

# The Advanced Placement Examination in Chemistry

## Part II - Free Response Questions & Answers 1970 to 2005

### Solids, Liquids & Solutions

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Compiled for the Macintosh and PC by:

Harvey Gendreau  
Framingham High School  
115 "A" Street  
Framingham, MA 01701-4195  
508-620-4963  
419-735-4782 (fax)

508-877-8723 (home office)  
www.apchemistry.com  
hgendrea@framingham.k12.ma.us  
hgendreau@rcn.com

Requests for copies of these questions and answers as e-mail attachments for either the Macintosh or the PC (MS-Office files) should be sent to:

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# Solids, Liquids, & Solutions

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1970

What is meant by the lattice energy of an ionic compound? What quantities need to be determined and how are they used to calculate the lattice energy of an ionic compound.

Answer:

Lattice energy - quantity of energy released in the formation of one mole of an ionic solid from its separated gaseous ions.

The energy quantities needed to be determined:

sublimation of solid metal

ionization of gaseous atomic metal (ionization energy)

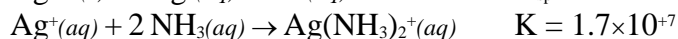
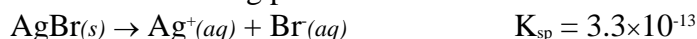
dissociation of gaseous non-metal

ion formation by gaseous atomic non-metal (electron affinity)

They are used with Hess's Law to determine the combination of gaseous ions. This is the Born-Haber Cycle.

1971

Solve the following problem



(a) How many grams of silver bromide, AgBr, can be dissolved in 50 milliliters of water?

(b) How many grams of silver bromide can be dissolved in 50 milliliters of 10 molar ammonia solution?

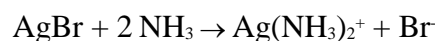
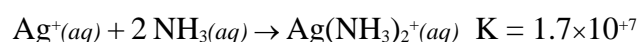
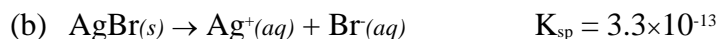
Answer:

$$(a) [\text{Ag}^+][\text{Br}^-] = K_{sp} = 3.3 \times 10^{-13} = X^2$$

$$X = 5.7 \times 10^{-7} \text{ M} = [\text{Ag}^+] = \text{mol/L AgBr that dissolve}$$

$$0.050 \text{ L} \propto \frac{5.7 \times 10^{-7} \text{ mol AgBr}}{1 \text{ L}} \propto \frac{187.8 \text{ g AgBr}}{1 \text{ mol AgBr}} =$$

$$= 5.4 \times 10^{-6} \text{ g AgBr}$$



$$K = K_{sp} \times K = 5.6 \times 10^{-6}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = [\text{Br}^-] = X \text{ M}; [\text{NH}_3] = (10 - 2X) \text{ M}$$

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = \frac{X \cdot X}{(10 - 2X)^2} = 5.6 \times 10^{-6}$$

$$X = 2.4 \times 10^{-2} \text{ M} = [\text{Br}^-] = \text{mol/L dissolved AgBr}$$

$$(2.4 \times 10^{-2} \text{ mol/L})(187.8 \text{ g/mol})(0.050 \text{ L}) = 0.22 \text{ g AgBr}$$

1971

Molarity and molality are two ways of expressing concentration.

(a) Clearly distinguish between them

(b) Indicate an experimental situation where expressing concentrations as molarity is particularly appropriate.

(c) Indicate an experimental situation where expressing concentration as molality is particularly appropriate.

Answer:

(a) molarity (M) - molar concentration; composition or concentration of a solution expressed as number of moles of solute per liter of solution.

molality (m) - solution concentration expressed as number of moles of solute per kilogram of solvent.

many possibilities, examples:

(b) Acid - base titrations

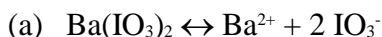
(c) Molecular weight determination by freezing point depression change.

1972 D

(a) How many moles of Ba(IO<sub>3</sub>)<sub>2</sub> is contained in 1.0 liter of a saturated solution of this salt at 25°. K<sub>sp</sub> of Ba(IO<sub>3</sub>)<sub>2</sub> = 6.5 × 10<sup>-10</sup>

(b) When 0.100 liter of 0.060 molar Ba(NO<sub>3</sub>)<sub>2</sub> and 0.150 liter of 0.12 molar KIO<sub>3</sub> are mixed at 25°C, how many milligrams of barium ion remains in each milliliter of the solution? Assume that the volumes are additive and that all activity coefficients are unity.

Answer:



$$K_{sp} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = 6.5 \times 10^{-10}$$

$$[\text{Ba}^{2+}] = X; [\text{IO}_3^-] = 2X; (X)(2X)^2 = 6.5 \times 10^{-10}$$

$$X = 5.5 \times 10^{-4} \text{ M} = \text{mol/L of dissolved Ba}(\text{IO}_3)_2$$

(b) initial mol Ba<sup>2+</sup> = (0.060 mol/L)(0.100L) = 0.0060 mol

initial mol IO<sub>3</sub><sup>-</sup> = (0.150L)(0.120 mol/L) = 0.0180 mol

# Solids, Liquids, & Solutions

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after reaction, essentially all  $\text{Ba}^{2+}$  reacts while  $\text{IO}_3^- = \{0.0180 - (2)(0.0060)\} \text{ mol} = 0.0060 \text{ mol}/0.250 \text{ L} = 0.024\text{M} [\text{IO}_3^-]$

$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{IO}_3^-]^2} = \frac{6.5 \times 10^{-10}}{(0.024)^2} = 1.1 \times 10^{-6} \text{ M}$$

$$\frac{1.1 \times 10^{-6} \text{ mol}}{100.0 \text{ mL}} \propto \frac{137340 \text{ mg Ba}^{2+}}{1 \text{ mol}} = 1.5 \times 10^{-4} \text{ mg / mL Ba}^{2+}$$

1973 D

The molar solubility of silver bromide is diminished by the addition of a small amount of solid potassium bromide to a saturated solution. However, the molar solubility of silver bromide is increased by the addition of solid potassium nitrate, a salt whose ions are not common to those of silver bromide.

Explain these experimental observations in terms of the principles involved.

Answer:

$\text{AgBr}(s) \leftrightarrow \text{Ag}^+(aq) + \text{Br}^-(aq)$ ; As KBr dissolves, the concentration of  $\text{Br}^-$  ions increase and force the equilibrium to shift to the left (LeChatelier's principle) where the concentrations of the ions in solution decrease and less can dissolve.

The diverse ("uncommon") ion effect – "the salt effect". As the total ionic concentration of a solution increases, interionic attractions become more important. Activities become smaller than the stoichiometric or measured concentrations. For the ions involved in the solution process this means that a higher concentration must appear in solution before equilibrium is established. - the solubility must increase.

1974 D

Two beakers, one containing 100 milliliters of a 0.10 molal solution of sucrose (a nonvolatile nonelectrolyte) the other containing 100 milliliters of pure water, are placed side by side in a closed system, such as under a bell jar. Explain in terms of the principles involved what changes, if any, occur to bring the system to equilibrium.

Answer:

(1) Volume of sugar solution increases; (2) volume of pure water decreases; (3) water beaker finally empty.

Raoult's Law, vapor pressure and volatility

Description of process (rates of vaporization and condensation)

1975 D

Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water. Salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain these facts from the standpoint of vapor pressure.

Answer:

An alcohol-water solution has a higher than normal (pure water) vapor pressure because alcohol is a volatile solute and contributes substantially to the vapor of the solution. The higher the vapor pressure, the lower the boiling point. A salt-water solution has a lower than normal vapor because salt is a non-volatile solute and solute-solvent interaction decrease the vapor of the solution, the lower the vapor pressure, the higher the boiling point.

1976 B

- Calculate the molality of a 20.0 percent by weight aqueous solution of  $\text{NH}_4\text{Cl}$ . (Molecular weight:  $\text{NH}_4\text{Cl} = 53.5$ )
- If this  $\text{NH}_4\text{Cl}$  solution is assumed to be ideal and is completely dissociated into ions, calculate the pressure of this solution at  $29.0^\circ\text{C}$ .
- Actually a solution of  $\text{NH}_4\text{Cl}$  of this concentration is not ideal. Calculate the apparent degree of dissociation of the  $\text{NH}_4\text{Cl}$  if the freezing point of this solution is  $-15.3^\circ\text{C}$ ? (Molal freezing point constant =  $1.86^\circ\text{C}$ )

Answer:

$$\frac{20.0}{80.0} \propto 1000 = 250 \text{ g NH}_4\text{Cl in } 1000 \text{ g H}_2\text{O}$$

$$(a) \quad \frac{250 \text{ g}}{1 \text{ kg H}_2\text{O}} \propto \frac{1 \text{ mol NH}_4\text{Cl}}{53.5 \text{ g}} = 4.67 \frac{\text{mol}}{\text{kg}} = 4.67 \text{ molal}$$

(b)  $P_1 = (P^\circ)(X_1)$

$$\text{mol ions} = (2)(4.67 \text{ mol}) = 9.34 \text{ mol}$$

$$1 \text{ kg water} = 55.6 \text{ mol water}$$

$$X_1 = \frac{55.6}{55.6 + 9.34} = 0.856$$

$$P_1 = (29.8 \text{ mm Hg})(0.856) = 25.5 \text{ mm Hg}$$

(c) Assume no dissociation.

