Chemistry 4000
Introduction to Inorganic Chemistry: The Different Perspectives of Bonding
Exam 3
Name: ______________________________

Show your work for maximum credit.

1. Identify the following. (17 points)

A. This solid-state lattice defect can result in a bluish tint to the compound.

F - center defect

B. This Acid-Base theory is specific to solutions in which water is the solvent.

Arrhenius

C. This Acid-Base theory focuses on the polarizability of species.

Hard - Soft Acid Base Theory

D. The product of K_a and K_b is.

$K_a \times K_b = K_w$

E. This type of bond is due to the electron pair coming exclusively from the Lewis Base.

Dative bond

F. He is famous for introducing the field of coordination chemistry with his model for cobalt compounds.

Alfred Werner

G. This is the coordination sphere that involves the direct bonding of ligands to metals.

Primary coordination sphere

H. The root of this coordination chemistry property comes from Latin, meaning "tooth".

Denticity

I. The ability of some metals to induce hydrolysis makes them this type of acid.

Bronsted Lowry

J. These types of isomers do not involve all bonds between the same atoms.

structural or constitutional isomers

K. The chelate effect is most relevant for chelators that form rings of these number of atom members. 5-membered or 6-membered rings

L. This Boron-based anion is an example of a "least coordinating anion."

BArf

M. This is the temperature below which a superconductor loses its resistivity.

Critical temperature (T_c)

N. This property of the charge of ionic compounds in solid state lattices is retained regardless of the defects that we discussed in lecture.

Charge Neutrality

O. This is an intrinsic semiconductor.

Element/Material with an innate semiconductor property due to having a band gap of 105 kJ/mol.

P. This is a p-type extrinsic semiconductor.

Material that is an intrinsic semiconductor to which a dopant has been added that is less χ and that has orbitals that can accept e^-. The dopant effectively lowers the band gap and movement of e^-s into the dopant orbitals provides a positive charge to the host.

2. Using a Born-Haber cycle, calculate the enthalpy of formation of fluorite (CaF_2). (12 points)

$$\begin{tikzcd} Ca & F_2 \arrow[d] \\ 2+ & 1- \end{tikzcd}$$

Ca^{2+}: Coordination number of 8

F^-: Coordination number of 4

6

$$\begin{tikzcd}
Ca_{(g)} \arrow[rrr, "\Delta H_{IE1} ; \Delta H_{IE2}"] & & & Ca^{2+}_{(g)} \\
& & & + \\
& & 2F_{(g)} \arrow[r, "2\Delta H_{EA}"] & 2F^{-}_{(g)} \arrow[d, "\Delta U"] \\
Ca_{(s)} \arrow[uuu, "\Delta H_{sub}"] & + & F_{2\,(g)} \arrow[u, "\Delta H_{atom}"] \arrow[r, "\Delta H_f"] & CaF_2
\end{tikzcd}$$

2

$$\Delta U = \overset{A}{\left(\frac{N M Z_+ Z_-}{r_0}\right)} \overset{B}{\left(\frac{e^2}{4\pi \epsilon_0}\right)} \overset{C}{\left(1 - \frac{30\,pm}{r_0}\right)} = A \times B \times C$$

$$= -2{,}524 \frac{kJ}{mol}$$

$r_0 = r_{Ca^{2+}(C.N.=8)} + r_{F^-(C.N.=4)} = 126pm + 117pm = 243pm$

$N = 6.02 \times \frac{10^{23}}{mol}$ $M = 2.51939$

$A: -1.248 \times 10^{22}\ pm^{-1}\ mol^{-1}$ $C: 0.8765$

$B = 2.307 \times 10^{-19}\ kJ\ pm$

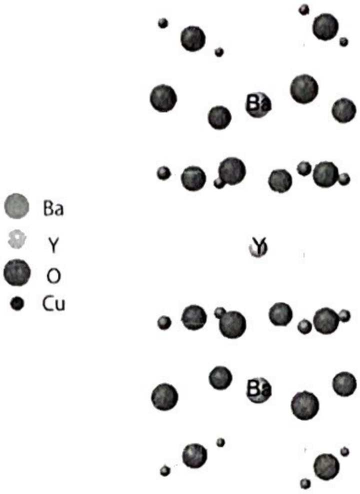
4

$\Delta H_{sub} + \Delta H_{atom} + \Delta H_{IE1} + \Delta H_{IE2} + 2\Delta H_{EA} + \Delta U = \Delta H_f$ (kJ/mol)

