the solute, so we use molarity for equilibrium constants and rate expressions, for example.

3. D

Multiplying the concentration of a solution in molarity times the volume of a solution will give you the moles of solute in the solution (moles per liter times liters equals moles).

$$MV = \text{moles of solute}$$

$$(2.0 \text{ M})(0.25 \text{ L}) = 0.5 \text{ mol NaOH}$$

The molecular weight of NaOH is 40 g mol^{-1} .

$$(0.5 \text{ mol})(40 \text{ g mol}^{-1}) = 20 \text{ g NaOH}$$

4. A

When a solution is diluted, you know that the amount of solute stays the same. This proposition takes the form of the *dilution equation*, which is basically that the product of the molarity and volume will be constant given that the amount of solute isn't changing.

$$M_1 V_1 = M_2 V_2$$

$$(0.5 \text{ M})(0.035 \text{ L}) = (0.35 \text{ M}) V_2$$

$$V_2 = 0.05 \text{ L}$$

So we need to add 15ml in order to increase the volume from 35ml to 50ml.

5. B

The molecular weight of AgNO_3 is 170 g mol^{-1} . An essential art in chemical stoichiometry is knowing that just as molecular weight allows you to convert moles to grams, the reciprocal of the molecular weight is the conversion factor to convert grams to moles.

$$8.5 \text{ g AgNO}_3 \frac{1 \text{ mol AgNO}_3}{170 \text{ g AgNO}_3} = 0.05 \text{ mol AgNO}_3$$

That makes our question easier. How many milliliters of 0.1 M AgNO_3 solution contain 0.05 mol AgNO_3 ?

$$MV = \text{moles of solute}$$

$$(0.1 \text{ M}) V = 0.05 \text{ mol AgNO}_3$$

$$V = 0.5 \text{ L}$$

6. C

Of all the choices, only choice 'C' is definitely true. A saturated solution is at equilibrium. The rate of dissolution and the rate of reforming the solid solute are equal. The other choices *may* be true.

7. C

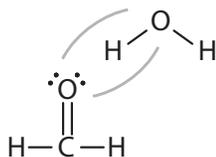
An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. Many Brønsted acids are electrolytes. Water itself is an electrolyte, which explains the conductivity of pure deionized water, the prototypical electrolyte is a salt. A salt solution conducts electricity through the movement of ions.

8. D

With methanol it's easy to see. A hydroxyl group is great at hydrogen bonding, so methanol with hydrogen bond with the water. With acetone and formaldehyde, it's a little harder to see at first, but they also will hydrogen bond with the water. This is true even though the type of intermolecular force which you will see prevailing in pure acetone or pure formaldehyde is dipole-dipole interaction. There is no hydrogen bonding in the pure forms of those substances because there are no functional groups in which a hydrogen is bound to a very electronegative element such as hydroxyl or amine groups.



However, in aqueous solution, the carbonyl oxygen will act as a *hydrogen bond receiver*.



9. B

One of the correlatives of Le Chatelier's Principle is that increasing temperature will shift an equilibrium to favor the endothermic direction. If a solution process were endothermic, solubility would *increase* with increasing temperature. In the case of lithium selenite, however, solubility decreases with increasing temperature. This means that the endothermic direction isn't the solution process but precipitation. Therefore, the solution process must be exothermic. This is an old favorite. If solubility does down with temperature, the solution process is exothermic.

10. A

Henry's Law has the mathematical form:

$$C_g = k P_g$$

11. B

One of the most important correlatives of Le Chatelier's principle is that increasing temperature shifts an equilibrium to favor the endothermic direction of a chemical process. Therefore, if solubility increases with temperature, we can conclude that the process of dissolving the particular solvent in that particular solvent is endothermic.

12. D

The solution became warm. This tells us that dissolving LiCl in water is an exothermic process. If the solution process is exothermic, solubility decreases when the temperature increases. According to Le Chatelier's principle, increased temperature favors the endothermic direction of a reaction process, which in this case would be precipitation. If the amount of solute added would saturate the solution at ambient temperature, this is more than the solvent can accommodate now that the temperature is elevated. It will take patience, allowing the solution to cool, to dissolve the LiCl.

