Physical Equilibrium

\[ \Delta G \ & \text{phase changes} \]

CHEM 102
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\[ \Delta G : H_2O(l) \rightleftharpoons H_2O(g) \]

\[ \begin{align*}
\Delta G &\approx \Delta H - T \Delta S \\
\Delta G &_{298} = 5.65 \text{kJ/mol} \\
\Delta G &_{298} = 23.36 \text{kJ/mol} \\
\Delta S &_{0} = 28.9 \text{J/mol K} \\
\Delta S &_{0} = 97.5 \text{J/mol K}
\end{align*} \]

\[ \Delta G \ & \text{phase changes:} \]

Example: \( H_2O(l) \rightleftharpoons H_2O(g) \)

\[ \begin{align*}
\text{For } P &= 1 \text{ atm}; \quad T < 373 \text{ K} (100 ^\circ \text{C}) \quad \Delta G > 0 \\
\text{(we know water doesn’t boil below 100 \(^\circ\text{C}\))}
\end{align*} \]

\[ \begin{align*}
\text{For } P &= 1 \text{ atm}; \quad T > 373 \text{ K} \quad \Delta G < 0 \\
\text{For } P &= 1 \text{ atm}; \quad T = 373 \text{ K} \quad \Delta G = 0
\end{align*} \]

At the boiling point, the liquid and vapor are in equilibrium. The boiling point is defined as the temp. at which the liquid and vapor phases are at equilibrium at 1 atm.

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\end{align*} \]

\[ \begin{align*}
\text{We saw that at } 298 \text{ K, } \Delta G &> 0 \\
\text{But } \langle \Delta H_{298}/\Delta S_{298} \rangle &= \langle 44.0/0.119 \rangle \text{ K} = 370 \text{ K} \text{ this is close to } 373 \text{ K, the boiling point! Why?} \\
\text{rearrange: } \Delta H_{298} &= (370 \text{ K}) \Delta S_{298} \\
\Delta H_{298} &= (370 \text{ K}) \Delta S_{298} = 0 \\
\text{recall: } \Delta H_{373} &= \Delta G_{373} = 0 \text{ (why?)} \\
\text{if } \Delta H_{373} &= \Delta H_{298} \text{ and } \Delta S_{373} = \Delta S_{298} \\
\text{then } \Delta G_{373} &= 0 = \Delta H_{298} - (373 \text{ K})\Delta S_{298}
\end{align*} \]

Generalization

\[ \Delta H \text{ and } \Delta S \text{ often don’t change much for a process or reaction from } \Delta H_{298} \text{ and } \Delta S_{298} \]

\[ \text{Often, can estimate for } \Delta G \text{ at other temps.: } \]

\[ \Delta G(T) \approx \Delta H_{298} - T\Delta S_{298} \]

Ex: Phase transitions for NH₃

The molar enthalpy and entropy of melting and vaporization for ammonia are given below. Estimate the melting and boiling points of ammonia.

\[\begin{align*}
\text{NH}_3(s) &\rightarrow \text{NH}_3(l) \quad \text{NH}_3(l) \rightleftharpoons \text{NH}_3(g) \\
\Delta H^\circ &\approx 5.65 \text{kJ/mol} \quad 23.36 \text{kJ/mol} \\
\Delta S^\circ &\approx 28.9 \text{J/mol K} \quad 97.5 \text{J/mol K}
\end{align*}\]
Example: Allotropes of Tin

Solid tin exists in two common forms (allotropes), “white” and “gray” tin. The standard molar enthalpy and molar free energy for the transformation between these two allotropes are given below.

\[
\text{Sn}_{\text{white}} \rightarrow \text{Sn}_{\text{gray}}
\]

\[
\Delta H^\circ = -2.090 \text{ kJ/mol}; \quad \Delta G^\circ = 0.130 \text{ kJ/mol}
\]

(a) Under standard conditions (298 K, 1 atm), which allotrope is thermodynamically stable?

(b) The standard molar entropy, \(S^\circ\), of gray tin is 44.14 J mol\(^{-1}\) K\(^{-1}\). What is the standard molar entropy of white tin?

(c) The melting point of tin is 505 K. For temperatures below 505 K, give the temperature ranges (if any) over which white and gray tin are the most stable allotropes.

Phase Diagrams

- All phase changes are determined by \(\Delta G\), phases are in equilibrium when \(\Delta G = 0\).
- P-T phase diagrams tell us what phases are stable at various values of \(T\) and \(P\).
- A line separating two regions of a phase diagram represents the temperatures and pressures where \(\Delta G = 0\) for the change from one phase to another.

Free Energies and Phase Diagrams

P-T Phase diagram for \(\text{H}_2\text{O}\)

P-T Phase diagram for \(\text{CO}_2\)

note: normal boiling point is not defined for \(\text{CO}_2\).
Phase diagram for NH₃
The triple point for ammonia occurs at 195.4 K, 0.60 atm. Draw an approximate phase (P-T) diagram for ammonia; label the gas, liquid, and solid regions. Include a dashed line on your drawing corresponding to a pressure of 1 atm. Be sure that the points you have obtained from part (a) and the triple point appear at the proper places on your drawing. \( T_m = 195.5 \text{ K}, T_b = 239.6 \text{ K} \)

Example - continued
(a) At 368.5 K, \( \Delta H = 402 \text{ J/mol} \) for this process. What is \( \Delta S \) for this process at 368.5 K?
(b) What must be the sign of \( \Delta G^\circ \) for this process? Estimate the value of \( \Delta G^\circ \).
(c) Bonus! Monoclinic sulfur is a little less dense than orthorhombic sulfur: \( \Delta V \equiv + 0.4 \text{ cm}^3/\text{mol} \)
For a \( P = 100 \text{ bar} \), estimate the transition temp. (Hint: assume \( \Delta E \) and \( \Delta S \) don’t depend on pressure.) 1.0 L-bar = 100 J

