1. Which of the following statements are true and which – false? For the false statements, provide a correction and a brief explanation. (11 points)
   a. If antimony (Sb), an element found in group 5 (5A), is a semiconductor, arsenic (As) must be a metal that conducts electricity.

① False. As is smaller than Sb, so must have an even larger band gap. ①

   b. Water containing dissolved $CaCl_2$ has higher vapor pressure than pure water at a given temperature.

① False. According to $P_A = P_A^\circ X_A$, it will have lower VP ①

   c. Exothermic reactions have greater reaction rates than endothermic reactions.

① False. ΔH_{rxn} doesn't affect rate of rxn. ①

   d. A substance that has a triple point at a pressure above 1 atm will sublime under normal conditions.

① True

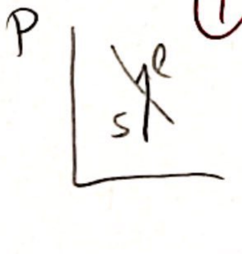
   e. Germanium doped with phosphorus is a n-type semiconductor.

① True

   f. Molecular solids usually have lower melting points than network solids.

① True

   g. If the phase diagram for a substance has a solid-liquid line with a negative slope, we can conclude that the substance is denser as a solid than as a liquid.

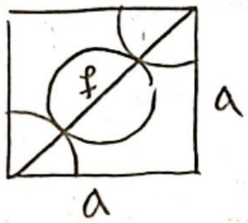


① False. A solid-liquid line with a negative slope means pressure will turn s to l – so l is denser. ①

2. Manganese crystallizes in a face-centered cubic system. The radius of the manganese atom is 1.30×10^{-8} cm. What is the density of manganese? (10 points)

$$\overset{①}{4\text{ Mn atoms}} \times \overset{①}{\frac{1\text{ mol}}{6.022\times10^{23}\text{ atoms}}} \times \overset{①}{\frac{54.938\text{ g}}{1\text{ mol}}} =$$

$$3.65\times10^{-22}\text{ g}$$



$f = 4r$ ①

$f^2 = 2a^2$ ①

$$(4r)^2 = 2a^2 \Rightarrow \overset{①}{\left[4(1.30\times10^{-8}\text{ cm})\right]^2} = 2a^2 \quad ①$$

$$\Rightarrow a = 3.68\times10^{-8}\text{ cm} \quad ①$$

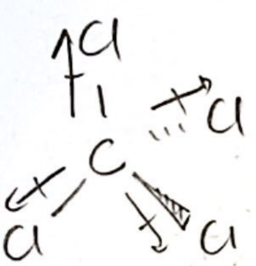
$$V = a^3 = (3.68\times10^{-8}\text{ cm})^3 = 4.97\times10^{-23}\text{ cm}^3 \quad ①$$

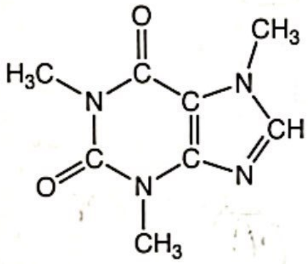
$$d = \frac{m}{V} = \frac{3.65\times10^{-22}\text{ g}}{4.97\times10^{-23}\text{ cm}^3} = \boxed{7.34\text{ g/cm}^3}$$

①

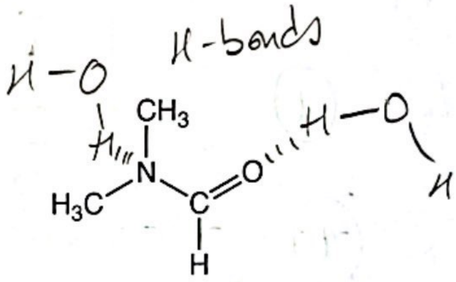
3. In the organic chemistry lab, students often perform a procedure called "liquid-liquid extraction". Consider the liquid-liquid extraction of caffeine (structure provided below). In the beginning of the procedure, caffeine is found in an aqueous solution (that is, dissolved in water). This solution is vigorously mixed with a liquid that is immiscible with water. After mixing, water and the liquid form two layers (since they are immiscible) and a significant amount of caffeine ends up extracted from water into this liquid.
   a. Which of the following liquids can be used in liquid-liquid extraction (i.e., is/are likely immiscible with water)? Briefly explain your answer. (6 points)
      i. Carbon tetrachloride, CCl_4
      ii. Ethanol, CH_3CH_2OH
      iii. N,N-dimethylformamide (see structure below)

all dipoles cancel





caffeine



N,N-dimethylformamide

①

CCl_4 is immiscible with H_2O. H_2O is very polar while CCl_4 is nonpolar ①

① CH_3CH_2OH is miscible with H_2O. It can H-bond like H_2O. ①

DMF is miscible with H_2O. ① It's quite polar. ① (can H-bond to H_2O)

   b. One solvent that is often used in extraction of caffeine from water is dichloromethane, CH_2Cl_2. Provide a plausible explanation why caffeine can be extracted into CH_2Cl_2. That is, why would caffeine have better solubility in CH_2Cl_2 than in water? (2 points)

①

Neither caffeine nor CH_2Cl_2 is as polar as H_2O.
① They are both polar, non H-bonding - more similar to each other than to H_2O.

