Comments in *italics* are not part of the expected answer.

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.

a) Copper (I) perchlorate solution and potassium bromide solution

$$Cu^{+}\,(aq) + Br^{-}\,(aq) \rightarrow CuBr(s)$$

Most chloride, bromide, and iodide salts are soluble, but Cu^{+} is one of the cations that forms precipitates. All potassium salts are soluble; all perchlorate salts are soluble.

b) Solid aluminum carbonate and aqueous sulfuric acid

$$Al_2(CO_3)_3\,(s) + 6\,H^{+}\,(aq)\ [\rightarrow 2\,Al^{3+}(aq) + 3\,H_2CO_3(aq)\ ] \rightarrow\ 2\,Al^{3+}\,(aq) + 3\,H_2O\,(\ell) + 3\,CO_2\,(g)$$

Sulfuric acid is strong: written as ions. Sulfate salts are generally soluble, so no precipitate there.

ok to omit the intermediate step, shown in square brackets. You could also write

$$Al_2(CO_3)_3\,(s) + 3\,H^{+}\,(aq) + 3\,HSO_4^{-}\,(aq)\ \rightarrow\ 2\,Al^{3+}\,(aq) + 3\,SO_4^{2-}\,(aq)\ + 3\,H_2O\,(\ell) + 3\,CO_2\,(g)$$

c) Barium nitrate solution and sodium sulfite solution

$$Ba^{2+}\,(aq) + SO_3^{2-}\,(aq) \rightarrow\ BaSO_3\,(s)$$

Nitrate salts are soluble. Sulfites are generally insoluble.

d) Aqueous ammonia solution and hydrochloric acid solution

$$NH_3\,(aq) + H^{+}\,(aq)\ \rightarrow\ NH_4^{+}\,(aq)$$

Ammonia is a weak base, a proton acceptor; HCl is a strong acid.

e) Solid Iron (III) hydroxide is mixed with aqueous acetic acid

$$Fe(OH)_3\,(s) + 3\,CH_3COOH\,(aq)\ \rightarrow Fe^{3+}\,(aq) + 3\,H_2O\,(\ell) + 3\,CH_3COO^{-}\,(aq)$$

CH_3COOH may also be written HOAc or $HC_2H_3O_2$. *One H^{+} available per molecule.*

Hydroxide salts dissolve in any acid, forming water. Acetic acid is weak, so molecular.
Acetate salts are soluble.

SOME GENERAL REMINDERS:

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

Except in special circumstances (like H_2CO_3 making H_2O and 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 ↓ instead.*

Denoting dissolved species in water with (aq) is required, for now.

When balancing equations, it is easier to balance units (e.g. acetates) than element-by-element.

Check that overall charge is balanced, this frequently shows when there are errors.

Question 2 (25 points) **ANSWERS**

2,4,6-trinitrotoluene, better known by its initials, TNT, is explosive, since it can quickly change from a solid into hot expanding gases. Some of the carbon is converted to soot, C(s). The volume of the soot is negligible. The molar mass of TNT is 227.133.

a) (4) Balance the reaction for the explosion:

_1_ $C_7H_5N_3O_6$ (s) → _3/2_ N_2 (g) + _7/2_ CO(g) + _5/2_ H_2O(g) + _7/2_ C(s)

first balance N and H, since they each appear in only one product, Next balance O, finally C.
For convenience, one can double all coefficients to get integers, but this is not required:

_2_ $C_7H_5N_3O_6$(s) → _3_ N_2(g) + _7_ CO(g) + _5_ H_2O(g) + _7_ C(s)

b) (10) 145 g of TNT is in an otherwise empty 250.0 mL bottle. If the temperature is 275°C after the TNT explodes, what is the pressure inside the bottle (before it breaks)?

145 g/ (227.133 g/mole) = 0.63<u>8</u>392 moles TNT, *a solid, which reacts and is gone!*

<u>*Method I*</u>*. work with* <u>*total*</u> *moles* <u>*gas*</u>*: C(s) is not a gas: not included!*

(total moles gas made) / (moles TNT used) = (3+7+5) / 2 = 15/2

total moles of gas after the explosion = (15/2)(0.638392) = 4.7<u>8</u>7939 moles

Use the ideal gas law to find P:

P = nRT/V = (4.7<u>8</u>7939 moles)(0.08205745 L-atm/K-mol)(548.15 K)/(0.250 L) = 86<u>1</u>.44 → <u>861 atm</u>.

