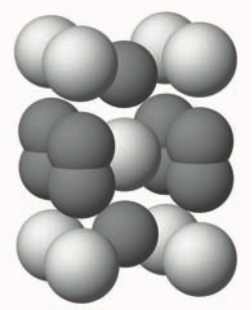
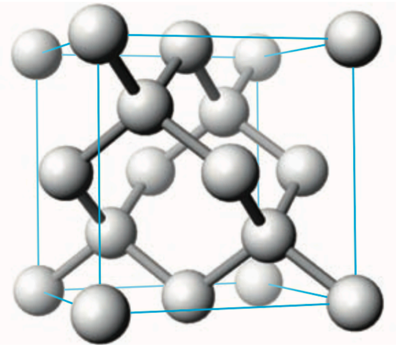
1. The unit cell shown here is for calcium carbide. How many calcium atoms and how many carbon atoms are in each unit cell? What is the formula of calcium carbide? (Calcium ions are silver in color and carbon atoms are gray.)



8 Ca atoms at corners x 1/8 = 1 Ca atom
1 Ca atom in the body
2 C atoms in the body
8 C atoms on edges x ¼ = 2 C atoms
Ca_2C_4 = **CaC_2**

2. The solid structure of silicon is shown below.
   a. Describe this crystal as PC, BCC or FCC. What type of holes are occupied in the lattice?
   b. Calculate the density of silicon in g cm^{-3} (given that the cube edge has a length of 543.1 pm).



8 Si atoms on corners x 1/8 = 1 Si atom
4 Si atoms in the body
6 Si atoms on faces x ½ = 3 Si atoms
Total = 8 Si atoms per unit cell

Si atoms occupy **tetrahedral holes** in a **FCC unit cell**.

$$8\ Si\ atoms \times \frac{1\ mol\ Si}{6.022 \times 10^{23}\ Si\ atoms} \times \frac{28.0855\ g}{1\ mol\ Si}$$
$$= 3.731 \times 10^{-22} g\ (mass\ of\ unit\ cell)$$

$$V\ (unit\ cell) = 543.1^3\ pm^3 \times \frac{1\ m^3}{(10^{12}\ pm)^3} \times \frac{(100\ cm)^3}{1\ m^3} = 1.602 \times 10^{-22} cm^3$$
$$\frac{3.731 \times 10^{-22}\ g}{1.602 \times 10^{-22} cm^3} = \mathbf{2.329\ g/cm^3}$$

3. Sodium metal adopts a body-centered cubic structure with a density of 0.97 g/cm^3. Use this information to estimate the atomic radius of sodium.

   BCC = 2 Na atoms in unit cell (1 in body, 8 in corners x 1/8)

$$2\ Na\ atoms \times \frac{1\ mol\ Na}{6.022 \times 10^{23}\ \ Na\ atoms} \times \frac{22.990\ g}{1\ mol\ Na}$$

$$= 7.635 \times 10^{-23}\ g\ (mass\ of\ unit\ cell)$$

$$7.635 \times 10^{-23}\ g\ \times \frac{1\ cm^3}{0.97\ g} = 7.9 \times 10^{-23}\ cm^3\ (V\ of\ unit\ cell)$$

   BCC = atoms touch along the body diagonal (BD)
   Let Na = atomic radius of Na
   BD = 4Na
   A right triangle forms between BD, a face diagonal (FD) and a unit cell edge (a)
   $a^2 + FD^2 = BD^2 \rightarrow a^2 + FD^2 = 16Na^2$

$$a = \sqrt[3]{7.9 \times 10^{-23} cm^3} \times \frac{1\ m}{100\ cm} \times \frac{10^{12}\ pm}{1\ m} = 430\ pm$$

   A right triangle forms between FD and two unit cell edges (a)
   $a^2 + a^2 = FD^2 \rightarrow 2(430\ pm)^2 = FD^2 \rightarrow FD = 610\ pm$

   $a^2 + FD^2 = 16Na^2 \rightarrow (430\ pm)^2 + (610\ pm)^2 = 16Na^2 \rightarrow$ **Na = 190 pm**

4. Vanadium metal has a density of 6.11 g/cm^3. Assuming the vanadium atomic radius is 132 pm, is the vanadium unit cell primitive cubic, body-centered cubic or face-centered cubic?

If V unit cell was PC, there would be 1 V atom per unit cell and the V atoms would touch along the unit cell edge.

