Problems

12.1 The high-spin d^4 complex $[Cr(H_2O)_6]^{2+}$ is *labile*, but the low-spin d^4 complex ion $[Cr(CN)_6]^{4-}$ is *inert*. Explain.

12.2 Why is the existence of a series of entering groups with different rate constants evidence for an associative mechanism (A or I_a)?

12.3 Predict whether these complexes would be labile or inert and explain your choices. The magnetic moment is given in Bohr magnetons μ_B after each complex.

Ammonium oxopentachlorochromate(V)	1.82
Potassium hexaiodomanganate(IV)	3.82
Potassium hexacyanoferrate(III)	2.40
Hexaammineiron(II) chloride	5.45

12.4 The yellow "prussiate of soda" $Na_4\,[Fe(CN)_6]$ has been added to table salt as an anticaking agent. Why have there been no apparent toxic effects, even though this compound contains cyano ligands?

12.5 Consider the half-lives of substitution reactions of the pairs of complexes:

Half-Lives Shorter than 1 Minute	**Half-Lives Longer than 1 Day**
$[Cr(CN)_6]^{4-}$	$[Cr(CN)_6]^{3-}$
$[Fe(H2O)_6]^{3+}$	$[Fe(CN)_6]^{4-}$
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_5(H_2O)]^{3+}$(H_2O exchange)

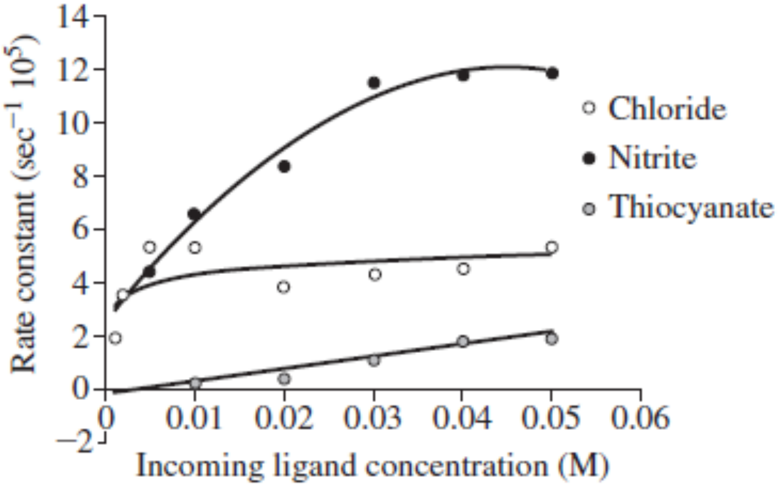
Interpret the differences in half-lives in terms of the electronic structures of each pair.

12.6 The general rate law for substitution in square-planar Pt(II) complexes is valid for the reaction

$$[Pt(NH_3)_4]^{2+} + Cl^- \rightarrow [Pt(NH_3)_3Cl]^+ + NH_3$$

Design the experiments needed to verify this and to determine the rate constants. What experimental data are needed, and how are the data to be treated?

12.7 The graph shows plots of k_{obs} versus $[X^-]$ for the anations $Co(en)_2(NO_2)(DMSO)]^{2+} + X^- \rightarrow [Co(en)_2(NO_2)X]^+ + DMSO$. The rate for DMSO exchange was determined as 30×10^{-5} sec $^{-1}$. (Graph created using data from W. R. Muir, C. H. Langford, *Inorg. Chem.*, **1968**, *7*, 1032.)



All three reactions are presumed to have the same mechanism.

a. Why is the DMSO exchange so much faster than the other reactions?
b. Why are the curves shaped as they are?
c. Explain what the limiting rate constants (at high concentration) are in terms of the rate laws for *D* and I_d mechanisms.
d. The limiting rate constants are 5.0×10^{-5} s^{-1} and 12.0×10^{-5} s^{-1} for Cl^- and NO_2^- respectively. For SCN^-, the limiting rate constant can be estimated as 1×10^{-5} s^{-1}. Do these values constitute evidence for an I_d mechanism?