6

4. An experiment was conducted to study the rate of the reaction

$$H_2SeO_3\,(aq) + 6\,I^-\,(aq) + 4\,H^+\,(aq) \rightarrow Se\,(s) + 2\,I_3^-\,(aq) + 3\,H_2O\,(l)$$

The results are found in the table below. All the reactions took place at the same temperature.

$[H_2SeO_3]_0$ (M)	$[I^-]_0$ (M)	$[H^+]_0$ (M)	Initial rate (M s^{-1})
1.00×10^{-4}	3.00×10^{-2}	2.00×10^{-2}	5.30×10^{-7}
2.00×10^{-4}	3.00×10^{-2}	2.00×10^{-2}	1.06×10^{-6}
3.00×10^{-4}	3.00×10^{-2}	4.00×10^{-2}	6.36×10^{-6}
3.00×10^{-4}	3.00×10^{-2}	8.00×10^{-2}	2.54×10^{-5}
3.00×10^{-4}	6.00×10^{-2}	8.00×10^{-2}	2.04×10^{-4}

a. Evaluate the orders of H_2SeO_3, I^- and H^+ in this reaction. (6 points)

① $[H_2SeO_3] \times 2 \rightarrow \text{rate} \times \frac{10.6}{5.3} = \times 2 \Rightarrow \boxed{\text{1st order}}$

① $[I^-] \times 2 \rightarrow \text{rate} \times \frac{20.4}{2.54} = \times 8 = \times 2^3 \Rightarrow \boxed{\text{3rd order}}$

① $[H^+] \times 2 \rightarrow \text{rate} \times \frac{25.4}{6.36} = \times 4 \Rightarrow \boxed{\text{2nd order}}$

Order of H_2SeO_3 = 1 ① Order of I^- = 3 ① Order of H^+ = 2 ①

b. Calculate the rate constant k for this temperature with appropriate units. (4 points)

$\text{rate} = k[H_2SeO_3][I^-]^3[H^+]^2$ ①

① $5.30 \times 10^{-7}\ M s^{-1} = k(1.00 \times 10^{-4}\ M)(3.00 \times 10^{-2}\ M)^3(2.00 \times 10^{-2}\ M)^2$

$k = 4.91 \times 10^5 \frac{M s^{-1}}{M^6} = \boxed{4.91 \times 10^5\ M^{-5} s^{-1}}$

① ①

5. The rate equation for the reaction A → products is $-d[A]/dt = k[A]^2$. If [A] = 0.400 M initially and 0.250 M after 15.0 min, what will [A] be after 175 min? (6 points)

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$ ①

$$\frac{1}{0.250\,M} - \frac{1}{0.400\,M} = k(15.0\text{ min}) \Rightarrow k = 0.100\ M^{-1}\text{min}^{-1}$$ ① ①

$$\frac{1}{[A]} - \frac{1}{0.400\,M} = (0.100\ M^{-1}\text{min}^{-1})(175\text{ min})$$ ①

$$\frac{1}{[A]} = 20.0\ M^{-1} \Rightarrow \boxed{[A] = 0.0500\ M}$$ ① ①

6. Arrange the following aqueous solutions in order of increasing osmotic pressure at 25 °C (from lowest to highest). Assume complete dissociation of ionic compounds. Briefly show your work (no need to show very detailed calculations, just your thought process). (5 points)

a. 0.030 M urea (CON_2H_4)
b. 0.010 M glucose ($C_6H_{12}O_6$) + 0.005 M sucrose ($C_{12}H_{22}O_{11}$)
c. 0.005 M Na_3PO_4
d. 0.020 M KCl

urea : effectively 0.030 M
glucose + sucrose : 0.015 M
Na_3PO_4 : $0.005 \times 4 = 0.020$ M
KCl : $0.020 \times 2 = 0.040$ M

the higher the concentration, the higher the Π (constant T) ①

②

$$\underset{g+s}{\overset{0.015}{b}} < \underset{Na_3PO_4}{\overset{0.02}{c}} < \underset{urea}{\overset{0.03}{a}} < \underset{KCl}{\overset{0.04}{d}}$$

