

8 Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

- Q8.1** Why is it reasonable to show the μ versus T segments for the three phases as straight lines as is done in Figure 8.1? More realistic curves would have some curvature. Is the curvature upward or downward on a μ versus T plot? Explain your answer.

$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$. Because S increases slowly with T , the realistic curves will curve downward, but not very rapidly.

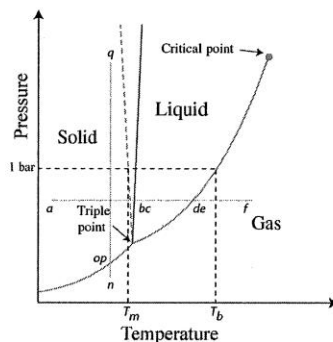
- Q8.2** Why do the temperature versus heat curves in the solid, liquid, and gas regions of Figure 8.7 have different slopes?

The slope of these curves are equal to the inverse of $C_{p,m}$, which has different values for the three phases as can be seen in Figure 2.9.

- Q8.3** Figure 8.7 is not drawn to scale. What would be the relative lengths on the q_p axis of the liquid + solid, liquid, and liquid + gas segments for water if the drawing were to scale and the system consisted of H_2O ?

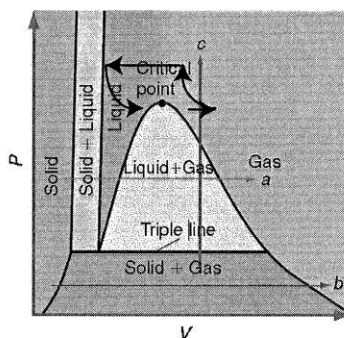
For the liquid + solid segment, the length of the segment is ΔH_{fusion} ; for the liquid segment, the length is $C_{p,m}^{\text{liquid}} \Delta T$; and for the liquid + gas segment, the length is $\Delta H_{\text{vaporization}}$. Numerically, for water, using Table 8.2, the relative lengths are 6010 J mol^{-1} , 7530 J mol^{-1} , and 40650 J mol^{-1} .

- Q8.4** Show the paths $n \rightarrow o \rightarrow p \rightarrow q$ and $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f$ of the P - V - T phase diagram of Figure 8.15 in the P - T phase diagram of Figure 8.4.



- Q8.5** At a given temperature, a liquid can coexist with its gas at a single value of the pressure. However, you can sense the presence of $\text{H}_2\text{O}(g)$ above the surface of a lake by the humidity, and it is still there if the barometric pressure rises or falls at constant temperature. How is this possible?
- The statement that at a given temperature, a liquid can coexist with its gas at a single value of the pressure holds for a system with only one substance. For the case described, the system consists of water and air. The change in barometric pressure is equivalent to an external pressure exerted on a liquid. As discussed in Section 8.7, this will change the vapor pressure only slightly.
- Q8.6** Why are the triple point temperature and the normal freezing point very close in temperature for most substances? This is the case because the freezing point changes only slightly with pressure.
- Q8.7** Give a molecular level explanation as to why the surface tension of $\text{Hg}(l)$ is not zero.
- Hg atoms have a strong attractive interaction. The atoms at the surface of a droplet have fewer nearest neighbors than an atom in the liquid. They experience a net force perpendicular to the surface that will lead to a pressure increase inside the droplet.
- Q8.8** A vessel containing a liquid is opened inside an evacuated chamber. Will you see a liquid–gas interface if the volume of the initially evacuated chamber is (a) less than the critical volume, (b) a factor of 10 larger than the critical volume, and (c) a factor of 1.05 larger than the critical volume?
- (a) No, because the liquid and gas are not distinguishable above the critical density.
(b) No, because all the liquid will evaporate.
(c) Yes, because the density is less than the critical density.
- Q8.9** Why are there no points in the phase diagram for sulfur in Figure 8.11 that show rhombic and monoclinic solid phases in equilibrium with liquid and gaseous sulfur?
- According to the Gibbs phase rule, four phases of a pure substance cannot coexist.
- Q8.10** What is the physical origin of the pressure difference across a curved liquid–gas interface?
- The origin is the cohesive forces in the liquid. Across an interface, the resultant force vector is not zero in magnitude. If the interface is curved, the resultant force tends to minimize the surface area, leading to a pressure difference across the interface.
- Q8.11** A triple point refers to a point in a P – T phase diagram for which three phases are in equilibrium. Do all triple points correspond to a gas–liquid–solid equilibrium?
- No. If there are several solid phases, there can be a triple point corresponding to equilibrium among three solid phases.
- Q8.12** Why does the liquid–gas coexistence curve in a P – T phase diagram end at the critical point?
- At the critical point, the gas and liquid have the same density, and can no longer be distinguished. This is also true for all points on the liquid–gas coexistence curve extended beyond the critical point.
- Q8.13** How can you get a P – T phase diagram from a P – V – T phase diagram?
- You get a P – T phase diagram by projecting a P – V – T phase diagram on the P – T plane.
- Q8.14** Why does the triple point in a P – T diagram become a triple line in a P – V diagram?
- This is the case because a gas and a liquid are in equilibrium for the range of values of volume from that of the pure liquid to that of the pure gas at a given temperature.
- Q8.15** Why does water have several different solid phases, but only one liquid and one gaseous phase?
- Liquid and gaseous phases are disordered, so that except for special cases such as superfluid and normal $\text{He}(l)$, there is no way to distinguish two different liquid or gaseous samples of the same pure substance.

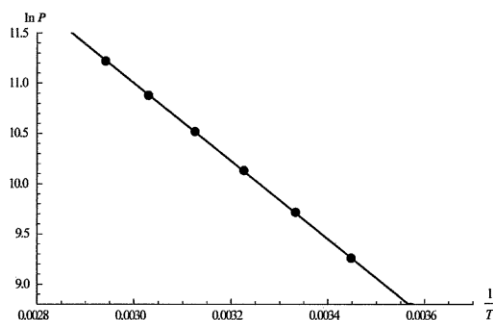
- Q8.16** As the pressure is increased at -45°C , ice I is converted to ice II. Which of these phases has the lower density?
The higher density phase is more stable as the pressure is increased, according to LeChatelier's principle. Therefore ice I is the less dense phase.
- Q8.17** Why is $\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$?
Because H is a state function, ΔH has the same value for solid \rightarrow gas or solid \rightarrow liquid \rightarrow gas as long as the initial and final states are the same for these two processes.
- Q8.18** Make a graph of the densities of a liquid and its gas as a function of the temperature from low temperatures up to the critical point. Explain the behavior at the critical point.
This information is shown in Figure 8.5. As the critical point is approached from lower temperatures, the density of the gas increases and that of the liquid decreases. The densities are identical at the critical point.
- Q8.19** What can you say about $\Delta H_{\text{vaporization}}$ of a liquid as the temperature approaches the critical temperature?
 $\Delta H_{\text{vaporization}}$ decreases slowly far from the critical temperature and rapidly as it approaches the critical temperature where it has the value zero.
- Q8.20** Is the following statement correct? *Because dry ice sublimates, carbon dioxide has no liquid phase.* Explain your answer.
It is not correct. Carbon dioxide has a liquid phase above the triple point, but not at 298 K.
- Q8.21** Make a drawing indicating the four-step process *d* of Figure 8.4 in Figure 8.13.



Numerical Problems

- P8.1** Use the vapor pressures of tetrachloromethane given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

T (K)	P (Pa)	T (K)	P (Pa)
280.	6440.	320.	37130.
290.	10540	330.	53250.
300.	16580	340.	74520.
310.	25190		



A least squares fit of $\ln P$ versus $1/T$ in units of K^{-1} gives the result $\Delta H_{\text{vaporization}} = 32.3 \text{ kJ mol}^{-1}$.

P8.2 The vapor pressure of ethanol(*l*) is given by

$$\ln\left(\frac{P}{\text{Pa}}\right) = 23.58 - \frac{3.6745 \times 10^3}{\frac{T}{\text{K}} - 46.702}$$

- Calculate the standard boiling temperature.
- Calculate $\Delta H_{\text{vaporization}}$ at 298 K and at the standard boiling temperature.

$$(a) \quad \ln\left(\frac{P}{\text{Pa}}\right) = 20.767 - \frac{2.7738 \times 10^3}{\frac{T}{\text{K}} - 53.08} = \ln 10^5 \text{ at } T_b$$

$$T_b = \frac{2.7738 \times 10^3}{20.767 - \ln(10^5)} + 53.08 = 351 \text{ K}$$

$$(b) \quad \Delta H_{\text{vaporization}}(298 \text{ K}) = RT^2 \frac{d \ln P}{dT} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (298 \text{ K})^2 \times 3.6745 \times 10^3}{(298 - 46.702)^2}$$

$$= 43.0 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta H_{\text{vaporization}}(351 \text{ K}) = RT^2 \frac{d \ln P}{dT} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (352.8 \text{ K})^2 \times 3.6745 \times 10^3}{(352.8 - 46.702)^2}$$

$$= 40.6 \text{ kJ mol}^{-1} \text{ at } 351 \text{ K}$$

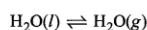
P8.3 In Section 8.8, it is stated that the maximum height of a water column in which cavitation does not occur is -9.7 m . Show that this is the case at 298 K.

