

NOTE: THIS SOLUTION TO THE "STRUCTURE" PORTION OF QUIZ NO. 1 WAS PREPARED WITH A TUTORIAL INTENT. YOU WERE NOT EXPECTED TO WRITE THIS MUCH - NOR WAS THIS NECESSARY!

1. Structure. (50 points)

a. Consider an ionic compound with composition AB_2 in which cation A has 4-fold tetrahedral coordination.

i. (6 points) What is the coordination number of B?

FOR A STRUCTURE OF COMPOSITION $A_n B_m$ (IN WHICH A'S ARE COORDINATED ONLY BY B - AND VICE VERSA - AND IN WHICH ALL A'S HAVE THE SAME COORDINATION AND ALL B'S HAVE THE SAME COORDINATION NUMBER) THE RATIO OF COORDINATION NUMBER IS

$$N_A : N_B = m : n$$

FOR THIS COMPOSITION, THEREFORE

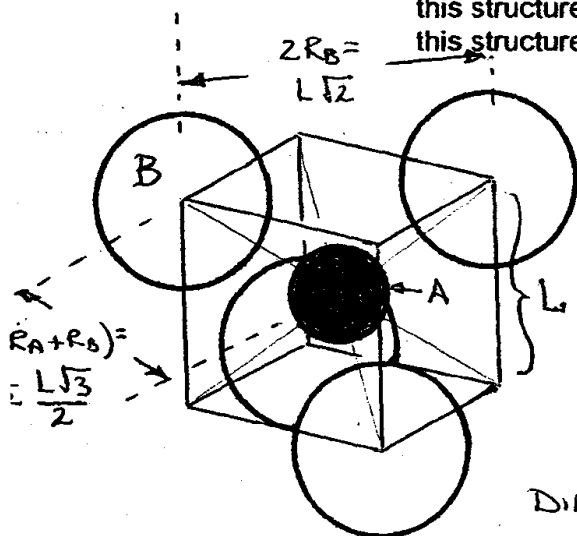
$$CN_A : CN_B = 2 : 1$$

$$\text{if } CN_A = 4 \quad \underline{CN_B = 2}$$

← THIS FOLLOWS FROM THE "COMPOSITION" OF A BOND

$$A \frac{1}{CN_A} B \frac{1}{CN_B} \times CN_A CN_B = A_{CN_B} B_{CN_A}$$

ii. (6 points) From the geometry of the coordination polyhedra that are present in this structure, compute the range of the ratios of ionic radii, R_A/R_B , for which this structure may form.



FOR $CN_A = 4$ EXPECTED COORDINATION POLYHEDRON IS

A TETRAHEDRON (B'S HAVE MAXIMUM SEPARATION FOR THIS ARRANGEMENT). TO FACILITATE THE EVALUATION OF CRITICAL CONTACTS, LET THE TETRAHEDRON BE INSCRIBED IN A CUBE OF EDGE L

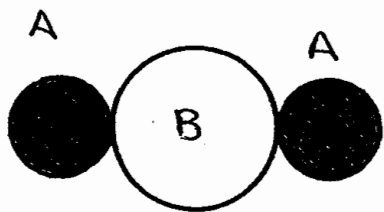
THE A AND B IONS ARE ALWAYS IN CONTACT (PAULING'S RULE NO. 1) THIS CONTACT OCCURS ALONG THE BODY DIAGONAL OF THE CUBE $\therefore 2(R_A + R_B) = L\sqrt{3}$

R_B CAN INCREASE RELATIVE TO R_A UNTIL B'S TOUCH ALONG A FACE DIAGONAL

$$2R_B = L\sqrt{2}$$

$$\frac{2(R_A + R_B)}{2R_B} = \frac{R_A}{R_B} + \frac{R_B}{R_B} = \frac{L\sqrt{3}}{L\sqrt{2}}$$

$$\underline{R_A/R_B = \sqrt{3/2} - 1 = 0.225}$$



FOR $CN_B = 2$ THE ARRANGEMENT WILL BE LINEAR (KEEPS A'S AT MAXIMUM SEPARATION)
THERE WILL BE NO CONSTRAINT ON R_A/R_B

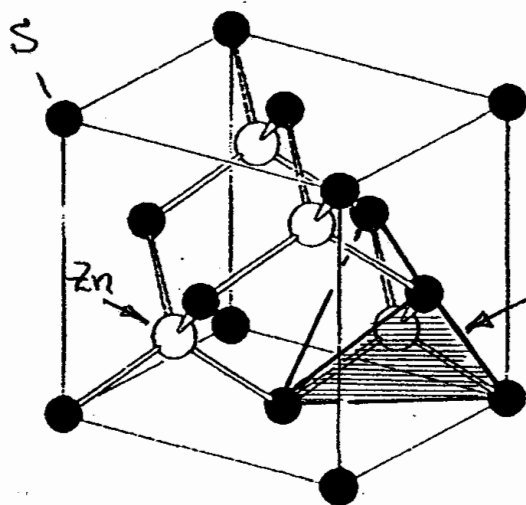
AS A MAY BE AS LARGE OR AS SMALL AS WE WISH RELATIVE TO B WITHOUT THE IONS MAKING CONTACT.