$192 + 158 + 589.8 + 1{,}145.4 + 2(-328) + -2{,}524 = \Delta H_f$

-1095 kJ/mol $= \Delta H_f$

3. Shown below is **one** unit cell for a superconductor. Yes, the whole thing is a unit cell and thus keep in mind that there are only four corners at the top and bottom of the cell. (14 points)



A. How many Cu^{n+} ions lie within one unit cell?

2 # of Cu = $\underset{1}{8(\frac{1}{8})}$ corner + $\underset{2}{8(\frac{1}{4})}$ edge = 3

B. How many Ba^{2+} ions lie within one unit cell?

1 2 inside

C. How many Y^{3+} ions lie within one unit cell?

1 1 inside

D. How many O^{2-} ions lie within one unit cell?

2 # of O^{2-} = $\underset{3}{12(\frac{1}{4})}$ edge + $\underset{4}{8(\frac{1}{2})}$ face = 7

E. What is the empirical formula for the superconductor?

2 $Ba_2YCu_3O_7$

F. Using **your** empirical formula, how many Cu^{2+} and Cu^{3+} ions should there be to have an overall net charge of zero?

$\underset{4+}{2(2+)} + \underset{3+}{1(3+)} + 3\text{"}\underset{2+/3+}{Cu^{n+}}\text{"} + \overset{14-}{7(2-)} = 0$ 3 "Cu^{n+}" = +7

2 $x\,Cu^{2+} + (3-x)\,Cu^{3+} \Rightarrow x(2+) + (3-x)(3+) = +7$ $2+x + 9+ - 3+x = +7$

$2+ = 1+x$

$2 = x$

$\therefore \underbrace{2\,Cu^{2+} + 1\,Cu^{3+}}_{+7}$

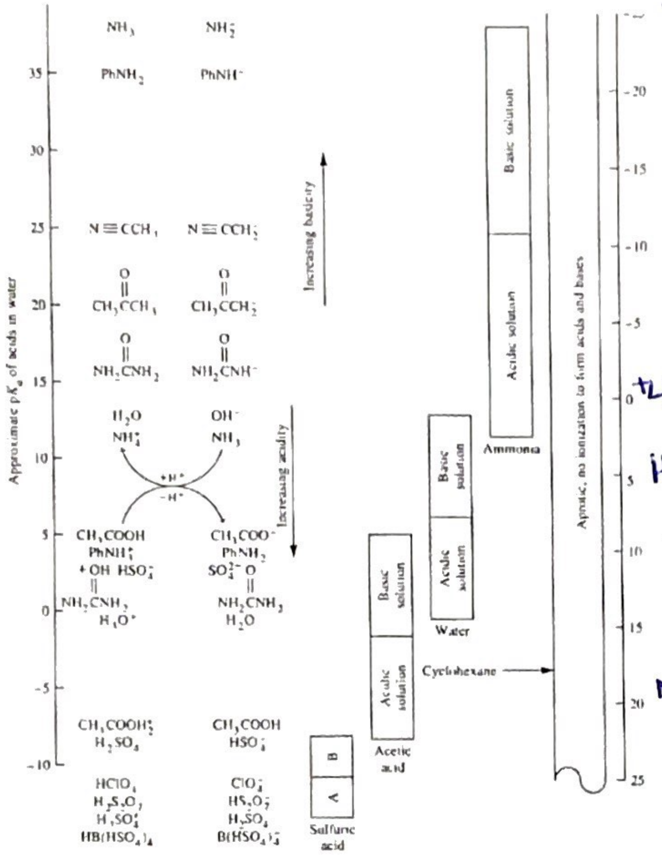
G. With respect to the $Cu^{2+/3+}$ ions, in what type of hole is Ba^{2+} located?

2 Cubic (C.N. = 8)

H. With respect to the O^{2-} ions, in what type of hole is Y^{3+} located?

2 Cubic (C.N. = 8)

4. Please write the appropriate acid/base reaction expression to define the behavior of the solutes $H_2S_2O_7$, NH_3, NaOH, and urea (NH_2CONH_2) in the following set of solvents. (14 points)



+2

A. cyclohexane (C_6H_{12})

The solutes are not acids or bases in cyclohexane.