<u>*Method II*</u>*. calculate each partial pressure, and add*

Moles CO = (7/2)(moles TNT) = 2.2<u>3</u>4372 moles

$P_{CO} = n_{CO}$ RT/V = (2.234372 moles)(0.08205745 L-atm/K-mol)(548.15 K)/(0.250 L) = 40<u>2</u>.00 atm

Moles N_2 = (3/2)(moles TNT) = 0.957588 moles

$P_{N2} = n_{N2}$ RT/V = (0.95<u>7</u>588 moles)(0.08205745 L-atm/K-mol)(548.15 K)/(0.250 L) = 17<u>2</u>.28 atm

Moles H_2O = (5/2)(moles TNT) = 1.595980 moles

$P_{H2O} = n_{H2O}$ RT/V = (1.595980 moles)(0.08205745 L-atm/K-mol)(548.15 K)/(0.250 L) = 28<u>7</u>.147 atm

Add: $P = P_{N2} + P_{CO} + P_{H2O}$ = 861.44 atm → <u>861 atm</u> *(boom!)*

c) (5) What is the partial pressure of CO(g) in the bottle?

Moles CO = (7/2)(moles TNT) = 2.2<u>3</u>4372 moles

$P_{CO} = n_{CO}$ RT/V = (2.2<u>3</u>4372 moles)(0.08205745 L-atm/K-mol)(548.15 K)/(0.250 L) = <u>402 atm</u>

<u>Alternatively</u>, observe that 7/15 of the product gas is CO (X_{CO} = 7/15), so using P_{total}:

$P_{CO} = X_{CO}$ P = (7/15)(861) = 402 atm

d) (6) What is the mole fraction of N_2 in the gas?

From the balanced reaction, 3 moles N_2 are formed per 15 moles gas, and no other gas is present, so X_{N2} = 3/15 = 0.20, (whatever amount of TNT explodes).

<u>or</u> find P_{N2} as above and divide by P_{tot}: $X_k = P_k/P$ = 172.28/861.44 = 0.20

<u>or</u> find n_{N2} as above → $X_{N2} = n_{N2} / n_{tot}$ = 0.957588 / 4.787939 = 0.20

Question 3 (25 points) **ANSWERS**

(The three parts of this question are independent of each other.)

a) (8) 0.494 g of anthracene, $C_{10}H_8(s)$, is dissolved in 10.0 g of benzene. What is the freezing point of the solution?

Molecular weight (molar mass) of anthracene = 10(12.011) + 8(1.00794) = 128.188 g/mole

(0.494 g) / (128.188 g/mole) = $0.0038\underline{5}3715$ moles in 0.0100 kg; so m = $0.38\underline{5}37$

$\Delta T = K_f m = (5.12)(0.38\underline{5}37) = 1.97$ *Anthracene is a molecular substance, not ionic, so i = 1*

$T_f = T_f° - \Delta T_f = 5.\underline{5} - 1.9\underline{7} = \underline{3.5°C}$ *Be careful about signs: the freezing point is* ***depressed****.*

b) (10) The walls of erythrocytes (red blood cells) are semipermeable. Placed in salt solution they shrink by osmosis if the outside concentration is high and swell if the outside concentration is low. An isotonic solution results in neither shrinking nor swelling. The isotonic NaCl solution freezes at –0.406°C. Calculate the osmotic pressure at 25°C of erythrocytes under these conditions. Since these are relatively dilute aqueous solutions, you may make the approximation that molarity and molality are equal.

$\Delta T_f = K_f m$, $\Delta T_t = T_f° - T_f = (0°C - (-0.406°C) = 0.406°C \rightarrow m = 0.406/(1.86) = 0.218 \approx c$

This is the total concentration of dissolved particles.

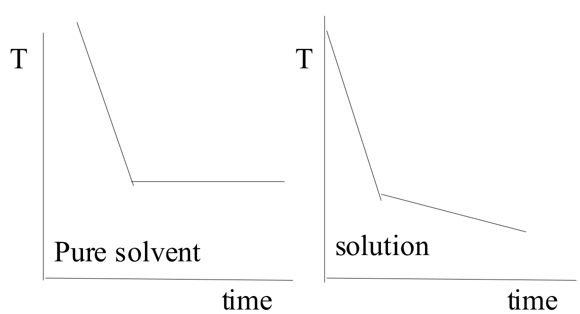
$\Pi = cRT$ = (0.218 moles/L)(0.082054 L-atm/K-mole)(298.15 K) = $\underline{5.34 \text{ atm} = 4060 \text{ mmHg}}$

Does this seem too high? It is not: osmotic pressures inside cells are huge: cells put in water burst!

What about the fact that NaCl ionizes? m calculated and used above is total molality of dissolved particles (Na^+ and Cl^-), which is what determines all colligative properties, including Π.