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$$\Delta T = k_f m = (1.86)(4.67) = 8.69^\circ\text{C}$$

of fused salt,  
etc.

$$i = 15.3 / 8.69 = 1.76$$

$$(1.76 - 1.00)(100) = 76\% \text{ dissociated}$$

1977 D

The solubility of  $\text{Zn(OH)}_2$  is not the same in the following solutions as it is in pure water. In each case state whether the solubility is greater or less than that in water and briefly account for the change in solubility.

- (a) 1-molar  $\text{HCl}$  (c) 1-molar  $\text{NaOH}$   
(b) 1-molar  $\text{Zn(NO}_3)_2$  (d) 1-molar  $\text{NH}_3$

Answer:

- (a) greater:  $\text{Zn(OH)}_2(s) + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + 2 \text{H}_2\text{O}$   
(b) lower: increased  $[\text{Zn}^{2+}]$  decreases  $[\text{OH}^-]$  and decreases the amount of  $\text{Zn(OH)}_2$  in solution.  $K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2$   
(c) greater:  $\text{Zn(OH)}_2(s) + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}$  (Can also site common ion effect)  
(d) greater:  $\text{Zn(OH)}_2(s) + 4 \text{NH}_3 \rightarrow \text{Zn(NH}_3)_4^{2+} + \text{OH}^-$

1977 D

The state of aggregation of solids can be described as belonging to the following four types:

- (1) ionic (3) covalent network  
(2) metallic (4) molecular

For each of these types of solids, indicate the kinds of particles that occupy the lattice points and identify forces among these particles. How could each type of solid be identified in the laboratory?

Answer:

|                  | Particles  | Binding Forces                                      | Experimental Identification              |
|------------------|------------|---|--|
| ionic            | + & - ions | electrostatic attraction                            | conductivity of fused salt               |
| metallic         | + ions     | electrostatic attraction between ions and electrons | conductivity of the solid                |
| covalent network | atoms      | covalent bonds                                      | high melting pt., extreme hardness, etc. |
| molecular        | molecules  | van der Waals                                       | low melting pt., non-conductivity        |

1978 D

The freezing point and electrical conductivities of three aqueous solutions are given below.

| Solution<br>(0.010 molal) | Freezing Point | Electrical Conductivity |
|---------------------------|----------------|-------------------------|
| sucrose                   | -0.0186°C      | almost zero             |
| formic acid               | -0.0213°C      | low                     |
| sodium formate            | -0.0361°C      | high                    |

Explain the relationship between the freezing point and electrical conductivity for each of the solutions above. Account for the differences in the freezing points among the three solutions.

Answer:

sucrose

a non electrolyte

0.010 mol/kg lowers freezing point 0.0186°C

formic acid

a weak electrolyte; low conductance as a result of low ion concentration

$m_{\text{total}} > 0.010$  molal due to partial ionization and  $\Delta T_f$  somewhat greater than 0.0186°C

sodium formate

a salt and strong electrolyte

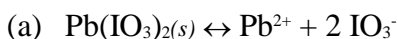
approximately 100% dissociation into ions,  $m_{\text{total}}$  approaching 0.02 molal

1979 A

A saturated solution of lead iodate in pure water has a lead ion concentration of  $4.0 \times 10^{-5}$  mole per liter at 20°C.

- (a) Calculate the value for the solubility-product constant of  $\text{Pb(IO}_3)_2$  at 25°C.  
(b) Calculate the molar solubility of  $\text{Pb(IO}_3)_2$  in a 0.10 molar  $\text{Pb(NO}_3)_2$  solution at 25°C.  
(c) To 333 milliliters of a 0.120-molar  $\text{Pb(NO}_3)_2$  solution, 667 milliliters of 0.435-molar  $\text{KIO}_3$  is added. Calculate the concentrations of  $\text{Pb}^{2+}$  and  $\text{IO}_3^-$  in the solution at equilibrium at 25°C.

Answer:



$$K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = (4.0 \times 10^{-5})(8.0 \times 10^{-5})^2$$

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$$= 2.6 \times 10^{-13}$$

$$(b) [Pb^{2+}] = (0.10 + X) M \approx 0.10 M$$

$$[IO_3^-]^2 = (2X) M$$

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = 2.6 \times 10^{-13} = (0.10)(2X)^2$$

$X = 8.1 \times 10^{-7} M = \text{mol Pb}(\text{IO}_3)_2 \text{ dissolved per L solution.}$

$$(c) \text{ initial mol Pb}^{2+} = 0.0400 \text{ mol}$$

$$\text{initial mol IO}_3^- = 0.290 \text{ mol}$$

ppt must occur; after ppt, mole  $\text{IO}_3^-$  in solution =  $(0.290 - 0.080) \text{ mol} = 0.210 \text{ mol}$

$$[\text{IO}_3^-] = 0.210 M \text{ since the volume is 1.00 L}$$

$$K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = 2.6 \times 10^{-13} = [\text{Pb}^{2+}](0.210)^2$$

$$[\text{Pb}^{2+}] = 5.8 \times 10^{-12} M$$

1980 B

(a) A solution containing 3.23 grams of an unknown compound dissolved in 100.0 grams of water freezes at  $-0.97^\circ\text{C}$ . The solution does not conduct electricity. Calculate the molecular weight of the compound. (The molal freezing point depression constant for water is  $1.86^\circ\text{C kg mole}^{-1}$ )

(b) Elemental analysis of this unknown compound yields the following percentages by weight H=9.74%; C=38.70%; O=51.56%. Determine the molecular formula for the compound.

(c) Complete combustion of a 1.05 gram sample of the compound with the stoichiometric amount of oxygen gas produces a mixture of  $\text{H}_2\text{O}(g)$  and  $\text{CO}_2(g)$ . What is the pressure of this gas mixture when it is contained in a 3.00 liter flask at  $127^\circ\text{C}$ ?

Answer:

$$(a) \Delta T_f = k_f m; 0.97^\circ\text{C} = (1.86^\circ\text{C} m^{-1})(m)$$

$$m = 0.52 \text{ mol solute/kg solvent}$$

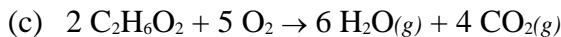
In this solution, 3.23 g solute in 100.0 g water or 32.3 g solute in 1 kg of water

$$\text{mol. wt.} = \frac{32.3 \text{ g}}{1 \text{ kg solvent}} \propto \frac{1 \text{ kg solvent}}{0.52 \text{ mol}} = 62 \frac{\text{g}}{\text{mol}}$$

$$(b) \frac{62 \text{ g}}{1 \text{ mol cmpd}} \propto \frac{0.0974 \text{ g H}}{1 \text{ g cmpd}} \propto \frac{1 \text{ mol H}}{1 \text{ g H}} = \frac{6.0 \text{ mol H}}{1 \text{ mol cmpd}}$$

$$\frac{62 \text{ g}}{1 \text{ mol cmpd}} \propto \frac{0.3870 \text{ g C}}{1 \text{ g cmpd}} \propto \frac{1 \text{ mol C}}{12 \text{ g C}} = \frac{2.0 \text{ mol C}}{1 \text{ mol cmpd}}$$

$$\frac{62 \text{ g}}{1 \text{ mol cmpd}} \propto \frac{0.5156 \text{ g O}}{1 \text{ g cmpd}} \propto \frac{1 \text{ mol O}}{16 \text{ g O}} = \frac{2.0 \text{ mol O}}{1 \text{ mol cmpd}}$$



$$1.05 \text{ g C}_2\text{H}_6\text{O}_2 \propto \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62 \text{ g C}_2\text{H}_6\text{O}_2} \propto \frac{10 \text{ mol gas}}{2 \text{ mol C}_2\text{H}_6\text{O}_2} =$$

$$= 0.0847 \text{ mol gas}$$

$$P = (nRT) / V$$

$$P = \frac{(0.0847 \text{ mol})(0.08205 \frac{\text{L atm}}{\text{mol K}})(400 .K)}{3.00 \text{ L}} = 0.926 \text{ atm.}$$

1980 D

Account for the differences in solubility described in each of the following experimental observations:

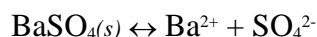
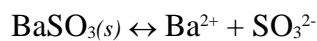
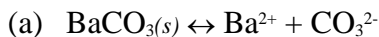
(a)  $\text{BaCO}_3$ ,  $\text{BaSO}_3$ , and  $\text{BaSO}_4$  are only slightly soluble in water, but the first two dissolve in HCl solution whereas  $\text{BaSO}_4$  does not.

(b)  $\text{CuS}$  cannot be dissolved by warm dilute HCl but it does dissolve in warm dilute  $\text{HNO}_3$ .

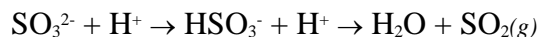
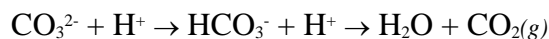
(c)  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$  and  $\text{PbCl}_2$  are only slightly soluble in water, but  $\text{AgCl}$  does dissolve in ammonia solution whereas the other two do not.

(d)  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  are only slightly soluble in water, but  $\text{Al}(\text{OH})_3$  dissolves in concentrated NaOH whereas  $\text{Fe}(\text{OH})_3$  does not.

Answer:



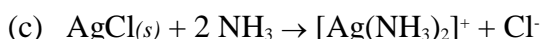
Dissolving takes place if equilibrium is shifted to the right.



In these two cases, equilibrium is shifted to the right by the production of a removed product (a gas).

