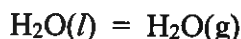


1. For the evaporation of water at 25 °C



show $\Delta H^\circ = 44,012 \text{ J mol}^{-1}$, $\Delta G^\circ = 8,557 \text{ J mol}^{-1}$, and $K = p_{\text{H}_2\text{O}} = 0.0317 \text{ bar}$.

- [3] Data at 298.15 K (25 °C):

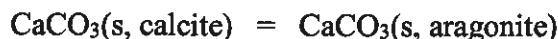
$$\begin{array}{ll} \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -285,830 \text{ J mol}^{-1} & \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -241,818 \text{ J mol}^{-1} \\ \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -237,129 \text{ J mol}^{-1} & \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -228,572 \text{ J mol}^{-1} \end{array}$$

2. a) The equilibrium constant for $\text{H}_2\text{O}(l) = \text{H}_2\text{O}(g)$ gives the pressure of water vapor in equilibrium with liquid water at a given temperature: $K = p_{\text{H}_2\text{O}}$.

Assuming ΔH° is constant, use the van't Hoff equation $\text{dln}K / \text{d}(1/T) = -\Delta H^\circ/R$ to show

[7]
$$\ln p_{\text{H}_2\text{O}}(\text{at } T) = \ln p_{\text{H}_2\text{O}}(\text{at } 298.15 \text{ K}) - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{298.15 \text{ K}} \right)$$

- b) Use the expression for $\ln p_{\text{H}_2\text{O}}(\text{at } T)$ to calculate the vapor pressure of water at 100 °C.
- c) Water boils at 100 °C and 1.00 atm (1.01325 bar). The vapor pressure of water at 100 °C calculated in part b is slightly in error. Why?
- d) A tank contains water at 80 °C and a pressure of 0.70 bar. Is the water in the tank liquid, vapor, or both? Justify your answer.
3. a) Calcium carbonate (CaCO_3) is found in nature in two different crystalline forms: calcite and aragonite. Use the value of ΔG° for the reaction



to show calcite is the more stable form of calcium carbonate at 25 °C and 1 bar.

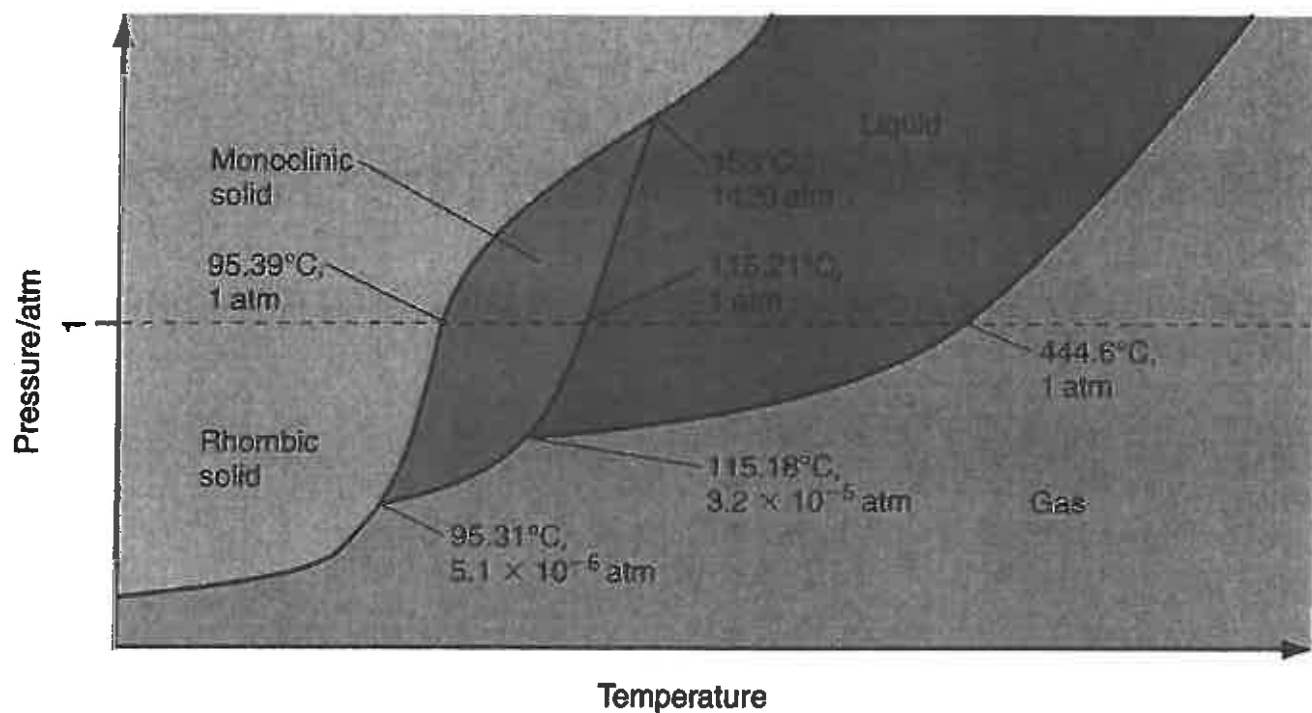
- b) Calcite initially at 25 °C and 1 bar is heated at 1 bar. Will aragonite form? If so, at what temperature? (*Hint: $\text{d}\Delta G^\circ/\text{d}T = -\Delta S^\circ$*)
- c) Calcite initially at 25 °C and 1 bar is compressed at 25 °C. Will aragonite form? If so, at what pressure? [*Hint: $(\partial\Delta G/\partial p)_T = \Delta V$*] Does this suggest where aragonite might have formed?

