• P6.5) The pressure dependence of \( G \) is quite different for gases and condensed phases. Calculate \( G_m(C, \text{ solid, graphite, 100 bar, 298.15 K}) \) and \( G_m(\text{He, g, 100 bar, 298.15 K}) \) relative to their standard state values. By what factor is the change in \( G_m \) greater for \( \text{He} \) than for graphite?

\[
\Delta G_m = G_m(P, T^0) - G_m(P^0, T^0) = \int_{P_0}^{P} V_m dP^n
\]

\[
\Delta G_m(\text{graphite}) = [Q1] \\
\Delta G_m(\text{He}) = [Q2]
\]
P6.8) Calculate $\Delta G^0$ and $\Delta A^0$ for the reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(l)$ at 298 K from the combustion enthalpy of methane and the entropies of the reactants and products.

- $\Delta G^0$ reaction is easy to obtain.
- $\Delta G^0 = \Delta H^0_{\text{reaction}} - T\Delta S^0_{\text{reaction}}$

The question is how to get $\Delta A^0$ reaction

- $\Delta A^0_{\text{reaction}} = \Delta G^0_{\text{reaction}} - \Delta(PV)$

Q. How do you get this $\Delta(PV)$?
We had a similar question between $U$ and $H$.

---

6.7 Expressing Chemical Equilibrium in Terms of the $\mu_i$

- $m_A A + m_B B + m_C C \ldots \rightarrow m_M M + m_N N + m_O O$
- We write the reaction in an abbreviated form as $-m_A A - m_B B - m_C C \ldots + m_M M + m_N N + m_O O = 0 \rightarrow$
- $\sum v_i X_i = 0$ ($v_i = -m_i$ if $X_i$ is a reactant; $v_i = m_i$ if $X_i$ is a product).
- $dG$ associated with change in $n_i$ is given by $dG = \sum \mu_i dn_i$ (*)

Now, we introduce **extent of the reaction** $\xi$ ($0 \leq \xi \leq 1$)

- $n_i = n_i^{\text{initial}} + \xi v_i$ $\rightarrow$ $dn_i = v_i \, d\xi$

- $n_i = n_i^{\text{initial}} + \xi v_i = m_i(1 - \xi)$ for reactant
- $= m_i \xi$ for product

when 100$\xi$ % of reactants reacted.
HW Q2 (text P126-127)

• $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$

\[ (2 - 2\xi) \text{ mole} \quad \xi \text{ mole} \]

\[ G_{\text{pure}} = (2 - 2\xi)G_{m,\text{NO}_2}^0 + \xi G_{m,\text{N}_2\text{O}_4}^0 \]

\[ G_{\text{mixture}} = G_{\text{pure}} + \Delta G_{\text{mix}} \]

\[ \Delta G_{\text{mix}} = n_{\text{NO}_2}RT\ln(x_{\text{NO}_2}) + n_{\text{N}_2\text{O}_4}RT\ln(x_{\text{N}_2\text{O}_4}) \]

Q1. How much is $\Delta G_{\text{reaction}}^0$?

$\Delta G_{\text{reaction}}^0 = [Q1]$  

Q2. How much is $\Delta G_{\text{reaction}}$?

$\Delta G_{\text{reaction}} = [Q2]$

Q3. Where is the equilibrium point?

---

HW Q3 (text P126-127)

• $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$

\[ (2 - 2\xi) \text{ mole} \quad \xi \text{ mole} \]

\[ G_{\text{pure}} = (2 - 2\xi)G_{m,\text{NO}_2}(T) + \xi G_{m,\text{N}_2\text{O}_4}(T) \]

\[ G_{\text{mixture}} = G_{\text{pure}} + \Delta G_{\text{mix}} \]

\[ \Delta G_{\text{mix}} = n_{\text{NO}_2}RT\ln(x_{\text{NO}_2}) + n_{\text{N}_2\text{O}_4}RT\ln(x_{\text{N}_2\text{O}_4}) \]

Q1. How do you read $G_{m,\text{N}_2\text{O}_4}$ from the graph below?

