1. (a) Naturally occurring uranium is only 0.720% ^{235}U, where as most of the rest is ^{238}U, which is not suitable for the fission process. A process of gaseous effusion was developed using the volatile hexa-fluorouranium compound (b.p. ~ 56.5 °C). How many effusion steps are necessary to yield 99.0% pure U-235 hexafluoride compound?

$$\frac{\textbf{Rate of effusion for gas 1}}{\textbf{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \qquad n \ln(1.0043) = \ln(137.50)$$

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \qquad n = \frac{\ln(137.50)}{\ln(1.0043)} = \boxed{1148}$$

(b) Suppose we have a 12.2 L sample containing 0.50 mole of O_2 gas at a pressure of 1 atm and a temperature of 25 °C. If all this O_2 were converted into ozone at the same T and P, what would be the volume of ozone? Avogadro's Law $V \propto n$

$$3O_2(g) \rightarrow 2O_3(g)$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$V_2 = 12.2 * 2 / 3 = 8.13$ (L)

(c) The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95K, and the pressure is 162 kPa. Assuming ideal behavior, calculate the density of Titan's atmosphere.

$$PM = dRT, \quad d = PM/RT = \frac{162\ (\text{kPa}) * 28.6\ (\text{g/mol})}{8.314(\text{m}^3\text{-Pa/mol-K}) * 95(\text{K})} = 5.9\ (\text{kg/m}^3)\ (\text{g/L})$$

(d) Predict whether each process is spontaneous as described, spontaneous in the reverse direction, or at equilibrium:

(i) Water at 40 ºC gets hotter when a piece of metal heated to 150 ºC is added.

(ii) Water at room temperature decomposes into $H_2(g)$ and $O_2(g)$.

(iii) Benzene vapor at a pressure of 101.3 kPa condenses to liquid benzene at the normal boiling point of benzene, 80.1 ºC.

(a) This process is spontaneous. Whenever two objects at different temperatures are brought into contact, heat is transferred from the hotter object to the colder one.
(b) Experience tells us that this process is not spontaneous—we certainly have never seen hydrogen and oxygen gases spontaneously bubbling up out of water! Rather, the *reverse* process—the reaction of H_2 and O_2 to form H_2O—is spontaneous.

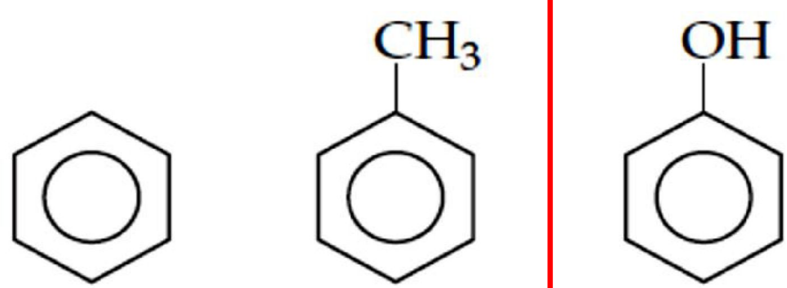
(c) The normal boiling point is the temperature at which a vapor at 101.3 kPa is in equilibrium with its liquid. Thus, this is an equilibrium situation. If the temperature were below 80.1 °C, condensation would be spontaneous.

(e) Fill out the following table:

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	*Process Spontaneous?*
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

1. (a) Naturally occurring uranium is only 0.720% ^{235}U, where as most of the rest is ^{238}U, which is not suitable for the fission process. A process of gaseous effusion was developed using the volatile hexa-fluorouranium compound (b.p. ~ 56.5 °C). How many effusion steps are necessary to yield 99.0% pure U-235 hexafluoride compound?