\therefore FOR TETRAHEDRAL PACKING OF B AROUND A $0.225 \leq R_A/R_B \leq \infty$
FOR LINEAR ARRANGEMENT OF A AROUND B $0 \leq R_A/R_B \leq \infty$

THUS THE NET RANGE OF RADIUS RATIO IS $0.225 \leq R_A/R_B \leq \infty$

b. The packing of ions in the cubic structure of ZnS is shown in the figure below. The appropriate ionic radii for Zn^{2+} and S^{2-} are 0.60 and 1.84 Å, respectively.

i. (6 points) What is the coordination number of Zn^{2+} ?



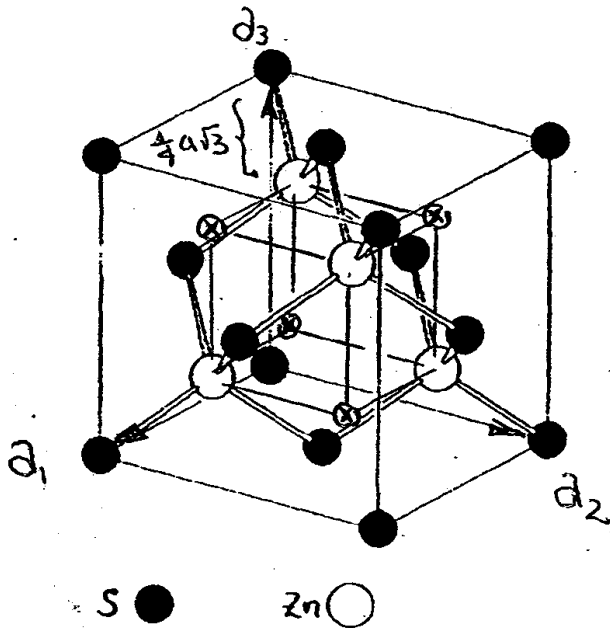
Zn has four S NEIGHBORS AT THE CORNERS OF A TETRAHEDRON

$$CN_{Zn} = 4$$



(PARENTHEICAL NOTE: NOW THAT THE PRESSURE of the quiz is ABSENT, THE REFLECTIVE STUDENT MIGHT WONDER "HEY! YOU CLAIMED ANIONS ARE LARGER THAN CATIONS! IN FACT, YOU SAY $R_{Zn^{2+}} = 0.60 \text{ \AA}$ AND $R_{S^{2-}} = 1.84 \text{ \AA}$. HOW COME, THEN, IS THE "S" CIRCLE IN YOUR FIGURE SMALLER AND BLACK (ZINC COLORED?) AND THE "Zn" CIRCLE LARGER??" GOOD QUESTION. THE ANSWER IS THAT I PREPARED THIS FIGURE SOME TIME AGO FOR A CHAPTER IN A BOOK. FOR PURPOSES OF THIS PROBLEM, HOWEVER, I WANTED TO AVOID POSSIBLE CONFUSION BY SHOWING ALL OF THE NEIGHBORS THAT SURROUND THE "ZINC" ATOM. THE EASIEST WAY OF DOING THIS WAS TO MERELY CHANGE THE LABELS ON THE ATOMS.)

- ii. (6 points) Zn^{2+} may be regarded as occupying interstices that occur between the larger close-packed S^{2-} ions. What fraction of the total number of available sites of this type that Zn^{2+} occupies are actually occupied?



THE S IONS ARE IN FACE-CENTERED CUBIC PACKING AND THERE ARE 4 S^{2-} PER CELL. IN i . WE DETERMINED THAT THE Zn^{2+} IONS ARE TETRAHEDRALLY COORDINATED.

IN ANY CLOSE PACKED ARRAY OF SPHERES THERE ARE TWICE AS MANY TETRAHEDRAL INTERSTICES AS SPHERES, \therefore EIGHT PER CELL.