Combining Equations (8.28) and (8.31),

$$h = \frac{P_{\text{inner}} - P_{\text{outer}}}{\rho g}$$

bubbles will form when P_{outer} has the value of the vapor pressure of water.

For the equilibrium



$$\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = -228.6 \text{ kJ mol}^{-1} + 237.1 \text{ kJ mol}^{-1} = 8.5 \text{ kJ mol}^{-1}$$

For this equilibrium

$$\ln K_P = -\frac{\Delta G_R^\circ}{RT} = P_{H_2O, g}$$

$$\frac{P}{1 \text{ bar}} = \exp\left(\frac{-8.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}\right)$$

$$P = 0.032 \text{ bar} = 3242 \text{ Pa}$$

Suppose that $P_{\text{inner}} = 1 \text{ atm} = 101325 \text{ Pa}$.

Using $\rho = 998 \text{ kg m}^{-3}$,

$$h = \frac{(101325 - 3242) \text{ Pa}}{998 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}} = 10.0 \text{ m}$$

- P8.4** Use the vapor pressures for tetrachloromethane given in the following table to estimate the temperature and pressure of the triple point and also the enthalpies of fusion, vaporization, and sublimation.

Phase	T (K)	P (Pa)
Solid	230.	225.7
Solid	250.	905
Liquid	280.	6440
Liquid	340.	62,501

To estimate $\Delta H_{\text{sublimation}}$, use the vapor pressures of the solid phase.

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

$$\Delta H_{\text{sublimation}} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{225.7 \text{ Pa}}{905 \text{ Pa}} \right)}{\frac{1}{230. \text{ K}} - \frac{1}{250. \text{ K}}}$$

$$= 33.2 \text{ kJ mol}^{-1}$$

To estimate $\Delta H_{\text{vaporization}}$, use the vapor pressures of the liquid phase.

$$\Delta H_{\text{vaporization}} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{62,501 \text{ Pa}}{6440 \text{ Pa}} \right)}{\frac{1}{280. \text{ K}} - \frac{1}{340. \text{ K}}}$$

$$\Delta H_{\text{vaporization}} = 30.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{fusion}} = \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}}$$

$$= 33.2 \text{ kJ mol}^{-1} - 30.0 \text{ kJ mol}^{-1}$$

$$= 3.2 \text{ kJ mol}^{-1}$$

At the triple point, the solid and liquid have the same vapor pressure.

$$\begin{aligned} \ln\left(\frac{P_{\text{solid}}}{P_{\text{solid, ref}}}\right) &= \frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_{\text{solid, ref}}} - \frac{1}{T}\right) \\ \ln\left(\frac{P_{\text{liquid}}}{P_{\text{liquid, ref}}}\right) &= \frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_{\text{liquid, ref}}} - \frac{1}{T}\right) \\ \frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_{\text{solid, ref}}} - \frac{1}{T}\right) + \ln P_{\text{solid, ref}} &= \frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_{\text{liquid, ref}}} - \frac{1}{T}\right) + \ln P_{\text{liquid, ref}} \\ \frac{1}{T} &= \frac{1}{\Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}}} \left(\frac{\Delta H_{\text{sublimation}}}{T_{\text{solid, ref}}} - \frac{\Delta H_{\text{vaporization}}}{T_{\text{liquid, ref}}} + R \ln P_{\text{solid, ref}} - R \ln P_{\text{liquid, ref}} \right) \end{aligned}$$

for

$$P_{\text{solid, ref}} = 225.7 \text{ Pa}, \quad P_{\text{liquid, ref}} = 6440 \text{ Pa}$$

$$T_{\text{solid, ref}} = 230. \text{ K}, \quad T_{\text{liquid, ref}} = 280. \text{ K}$$

$$\begin{aligned} \frac{1}{T_{\text{tp}}} &= \frac{1}{(33.2 - 30.0) \times 10^3 \text{ J mol}^{-1}} \times \left[\frac{33.2 \times 10^3 \text{ J mol}^{-1}}{230. \text{ K}} - \frac{30.0 \times 10^3 \text{ J mol}^{-1}}{280. \text{ K}} \right. \\ &\quad \left. + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\left(\frac{225.7 \text{ Pa}}{6440 \text{ Pa}}\right) \right] \\ &= 2.92 \times 10^{-3} \text{ K}^{-1} \\ T_{\text{tp}} &= 342 \text{ K} \end{aligned}$$

The pressure at the triple point can be obtained from either the equation for vapor pressure of the solid or the liquid phases.

$$P_{\text{solid}}(T) = P_{\text{solid, ref}} \exp\left[\frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_{\text{solid, ref}}} - \frac{1}{T}\right)\right]$$

$$P_{\text{tp}} = 225.7 \text{ Pa} \times \exp\left[\frac{33.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{230. \text{ K}} - \frac{1}{342 \text{ K}}\right)\right]$$

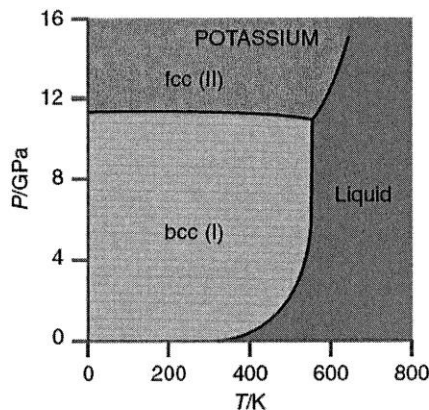
$$P_{\text{tp}} = 6.70 \times 10^4 \text{ Pa}$$

P8.5 Within what range can you restrict the values of P and T if the following information is known about CO_2 ? Use Figure 8.12 to answer this question.

- As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.
 - An interface delineating liquid and gaseous phases is observed throughout the pressure range between 6 and 65 atm.
 - Solid, liquid, and gas phases coexist at equilibrium.
 - Only a liquid phase is observed in the pressure range from 10. to 50. atm.
 - An increase in temperature from $-80.^\circ$ to $20.^\circ\text{C}$ converts a solid to a gas with no intermediate liquid phase.
- The temperature and pressure are greater than the values for the triple point, -56.6°C and 5.11 atm.
 - The temperature lies between the values for the triple point and the critical point.

- (c) The system is at the triple point, -56.6°C and 5.11 atm.
 (d) The temperature lies between the values for the triple point and the critical point.
 (e) The pressure is below the triple point pressure value of 5.11 atm.

P8.6 A P - T phase diagram for potassium is shown below.



- a. Which phase has the higher density, the fcc or the bcc phase? Explain your answer.
 According to Le Chatelier's principle, for a given temperature, the phase with the higher density will be found at higher pressure. Therefore the fcc phase is more dense.
- b. Indicate the range of P and T in the phase diagram for which fcc and liquid potassium are in equilibrium. Does fcc potassium float on or sink in liquid potassium? Explain your answer.
 fcc and liquid potassium are in equilibrium on the liquid–solid coexistence line existing upward from the triple point. The fcc phase will sink in the liquid because the slope of the two phase liquid–solid coexistence line is positive.
- c. Redraw this diagram for a different pressure range and indicate where you expect to find the vapor phase. Explain how you chose the slope of your liquid–vapor coexistence line.
 The phase diagram would look like Figure 8.4 except that there is a second triple point at which the liquid and the fcc and bcc solid phases coexist. The vapor phase is found at much lower pressures and higher temperatures. The slope of the vapor–liquid coexistence line is always positive because the vapor pressure increases rather than decreases with increasing temperature.