Let r = atomic radius of V
Let a = unit cell edge

$$1\ V\ atom \times \frac{1\ mol\ V}{6.022 \times 10^{23}\ \ V\ atoms} \times \frac{50.942\ g}{1\ mol\ V}$$
$$= 8.459 \times 10^{-23}\ g\ (mass\ of\ unit\ cell)$$

$$8.459 \times 10^{-23}\ g\ \times \frac{1\ cm^3}{6.11\ g} = 1.38 \times 10^{-23}\ cm^3\ (volume\ of\ unit\ cell)$$

$$a = \sqrt[3]{1.38 \times 10^{-23} cm^3} \times \frac{1\ m}{100\ cm} \times \frac{10^{12}\ pm}{1\ m} = 240.pm$$

2r = a → 2r = 240. pm → r = 120. pm (compare to given r = 132 pm)

If V unit cell was FCC, there would be 4 V atoms per unit cell and the V atoms would touch along the face diagonal (FD).

$$4\ V\ atoms \times \frac{1\ mol\ V}{6.022 \times 10^{23}\ \ V\ atoms} \times \frac{50.942\ g}{1\ mol\ V}$$
$$= 3.384 \times 10^{-22}\ g\ (mass\ of\ unit\ cell)$$
$$3.384 \times 10^{-22}\ g\ \times \frac{1\ cm^3}{6.11\ g} = 5.54 \times 10^{-23}\ cm^3\ (volume\ of\ unit\ cell)$$
$$a = \sqrt[3]{5.54 \times 10^{-23} cm^3} \times \frac{1\ m}{100\ cm} \times \frac{10^{12}\ pm}{1\ m} = 381\ pm$$

$a^2 + a^2 = (FD)^2$
FD = 4r
$2(381\ pm)^2 = 16r^2$ → r = 135 pm (compare to given r = 132 pm)

If V unit cell was BCC, there would be 2 V atoms per unit cell and the V atoms would touch along the body diagonal (BD).

$$2\ V\ atoms \times \frac{1\ mol\ V}{6.022 \times 10^{23}\ \ V\ atoms} \times \frac{50.942\ g}{1\ mol\ V}$$
$$= 1.692 \times 10^{-22}\ g\ (mass\ of\ unit\ cell)$$

$$1.692 \times 10^{-22}\ g\ \times \frac{1\ cm^3}{6.11\ g} = 2.77 \times 10^{-23}\ cm^3\ (volume\ of\ unit\ cell)$$

$$a = \sqrt[3]{2.77 \times 10^{-23} cm^3} \times \frac{1\ m}{100\ cm} \times \frac{10^{12}\ pm}{1\ m} = 302\ pm$$

$a^2 + (FD)^2 = (BD)^2$
$a^2 + a^2 = (FD)^2$
$2(302\ \text{pm})^2 = (FD)^2 \rightarrow FD = 428\ \text{pm}$
$(302\ \text{pm})^2 + (428\ \text{pm})^2 = (BD)^2 \rightarrow BD = 524\ \text{pm}$
524 pm = 4r → r = 131 pm (best match, compares the best to 132 pm)
V must be BCC.

5. Rationalize why chalk (calcium carbonate) has a higher melting point that motor oil (large compounds made of C and H), which has a higher melting point than water, which engages in relatively strong hydrogen-bonding interactions.

$CaCO_3$ is an ionic compound.
Motor oil is made of molecular compounds.
Water is a molecular compound.

Attractions between ions in ionic solids are very strong and a lot of energy would be required for these ions to be separated (typically a few thousands kJ/mol), which would need to happen for the solid to melt. This is why ionic solids like $CaCO_3$ have high melting points.

Motor oil and water both involve molecular compounds. The compounds making up motor oil are relatively nonpolar and interact primarily via London dispersion forces (LDFs). Water, on the other hand, can make hydrogen bonds. A single hydrogen bond is stronger than a single LDF as you know from Chem 103. Motor oil has the higher melting point because it is made up of large molecules. Each molecule would engage in many LDFs, so the amount of energy required to break these forces would be greater the amount of energy needed to break up the 4 hydrogen bonds each water molecule is involved in.

6. For each of the following pairs of semiconductors, which one will have the larger band gap: (a) CdS or CdTe? (b) GaN or InP? (c) GaAs or InAs?

   (a) CdS, (b) GaN, (c) GaAs

7. The melting point of a fictional substance X is 225 ˚C at 10.0 atm. If the density of the solid phase of X is 2.67 g/cm^3 and the density of the liquid phase is 2.78 g/cm^3 at 10.0 atm, predict whether the normal melting point of X will be less than, equal to, or greater than 225 ˚C. Explain.