12.8

a. The CO exchange reaction $Cr(^{12}CO)_6 + {}^{13}CO \rightarrow Cr(^{12}CO)_5(^{13}CO) + {}^{12}CO$ has a rate that is first order in the concentration of $Cr(^{12}CO)_6$ but independent of the concentration of ^{13}CO. What does this imply about the mechanism of this reaction?

b. The reaction $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ [$R = P(n\text{-}C_4H_9)_3$] has the rate law of $= k_1[Cr(CO)_6] + k_2[Cr(CO)_6][PR_3]$. Why does this rate law have two terms?

c. For the general reaction in part **b**, will bulkier ligands tend to favor the first order or second order pathway? Explain briefly.

12.9 Account for the observation that two separate water exchange rates are found for $[Cu(H_2O)_6]^{2+}$ in aqueous solution.

12.10 The ligand exchange mechanism of the solvated lithium cations $[Li(H_2O)_4]^+$ and $[Li(NH_3)_4]^+$ has been studied using DFT calculations (R. Puchta, M. Galle, N. van E. Hommes, E. Pasgreta, R. van Eldik, *Inorg. Chem.*, **2004**, 43, 8227.). Describe how water exchange is postulated to occur with the inclusion of the pertinent structures. What parameter most strongly supports a limiting associative substitution mechanism? How is the proposed mechanism for ligand exchange in $[Li(NH_3)_4]^+$ different? Why is the $[Li(NH_3)_4]^+$ mechanism postulated as associative interchange?

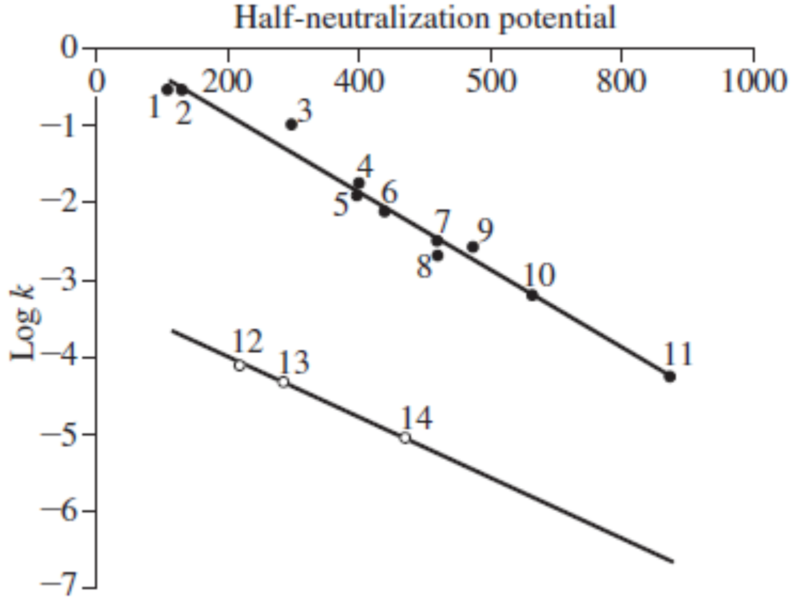
12.11 Data for the reaction

$$Co(NO)(CO)_3 + As(C_6H_5)_3 \rightarrow Co(NO)(CO)_2[As(C_6H_5)_3] + CO$$

in toluene at 45 °C are given in the table. In all cases, the reaction is pseudo–first order in $Co(NO)(CO)_3$. Determine the rate constant(s) and discuss their probable significance (See E. M. Thorsteinson, F. Basolo, *J. Am. Chem. Soc.*, **1966**, *88*, 3929).

$[As(C_6H_5)_3]$ *(M)*	**k (10^{-5} s^{-1})**
0.014	2.3
0.098	3.9
0.525	12
1.02	23

12.12 A plot of the log of the rate constant for substitution of CO on Co(NO)(CO)$_3$ by phosphorus and nitrogen ligands in nitromethane at 298 K, versus the half-neutralization potential of the ligands, a measure of ligand basicity, is below. Explain the linearity of such a plot and why there are two different lines. Incoming nucleophilic ligands: (1) P(C$_2$H$_5$)$_3$, (2) P(*n*-C$_4$H$_9$)$_3$, (3) P(C$_6$H$_6$)(C$_2$H$_5$)$_2$, (4) P(C$_6$H$_5$)$_2$(C$_2$H$_5$), (5) P(C$_6$H$_5$)$_2$ (*n*-C$_4$H$_9$), (6) P(*p*-CH$_3$OC$_6$H$_4$)$_3$, (7) P(O-*n*-C$_4$H1$_9$)$_3$, (8) P(OCH$_3$)$_3$, (9) P(C$_6$H$_5$)$_3$, (10) P(OCH$_2$)$_3$ CCH$_3$, (11) P(OC$_6$H$_5$)$_3$, (12) 4-picoline, (13) pyridine, (14) 3-chloropyridine. (Graph created with data from E. M. Thorsteinson, F. Basolo, *J. Am. Chem. Soc.*, **1966**, *88*, 3929.)



