ADVANCED CHEMISTRY

INORGANIC CHEMISTRY – SPRING – WEEK 4

Worksheet

ΔH [KJ/mol]

(1)

		ΔH [KJ/mol]
$AgBr(s)$	$\longrightarrow Ag(s) + \frac{1}{2}Br_2(l)$	$+100.37$
$Ag(s)$	$\longrightarrow Ag(g)$	284.55
$Ag(g)$	$\longrightarrow Ag^+(g) + e^-$	730.9
$\frac{1}{2}Br_2(l)$	$\longrightarrow \frac{1}{2}Br_2(g)$	$\frac{1}{2}(30.907)$
$\frac{1}{2}Br_2(g)$	$\longrightarrow Br(g)$	$\frac{1}{2}(192.86)$
$Br(g) + e^-$	$\longrightarrow Br^-(g)$	-324.5

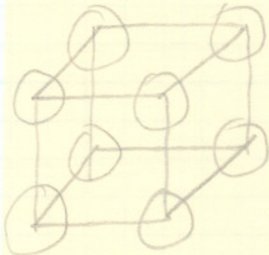
(+) ↓

$$AgBr(s) \longrightarrow Ag^+(g) + Br^-(g)$$

$$\Delta H^\circ_{lattice} = \left[100.37 + 284.55 + 730.9 + \frac{1}{2}(30.907) + \frac{1}{2}(192.86) - 324.5\right] KJ/mol$$

$$= \underline{\underline{903.204\ KJ/mol}}$$

(2) Assume that the unit cell is a primitive cube



Each corner has an atom

$\left(8 \text{ corners} \times \frac{1}{8}\right) = 1$ atom of Fe in unit cell.

$$\text{mass of 1 Fe atom} = \left(55.85\frac{g}{mol}\right) \times \left(\frac{1\,mol}{6.02 \times 10^{23}\text{ atoms}}\right)$$

$$= 9.277 \times 10^{-23}\ g/\text{atom}$$

$$\text{volume of unit cell} = a \times b \times c = a \times a \times a = a^3$$

$$= (287\,pm)^3$$

$$= (287\,pm)^3 \times \left(\frac{m}{10^{12}\,pm}\right)^3 \left(\frac{10^2\,cm}{m}\right)^3$$

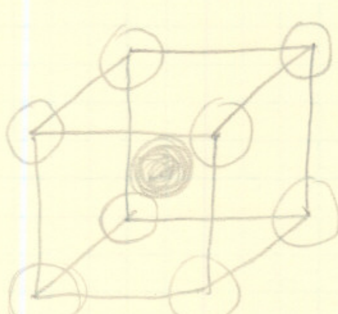
$$= 2.36 \times 10^{-23}\ cm^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{9.277 \times 10^{-23}\ g}{2.36 \times 10^{-23}\ cm^3}$$

$$= 3.924\ g/cm^3$$

does not agree with the given density data.

Assume that the unit cell is a body centered cube (bcc)



$$\left.\begin{array}{l}\#\text{ of atoms}\\ \text{in the unit cell}\end{array}\right\} = \left(8 \text{ corners} \times \frac{1}{8}\right) + 1 \text{ in center}$$

$$= 2 \text{ atoms}$$

$$\text{mass} = 2 \times 9.277 \times 10^{-23}\ g$$

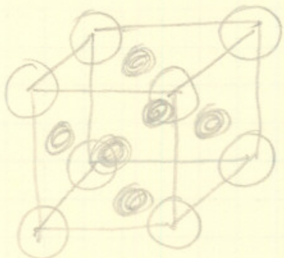
$$= 1.8554 \times 10^{-22}\ g$$

volume = $a^3 = 2.36 \times 10^{-23}\ cm^3$

density = $\dfrac{1.8554 \times 10^{-22}\ g}{2.36 \times 10^{-23}\ cm^3} = \underline{\underline{7.86\ g/cm^3}}$

agrees with given density data

Assume the unit cell is face centered cubic (fcc)



# of atoms in unit cell =

$\left(\frac{1}{8} \times 8 \text{ atoms in corners}\right) + \left(\frac{1}{2} \times 6 \text{ on faces}\right)$

$1 + 3 = 4$ atom

mass of unit cell = $4 \times 9.277 \times 10^{-23}\ g$

$= 3.7108 \times 10^{-22}\ g$

volume = $a \times b \times c = a^3 = 2.36 \times 10^{-23}\ cm^3$

density = $\dfrac{3.7108 \times 10^{-22}\ g}{2.36 \times 10^{-23}\ cm^3} = \underline{15.72\ g/cm^3}$

does not agree with given density data

∴ The unit cell must be body centered cubic.