$0.72 * (\frac{\sqrt{238}}{\sqrt{235}})^{n} = 9$

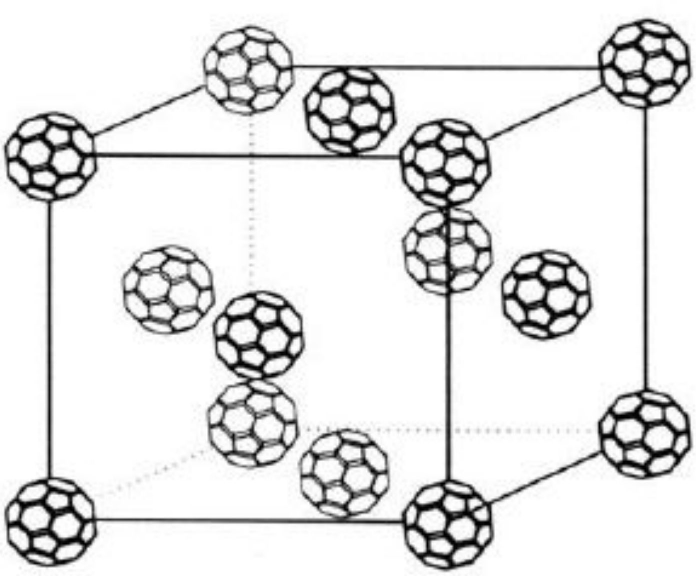


(b) Suppose we hav ... gas
at a pressure of 1 ... vere
converted into ozo ... lume
of ozone?

	Benzene	Toluene	Phenol
Melting point (°C)	5	–95	43
Boiling point (°C)	80	111	182

$V_2 = 12.2 * 2 / 3 = 8.13\ (L)$

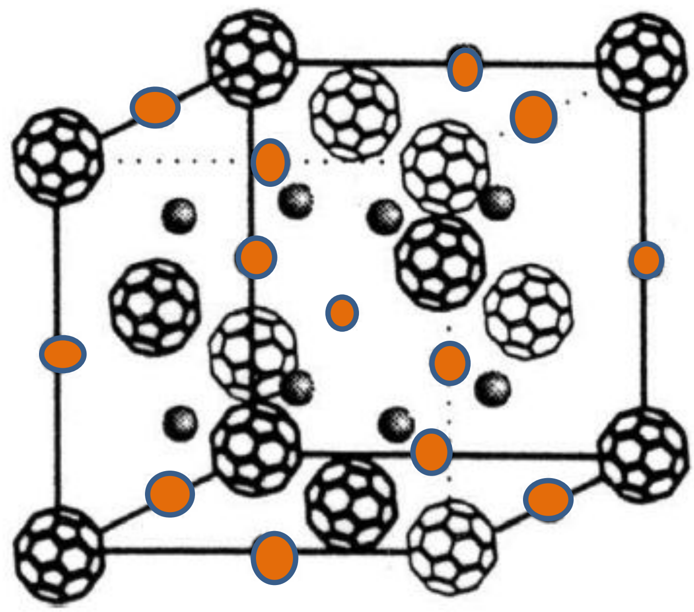
(c) The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is



Assuming ideal behavior,
nosphere.

$\frac{28.6\ (g/mol)}{a/mol\text{-}K) * 95(K)} = 5.9\ (kg/m^3)\ (g/L)$

(d) When C_{60} solid is exposed to potassium vapor, it is reduced to a solid containing C_{60}^{3-} anions in fcc arrangements and potassium ions filled in all octahedral and tetrahedral interstitial sites. How many potassium ions are filling in the octahedral sites? What is the chemical composition of the resulting compound?



1. (a) Naturally occurring uranium is only 0.720% ^{235}U, where as most of the rest is ^{238}U, which is not suitable for the fission process. A process of gaseous effusion was developed using the volatile hexa-fluorouranium compound (b.p. ~ 56.5 °C). How many effusion steps are necessary to yield 99.0% pure U-235 hexafluoride compound?

$0.72 * (\frac{\sqrt{238}}{\sqrt{235}})^n = 99$, $n * log\ (\frac{\sqrt{238}}{\sqrt{235}}) = log(\frac{99}{0.72})$, $n = 777$

(b) Suppose we have a 12.2 L sample containing 0.50 mole of O_2 gas at a pressure of 1 atm and a temperature of 25 °C. If all this O_2 were converted into ozone at the same T and P, what would be the volume of ozone?

$V_2 = 12.2 * 2 / 3 = 8.13$ (L)

(c) The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95K, and the pressure is 162 kPa. Assuming ideal behavior, calculate the density of Titan's atmosphere.

