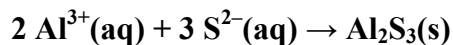


## Question 1 (24 points)

## ANSWERS

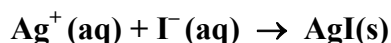
Write *balanced net ionic equations* describing the predominant reaction(s) that occur when the substances below are mixed in aqueous solution.

Solutions of aluminum nitrate and sodium sulfide are mixed



*Nitrates are soluble, sodium salts are soluble; sulfides are generally insoluble.*

Sodium iodide solution is mixed with silver nitrate solution



*Sodium salts are soluble; nitrate salts are soluble: reactants are all ions.*

*Most halide salts are soluble, but silver is one of the metal cations that forms insoluble halides.*

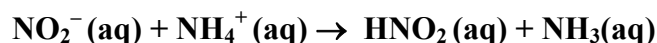
A solution of acetic acid is mixed with lead hydroxide.



*Reactants: hydroxides are generally insoluble, HOAc is weak*

*products: acetates are soluble; but  $\text{H}^+$  and  $\text{OH}^-$  will always combine to make water.*

Solutions of sodium nitrite and ammonium chloride are mixed.



*Reactants: "solutions of" salts, so we write ions.*

*sodium salts are soluble and ammonium salts are soluble, so no precipitates form.*

*But  $\text{NH}_4^+$  is acidic, so it reacts with the weak base  $\text{NO}_2^-$ , forming the weak acid  $\text{HNO}_2$ .*

### SOME GENERAL REMINDERS:

*Solutions of soluble salts contains ions. Solutions of strong acids contain ions.*

*Except in special circumstances (like  $\text{H}_2\text{CO}_3$  making  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ), don't modify the core ion: it is either in a salt, in solution, or in a weak acid or base! These are not redox reactions!*

*For weak acids, the predominant species in solution is the molecular acid, HA.*

*Always write ions in solution **with their charges**, and ions in salts or weak acids **without**.*

*Always show solids with (s). When a solid **forms**, you may write  $\downarrow$  instead.*

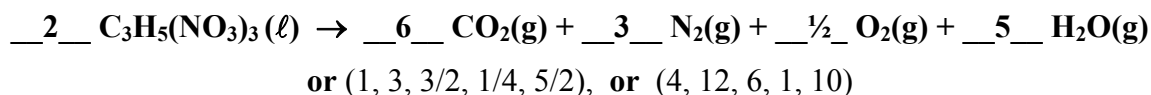
*Denoting dissolved species in water with (aq) is optional; if a phase is not specified (aq) is implied.*

## Question 2 (25 points)

## ANSWERS

Nitroglycerine is a shock-sensitive liquid: when disturbed, it explodes violently. Its molecular weight is 227.09.

a) (4) Balance the chemical equation for the explosion:



b) (8) 28.4 g (one ounce) of nitroglycerin explodes. How many moles of gas are produced?

$$\text{moles nitroglycerin} = (28.4 \text{ g}) / (227.09 \text{ g/mole}) = 0.1250655 \text{ moles}$$

The quick way to find total moles is to use the stoichiometry of the balanced equation:

for every two moles of nitroglycerin that react,  $6 + 5 + 3 + 0.5 = 14.5$  moles of gas are formed.

therefore moles of gas formed =  $(14.5/2) \times 0.125065 = 0.90672 \rightarrow \underline{0.907 \text{ moles gas}}$

Alternatively, you can calculate moles of each product, and then add:

$$\text{moles CO}_2 \text{ formed} = 3 (\text{moles nitroglycerin reacting}) = 0.375195$$

$$\text{moles H}_2\text{O formed} = 5/2 (\text{moles nitroglycerin reacting}) = 0.31266$$

$$\text{moles N}_2 \text{ formed} = 3/2 (\text{moles nitroglycerin reacting}) = 0.187597$$

$$\text{moles O}_2 \text{ formed} = 1/4 (\text{moles nitroglycerin reacting}) = 0.03125 \quad \text{sum} = \underline{0.907 \text{ moles}}$$