Solid is less dense than liquid → negative solid-liquid line slope

$$\frac{\Delta y}{\Delta x} < 0 \rightarrow \frac{1\ atm - 10.0\ atm}{x - 225\ ^\circ C} < 0 \rightarrow x - 225\ ^\circ C > 0 \rightarrow \boldsymbol{x > 225\ ^\circ C}$$

That means at 1 atm, the temperature (x) has to be greater than 225 ˚C.

8. Consider the following data for xenon:

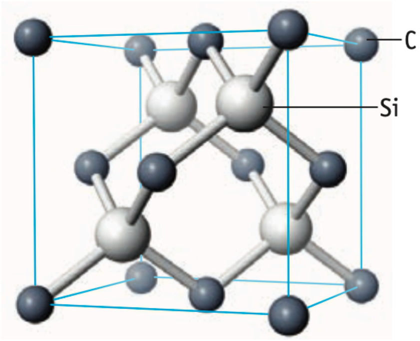
Triple point: –121 ˚C, 280 torr
Normal melting point: –112 ˚C
Normal boiling point: –107 ˚C

What is more dense, Xe (s) or Xe (l)?

$$slope\ of\ s-l\ line = \frac{\Delta y}{\Delta x} = \frac{280\ torr - 760\ torr}{-121\ ^\circ C + 112\ ^\circ C} > 0$$

Xe (s)

9. The solid state structure of silicon carbide, SiC, is shown below. Knowing that the Si–C bond length is 188.8 pm (and the Si–C–Si bond angle is 109.5˚), calculate the density of SiC.



Unit cell of SiC.

To get the density, we need to find the mass of the unit cell (in g) and the volume of the unit cell (in cm^3).

Inside the unit cell there are 8 C atoms on the corners x 1/8 = 1 C atom, as well as 6 C atoms on the faces x ½ = 3 C atoms (total 4 C atoms)

There are 4 Si atoms inside the body.

Overall = 4 SiC units

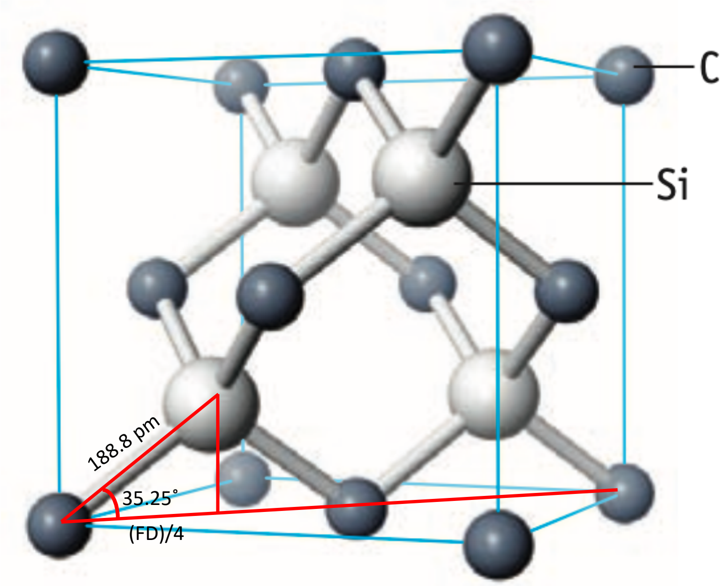
$$4\ SiC\ units \times \frac{1\ mol\ SiC}{6.022 \times 10^{23}\ SiC\ units} \times \frac{40.0965\ g}{1\ mol\ SiC}$$
$$= 2.663 \times 10^{-22}\ g\ (mass\ of\ unit\ cell)$$

Let a = side of the unit cell.

Let FD = face diagonal

An equilateral triangle forms between 2 Si–C bonds and half the face diagonal ($\frac{FD}{2}$). The C–Si–C angle is 109.5˚, so the two remaining angles are $\frac{180^\circ - 109.5^\circ}{2} = 35.25^\circ$each.

The height of that equilateral triangle perpendicular to $\frac{FD}{2}$ bisects it in two ($\frac{FD}{4}$).



Unit cell of SiC.