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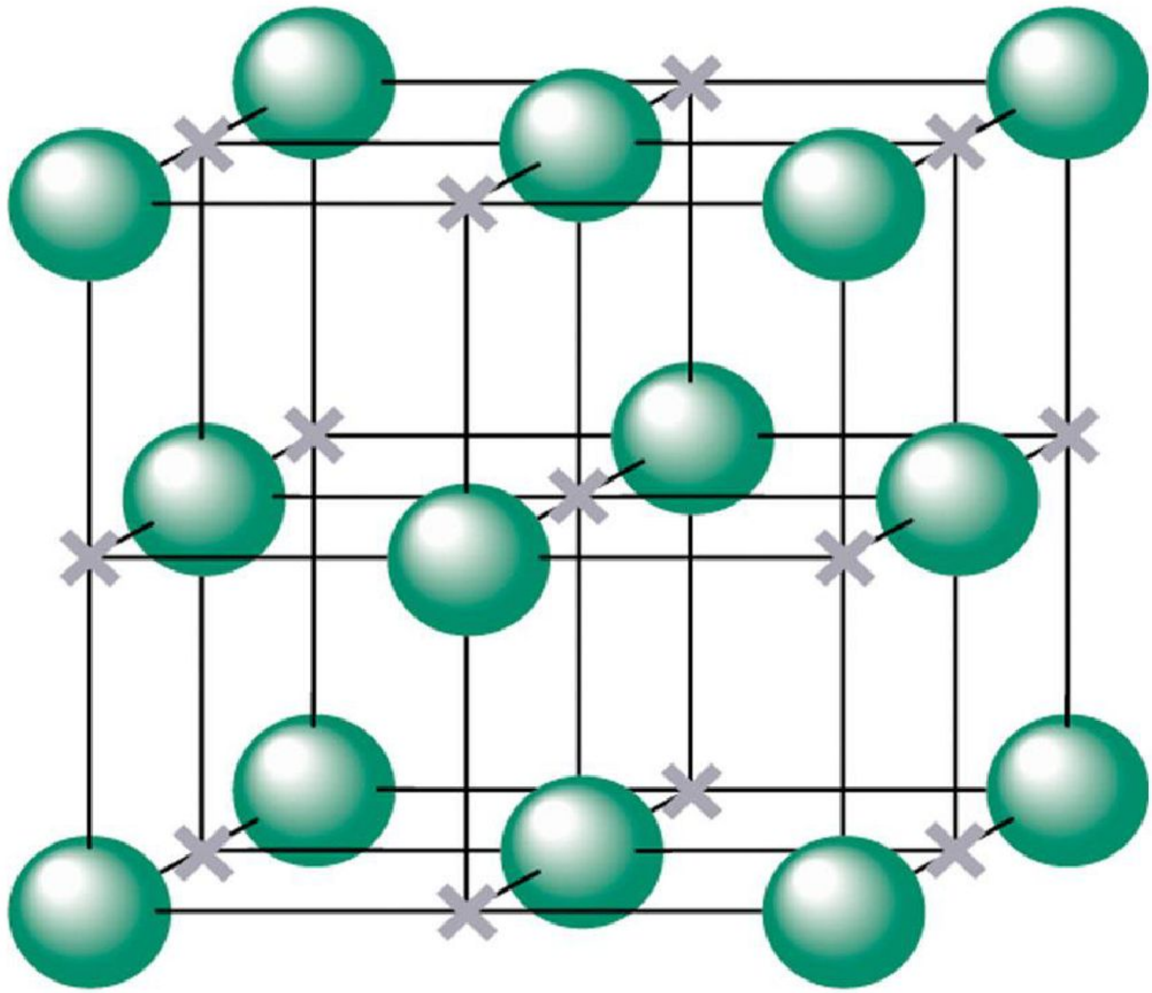
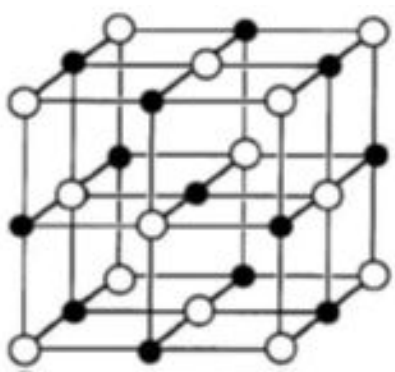
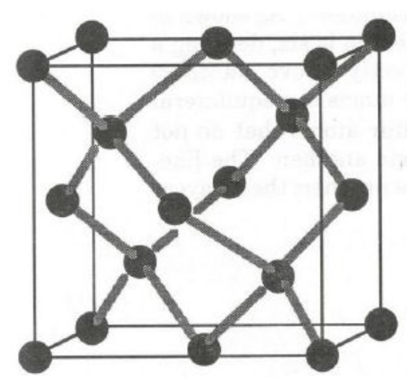