Conservation of matter does NOT imply that moles of *molecules* do not change in a reaction!

c) (5) One ounce of nitroglycerin explodes in an empty rigid 3.00 L container. What is the final pressure, if the final temperature is 75°C?

$$PV = nRT, \text{ so } P = nRT/V = (0.90672 \text{ moles})(0.0820578 \text{ L-atm/K-mol})(348.15 \text{ K}) / (3.00 \text{ L})$$

$$P = 8.63452 \rightarrow \underline{8.63 \text{ atm}} \quad (\text{This large sudden pressure causes the explosion. Boom!})$$

It is wrong to use moles of nitroglycerine here: why?

(1) it is a *reactant* and is gone after the explosion, and

(2) it was a liquid; even if you wanted to find the initial P, you could not use the ideal gas law!

d) (5) What is the mole fraction of CO<sub>2</sub> in the container after the explosion?

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{total}}} = \frac{0.375195}{0.90672} = 0.41379 \rightarrow \underline{0.414}$$

One could also use the equation  $X_i^{\text{gas}} = P_i / P_{\text{total}}$ . Alternatively, since the only gases present are products, and since there are 3 moles CO<sub>2</sub> formed for every 7.25 moles of total gas, we could calculate this as  $3/7.25 = 0.41379$ . This result would not have a limited number of significant figures, since the stoichiometric coefficients are integers or ratios of integers.

*Mole fractions must be in the interval 0 to 1; anything else is obviously WRONG!*

e) (4) What is the partial pressure of N<sub>2</sub> in the container after the explosion?

$$\text{Two possible methods: } P_{\text{N}_2} = X_{\text{N}_2} P = (3/14.5)(8.63452) = \underline{1.78 \text{ atm}}$$

$$\text{or } P_{\text{N}_2} = n_{\text{N}_2} RT / V = (0.187597)(0.082058 \text{ L-atm/K-mol})(348.15 \text{ K}) / (3.00 \text{ L}) = 1.78 \text{ atm}$$

## Question 3 (25 points)

## ANSWERS

THE TWO PARTS OF THIS QUESTION ARE INDEPENDENT OF ONE ANOTHER.

- A) (11) Two students are discussing the salt  $\text{KMnO}_4$  (formula weight 158.0339 g/mole). Sarah argues it dissolves forming ions  $\text{K}^+$ ,  $\text{Mn}^{7+}$ , and  $\text{O}^{2-}$ . Deena thinks it forms  $\text{K}^+$  and  $\text{MnO}_4^-$ . They decide to resolve the issue by experiment. They weigh 1.58 grams of the salt, and dissolve it in 100 g water. Predict the freezing point of the solution, as expected by each student.

1.58 g = 0.0100 moles solute in 100 g (= 0.100 kg) solvent, so

molality is  $m = (0.010 \text{ moles}) / (0.100 \text{ kg}) = 0.100 \text{ m}$

$\Delta T_f = i K_f m$ . Sarah predicts  $i = 6$  (1  $\text{K}^+$ , 1  $\text{Mn}^{7+}$ , and 4  $\text{O}^{2-}$ ), while Deena predicts  $i = 2$ .

Deena predicts  $\Delta T_f = 2(1.86)(0.100) = 0.372^\circ \rightarrow T_f = T_f^\circ - \Delta T = \underline{-0.372^\circ\text{C}}$

Sarah's would be a factor of three larger:  $\Delta T_f = 1.116^\circ \rightarrow T_f = \underline{-1.12^\circ\text{C}}$ .

*The experiment would show that Deena is correct.*

- B) (14) A 100.0 mL solution of a soluble polysaccharide (a non-electrolyte) was prepared by dissolving 0.0516 g of the substance in water. When the osmotic pressure was measured at  $25^\circ\text{C}$ , the solution rose 3.305 cm above the surface of the water. What is the approximate molecular weight of the polysaccharide?