Q2. How about $G_{m,\text{NO}_2}$?

\[ T = 350 \text{ K} \]

\[ x_{\text{NO}_2} = \frac{n_{\text{NO}_2}}{n_{\text{NO}_2} + n_{\text{N}_2\text{O}_4}} = \frac{(2-2\xi)}{(2-\xi)} \]

\[ x_{\text{N}_2\text{O}_4} = \frac{n_{\text{N}_2\text{O}_4}}{n_{\text{NO}_2} + n_{\text{N}_2\text{O}_4}} = \frac{\xi}{(2-\xi)} \]

Q3. Where is the equilibrium point?
6.7 Expressing Chemical Equilibrium in Terms of the $\mu_i$

- $m_A A + m_B B + m_C C \ldots \rightarrow m_M M + m_N N + m_O O$
- We write the reaction in an abbreviated form as
  - $-m_A A - m_B B - m_C C \ldots + m_M M + m_N N + m_O O = 0$ \rightarrow
- $\sum \nu_i X_i = 0$ ($\nu_i = -m_i$ if $X_i$ is a reactant; $\nu_i = m_i$ if $X_i$ is a product).
- $dG$ associated with change in $n_i$ is given by
  \[ dG = \sum \mu_i \nu_i \, dn_i \quad (*) \]

Now, we introduce **extent of the reaction** $\xi$ ($0 \leq \xi \leq 1$)

\[ n_i = n_i^{\text{initial}} + \xi \nu_i \rightarrow dn_i = \nu_i \, d\xi \]

From (*)

\[ dG = \sum \mu_i \nu_i \, d\xi = \Delta G_{\text{reaction}} \, d\xi \]

\[ (\partial G / \partial \xi)_{T,P} = \sum \nu_i \mu_i = \Delta G_{\text{reaction}}. \]

$(\partial G / \partial \xi)_{T,P} = 0 \rightarrow$ System reaches equilibrium.

---

**Reaction Gibbs Energy (p127)**

- **For a compound**, consider a formation reaction from elements $(A, B)$: $A + 2B \rightarrow C$
  \[ \Delta G_f^0 = G_{m,C}^0 - G_{m,A}^0 - 2G_{m,B}^0 \]

- **For a reaction** $(P_A=P_B=P_C=P_D=1\text{bar})$: $A + 2B \rightarrow C + 2D$
  \[ \Delta G_{\text{reaction}} = G_{m,C}^0 + 2G_{m,D}^0 - G_{m,A}^0 - 2G_{m,B}^0 \]
  \[ = \Delta G_{f,C}^0 + 2 \Delta G_{f,D}^0 - \Delta G_{f,A}^0 - 2 \Delta G_{f,B}^0 \]

In general,
  \[ \Delta G_{\text{reaction}} = \sum \nu_i \Delta G_{f,i}^0 \]

- $\Delta G_f^0 = G_{m,\text{product}}^0 + \sum \nu_i G_{m,\text{reactant}}^0$

For a pure element, $\Delta G_f^0 = [Q1]$
6.8 Calculating \( \Delta G_{\text{reaction}} \) and Introducing the Equilibrium Constant for a Mixture of Ideal Gas

\[ \begin{align*}
\Delta G_{\text{reaction}} &= \sum v_i \Delta G_{f.i} = 3 \Delta G_{f.C}(P_C) + \Delta G_{f.D}(P_D) \\
&\quad - 2 \Delta G_{f.A}(P_A) - \Delta G_{f.B}(P_B) \\
&= 3 \mu_0^C + 3R \ln(P_C/P^0) + \mu_0^D + R \ln(P_D/P^0) \\
&\quad - 2 \mu_0^A - 2R \ln(P_A/P^0) - \mu_0^B - R \ln(P_B/P^0) \\
&= 3 \mu_0^C + \mu_0^D - 2 \mu_0^A - \mu_0^B
\end{align*} \]

\[ \begin{align*}
\Delta G_{\text{reaction}} &= \sum v_i \Delta G_{f.i} = \Delta G_{\text{reaction}}^0 + [Q1] \\
Q. \text{What is } \Delta G_{\text{reaction}}^0 ?
\end{align*} \]