12.13 *cis*-PtCl$_2$(PEt$_3$)$_2$ is stable in benzene solution. However, small amounts of free triethylphosphine catalyze establishment of an equilibrium with the *trans* isomer:

$$cis\text{-}\mathrm{PtCl_2(PEt_3)_2} \rightleftharpoons trans\text{-}\mathrm{PtCl_2(PEt_3)_2}$$

For the conversion of *cis* to *trans* in benzene at 25 °C, $\Delta H° = 10.3$ kJ mol^{-1} and $\Delta S° = 55.6$ J mol^{-1} K^{-1}.

a. Calculate the free energy change, $\Delta G°$ and the equilibrium constant for this isomerization.
b. Which isomer has the higher bond energy? Is this answer consistent with what you would expect on the basis of π bonding in the two isomers? Explain briefly.
c. Why is free triethylphosphine necessary to catalyze the isomerization?

12.14 This table shows the effect of changing ligands on the dissociation rates of CO *cis* to those ligands. Explain the effect of these ligands on the rates of dissociation. Include the effect of these ligands on $Cr - CO$ bonding and on the transition state, presumed to be square-pyramidal. (See J. D. Atwood, T. L. Brown, *J. Am. Chem. Soc*., **1976**, *98*, 3160).

Compound	***k*(s^{-1})for CO Dissociation**
$Cr(CO)_6$	1×10^{-12}
$Cr(CO)_5(PPh_3)$	3.0×10^{-10}
$[Cr(CO)_5I]^-$	-5
$[Cr(CO)_5Br]^-$	2×10^{-5}
$[Cr(CO)_5Cl]^-$	1.5×10^{-4}

12.15 When the two isomers of $Pt(NH_3)_2Cl_2$ react with thiourea $[tu = S = (NH_2)_2]$, one product is $[Pt(tu)_4]^{2+}$ and the other is $[Pt(NH_3)_2(tu)_2]^{2+}$. Identify the initial isomers and explain the results.

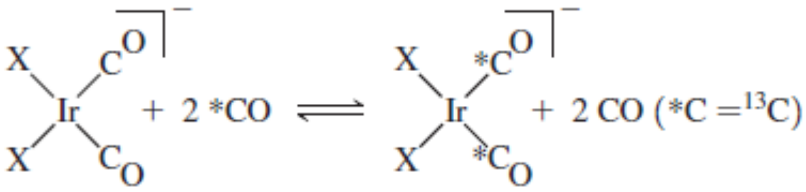
12.16 Predict the products (equimolar mixtures of reactants):

a. $[Pt(CO)Cl_3]^- + NH_3 \rightarrow$
b. $[Pt(NH_3)Br_3]^- + NH_3 \rightarrow$
c. $[(C_2H_4)PtCl_3]^- + NH_3 \rightarrow$

12.17

a. Design a sequence of reactions, beginning with $[PtCl_4]^{2-}$, that will result in Pt(II) complexes with four different ligands—py, NH_3, NO_2^-, and CH_3NH_2—with two different sets of *trans* ligands. (CH_3NH_2 is similar to NH_3 in its *trans* effect.)
b. Pt(II) can be oxidized to Pt(IV) by Cl_2 with no change in configuration (chloride ions are added above and below the plane of the Pt(II) complex). Predict the results if the two compounds from (a) are reacted with Cl_2 and then with 1 mole of Br^- for each mole of the Pt compound.