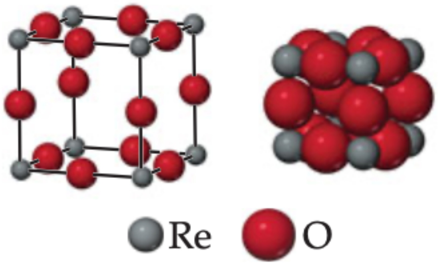
$$\cos(35.25^\circ) = \frac{\frac{FD}{4}}{188.8pm} \rightarrow FD = 616.7\ pm$$

$a^2 + a^2 = (FD)^2 \rightarrow 2a^2 = (616.7\text{ pm})^2 \rightarrow a = 436.1\text{ pm}$

$$V\ (unit\ cell) = 436.1^3\ pm^3 \times \frac{1\ m^3}{(10^{12}\ pm)^3} \times \frac{(100\ cm)^3}{1\ m^3} = 8.293 \times 10^{-23} cm^3$$

$$\frac{2.663 \times 10^{-22}\ g}{8.293 \times 10^{-23} cm^3} = \mathbf{3.211\ g/cm^3}$$

10. Rhenium oxide crystallizes with a structure that has a primitive cubic lattice, as shown here. In the image on the left, the sizes of the ions have been reduced to show the entire unit cell.



   a. How many atoms of each type are there per unit cell?
   b. Use the ionic radii of rhenium (0.70 Å) and oxygen (1.26 Å) to estimate the length of the edge of the unit cell (1 Å = 10^{-10} m).
   c. Use your answers to parts (a) and (b) to estimate the density of this compound.

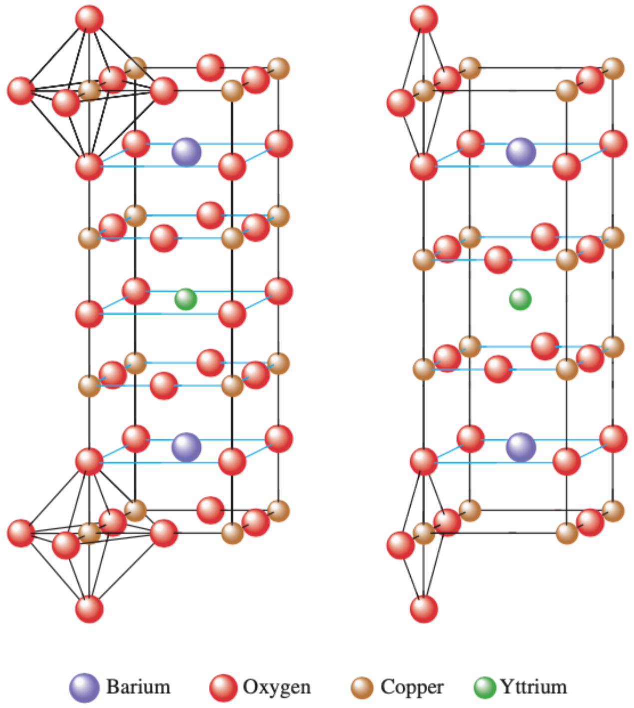
8 Re atoms on corners x 1/8 = **1 Re atom**
12 O atoms on edges x ¼ = **3 O atoms**
Atoms touch along the edge (a).
Let Re = atomic radius of Re and O = atomic radius of O.
a = 2Re + 2O = 2(0.70 Å) + 2(1.26 Å) = **3.92 Å**

$$1\ ReO_3\ unit \times \frac{1\ mol\ ReO_3}{6.022 \times 10^{23}\ \ ReO_3\ units} \times \frac{234.205\ g}{1\ mol\ ReO_3}$$
$$= 3.889 \times 10^{-22}\ g\ (mass\ of\ unit\ cell)$$

$$V\ (unit\ cell) = 3.92^3\ \text{Å}^3 \times \frac{1\ m^3}{(10^{10}\ \text{Å})^3} \times \frac{(100\ cm)^3}{1\ m^3} = 6.02 \times 10^{-23} cm^3$$

$$\frac{3.889 \times 10^{-22}\ g}{6.02 \times 10^{-23} cm^3} = \mathbf{6.46\ g/cm^3}$$

11. Materials containing the elements Y, Ba, Cu and O that are superconductors (electrical resistance equals zero) at temperatures above that of liquid nitrogen were recently discovered. The structures of these materials are based on the perovskite structure. Were they to have the ideal perovskite structure, the superconductor would have the structure shown in part (a) of the figure. These materials, however, do not act as superconductors unless they are deficient in oxygen. The structure of the actual superconducting phase appears to be that shown in part (b) of the figure.
    d. What is the formula of this ideal perovskite material?
    e. What is the formula of the actual superconductor?