P8.7 A cell is roughly spherical with a radius of 20.0×10^{-6} m. Calculate the work required to expand the cell surface if the radius increases by a factor of three. Assume the cell is surrounded by pure water and that $T = 298.15$ K.

$$Area_1 = 4\pi r_1^2 = 4\pi(20.0 \times 10^{-6} \text{ m})^2 = 5.03 \times 10^{-9} \text{ m}^2$$

$$r_2 = 3r_1 = 60.0 \times 10^{-6} \text{ m}$$

$$Area_2 = 4\pi r_2^2 = 4\pi(60.0 \times 10^{-6} \text{ m})^2 = 4.52 \times 10^{-8} \text{ m}^2$$

$$w_{rev} = \Delta A = \gamma(Area_2 - Area_1) = 71.99 \text{ mN m}^{-1} \times (4.52 \times 10^{-8} \text{ m}^2 - 5.03 \times 10^{-9} \text{ m}^2) \\ = 2.89 \times 10^{-9} \text{ J}$$

The surface tension of water is listed in Table 8.5.

P8.8 It has been suggested that the surface melting of ice plays a role in enabling speed skaters to achieve peak performance. Carry out the following calculation to test this hypothesis. At 1 atm pressure, ice melts at 273.15 K, $\Delta H_{\text{fusion}} = 6010. \text{ J mol}^{-1}$, the density of ice is $920. \text{ kg m}^{-3}$, and the density of liquid water is 997 kg m^{-3} .

- What pressure is required to lower the melting temperature by 4.0°C ?
- Assume that the width of the skate in contact with the ice has been reduced by sharpening to $19 \times 10^{-3} \text{ cm}$, and that the length of the contact area is 18 cm. If a skater of mass 78 kg is balanced on one skate, what pressure is exerted at the interface of the skate and the ice?
- What is the melting point of ice under this pressure?
- If the temperature of the ice is -4.0°C , do you expect melting of the ice at the ice-skate interface to occur?

$$\begin{aligned} \left(\frac{dP}{dT}\right)_{\text{fusion}} &= \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{\Delta S_{\text{fusion}}}{\frac{M}{\rho_{\text{H}_2\text{O},l}} - \frac{M}{\rho_{\text{H}_2\text{O},s}}} = \frac{22.0 \text{ J mol}^{-1} \text{ K}^{-1}}{\frac{18.02 \times 10^{-3} \text{ kg}}{997 \text{ kg m}^{-3}} - \frac{18.02 \times 10^{-3} \text{ kg}}{920 \text{ kg m}^{-3}}} \\ &= -1.45 \times 10^7 \text{ Pa K}^{-1} = -145 \text{ bar K}^{-1} \end{aligned}$$

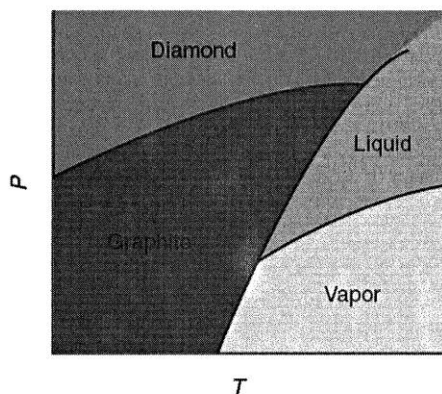
The pressure must be increased by 582 bar to lower the melting point by 4.0°C .

$$(b) \quad P = \frac{F}{A} = \frac{78 \text{ kg} \times 9.81 \text{ m s}^{-2}}{18 \times 10^{-2} \text{ m} \times 19 \times 10^{-3} \text{ m}} = 2.24 \times 10^7 \text{ Pa} = 2.24 \times 10^2 \text{ bar}$$

$$(c) \quad \Delta T = \left(\frac{dT}{dP}\right)_{\text{fusion}} \Delta P = \frac{-1^\circ\text{C}}{145 \text{ bar}} \times 2.24 \times 10^2 \text{ bar} = 1.5^\circ\text{C}; \quad T_m = -1.5^\circ\text{C}$$

- No, because the lowering of the melting temperature is less than the temperature of the ice.

P8.9 Answer the following questions using the P - T phase diagram for carbon sketched below.



- Which substance is denser, graphite or diamond? Explain your answer.
According to Le Chatelier's principle, for a given temperature, the phase with the higher density will be found at higher pressure. Therefore diamond is more dense than graphite.
- Which phase is more dense, graphite or liquid carbon? Explain your answer.
Graphite is more dense because the slope of the graphite-liquid coexistence line is positive.

- c. Why does the phase diagram have two triple points? Explain your answer.

Multiple triple points are possible only if there are several solid phases or in rare cases more than one liquid phase.

- P8.10** You have a compound dissolved in chloroform and need to remove the solvent by distillation. Because the compound is heat sensitive, you hesitate to raise the temperature above 5.00°C and decide on vacuum distillation. What is the maximum pressure at which the distillation takes place?

We can calculate the vapor pressure of chloroform at the given temperature using the data in Table 8.3.

$$\ln P = a_1 - \frac{a_2}{T/K + a_3} = 20.907 - \frac{2696.1}{278.15 - 46.926} = \ln(10^5) = 9.2469$$

$$P = 10.4 \times 10^3 \text{ Pa}$$

- P8.11** Use the vapor pressures for hexane given in the following table to estimate the temperature and pressure of the triple point and also the enthalpies of fusion, vaporization, and sublimation.

Phase	<i>T</i> (K)	<i>P</i> (Pa)
Solid	168	0.1296
Solid	178	1.111
Liquid	290.	1.400×10^4
Liquid	320.	4.822×10^4

$$\Delta H_{\text{sublimation}} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\left(\frac{1.111 \text{ Pa}}{0.1296 \text{ Pa}}\right)}{\left(\frac{1}{178 \text{ K}} - \frac{1}{168 \text{ K}}\right)} = 53.4 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vaporization}} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\left(\frac{4.822 \times 10^4 \text{ Pa}}{1.400 \times 10^4 \text{ Pa}}\right)}{\left(\frac{1}{320. \text{ K}} - \frac{1}{290. \text{ K}}\right)} = 31.8 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{fusion}} = (53.4 - 31.8) \text{ kJ mol}^{-1} = 21.6 \text{ kJ mol}^{-1}$$

To calculate the triple point temperature, take

$$T_{\text{solid, ref}} = 168 \text{ K} \quad P_{\text{solid, ref}} = 0.1296 \text{ Pa}$$

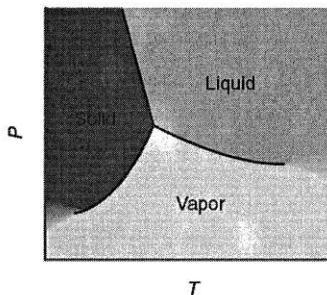
$$T_{\text{liquid, ref}} = 290. \text{ K} \quad P_{\text{liquid, ref}} = 1.400 \times 10^4 \text{ Pa}$$

$$\frac{1}{T_{\text{tp}}} = \frac{1}{(53.4 - 31.8) \times 10^3 \text{ J mol}^{-1}} \times \left[\frac{53.4 \times 10^3 \text{ J mol}^{-1}}{168 \text{ K}} - \frac{31.8 \times 10^3 \text{ J mol}^{-1}}{290. \text{ K}} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\left(\frac{0.1296 \text{ Pa}}{1.400 \times 10^4 \text{ Pa}}\right) \right]$$

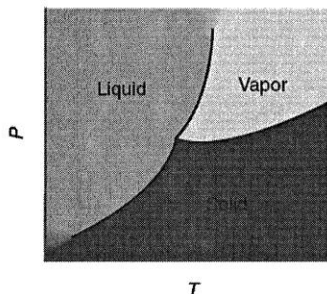
$$\frac{1}{T_{\text{tp}}} = 0.005179 \text{ K}^{-1}, \quad T_{\text{tp}} = 193 \text{ K}$$

$$P_{\text{tp}} = 0.1296 \text{ Pa} \times \exp\left[\frac{53.46 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{168 \text{ K}} - \frac{1}{193 \text{ K}}\right) \right] = 18.7 \text{ Pa}$$

- P8.12** Are the two P - T phase diagrams below likely to be observed for a pure substance? If not, explain all features of the diagram that will not be observed.



(a)



(b)

- (a) No. The liquid-vapor coexistence line has a negative slope, indicating that the vapor pressure of the liquid decreases with increasing temperature. The fact that the vapor phase exists at higher pressures than the solid phase would mean that the vapor is more dense than the solid, which is incorrect. The diagram indicates a solid-vapor critical point, which cannot exist. As the liquid is cooled, it vaporizes, which is physically unreasonable.
- (b) No. Below the triple point, the liquid solidifies as the temperature increases, which is incorrect. As the pressure increases at constant temperature, the solid sublimes, which is incorrect. Above the triple point, the vapor solidifies at constant pressure as the temperature increases, which is incorrect. The diagram indicates a solid-liquid critical point, which cannot exist.