HALF OF THE TETRAHEDRAL SITES (FOUR — COUNTING THEM UP) ARE OCCUPIED

THUS ONE-HALF OF THE AVAILABLE TETRAHEDRAL SITES ARE OCCUPIED

THE UNOCCUPIED TETRAHEDRAL SITES ARE MARKED BY ○

IF THEY ARE HARD TO APPRECIATE IN THE (BY NOW) PRETTY-CLUTTERED DIAGRAM

THEIR COORDINATES ARE

<u>OCCUPIED SITES:</u>	$\left\{ \begin{array}{ll} \frac{3}{4} \frac{1}{4} \frac{1}{4} & \frac{1}{4} \frac{3}{4} \frac{1}{4} \\ \frac{1}{4} \frac{1}{4} \frac{3}{4} & \frac{3}{4} \frac{3}{4} \frac{3}{4} \end{array} \right.$
<u>UNOCCUPIED SITES:</u>	$\left\{ \begin{array}{ll} \frac{1}{4} \frac{1}{4} \frac{1}{4} & \frac{3}{4} \frac{3}{4} \frac{1}{4} \\ \frac{3}{4} \frac{1}{4} \frac{3}{4} & \frac{1}{4} \frac{3}{4} \frac{3}{4} \end{array} \right.$

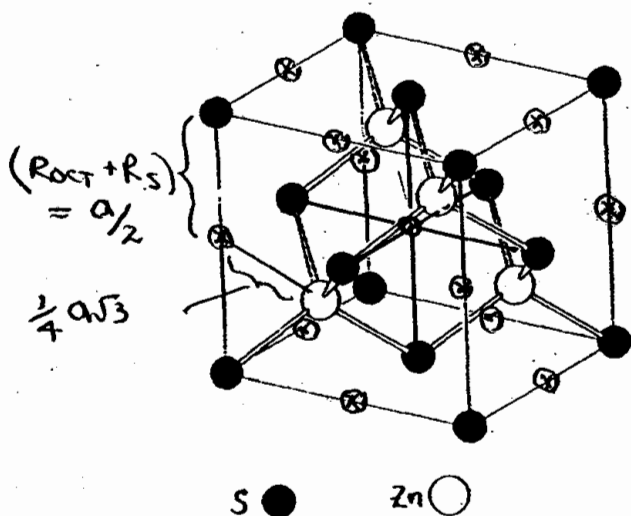
WHERE, IN THE ABOVE, x, y, z ARE THE FRACTIONAL COORDINATES ALONG THE CELL EDGES a_1, a_2, a_3

- iii. (6 points) Compute the length of the edge of the cubic cell for ZnS.

THE Zn AND S IONS ARE IN CONTACT ALONG THE BODY DIAGONAL OF THE CELL $R_{Zn} + R_S = \frac{1}{4} a \sqrt{3} \quad \therefore a = \frac{4}{\sqrt{3}} (R_{Zn} + R_S)$
 $= \frac{4}{\sqrt{3}} (0.60 + 1.84)$

$a = 5.635 \text{ \AA}$

- iv. (6 points) There is a second, different site among the S^{2-} ions that is not occupied in this structure. Compute the maximum radius of an ion that could occupy this site without distortion of the arrangement of the ions in ZnS.



IN EVERY CLOSE-PACKED ARRAY OF SPHERES, REGARDLESS OF STACKING SEQUENCE, THERE ARE TWO TETRAHEDRAL SITES PER CLOSE-PACKED SPHERE AND ONE OCTAHEDRALLY-COORDINATED SITE. WE SHOULD, ACCORDINGLY, BE ABLE TO LOCATE FOUR SITES WITHIN THE CELL OF ZnS THAT HAVE SIX NEIGHBORS

IF THESE SITES WERE OCCUPIED AMONG THE FCC S^{2-} IONS WE WOULD HAVE THAT ALL-TIME FAVORITE THE ROCK SALT STRUCTURE TYPE AND WE KNOW EXACTLY WHERE THESE SITES RESIDE: AT THE CENTER OF THE CELL AND MIDPOINT OF EVERY EDGE $[(1 + \frac{1}{4} \times 12) = 4]$

THE Zn^{2+} IONS IN THE TETRAHEDRAL SITES HOLD THE SULFUR IONS APART THEREBY PROVIDING THE CELL EDGE THAT WE COMPUTED IN PART iii. THE RADIUS OF THE LARGEST SPHERE THAT CAN BE PLACED IN THE OCTAHEDRAL SITE IS THIS

$$R_{oct} = \frac{a}{2} - R_s = \frac{5.635}{2} - 1.84 = 0.978 \text{ \AA}$$

$$R_{oct} = 0.978 \text{ \AA}$$

(NOTE THAT THIS IS MUCH LARGER THAN THE RADIUS OF THE Zn^{2+} ION. THE OCTAHEDRALLY-COORDINATED SITE IS ^{ALWAYS} LARGER THAN THE TETRAHEDRAL SITE.)

WE PROBABLY DID THIS CORRECTLY. (AS ANIONS ARE LARGER THAN CATIONS THE CONTACT THAT WE CONSIDERED ABOVE SHOULD PLACE THE LIMIT ON THE SIZE OF THE SPHERE THAT CAN BE ACCOMMODATED IN THE OCTAHEDRAL SITE) JUST TO BE CERTAIN, HOWEVER, LET'S CALCULATE HOW LARGE - OTHER CONTACTS NOT HAPPENING FIRST - THE SPHERE COULD BECOME BEFORE IT TOUCHED THE Zn^{2+} ION IN A TETRAHEDRAL SITE THIS DISTANCE IS $\frac{1}{4} a\sqrt{3}$ SO $R = \frac{1}{4} a\sqrt{3} - R_{Zn^{2+}}$

$= \frac{\sqrt{3}}{4} (5.635) - 0.60 = 1.07 \text{ \AA}$ - WHICH IS THE RADIUS OF S^{2-} . CLEARLY THE SPHERE WILL TOUCH THE S^{2-} ION FIRST.