6.8 Continued

\[ \begin{align*}
\Delta G_{\text{reaction}} &= \sum v_i \Delta G_{f.i} = \Delta G_{\text{reaction}}^0 + \sum v_i R \ln(P_i/P^0) \\
&= \Delta G_{\text{reaction}}^0 + RT \ln K_p \\
\text{Thermodynamic Equilibrium Const}
\end{align*} \]

\[ K_p = \exp(-\Delta G_{\text{reaction}}^0/RT) \] (at 298K)

When \( A \leftrightarrow B \) \( \Rightarrow K_p = P_A/P_B = \exp(-\Delta G^0/RT) \)
6.9 Calculating the Equilibrium Partial Pressure in a Mixture of Ideal Gases

\[ \text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g) \]

For the reaction above, derive an expression for \( K_p \) in terms of \( n_0 \), \( \xi \), and \( P \) assuming the reaction starts from \( n_0 \) mole of \( \text{Cl}_2 \).

\[
K_p = \exp\left(-\frac{\Delta G_{\text{reaction}}^0}{RT}\right)
\]

\[
\Delta G_{\text{reaction}}^0 = 2\Delta G_{f, \text{Cl}}^0 - \Delta G_{f, \text{Cl}_2}^0
\]

6.10 Variation of \( K_p \) with \( T \)

\[
\frac{d\ln(K_p)}{dT} = -\frac{d(\Delta G_{\text{reaction}}^0 / RT)}{dT} = -\frac{1}{R} \frac{d(\Delta G_{\text{reaction}}^0 / T)}{dT} = \frac{\Delta H_{\text{reaction}}^0}{RT^2}
\]

\[
\begin{align*}
\rightarrow dT &> 0 \text{ & } \Delta H > 0 \rightarrow d\ln(K_p) > 0 \\
\text{More product} &\\
\end{align*}
\]

\[
\begin{align*}
\rightarrow dT &> 0 \text{ & } \Delta H < 0 \rightarrow d\ln(K_p) < 0 \\
\text{Less product} &
\end{align*}
\]

\[
\Delta\ln(K_p) = \ln\{K_p(T_{\text{fin}})\} - \ln\{K_p(T_{\text{ini}})\} = \int_{T_{\text{ini}}}^{T_{\text{fin}}} \frac{\Delta H_{\text{reaction}}^0}{RT^2} \, dT
\]

\[
= \left[ -\frac{\Delta H_{\text{reaction}}^0}{RT} \right]_{T_{\text{ini}}}^{T_{\text{fin}}} = -\frac{\Delta H_{\text{reaction}}^0}{RT} \left[ \frac{1}{T_{\text{fin}}} - \frac{1}{298} \right]
\]

\[
\begin{align*}
\ln\{K_p(T_{\text{fin}})\} &= \ln\{K_p(298)\} - \frac{\Delta H_{\text{reaction}}^0}{R} \left[ \frac{1}{T_{\text{fin}}} - \frac{1}{298} \right]
\end{align*}
\]

\[
\Delta G_{\text{reaction}}(T)/RT_f = -\Delta G_{\text{reaction}}^0/RT_0
\]
7.10 Conformational Transitions of Biological Polymers

\[ N \leftrightarrow D \]
\[ C_{\text{in}}(1-f_D) \quad C_{\text{in}}f_D \]

\[ K = \frac{C_D}{C_N} = \frac{f_D C_{\text{in}}}{f_N C_{\text{in}}} = \frac{f_D}{1-f_D} \]

At \( T_m \rightarrow K = 1 \) & \( f_D = 0.5 \)

- **HW 7 P6.18** Many biological macromolecules undergo a transition called *denaturation*. Denaturation is a process whereby a structured, biological active molecule, called the native form, unfolds or becomes unstructured and biologically inactive. The equilibrium is \( N \) (Native) \( \leftrightarrow \) \( D \) (Denatured)

- For a protein at \( pH = 2 \), the enthalpy change associated with denaturation is \( \Delta H^\circ = 418.0 \text{ kJ mol}^{-1} \) and the entropy change is \( \Delta S^\circ = 1.3 \text{ kJ K}^{-1} \text{ mol}^{-1} \).

  a. Calculate the Gibbs energy change for the denaturation of the protein at \( pH = 2 \) and \( T = 303 \text{ K} \). Assume the enthalpy and entropy are temperature independent between 298.15 and 303 K.