13. C

Freezing-point depression is the decrease of the freezing point of a solvent that occurs on the addition of a non-volatile solute. The change in the freezing point is given by the following formula:

$$\Delta T_F = K_F \cdot m \cdot i$$

ΔT_F , the freezing-point depression, is defined as T_F (pure solvent) - T_F (solution).

K_F , the cryoscopic constant, is dependent on the properties of the solvent, not the solute. For water, $K_F = 1.853 \text{ K}\cdot\text{kg}/\text{mol}$.

m is the molality (moles solute per kilogram of solvent).

i is the van 't Hoff factor.

For the MCAT, when you're dealing with the dissociation of a strong electrolyte, it's not a bad working assumption to assume complete dissociation and just

say $i = 2$. Each mole dissolved yields two moles of particles in the solution. For MgBr_2 we would say $i = 3$.

However, in this particular question we are given to see the particular issue that can come up, especially for more concentrated electrolyte solutions, where the van't Hoff factor is not a whole number. For an ideal solution of an ionic compound dissolved in water, the van't Hoff factor is equal to the number of discrete ions in a formula unit of the substance. This is true for ideal solutions only, as occasionally ion pairing occurs in solution in real solutions. At a given instant a small percentage of the ions are paired and count as a single particle. Ion pairing occurs to some extent in all electrolyte solutions. This causes the measured van't Hoff factor to be less than that predicted in an ideal solution.

If the van't Hoff factor were actually 2 here, the freezing point depression would be 3.72°C instead of 3.5°C . This is because the *degree of dissociation*, α , is less than 100%. If n equals the ideal van't Hoff factor, 2, then the actual van't Hoff factor can be determined from degree of dissociation as below.

$$i = 1 + \alpha(n - 1)$$

We don't need to do math to confirm the degree of dissociation is 88% because choices 'A' and 'B' are both saying the same thing which is inconsistent with the observed freezing point depression of 3.5°C .

14. B

While it should be apparent by inspection that combining a concentrated CaCl_2 solution with a saturated solution of CaCO_3 will lead to precipitation of CaCO_3 , it's a good exercise to do the math. In the saturated solution of CaCO_3 , the concentrations of the two ions are equal. In the saturated solution, each concentration equals the square root of K_{sp} .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.9 \times 10^{-9}$$

$$x^2 = 4.9 \times 10^{-9}$$

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = 7.0 \times 10^{-5} \text{ M}$$

If we combine 0.5 L of this CaCO_3 solution with a 0.5 L solution of 0.2 M CaCl_2 , we will have 1.0 L solution that is $3.5 \times 10^{-5} \text{ M}$ for CO_3^{2-} and 0.1M for Ca^{2+} . Note, firstly, that in combining the two 0.5L solutions we doubled the volume, which halved the concentrations from the contributing solutions. Secondly, because the 0.1M Ca^{2+} from the CaCl_2 is so much greater than the $3.5 \times 10^{-5} \text{ M}$ Ca^{2+} from the CaCO_3 solution, we can ignore this contribution and treat the concentration after admixture as 0.1M. In summary, we have a solution with 0.1M Ca^{2+} and $3.5 \times 10^{-5} \text{ M}$ CO_3^{2-} . Therefore, we have the following ion product.

$$Q_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 3.5 \times 10^{-6}$$

This is greater than the solubility product.

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.9 \times 10^{-9}$$

If the ion product, Q_{sp} , is greater than the solubility product, K_{sp} , there are more ions in the solution than the equilibrium, saturated state, so it will precipitate.