$\text{SO}_4^{2-} + \text{H}^+$  do not react since  $\text{SO}_4^{2-}$  is a weak Bronsted base.

(b) Warm dilute  $\text{HNO}_3$  oxidizes  $\text{S}^{2-}$  to  $\text{S}^0$  (or higher). This reaction shifts the equilibrium between  $\text{CuS}(s)$  and its ions toward the ions.



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silver ions complex with ammonia to form the soluble  $[\text{Ag}(\text{NH}_3)_2]^+$ , neither  $\text{Hg}_2^{2+}$  nor  $\text{Pb}^{2+}$  form such complexes.

- (d)  $\text{Al}(\text{OH})_3(s) + \text{OH}^- \rightarrow \text{Al}(\text{OH})_4^-$  (or similar)

$\text{Al}(\text{OH})_3$  is amphoteric. The product is a hydroxoaluminate ion,  $\text{Fe}(\text{OH})_3$  is not amphoteric.

1984 C

Give a scientific explanation for the following observations. Use equations or diagrams if they are relevant.

- (a) It takes longer to cook an egg until it is hard-boiled in Denver (altitude 1 mile above sea level) than it does in New York City (near sea level).  
 (b) Burn coal containing a significant amount of sulfur leads to acid rain.  
 (c) Perspiring is a mechanism for cooling the body.  
 (d) The addition of antifreeze to water in a radiator decreases the likelihood that the liquid in the radiator will either freeze or boil.

Answer:

- (a) Water boils at a lower temperature in Denver than in NYC because the atmospheric pressure is less at high altitudes. At a lower temperature, the cooking process is slower, so the time to prepare a hard-boiled egg is longer.

- (b)  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  (as coal is burned)

$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$  (in the atmosphere)

$\text{H}_2\text{SO}_3$  is sulfurous acid.

- (c) Vaporization or evaporation of sweat from the skin is an endothermic process and takes heat from the body and so cool the skin.

- (d) Colligative properties, which depend on the number of particles present, are involved.

Solute (the antifreeze) causes the lowering of the vapor pressure of the solvent. When the vapor pressure of the solvent is lowered, the freezing point is lowered and the boiling point is raised.

1985 B

The formula and the molecular weight of an unknown hydrocarbon compound are to be determined by elemental analysis and the freezing-point depression method.

- (a) The hydrocarbon is found to contain 93.46 percent carbon and 6.54 percent hydrogen. Calculate the empirical formula of the unknown hydrocarbon.

- (b) A solution is prepared by dissolving 2.53 grams of p-dichlorobenzene (molecular weight 147.0) in 25.86 grams of naphthalene (molecular weight 128.2). Calculate the molality of the p-dichlorobenzene solution.

- (c) The freezing point of pure naphthalene is determined to be  $80.2^\circ\text{C}$ . The solution prepared in (b) is found to have an initial freezing point of  $75.7^\circ\text{C}$ . Calculate the molal freezing-point depression constant of naphthalene.

- (d) A solution of 2.42 grams of the unknown hydrocarbon dissolved in 26.7 grams of naphthalene is found to freeze initially at  $76.2^\circ\text{C}$ . Calculate the apparent molecular weight of the unknown hydrocarbon on the basis of the freezing-point depression experiment above.

- (e) What is the molecular formula of the unknown hydrocarbon?

Answer:

- (a) Assume 100. g sample of the hydrocarbon

$$93.46 \text{ g C} \propto \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.782 \text{ mol C}$$

$$6.54 \text{ g H} \propto \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.49 \text{ mol H}$$

$$\frac{7.782 \text{ mol C}}{6.49 \text{ mol H}} = \frac{1.20}{1.00}; \text{ C}_{1.20}\text{H}_{1.00} = \text{C}_6\text{H}_5$$

- (b)

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{2.53 \text{ g} \propto \frac{1 \text{ mol}}{147.0 \text{ g}}}{0.02586 \text{ kg}} = 0.666 \text{ molal}$$

- (c)  $\Delta T_f = (80.2 - 75.7)^\circ\text{C} = 4.5^\circ\text{C}$

$$k_f = \Delta T_f / m = 4.5^\circ\text{C} / 0.666 \text{ molal} = 6.8^\circ\text{C/molal}$$

- (d)  $\Delta T_f = (80.2 - 76.2)^\circ\text{C} = 4.0^\circ\text{C}$

$$\frac{1}{4.0^\circ\text{C}} \propto \frac{6.8^\circ\text{C} \cdot \text{kg solvent}}{1 \text{ mol solute}} \propto \frac{2.43 \text{ g solute}}{0.0267 \text{ kg solvent}} =$$

$$= 154 \text{ g/mol}$$

- (e)  $\text{C}_6\text{H}_5 = 77$

$$\# \text{ empirical units/mol} = 154/77 = 2$$

$$\text{molecular formula} = (\text{C}_6\text{H}_5)_2 = \text{C}_{12}\text{H}_{10}$$

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1986 D

Give a scientific explanation for each of the following observations. Use equations or diagrams if they seem relevant.

- (a) Graphite is used to make electrodes, while diamond, another allotrope of carbon, is a very poor conductor of electricity.
- (b) Putting rock salt on an icy driveway melts the ice even when the air temperature is  $-10^{\circ}\text{C}$ .
- (c) [question and answer in the GASES section]
- (d) Carbon dioxide, rather than a stream of water, should be used to extinguish an oil fire.

Answer:

- (a) Distinction or correctly implied distinction between the structures of graphite and diamond.  
Freedom of movement of electrons in graphite resulting from the structure.
- (b) The rock salt forms a concentrated solution with very little water from the ice. The solution now has a freezing point lower than the temperature of the ice, therefore, the ice melts.
- (c) [question and answer in the GASES section]
- (d) Carbon dioxide is more dense than air and so pushes the air away from the fire.

Water is more dense than the oil and so ends up below the oil, leaving the oil still in contact with the air; or the hot burning oil quickly vaporizes the water creating steam that spatters the oil into the air.

1987 D

In 1884 the Swedish chemist Svante Arrhenius proposed that salts dissociate into two or more separate, independent, ionic fragments when they dissolve in water.

- (a) Give one piece of experimental evidence that more than 1 mole of particles is formed when 1 mole of a salt dissolves in water.
- (b) Give one piece of experimental evidence that the particles formed when a salt dissolves in water are charged.
- (c) Explain why the heat of neutralization is always the same when 1 mole of any monoprotic strong

acid reacts with enough strong base to form a neutral solution.

- (d) Explain why hydrogen chloride,  $\text{HCl}$ , dissociated when it dissolves in water but not when it dissolves in benzene.

Answer:

- (a) The freezing point depression (or any colligative effect) that occurs when a mole of a salt is dissolved is greater than when a mole of a non-dissociated substance is dissolved. (The greater the number of solute particles the greater the colligative effect.)
- (b) The solution of a salt conducts electricity.
- (c) Every neutralization between a strong acid and a strong base involves the same reaction:



since both the strong acid and the strong base are completely dissociated. Spectator ions have no appreciable effect.

- (d) Because of the polar nature of water, it is capable of solvating the ions that result from the dissociation, whereas the nonpolar benzene interacts very weakly with these ions. OR

Because of the greater dielectric constant of water, it is better able to separate the ions.

1988 D

The normal boiling and freezing points of argon are  $87.3\text{ K}$  and  $84.0\text{ K}$ , respectively. The triple point is at  $82.7\text{ K}$  and  $0.68\text{ atmospheres}$ .

- (a) Use the data above to draw a phase diagram for argon. Label the axes and label the regions in which the solid, liquid and gas phases are stable. On the phase diagram, show the position of the normal boiling point.
- (b) Describe any changes that can be observed in a sample of solid argon when the temperature is increased from  $40\text{ K}$  to  $160\text{ K}$  at a constant pressure of  $0.50\text{ atmospheres}$ .
- (c) Describe any changes that can be observed in a sample of liquid argon when the pressure is reduced from  $10\text{ atmospheres}$  to  $1\text{ atmosphere}$  at a constant temperature of  $100\text{ K}$ , which is well below the critical temperature.

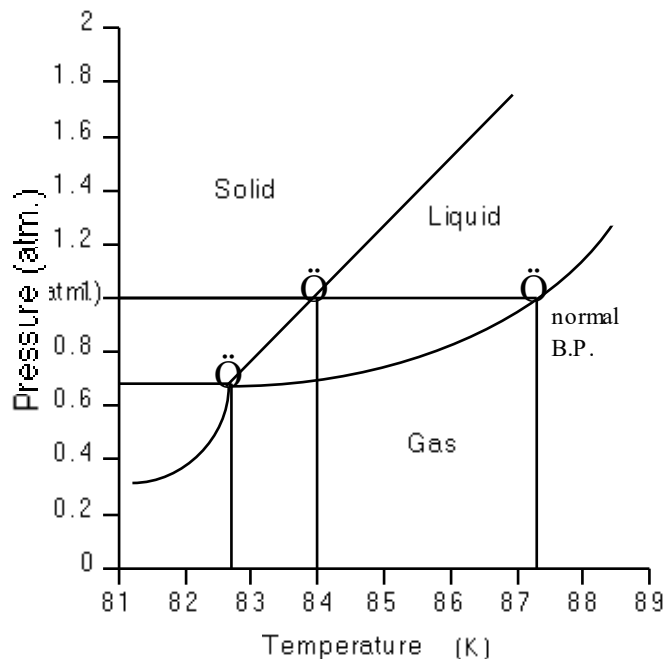
# Solids, Liquids, & Solutions

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- (d) Does the liquid phase of argon have a density greater than, equal to, or less than the density of the solid phase? Explain your answer, using information given in the introduction to this question.