③ for 4 in correct order
② for 3
① for 2

7. For the first-order reaction

$N_2O_5\,(g) \rightarrow 2\,NO_2\,(g) + \frac{1}{2}\,O_2\,(g)$

the half-life is 22.5 h at 20. °C and 1.5 h at 40. °C.

a. Calculate the rate constants for this reaction at 20. °C and 40. °C. Compare their values and briefly explain why one of them is larger than the other. (3 points)

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{22.5\,h} = 0.0308\,h^{-1} \text{ for } 20.°C \quad ①$$

$$= \frac{\ln 2}{1.5\,h} = 0.46\,h^{-1} \text{ for } 40.°C$$

The rate constant is higher at the higher T ① because rates are higher at higher T (more particles possess sufficient energy to overcome E_a) ①

b. Calculate the activation energy of this reaction with appropriate units. (6 points)

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad ①$$

①

$$\ln\frac{0.46\,h^{-1}}{0.0308\,h^{-1}} = -\frac{E_a}{8.314\,J\,K^{-1}\,mol^{-1}}\left(\frac{1}{313\,K} - \frac{1}{293\,K}\right)$$

① ①

$$E_a = 103000\,J\,mol^{-1} = 103\,kJ\,mol^{-1}$$

① ①

8. A forensic chemist is given a white powder for analysis. She dissolves 0.50 g of the substance in 8.0 g of benzene. The solution freezes at 3.9 °C. (For benzene, normal freezing point = 5.5 °C and K_f = 5.12 °C m^{-1}).
   a. Can the chemist conclude that the compound is cocaine? ($C_{17}H_{21}NO_4$)? Support your answer with a calculation. (7 points)

①

① $\Delta T = Km = 5.5\,°C - 3.9\,°C = (5.12\,°C\,m^{-1})\,m$

$m = 0.31$ mol/kg ①

$8.0\,g \times \frac{1\,kg}{1000\,g} \times \frac{0.31\,mol}{1\,kg} = 2.5 \times 10^{-3}\,mol$ ①

$\frac{0.50\,g}{2.5 \times 10^{-3}\,g\,mol^{-1}} = \boxed{200\,g/mol}$ ①

cocaine $\simeq 303\,g\,mol^{-1}$ ①

no ①

   b. Name one assumption that is made in this analysis. (1 point)

P = 1 atm   ideal solution

pure substance (or i = 1)   ①

nonvolatile solute

9. Calculate the lattice enthalpy of potassium chloride (KCl) from the following data. Write a chemical equation for each process when it is missing. (12 points)

	Process		Enthalpy (kJ/mol product)	Equation
✓	Sublimation of K	flip	+79.2	$K(s) \rightarrow K(g)$
✓	First ionization energy of K	flip	+418.7	② $K(g) \to K^+(g) + e^-$
✓	Formation of KCl (s)	keep	−435.7	② $K(s) + \frac{1}{2}Cl_2(g) \to KCl(s)$
✓	Formation of Cl (g)	flip	+121.4	$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$
✓	Electron affinity of Cl	flip	−348	$Cl(g) + e^- \rightarrow Cl^-(g)$
	Lattice enthalpy of KCl		x	② $K^+(g) + Cl^-(g) \to KCl(s)$

$\boxed{K^+(g)} + \cancel{e^-} \to \cancel{K(g)}$ -418.7 ①

$\boxed{Cl^-(g)} \to \cancel{Cl(g)} + \cancel{e^-}$ $+348$ ①

$\cancel{K(s)} + \frac{1}{2}\cancel{Cl_2(g)} \to \boxed{KCl(s)}$ -435.7 ①

$\cancel{K(g)} \to \cancel{K(s)}$ -79.2 ①

$\cancel{Cl(g)} \to \frac{1}{2}\cancel{Cl_2(g)}$ -121.4 ①

$\Delta H = (-418.7 + 348 - 435.7 - 79.2 - 121.4)\ kJ/mol$

$= \boxed{-707\ kJ\ mol^{-1}}$ ①

10. The standard enthalpy of solution ($\Delta H^\circ_{solution}$) of LiCl is –37.1 kJ/mol. Recall that the dissolution of an ionic solid MX in water, MX (s) → MX (aq), can be described as a two-step process:

$MX(s) \rightarrow M^+(g) + X^-(g)$ ΔH°_1
$M^+(g) + X^-(g) \rightarrow MX(aq)$ ΔH°_2

a. What is the sign of ΔH°_1? Provide a brief explanation. (2 points)

$\Delta H_1 > 0$. To break bonds, it must absorb energy.