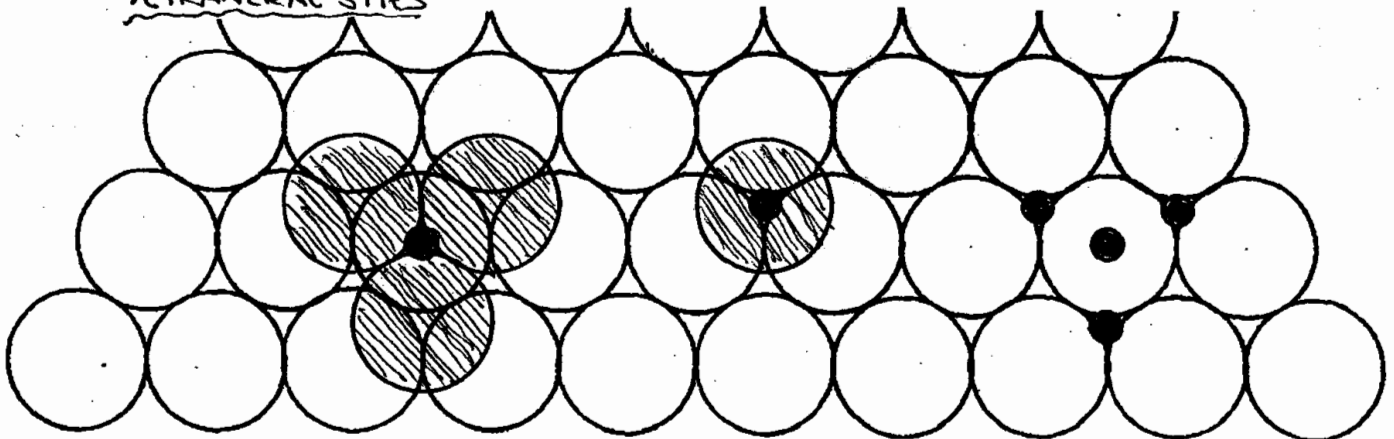
- c. The two compounds $Mg(OH)_2$ (brucite) and $Al(OH)_3$ (Gibbsite) have structures built from two-dimensional sheets of hydroxyl ions. The hydrogen atom is so small that OH^- may be regarded as a spherical ion of charge -1 . In both of these structures the isolated two-dimensional sheets consist of a pair of close-packed OH^- layers that are arranged one above the other in close packing. The cations occupy certain of the interstitial sites between the pair of layers. The layers are loosely held together by weak Van der Waals forces.

The diagrams shown on the following pages provide a set of circles representing a first close-packed sheet of OH^- ions. Superposed on this (to keep things from becoming too messy) are a partial set of triangles that connect the centers of the location of the second layer of OH^- ions.

Let us now employ Pauling's Rules concerning bond strength to deduce the likely structures of $Mg(OH)_2$ and $Al(OH)_3$ using, in addition, what we know about the interstices available in close-packed arrays and the sharing of elements of coordination polyhedra in a stable structure.

- i. (6 points) Mark on one of the diagrams the location of interstitial sites that are available.