Answer:

(a)



- (b) The argon sublimes.  
 (c) The argon vaporizes.  
 (d) The liquid phase is less dense than the solid phase. Since the freezing point of argon is higher than the triple point temperature, the solid-liquid equilibrium line slopes to the right with increasing pressure. Thus, if a sample of liquid argon is compressed (pressure increased) at constant temperature, the liquid becomes a solid. Because increasing pressure favors the denser phase, solid argon must be the denser phase.

1989 D

Consider three unlabeled bottles, each contain small pieces of one of the following metals.

- Magnesium
- Sodium
- Silver

The following reagents are used for identifying the metals.

- Pure water
- A solution of 1.0 molar HCl

- A solution of concentrated HNO<sub>3</sub>

- (a) Which metal can be easily identified because it is much softer than the other two? Describe a chemical test that distinguishes this metal from the other two, using only one of the reagents above. Write a balanced chemical equation for the reaction that occurs.
- (b) One of the other two metals reacts readily with the HCl solution. Identify the metal and write the balanced chemical equation for the reaction that occurs when this metal is added to the HCl solution. Use the table of standard reduction potentials (attached) to account for the fact that this metal reacts with HCl while the other does not.
- (c) The one remaining metal reacts with the concentrated HNO<sub>3</sub> solution. Write a balanced chemical equation for the reaction that occurs.
- (d) The solution obtained in (c) is diluted and a few drops of 1 M HCl is added. Describe what would be observed. Write a balanced chemical equation for the reaction that occurs.

Answer:

- (a) Sodium is softest of the three.  
 Na added to water → gas and base  

$$\text{Na} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{NaOH}$$
- (b) Mg reacts with HCl.  $\text{Mg} + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$   
 Reduction potentials, E°: Mg = -2.37v; Ag = +0.80v. Mg, not Ag, reacts with HCl
- (c)  $\text{Ag} + 4 \text{H}^+ + \text{NO}_3^- \rightarrow 3 \text{Ag}^+ + \text{NO} + 2 \text{H}_2\text{O}$  **OR**  
 $\text{Ag} + 2 \text{H}^+ + \text{NO}_3^- \rightarrow \text{Ag}^+ + \text{NO}_2 + \text{H}_2\text{O}$
- (d) A white precipitate forms:  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}_{(s)}$

1990 A

The solubility of iron(II) hydroxide, Fe(OH)<sub>2</sub>, is 1.43×10<sup>-3</sup> gram per litre at 25°C.

- (a) Write a balanced equation for the solubility equilibrium.
- (b) Write the expression for the solubility product constant, K<sub>sp</sub>, and calculate its value.
- (c) Calculate the pH of a saturated solution of Fe(OH)<sub>2</sub> at 25°C.
- (d) A 50.0 millilitre sample of 3.00×10<sup>-3</sup> molar FeSO<sub>4</sub> solution is added to 50.0 millilitres of 4.00×10<sup>-6</sup> molar NaOH solution. Does a precipitate of

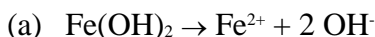


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Fe(OH)<sub>2</sub> form? Explain and show calculations to support your answer.

Answer:



(b)  $\frac{1.43 \times 10^{-3} \text{ g}}{\text{L}} \times \frac{1 \text{ mol}}{89.9 \text{ g}} = 1.59 \times 10^{-5} \text{ mol/L Fe(OH)}_2$

$= 1.59 \times 10^{-5} \text{ M} = [\text{Fe}^{2+}]$

$= 3.18 \times 10^{-5} \text{ M} = [\text{OH}^-]$

$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (1.59 \times 10^{-5})(3.18 \times 10^{-5})^2$

$= 1.61 \times 10^{-14}$

(c)  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.18 \times 10^{-5}} = 3.14 \times 10^{-10} \text{ M}$

$\text{pH} = -\log[\text{H}^+] = 9.50$

OR

$\text{pOH} = -\log[\text{OH}^-] = -\log(3.18 \times 10^{-5}) = 4.50$

$\text{pH} = 14 - \text{pOH} = 9.50$

(d) 50.0 mL of  $3.00 \times 10^{-3} \text{ M Fe}^{2+}$  diluted of 100.0 mL =  $1.50 \times 10^{-3} \text{ M Fe}^{2+}$

50.0 mL of  $4.00 \times 10^{-6} \text{ M OH}^-$  diluted of 100.0 mL =  $2.00 \times 10^{-6} \text{ M OH}^-$

$Q = [\text{Fe}^{2+}][\text{OH}^-]^2 = (1.50 \times 10^{-3})(2.00 \times 10^{-6})^2$

$= 6.00 \times 10^{-15}$

Precipitate will NOT form since  $Q < K_{sp}$

1993 A

Elemental analysis of an unknown pure substance indicated that the percent composition by mass is as follows.

| Element  | Percent by Mass |
|----------|-----------------|
| Carbon   | 49.02%          |
| Hydrogen | 2.743%          |
| Chlorine | 48.23%          |

A solution that is prepared by dissolving 3.150 grams of the substance in 25.00 grams of benzene, C<sub>6</sub>H<sub>6</sub>, has a freezing point of 1.12°C. (The normal freezing point of benzene is 5.50°C and the molal freezing-point depression constant, K<sub>f</sub>, for benzene is 5.12°C/molal.)

(a) Determine the empirical formula of the unknown substance.

(b) Using the data gathered from the freezing-point depression method, calculate the molar mass of the unknown substance.

(c) Calculate the mole fraction of benzene in the solution described above.

(d) The vapor pressure of pure benzene at 35°C is 150. millimeters of Hg. Calculate the vapor pressure of benzene over the solution described above at 35°C.

Answer:

(a) moles / 100 g C H Cl  
 49.02/12.01 2.743/1.008 48.23/35.45  
 = 4.081 = 2.722 = 1.360  
 mol ratio 3 2 1  
 empirical formula: C<sub>3</sub>H<sub>2</sub>Cl

(b)  $\Delta T_f = (K_f)(m)$

$4.38^\circ = (5.12^\circ/\text{molal}) \times \frac{3.150\text{g/molmass}}{0.02500\text{kg}} = 147\text{g/mol}$

(c) mol fraction = mol benzene / total mol

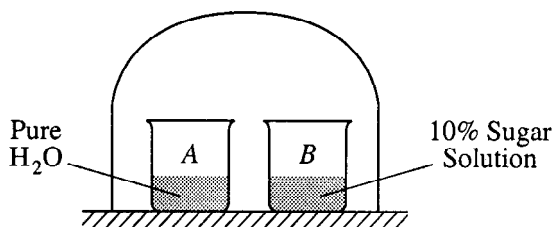
$= \frac{25.00/78.11}{\frac{3.150}{147} + \frac{25.00}{78.11}} = 0.938$

(d) vapor pressure = mol fraction  $\times$  P<sub>o</sub>

$= (0.938)(150 \text{ mm}) = 141 \text{ mm Hg}$

1994 D (Required)

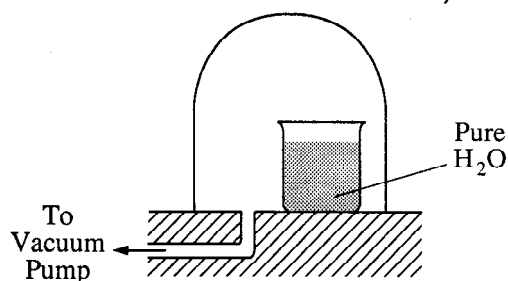
Discuss the following phenomena in terms of the chemical and physical properties of the substances involved and general principles of chemical and physical change.



(a) As the system shown above approaches equilibrium, what change occurs to the volume of water in beaker A? What happens to the concentration of the sugar solution in beaker B? Explain why these changes occur.

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(ii) The TTE will be the bottom layer because its density is greater than the water.

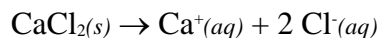
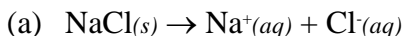
(iii) The non-polar iodine will dissolve better in the non-polar TTE and form a pinkish-purple tint.

1994 D

For each of the following, use appropriate chemical principles to explain the observation.

- (a) Sodium chloride may be spread on an icy sidewalk in order to melt the ice; equimolar amounts of calcium chloride are even more effective.
- (b) At room temperature,  $\text{NH}_3$  is a gas and  $\text{H}_2\text{O}$  is a liquid, even though  $\text{NH}_3$  has a molar mass of 17 grams and  $\text{H}_2\text{O}$  has a molar mass of 18 grams.
- (c) C (graphite) is used as a lubricant, whereas C (diamond) is used as an abrasive.
- (d) Pouring vinegar onto the white residue inside a kettle used for boiling water results in a fizzing/bubbling phenomenon.

Answer:

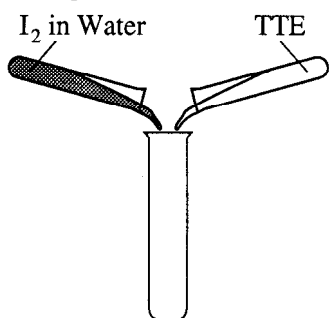


The freezing point of an aqueous solution is lower than the freezing point of water. A higher molality of a solution lowers the freezing point more and an equimolar amount of the two solids gives a larger molal solution from the calcium chloride as illustrated by the above equations.