$\Pi = 3.305 \text{ cm H}_2\text{O} = 33.05 \text{ mmH}_2\text{O}$ .

*An osmosis apparatus is in effect a water barometer. The barometric formula is  $P = gph$*

*if measuring the same pressure with a water and mercury barometer,  $\rho_1 h_1 = \rho_2 h_2$*

$h(\text{mmHg}) = h(\text{mmH}_2\text{O})(\rho_{\text{water}}/\rho_{\text{Hg}}) = h(\text{mmH}_2\text{O}) / 13.6$  {mercury is 13.6 times as dense as water}

$\Pi = (33.05 \text{ mmH}_2\text{O}) / 13.6 = 2.430 \text{ mmHg}$

$\Pi = cRT \rightarrow c = \Pi/RT = (2.43 \text{ mmHg}) / (62.365 \text{ L}\cdot\text{mmHg}/\text{mole}\cdot\text{K})(298.15 \text{ K})$

$= 1.30689 \times 10^4 \text{ mole/L}$

$(1.30689 \times 10^4 \text{ moles/L})(0.100 \text{ L}) = 1.30689 \times 10^{-5} \text{ moles in the } 0.0516 \text{ g sample.}$

Molecular weight =  $(0.0516 \text{ g}) / (1.30689 \times 10^{-5} \text{ moles}) = \underline{3950 \text{ g/mole}}$  [3 sig. figs.]

*A single equation can put it all together (see below), but I find it easier to proceed stepwise.*

$\Pi = cRT$ ,  $c = n/V$ ,  $M = w/n$ , so  $\Pi = (w/MV) RT \rightarrow M = wRT/\Pi V$

## Question 4 (25 points)

## ANSWERS

Catechol,  $C_6H_5O_2$  (molar mass 110.11), is a non-volatile molecular substance present in many plants. It can be extracted by soaking the leaves in the solvent nitrobenzene,  $C_6H_5NO_2$  (molar mass 123.11).

a) (10) A sample of leaves is soaked in 80.0 g of nitrobenzene. The resulting solution is filtered, and its freezing point is measured to be  $3.4^\circ\text{C}$ . How many grams of catechol were extracted?

Solvent is nitromethane:  $K_f = 7.0$  deg/molal, and  $T_f^\circ = 5.7^\circ\text{C}$ .

$$\Delta T = K_f m, \text{ so } m = \Delta T / K_f = (5.7 - 3.4) / 7.0 = 2.3 / 7.0 = 0.32857 \rightarrow 0.33 \text{ m}$$

$$m = (\text{moles solute}) / (\text{kg solvent}), \text{ so moles solute} = (m)(\text{kg solvent}) = (0.32857)(0.080) = 0.0262857$$

$$\text{grams catechol} = (\text{moles})(\text{molar mass}) = (0.0262857)(110.11) = 2.89432 \rightarrow \underline{2.9 \text{ grams catechol}}$$

*No factor of  $i$  here: the solute is molecular, so  $i = 1$ .*

b) (15) 10.0 mL of the same catechol-nitrobenzene solution is found to weigh 12.0 grams. What is the molarity of the solution? (If you were not able to solve part a, assume that 3.2 grams of catechol dissolved in 80 g of nitrobenzene.)

Molarity  $\equiv$  (moles solute)/(L solution)

Method I. Working with the original solution, the total mass is  $80.0 + 2.9 = 82.9$  grams.

The density of the solution in gram/mL is  $(12.0 \text{ g}) / (10.0 \text{ mL}) = 1.20 \text{ g/mL}$ .

so the volume of the total sample is  $(82.9 \text{ grams}) / (1.20 \text{ g/mL}) = 69.0833 \text{ mL} = 0.0690833 \text{ L}$ .

Therefore its molarity is (moles)/(L) =  $(0.0262857) / (0.0690833) = 0.380492 \rightarrow \underline{0.38 \text{ M}}$

Method II. Working with the original solution, the total mass is  $80.0 + 2.9 = 82.9$  grams.