TETRAHEDRAL SITES AND OCTAHEDRAL SITES ARE PRESENT
AMONG SPHERES PLACED IN A CLOSE-PACKED ARRAY
TETRAHEDRAL SITES

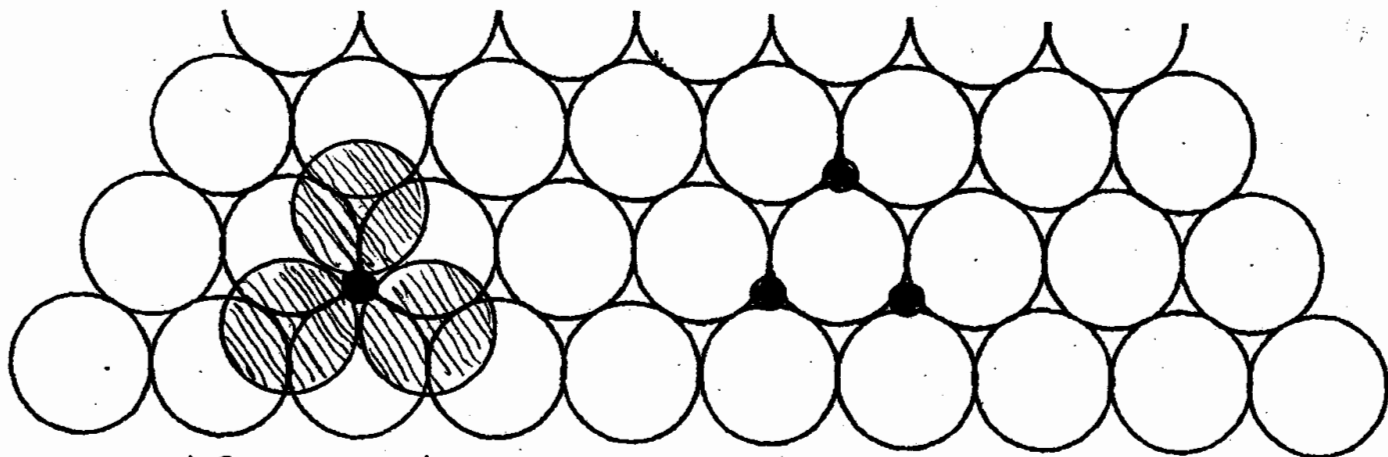


A TETRAHEDRAL SITE IS LOCATED DIRECTLY ABOVE EACH SPHERE IN THE INITIAL SHEET. (THIS TETRAHEDRON POINTS DOWN)

A TETRAHEDRAL SITE IS LOCATED IN THREE POSITIONS THAT SURROUND EACH SPHERE IN THE INITIAL SHEET (ONLY ONE IS SHOWN) (THIS TETRAHEDRON POINTS UP)

ALL TOGETHER FOUR TETRAHEDRAL SITES SURROUND EACH SPHERE. THESE SITES ARE SHARED BETWEEN FOUR SPHERES

THUS $4 \times \frac{1}{4} = 1$
TETRAHEDRAL SITE PER SPHERE



A SITE SITS IN THE MIDDLE of a TRIANGLE of SPHERES THAT HAS ANOTHER TRIANGLE of SPHERES IN AN OPPOSED ORIENTATION DIRECTLY ABOVE. THESE SIX SPHERES FORM AN OCTAHEDRON THAT SITS ON ONE of ITS TRIANGULAR FACES

Each SITE is "shared" SIX WAYS with the OTHER SPHERES that form the OCTAHEDRON so there are 3 SITES PER SPHERE $\times \frac{1}{6}$ SPHERE PER SITE =

THREE OCTAHEDRAL SITES SURROUND EACH SPHERE IN THE INITIAL SHEET (ONLY ONE WAS SHOWN TO THE LEFT) NOTE THAT THE CENTRAL SPHERE IN THE INITIAL LAYER PARTICIPATES IN THE TRIANGULAR FACE of the OCTAHEDRON IN ALL of the THREE POSSIBLE WAYS (THE SPHERE AT THE BOTTOM ∇ the SPHERE AT UPPER LEFT ∇ AND the SPHERE AT UPPER RIGHT ∇) for the THREE SITES ABOVE IT)

$$\frac{1}{2} \text{ OCTAHEDRAL SITE PER SPHERE}$$

- ii. (8 points) For $\text{Mg}(\text{OH})_2$ and then, separately, for $\text{Al}(\text{OH})_3$, deduce a likely pattern of site filling and show that Pauling's Rule for bond strength summation is satisfied. If some of the available sites of a set of interstices of a particular type are unfilled, please be sure to indicate that pattern of unoccupied sites.

{ FOR $\text{Mg}(\text{OH})_2$ THERE ARE TWICE AS MANY $(\text{OH})^-$ AS Mg^{2+} (PER FORMULA UNIT, PER KILOGRAM, PER UNIT CELL OR PER CRYSTAL!)
 FOR $\text{Al}(\text{OH})_3$ THERE ARE THREE TIMES AS MANY $(\text{OH})^-$ AS Al^{3+}

AS DETERMINED ABOVE, THE INTERSTITIAL SITES BETWEEN TWO CLOSEPACKED SHEETS IN AN ISOLATED TWO LAYER SLAB PROVIDE

{ ONE TETRAHEDRAL SITE / SPHERE
 ONE-HALF OCTAHEDRAL SITE / SPHERE

(NOTE: WE HAVE, IN OTHER CONTEXTS, MADE THE STATEMENT "TWO TETRAHEDRAL SITES PER SPHERE IN ANY CLOSEPACKED ARRAY AND ONE OCTAHEDRAL SITE" THIS, HOWEVER, IS FOR A SPHERE IN A THREE-DIMENSIONAL ARRAY, THE NUMBER of SITES BETWEEN A GIVEN SPHERE AND THE LAYER ABOVE, SAY, IS INDEED ONE AND ONE-HALF, RESPECTIVELY, WITH THE SAME NUMBER of SITES AGAIN, ON THE OTHER SIDE of OUR SPHERE, BETWEEN ITS LAYER AND THE LAYER BELOW!!)