- P8.13** Autoclaves that are used to sterilize surgical tools require a temperature of $120.^\circ\text{C}$ to kill some bacteria. If water is used for this purpose, at what pressure must the autoclave operate?

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{393.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right) = 0.6667$$

$$\frac{P_f}{P_i} = 1.95; \quad P_f = 1.95 \text{ atm}$$

- P8.14** You have collected a tissue specimen that you would like to preserve by freeze drying. To ensure the integrity of the specimen, the temperature should not exceed -5.00°C . The vapor pressure of ice at 273.16 K is 624 Pa. What is the maximum pressure at which the freeze drying can be carried out?

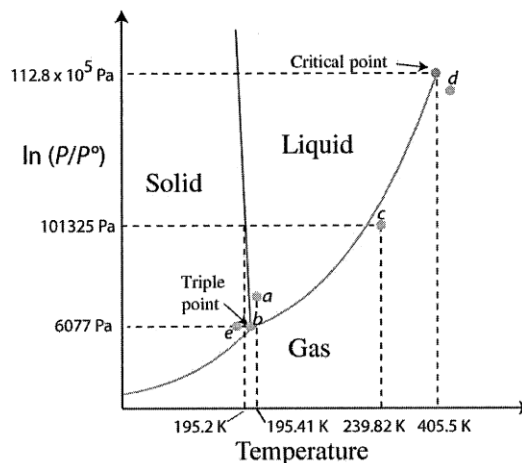
$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{6.008 \times 10^3 \text{ J mol}^{-1} + 40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{268.15 \text{ K}} - \frac{1}{273.16 \text{ K}} \right) = -0.3838$$

$$\frac{P_f}{P_i} = 0.681; \quad P_f = 0.681 \times 624 \text{ Pa} = 425 \text{ Pa}$$

- P8.15** The phase diagram of NH_3 can be characterized by the following information. The normal melting and boiling temperatures are 195.2 and 239.82 K, respectively; the triple point pressure and temperature are 6077 Pa and 195.41 K, respectively. The critical point parameters are 112.8×10^5 Pa and 405.5 K. Make a sketch of the P - T phase diagram (not necessarily to scale) for NH_3 . Place a point in the phase diagram for the following conditions. State which and how many phases are present.

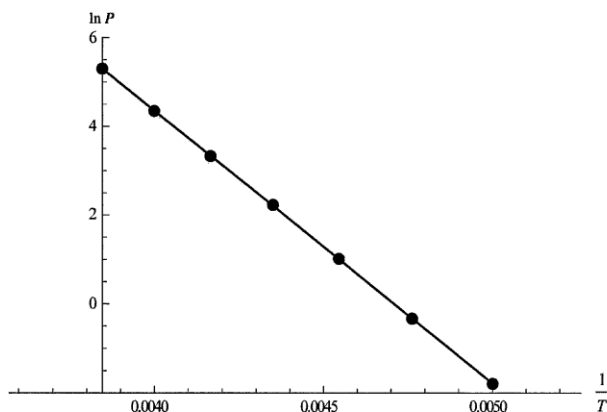
- 195.41 K, 9506 Pa
- 195.41 K, 6077 Pa
- 245.45 K, 101,325 Pa
- 415 K, 105×10^5 Pa
- 185.5 K, 6077 Pa



- | | |
|---------------------------------|----------------------------------|
| (a) 195.41 K, 9506 Pa | single phase liquid |
| (b) 195.41 K, 6077 Pa | triple point: gas, liquid, solid |
| (c) 245.45 K, 101,325 Pa | single phase gas |
| (d) 415 K, 105×10^5 Pa | single phase supercritical fluid |
| (e) 185.5 K, 6077 Pa | single phase solid |

- P8.16** Use the vapor pressures of ice given here to calculate the enthalpy of sublimation using a graphical method or a least squares fitting routine.

T (K)	P (Torr)
200.	0.1676
210.	0.7233
220.	2.732
230.	9.195
240.	27.97
250.	77.82
260.	200.2



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_m^{\text{sublimation}} = 51.1 \text{ kJ mol}^{-1}$.

- P8.17** Calculate the vapor pressure for a mist of spherical water droplets of radius (a) $1.95 \times 10^{-8} \text{ m}$ and (b) $2.25 \times 10^{-6} \text{ m}$ at 298 K. The vapor pressure of water at this temperature is 25.2 Torr.

$$\text{a. } \Delta P = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ N m}^{-1}}{1.95 \times 10^{-8} \text{ m}} = 7.38 \times 10^6 \text{ Pa}$$

$$P_{\text{inside}} = P_{\text{vapor}} + \Delta P = 3.32 \times 10^3 \text{ Pa} + 7.38 \times 10^6 \text{ Pa} = 7.39 \times 10^6 \text{ Pa}$$

Using Equation (8.25),

$$\ln\left(\frac{P}{P_0}\right) = \frac{M(P - P_0)}{\rho RT} = \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} \times \frac{(7.39 \times 10^6 - 3.32 \times 10^3) \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.05381$$

$$P = 1.055 P_0 = 3.50 \times 10^3 \text{ Pa or } 26.6 \text{ Torr}$$

$$\text{b. } \Delta P = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ N m}^{-1}}{2.25 \times 10^{-6} \text{ m}} = 6.40 \times 10^4 \text{ Pa}$$

$$P_{\text{inside}} = P_{\text{vapor}} + \Delta P = 3.32 \times 10^3 \text{ Pa} + 6.40 \times 10^4 \text{ Pa} = 6.73 \times 10^4 \text{ Pa}$$

Using Equation (8.25),

$$\ln\left(\frac{P}{P_0}\right) = \frac{M(P - P_0)}{RT} = \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1} \times (6.73 \times 10^4 - 3.3 \times 10^3) \text{ Pa}}{998 \text{ kg m}^{-3} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.0004664$$

$$P = 1.00047 P_0 = 3.32 \times 10^3 \text{ Pa or } 25.2 \text{ Torr}$$

- P8.18** The vapor pressure of a liquid can be written in the empirical form known as the Antoine equation, where $A(1)$, $A(2)$, and $A(3)$ are constants determined from measurements:

$$\ln \frac{P(T)}{\text{Pa}} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)}$$

Starting with this equation, derive an equation giving $\Delta H_m^{\text{vaporization}}$ as a function of temperature.

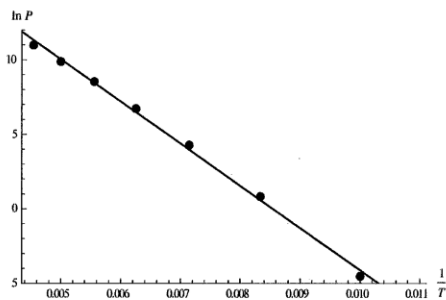
For a liquid–gas equilibrium involving a single species, $K_p = \frac{P}{P^\circ}$.

$$\Delta H = -R \frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = RT^2 \frac{d \ln K_p}{dT} = RT^2 \frac{d\left(A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)}\right)}{dT}$$

$$\Delta H = \frac{RT^2 A(2)}{\left[\frac{T}{\text{K}} + A(3)\right]^2}$$

- P8.19** Use the following vapor pressures of propane given here to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

T (K)	P (Torr)
100.	0.01114
120.	2.317
140.	73.91
160.	838.0
180.	5054
200.	2.016×10^4
220.	6.046×10^4



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 23.5 \text{ kJ mol}^{-1}$.

- P8.20** The vapor pressure of liquid benzene is 20,170 Pa at 298.15 K, and $\Delta H_{\text{vaporization}} = 30.72 \text{ kJ mol}^{-1}$ at 1 atm pressure. Calculate the normal and standard boiling points. Does your result for the normal boiling point agree with that in Table 8.3? If not, suggest a possible cause.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_{\text{vaporization}}}{R \left(\frac{\Delta H_{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 101,325 \text{ Pa}$.

$$T_{b, \text{normal}} = \frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} - \ln \frac{101325}{20170} \right)} = 342.8 \text{ K}$$

At the standard boiling point, $P = 10^5 \text{ Pa}$.

$$T_{b, \text{standard}} = \frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} - \ln \frac{10^5}{20170} \right)} = 342.4 \text{ K}$$

The result for the normal boiling point is $\sim 10 \text{ K}$ lower than the value tabulated in Table 8.3. The most probable reason for this difference is that the calculation above has assumed that $\Delta H_{\text{vaporization}}$ is independent of T .

