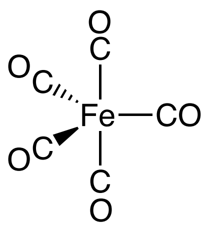
Chemistry 6330
Problem Set 1 Answers

1.

(a) T_d

(b) C_{3v}

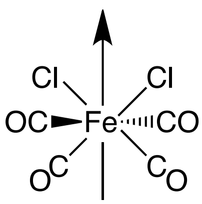
(c) C_{2v}



(d) D_{3h}

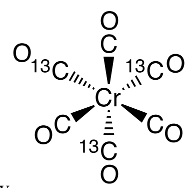
(e) O_h

(f) C_{4v}

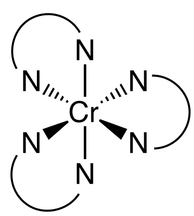


(g) C_{2v}

(h) D_{4h}



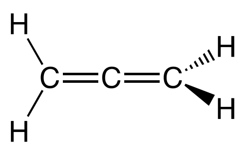
(i) C_{3v}



(j) C_{2v}

(k) D_3

(l) C_{2v}



(m) C_{2h}

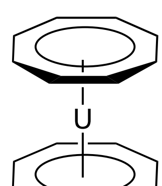
(n) D_{2d}

(o) C_{3v}

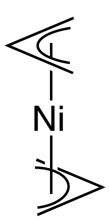
(p) C_s

(q) D_{5d}

(r) D_{8h}

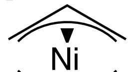


(s) C_{2h}

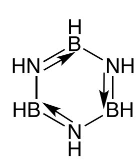


or

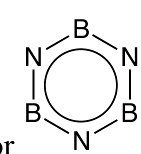
top-down view



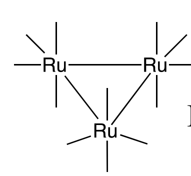
(t) D_{3h}



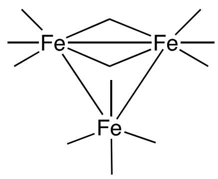
or

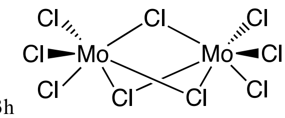


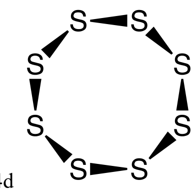
(u)

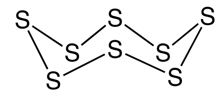


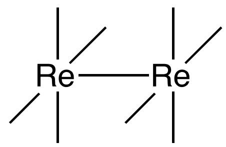
D_{3h}

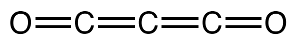
(v) C_{2v} 

(w) D_{3h} 

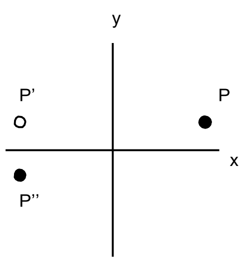
(x) D_{4d} 

or 

(y) D_{4h} 

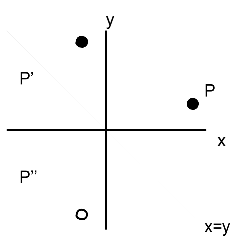
(z) $D_{\infty h}$ 

2. (a) C_2^y (a, b, c) $\rightarrow$ (-a, b, -c)
C_2^x (-a, b, -c) $\rightarrow$ (-a, -b, c)
$C_2^x\, C_2^y \rightarrow$ (-a, -b, c) = C_2^z (a, b, c)



$C_2^x\, C_2^y = C_2^z$

(b) C_4^z (a, b, c) $\rightarrow$ (-b, a, c)
C_2^x (-b, a, c) $\rightarrow$ (-b, -a, -c)
$C_2^x\, C_4^z$ (a, b, c) $\rightarrow$ (-b, -a, -c)

