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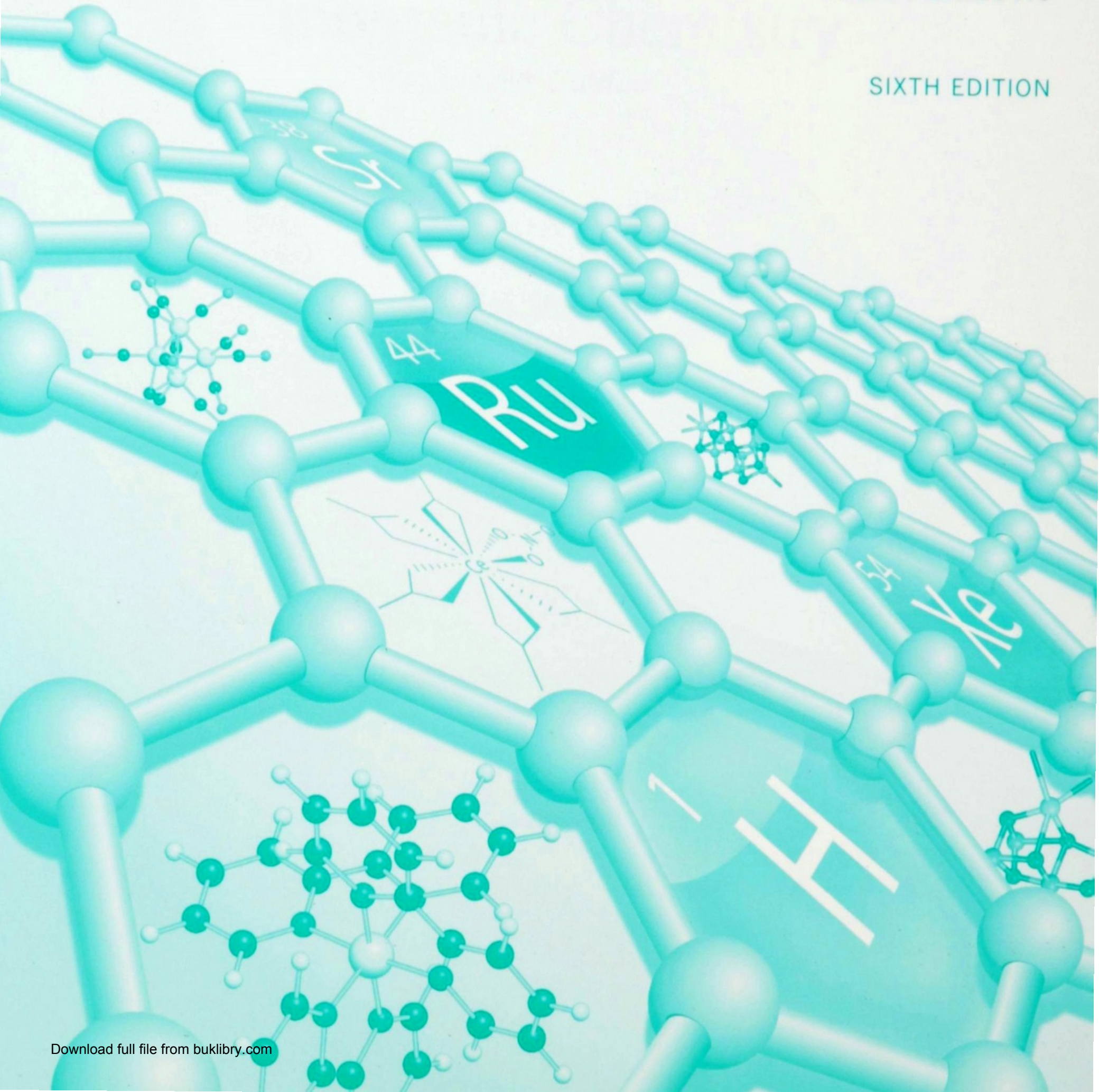
Solutions Manual to Accompany

Inorganic Chemistry

Alen Hadzovic

SIXTH EDITION



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Alen Hadzovic
University of Toronto

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E3.43 Ag_2S and CuBr (low-oxidation-number metal chalcogenide and halide) would be a p-type, and VO_2 (high-oxidation-number transition metal oxide) would be an n-type.

E3.44 In KC_8 potassium donates the electrons to the upper band which was originally empty in the graphite structure. In C_8Br bromine removes some electrons from the filled lower band in the graphite structure. In either case the net result is a partially filled band (formed either by addition of electrons to the originally empty band or by removal of electrons from the initially filled band) and both KC_8 and C_8Br should have metallic properties.