- P8.21** Benzene(*l*) has a vapor pressure of 0.1269 bar at 298.15 K and an enthalpy of vaporization of $30.72 \text{ kJ mol}^{-1}$. The $C_{p,m}$ of the vapor and liquid phases at that temperature are 82.4 and $136.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Calculate the vapor pressure of $\text{C}_6\text{H}_6(\text{l})$ at 340.0 K assuming

- that the enthalpy of vaporization does not change with temperature.
 - that the enthalpy of sublimation at temperature T can be calculated from the equation $\Delta H_{\text{vaporization}}(T) = \Delta H_{\text{vaporization}}(T_0) + \Delta C_p(T - T_0)$ assuming that ΔC_p does not change with temperature.
- (a) If the enthalpy of vaporization is constant

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

$$\ln P_2 = \ln(0.1269) - \frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{340. \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = -0.5389$$

$$P_2 = 0.583 \text{ bar}$$

- (b) If the enthalpy of vaporization is given by

$$\Delta H_{\text{vaporization}}(T) = \Delta H_{\text{vaporization}}(T_0) + \Delta C_p(T - T_0)$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}}{RT^2} dT = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}(T_1) + \Delta C_P(T - T_1)}{RT^2} dT$$

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

$$\ln P_2 = \ln(0.4741) - \frac{30.72 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{340. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(82.4 - 136) \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{340. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(82.4 - 136) \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \ln \frac{340. \text{ K}}{298.15 \text{ K}}$$

$$\ln P_2 = -0.59218$$

$$P_2 = 0.553 \text{ bar}$$

P8.22 Use the values for $\Delta G_f^\circ(\text{CCl}_4, l)$ and $\Delta G_f^\circ(\text{CCl}_4, g)$ from Appendix B to calculate the vapor pressure of CCl_4 at 298.15 K.

For the transformation $\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g)$

$$\ln K_P = \ln \frac{P_{\text{C}_6\text{H}_6(g)}}{P^\circ} = -\frac{\Delta G_f^\circ(\text{C}_6\text{H}_6, g) - \Delta G_f^\circ(\text{C}_6\text{H}_6, l)}{RT}$$

$$= -\frac{-62.500 \times 10^3 \text{ J mol}^{-1} + 66.800 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -1.7347$$

$$K_P = \frac{P_{\text{C}_6\text{H}_6(g)}}{1 \text{ bar}} = 0.176 \quad P_{\text{C}_6\text{H}_6(g)} = 0.176 \text{ bar}$$

P8.23 Calculate the vapor pressure of water droplets of radius 1.00×10^{-8} m at 360. K in equilibrium with water vapor. Use the tabulated value of the density and the surface tension at 298 K from Appendix B for this problem. (*Hint:* You need to calculate the vapor pressure of water at this temperature.)

We first calculate the vapor pressure of water at 298 K using Table 8.3.

$$\ln \frac{P(T)}{P_a} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} = 23.58 - \frac{3.6745 \times 10^3}{360. - 46.702} = 11.0373$$

$$P = 6.21 \times 10^4 \text{ Pa}$$

We next calculate the pressure difference across the interface using Equation (8.29).

$$\Delta P = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ N m}^{-1}}{1.00 \times 10^{-8} \text{ m}} = 1.44 \times 10^7 \text{ Pa}$$

$$P_{\text{inside}} = P_{\text{vapor}} + \Delta P = 6.21 \times 10^4 \text{ Pa} + 1.44 \times 10^7 \text{ Pa} = 1.45 \times 10^7 \text{ Pa}$$

We calculate the increase in the vapor pressure using Equation (8.25).

$$\ln \left(\frac{P}{P_0} \right) = \frac{M(P - P_0)}{RT} = \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} \times \frac{(1.45 \times 10^7 - 6.21 \times 10^4) \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 360. \text{ K}} = 0.08686$$

$$P = 1.091 P_0 = 6.78 \times 10^4 \text{ Pa}$$

P8.24 The vapor pressure of an unknown solid is approximately given by $\ln(P/\text{Torr}) = 22.413 - 2211(K/T)$, and the vapor pressure of the liquid phase of the same substance is approximately given by $\ln(P/\text{Torr}) = 18.352 - 1736(K/T)$.

- Calculate $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.
- Calculate ΔH_{fusion} .
- Calculate the triple point temperature and pressure.

(a) From Equation (8.19),

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{sublimation}}}{RT^2}$$

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = \frac{d \ln P}{dT} \frac{dT}{d\left(\frac{1}{T}\right)} = -T^2 \frac{d \ln P}{dT} = -\frac{\Delta H_{\text{sublimation}}}{R}$$

For this specific case

$$\frac{\Delta H_{\text{sublimation}}}{R} = 2211 \quad \Delta H_{\text{sublimation}} = 18.4 \times 10^3 \text{ J mol}^{-1}$$

Following the same procedure as above,

$$\frac{\Delta H_{\text{vaporization}}}{R} = 1736 \quad \Delta H_{\text{vaporization}} = 14.4 \times 10^3 \text{ J mol}^{-1}$$

- (b) Calculate ΔH_{fusion} .

$$\begin{aligned} \Delta H_{\text{fusion}} &= \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}} \\ &= 18.4 \times 10^3 \text{ J mol}^{-1} - 14.4 \times 10^3 \text{ J mol}^{-1} \\ &= 4.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

- (c) Calculate the triple point temperature and pressure.

At the triple point, the vapor pressures of the solid and liquid are equal. Therefore

$$\begin{aligned} 22.413 - 2211 \frac{\text{K}}{T_{\text{tp}}} &= 18.352 - 1736 \frac{\text{K}}{T_{\text{tp}}} \\ T_{\text{tp}} &= 117 \text{ K} \\ \ln \frac{P_{\text{tp}}}{\text{Torr}} &= 22.413 - \frac{2211}{117} = 3.5101 \\ P_{\text{tp}} &= 33.5 \text{ Torr} \end{aligned}$$

P8.25 For water, $\Delta H_{\text{vaporization}}$ is $40.656 \text{ kJ mol}^{-1}$, and the normal boiling point is 373.12 K . Calculate the boiling point for water on the top of Mt. Everest (elevation 8848 m), where the normal barometric pressure is 253 Torr .

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_{\text{vaporization}}}{R \left(\frac{\Delta H_{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 760 \text{ Torr}$.

$$T_{b, \text{normal}} = \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 373.12 \text{ K}} - \ln \frac{253 \text{ Torr}}{760 \text{ Torr}} \right)} = 344 \text{ K}$$

- P8.26** Calculate the difference in pressure across the liquid-air interface for a (a) mercury and (b) methanol droplet of radius 125 nm.

From Equation (8.26),

$$P_{\text{inner}} - P_{\text{outer}} = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ N m}^{-1}}{125 \times 10^{-9} \text{ m}} = 3.53 \times 10^5 \text{ Pa for methanol}$$

$$P_{\text{inner}} - P_{\text{outer}} = \frac{2\gamma}{r} = \frac{2 \times 485.5 \times 10^{-3} \text{ N.m}^{-1}}{125 \times 10^{-9} \text{ m}} = 7.77 \times 10^6 \text{ Pa for mercury}$$

- P8.27** Calculate the vapor pressure of $\text{CH}_3\text{OH}(l)$ at 298.15 K if He is added to the gas phase at a partial pressure of 200. bar using the data tables. By what factor does the vapor pressure change?

$$\ln \frac{P(298.15 \text{ K})}{\text{Pa}} = 23.593 - \frac{3697.1}{298.15 - 31.317}$$

$$\frac{P(298.15 \text{ K})}{\text{Pa}} = 1.68 \times 10^4$$

We calculate the increase in the vapor pressure using Equation (8.25).

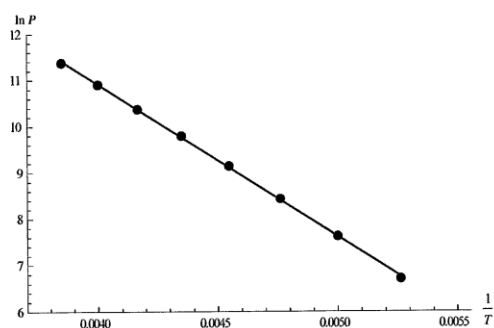
$$\ln \left(\frac{P}{P_0} \right) = \frac{V_m^{\text{liquid}} (P - P_0)}{RT} = \frac{M}{\rho_{\text{liquid}}} \frac{(P - P_0)}{RT}$$

$$\ln \left(\frac{P}{P_0} \right) = \frac{32.04 \times 10^{-3} \text{ kg mol}^{-1}}{791.4 \text{ kg m}^{-3}} \times \frac{(200. \times 10^5 \text{ Pa} - 1.68 \times 10^4 \text{ Pa})}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = 10.0563$$

$$P = 1.386 P_0 = 1.386 \times 1.68 \times 10^4 \text{ Pa} = 2.33 \times 10^4 \text{ Pa}$$

- P8.28** Use the vapor pressures of $\text{SO}_2(l)$ given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

T (K)	P (Pa)	T (K)	P (Pa)
190.	824.1	230.	17950
200.	2050.	240.	32110
210.	4591	250.	54410
220.	9421	260.	87930



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 27.4 \text{ kJ mol}^{-1}$.