15. A

The solubility product, K_{sp} , is a simplified equilibrium constant representing the equilibrium state of a salt solution, the saturated solution. In other words, the product of the ion concentrations of a saturated solution equals K_{sp} . If the ion product is less than K_{sp} , more could dissolve. If the ion product is greater than K_{sp} , the solution is precipitating.

$$[\text{Pb}^{2+}][\text{CO}_3^{2-}] = 7.4 \times 10^{-14}$$

$$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = 2.0 \times 10^{-8}$$

In saturated PbCO_3 solution, the concentration $[\text{Pb}^{2+}]$ equals $[\text{CO}_3^{2-}]$. This is because when PbCO_3 dissolves, the ions dissociate in 1:1 stoichiometric ratio. Additionally, each of these concentrations equals the square root of 7.4×10^{-14} .

Analogous statements are true for the saturated PbSO_4 solution. In this solution, the respective $[\text{Pb}^{2+}]$ and $[\text{SO}_4^{2-}]$ concentrations equal the square root of 2.0×10^{-8} .

The concentrations of ions in the PbCO_3 solution are

on the order of 10^{-7} M. The concentrations of ions in the PbSO_4 solution are on the order of 10^{-4} M. If we combine the two solutions in equal mixture, the ion concentrations will be halved. Without the need for arithmetic, it's easy to see that in the final, combined solution, the ion product of PbSO_4 will be below its K_{sp} , but the ion product of PbCO_3 will be above its K_{sp} . This is because the carbonate ions now find themselves in a solution with lead ions on the order of 10^{-4} M. This will put the ion product of PbCO_3 on the order of 10^{-11} , so it is going to precipitate.

16. C

The basic conceptual vocabulary in physics and chemistry really isn't that large, so most of the challenge in a problem is often to translate the real world scenario presented into the simpler language of fundamental relationships. The key here is to recognize that the observation that bubbling the air through the ether resulted in a loss of mass of the solution 95% of the loss when bubbling the air through the pure ether is basically telling you that dissolving the solute in the ether *decreased its vapor pressure* to 95% of its original value. Therefore, from Raoult's Law, we know that the mole fraction of ether in the second experiment is 95% of the original value. Recognizing what the problem is about is the first step. It's about vapor pressure lowering governed by Raoult's Law. The vapor pressure of the solvent in the solution is proportional to the mole fraction of solvent.

$$P_A = X_A P_A^0$$

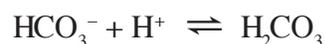
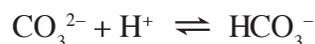
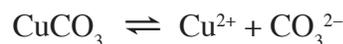
P_A^0 is the vapor pressure of the pure solvent. X_A is the mole fraction of solvent in the solution. P_A is the vapor pressure of the solution.

We can conclude that the mole fraction of ether in the solution is 95%.

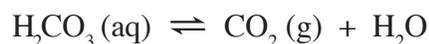
The spacing of the answers is an invitation to use mental math. 150g of diethyl ether is 2 moles (MW = 74 g mol⁻¹). If this amount of ether represents 95% of the moles of the solution, then our added substance represents approximately 0.1 mol, one twentieth of 2 moles. If 9g represents 0.1 mole, its molecular weight must be approximately 90g.

17. C

Lowering the pH will increase the solubility of an insoluble or sparingly soluble electrolyte, such as copper(II) carbonate, whose anion is the conjugate base of a weak acid. The shifting acid base equilibrium to accommodate the lower pH will promote the solution process by removing the anion from the solution.

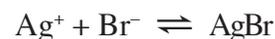
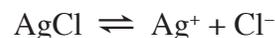


Additionally, a process leading to formation of excess carbon dioxide will be a gas evolution reaction. Carbonic acid decomposes forming carbon dioxide and water. Because of its importance in physiology, this is one of the MCAT's very favorite chemical reactions.



18. B

When the solid AgCl is introduced to the solution, Ag^+ and Cl^- ions will start dissociating and entering the aqueous phase. This solution process will be driving towards the K_{sp} of AgCl , but it won't be permitted to reach it, because long before the ion products reaches that value, the ion product of Ag^+ and Br^- will cross the threshold of the K_{sp} of AgBr . Not only is the K_{sp} of AgBr lower than that of AgCl (it's less soluble), but the solution is concentrated for Br^- . AgBr starts to precipitate. The precipitation of AgBr will couple with dissolution of AgCl until all of the AgCl has dissolved.