- (b) Water is more polar than ammonia creating stronger attractions (IMF) between molecules and making it a liquid.
- (c) Diamond, the hardest naturally occurring substance, has each carbon atom surrounded by a tetrahedral arrangement of other carbon atoms (see drawing). The network solid structure is stabilized by covalent bonds, formed by the overlap of  $sp^3$  hybridized carbon atomic orbitals. A diamond has uniform very strong bonds in all directions in the crystal.

- (b) A bell jar connected to a vacuum pump is shown above. As the air pressure under the bell jar decreases, what behavior of water in the beaker will be observed? Explain why this occurs.

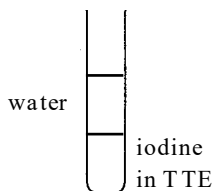
- (c) [see Redox section]



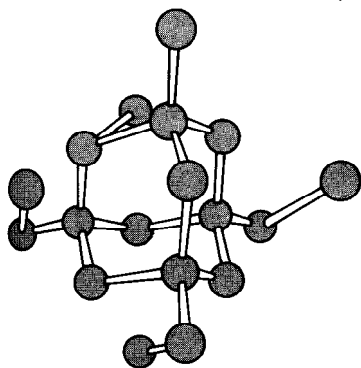
- (d) A water solution of  $\text{I}_2$  is shaken with an equal volume of a nonpolar solvent such as TTE (trichlorotrifluoroethane). Describe the appearance of this system after shaking. (A diagram may be helpful.) Account for this observation.

Answer:

- (a) volume of water decreases while the concentration of sugar solution decreases.  
Pure water has a higher vapor pressure than does the 10% sugar solution and when equilibrium is reached the water will evaporate and the solution will increase in volume.
- (b) The water will boil when the pressure in the bell jar reaches the vapor pressure of the water. Boiling occurs when the vapor pressure of the liquid is in equilibrium with the pressure above the liquid.
- (d) (i) Water and TTE will form separate layers because the polar water is not miscible with the non-polar TTE.

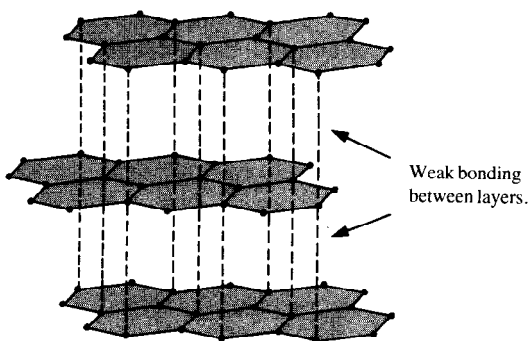


# Solids, Liquids, & Solutions

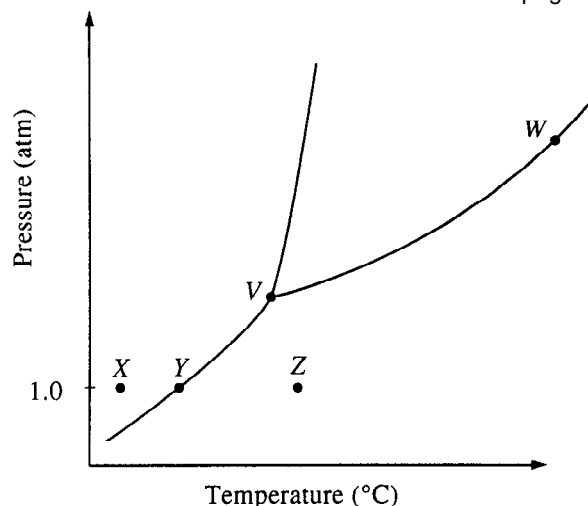


Diamond

Graphite has a different kind of bonding based on layers of carbon atoms arranged in fused six-member rings (see drawing). Each carbon atom in a layer is surrounded by three other carbons in a trigonal planar arrangement with  $120^\circ$  bond angles. The slipperiness is caused by noting that graphite has very strong bonds within layers but little bonding between the layers which allows the layers to slide past one another quite readily.



Graphite



The phase diagram for a pure substance is shown above. Use this diagram and your knowledge about changes of phase to answer the following questions.

- What does point V represent? What characteristics are specific to the system only at point V?
- What does each point on the curve between V and W represent?
- Describe the changes that the system undergoes as the temperature slowly increases from X to Y to Z at 1.0 atmosphere.
- In a solid-liquid mixture of this substance, will the solid float or sink? Explain.

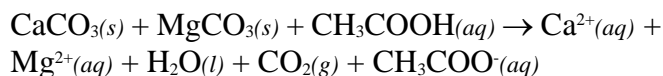
Answer:

- Triple point. All three states of the substance co-exist (equilibrium); the solid and the liquid have identical vapor pressures.
- Curve VW represents the equilibrium between the liquid and its vapor. Along this line the liquid will be boiling. The points represent the vapor pressure of the liquid as a function of temperature.
- At point X the substance is a solid, as its temperature increases (at constant pressure), at point Y the solid is in equilibrium with its vapor and will sublime. From point Y to Z it exist only as a vapor.
- Sink. A positive slope of the solid-liquid line indicates that the solid is denser than its liquid and, therefore, will sink.

1995 D (repeated in the thermo section)

Lead iodide is a dense, golden yellow, slightly soluble solid. At  $25^\circ\text{C}$ , lead iodide dissolves in water forming a system represented by the following equation.

- Calcium and magnesium carbonates are left behind from the evaporation of hard water. These carbonates decompose and release carbon dioxide gas when reacted with the acetic acid in the vinegar.



1995 D

# Solids, Liquids, & Solutions

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- (a) How does the entropy of the system  $\text{PbI}_{2(s)} + \text{H}_2\text{O}(l)$  change as  $\text{PbI}_{2(s)}$  dissolves in water at  $25^\circ\text{C}$ ? Explain
- (b) If the temperature of the system were lowered from  $25^\circ\text{C}$  to  $15^\circ\text{C}$ , what would be the effect on the value of  $K_{sp}$ ? Explain.
- (c) If additional solid  $\text{PbI}_2$  were added to the system at equilibrium, what would be the effect on the concentration of  $\text{I}^-$  in the solution? Explain.
- (d) At equilibrium,  $\Delta G = 0$ . What is the initial effect on the value of  $\Delta G$  of adding a small amount of  $\text{Pb}(\text{NO}_3)_2$  to the system at equilibrium? Explain.

Answer:

- (a) Entropy increases. At the same temperature, liquids and solids have a much lower entropy than do aqueous ions. Ions in solutions have much greater “degrees of freedom and randomness”.
- (b)  $K_{sp}$  value decreases.  $K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2$ . As the temperature is decreased, the rate of the forward (endothermic) reaction decreases resulting in a net decrease in ion concentration which produces a smaller  $K_{sp}$  value.
- (c) No effect. The addition of more solid  $\text{PbI}_2$  does not change the concentration of the  $\text{PbI}_2$  which is a constant (at constant temperature), therefore, neither the rate of the forward nor reverse reaction is affected and the concentration of iodide ions remains the same.
- (d)  $\Delta G$  increases. Increasing the concentration of  $\text{Pb}^{2+}$  ions causes a spontaneous increase in the reverse reaction rate (a “shift left” according to LeChâtelier’s Principle). A reverse reaction is spontaneous when the  $\Delta G > 0$ .

1996 B

Concentrated sulfuric acid (18.4-molar  $\text{H}_2\text{SO}_4$ ) has a density of 1.84 grams per milliliter. After dilution with water to 5.20-molar, the solution has a density of 1.38 grams per milliliter and can be used as an electrolyte in lead storage batteries for automobiles.

- (a) Calculate the volume of concentrated acid required to prepare 1.00 liter of 5.20-molar  $\text{H}_2\text{SO}_4$ .
- (b) Determine the mass percent of  $\text{H}_2\text{SO}_4$  in the original concentrated solution.

- (c) Calculate the volume of 5.20-molar  $\text{H}_2\text{SO}_4$  that can be completely neutralized with 10.5 grams of sodium bicarbonate,  $\text{NaHCO}_3$ .
- (d) What is the molality of the 5.20-molar  $\text{H}_2\text{SO}_4$ ?

Answer:

- (a)  $M_1V_1 = M_2V_2$ ;  $(5.20 \text{ M})(1.00 \text{ L}) = (18.4 \text{ M})(V_2)$   
 $V_2 = 0.283 \text{ L}$
- (b)  $18.4 \text{ mol/L} \times 98.1 \text{ g H}_2\text{SO}_4/\text{mol} = 1805 \text{ g H}_2\text{SO}_4$   
 $1 \text{ L} \times 1.84 \text{ g/mL} \times 1000 \text{ mL/L} = 1840 \text{ g solution}$   
 $\text{mass \%} = 1805 \text{ g}/1840 \text{ g} \times 100 = 98.1\%$
- (c)  $2 \text{ NaHCO}_3 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{ H}_2\text{O} + \text{Na}_2\text{SO}_4 + 2 \text{ CO}_2$   
 $10.5 \text{ g NaHCO}_3 \times 1 \text{ mol NaHCO}_3/84.0 \text{ g NaHCO}_3 \times 1 \text{ mol H}_2\text{SO}_4/2 \text{ mol NaHCO}_3 \times 1 \text{ L}/5.20 \text{ mol H}_2\text{SO}_4 = 0.0120 \text{ L}$
- (d)  $\text{molality} = \text{mol solute}/\text{kg solvent}$   
 $5.20 \text{ mol/L} \times 98.1 \text{ g H}_2\text{SO}_4/\text{mol} = 510 \text{ g H}_2\text{SO}_4$   
 $1 \text{ L} \times 1.38 \text{ g/mL} \times 1000 \text{ mL/L} = 1380 \text{ g solution}$   
 $1380 \text{ g solution} - 510 \text{ g H}_2\text{SO}_4 = 870 \text{ g solvent}$   
 $5.20 \text{ mol H}_2\text{SO}_4/0.870 \text{ kg solvent} = 5.98 \text{ m}$

1998 A (Required)

Solve the following problem related to the solubility equilibria of some metal hydroxides in aqueous solution.