One could solve the problem using i = 2 which says that the nominal NaCl molality m is 0.109. But then the same factor i = 2 would be included in the osmotic pressure calculation.

c) (7) The freezing point of a pure solvent is constant, from the first formation of crystals until the sample is frozen solid. The freezing point of a solution continues to fall as solid forms. Sketch cooling curves for both solvent and solution to show this behavior (label the axes). Explain in one or two clear sentences why the freezing point of a solution is not constant.



When a solution begins to freeze, pure solvent freezes first. Thus the **concentration of the remaining liquid increases**. Since freezing point decreases with concentration ($\Delta T_f = K_f m$), the freezing point falls.

{T vs. time will fall more steeply *after* all the solvent or solution has frozen, but you did not observe that in lab, nor was it part of the question.}

The solution has a lower freezing point than the pure solvent because entropy is higher in the (mixed) solution. But this is not what I asked. I asked why the freezing point falls during the cooling.

Question 4 (30 points) **ANSWERS**

A. (21) Concentrated aqueous ammonia purchased from a chemical supplier is 14.8 M, with density 0.885 g/mL. Find its concentration in the following units:

Molality ___23.4 m_____ Mole fraction __0.296_____ % by weight ___28.5%_____

Aqueous means water is the solvent; ammonia is the solute. 0.885 g/mL is the solution density.

Molecular weight NH_3 = 14.0067 + 3(1.00794) = 17.03052 g NH_3 / mole NH_3

Molecular weight H_2O = 15.9994 + 2(1.00794) = 18.01528 g H_2O / mole H_2O

Molarity = (moles solute)/(L solution)

Consider exactly 1 Liter (1000 mL) of solution *Specify the amount you use! Other choice next page.*

it contains 14.8 moles NH_3

it weighs (1000 mL solution) × (0.885 g/mL) = 885 grams of solution

reminder: the density of a solution is (mass solution)/(volume of solution)

how many grams NH_3? (14.8 moles)(17.03052 g NH_3 /mole NH_3) = 252.051 g NH_3

grams water = (total grams – grams NH_3) = (885 – 252) = 633 grams H_2O = 0.633 kg H_2O

molality = (moles NH_3) / (kg water) = 14.8 / 0.633 = 23.4 m

Find mole fraction: continue to work with the same one liter of solution:

(633 grams water)/(18.01528 g H_2O/mole H_2O) = 35.133 moles water

total moles = 14.8 + 35.133 = 49.9

→ **mole fraction NH_3 = (moles NH_3)/(total moles)** = 14.8 / 49.9 = 0.29637 → 0.296

Find % by weight: still working with the same 1000 mL of solution

There are 252.05 grams of NH_3 in 885 grams solution;

% by weight = 100 × (grams solute/grams solution) = 100 × (252.05/885) = 28.48 → 28.5%

[*You can start with different amounts in each part, but it is much quicker to build on what you know.*]

It is essential each step along the way to carefully specify grams of what, moles of what, etc.
This helps prevent errors like dividing (grams of solute) by (density of solution), a meaningless result.

B. (9) Give detailed instructions for preparing 250.0 mL of 2.00 M NH_3, starting with the 14.8 M concentrated solution.

250 mL × 2.00 M = 500 mmoles NH_3 needed *or* (0.250 L)(2.00 M) = 0.500 moles NH_3)

In a 14.8 M solution, 500 mmoles = (14.8 M)(V mL) → V = 500/14.8 = 33.7837 → 33.8 mL.

Shortcut: constant moles, so $M_1V_1 = M_2V_2 \rightarrow V_2 = V_1(M_1/M_2)$ = (250 mL)(2.0/14.8) = 33.8 mL

Recipe: using a buret*, measure 33.8 mL of 14.8 M NH_3 into a clean beaker or weighing bottle.

Transfer quantitatively to a 250 mL volumetric flask (use a funnel, rinse three times with water).

Fill part way with distilled water; mix thoroughly.