  \[ \Delta G_D^\circ (298K) = \left[ Q1 \right] \]

  \[ \Delta G_D(T_2) = T_2 \left[ \Delta G_D(T_1) / T_1 \right] + \left[ Q2 \right] \]

  b. Calculate the equilibrium constant for the denaturation of protein at \( pH = 2 \) and \( T = 303 \text{ K} \).

  \[ K_D(T_2) = \exp(- \Delta G_D/(RT_2)) \]

  c. Based on your answers for parts (a) and (b), is protein structurally stable at \( pH = 2 \) and \( T = 303 \text{ K} \)?
6.11 Equilibria Involving Ideal Gases and Solid or Liquid Phase

- We consider equilibrium in a thermal decomposition of CaCO₃:
  \[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

In this case, gas (CO₂) is in equilibrium with two solid phase (CaCO₃ & CaO)

\[ \Delta G_{\text{reaction}} = \sum \gamma_i \mu_i = 0 \]

\[ 0 = \mu_{\text{eq}(\text{CaO},s,P)} + \mu_{\text{eq}(\text{CO}_2,g,P)} - \mu_{\text{eq}(\text{CaCO}_3,s,P)} \]

\[ 0 = \mu^0_{\text{eq}(\text{CaO},s)} + \mu^0_{\text{eq}(\text{CO}_2,g)} - \mu^0_{\text{eq}(\text{CaCO}_3,s)} + RT \ln \left( \frac{P_{\text{CO}_2}}{P^0} \right) \]

\[ \Delta G^0_{\text{reaction}} = -RT \ln \left( \frac{P_{\text{CO}_2}}{P^0} \right) \]

6.12 Expressing the Equilibrium Constant in Terms of Mole Fraction

\[ K_p = \left( \frac{P_{\text{eq}}}{P^0} \right)^{nc} \left( \frac{P_{\text{eq}}}{P^0} \right)^{nD} = \left( \frac{X_{\text{eq}}P}{P^0} \right)^{nc} \left( \frac{X_{\text{eq}}P}{P^0} \right)^{nD} \]

\[ = \left( \frac{X_{\text{eq}}}{X^\Delta} \right)^{nc} \left( \frac{X_{\text{eq}}}{X^\Delta} \right)^{nD} \left( P \right)^{mc+mD-mA-mB} \]

\[ = K_X \left( \frac{P}{P^0} \right)^{\Delta \nu} \]

\[ K_X = K_p \left( \frac{P}{P^0} \right)^{\Delta \nu} \]
**HW7 P6.14**  Consider the equilibrium
\[ \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2}\text{O}_2(g) \]
One mole of \( \text{NO}_2(g) \) is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the contents of the vessel gives the following results:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( P_{\text{NO}}/P_{\text{NO}_2} )</th>
<th>( \frac{P_{\text{NO}}}{P_{\text{NO}_2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 K</td>
<td>0.872</td>
<td>0.872</td>
</tr>
<tr>
<td>800 K</td>
<td>2.50</td>
<td>2.50</td>
</tr>
</tbody>
</table>

\[ P_{\text{NO}} = x_{\text{NO}} = n_{\text{NO}} = \frac{y}{1-y} \]

**a. Calculate \( K_p \) at 700 and 800 K.**

\[
K_p = \frac{\left( \frac{p(\text{NO})}{p^{1/2} \text{p}} \right)^{1/2} \left( \frac{p(\text{O}_2)}{p} \right)^{1/2}}{\left( \frac{p(\text{NO}_2)}{p} \right)^{1/2}} = \frac{p(\text{NO})}{p(\text{NO}_2)} \times \frac{p(\text{O}_2)}{p} = \frac{(x_{\text{NO}})(x_{\text{O}_2})}{x_{\text{NO}_2}} \times \frac{p^{1/2}}{p^{1/2}}
\]

**b. Calculate \( \Delta G^0_{\text{reaction}} \) for this reaction at 298.15 K, assuming that \( \Delta H^0_{\text{reaction}} \) is independent of temperature.**

