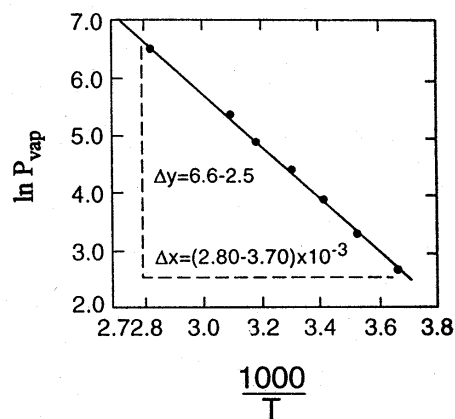


38. A molecule at the surface of a waterdrop is subject to attractions only by molecules below it and to each side. The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and causes the droplet to assume the shape that has the minimum surface area, a sphere.
40.  $\text{CO}_2$  is a gas at room temperature. As mp and bp increase, the strength of the intermolecular forces also increases. Therefore, the strength of forces is  $\text{CO}_2 < \text{CS}_2 < \text{CSe}_2$ . From a structural standpoint this is expected. All three are linear, nonpolar molecules. Thus, only London dispersion forces are present. Since the molecules increase in size from  $\text{CO}_2 < \text{CS}_2 < \text{CSe}_2$ , the strength of the intermolecular forces will increase in the same order.
80. We graph  $\ln P_{\text{vap}}$  vs  $1/T$ . The slope of the line equals  $-\Delta H_{\text{vap}}/R$ .

T(K)	$10^3/T$ ( $\text{K}^{-1}$ )	$P_{\text{vap}}$ (torr)	$\ln P_{\text{vap}}$
273	3.66	14.4	2.67
283	3.53	26.6	3.28
293	3.41	47.9	3.87
303	3.30	81.3	4.40
313	3.19	133	4.89
323	3.10	208	5.34
353	2.83	670.	6.51



$$\text{slope} = \frac{6.6 - 2.5}{(2.80 \times 10^{-3} - 3.70 \times 10^{-3}) \text{ K}^{-1}} = -4600 \text{ K}$$

$$-4600 \text{ K} = \frac{-\Delta H_{\text{vap}}}{R} = \frac{-\Delta H_{\text{vap}}}{8.3145 \text{ J/K} \cdot \text{mol}}, \quad \Delta H_{\text{vap}} = 38,000 \text{ J/mol} = 38 \text{ kJ/mol}$$

To determine the normal boiling point, we can use the following formula:

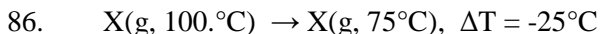
$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

At the normal boiling point, the vapor pressure equals 1.00 atm or 760. torr. At 273 K, the vapor pressure is 14.4. torr (from data in the problem).

$$\ln\left(\frac{14.4}{760.}\right) = \frac{38,000 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{T_2} - \frac{1}{273 \text{ K}} \right), \quad -3.97 = 4.6 \times 10^3 (1/T_2 - 3.66 \times 10^{-3})$$

$$82. \quad \ln\left(\frac{P_2}{1.00}\right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{373 \text{ K}} - \frac{1}{623 \text{ K}} \right), \quad \ln P_2 = 5.27, \quad P_2 = e^{5.27} = 194 \text{ atm}$$

$$!8.6 \times 10^{-4} + 3.66 \times 10^{-3} = 1/T_2 = 2.80 \times 10^{-3}, \quad T_2 = 357 \text{ K} = \text{normal boiling point}$$



$$q_1 = s_{\text{gas}} \times m \times \Delta T = \frac{1.0 \text{ J}}{\text{g}^{\circ}\text{C}} \times 250. \text{ g} \times (!25.^{\circ}\text{C}) = !6300 \text{ J} = !6.3 \text{ kJ}$$

$$X(g, 75.^{\circ}\text{C}) \rightarrow X(l, 75.^{\circ}\text{C}), \quad q_2 = 250. \text{ g} \times \frac{1 \text{ mol}}{75.0 \text{ g}} \times \frac{-20. \text{ kJ}}{\text{mol}} = !67 \text{ kJ}$$