②

b. What is the sign of ΔH°_2? Provide a brief explanation. (2 points)

②

$\Delta H_2 < 0$. IMFs are formed, (ion-dipole attractions between M^+, X^- and H_2O) so energy is released.

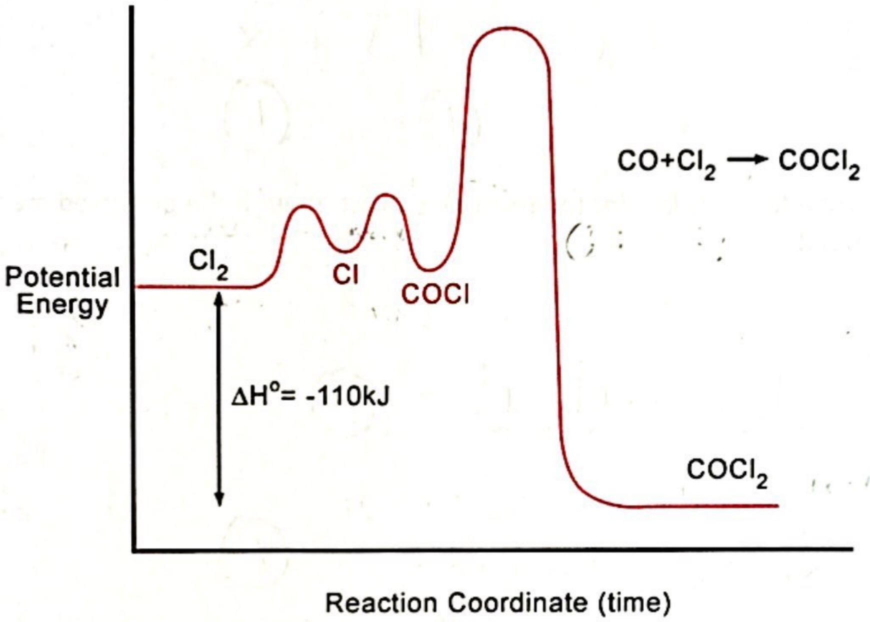
c. Use the $\Delta H^\circ_{solution}$ value for LiCl to explain how the absolute values of ΔH°_1 and ΔH°_2 compare to each other for this compound. That is, clearly state whether $|\Delta H^\circ_1| = |\Delta H^\circ_2|$, $|\Delta H^\circ_1| > |\Delta H^\circ_2|$, or $|\Delta H^\circ_1| < |\Delta H^\circ_2|$. Provide a brief explanation. (2 points)

$|\Delta H_2| > |\Delta H_1|$ ①

For LiCl, $\Delta H_1 + \Delta H_2 < 0$,

① so the negative second component must be larger.

11. The reaction coordinate diagram and a proposed mechanism for the multistep reaction $CO + Cl_2 \rightarrow COCl_2$ are provided below:



1. $Cl_2 \xrightleftharpoons[k_{-1}]{k_1} 2\,Cl$
2. $Cl + CO \xrightleftharpoons[k_{-2}]{k_2} COCl$
3. $COCl + Cl \xrightarrow{k_3} COCl_2$

a. Which is the rate-determining step? Briefly explain your answer. (2 points)

step 3 - highest E_a ① ①

b. List all the intermediates in this reaction. (2 points)

① Cl, COCl ①

c. List two aspects of the reaction coordinate diagram that could change and one that would remain unchanged if a catalyst was added. (3 points)

① E_a will change
① Mechanism (number of steps) can change
① ΔH_{rxn} will not change

d. **If the activation energy of the forward reaction is x kJ/mol, what is the activation energy of the reverse reaction in terms of x? (2 points)**

$$E_a = 110\ kJ + x$$

① ①

e. **Provide a rate law for the reaction consistent with the proposed mechanism. (6 points)**

$$rate = k_3[COCl][Cl]$$ ①

$$k_2[Cl][CO] = k_{-2}[COCl]$$ ①

$$[COCl] = \frac{k_2}{k_{-2}}[Cl][CO]$$ ①

$$k_1[Cl_2] = k_{-1}[Cl]^2$$ ①

$$[Cl]^2 = \frac{k_1}{k_{-1}}[Cl_2]$$ ①

$$rate = \frac{k_3 k_2}{k_{-2}}[Cl]^2[CO] = \frac{k_3 k_2 k_1}{k_{-2} k_{-1}}[Cl_2][CO]$$ ①