19. B

To solve this problem, first we will need to determine the concentration of Ag^+ in the combined solution after admixture. We will then use this Ag^+ concentration along with the K_{sp} of AgBr given in the passage

to determine the concentration of Br^- great enough to lead to precipitation.

Firstly, to determine the concentration of Ag^+ in the combined solution, we divide the moles of Ag^+ (concentration of the 1st solution times its volume) by the new combined solution volume. The dilution is not hard to compute in your head, but it's good to see it worked it out to be ready for dilutions that may be a little more complicated.

$$\frac{(0.1\text{L})(0.3 \text{ mol L}^{-1} \text{Ag}^+)}{(0.1\text{L} + 0.05\text{L})} = \frac{3 \times 10^{-2} \text{ mol}}{1.5 \times 10^{-1} \text{ L}} = 2 \times 10^{-1} \text{ M}$$

Now we can use K_{sp} to determine the minimum concentration of Br^- to observe precipitation.

$$K_{\text{sp}} = (2.0 \times 10^{-1})[\text{Br}^-] = 4.1 \times 10^{-13}$$

$$[\text{Br}^-] = 2.0 \times 10^{-12} \text{ M}$$

We have found the minimum concentration of Br^- in the combined solution to observe precipitation. However, this concentration doesn't represent the detection limit. That detection limit is the concentration of Br^- in the original 50ml sample which corresponds to this. Although you might see that the original threshold concentration would have been three times greater, having diluted from 50ml to 150ml.

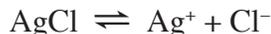
$$\frac{(0.05\text{L})(\text{original concentration})}{(0.1\text{L} + 0.05\text{L})} = 2.0 \times 10^{-12} \text{ M}$$

$$\text{original concentration} = 6.0 \times 10^{-12} \text{ M}$$

This is the threshold concentration in the original 50ml sample for precipitation after admixture.

20. A

$[\text{Ag}(\text{NH}_3)_2]^+$ is a complex ion. It has a metal ion at its center with a number of other molecules or ions surrounding it, attached via coordinate covalent bonds. The solution process for a weak electrolyte may be coupled with formation of a complex ion.



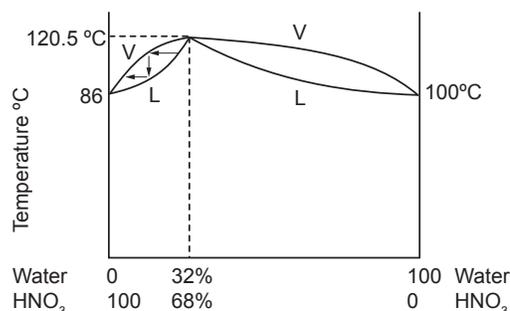
The question stem indicated that diamminesilver(I) ion is very stable, so the equilibrium of complex ion formation will lie to the right. This will remove silver ions from the solution, driving the dissolution of AgCl forward by mass action.

21. A

At at 95.4% ethanol, the ethanol-water mixture has a boiling point of 78.15°C. This is lower than the boiling point of 81.3°C for pure ethanol. The standard boiling point describes the temperature at which the vapor pressure of a liquid comes to equal 1atm. For the mixture to have a lower boiling point than pure ethanol, it must have a higher vapor pressure.

22. A

These types of phase diagrams depicting minimum and maximum boiling azeotropes are Chem 101 classics, so it's good to know your way around them. The diagrams show how the composition of the vapor coming off the liquid at a given temperature may differ from the composition of the liquid itself. Notice first leftward arrow in the diagram below. The vapor of a 75% nitric acid solution has more nitric acid than the liquid itself. When we condense that liquid, the downward arrow, the liquid is enriched for nitric acid. The process can continue with another round, which will yield even greater enrichment for nitric acid.



Notice that for a 75% nitric acid solution, being on the left side of the maximum boiling azeotrope, we would be unable produce pure water by fractional distillation.