$$X(l, 75.^{\circ}\text{C}) \rightarrow X(l, -15.^{\circ}\text{C}), \quad q_3 = \frac{2.5 \text{ J}}{\text{g}^{\circ}\text{C}} \times 250. \text{ g} \times (-90.^{\circ}\text{C}) = -56,000 \text{ J} = !56 \text{ kJ}$$

$$X(l, !15.^{\circ}\text{C}) \rightarrow X(s, !15.^{\circ}\text{C}), \quad q_4 = 250. \text{ g} \times \frac{1 \text{ mol}}{75.0 \text{ g}} \times \frac{-5.0 \text{ kJ}}{\text{mol}} = !17 \text{ kJ}$$

$$X(s, !15.^{\circ}\text{C}) \rightarrow X(s, !50.^{\circ}\text{C}), \quad q_5 = \frac{3.0 \text{ J}}{\text{g}^{\circ}\text{C}} \times 250. \text{ g} \times (!35.^{\circ}\text{C}) = !26,000 \text{ J} = !26 \text{ kJ}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = -6.3 ! 67 - 56 ! 17 ! 26 = !172 \text{ kJ}$$

92. a. 3

b. Triple point at  $95.31^{\circ}\text{C}$ : rhombic, monoclinic, gas

Triple point at  $115.18^{\circ}\text{C}$ : monoclinic, liquid, gas

Triple point at  $153^{\circ}\text{C}$ : rhombic, monoclinic, liquid

c. From the phase diagram, the monoclinic solid phase is stable at  $T = 100^{\circ}\text{C}$  and  $P = 1$  atm.

d. Normal melting point =  $115.21^{\circ}\text{C}$ ; normal boiling point =  $444.6^{\circ}\text{C}$ ; The normal melting and boiling points occur at  $P = 1.0$  atm.

e. Rhombic is the densest phase since the rhombic-monoclinic equilibrium line has a positive slope and since the solid-liquid lines also have positive slopes.

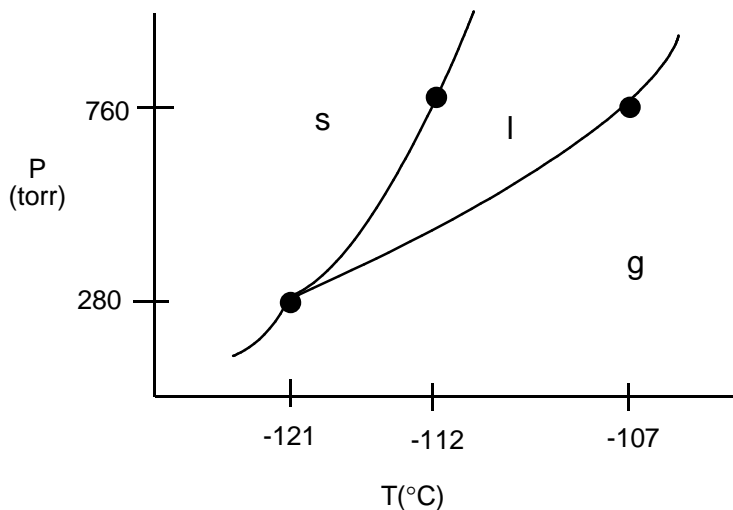
f. No;  $P = 1.0 \times 10^{-5}$  atm is at a pressure somewhere between the  $95.31^{\circ}\text{C}$  and  $115.18^{\circ}\text{C}$  triple points. At this pressure, the rhombic and gas phases are never in equilibrium with each other, so rhombic sulfur cannot sublime at  $P = 1.0 \times 10^{-5}$  atm. However, monoclinic sulfur can sublime at this pressure.

g. From the phase diagram, we would start off with gaseous sulfur. At  $100^{\circ}\text{C}$  and  $\sim 1 \times 10^{-5}$  atm,  $S(g)$  would convert to the solid monoclinic form of sulfur. Finally at  $100^{\circ}\text{C}$  and some large pressure less than 1420 atm,  $S(s, \text{monoclinic})$  would convert to the solid rhombic form of sulfur. Summarizing, the phase changes are  $S(g) \rightarrow S(\text{monoclinic}) \rightarrow S(\text{rhombic})$ .

