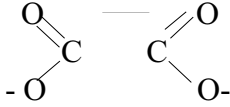
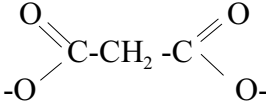


Answer all questions in the blue books

- Although sodium nitride, Na_3N , was first prepared in 2002 years before a thermodynamic analysis using a Born-Haber cycle showed that the compound might be stable. Draw out a Born-Haber cycle and calculate the enthalpy of formation for Na_3N given the following information: $\Delta H_{\text{sub}} = 108 \text{ kJ/mol}$, $I_1 = 495.8 \text{ kJ/mol}$, $\Delta H_{\text{diss}} = 946 \text{ kJ/mol}$, $A_1 + A_2 + A_3 = 2122 \text{ kJ/mol}$, $U^\circ = -4422 \text{ kJ/mol}$. (10)
- Briefly explain the band theory of metals using Li as an example?
 - What is meaning of the acronyms: hcp, ccp, and fcc? For type A lattices what is the coordination number for each case? (12)
- Which is the strongest acid in each series?
 - HSO_4^- , H_2AsO_3 , H_2SO_4 , H_2SeO_3 , H_6TeO_6
 - NH_4^+ , HF , H_2Se , HIO_2 , HBr
 - HClO_4 , HClO_3 , HClO , HFO , HIO
 - Write balanced equations for each base in water indicating by means of equilibrium arrows or a single arrow which base is totally associated, and identifying the conjugate acid of the base? (1) O^{2-} (2) F^- (3) H^- (12)
- Explain the trend in thermodynamic stability from the attached equilibrium constant data. The reaction in every case is $\text{M}^{2+} + \text{L}^{2-} \rightleftharpoons \text{ML}$

	oxalate	malonate
		
Log K_{eq}	4.96	6.18
	6.23	5.80
 - The experimental log K values for the stepwise formation of cadmium ammine complexes follows the order $K_1 = 2.65$, $K_2 = 2.10$, $K_3 = 1.44$, and $K_4 = 0.93$. What is the reaction and the numerical value of the formation constant for $\log\beta_3$?
 - Give an explanation why in part (b) the magnitude of the stepwise constants decrease from K_1 to K_4 ? (12)
- Give a reasonable explanation for the two reactions:

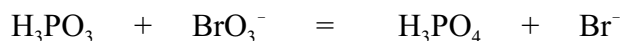
$$\text{Pd}^{2+} + \text{SCN}^- \rightarrow [\text{PdSCN}]^+$$

$$\text{Fe}^{3+} + \text{SCN}^- \rightarrow [\text{FeNCS}]^{2+}$$
 - Write balance equations for the reactions:

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow$$

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow$$
 (7)

6. (a) Balance the reaction writing the two half-reactions and show which is the oxidation and which is the reduction?



- (b) Given the couples $E^\circ(\text{BrO}_3^-/\text{Br}^-) = +1.42\text{V}$ and $E^\circ(\text{H}_3\text{PO}_4/\text{H}_3\text{PO}_3) = -0.28\text{V}$ calculate E° for the reaction you balanced in part (a)? Is the reaction spontaneous?
- (c) What will be $E(\text{BrO}_3^-/\text{Br}^-)$ when the pH of the solution is 3 and other variables are at standard conditions? Does BrO_3^- become a better oxidizing agent?
- (d) Will E for the reaction in part (a) at pH 3 differ from E° ? (13)

7. (a) Given the Latimer Diagram:
- $$\text{Cu}^{2+} \xrightarrow{+0.15} \text{Cu}^+ \xrightarrow{+0.52} \text{Cu}$$
-

construct the Frost diagram for Cu, Cu^+ , and Cu^{2+} .

- (b) From your diagram estimate if Cu and Cu^{2+} will comproportionate in aqueous solution? (8)
8. For each of the non-aqueous solvents write the auto ionization equation and indicate the acidic and basic species: (a) NH_3 (b) HF (c) CH_3COOH (d) BrF_3 (8)
9. Write balanced equations to explain the following observations:
- (a) AlF_3 has a low solubility in liquid HF but a combination of AlF_3 and NaF leads to dissolution of the reagents. When BF_3 is added to the solution a precipitate forms.
- (b) When Na is added to liquid ammonia a deep blue solution forms, but addition of a catalytic amount of Fe(III) salt produces a gray precipitate and evolution of a gas other than $\text{NH}_3(\text{g})$. (8)
- 10.(a) Write equations for the industrial preparation of hydrogen from methane and be sure to give conditions where appropriate?
- (b) The stretching frequency for the O-H bond changes as the phases of water change from gas to liquid to solid. What trend in frequency is observed and why?
- (c) For deuterium, $I = 1$. In a fully labeled sample of CDCl_3 , what is observed in the ^{13}C NMR spectrum? (10)