+4

B. sulfuric acid (H_2SO_4)

$H_2S_2O_7 + H_2SO_4 \rightleftarrows HS_2O_7^- + H_3SO_4^+$

$NH_3 + H_2SO_4 \rightarrow NH_4^+ + HSO_4^-$

$OH^- + H_2SO_4 \rightarrow HSO_4^- + H_2O$

$NH_2CONH_2 + H_2SO_4 \rightarrow NH_3CONH_2^+ + HSO_4^-$

C. dihydrogen monoxide (Very deadly)

$H_2S_2O_7 + H_2O \rightarrow HS_2O_7^- + H_3O^+$

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$OH^- + H_2O$ "No reaction" because already leveled. Strong base.

$NH_2CONH_2 + H_2O$ No reaction

D. acetic acid (CH_3COOH)

$H_2S_2O_7 + CH_3COOH \rightarrow HS_2O_7^- + CH_3COOH_2^+$

$NH_3 + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$

$OH^- + CH_3COOH \rightarrow H_2O + CH_3COO^-$

$NH_2CONH_2 + CH_3COOH \rightleftarrows NH_2CONH_3^+ + CH_3COO^-$

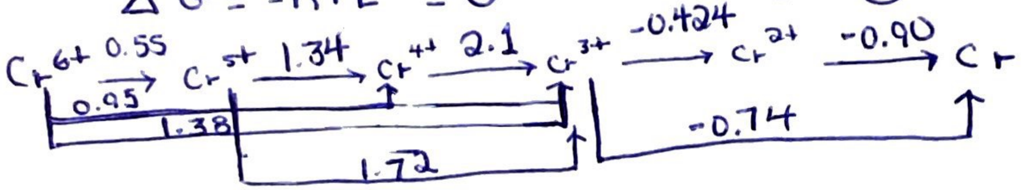
5. Organize the following information into a Latimer diagram. Identify which electron transfer steps are thermodynamically favorable. (10 points)

2

	E° (V) vs SHE	Favorable?
$Cr^{6+} + e^- \rightarrow Cr^{5+}$ ✓	0.55	Yes
$Cr^{6+} + 2e^- \rightarrow Cr^{4+}$ ✓	0.95	Yes
$Cr^{6+} + 3e^- \rightarrow Cr^{3+}$ ✓	1.38	Yes
$Cr^{5+} + e^- \rightarrow Cr^{4+}$ ✓	1.34	Yes
$Cr^{5+} + 2e^- \rightarrow Cr^{3+}$ ✓	1.72	Yes
$Cr^{4+} + e^- \rightarrow Cr^{3+}$ ✓	2.1	Yes
$Cr^{3+} + e^- \rightarrow Cr^{2+}$ ✓	-0.424	No
$Cr^{3+} + 3e^- \rightarrow Cr$ ✓	-0.74	No
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.90	No

$\Delta G = -nFE^\circ = \ominus$ Favorable $\therefore E^\circ = \oplus$

8



6. Please name the following coordination compounds. (10 points)

4+ 2- 2-

a. $[PtClBr(NH_3)_2(H_2O)_2]Cl_2$

2+

bisammine bisaqua bromo chloroplatinum (IV) chloride

1-

b. $Na[NiBr_3(H_2O)]$ Sodium aquatribromonickelate (II)

1+ 2+ 3-

c. $Fe(CN)_2(en)_2$ 0 dicyano bis(ethylenediamine) iron (II)

2+ 2-

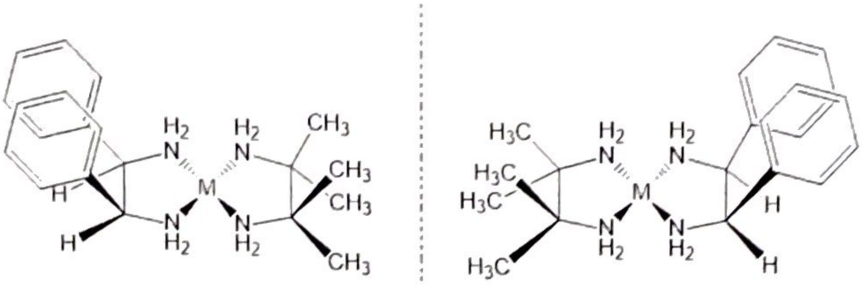
3+ 3-

d. $[Co(CO)_6][CoF_6]$ (The cationic sphere has a charge of +3)

hexacarbonyl cobalt(III) hexafloro cobaltate (III)