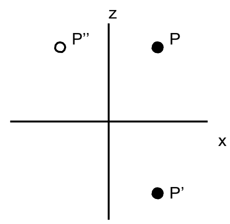


$C_2^x\, C_4^z = C_2^{x\,=\,-y}$

(c) σ_z (a, b, c) $\rightarrow$ (a, b, -c)

i (a, b, -c) $\rightarrow$ (-a, -b, c)

i $\cdot$ σ_z (a, b, c) $\rightarrow$ (-a, -b, c) = C_2^z (a, b, c)□□□□



i $\cdot$ σ_z = C_2^z

(d) i (a, b, c) $\rightarrow$ (-a, -b, -c)

C_4^x i (-a, -b, -c) $\rightarrow$ (-a, c, -b)

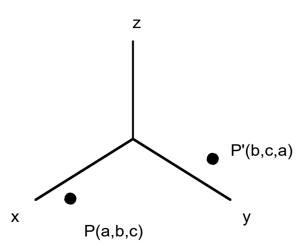
C_4^x i = S_4^3(x)

(e) $\sigma_{x=y}$ (a, b, c) $\rightarrow$ (b, a, c)

C_4^x(b, a, c) $\rightarrow$ (b, -c, a)

C_4^x $\sigma_{x=y}$ (a, b, c) (b, -c, a)

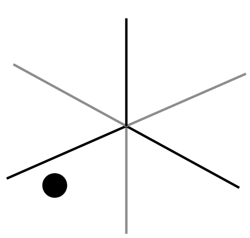
This product is unlike any that we discussed in class <u>for it permutes all three c</u>oordinates. One way of approaching this problem is to recognize that C_4^x and $\sigma_{x=y}$ are both operations of the O_h point group. Thus, the product must also be in O_h by closure. Consider the C_3 operations. These do not lie on the coordinate axes; rather, they go through the faces of the octahedron along the lines x=y=z, etc:



C_3 is perpendicular to page

The C_3 rotation takes x $\rightarrow$ y, y $\rightarrow$ z, z $\rightarrow$ x, so the point (a, b, c) is transformed into (b, c, a) as shown. We are close!

Because we are combining a proper rotation and a reflection, we might expect an improper rotation to result. The S_6 operations are defined on the same axes as the C_3 operations, e.g.



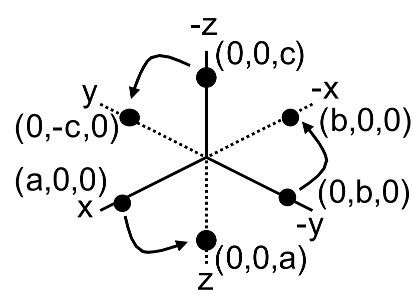
This transformation is harder to see (you might want to use a three-dimensional model) but the effect is to permute the labels <u>and</u> to change one sign. We are closer!

We now need the correct S_6 operation (there are 8 of them.) I think the easiest way to do this is to consider what must happen to points lying on the principal axes. Because we are looking for (a, b, c) $\rightarrow$ (b, -c, a), we see that a point on the x axis (a, 0, 0) should be transformed to the z axis (0, 0, a). Similarly, (0, b, 0) $\rightarrow$ (b, 0, 0) and (0, 0, c) $\rightarrow$ should go into (0, -c, 0)

Thus, we see the answer:

$C_4^x\ \sigma_{x=y} = S_6(x = -y = -z)$

Note: This problem allows me to point out an interesting feature of the O_h point group. The 48 operations of O_h correspond to taking the point (a, b, c) into all possible permutations of (a, b, c), each proceeded by a + or a -.



Thus:

$$(a, b, c) \rightarrow (-a, -b, -c)$$
$$(-a, -c, -b)$$
$$\vdots$$
etc.

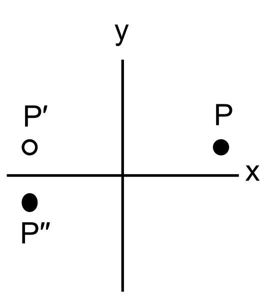
There are 6 permutation of (a, b, c) (given by 3!/0!) and 2^3 = 8 choices of signs for each permutation. The 6x8 possibilities are the 48 operations of O_h.