P8.29 Prove that a substance for which the solid–liquid coexistence curve has a negative slope contracts upon melting.

The Clapeyron equation states that $\frac{dP}{dT} = \frac{\Delta S}{\Delta V_m}$. Therefore

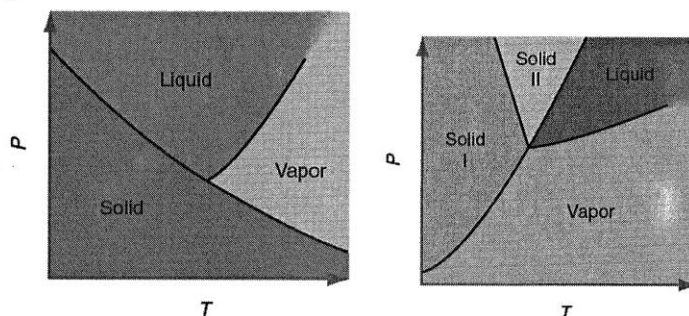
$$\Delta V_m = \frac{\Delta S_{\text{fusion}}}{\left(\frac{dP}{dT}\right)}$$

We know that $\Delta S_{\text{fusion}} > 0$.

Therefore, if

$$\left(\frac{dP}{dT}\right) < 0, \Delta V_m < 0$$

P8.30 Are the two P – T phase diagrams below likely to be observed for a pure substance? If not, explain all features of the diagram that will not be observed.



(a)

(b)

- (a) No. The solid–vapor line must have a positive slope because the volume increases upon sublimation. The slope of the liquid–solid coexistence line can be positive or negative, but will be much larger in magnitude than the slope of the vapor–solid coexistence line.
- (b) No. Four phases of a pure substance cannot coexist according to the Gibbs phase rule.

P8.31 The vapor pressure of methanol(l) is 16.94×10^3 Pa at 298.15 K. Use this value to calculate $\Delta G_f^\circ(\text{CH}_3\text{OH}, g) - \Delta G_f^\circ(\text{CH}_3\text{OH}, l)$. Compare your result with those in Table 4.1.

$$\Delta G_f^\circ(\text{CH}_3\text{OH}, g) - \Delta G_f^\circ(\text{CH}_3\text{OH}, l) = -RT \ln K_p = \ln \frac{P_{\text{CH}_3\text{OH}, g}}{P^\circ}$$

$$\Delta G_f^\circ(\text{CH}_3\text{OH}, g) - \Delta G_f^\circ(\text{CH}_3\text{OH}, l) = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{1.69 \times 10^4 \text{ Pa}}{10^5 \text{ Pa}}$$

$$\Delta G_f^\circ(\text{CH}_3\text{OH}, g) - \Delta G_f^\circ(\text{CH}_3\text{OH}, l) = 4.40 \times 10^3 \text{ J mol}^{-1}$$

From the tables, $\Delta G_f^\circ(\text{C}_2\text{H}_5\text{OH}, g) - \Delta G_f^\circ(\text{C}_2\text{H}_5\text{OH}, l) = -162.3 \text{ kJ mol}^{-1} + 166.6 \text{ kJ mol}^{-1} = 4.30 \text{ kJ mol}^{-1}$. This result is in good agreement with the ΔG_f° values calculated above.

P8.32 Within what range can you restrict the values of P and/or T if the following information is known about sulfur? Use Figure 8.11 to answer this problem.

- Only the rhombic solid phase is observed for $P = 1$ atm.
- When the pressure on the vapor is increased, the monoclinic solid phase is formed.
- Solid, liquid, and gas phases coexist at equilibrium.

- d. As the temperature is increased, the rhombic solid phase is converted to the monoclinic solid phase.
 e. As the temperature is increased at 1 atm, the rhombic solid phase is converted to the liquid directly.
- (a) $95.39^\circ\text{C} < T$
 (b) $95.31^\circ\text{C} < T < 115.18^\circ\text{C}$, $5.1 \times 10^{-6} \text{ atm} < P < 3.2 \times 10^{-5} \text{ atm}$
 (c) $P = 3.2 \times 10^{-5} \text{ atm}$, $T = 115.18^\circ\text{C}$
 (d) $153^\circ\text{C} > T > 95.31^\circ\text{C}$; $1420 \text{ atm} > P > 5.1 \times 10^{-6} \text{ atm}$
 (e) $T > 153^\circ\text{C}$; $P > 1420 \text{ atm}$

P8.33 The normal melting point of H_2O is 273.15 K, and $\Delta H_{\text{fusion}} = 6010 \text{ J mol}^{-1}$. Calculate the change in the normal freezing point at 100. and 500. bar compared to that at 1 bar assuming that the densities of the liquid and solid phases remain constant at 997 and 917 kg m^{-3} , respectively. Explain why your answer is positive (or negative).

$$\begin{aligned} \left(\frac{dP}{dT}\right)_{\text{fusion}} &= \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}} M \left(\frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}}\right)} \\ &= \frac{6010 \text{ J mol}^{-1}}{273.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{997 \text{ kg m}^{-3}} - \frac{1}{917 \text{ kg m}^{-3}}\right)} = -1.40 \times 10^7 \text{ Pa K}^{-1} \\ \left(\frac{dP}{dT}\right)_{\text{fusion}} &= -140. \text{ bar K}^{-1} \\ \Delta T &= \frac{\Delta P}{140. \text{ bar K}^{-1}} = -0.717 \text{ K at 100. bar and } -3.58 \text{ K at 500. bar} \end{aligned}$$

ΔT is negative because the liquid is more dense than the solid.

P8.34 Carbon tetrachloride melts at 250. K. The vapor pressure of the liquid is 10,539 Pa at 290. K and 74,518 Pa at 340. K. The vapor pressure of the solid is 270. Pa at 232 K and 1092 Pa at 250. K.

- a. Calculate $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.
 b. Calculate ΔH_{fusion} .
 c. Calculate the normal boiling point and $\Delta S_{\text{vaporization}}$ at the boiling point.
 d. Calculate the triple point pressure and temperature.

(a) $\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i}\right)$

$$\Delta H_{\text{vaporization}} = -\frac{R \ln \frac{P_f}{P_i}}{\left(\frac{1}{T_f} - \frac{1}{T_i}\right)}$$

$$\Delta H_{\text{vaporization}} = -\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{74,518 \text{ Pa}}{10,539 \text{ Pa}}}{\left(\frac{1}{340. \text{ K}} - \frac{1}{290. \text{ K}}\right)} = 32.1 \times 10^3 \text{ J mol}^{-1}$$

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\Delta H_{\text{sublimation}} = -\frac{R \ln \frac{P_f}{P_i}}{\left(\frac{1}{T_f} - \frac{1}{T_i} \right)}$$

$$\Delta H_{\text{sublimation}} = -\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{1092 \text{ Pa}}{270 \text{ Pa}}}{\left(\frac{1}{250 \text{ K}} - \frac{1}{232 \text{ K}} \right)} = 37.4 \times 10^3 \text{ J mol}^{-1}$$

$$(b) \quad \Delta H_{\text{fusion}} = \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}} = 37.4 \times 10^3 \text{ J mol}^{-1} - 32.1 \times 10^3 \text{ J mol}^{-1}$$

$$= 5.4 \times 10^3 \text{ J mol}^{-1}.$$

$$(c) \quad \ln \frac{P_f}{P_i} = -\frac{\Delta H_{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_{\text{vaporization}}}{R \left(\frac{\Delta H_{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 101325 \text{ Pa}$.

$$T_{b, \text{normal}} = \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 340 \text{ K}} - \ln \frac{101325 \text{ Pa}}{74518 \text{ Pa}} \right)} = 349.5 \text{ K}$$

$$\Delta S_{\text{vaporization}} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{vaporization}}} = \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{349.5 \text{ K}} = 91.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