Therefore the fraction by weight of solute in the solution is  $(2.9 / 82.9) = (0.0349819)$

Thus 10 mL of solution (12 grams) has  $(0.0349819)(12 \text{ g}) = 0.419783$  grams solute (catechol)

$(0.419783 \text{ g}) / (110.11 \text{ g/mole}) = 0.0038124$  moles catechol in 10 mL solution

molarity =  $(0.0038124 \text{ moles}) / (0.010 \text{ L}) = \underline{0.38 \text{ M}}$

If you used 3.2 grams:  $(3.2 \text{ grams}) / (110.11 \text{ g/mole}) = 0.0290618$  moles solute

$80.0 + 3.2 = 83.2$  grams solution  $\rightarrow (83.2 \text{ g}) / (1.20 \text{ g/mL}) = 69.333 \text{ mL solution}$

$(0.0290618 \text{ moles}) / (0.06933 \text{ mL}) = 0.419161 \text{ M} \rightarrow \underline{0.42 \text{ M}}$

*Write the definitions, including moles of what, L or kg of what. This serves two purposes: (1) I give partial credit for correct definitions, and (2) it helps you think through how to solve the problem.*

*Note that using a molar mass to convert between mass and moles works ONLY for pure substances.*

*A solution does not have a molecular weight: adding the molecular weights gives you a useless quantity.*

## Question 5 (26 points)

## ANSWERS

At 50°C the vapor pressure of pure ethyl acetate (A) is 280.4 mmHg, while that of pure ethyl iodide (I) is 353.4 mmHg.

- a) (8) Assuming that when mixed they form an ideal solution, draw the P-X diagram for mixtures of ethyl acetate and ethyl iodide at 50°C. Label the axes and all lines, points, or curves.

*Graph must use the numbers above.*

*ok if axes reversed,*

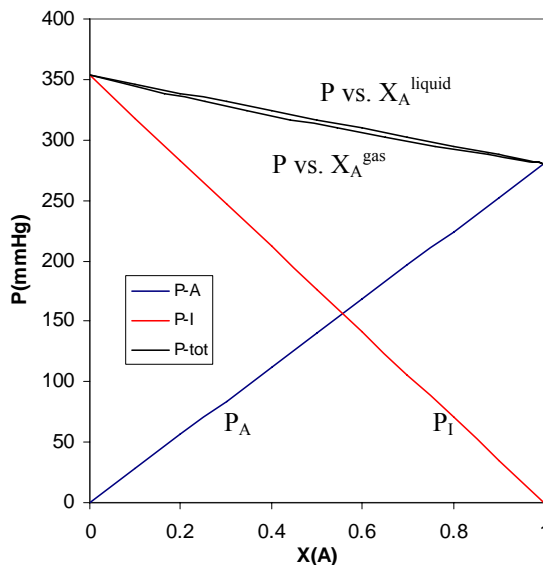
*You must say which X you use here I chose the acetate (A).*

*P vs.  $X_A^{liq}$  (liquidus) is a line;*

*below it is P vs.  $X_A^{gas}$  (bubble point curve).*

*I show calculated values; since the two  $P^\circ$ 's are similar, the two curves are unusually close.*

*I did not expect calculations, so your bubble point curve may be considerably more curvy.*



- b) (12) In a solution which is 63.3 mole % ethyl iodide, the vapor pressure of ethyl iodide is found to be 239.1 mmHg, that of ethyl acetate 122.9 mmHg. Does ethyl acetate obey Raoult's law? Explain.

Raoult's law says:  $P_k = X_k^l P_k^\circ$  {subscripts and superscripts are essential to the meaning!}

For  $k = A$ :  $P_A$  (ideal) =  $(1 - 0.633)(280.4) = (0.367)(280.4) = 102.92 \rightarrow 102.9$  mmHg

Since the experimental pressure is 122.9 mmHg, ethyl acetate does not obey Raoult's law.