Answers to Selected Tutorial Problems

T3.2 The Madelung constant is in a sense a geometrical factor that depends on the position of ions within a unit cell. The electrostatic potential in which Na^+ ions resides is given by:

$$V = \frac{z^2e^2}{4\pi\varepsilon_o d}$$

where in this case d is the distance between Na^+ and the neighbouring atoms we are considering. The first neighbours are 6 Cl^- ions at the distance d. Thus the potential energy of a single Na^+ surrounded by six anions is:

$$V_1 = -\frac{6z^2e^2}{4\pi\varepsilon_o d}$$

Next, we have 12 Na^+ ions (the ones located on the faces of the cubic unit cell). Using Pythagoras's theorem we can show that they are at the distance of $d\sqrt{2}$ from the same Na^+ we looked at above (see Figure T3.2 below). This is a repulsive interaction for which we get the following potential V_2:

$$V_2 = +\frac{12z^2e^2}{4\pi\varepsilon_o \sqrt{2}d}$$

Next to consider are eight Cl^- ions at the middle of each edge of the unit cell. Again, using Pythagoras's theorem we can see that the distance between them and our Na^+ is $d\sqrt{3}$. The potential V_3 is thus:

$$V_3 = -\frac{8z^2e^2}{4\pi\varepsilon_o \sqrt{3}d}$$

This process can be continued in the same manner until V_6, which would give all six terms in the Madelung series given in this project (Figure P3.2 shows the distances involved in calculation of all V_n).

To find the total potential for Na^+ cation we have to sum V_1, V_2, V_3, etc.:

$$\begin{aligned} V_{tot} &= V_1 + V_2 + V_3 + ... = \\ &= -\frac{6z^2e^2}{4\pi\varepsilon_0 d} + \frac{12z^2e^2}{4\pi\varepsilon_0 d\sqrt{2}} - \frac{8z^2e^2}{4\pi\varepsilon_0 d\sqrt{3}} + ... = \\ &= -\frac{z^2e^2}{4\pi\varepsilon_0 d}\left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - ...\right) \end{aligned}$$

The value of the series in the brackets is called the Madelung constant for NaCl type structure.

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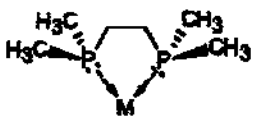
Monodentate

Bidentate

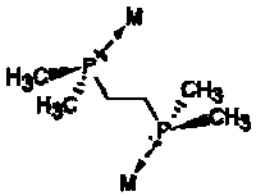
E7.8 Linkage isomers can arise with ambidentate ligands. Ambidentate ligands are ligands that have two different atoms within the molecule that can serve as a Lewis basic donor atom. An example is the thiocyanide anion NCS^-. It can bond to a metal either through the nitrogen's lone pair or through the sulphur's lone pair, depending on the electronics of the metal. If the metal is soft, then the softer-base sulphur is preferred; if the metal is hard, then the hard-base nitrogen is preferred.

NCS–M (thiocyanato-κ*S*) SCN–M (thiocyanato-κ*N*)

E7.9 **(a)** Bisdimethylphosphino ethane (dmpe) bonds to a metal through lone pairs on two phosphorus atoms; thus dmpe is a bidentate, chelating ligand that could also be a bridging ligand due to free rotation around single bonds.



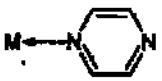
bidentate, chelating dmpe



bridging dmpe

(b) 2,2′-Bipyridine (bpy) is a bidentate, chelating ligand that is able to bond to a metal through both of its nitrogen atoms.

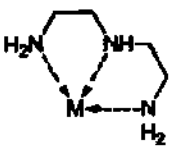
(c) Pyrazine is a monodentate ligand even though it has two Lewis basic sites. Because of the location of the nitrogen atoms, the ligand can only bond to one metal; it can, however, bridge two metals, as shown below.



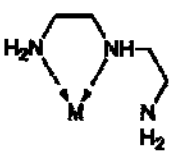
monodentate pyrazine

bridging pyrazine

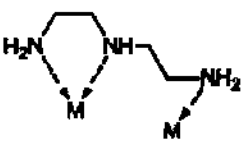
(d) Diethylenetriamine (dien) ligand has three Lewis basic nitrogen atoms, thus it could be a tridentate ligand that forms two chelating rings with one metal. It can, however, also act as a bidentate ligand (bonding using only two N atoms) forming one chelate ring and could be a bridging ligand if the third nitrogen atom is bonded to the second metal (in theory, all three nitrogen atoms could bind to three different metallic centres as well):



tridentate, chelating dien



bidentate, chelating dien



bidentate and bridging dien

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$$\{[Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_5]^{2+}, H_2O\} \rightarrow [(NH_3)_5\underset{Co(III)}{Co}–N=N=N–\underset{V(II)}{V}(OH_2)_5]^{4+} + H_2O$$

$$[(NH_3)_5\underset{Co(III)}{Co}–N=N=N–\underset{V(II)}{V}(OH_2)_5]^{4+} \rightarrow [(NH_3)_5\underset{Co(II)}{Co}–N=N=N–\underset{V(III)}{V}(OH_2)_5]^{4+}$$

$$H_2O + [(NH_3)_5\underset{Co(II)}{Co}–N=N=N–\underset{V(III)}{V}(OH_2)_5]^{4+} \rightarrow [Co(NH_3)_5(OH_2)]^{2+} + [V(N_3)(OH_2)_5]^{2+}$$