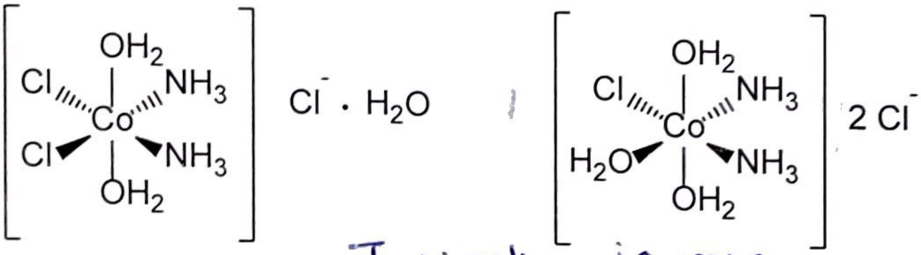
7. What type of isomers are the following pairs? (8 points)

a.



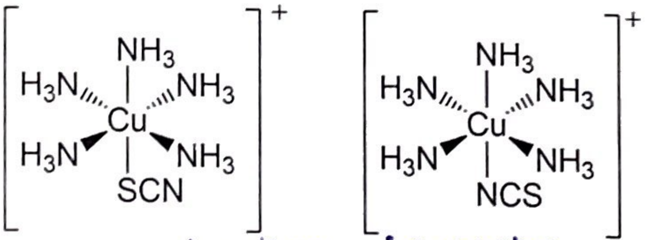
Not isomers. Same compound.

b.



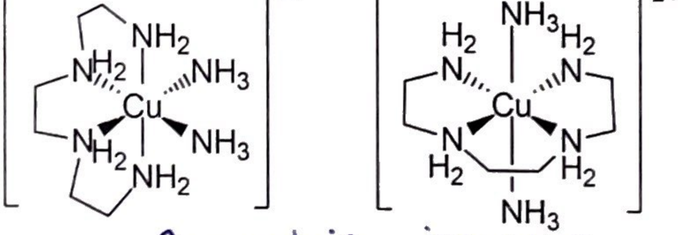
Ionization isomers

c.



Linkage isomers

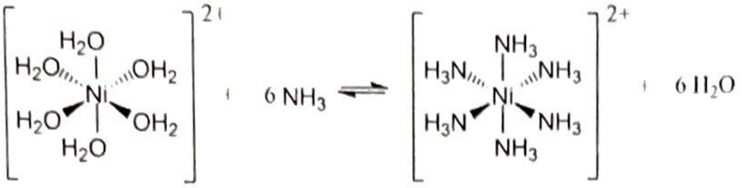
d.



Geometric isomers

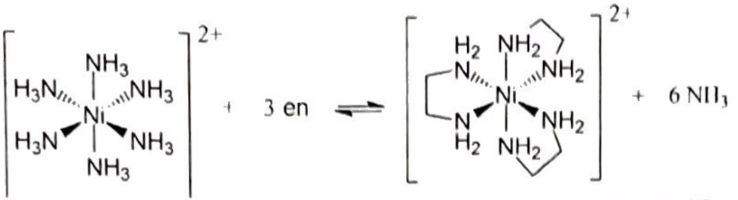
8. Refer to the two complexation reactions below to address the following. (15 points)

A.



$\beta_A = 2.0 \times 10^8$

B.



$\beta_B = 6.02 \times 10^{11}$

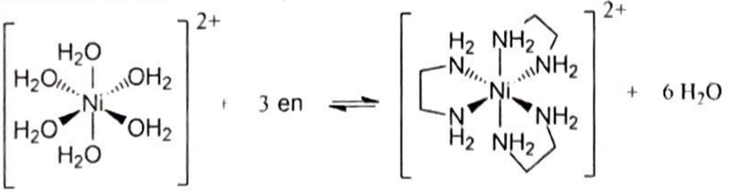
a. For reaction B, ΔH° = -12.1 kJ/mol and at T = 298K, -TΔS° = -55.1 kJ/mol. Determine the value of ΔG° and explain what thermodynamic parameter is driving this reaction and why.