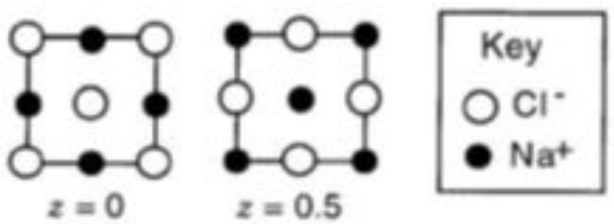
X **Octahedral Holes**

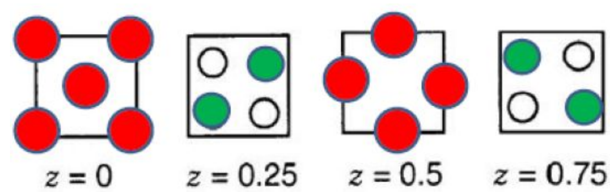
3. Silicon is the fundamental component of integrated circuits and has the same structure as diamond. Galena is a mineral composed of lead(II) sulfide and adopts NaCl structure.

(a) Describe diamond and NaCl structure, respectively.







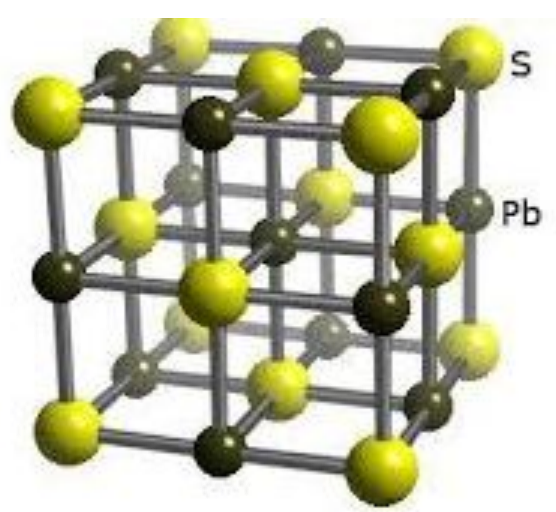


(b) Is diamond a semiconductor? What makes silicon a semiconductor?

NO !

(c) Write the chemical formula for lead(II) sulfide. How many lead(II) ions are there in a face-centered cubic cell?