(f) σ_y (a, b, c) $\rightarrow$ (a, -b, c)

σ_x (a, -b, c) $\rightarrow$ (-a, -b, c)

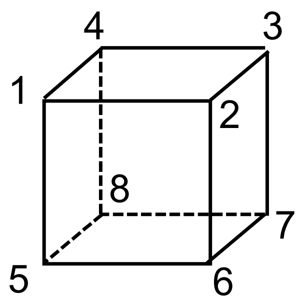
$\sigma_x\ \sigma_y$ (a, b, c) $\rightarrow$ (-a, -b, c) = C_2^z (a, b, c)

Rotation:



In general, the product of two planes generates an axis along their line of intersection.

3 (a)



$$\underline{E} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(b) C_3 (defined through vertices 1 and 7, with 1 being the positive side of axis)

$$\underline{C_3} \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{bmatrix} \rightarrow \begin{bmatrix} 1 \\ 4 \\ 8 \\ 5 \\ 2 \\ 3 \\ 7 \\ 6 \end{bmatrix} \qquad \underline{C_3} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

(c) C_4 (defined perpendicular to 1-2-3-4 face, ccw rotation)

$$\underline{C_4} \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{bmatrix} \rightarrow \begin{bmatrix} 2 \\ 3 \\ 4 \\ 1 \\ 6 \\ 7 \\ 8 \\ 5 \end{bmatrix} \qquad \underline{C_4} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

(d) i

$$\underline{i}\begin{bmatrix}1\\2\\3\\4\\5\\6\\7\\8\end{bmatrix}\rightarrow\begin{bmatrix}7\\8\\5\\6\\3\\4\\1\\2\end{bmatrix} \qquad \underline{i}=\begin{bmatrix}0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&1\\0&0&0&0&1&0&0&0\\0&0&0&0&0&1&0&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&1\\1&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0\end{bmatrix}$$

(e) S_4 (defined along C_4)

$$\underline{S_4}\begin{bmatrix}1\\2\\3\\4\\5\\6\\7\\8\end{bmatrix}\rightarrow\begin{bmatrix}6\\7\\8\\5\\2\\3\\4\\1\end{bmatrix} \qquad \underline{S_4}=\begin{bmatrix}0&0&0&0&0&1&0&0\\0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&1\\0&0&0&0&1&0&0&0\\0&1&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&0\\1&0&0&0&0&0&0&0\end{bmatrix}$$

(f) S_6 (defined along C_3)

$$\underline{S_6}\begin{bmatrix}1\\2\\3\\4\\5\\6\\7\\8\end{bmatrix}\rightarrow\begin{bmatrix}7\\3\\4\\8\\6\\2\\1\\5\end{bmatrix} \qquad \underline{S_6}=\begin{bmatrix}0&0&0&0&0&0&1&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&0\\0&0&0&0&0&0&0&1\\0&0&0&0&0&1&0&0\\0&1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0\\0&0&0&0&1&0&0&0\end{bmatrix}$$

(g) σ_h (perpendicular to C_4)

$$\underline{\sigma_h}\begin{bmatrix}1\\2\\3\\4\\5\\6\\7\\8\end{bmatrix}\rightarrow\begin{bmatrix}5\\6\\7\\8\\1\\2\\3\\4\end{bmatrix} \qquad \underline{\sigma_h}=\begin{bmatrix}0&0&0&0&1&0&0&0\\0&0&0&0&0&1&0&0\\0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&1\\1&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&0\end{bmatrix}$$

(h) σ_d (defined by vertices 1,3,5,7)

$$\underline{\sigma_d}\begin{bmatrix}1\\2\\3\\4\\5\\6\\7\\8\end{bmatrix} \rightarrow \begin{bmatrix}1\\4\\3\\2\\5\\8\\7\\6\end{bmatrix} \qquad \underline{\sigma_d} = \begin{bmatrix}1&0&0&0&0&0&0&0\\0&0&0&1&0&0&0&0\\0&0&1&0&0&0&0&0\\0&1&0&0&0&0&0&0\\0&0&0&0&1&0&0&0\\0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0\\0&0&0&0&0&1&0&0\end{bmatrix}$$