93. a. two

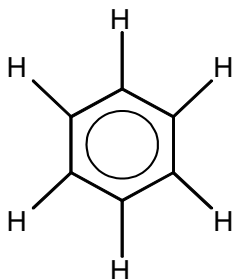
- b. Higher pressure triple point: graphite, diamond and liquid; Lower pressure triple point: graphite, liquid and vapor
- c. It is converted to diamond (the more dense solid form).
- d. Diamond is more dense, which is why graphite can be converted to diamond by applying pressure.

96.



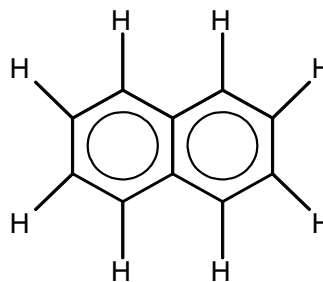
From the three points given, the slope of the s-l boundary line is positive so Xe(s) is more dense than Xe(l). Also, the positive slope of this line tells us that the melting point of Xe increases as pressure increases. The same direct relationship exists for the boiling point of Xe as the l-g boundary line also has a positive slope.

98. Benzene



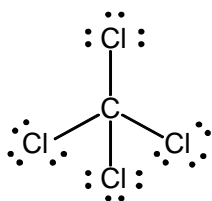
LD forces only

Naphthalene



LD forces only

**Note:** London dispersion forces in molecules like benzene and naphthalene are fairly large. The molecules are flat, and there is efficient surface area contact among molecules. Large surface area contact leads to stronger London dispersion forces.

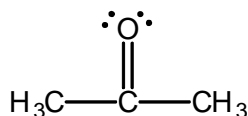


Carbon tetrachloride ( $\text{CCl}_4$ ) has polar bonds but is a nonpolar molecule.  $\text{CCl}_4$  only has LD forces.

In terms of size and shape:  $\text{CCl}_4 < \text{C}_6\text{H}_6 < \text{C}_{10}\text{H}_8$

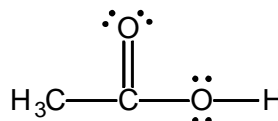
The strengths of the LD forces are proportional to size and are related to shape. Although  $\text{CCl}_4$  is fairly large, its overall spherical shape gives rise to relatively weak LD forces as compared to flat molecules like benzene and naphthalene. The physical properties given in the problem are consistent with the order listed above. Each of the physical properties will increase with an increase in intermolecular forces.

Acetone



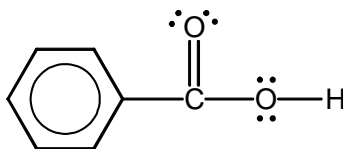
LD, dipole

Acetic Acid



LD, dipole, H bonding

Benzoic acid



LD, dipole, H bonding

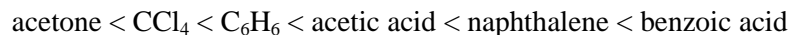
We would predict the strength of intermolecular forces for the last three molecules to be:

acetone < acetic acid < benzoic acid

and  
 polar          H bonding          H bonding, but large LD forces because of greater size  
 shape.

This ordering is consistent with the values given for bp, mp, and  $\Delta H_{\text{vap}}$ .

The overall order of the strengths of intermolecular forces based on physical properties are:



The order seems reasonable except for acetone and naphthalene. Since acetone is polar, we would not expect it to boil at the lowest temperature. However, in terms of size and shape, acetone is the smallest molecule, and the LD forces in acetone must be very small compared to the other molecules. Naphthalene must have very strong LD forces because of its size and flat shape.

107.  $\Delta H = q_p = 30.79 \text{ kJ}$ ;  $\Delta E = q_p + w$ ,  $w = -P\Delta V$

$$w = -P\Delta V = -1.00 \text{ atm} (28.90 \text{ L}) = -28.9 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -2930 \text{ J}$$

$$\Delta E = 30.79 \text{ kJ} + (-2.93 \text{ kJ}) = 27.86 \text{ kJ}$$