(d) From Example Problem 8.2,

$$T_p = \frac{(\Delta H_{\text{vaporization}} - \Delta H_{\text{sublimation}})}{R \left(\ln \frac{P^{\text{liquid}}}{P^\circ} - \ln \frac{P^{\text{solid}}}{P^\circ} - \frac{\Delta H_{\text{sublimation}}}{RT_i^{\text{solid}}} + \frac{\Delta H_{\text{vaporization}}}{RT_i^{\text{liquid}}} \right)}$$

$$T_p = \frac{(32.1 \times 10^3 \text{ J mol}^{-1} - 37.4 \times 10^3 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \left(\ln \frac{10539 \text{ Pa}}{10^5 \text{ Pa}} - \ln \frac{270 \text{ Pa}}{10^5 \text{ Pa}} - \frac{37.4 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 232 \text{ K}} + \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 290 \text{ K}} \right)} = 264 \text{ K}$$

$$\ln \frac{P_{lp}}{10539 \text{ Pa}} = -\frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{264 \text{ K}} - \frac{1}{290. \text{ K}} \right) = -1.3112$$

$$\frac{P_{lp}}{10539 \text{ Pa}} = 0.269$$

$$P_{lp} = 2.84 \times 10^3 \text{ Pa}$$

- P8.35** In Equation (8.16), $(dP/dT)_{\text{vaporization}}$ was calculated by assuming that $V_m^{\text{gas}} \gg V_m^{\text{liquid}}$. In this problem, you will test the validity of this approximation. For water at its normal boiling point of 373.12 K, $\Delta H_{\text{vaporization}} = 40.656 \times 10^3 \text{ J mol}^{-1}$, $\rho_{\text{liquid}} = 958.66 \text{ kg m}^{-3}$, and $\rho_{\text{gas}} = 0.58958 \text{ kg m}^{-3}$. Compare the calculated values for $(dP/dT)_{\text{vaporization}}$ with and without the approximation of Equation (8.19). What is the relative error in making the approximation?

$$\left(\frac{dP}{dT} \right)_{\text{vaporization}} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{vaporization}} M \left(\frac{1}{\rho_{\text{gas}}} - \frac{1}{\rho_{\text{liquid}}} \right)}$$

$$\left(\frac{dP}{dT} \right)_{\text{vaporization}} = \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{0.58958 \text{ kg m}^{-3}} - \frac{1}{958.66 \text{ kg m}^{-3}} \right)}$$

$$= 3567 \text{ Pa K}^{-1}$$

$$\left(\frac{dP}{dT} \right)_{\text{vaporization}} \approx \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{0.58958 \text{ kg m}^{-3}} \right)} = 3564 \text{ Pa K}^{-1}$$

$$\text{Relative Error} = 100 \times \frac{3567 \text{ Pa K}^{-1} - 3564 \text{ Pa K}^{-1}}{3567 \text{ Pa K}^{-1}} = 0.061\%$$

- P8.36** The densities of a given solid and liquid of molar mass 122.5 g mol^{-1} at its normal melting temperature of 427.15 K are 1075 and 1012 kg m^{-3} , respectively. If the pressure is increased to 120. bar, the melting temperature increases to 429.35 K. Calculate $\Delta H_{\text{fusion}}^\circ$ and $\Delta S_{\text{fusion}}^\circ$ for this substance.

$$\frac{\Delta P}{\Delta T} \approx \frac{\Delta S}{\Delta V}; \quad \Delta S \approx \frac{\Delta P}{\Delta T} \Delta V$$

$$\Delta S_{\text{fusion}} = \frac{\Delta P}{\Delta T} M \left(\frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}} \right)$$

$$\Delta S_{\text{fusion}} = \frac{119 \times 10^5 \text{ Pa}}{429.35 \text{ K} - 427.15 \text{ K}} \times 122.5 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{1012 \text{ kg m}^{-3}} - \frac{1}{1075 \text{ kg m}^{-3}} \right)$$

$$= 38.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{\text{fusion}} = T_{\text{fusion}} \Delta S_{\text{fusion}} = 427.15 \text{ K} \times 38.4 \text{ J K}^{-1} \text{ mol}^{-1} = 16.4 \times 10^3 \text{ J mol}^{-1} \text{ at 1 bar}$$

- P8.37** The variation of the vapor pressure of the liquid and solid forms of a pure substance near the triple point are given by $\ln \frac{P_{\text{solid}}}{\text{Pa}} = -8750 \frac{\text{K}}{T} + 34.143$ and $\ln \frac{P_{\text{liquid}}}{\text{Pa}} = -4053 \frac{\text{K}}{T} + 21.10$. Calculate the temperature and pressure at the triple point.

At the triple point, $P_{\text{solid}} = P_{\text{liquid}}$.

$$-8750 \frac{\text{K}}{T} + 34.143 = -4053 \frac{\text{K}}{T} + 21.10$$

$$13.043 = 4697 \frac{\text{K}}{T}$$

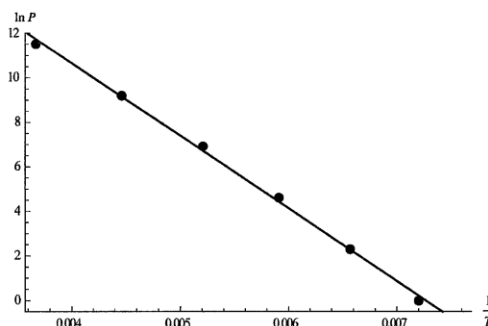
$$T_p = 360. \text{K}$$

$$\ln \frac{P_p}{\text{Pa}} = \frac{-8750.}{360.} + 34.143 = 9.84534$$

$$\frac{P_p}{\text{Pa}} = 1.89 \times 10^4$$

P8.38 Use the vapor pressures of *n*-butane given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

T (°C)	P (Pa)	T (°C)	P (Pa)
-134.3	1.00	-49.10	1.000×10^4
-121.9	10.00	-0.800	1.000×10^5
-103.9	100.0		
-81.10	1000.		



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 27.1 \text{ kJ mol}^{-1}$.

P8.39 At 298.15 K, $\Delta G_f^\circ(\text{HCOOH}, g) = -351.0 \text{ kJ mol}^{-1}$ and $\Delta G_f^\circ(\text{HCOOH}, l) = -361.4 \text{ kJ mol}^{-1}$. Calculate the vapor pressure of water at this temperature.

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{HCOOH}, g) - \Delta G_f^\circ(\text{HCOOH}, l) = -351.0 \text{ kJ mol}^{-1} + 361.4 \text{ kJ mol}^{-1} \\ &= 10.4 \text{ kJ mol}^{-1} \end{aligned}$$

$$\ln \frac{P}{P^\circ} = -\frac{\Delta G^\circ}{RT} = \frac{10.4 \text{ kJ mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -4.1956$$

$$P = 1.51 \times 10^{-2} \text{ bar}$$

P8.40 In this problem, you will calculate the differences in the chemical potentials of ice and supercooled water, and of steam and superheated water, all at 1 atm pressure shown schematically in Figure 8.1. For this problem, $S_{H_2O,s}^\circ = 48.0 \text{ J mol}^{-1} \text{ K}^{-1}$, $S_{H_2O,l}^\circ = 70.0 \text{ J mol}^{-1} \text{ K}^{-1}$, and $S_{H_2O,g}^\circ = 188.8 \text{ J mol}^{-1} \text{ K}^{-1}$.