12.18 The rates of exchange of CO on *cis* square-planar Ir complexes have been observed for the following reaction at 298 K:



The observed rate constants were:

X	***k*(L/mol s)**
Cl	1,080
Br	12,700
I	98,900

All three reactions have large negative values of entropy of activation, ΔS

a. Is this reaction associative or dissociative?
b. On the basis of the data, which halide ligand exerts the strongest *trans* effect? (See R. Churlaud, U. Frey, F. Metz, A. E. Merbach, *Inorg. Chem*., **2000**, *39*, 304.)

12.19 The rate constant for electron exchange between $V^{2+}(aq)$ and $V^{3+}(aq)$ is observed to depend on the hydrogen ion concentration:

$$k = a + b/[H^+]$$

Propose a mechanism, and express *a* and *b* in terms of the rate constants of the mechanism. (Hint: $V^{3+}(aq)$ hydrolyzes more easily than $V^{2+}(aq)$.)

12.20 Is the reaction $[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+}$ likely to proceed by an inner-sphere or outer-sphere mechanism? Explain your answer.

12.21 The rate constants for the exchange reaction

$$CrX^{2+} + {}^*Cr^{2+} \rightarrow {}^*CrX^{2+} + Cr^{2+}$$
$$({}^*Cr \text{ is radioactive } {}^{51}Cr)$$

are given in the table for reactions at 0 °C and 1$HClO_4$. Explain the differences in the rate constants in terms of the probable mechanism of the reaction.

X^-

X^- *k* (M^{-1} s^{-1}) F^- 1.2 × 10^{-3} Cl^- 11 Br^- 60 NCS^- 1.2 × 10^{-4} (at 24 °C) N_3^- > 1.2

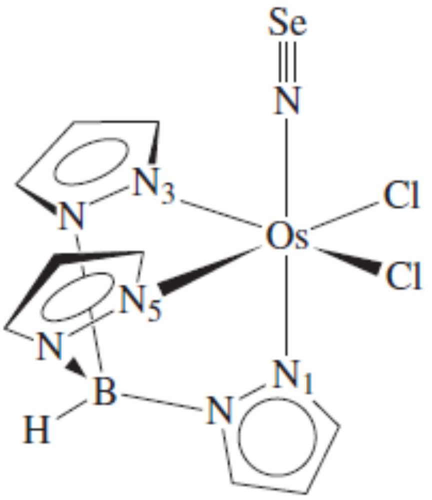
- **12.22** The first complex of the ligand NSe (selenonitrosyl), $TpOs(NSe)Cl_2$ [Tp = hydrotris (1-pyrazolyl)borate], is shown. The osmium–nitrogen distances are:

Os–N(1): 210.1(7) pm

Os–N(3): 206.6(8) pm

Os–N(5): 206.9(7) pm

a. Which ligand, Cl or NSe, has the larger *trans* influence? Explain briefly.
b. The nitrogen–selenium distance in this compound is among the shortest N — Se distances known. Why is this distance so short? (See T. J. Crevier, S. Lovell, J. M. Mayer, A. L. Rheingold, I. A. Guzei, *J. Am. Chem. Soc.*, **1998**, *120*, 6607.)



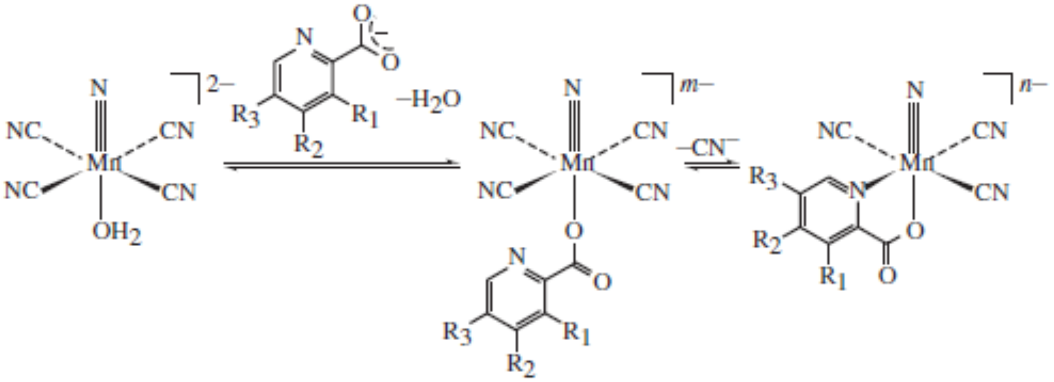
- **12.23** Exchange of an H_2O ligand on $[(CO)_3Mn(H_2O)_3]^+$ is much more rapid than on the analogous $[(CO)_3Re(H_2O)_3]^+$. The activation volume (change in volume on formation of the activated complex) is -4.5 ± 0.4 cm^3mol^{-1}. The Mn complex has infrared bands at 2051 and 1944 cm^{-1} that can be attributed to C — O stretching vibrations. (See U. Prinz, A. E. Merbach, O. Maas, K. Hegetschweiler, *Inorg. Chem.*, **2004**, *43*, 2387.)