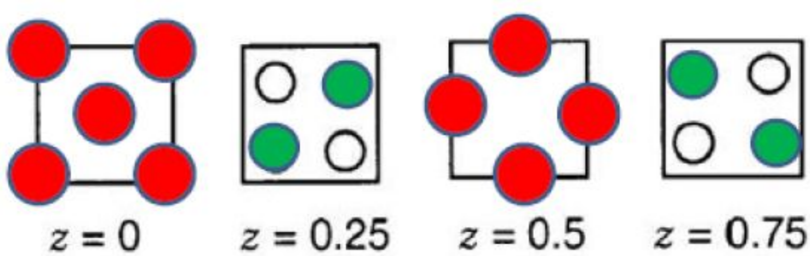
FCC: 陽離子 4顆
陰離子 4顆

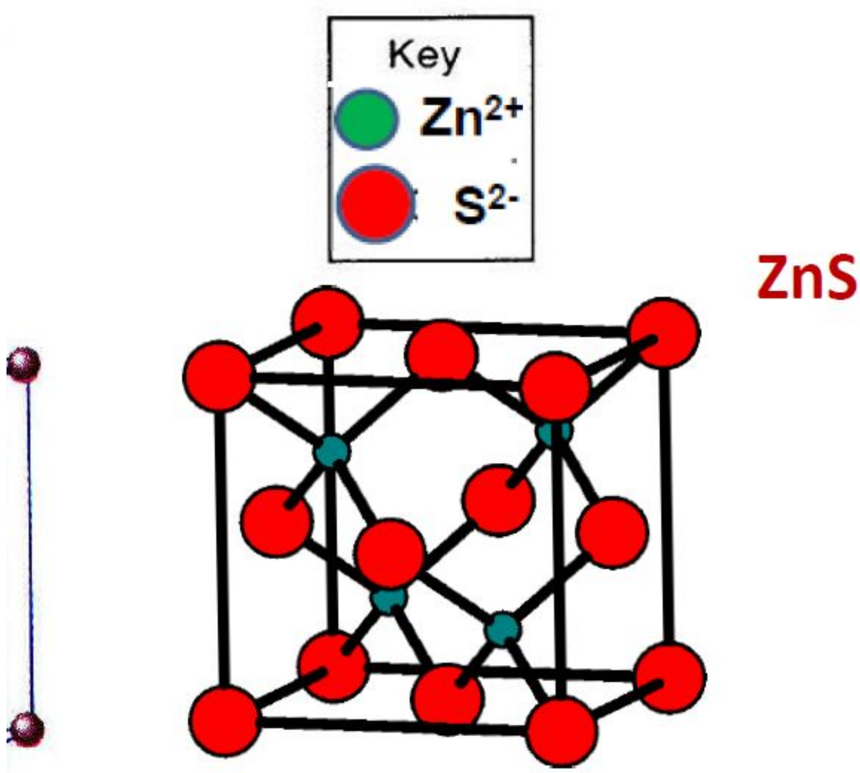


(d) Is NaCl a conductor, semiconductor, or insulator? Explain.

$NaCl_{(s)}$固體不導電 insulator
$NaCl_{(L)}$融溶態導電 conductor
$NaCl_{(aq)}$水溶液導電，電解質 electrolyte

(e) Is the structure of Zinc blende related to NaCl or diamond? Why?   Zinc blende 閃鋅礦 ZnS





4. (i) For each categories of alloys, give an example with a chemical formula:

(a) substitutional alloy (b) interstitial alloy (c) intermetallic compound

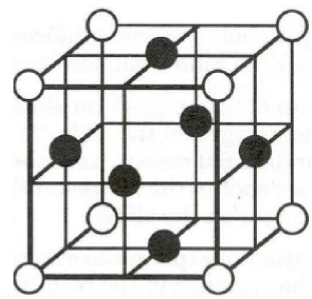
(ii) Is NiTi memory alloy an intermetallic compound? Explain.

(iii) Is the structure of NiTi a body-centered cubic? Explain.

(iv) Is the figure shown to the right a fcc structure? Explain.

If the black solid circle is named A and the open circle B.

What is the chemical composition of this structure?

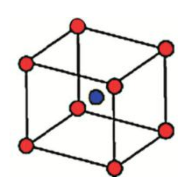


(i) (a) substitutional alloy = FeNi、CuZn 、AuAg

(b) interstitial alloy = FeSi 、Fe_3C

(c) intermetallic compound = $SmCo_5$ Ni_3Al Nb_3Sn

(ii) Yes, The ordering of atoms in NiTi. And it differs greatly from the properties of Ni and Ti metals.



(iii) No, the atom at the body center was not the same kind of atom as those on the corners of the cell.

(iv) No, the atom at the face was not the same kind of atom as those on the corners of the cell.

A= 6*(1/2)=3 ; B=8*(1/8)=1 A_3B

5. Write chemical reactions for the following process:

(i) Solid UO_2 reacts with gaseous HF to form gaseous UF_4 and water, and the product of UF_4 are further reacts with fluorine gas to form hexa-fluorouranium solid, which will be utilized for the extraction of U-235.

(i) A gaseous compound containing metallic element

$$UO_2\,(s) + 4\,HF\,(g) \Leftrightarrow UF_4(g) + 2\,H_2O\,(g)$$

$$UF_4\,(g) + F_2\,(g) \Leftrightarrow UF_6(s)$$

(ii) Automobile air bags are inflated by nitrogen gas generated by the decomposition of NaN_3. The sodium that is formed is removed by reaction with potassium nitrate to form K_2O, which can further react with SiO_2 to form stable K_2SiO_3.

(ii) $$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$$

$$10\ Na + 2\,KNO_3 \rightarrow K_2O + 5\,Na_2O + N_2\,(g)$$

$$K_2O + 2\,SiO_2 \rightarrow K_2SiO_3$$

鋁熱劑

(iii) Thermite reactions which involve Fe_2O_3 and CuO, respectively. Are they spontaneous process? How?