The pathway for outer-sphere electron transfer is shown below:

$$[Co(N_3)(NH_3)_5]^{2+} + [V(OH_2)_6]^{2+} \rightarrow \{[Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_6]^{2+}\}$$

$$\{[Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_6]^{2+}\} \rightarrow \{[Co(N_3)(NH_3)_5]^{+}, [V(OH_2)_6]^{3+}\}$$

$$\{[Co(N_3)(NH_3)_5]^{+}, [V(OH_2)_6]^{3+}\} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{2+} + [V(OH_2)_6]^{3+} + N_3^-$$

In both cases, the cobalt-containing product is the aqua complex because H_2O is present in abundance, and high-spin d^7 complexes of Co(II) are substitution labile. However, something that distinguishes the two pathways is the composition of the vanadium-containing product. If $[V(N_3)(OH_2)_5]^{2+}$ is the product, then the reaction has proceeded via an inner-sphere pathway. If $[V(OH_2)_6]^{3+}$ is the product, then the electron-transfer reaction is outer-sphere. The complex $[V(N_3)(OH_2)_5]^{2+}$ is inert enough to be experimentally observed before the water molecule displaces the azide anion to give $[V(OH_2)_6]^{3+}$.

E21.18 The direct transfer of a ligand from the coordination sphere of one redox partner (in this case the oxidizing agent, $[Co(NCS)(NH_3)_5]^{2+}$) to the coordination sphere of the other (in this case the reducing agent, $[Fe(OH_2)_6]^{2+}$) signals an inner-sphere electron-transfer reaction. Even if the first formed product $[Fe(NCS)(OH_2)_5]^{2+}$ is short lived and undergoes hydrolysis to $[Fe(OH_2)_6]^{3+}$, its fleeting existence demands that the electron was transferred across a Co–(NCS)–Fe bridge.

E21.19 In the case of reactions with Co(II), the difference in the rate of reduction can be explained by different mechanisms for the two reactions. The reduction of $[Co(NH_3)_5(OH)]^{2+}$ proceeds via inner-sphere mechanism: Co(II) complexes are labile (see Fig. 21.1) whereas $[Co(NH_3)_5(OH)]^{2+}$ has OH^- ligand that can serve as a bridging ligand. The $[Co(NH_3)_5(H_2O)]^{3+}$ has no bridging ligands and the only mechanistic pathway for the electron-transfer is outer sphere.
On the other hand, both reactions with $[Ru(NH_3)_6]^{2+}$ as a reducing agent likely proceed via the same mechanism, the outer-sphere mechanism because Ru(II) complex, being a complex of the second row transition element with high LFSE, is more inert than Co(II) complex.

E21.20 Using the Marcus cross-relation (Equation 21.16), we can calculate the rate constants. In this equation $[k_{12} = [k_{11} \cdot k_{22} \cdot K_{12} \cdot f_{12}]^{1/2}$, the values of k_{11} and k_{22} can be obtained from Table 21.12. We can assume f_{12} to be unity. The redox potential data allows us to calculate K_{12} because $E° = [RT/\nu F]\ln K$. The value of $E°$ can be calculated by subtracting the anodic reduction potential (the V^{3+}/V^{2+} couple serves as the anode) from the cathodic one.
(a) $[Ru(NH_3)_6]^{3+}$ $k = 4.53 \times 10^3\ dm^3mol^{-1}s^{-1}$
(b) $[Co(NH_3)_6]^{3+}$ $k = 1.41 \times 10^{-2}\ dm^3mol^{-1}s^{-1}$
Relative sizes? The reduction of the Ru complex is more thermodynamically favoured than the reaction of the Co complex, and it is faster as evident from its larger k value.

E21.21 Using the Marcus cross-relation (Equation 21.16), we can calculate the rate constants. In this equation $[k_{12} = [k_{11} \cdot k_{22} \cdot K_{12} \cdot f_{12}]^{1/2}$, the values of k_{11} and k_{22} can be obtained from Table 21.12. We can assume f_{12} to be unity. The redox potential data allows us to calculate K_{12} because $E° = [RT/\nu F]\ln K$. The value of $E°$ can be calculated by subtracting the anodic reduction potential (the Cr^{3+}/Cr^{2+} couple serves as the anode) from the cathodic one.
(a) k_{11} (Cr^{3+}/Cr^{2+}) = $1 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$; k_{22} (Ru^{3+}/Ru^{2+} for the hexamine complex) = $6.6 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$; $f_{12} = 1$; $K_{12} = e^{[nF\,\varepsilon°/RT]}$ where $\varepsilon° = 0.07\ V - (-0.41V) = 0.48\ V$; $n = 1$; $F = 96485\ C$; $R = 8.31\ J\ mol^{-1}K^{-1}$ and $T = 298$

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