a. Suggest why the Mn complex reacts more rapidly than the analogous Re complex.

b. Is the activation volume more consistent with an *A* (or I_a) or a *D* (or I_d) mechanism? Explain.

c. On the basis of the IR spectrum, is the reactant more likely a *fac* or *mer* isomer?

- **12.24** The mechanism of substitution reactions of *trans*-$[MnN(H_2O)(CN)_4]^{2-}$ with pyridine dicarboxylate ligands has been explored (H. J. van der Westhuizen, R. Meijboom, M. Schutte, A. Roodt, *Inorg. Chem.*, **2010**, *49*, 9599). The rate determining step is the second one, resulting in chelation and loss of cyanide. Attachment of the carboxylate oxygen to the Mn(V) center of *trans*-$[MnN(H_2O)(CN)_4]^{2-}$ is extremely fast.



The following kinetics data were obtained at roughly 298 K, where k_1 is the rate constant associated with the overall forward reaction.

	m	n	k_1 (M^{-1} s^{-1})	$\Delta S_{activation}$(J $mol^{-1}K^{-1}$)
$R_1 = H$, $R_2 = H$, $R_3 = H$	3	2	1.15(4) × 10^{-3}	43(3)
R1 = CO_2^-, $R_2 = H$, $R_3 = H$	4	3	1.11(1) × 10^{-3}	20(4)
$R_1 = H$, $R_2 = CO_2^-$, $R_3 = H$	4	3	8.5(5) × 10^{-4}	115(14)
$R_1 = H$, $R_2 = H$, $R_3 = CO_2^-$	4	3	1.08(4) × 10^{-3}	60(2)

Do you expect the rate determining step (chelation of the pyridine carboxylate and loss of cyanide) to proceed by dissociative or association activation? Explain.

- **12.25** The two-electron oxidation of U^{4+} by $[PtCl_6]^{2-}$ in aqueous solution is postulated to proceed via an inner-sphere mechanism (R. M. Hassan, *J. Phys. Chem. A.*, **2011**, *115*, 13338).

    a. What are the orders with respect to $[U^{4+}]$ and $[PtCl_6{}^{2-}]$? What data were used to determine these orders?
    b. The initial combination of $[PtCl_6]^{2-}$ and U^{4+} is postulated to release two protons prior to the electron transfer step. How is this ionization proposed to increase the electron transfer rate? What is the most likely structure of the bridging species that facilitates the electron transfer from $[U^{4+}]$ to Pt^{4+}?

- **12.26** The reduction of $[Co(edta)]^-$ by $[Fe(CN)_6]^{2-}$ is facile in water, but is remarkably "switched off" when conducted in reverse micelle microemulsions (M. D. Johnson, B. B. Lorenz, P. C. Wilkins, B. G. Lemons, B. Baruah, N. Lamborn, M. Stahla, P. B. Chatterjee, D. T. Richens, D. C. Crans, *Inorg. Chem.*, **2012**, *51*, 2757.).

    a. Is the electron transfer mechanism for these two reactants believed to be inner-sphere or outer-sphere?
    b. These reactions were carried out under pseudo-first order conditions. Why do plots of k_{obs} versus $[Fe(CN)_6]^{2-}$ from these experiments exhibit linear relationships? What does the *y*-intercept of 0 communicate about these electron transfer reactions? How is k_{obs} related to the bimolecular rate constant k_1 for the reduction of $[Co(edta)]^-$?
    c. What is the hypothesis for the suppressed reduction of $[Co(edta)]^-$ by $[Fe(CN)_6]^{2-}$ when attempted in reverse micelle microemulsions?