LET'S NOW PUT THIS INFORMATION TOGETHER TO SEE HOW THE PACKING WILL WORK FOR THE TWO COMPOUNDS

	Mg(OH) ₂	Al(OH) ₃
If TETRAHEDRAL SITES ARE OCCUPIED (ONE SITE/SPHERE)	COMPOSITION REQUIRES $\frac{1}{2}$ Mg PER (OH) SPHERE ∴ ONE-HALF OF THE AVAILABLE TETRAHEDRAL SITES WOULD BE OCCUPIED.	COMPOSITION REQUIRES $\frac{1}{3}$ Al PER (OH) SPHERE ∴ ONE-THIRD OF THE AVAILABLE TETRAHEDRAL SITES WOULD BE OCCUPIED
If OCTAHEDRAL SITES ARE OCCUPIED (ONE-HALF SITE/SPHERE)	COMPOSITION REQUIRES $\frac{1}{2}$ Mg PER (OH) SPHERE ∴ ALL OCTAHEDRAL SITES WOULD BE OCCUPIED	COMPOSITION REQUIRES $\frac{1}{3}$ Al PER (OH) SPHERE ∴ ON AVERAGE THERE WILL BE $\frac{1}{3}$ Al PER HALF OCTAHEDRAL SITE OR $\frac{2}{3}$ Al PER OCTAHEDRAL SITE OR ONLY $\frac{2}{3}$ OF ALL AVAILABLE OCTAHEDRAL SITES WOULD BE OCCUPIED BY A WHOLE Al ION

NOW LET'S USE PAULING'S RULE CONCERNING BOND STRENGTH TO SEE WHICH OF THESE POSSIBILITIES CAN WORK.

<u>RATION IN TETRAHEDRAL SITE</u>	$S_{Mg^{2+}} = \frac{+2}{4} = \frac{1}{2}$ EVERY OH ⁻ SHOULD HAVE TWO Mg ²⁺ NEIGHBORS SO THAT $\sum S_{Mg} = 1$ PROMISING! - LET'S SEE IF WE CAN MAKE SUCH A DISTRIBUTION	$S_{Al^{3+}} = \frac{+3}{4}$ THIS IS IMPOSSIBLE NO MORE THAN ONE Al ³⁺ NEIGHBOR COULD TOUCH AN OH ⁻ (SO NOTHING WOULD HOLD THE STRUCTURE TOGETHER) AND THIS COULD NOT PROVIDE $\sum S = 1 \cdot \frac{3}{4}$ TO SATISFY THE CHARGE OF OH ⁻
<u>CATION IN OCTAHEDRAL SITE</u>	$S_{Mg^{2+}} = \frac{+2}{6} = \frac{1}{3}$ EVERY OH ⁻ SHOULD HAVE THREE Mg ²⁺ NEIGHBORS SHOULD WORK!	$S_{Al^{3+}} = \frac{+3}{6} = \frac{1}{2}$ EACH OH ⁻ SHOULD HAVE TWO Al ³⁺ NEIGHBORS SHOULD WORK!

BEFORE ATTEMPTING TO DRAW A PATTERN OF OCCUPIED SITES LET'S LOOK AT THE PROBLEM IN STILL A DIFFERENT WAY - WITH THE REASONING OF PROBLEM (C) WHICH CONNECTED COMPOSITION TO RATIOS OF COORDINATION NUMBERS

FOR Mg(OH)₂ CN_{Mg} : CN_{OH} = 2 : 1

BUT ONLY TETRAHEDRAL AND OCTAHEDRAL SITES ARE AVAILABLE THIS $\left. \begin{matrix} 4 : 2 \\ \text{OR} \\ 6 : 3 \end{matrix} \right\}$ ARE POSSIBLE

⇒ SAME RESULT AS ABOVE!