(iii)

$$Fe_2O_3 + 2\ Al \rightarrow 2\ Fe + Al_2O_3$$

$$3CuO + 2Al \rightarrow 3Cu + Al_2O_3$$

Yes, because Aluminum forms stronger bonds with oxygen than iron and Copper. Exothermic process

(iv) Disproportionation reaction of concentrated hydrogen peroxide, which is an highly exothermic process. Is it a spontaneous reduction process? Why?

(iv)

Hydrogen peroxide (Figure 22.14) is the most familiar and commercially important peroxide. Pure hydrogen peroxide is a clear, syrupy liquid that melts at −0.4 °C. Concentrated hydrogen peroxide is dangerously reactive because the decomposition to water and oxygen is very exothermic:

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g) \quad \Delta H^\circ = -196.1\text{ kJ}$$

This is an example of a **disproportionation** reaction, in which an element is simultaneously oxidized and reduced. The oxidation number of oxygen changes from −1 to −2 and 0.

Yes, because Exothermic process

6. We learned that chemical processes are favored by positive entropy changes and by negative enthalpy changes. The special stability associated with the formation of chelates, called the *chelate effect*, can be explained by comparing the entropy changes that occur with mono-dentate ligands with the entropy changes that occur with polydentate ligands. For the reaction in which two H_2O ligands of the square-planar Cu(II) complex $[Cu(H_2O)_4]^{2+}$ are replaced by monodentate NH_3 ligands at

$$[Cu(H_2O)_4]^{2+}(aq) + 2\,NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + 2\,H_2O(l) \quad (1)$$

$$\Delta H^\circ = -46\text{ kJ}; \quad \Delta S^\circ = -8.4\text{ J/K}$$

(a) What do these thermodynamic data tell you about the relative abilities of water and ammonia molecules to serve as ligands? Why is the entropy changes slightly negative?

(b) Calculate Gibbs free energy and the equilibrium constant of the reaction at 27 ºC. What does them tell you about the tendency of the reaction at equilibrium?

$$[Cu(H_2O)_4]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_2(en)]^{2+}(aq) + 2\,H_2O(l) \quad (2)$$

$$\Delta H^\circ = -54\text{ kJ}; \quad \Delta S^\circ = +23\text{ J/K}$$

The following shows a reaction when two H_2O ligands of the square-planar Cu(II) complex $[Cu(H_2O)_4]^{2+}$ are replaced by a single bidentate ethylenediamine (en) ligand at 27 ºC:

(c) Give the reason why the reaction leads to a positive entropy change for the equilibrium.

(d) Combine the above two equations (1) and (2) using Hess's Law to calculate the enthalpy, entropy, and free-energy changes that occur for en to replace ammonia as ligands on Cu(II):

$$[Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_2(en)]^{2+}(aq) + 2\,NH_3(aq)$$

$$\boxed{\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}}$$

$$\Delta G^\circ = -RT\ln K$$

Ch23 p1045.

A CLOSER LOOK **Entropy and the Chelate Effect**

We learned in Section 19.5 that chemical processes are favored by positive entropy changes and by negative enthalpy changes. The special stability associated with the formation of chelates, called the *chelate effect*, can be explained by comparing the entropy changes that occur with monodentate ligands with the entropy changes that occur with polydentate ligands.

We begin with the reaction in which two H_2O ligands of the square-planar Cu(II) complex $[Cu(H_2O)_4]^{2+}$ are replaced by monodentate NH_3 ligands at 27 °C:

$$[Cu(H_2O)_4]^{2+}(aq) + 2\,NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + 2\,H_2O(l)$$

$$\Delta H^\circ = -46\text{ kJ};\quad \Delta S^\circ = -8.4\text{ J/K};\quad \Delta G^\circ = -43\text{ kJ}$$

The thermodynamic data tell us about the relative abilities of H_2O and NH_3 to serve as ligands in this reaction. In general, NH_3 binds more tightly to metal ions than does H_2O, so this substitution reaction is exothermic ($\Delta H < 0$). The stronger bonding of the NH_3 ligands also causes the $[Cu(H_2O)_2(NH_3)_2]^{2+}$ ion to be more rigid, which is probably the reason ΔS° is slightly negative.