- a. By what amount does the chemical potential of water exceed that of ice at -2.25°C ?
- b. By what amount does the chemical potential of water exceed that of steam at 102.25°C ?
- (a) $\Delta\mu = \Delta G_m = -\Delta S_m \Delta T$ at constant P
 $\Delta\mu = \Delta G_m = -(S_{H_2O,l}^\circ - S_{H_2O,s}^\circ)(\Delta T) = -(70.0 \text{ J K}^{-1} \text{ mol}^{-1} - 48.0 \text{ J K}^{-1} \text{ mol}^{-1})(-2.25^\circ\text{C})$
 $= 49.5 \text{ J mol}^{-1}$
- (b) $\Delta\mu = \Delta G_m = -(S_{H_2O,l}^\circ - S_{H_2O,g}^\circ)(\Delta T) = -(70.0 \text{ J K}^{-1} \text{ mol}^{-1} - 188.8 \text{ J K}^{-1} \text{ mol}^{-1})(2.25^\circ\text{C})$
 $= 267 \text{ J mol}^{-1}$

P8.41 Calculate the vapor pressure of a droplet of benzene of radius $1.25 \times 10^{-8} \text{ m}$ at 38.0°C in equilibrium with its vapor. Use the tabulated value of the density and the surface tension at 298 K from Appendix B for this problem. (*Hint:* You need to calculate the vapor pressure of benzene at this temperature.)

$$\ln \frac{P(T)}{P_0} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} = 20.767 - \frac{2.7738 \times 10^3}{311.15 - 53.08} = 10.0188$$

$$P = 2.24 \times 10^4 \text{ Pa}$$

Using Equation (8.29),

$$\Delta P = \frac{2\gamma}{r} = \frac{2 \times 28.22 \times 10^{-3} \text{ N m}^{-1}}{1.25 \times 10^{-8} \text{ m}} = 4.52 \times 10^6 \text{ Pa}$$

$$P_{\text{inside}} = P_{\text{vapor}} + \Delta P = 2.24 \times 10^4 \text{ Pa} + 4.52 \times 10^6 \text{ Pa} = 4.54 \times 10^6 \text{ Pa}$$

For a very large droplet, $\Delta P \rightarrow 0$, the vapor pressure is $2.24 \times 10^4 \text{ Pa}$. For the small droplet, the vapor pressure is increased by the factor

$$\ln \left(\frac{P}{P_0} \right) = \frac{M(P - P_0)}{\rho RT} = \frac{78.11 \times 10^{-3} \text{ kg mol}^{-1}}{876.5 \text{ kg m}^{-3}} \times \frac{(4.54 \times 10^6 - 2.24 \times 10^4) \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 311.15 \text{ K}}$$

$$= 0.1555$$

$$P = 1.168 P_0 = 2.62 \times 10^4 \text{ Pa}$$

P8.42 Solid iodine, $\text{I}_2(s)$, at 25.0°C has an enthalpy of sublimation of $56.30 \text{ kJ mol}^{-1}$. The $C_{p,m}$ of the vapor and solid phases at that temperature are 36.9 and $54.4 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The sublimation pressure at 25.0°C is 0.30844 Torr . Calculate the sublimation pressure of the solid at the melting point (113.6°C) assuming

- a. that the enthalpy of sublimation and the heat capacities do not change with temperature.
- b. that the enthalpy of sublimation at temperature T can be calculated from the equation $\Delta H_{\text{sublimation}}(T) = \Delta H_{\text{sublimation}}(T_0) + \Delta C_p(T - T_0)$ and ΔC_p does not change with T .
- (a) If the enthalpy of sublimation is constant

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

$$\ln P_2 = \ln 0.30844 - \frac{56.30 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$P_2 = 56.1 \text{ Torr}$$

(b) If the enthalpy of sublimation is given by

$$\Delta H_{\text{sublimation}}(T) = \Delta H_{\text{sublimation}}(T_0) + \Delta C_p(T - T_0)$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}}{RT^2} dT = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}(T_1) + \Delta C_p(T - T_1)}{RT^2} dT$$

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

$$\begin{aligned} \ln P_2 = \ln 0.30844 - \frac{56.30 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ + \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ + \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \ln \frac{386.8 \text{ K}}{298.15 \text{ K}} \end{aligned}$$

$$\ln P_2 = 3.964$$

$$P_2 = 52.5 \text{ Torr}$$

P8.43 Consider the transition between two forms of solid tin, $\text{Sn}(s, \text{gray}) \rightarrow \text{Sn}(s, \text{white})$. The two phases are in equilibrium at 1 bar and 18°C. The densities for gray and white tin are 5750 and 7280 kg m^{-3} , respectively, and the molar entropies for gray and white tin are 44.14 and 51.18 $\text{J K}^{-1} \text{ mol}^{-1}$, respectively. Calculate the temperature at which the two phases are in equilibrium at 350. bar.

In going from 1 atm, 18°C to 200 atm, T

$$\Delta G^{\text{gray}} = V_m^{\text{gray}} \Delta P - S^{\text{gray}} \Delta T$$

$$\Delta G^{\text{white}} = V_m^{\text{white}} \Delta P - S^{\text{white}} \Delta T$$

At equilibrium

$$\Delta G^{\text{gray}} - \Delta G^{\text{white}} = 0 = (V_m^{\text{gray}} - V_m^{\text{white}}) \Delta P - (S^{\text{gray}} - S^{\text{white}}) \Delta T$$

$$\begin{aligned} \Delta T = \frac{(V_m^{\text{gray}} - V_m^{\text{white}}) \Delta P}{(S^{\text{gray}} - S^{\text{white}})} &= \frac{M_{\text{Sn}} \left(\frac{1}{\rho_{\text{gray}}} - \frac{1}{\rho_{\text{white}}} \right) \Delta P}{\Delta S_{\text{transition}}} \\ &= \frac{118.71 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{5750 \text{ kg m}^{-3}} - \frac{1}{7280 \text{ kg m}^{-3}} \right) \times 349 \times 10^5 \text{ Pa}}{-7.04 \text{ J K}^{-1} \text{ mol}^{-1}} = -21.5^\circ \text{C} \\ T_f &= -3.5^\circ \text{C} \end{aligned}$$

P8.44 A reasonable approximation to the vapor pressure of krypton is given by $\log_{10}(P/\text{Torr}) = b - 0.05223(a/T)$. For solid krypton, $a = 10065 \text{ K}$ and $b = 7.1770$. For liquid krypton, $a = 9377.0 \text{ K}$ and $b = 6.92387$. Use these formulas to estimate the triple point temperature and pressure and also the enthalpies of vaporization, fusion, and sublimation of krypton.

At the triple point, the vapor pressures of the solid and liquid are equal.

$$7.1770 - 0.05223 \times \frac{10065}{T_{ip}} = 6.92387 - 0.05223 \times \frac{9377.0}{T_{ip}}$$

$$0.2531 = 0.05223 \times \frac{688}{T_{ip}}$$

$$T_{ip} = 142 \text{ K}$$

$$\log_{10} \frac{P_{ip}}{\text{Torr}} = 7.1770 - 0.05223 \times \frac{10065}{142} = 3.4678$$

$$P_{ip} = 2.94 \times 10^3 \text{ Torr}$$

We next calculate the enthalpies of sublimation and vaporization.

If the enthalpy of sublimation is given by

$$\Delta H_{\text{sublimation}}(T) = \Delta H_{\text{sublimation}}(T_0) + \Delta C_p(T - T_0)$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}}{RT^2} dT = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vaporization}}(T_1) + \Delta C_p(T - T_1)}{RT^2} dT$$

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

$$\ln P_2 = \ln 0.30844 - \frac{56.30 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \ln \frac{386.8 \text{ K}}{298.15 \text{ K}}$$

$$\ln P_2 = 3.964$$

$$P_2 = 52.5 \text{ Torr}$$

From Equation (8.19),

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{sublimation}}}{RT^2}$$

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = \frac{d \ln P}{dT} \frac{dT}{d\left(\frac{1}{T}\right)} = -T^2 \frac{d \ln P}{dT} = -\frac{\Delta H_{\text{sublimation}}}{R}$$

$$\frac{d \log_{10} P}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{\text{sublimation}}}{2.303 R}$$

For this specific case

$$\frac{\Delta H_{\text{sublimation}}}{R} = 0.05223 \times 2.303 \times 10065 \quad \Delta H_{\text{sublimation}} = 10.1 \times 10^3 \text{ J mol}^{-1}$$

Following the same reasoning

$$\frac{\Delta H_{\text{sublimation}}}{R} = 0.05223 \times 2.303 \times 9377 \quad \Delta H_{\text{sublimation}} = 9.38 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{\text{fusion}} = \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}} = 10.07 \times 10^3 \text{ J mol}^{-1} - 9.38 \times 10^3 \text{ J mol}^{-1}$$

$$= 0.69 \times 10^3 \text{ J mol}^{-1}$$

P8.45 20.0 g of water is in a container of 20.0 L at 298.15 K. The vapor pressure of water at this temperature is 23.76 Torr.

- a. What phases are present?
 - b. At what volume would only the gas phase be present?
 - c. At what volume would only the liquid phase be present?
- (a) Liquid and gaseous phases are present.
(b) Assuming the validity of the ideal gas law,

$$V = \frac{nRT}{P} = \frac{(20.0 \text{ g}/18.02 \text{ g mol}^{-1}) \times 62.35 \text{ Torr L mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{23.76 \text{ Torr}} = 868 \text{ L}$$

- (c) Only liquid will be present if the volume is decreased to a value at which water at its normal density fills the whole volume.

$$V = \frac{\text{mass}}{\text{density}} = \frac{20.0 \times 10^{-3} \text{ kg}}{998 \text{ kg m}^{-3}} = 0.0200 \text{ L}$$