FOR Al(OH)₃ CN_{Al} : CN_{OH} = 3 : 1

FOR FILLING OF TETRAHEDRAL & OCTAHEDRAL SITE CN_{Al} & CN_{OH} = $4 : \frac{3}{4}$ WON'T WORK OR 6 : 2 POSSIBLE

TETRAHEDRAL SITES

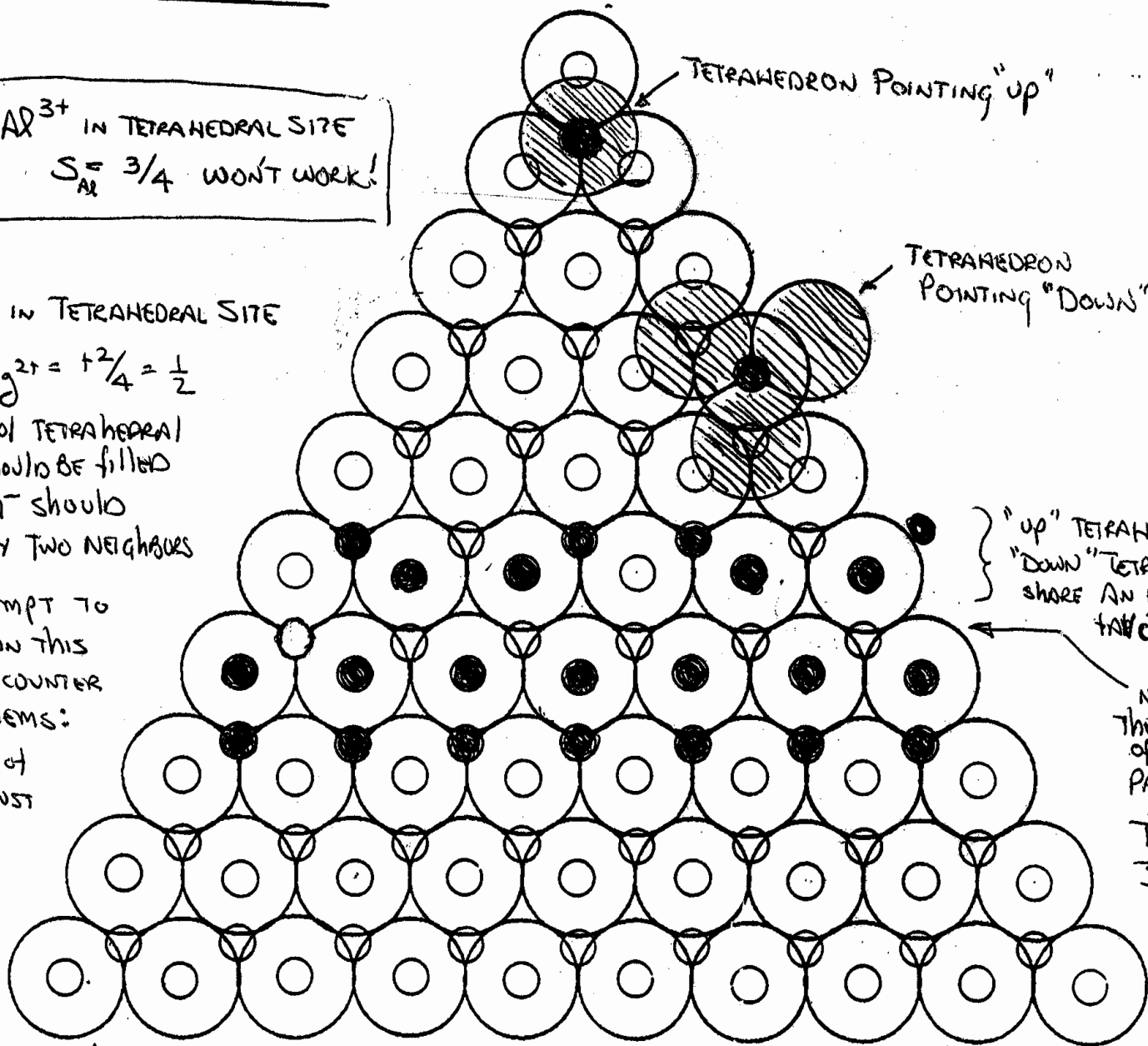
Al^{3+} IN TETRAHEDRAL SITE
 $S_{Al} = 3/4$ WON'T WORK!

Mg^{2+} IN TETRAHEDRAL SITE
 $S_{Mg^{2+}} = 1^2/4 = 1/2$

HALF OF TETRAHEDRAL
 SITES SHOULD BE FILLED
 EACH OH^- SHOULD
 HAVE ONLY TWO NEIGHBORS

IF WE ATTEMPT TO
 FILL SITES IN THIS
 FASHION WE ENCOUNTER
 SERIOUS PROBLEMS:

- ① SOME PAIRS OF TETRAHEDRAL MUST SHARE AN EDGE WHICH IS AN UNFAVORABLE LINKAGE
- ② THE PAIRS OF TETRAHEDRA HAVE NO BOND WHICH JOINS THEM TOGETHER.



TETRAHEDRON POINTING "DOWN"

TETRAHEDRON POINTING "UP"

"UP" TETRAHEDRA AND "DOWN" TETRAHEDRA SHARE AN EDGE, NOT FAVORABLE FOR CN=4

NOTHING HOLDS THESE ROWS OF TETRAHEDRA PAIRS TOGETHER

THIS IS JUST NOT GOING TO PROVE POSSIBLE!