Data at 25 °C:

$$\begin{array}{ll} \Delta H_{\text{fm}}^\circ(\text{aragonite}) = -1207.13 \text{ kJ mol}^{-1} & \Delta H_{\text{fm}}^\circ(\text{calcite}) = -1206.92 \text{ kJ mol}^{-1} \\ \Delta G_{\text{fm}}^\circ(\text{aragonite}) = -1127.75 \text{ kJ mol}^{-1} & \Delta G_{\text{fm}}^\circ(\text{calcite}) = -1128.79 \text{ kJ mol}^{-1} \\ S_{\text{m}}^\circ(\text{aragonite}) = 88.7 \text{ J K}^{-1} \text{ mol}^{-1} & S_{\text{m}}^\circ(\text{calcite}) = 92.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ V_{\text{m}}^\circ(\text{aragonite}) = 35.36 \text{ cm}^3 \text{ mol}^{-1} & V_{\text{m}}^\circ(\text{calcite}) = 36.93 \text{ cm}^3 \text{ mol}^{-1} \end{array}$$

4. Use the phase diagram for sulfur given below to answer this question.

- a) Give the equilibrium form of sulfur at 25 °C and 1 atm.
- b) Can monoclinic sulfur be converted to rhombic sulfur by increasing the temperature?
- [4]
- c) Can monoclinic sulfur be converted to rhombic sulfur by increasing the pressure?
- d) Give the minimum temperature and the maximum temperature at which monoclinic sulfur can exist under equilibrium conditions.



Q1) Liquid/Vapor equilibrium for water at 25 °C:



$$\Delta H^\circ = \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) - \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l)$$

$$= [-241,818 - (-285,830)] \frac{\text{J}}{\text{mol}} = \boxed{44,012 \frac{\text{J}}{\text{mol}}}$$

$$\Delta G^\circ = \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, g) - \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, l)$$

$$= [-228,572 - (-237,129)] \frac{\text{J}}{\text{mol}} = \boxed{8,557 \frac{\text{J}}{\text{mol}}}$$

equilibrium
constant

$$K = \exp(-\Delta G^\circ/RT)$$

$$= \exp\left(\frac{8557 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right)$$

$$K = \exp(-3.452) = \boxed{0.03168 \text{ bar}}$$

Q2) a) $\text{H}_2\text{O}(l) = \text{H}_2\text{O}(g) \quad K = P_{\text{H}_2\text{O}}$

$$\frac{d \ln K}{d \frac{1}{T}} = \frac{d \ln P_{\text{H}_2\text{O}}}{d \frac{1}{T}} = -\frac{\Delta H^\circ}{R}$$

(standard
enthalpy of
vaporization
= ΔH°)

integrate:

$$d \ln P_{\text{H}_2\text{O}} = -\frac{\Delta H^\circ}{R} d \frac{1}{T} \quad (\text{assuming } \Delta H^\circ \text{ is constant})$$

$$\int d \ln P_{\text{H}_2\text{O}} = -\frac{\Delta H^\circ}{R} \int d \frac{1}{T}$$

(Q2 a cont.)

$$\ln P_{H_2O}(\text{at } T) - \ln P_{H_2O}(\text{at } 298.15\text{K}) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{298.15\text{K}} \right)$$

b) use data at 25°C ($\Delta H^\circ = 44012 \frac{\text{J}}{\text{mol}}$, $P_{H_2O} = 0.0317\text{bar}$)
to estimate the normal boiling point ($p = 1\text{atm}$) of water.