Allotropes of Sulfur (Example)
At a pressure of 1 atm, orthorhombic sulfur is stable below 368.5 K, monoclinic sulfur is stable above 368.5 K, and these two forms are stand at equilibrium at 368.5 K (the transition temp.). Consider the process: \( S_{\text{orthorhombic}} \rightarrow S_{\text{monoclinic}} \)

Critical Properties

Gas-Liquid Equilibrium

\( G_{\text{sq}} = G_{\text{qg}} = G_{\text{gg}} \)}

\[ f = c \cdot p + 2 \]

One Component: \( f = 3 \cdot p \)

\[ f = \# \text{ of degrees of freedom} \]

\[ p = \# \text{ of phases} \]

\[ c = \# \text{ of components} \]
Recall: Henry’s Law
Solubility \(s\) of a gas in a liquid is proportional to the partial pressure of the gas:
\[ s = k_H P \]
- Henry’s constant, \(k_H\), depends on the strength of solvent-solute intermolecular forces and temperature.
- E.g., \(k_H\) for \(O_2\) in water is \(1.3 \times 10^{-3}\) mol\(\text{L}^{-1}\text{atm}^{-1}\) at 20 °C. Is the number of \(O_2\) molecules per liter greater in water or in air?

Boiling, Vapor Pressures
- The boiling point of a substance is temperature at which the equilibrium vapor pressure of the gas over the liquid reaches 1.0 atm.

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \]

Recall: \(\text{H}_2\text{O}\) Phase Diagram

\[ \Delta G, \Delta G^\circ, \text{and Equilibrium} \]
- Text gives this equation for any equilibrium:
\[ \Delta G = \Delta G^\circ + RT \ln Q \quad \text{p. 876 (eqn. 19.6)} \]
- \(\Delta G^\circ\) is the standard molar (\(P = 1\) bar, \(n = 1\) mol) free energy and “\(Q\)” is the reaction quotient. When a system is at equilibrium \(Q\) is numerically equal to \(K_{eq}\), the equilibrium constant.
- This expression can be applied the physical and chemical equilibria, as long as we are careful to use the correct expression the “equilibrium constant.”
Phase Equilibria

- For molecules or ions dissolved in solution, equilibria involve concentrations. For gases, equilibria involve pressures.
- When a solid or liquid is in equilibrium with a gas, the "concentration" of the condensed phase = 1.0. Also, when a solid is in equilibrium with dissolved species, the "concentration" of the solid = 1.0.

Gas-Liquid and Gas-Solid Equilibria

\[ H_2O(l) \rightleftharpoons H_2O(g) \quad \text{and} \quad CO_2(s) \rightleftharpoons CO_2(g) \]

- When gases are nearly ideal (usually OK), activity is numerically equal to pressure (in bar).
- There is no "concentration" of \( H_2O(l) \) or \( CO_2(s) \) in these expressions. As long as at least some \( H_2O(l) \) or \( CO_2(s) \) are present, the equilibrium vapor pressures of the gases will not depend on how much of the condensed phases there are.

Vapor Pressure, Quantitative Relationship

\[ H_2O(l) \rightleftharpoons H_2O(g) \]

- Now we can get the relationship between pressure and the "boiling temperature'.
- \( K = p_{H_2O} = \exp(-\Delta G_{vap}/RT) \Rightarrow \ln p_{H_2O} = -\Delta G_{vap}/RT \)

Temperature Dependence of \( K_{eq} \)

- \( \ln K_{eq} = -\Delta G/RT \) and \( \Delta G = \Delta H - T\Delta S \Rightarrow \)
- \( \ln K_{eq} \approx -\Delta H/RT + \Delta S/RT \)

For vapor pressure equilibrium, \( K_{eq} = P \) and the relevant enthalpy and entropy terms are \( \Delta H_{vap} \) and \( \Delta S_{vap} \).
- \( \ln (P_2/P_1) \approx - (\Delta H_{vap}/R)(1/T_2 - 1/T_1) \)
  The Clausius-Clapeyron equation
- Assume, as before, that \( \Delta H \) and \( \Delta S \) don’t change much as a function of temp. \( (\Delta H \approx \Delta H_{vap}; \Delta S \approx \Delta S_{vap}) \), then a plot of \( P \) vs. \( 1/T \) gives \( \Delta H_{vap} \) and \( \Delta S_{vap} \).

Problem

The normal boiling point of iodomethane, \( CH_3I \), is 42.43 °C and its vapor pressure at 0 °C is 140 torr. Calculate
(a) standard enthalpy of vaporization (\( \Delta H_{vap} \)) of iodomethane
(b) standard entropy of vaporization (\( \Delta S_{vap} \)) of iodomethane
(c) the vapor pressure of \( CH_3I \) at 25 °C

Problem

\[ CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \]

- limestone → lime

Given:
\( \Delta H = +178 \text{ kJ} \) at 25 °C, \( K_p = 1.39 \times 10^{-23} \)
- Give an estimate for \( K_p \) at 800 °C.
The process is in equilibrium when rate of ions (or molecules) leaving the solid = rate returning to the solid. That is, when dissolution rate = precipitation rate.

Solubility Product, $K_{sp}$

$$A_xX_y(s) \rightleftharpoons x \ X^{y+}(aq) + y \ X^{y-}(aq)$$

(eg., $\text{BaCl}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \ \text{Cl}^-(aq)$)

- What is the form for the equilibrium constant?

$$K_{eq} = \frac{\text{activities of products}}{\text{activities of reactants}} \quad \text{(at equilibrium)}$$

- Write the equilibrium constant expression.