Number of Fe atoms in unit cell = $\underline{\underline{2}}$

(3)

		# of atoms in unit cell	
8 "a" atoms in each corner	=	$8 \times \frac{1}{8}$	= 1 "a"
6 "b" atoms on each face	=	$6 \times \frac{1}{2}$	= 3 "b"
1 "c" atom at center	=	1×1	= 1 "c"
12 "d" atoms on each edge	=	$12 \times \frac{1}{4}$	= 3 "d"

$$ab_3cd_3$$

(4) octahedral hole has 6 nearest neighbors.
tetrahedral hole has 4 nearest neighbors.

In order to have 6 neighbors (instead of 4) around it, the octahedral hole must be larger than the tetrahedral hole.

(5) mass of a Ag atom $= \left(107.87 \frac{g}{mol}\right) \times \left(\frac{1 mol}{6.02 \times 10^{23} \text{ atoms}}\right)$

$= 1.792 \times 10^{-22}$ g/atom

volume $= \frac{1.792 \times 10^{-22} \text{ g}}{10.50 \text{ g/cm}^3}$

$= 1.707 \times 10^{-23} \text{ cm}^3$

length of one edge $= 2.575 \times 10^{-8}$ cm

$= 257.5$ pm

(5) unit cell edge = 408.7 pm.

∴ unit cell volume $= (408.7\ pm)^3 \times \left(\frac{m}{10^{12}\ pm}\right)^3 \left(\frac{10^2\ cm}{m}\right)^3$

$= 6.827 \times 10^{-23}\ cm^3$

mass = volume x density

$= (6.827 \times 10^{-23}\ cm^3)(10.50\ g/cm^3)$

$= 7.168 \times 10^{-22}\ g$

mass of 1 mol of Ag $= \frac{107.87\ g}{6.02 \times 10^{23}\ atoms}$

# of atoms of Ag in $7.168 \times 10^{-22}\ g$ $= \frac{7.168 \times 10^{-22}\ g}{\left(\frac{107.87\ g}{6.02 \times 10^{23}\ atoms}\right)}$

$= 4$ atoms

To have 4 atoms in the unit cell, it must be ~~have~~ fcc type.

for fcc unit cell $a = (\sqrt{8})\, r$

$r = \frac{a}{\sqrt{8}} = \frac{408.7\ pm}{\sqrt{8}}$

$\underline{r = 1.44\ pm}$

⑥ In a fcc structure

there are 4 atoms

8 tetrahedral holes

4 octahedral holes

If the chemical formula is AB_2 then all the tetrahedral holes must be filled.

⑦ As an atom loses electrons, the nucleus attracts the remaining electrons to itself more strongly (due to high proton : electron ratio). Therefore cations are smaller in size than neutral atoms.

As an atom gains more electrons, the extra electrons push each other apart, increasing the size of the anion compared to the neutral atom

$$M > M^{+} > M^{2+} > M^{3+}$$

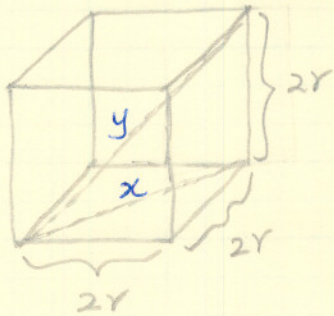
⟶ size decreases

$$X < X^{-} < X^{2-} < X^{3-}$$

⟶ size increases.

Chapter 7

(8)



In a primitive cube

$a = b = c = 2r$

x = length of face diagonal

y = length of body diagonal

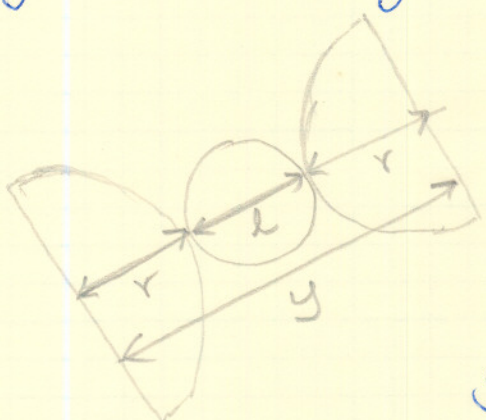
Using Pythagorus theorem:

$$x^2 = (2r)^2 + 2r^2 = 8r^2$$

$$y^2 = x^2 + (2r)^2 = 8r^2 + 4r^2 = 12r^2$$

$$y = (\sqrt{12})r = 3.464r$$

y is the length of the body diagonal.



$\therefore y = r + l + r$

l = diameter of the sphere that would fit in the center of primitive cube

$$y = 2r + l$$

$$l = y - 2r = 3.464r - 2r = 1.464r$$

$$\frac{l}{2} = 0.732r$$

$\therefore$ Radius of the sphere that fits in the center $= \frac{l}{2} = \underline{0.732r}$