$\Delta G° = \Delta H° - T\Delta S° = -67.2\ kJ/mol$

The entropy more than the enthalpy is driving the reaction as there is a shift from 4 reactants to 7 products.

b. Determine the value of β_C for reaction C listed below.

C.



$\beta_C = B_A \times B_B$

$$= 1.2 \times 10^{20} = \frac{[Ni(en)_3^{2+}]}{[Ni^{2+}][en]^3}$$

c. Derive the K_2 expression for the complexation of NH_3 starting from the complex $Ni(H_2O)_6^{2+}$.

$Ni(NH_3)(H_2O)_5 + NH_3 \rightleftarrows Ni(NH_3)_2(H_2O)_4 + 1\ H_2O$

$$K_2 = \frac{[Ni(NH_3)_2^{2+}]}{[Ni(NH_3)^{2+}][NH_3]}$$

d. Derive the β_2 expression for the complexation of **en** starting from the complex $Ni(H_2O)_6^{2+}$.

$Ni(H_2O)_6^{2+} + 2en \rightleftarrows Ni(en)_2(H_2O)_2 + 4H_2O$

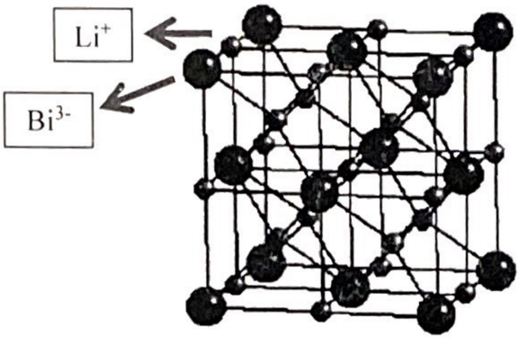
$$\beta_2 = \frac{[Ni(en)_2^{2+}]}{[Ni^{2+}][en]^2}$$

e. In general, would the affinity of the ammine be greater for Cu^{1+} or Ni^{2+}? Explain.

The ammine is an intermedicte Lewis base and prefers binding to Ni^{2+}, an intermedicte metal, then Cu^{1+}, a soft metal.

Extra Credit:

Calculate the enthalpy of formation of lithium bismuthide. (Five points)



12 Li^+ ions:
→ 8 Td
→ 4 Oh

4 Bi^{3-} ions
→ C.N. = 14

Li_3Bi

$r_{Li^+(CN=4)}$ = 60 pm

$r_{Bi^{3-}(C.N.=14)}$ = 282 pm

Unknown Madelung constant

r_o = 342 pm

ν = 4

$$\begin{tikzcd}
3Li_{(g)} \arrow[rr, "\Delta H_{IE}"] & & 3Li^+_{(g)} \\
& & + \\
& Bi_{(g)} \arrow[r, "\Delta H_{EA_1}, \Delta H_{EA_2} \Delta H_{EA_3}"] & 1Bi^{3-}_{(g)} \arrow[dd, "\Delta U"] \\
& Bi_{(l)} \arrow[u, "\Delta H_{vap}"] & \\
3Li_{(s)} \arrow[uuuu, "\Delta H_{sub}"] \; + & Bi_{(s)} \arrow[u, "\Delta H_{fus}"] \arrow[r, "\Delta H_f"] & Li_3Bi_{(s)}
\end{tikzcd}$$

$$\Delta U = \underbrace{\frac{120,200 \, \nu Z+Z-}{r_o}}_{-4217.54} \underbrace{\left(1 - \frac{34.5\text{pm}}{r_o}\right)}_{0.899123} \frac{kJ}{mol}$$

$$= -3,792.09 \frac{kJ}{mol}$$

$$3\Delta H_{sub} + 3\Delta H_{IE} + \Delta H_{fus} + \Delta H_{vap} + \Delta H_{EA_1} + \Delta H_{EA_2} + \Delta H_{EA_3} + \Delta U = \Delta H_f \frac{kJ}{mol}$$

$$3(162) + 3(520.2) + 11.30 + 179 + -91.2 + 422 + 880 + -3,792 = \Delta H_f$$

$$-344 \frac{kJ}{mol} = \Delta H_f$$