Fill exactly to the mark with distilled water; mix again. {Essential points underlined.}

* *There is no such thing as a volumetric pipet that can deliver 33.8 mL.*

4.A) Other starting points to find the concentration:

Consider 100 g of solution: (multiply all by 10 if you start with 1000 g)

it has volume (100 g) / (0.885 g/mL) = 111.299 mL = 0.111299 L

moles NH_3 = (14.8 M)(0.111299 L) = 1.6723 moles NH_3

mass of NH_3 = (1.6723 moles NH_3)($17.030\underline{5}2$ g NH_3 / mole NH_3) = 28.48 g NH_3

Since masses are additive,(mass of water) = mass solution –mass NH_3) = 100 – 28.48 = 71.52 g H_2O

moles H_2O = (71.52 g H_2O)($18.015\underline{2}8$ g H_2O / mole H_2O) = 3.97 moles H_2O

molality = moles NH_3/kg water = 1.6723/0.07152 = 23.4

mole fraction = (moles NH_3)/(total moles) = 1.6723/(1.6723+3.97) = 0.296

% by weight = 100 x (grams NH_3)/(grams solution) = 100(28.48/100) = 28.48

Consider the amount of solution that contains one mole of ammonia NH_3:

14.8 moles / 1000 mL = 1 mole / x mL $\rightarrow$ x = 1000 mL/14.8 = 68.493 mL of solution.

(68.493 mL of solution)(0.885 g soln / mL solution) = 60.616 grams solution.

Since masses are additive

grams H_2O = 60.616 grams solution – 17.0305 g NH_3 = 43.586 grams H_2O

moles H_2O = (43.586 g H_2O)($18.015\underline{2}8$ g H_2O / mole H_2O) = 2.4194 moles H_2O

molality = moles NH_3/kg water = 1/0.043586 = 23.4

mole fraction = (moles NH_3)/(total moles) = 1/(1+ 2.4194) = 0.296

% by weight = 100 x (grams NH_3)/(grams solution) = 100 (43.586/60.616) = 28.48

There are other possible choices as well. But you see the pattern. So long as you are clear about your choice, and keep track of exactly what you are working with, you can get there.

Note: you cannot obtain moles of solution by dividing the mass of the solution my a molecular weight. Solutions do not have molecular weights, only pure substances do!

Masses and moles are additive, but volumes are not. If you do not understand this, please come see me.

Question 5 (21 points) **ANSWERS**

Parts A and B are independent of each other.

A. (13) The following data was collected for solutions of acetone (A) with ethyl ether (E) at 20°C.

X_E^{liquid}	0	0.15	0.25	0.50	0.80	0.90	1.00
P_A (mmHg)	298	265	243	182	88	45	0
P_E (mmHg)	0	101	150	250	357	401	441

a) (7) Are these solutions ideal? Show using a sample calculation at $X_E^{liq} = 0.25$. If not ideal, are the deviations positive or negative.

If ideal, then Raoult's law should hold: $P_E = X_E^{liq} P_E°$ (and same for A)

Where are the P° values? At the two ends of the table: $P_E° = 441$ and $P_A° = 298$ mmHg

At $X_E^{liq} = 0.25$, Raoult's law would predict $P_E^{ideal} = 0.25(441) = 110.25$ mmHg

but P_E^{real} at this X is 150 mmHg. This system is NOT ideal: the deviation is positive: $P^{real} > P^{ideal}$.

You must show the explicit comparison: what number you are comparing with your calculation.

b) (6) What is mole fraction of ethyl ether in the gas which is in equilibrium with a liquid with mole fraction of ethyl ether is 0.25?

$P_{total} = 243 + 150 = 393$; $X_E^{gas} = P_E / P_{total} = 150/393 = 0.381679 \rightarrow$ 0.382

U*sing Raoult's law here is wrong, since solution is not ideal, but here is the calculation if it were ideal:*

$P_E = 0.25(441) = 110.25$ mmHg, $P_A = 0.75(298) = 223.50$ mmHg, $P = 333.75$ mmHg,

$X_E^{gas} = P_E / P_{total} = 110.25/33.75 = 0.330337 \rightarrow$ 0.330 *This was given half credit, if done correctly*

B) (8) Mercury (II) chloride is unusual: although soluble, it is a weak electrolyte. Consider a solution with 0.015 moles of $HgCl_2$(s) dissolved in 100.0 g of water.

a) (3) What would be the freezing point of the solution it there were no ionization?

0.015 moles in 0.100 kg solvent → 0.15 molal

$\Delta T_f = K_f m = (1.86)(0.15) = 0.2\underline{7}9°$

$T_f = T_f° - \Delta T_f = 0.00 - 0.28 =$ –0.28°C

b) (3) What would be the freezing point of the solution if the salt ionized completely?

If $HgCl_2(aq) \rightarrow Hg^{2+} + 2\ Cl^-$, then i = 3. Therefore ΔT is three times that calculated above.

$\Delta T_f = 3(0.279) = 0.8\underline{3}7°$, $T_f = -0.84$°C

c) (2) Based on the facts described above, what freezing point would you expect to observe?

The observed freezing point would be close to –0.28°C: *weak electrolytes ionize to a very small extent.*