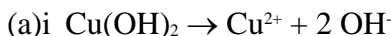
- (a) The solubility of  $\text{Cu}(\text{OH})_2(s)$  is  $1.72 \times 10^{-6}$  gram per 100. milliliters of solution at  $25^\circ\text{C}$ .
- (i) Write the balanced chemical equation for the dissociation of  $\text{Cu}(\text{OH})_2(s)$  in aqueous solution.
- (ii) Calculate the solubility (in moles per liter) of  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .
- (iii) Calculate the value of the solubility-product constant,  $K_{sp}$ , for  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .
- (b) The value of the solubility-product constant,  $K_{sp}$ , for  $\text{Zn}(\text{OH})_2$  is  $7.7 \times 10^{-17}$  at  $25^\circ\text{C}$ .
- (i) Calculate the solubility (in moles per liter) of  $\text{Zn}(\text{OH})_2$  at  $25^\circ\text{C}$  in a solution with a pH of 9.35.

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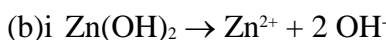
- (ii) At 25°C, 50.0 milliliters of 0.100-molar  $\text{Zn}(\text{NO}_3)_2$  is mixed with 50.0 milliliters of 0.300-molar NaOH. Calculate the molar concentration of  $\text{Zn}^{2+}(\text{aq})$  in the resulting solution once equilibrium has been established. Assume that volumes are additive.

Answer



$$\text{ii} \quad \frac{1.72 \times 10^{-6} \text{ g}}{0.100 \text{ L}} \propto \frac{1 \text{ mol}}{97.5 \text{ g}} = 1.76 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$

$$\text{iii} \quad K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 \\ = [1.76 \times 10^{-7}][3.53 \times 10^{-8}]^2 = 2.20 \times 10^{-20}$$



$$K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

$$\text{pH } 9.35 = \text{pOH } 4.65; [\text{OH}^-] = 10^{-\text{pOH}}$$

$$[\text{OH}^-] = 10^{-4.65} = 2.24 \times 10^{-5} \text{ M}$$

$$[\text{Zn}^{2+}] = \text{solubility of } \text{Zn}(\text{OH})_2 \text{ in } \frac{\text{mol}}{\text{L}}$$

$$[\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{7.7 \times 10^{-17}}{(2.24 \times 10^{-5})^2} = 1.5 \times 10^{-7} \text{ M}$$

$$\text{ii} \quad [\text{Zn}^{2+}]_{\text{init}} = 0.100 \text{ M} \times \frac{50 \text{ mL}}{100 \text{ mL}} = 0.0500 \text{ M}$$

$$[\text{OH}^-]_{\text{init}} = 0.300 \text{ M} \times \frac{50 \text{ mL}}{100 \text{ mL}} = 0.150 \text{ M}$$

X = conc. loss to get to equilibrium

$$K_{sp} = 7.7 \times 10^{-17} = (0.0500 - X)(0.150 - 2X)^2$$

$$[\text{Zn}^{2+}] = 0.0500 - X = 3.1 \times 10^{-14} \text{ M}$$

1998 B

An unknown compound contains only the three elements C, H, and O. A pure sample of the compound is analyzed and found to be 65.60 percent C and 9.44 percent H by mass.

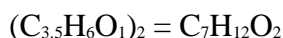
- (a) Determine the empirical formula of the compound.
- (b) A solution of 1.570 grams of the compound in 16.08 grams of camphor is observed to freeze at a temperature 15.2 Celsius degrees below the normal freezing point of pure camphor. Determine the molar mass and apparent molecular formula of the compound. (The molal freezing-point depression constant,  $K_a$ , for camphor is  $40.0 \text{ kg} \cdot \text{K} \cdot \text{mol}^{-1}$ .)

- (c) When 1.570 grams of the compound is vaporized at 300°C and 1.00 atmosphere, the gas occupies a volume of 577 milliliters. What is the molar mass of the compound based on this result?
- (d) Briefly describe what occurs in solution that accounts for the difference between the results obtained in parts (b) and (c).

Answer

$$\text{(a)} \quad \frac{65.60}{12.011} = 5.462 \quad \frac{9.44}{1.0079} = 9.37 \quad \frac{24.96}{16.00} = 1.56$$

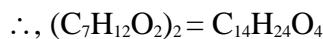
$$\frac{5.462}{1.56} = 3.50 \quad \frac{9.37}{1.56} = 6.00 \quad \frac{1.56}{1.56} = 1.00$$



$$\text{(b)} \quad \Delta T_{\text{FP}} = k_a m = k_a \frac{\frac{\text{mol solute}}{\text{kg solvent}}}{\frac{\text{g solvent}}{\text{molar mass}}} = k_a \frac{(\text{g solute})(\frac{1}{k_e})}{(\text{kg solvent})(\Delta T_{\text{FP}})}$$

$$\text{molar mass} = \frac{(1.570 \text{ g})(40.0 \frac{\text{kg} \cdot \text{K}}{\text{mol}})}{(0.01608 \text{ kg})(15.2 \text{ } ^\circ\text{C})} = 257 \text{ g/mol}$$

$$\text{C}_7\text{H}_{12}\text{O}_2 = 128 \text{ g/mol}; 257/128 = 2$$



$$\text{(c)} \quad \text{PV} = \frac{\text{grams}}{\text{molar mass}} \frac{\text{RT}}{\text{P} \propto \text{V}}$$

$$\text{molar mass} = \frac{\text{grams} \propto \text{R} \propto \text{T}}{\text{P} \propto \text{V}}$$

$$\frac{(1.570 \text{ g}) \propto 0.08205 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \propto 573 \text{ K}}{1.00 \text{ atm} \propto 0.577 \text{ L}} = 128 \text{ g/mol}$$

- (d) since the apparent molar mass from freezing point change is twice that determined by the vapor, the molecules of the compound must associate in camphor to form dimers, **OR** the compound must dissociate in the gas phase.

1998 D

Answer each of the following using appropriate chemical principles.

- (a) Why does it take longer to cook an egg in boiling water at high altitude than it does at sea level?

Answer

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- (a) At a high altitude the pressure is lower and the boiling point of water is lower. Since the temperature of the boiling water is less, it takes longer to cook the egg.

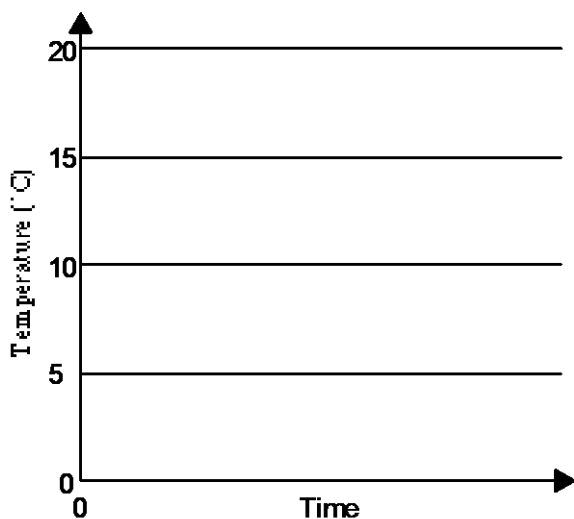
2000 D Required

The molar mass of an unknown solid, which is nonvolatile and a nonelectrolyte, is to be determined by the freezing-point depression method. The pure solvent used in the experiment freezes at  $10^{\circ}\text{C}$  and has a known molal freezing-point depression constant,  $K_f$ . Assume that the following materials are also available.