$$T = 373.15\text{K} \quad (100^\circ\text{C})$$

$$\ln P_{H_2O}(\text{at } 373.15\text{K}) = \ln P_{H_2O}(\text{at } 298.15\text{K}) - \frac{\Delta H^\circ}{R} \left(\frac{1}{373.15\text{K}} - \frac{1}{298.15\text{K}} \right)$$

$$\ln P_{H_2O}(\text{at } 373.15\text{K}) = \ln(0.0317) - \frac{44012 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{Kmol}}} \left(\frac{1}{373.15\text{K}} - \frac{1}{298.15\text{K}} \right)$$

$$\ln P_{H_2O}(\text{at } 373.15\text{K}) = -3.451 + 3.569 = 0.117$$

$$P_{H_2O}(\text{at } 373.15\text{K}) = e^{0.117} = \boxed{1.12\text{ bar}}$$

c) actual water vapor pressure at 373.15K is 1.00atm
(1.01325bar)

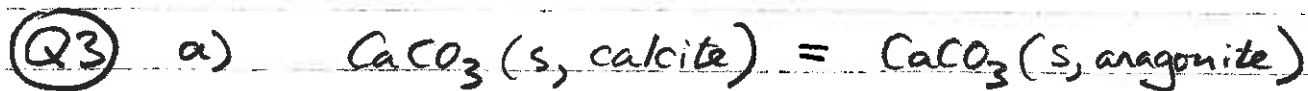
the calculated pressure of water is slightly higher, 1.12bar

Why? ΔH° was assumed to be constant for the
van't Hoff integration from 25° to 100°C , when in fact
 ΔH° ~~decreases~~ slightly with increasing T ($\Delta H^\circ \rightarrow 0$ at T_c)

$$\text{d) calculate } \ln P_{H_2O}(\text{at } 80^\circ\text{C}) = \ln(0.0317) - \frac{44012}{8.314} \left(\frac{1}{353.15} - \frac{1}{298.15} \right)$$
$$= -3.451 - 2.765 = -0.6862$$

$$P_{H_2O}(\text{at } 80^\circ\text{C}) = e^{-0.6862} = 0.503\text{ bar}$$

tank pressure 0.70bar
is higher only liquid



$$\Delta G^\circ = \Delta G_{\text{fm}}^\circ(\text{aragonite}) - \Delta G_{\text{fm}}^\circ(\text{calcite})$$

$$= [-1127.75 - (-1128.79)] \frac{\text{kJ}}{\text{mol}} = \boxed{1.04 \frac{\text{kJ}}{\text{mol}}}$$

$$\Delta G^\circ = 1040 \frac{\text{J}}{\text{mol}} \quad \text{at } 25^\circ\text{C, 1 bar} \quad \left(\begin{array}{c} \text{fixed} \\ T, P \end{array} \right)$$

$\Delta G_{T,P}^\circ > 0$ reaction is not spontaneous

calcite is the stable form of calcium carbonate

b) ΔG° is positive at 25°C . If the temperature is raised, will ΔG° become negative, indicating a spontaneous reaction and aragonite stable?

NO!

$$\frac{d\Delta G^\circ}{dT} = -\Delta S^\circ = -\left(S_m^\circ(\text{aragonite}) - S_m^\circ(\text{calcite})\right)$$

$$= -(88.7 - 92.9) \frac{\text{J}}{\text{K mol}} = +4.2 \frac{\text{J}}{\text{K mol}}$$

$\frac{d\Delta G^\circ}{dT} > 0 \Rightarrow$ aragonite is less stable as T is raised

c) If the pressure is raised, will ΔG° become negative?

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_m = V_m(\text{anag.}) - V_m(\text{calc.}) = (35.36 - 36.93) \frac{\text{cm}^3}{\text{mol}}$$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = -\left(1.57 \frac{\text{cm}^3}{\text{mol}} \times \frac{10^{-6} \text{m}^3}{\text{cm}^3}\right) = -1.57 \times 10^{-6} \frac{\text{m}^3}{\text{mol}} \quad (\text{SI units})$$

(Q3 c cont.)

$$\left(\frac{\partial \Delta G_r}{\partial P}\right)_T = -\left(1.57 \times 10^{-6} \frac{\text{J}}{\text{Pa}}\right) \left(\frac{10^5 \text{ Pa}}{\text{bar}}\right) = -0.157 \frac{\text{J}}{\text{bar}}$$

ΔG_r decreases by 0.157 J per bar as the pressure is raised. ΔG_r is +1040 J at 1 bar.

Pressure to make aragonite stable at 25 °C =

$$\frac{1040 \text{ J}}{0.157 \text{ J/bar}} = \boxed{6624 \text{ bar}}$$

(Q4) a) As the temperature is reduced at 1 atm, solid rhombic sulfur is stable.

b) No. Heating monoclinic sulfur forms liquid sulfur or sulfur vapor.

c) Yes. Raising the pressure converts monoclinic sulfur to rhombic sulfur.

d) minimum temperature for monoclinic sulfur
 $\boxed{95.31 \text{ °C}}$ (rhombic, monoclinic, vapor triple point)

maximum temperature for monoclinic sulfur
 $\boxed{153 \text{ °C}}$ (rhombic, monoclinic, liquid triple point)