(a) Ideal perovskite structure

(b) Actual structure of superconductor

Ideal structure:
2 Ba atoms in body
20 O atoms on edges x ¼ = 5 O atoms
8 O atoms on faces x ½ = 4 O atoms
8 Cu atoms on edges x ¼ = 2 Cu atoms
8 Cu atoms on corners x 1/8 = 1 Cu atom
1 Y atom in body

$YBa_2Cu_3O_9$

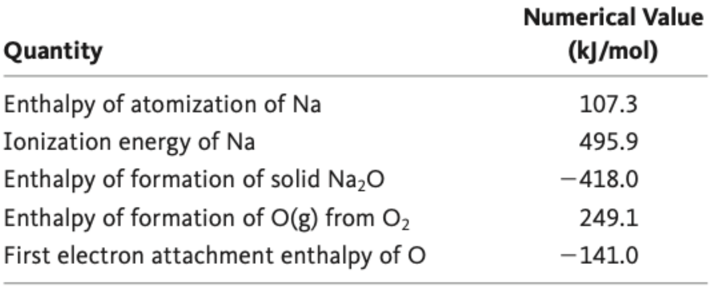
Actual structure:
2 Ba atoms in body
12 O atoms on edges x ¼ = 3 O atoms
8 O atoms on faces x ½ = 4 O atoms
8 Cu atoms on edges x ¼ = 2 Cu atoms
8 Cu atoms on corners x 1/8 = 1 Cu atom
1 Y atom in body

$YBa_2Cu_3O_7$

12. If you wanted to dope GaAs to make a n-type semiconductor with an element to replace Ga, which element(s) would you pick?

    An element with more electrons than Ga (group 4 element like C, Si, Ge…)

13. Using the thermochemical data below and an estimated value of –2481 kJ/mol for the lattice enthalpy for Na_2O, calculate the value for the second electron affinity of oxygen [O^- (g) + e– (g) → O^{2-} (g)].



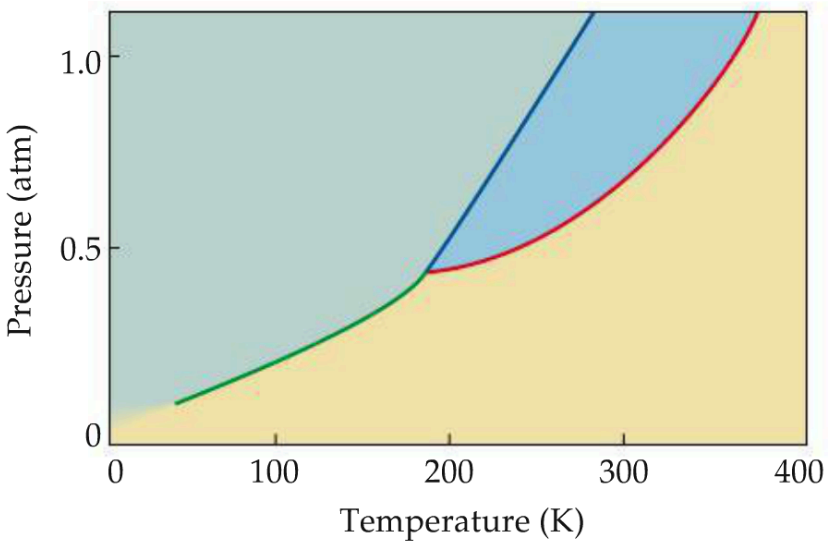
Quantity	**Numerical Value (kJ/mol)**
Enthalpy of atomization of Na	107.3
Ionization energy of Na	495.9
Enthalpy of formation of solid Na_2O	−418.0
Enthalpy of formation of O(g) from O_2	249.1
First electron attachment enthalpy of O	−141.0

$2\ Na^+ (g) + O^{2-} (g) \rightarrow Na_2O (s)$ ΔH = –2481 kJ (A) flip
$Na (s) \rightarrow Na (g)$ ΔH = +107.3 kJ (B) flip, x2
$Na (g) \rightarrow Na^+ (g) + e^-$ ΔH = +495.9 kJ (C) flip, x2
$2\ Na (s) + ½\ O_2 (g) \rightarrow Na_2O (s)$ ΔH = –418.0 kJ (D) keep
$½\ O_2 (g) \rightarrow O (g)$ ΔH = +249.1 kJ (E) flip
$O (g) + e^- \rightarrow O^- (g)$ ΔH = –141.0 kJ (F) flip