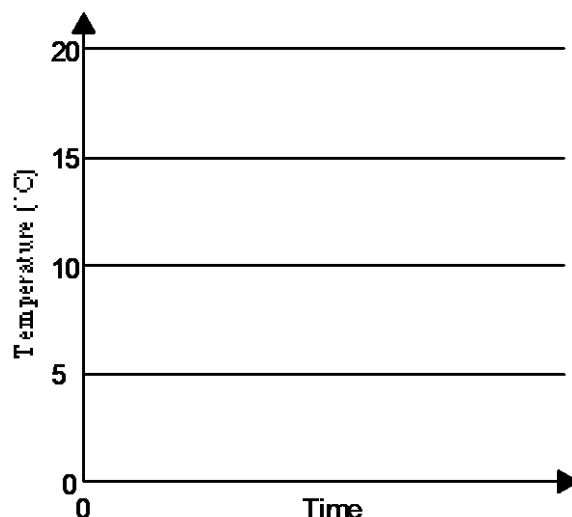
- test tubes      • stirrer      • pipet
- stopwatch      • graph paper
- thermometer      • balance      • beaker
- ice      • hot-water bath

- (a) Using the two sets of axes provided below, sketch cooling curves for (i) the pure solvent and for (ii) the solution as each is cooled from  $20^{\circ}\text{C}$  to  $0.0^{\circ}\text{C}$

Pure Solvent



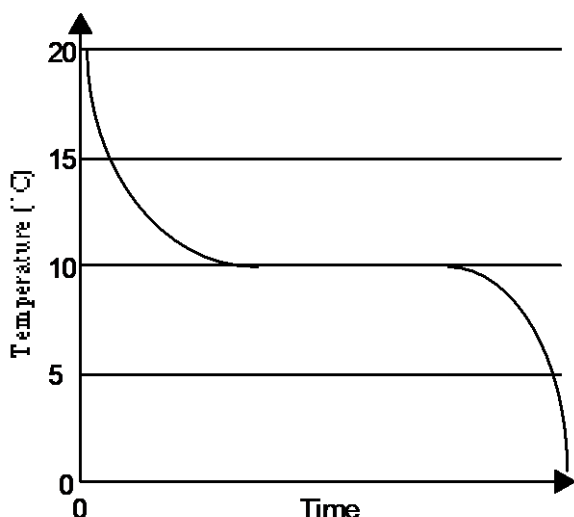
Solution



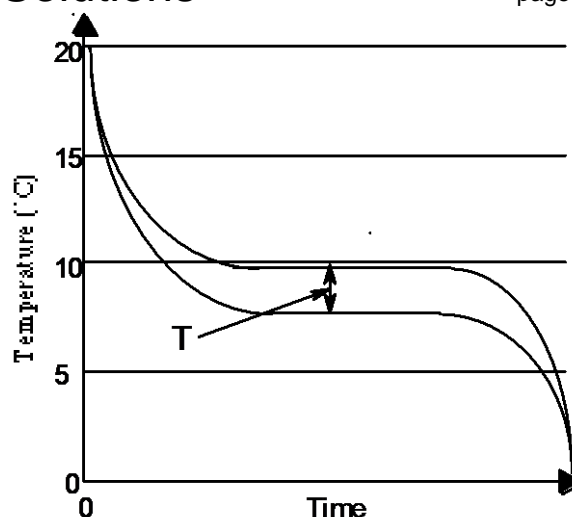
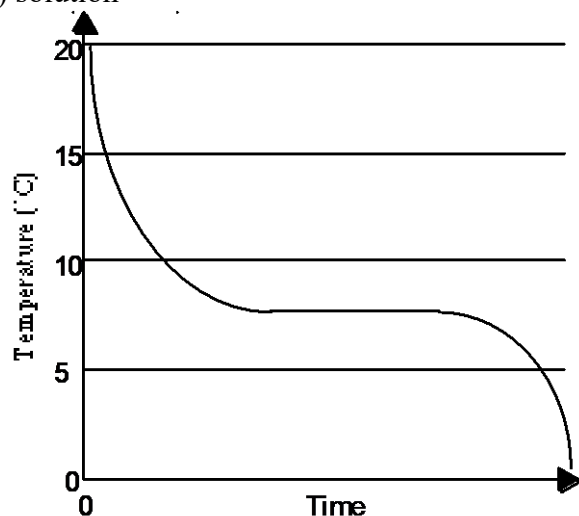
- (b) Information from these graphs may be used to determine the molar mass of the unknown solid.
- Describe the measurements that must be made to determine the molar mass of the unknown solid by this method.
  - Show the setup(s) for the calculation(s) that must be performed to determine the molar mass of the unknown solid from the experimental data.
  - Explain how the difference(s) between the two graphs in part (a) can be used to obtain information needed to calculate the molar mass of the unknown solid.
- (c) Suppose that during the experiment a significant but unknown amount of solvent evaporates from the test tube. What effect would this have on (the calculated value of the molar mass of the solid (*i.e.*, too large, too small, or no effect)? Justify your answer.
- (d) Show the setup for the calculation of the percentage error in a student's result if the student obtains a value of  $126 \text{ g mol}^{-1}$  for the molar mass of the solid when the actual value is  $120. \text{ g mol}^{-1}$ .

Answer:

- (a) (i) pure solvent



(ii) solution



(c) Too small. If solvent evaporates then its mass decreases and the recorded denominator in the equation in (b)(i) is larger than the expt. value and the resulting answer decreases.

$$(d) \% \text{ error} = \frac{(126 \text{ g} \cdot \text{mol}^{-1} - 120 \text{ g} \cdot \text{mol}^{-1})}{120 \text{ g} \cdot \text{mol}^{-1}} \times 100\%$$

## 2001 A Required

Answer the following questions relating to the solubility of the chlorides of silver and lead.

(a) At 10°C,  $8.9 \times 10^{-5}$  g of  $\text{AgCl}_{(s)}$  will dissolve in 100. mL of water.

(i) Write the equation for the dissociation of  $\text{AgCl}_{(s)}$  in water.

(ii) Calculate the solubility, in  $\text{mol L}^{-1}$ , of  $\text{AgCl}_{(s)}$  in water at 10°C.

(iii) Calculate the value of the solubility-product constant,  $K_{sp}$  for  $\text{AgCl}_{(s)}$  at 10°C.

(b) At 25°C, the value of  $K_{sp}$  for  $\text{PbCl}_{2(s)}$  is  $1.6 \times 10^{-5}$  and the value of  $K_{sp}$  for  $\text{AgCl}_{(s)}$  is  $1.8 \times 10^{-10}$ .

(i) If 60.0 mL of 0.0400 M  $\text{NaCl}_{(aq)}$  is added to 60.0 mL of 0.0300 M  $\text{Pb}(\text{NO}_3)_{2(aq)}$ , will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.

(ii) Calculate the equilibrium value of  $[\text{Pb}^{2+}_{(aq)}]$  in 1.00 L of saturated  $\text{PbCl}_2$  solution to which 0.250 mole of  $\text{NaCl}_{(s)}$  has been added. Assume that no volume change occurs.

(iii) If 0.100 M  $\text{NaCl}_{(aq)}$  is added slowly to a beaker containing both 0.120 M  $\text{AgNO}_3(aq)$

(b) (i) mass of pure solvent; freezing point of pure solvent; mass of unknown solid solute added to pure solvent; freezing point of resulting solution

(ii) determine the change in freezing point,  $\Delta T$

$$\Delta T = K_f \cdot m, \text{ where } m = \frac{\text{mol solute}}{1 \text{ kg of solvent}} \text{ and moles}$$

$$\text{solute} = \frac{\text{mass solute}}{\text{molar mass}}$$

$$\text{therefore, molar mass} = \frac{\text{mass of solute} \cdot K_f}{\text{kg solvent} \cdot \Delta T}$$

(iii) the change in temperature is the difference in the flat portions of the graph.

# Solids, Liquids, & Solutions

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and 0.150 M  $\text{Pb}(\text{NO}_3)_2(aq)$  at 25°C, which will precipitate first,  $\text{AgCl}(s)$  or  $\text{PbCl}_2(s)$ ? Show calculations to support your answer.

## Answer:

(a) (i)  $\text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^-$

$$(ii) \frac{8.9 \times 10^{-5} \text{ g}}{0.100 \text{ L}} \times \frac{1 \text{ mol}}{143.343 \text{ g}} = 6.2 \times 10^{-6} \text{ M}$$

$$(iii) K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (6.2 \times 10^{-6})^2 = 3.9 \times 10^{-11}$$

(b) (i) No

$$\frac{60.0 \text{ mL}}{(60.0 \text{ mL} + 60.0 \text{ mL})} \times \frac{0.0400 \text{ mol}}{1000 \text{ mL}} = 0.0200 \text{ M} \quad [\text{Cl}^-]$$

$$\frac{60.0 \text{ mL}}{(60.0 \text{ mL} + 60.0 \text{ mL})} \times \frac{0.0300 \text{ mol}}{1000 \text{ mL}} = 0.0150 \text{ M} \quad [\text{Pb}^{2+}]$$

$$\text{trial } K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (0.0150)(0.0200)^2 = 6.0 \times 10^{-6}; \text{ trial } K_{sp} < K_{sp}, \text{ no ppt.}$$

$$(ii) K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2, [\text{Pb}^{2+}] = K_{sp}/[\text{Cl}^-]^2$$

$$[\text{Pb}^{2+}] = \frac{1.6 \times 10^{-5}}{(0.250)^2} = 2.6 \times 10^{-4} \text{ M}$$

(iii)  $\text{AgCl}$

$$[\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{0.120} = 1.5 \times 10^{-9} \text{ M}$$

$\text{PbCl}_2$

$$[\text{Cl}^-] = \sqrt{\frac{K_{sp}}{[\text{Pb}^{2+}]}} = \sqrt{\frac{1.6 \times 10^{-5}}{0.150}} = 0.0103 \text{ M}$$

$\text{AgCl}$  will form a ppt when the  $[\text{Cl}^-]$  exceeds  $1.5 \times 10^{-9} \text{ M}$ . The formation of  $\text{PbCl}_2(s)$  requires a  $[\text{Cl}^-]$  that is over 6 million times more concentrated.

## 2001 D Required

Solution 1   Solution 2   Solution 3   Solution 4   Solution 5



0.10 M  $\text{Pb}(\text{NO}_3)_2$    0.10 M  $\text{NaCl}$    0.10 M  $\text{KMnO}_4$    0.10 M  $\text{C}_2\text{H}_5\text{OH}$    0.10 M  $\text{KC}_2\text{H}_3\text{O}_2$

Answer the questions below that relate to the five aqueous solutions at 25°C shown above.