We can use Equation 19.20, $\Delta G^\circ = -RT \ln K$, to calculate the equilibrium constant of the reaction at 27 °C. The result, $K = 3.1 \times 10^7$, tells us that the equilibrium lies far to the right, favoring replacement of H_2O by NH_3. For this equilibrium, therefore, the enthalpy change, $\Delta H^\circ = -46$ kJ, is large enough and negative enough to overcome the entropy change, $\Delta S^\circ = -8.4$ J/K.

Now let's use a single bidentate ethylenediamine (en) ligand in our substitution reaction:

$$[Cu(H_2O)_4]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_2(en)]^{2+}(aq) + 2\,H_2O(l)$$

$$\Delta H^\circ = -54\text{ kJ};\quad \Delta S^\circ = +23\text{ J/K};\quad \Delta G^\circ = -61\text{ kJ}$$

The en ligand binds slightly more strongly to the Cu^{2+} ion than two NH_3 ligands, so the enthalpy change here (−54 kJ) is slightly more negative than for $[Cu(H_2O)_2(NH_3)_2]^{2+}$(−46 kJ). There is a big difference in the entropy change, however: ΔS° is −8.4 J/K for the NH_3 reaction but +23 J/K for the en reaction. We can explain the positive ΔS° value using concepts discussed in Section 19.3. Because a single en ligand occupies two coordination sites, two molecules of H_2O are released when one en ligand bonds. Thus, there are three product molecules in the reaction but only two reactant molecules. The greater number of product molecules leads to the positive entropy change for the equilibrium.

The slightly more negative value of ΔH° for the en reaction (−54 kJ versus −46 kJ) coupled with the positive entropy change leads to a much more negative value of ΔG° (−61 kJ for en, −43 kJ for NH_3) and thus a larger equilibrium constant: $K = 4.2 \times 10^{10}$.

We can combine our two equations using Hess's law (Section 5.6) to calculate the enthalpy, entropy, and free-energy changes that occur for en to replace ammonia as ligands on Cu(II):

$$[Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_2(en)]^{2+}(aq) + 2\,NH_3(aq)$$

$$\Delta H^\circ = (-54\text{ kJ}) - (-46\text{ kJ}) = -8\text{ kJ}$$

$$\Delta S^\circ = (+23\text{ J/K}) - (-8.4\text{ J/K}) = +31\text{ J/K}$$

$$\Delta G^\circ = (-61\text{ kJ}) - (-43\text{ kJ}) = -18\text{ kJ}$$

Notice that at 27 °C, the entropic contribution ($-T\Delta S^\circ$) to the free-energy change, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Equation 19.12), is negative and greater in magnitude than the enthalpic contribution (ΔH°). The equilibrium constant for the NH_3–en reaction, 1.4×10^3, shows that the replacement of NH_3 by en is thermodynamically favorable.

The chelate effect is important in biochemistry and molecular biology. The additional thermodynamic stabilization provided by entropy effects helps stabilize biological metal–chelate complexes, such as porphyrins, and can allow changes in the oxidation state of the metal ion while retaining the structural integrity of the complex.

Related Exercises: 23.32, 23.98

7. About coordination compounds:

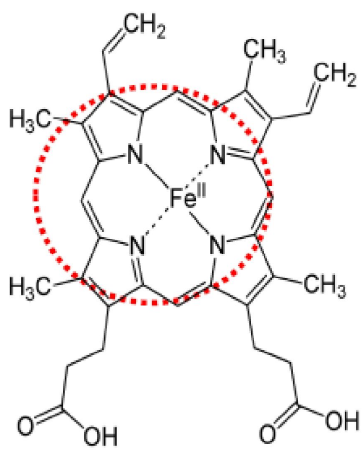
(a) Draw the coordination sphere for the Heme Complex.

(b) When gaseous O_2 is bubbled in the aqueous solution containing heme, what changes would occur to the central metal ion?

(c) Write the chemical reaction between hemoglobin (Hb) and oxygen.

(d) Read the following passage, extract key information and points, and make a summary of it in your own word. **Do not copy any sentences….**

(a)



Containing **ferrous** where the **Fe^{2+} ion is coordinated to four nitrogen atoms**

(b) **Fe^{2+} is oxidized to Fe^{3+} (an O_2 bridge between Fe^{2+} ions)**

(c) $Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$

(d) CO與Hb結合能力遠大於氧氣
故CO過多容易造成缺氧死亡
且CO無色無味難察覺