*(not asked: since  $P_{k, real} > P_{k, ideal}$  this is positive deviation from Raoult's law (part e below)*

*There is no reason to convert to atmospheres: it is easiest to stick with the given units.*

*It is not wrong to convert, you are just making extra work.*

- c) (4) What is the composition of the vapor in equilibrium with this 63.3% solution?

The definition of partial pressure is  $P_k = X_k^{gas} P_{total}$ , so

$X_I^{gas} = P_I / (P_I + P_A) = (239.1) / (239.1 + 122.9) = 0.660497 \rightarrow 0.660 = \underline{66.0\%}$  ethyl iodide

*This is a larger percentage than in the liquid: the vapor is richer in the more volatile component.*

*Use the real pressures here, not the incorrect ones calculated from Raoult's law!*

- e) (3) Is this solution ideal? Explain.

No: a solution is ideal only if Raoult's law holds.

$PV = nRT$  is the ideal gas law. It has nothing to do with whether a solution is ideal.

**General comments:** Don't be too discouraged if you did badly on this exam. Because the second exam covers a wide range of topics, it is not unusual for students in this course to find it especially difficult. But now is the time to go back over that material, review carefully what you did wrong and why, and make sure you now understand the concepts. It is also a good time to think about strategies (both preparing and test-taking) so you can do a better job on the third exam and the final.

Pull out and re-read the handout "What to do after taking an examination". Do not simply put this exam away: now is the time to learn from your errors (and reinforce what you did correctly).

**Advice for future exams, based on what I saw on this one:**

1) **THINK before you write.** Ask yourself very carefully what is being asked. Read the problem carefully a couple of times, and be sure you understand what is going on. Picture it in your mind.

2) **Write chemical equations**, even if I do not explicitly ask for them.

3) **ALWAYS write complete equations in symbolic form**, using standard notation. I give partial credit for the correct relevant equation, even if you do not use it correctly. For example in question 5, someone who wrote Raoult's law in part c and the definition of molarity in part d received some of the total credit. On the other hand, someone who did lots of calculations, but labeled nothing so I had no real way of figuring out what it all meant, got no credit.

4) **MEMORIZE the basic equations carefully**, and write them **completely** using the standard symbols. Examples (1) it is VERY important that Raoult's law relates the pressure of the gas to the mole fraction of that component *in the liquid*. Without the symbol *l* included with X the equation is not correct. (2) We use the terms "partial pressure" and "vapor pressure" interchangeably, but if you decide to use V instead of P for that quantity, you are very likely to get very confused. (3) In definitions of concentration, it is not sufficient to think "moles/kg": what is essential to know is moles *of what* per kg *of what*. Likewise the density of a solution tells you the grams of *the solution* per mL of *that solution*: it does not tell you about grams of *solute* or mL of *solvent*. In concentration problems, always distinguish carefully whether grams, volumes, and moles pertain to solute, solvent, or solution.

*Some common pitfalls:* Be careful you are clear in an equation whether M denotes molarity or molar mass. (That is why I prefer to use  $\Pi = cRT$  in osmosis problems, with *c* the molarity). Avoid using *m* for mass, since it is too easily confused with molality. Use *w* instead.

5) **Think about your assumptions:** be sure they are consistent. For example, in question 4, the information in the last part tells you about density of the solution, needed to get to molarity. But the whole sample considered in part a and b is not the weighed 10 mL sample. So you must either find out how many moles are in the 10 mL sample, or go back and find the volume of the original sample with 80 g solvent. Dividing the mass of *solvent* by the density of *solution* gives a meaningless number.

6) **Think about your calculated values.** Since the density of water is ~1 g/mL, there are 1000 g of water per L,  $(1000 \text{ g})/(18 \text{ g/mole}) = 55$  moles: the molarity of water in water is ~55 M. Molarities of solutes in aqueous solutions will never be this large. If you get a molarity like 1827 M, you should immediately recognize that an error was made, and tell me. Likewise, a mole fraction greater than one is clearly incorrect. No molecule can weigh less than 4 g/mole (about what H<sub>2</sub> weighs). I deduct extra points for egregious errors that are left without comment!