O– (g) + $e^- \rightarrow O^{2-}$ (g) ΔH = x

x = –A – 2B – 2C +D – E – F = +2481 kJ – 2(+107.3 kJ) – 2(+495.9 kJ) + (–418.0 kJ) – (+249.1 kJ – (–141.0 kJ) = **748.5 kJ**

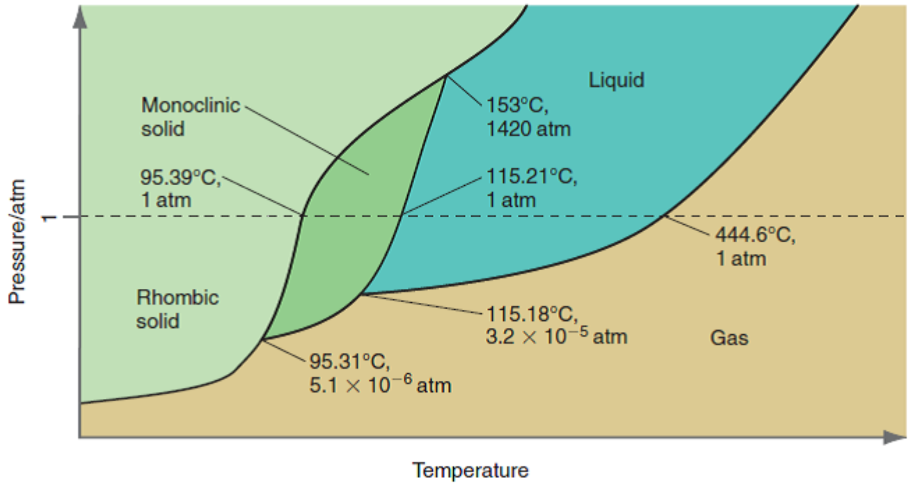
14. The phase diagram of a hypothetical substance is shown below.



a. Estimate the normal boiling point and freezing point of the substance.
b. What is the physical state of the substance under the following conditions? (i) T = 150 K, P = 0.2 atm; (ii) T = 100 K, P = 0.8 atm; (iii) T = 300 K, P = 1.0 atm
c. What is the triple point of the substance?

Normal BP ~ **360 K**
Normal FP ~ **250 K**
(i) gas, (ii) solid, (iii) liquid
TP ~ 0.45 atm, 190 K

15. Use the accompanying phase diagram for sulfur to answer the following questions (the phase diagram is not to scale)

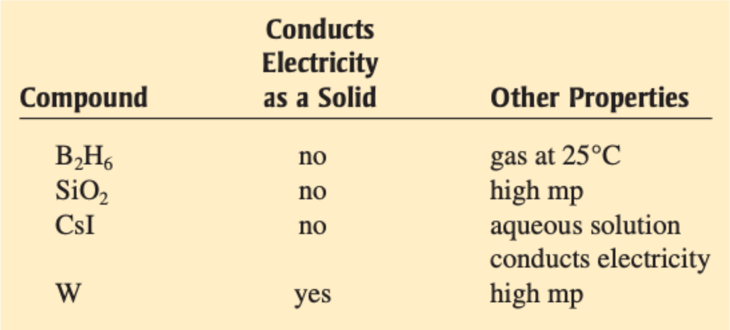


a. How many triple points are in the phase diagram?
b. What phases are in equilibrium at each of the triple points?
c. What phase is stable at 1.0 atm and room temperature?
d. Can monoclinic sulfur exist in equilibrium with sulfur vapor?

   e. What are the normal melting point and normal boiling point of sulfur?
   f. At a pressure of 1.0 x 10^{-5} atm, can rhombic sulfur sublime?
   g. What phase changes occur when the pressure of a sample of sulfur at 100. ˚C is increased from 1.0 x 10^{-8} atm to 1500 atm?

a. 3
b. Rhombic, monoclinic, liquid; rhombic, monoclinic, gas; monoclinic, liquid, gas
c. Rhombic
d. Yes
e. Normal MP: 115. 21 ˚C. Normal BP: 444.6 ˚C
f. No
g. Gas → monoclinic → rhombic

16. Consider the following data concerning four different substances. Label the four substances as either ionic, network, metallic or molecular solids.



Compound	Conducts Electricity as a Solid	Other Properties
B_2H_6	no	gas at 25°C
SiO_2	no	high mp
CsI	no	aqueous solution conducts electricity
W	yes	high mp

B_2H_6: molecular solid
SiO_2: network solid
CsI: ionic solid
W: metallic solid