- Which solution has the highest boiling point? Explain.
- Which solution has the highest pH? Explain.
- Identify a pair of the solutions that would produce a precipitate when mixed together. Write the formula of the precipitate.
- Which solution could be used to oxidize the  $\text{Cl}^-(aq)$  ion? Identify the product of the oxidation.
- Which solution would be the least effective conductor of electricity? Explain.

## Answer:

- solution 1,  $\text{Pb}(\text{NO}_3)_2$ . This compound will dissociate into three ions with the highest total particle molality. The greater the molality, the higher the boiling point. Solutions 2, 3, and 5 will produce two ions while solution 4 is molecular.
- solution 5,  $\text{KC}_2\text{H}_3\text{O}_2$ . The salt of a weak acid (in this case, acetic acid) produces a basic solution, and, a higher pH.
- solution 1,  $\text{Pb}(\text{NO}_3)_2$ , and solution 2,  $\text{NaCl}$ .  $\text{PbCl}_2$
- solution 3,  $\text{KMnO}_4$ ,  $\text{ClO}_3^-$
- solution 4,  $\text{C}_2\text{H}_5\text{OH}$ . Ethyl alcohol is covalently bonded and does not form ions in water. Therefore, the solution is not a better conductor of electricity than water, which is also covalently bonded.

## 2003 D Required

For each of the following, use appropriate chemical principles to explain the observations. Include chemical equations as appropriate.

- In areas affected by acid rain, statues and structures made of limestone (calcium carbonate) often show signs of considerable deterioration.
- When table salt ( $\text{NaCl}$ ) and sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) are dissolved in water, it is observed that
  - both solution have higher boiling points than pure water, and
  - the boiling point of 0.10 M  $\text{NaCl}(aq)$  is higher than that of 0.10 M  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$ .
- Methane gas does not behave as an ideal gas at low temperatures and high pressures.
- Water droplets form on the outside of a beaker containing an ice bath.

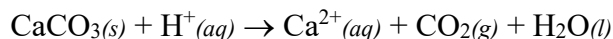


# Solids, Liquids, & Solutions

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Answer:

- (a) limestone reacts with acid to produce a soluble substance, a gas, and water which wash away



- (b) (i) a solution made from a non-volatile solute has a higher boiling point than the pure solvent because the solution has a lower vapor pressure than the water (Raoult's Law). the temperature of the solution has to be higher to produce enough vapor pressure to equal the atmospheric pressure (i.e., boiling)

(ii) the amount of boiling point elevation depends on the number of non-volatile particles in solution. since the salt dissociates into 2 particles for every NaCl that dissolves, it will increase the boiling point more than an equal concentration of sugar (a molecular cpd) that does not dissociate or ionize.

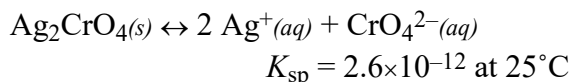
- (c) at low temperatures and high pressures, the methane molecules are slow and closer together. under these conditions, van der Waal forces become measurable and significant and creates a deviation from ideal behavior. at high pressure the volume of a real molecule is also significant.

- (d) a water vapor molecules collide with the cool beaker, the molecules lose kinetic energy, slow down, attract others, and condense into a liquid

## 2004 A Required

Answer the questions relating to the solubility's of two silver compounds,  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$

Silver chromate dissociates in water according to the following equation:



- (a) Write the equilibrium constant expression for the dissolving of  $\text{Ag}_2\text{CrO}_4$ .
- (b) Calculate the concentration in  $\text{mol L}^{-1}$ , of  $\text{Ag}^+$  in a saturated solution of  $\text{Ag}_2\text{CrO}_4$  at  $25^\circ\text{C}$ .
- (c) Calculate the maximum mass in grams of  $\text{Ag}_2\text{CrO}_4$  that can dissolve in 100. mL of water at  $25^\circ\text{C}$ .
- (d) A 0.100 mol sample of solid  $\text{AgNO}_3$  is added to 1.00 L saturated solution of  $\text{Ag}_2\text{CrO}_4$ . Assuming no volume change, does  $[\text{CrO}_4^{2-}]$  increase, de-

crease, or remain the same? Justify your answer.

In a saturated solution of  $\text{Ag}_3\text{PO}_4$  at  $25^\circ\text{C}$ , the concentration of  $\text{Ag}^+$  is  $5.3 \times 10^{-5} \text{ M}$ . The equilibrium constant expression for the dissolving of  $\text{Ag}_3\text{PO}_4$  is shown below:

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

- (e) Write the balanced equation for the dissolving of  $\text{Ag}_3\text{PO}_4$  in water.
- (f) Calculate the value of  $K_{sp}$  for  $\text{Ag}_3\text{PO}_4$  in water.
- (g) A 1.00 L sample of saturated  $\text{Ag}_3\text{PO}_4$  solution is allowed to evaporate at  $25^\circ\text{C}$  to a final volume of 500. mL. What is  $[\text{Ag}^+]$  in the solution? Justify your answer.

Answer:

(a)  $K_{sp} = [\text{Ag}^+]^2[\text{Cr}_2\text{O}_7^{2-}]$

(b)  $[\text{Cr}_2\text{O}_7^{2-}] = X; [\text{Ag}^+] = 2X$

$$(2X)^2(X) = K_{sp} = 2.6 \times 10^{-12}$$

$$X = 8.7 \times 10^{-5} \text{ mol L}^{-1}$$

$$2X = [\text{Ag}^+] = 1.7 \times 10^{-4} \text{ mol L}^{-1}$$

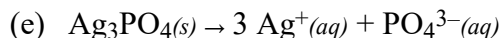
(c)  $\text{amt. Ag}_2\text{CrO}_4 = X = 8.7 \times 10^{-5} \text{ mol L}^{-1}$

$$(8.7 \times 10^{-5} \text{ mol L}^{-1})(331.74 \text{ g mol}^{-1}) =$$

$$= 0.0287 \text{ g L}^{-1}$$

$$\text{in 100 mL, } 100 \text{ mL} \times \frac{0.0287 \text{ g}}{1000 \text{ mL}} = 0.0029 \text{ g}$$

- (d) decrease, since the silver nitrate dissolves and produces an increase in  $[\text{Ag}^+]$ , this causes a LeChâtelier shift to the left and results in a decrease in the products, including chromate ions



(f)  $[\text{PO}_4^{3-}] = \frac{[\text{Ag}^+]}{3}$

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (5.3 \times 10^{-5})^3 \left( \frac{5.3 \times 10^{-5}}{3} \right)$$

$$= 2.6 \times 10^{-18}$$

- (g)  $[\text{Ag}^+] = 5.3 \times 10^{-5} \text{ M}$ . In a saturated solution the molar concentration is independent of the total volume. As the volume evaporates and becomes half, half of the  $\text{Ag}^+$  will precipitate out.

2005 B

# Solids, Liquids, & Solutions

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Answer the following questions about a pure compound that contains only carbon, hydrogen, and oxygen.

- (a) A 0.7549 g sample of the compound burns in  $O_{2(g)}$  to produce 1.9061 g of  $CO_{2(g)}$  and 0.3370 g of  $H_2O_{(g)}$ .

(i) Calculate the individual masses of C, H, and O in the 0.7549 g sample.

(ii) Determine the empirical formula for the compound.

- (b) A 0.5246 g sample of the compound was dissolved in 10.0012 g of lauric acid, and it was determined that the freezing point of the lauric acid was lowered by  $1.68^{\circ}C$ . The value of  $K_f$  of lauric acid is  $3.90^{\circ}C\ m^{-1}$ . Assume that the compound does not dissociate in lauric acid.

(i) Calculate the molality of the compound dissolved in the lauric acid.

(ii) Calculate the molar mass of the compound from the information provided.

(c) Without doing any calculations, explain how to determine the molecular formula of the compound based on the answers to parts (a)(ii) and (b)(ii).

- (d) Further tests indicate that a 0.10 M aqueous solution of the compound has a pH of 2.6. Identify the organic functional group that accounts for this pH.

Answer:

(a) (i)  $1.9061\ g \times \frac{12}{44} = 0.5198\ g\ of\ C$

$0.3370\ g\ H_2O \times \frac{2}{18} = 0.03744\ g\ of\ H$

$0.7549\ g\ sample$

$-0.5198\ g\ C$

$-0.0374\ g\ H$

$0.1977\ g\ of\ Oxygen$

(ii)  $0.5198\ g\ C \times \frac{1000\ mmol}{12.0\ g} = 43.32\ mmol\ C$

$0.0374\ g\ H \times \frac{1000\ mmol}{1.0\ g} = 37.4\ mmol\ H$

$0.1977\ g\ O \times \frac{1000\ mmol}{16.0\ g} = 12.36\ mmol\ O$

dividing each by 12.36 gives

$3.5\ C : 3\ H : 1\ Oxygen$ , OR  $7\ C : 6\ H : 2\ O$ , thus an empirical formula of  $C_7H_6O_2$

(b) (i)  $molality = \frac{\Delta T_f}{K_f} = \frac{1.68^{\circ}C}{3.90^{\circ}C\ m^{-1}} = 0.431\ m$

(ii)  $molar\ mass = \frac{g\ of\ solute}{kg\ solvent \cdot molality} =$

$= \frac{0.5246\ g}{0.0100012\ kg \cdot 0.431\ m} = 122\ g/mol$

- (c) from (a)(ii), the molar mass of  $C_7H_6O_2 = 122.0\ g/mol$

since the two molar mass are the same, the empirical formula = molecular formula

- (d) low pH indicates an organic acid containing the carboxyl functional group,  $-COOH$ .

[likely benzoic acid]