OCTAHEDRAL SITES

Mg²⁺ OCTAHEDRA

$$S_{Mg^{2+}} = +\frac{2}{6}$$

Each OH^- should
HAVE THREE Mg^{2+}
NEIGHBORS

Filling ALL AVAILABLE
OCTAHEDRAL SITES
WORKS JUST FINE !!

$$CN_{Mg^{2+}} = 6$$

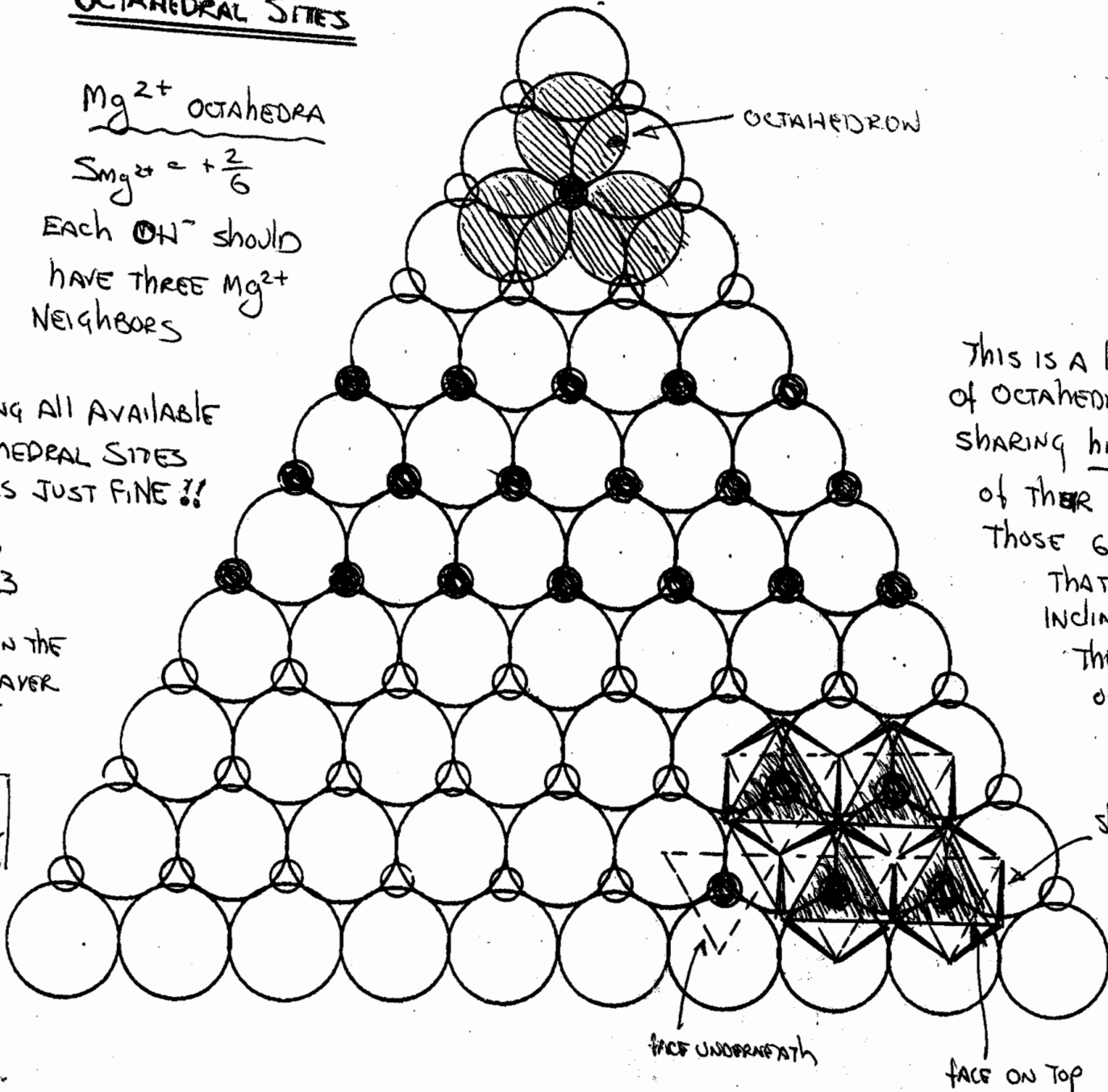
$$CN_{OH^-} = 3$$

Each OH^- IN THE
FIRST ANION LAYER
HAS 3 Mg^{2+}
NEIGHBORS

$$\sum S_{Mg} = 3 \cdot \frac{1}{3}$$

$$= 1 \checkmark$$

EACH OH^- IN
THE SECOND OH^-
LAYER HAS
3 Mg^{2+} BELOW IT!



OCTAHEDRAL SITES

Al³⁺ OCTAHEDRA

$$S_{Al^{3+}} = \frac{+3}{6} = \frac{1}{2}$$

Each OH⁻ should have two Al³⁺ neighbors. Therefore only two of the three octahedral sites around an OH⁻ should be filled

As the Al³⁺ cations will repel each other, it would be energetically favorable to have two filled sites in one row placed such they straddle the vacant site in the neighboring row — and vice versa

Two Al³⁺ coordinate each OH⁻

$$\sum S_{Al^{3+}} = 2 \times \frac{1}{2} = 1 \checkmark$$