---

**HW8 P6.15**

**a. Calculate \( K_p \) and \( \Delta H^0 \) at 1000 K.**

\[ \text{CO(g) + H}_2\text{O(g)} \leftrightarrow \text{CO}_2(g) + \text{H}_2(g) \]

At 1000 K, the composition of the reaction mixture is

<table>
<thead>
<tr>
<th>Substance (g)</th>
<th>CO(g)</th>
<th>H2(g)</th>
<th>CO2(g)</th>
<th>H2O(g)</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>27.1</td>
<td>27.1</td>
<td>22.9</td>
<td>22.9</td>
<td>Mole %</td>
</tr>
</tbody>
</table>

**b. Given the answer to part (a), use the \( \Delta H_J^0 \) of the reaction species to calculate \( \Delta G^0_{\text{reaction}} \) at 298.15 K. Assume that \( \Delta H^0_{\text{reaction}} \) is independent of temperature.**

\[ K_p = \frac{x_{\text{CO}} x_{\text{H}_2} x_{\text{H}_2\text{O}}}{x_{\text{CO}} x_{\text{H}_2\text{O}} x_{\text{CO}} x_{\text{H}_2\text{O}}} \times \left[ \text{Q1} \right] = \left[ \text{Q2} \right] \]

\[ \Delta G_{\text{reaction}}(T) = -RT \ln K_p(T) \]

\[
\ln \{ K_p(T_{\text{mo}}) \} = \ln \{ K_p(298 \text{ K}) \} - \frac{\Delta H^0_{\text{reaction}}}{R} \left[ \frac{1}{T_{\text{mo}}} - \frac{1}{298 \text{ K}} \right]
\]
6.7 Expressing Chemical Equilibrium in Terms of the $\mu_i$

- $m_A A + m_B B + m_C C \ldots \rightarrow m_M M + m_N N + m_O O$
- We write the reaction in an abbreviated form as 
  $-m_A A - m_B B - m_C C \ldots + m_M M + m_N N + m_O O = 0$
- $\sum \nu_i X_i = 0 \ (\nu_i = -m_i$ if $X_i$ is a reactant; $\nu_i = m_i$ if $X_i$ is a product).

Q11 From the following data at 298.15 K and 1 bar, choose the closest value to the standard formation enthalpy for CO(g).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction enthalpy (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A × $\text{Fe}_2\text{O}_3(s) + 3\text{C(graphite)} \rightarrow 2\text{Fe(s)} + 3\text{CO(g)}$</td>
<td>493</td>
</tr>
<tr>
<td>B × $\text{FeO(s)} + \text{C(graphite)} \rightarrow \text{Fe(s)} + \text{CO(g)}$</td>
<td>156</td>
</tr>
<tr>
<td>C × $\text{CO}_2(g) \rightarrow \text{CO(g)} + 1/2\text{O}_2(g)$</td>
<td>283</td>
</tr>
<tr>
<td>D × $\text{Fe(s)} + 1/2\text{O}_2(g) \rightarrow \text{FeO(s)}$</td>
<td>-266</td>
</tr>
</tbody>
</table>

$2A \text{Fe(s)} + 3A \text{CO(g)} - A \text{Fe}_2\text{O}_3(s) -3A \text{C(grap)} = 0$

$B \text{Fe(s)} + B \text{CO(g)} - B \text{FeO(s)} -B \text{C(grap)} = 0$

$C \text{CO(g)} + C/2 \text{O}_2(g) - C \text{CO}_2(g) = 0$

$D \text{FeO(s)} - D \text{Fe(s)} - D/2 \text{O}_2(g) = 0$

$(2A + B - D) \text{Fe(s)} + (3A + B + C) \text{CO(g)} - A\text{Fe}_2\text{O}_3 - (3A + B) \text{C(grap)} = 0$

$(-B + D) \text{FeO(s)} - C \text{CO}_2(g) + (C/2 - D/2) \text{O}_2(g) = 0$
7.1 What Determines the Relative Stability of the Solid, Liquid, and Gas Phase

• Phase: Solid $\rightarrow$ Liquid $\rightarrow$ Gas

Phase refers to “a form of matter that is uniform with respect to chemical composition and the state of aggregation”

Q. What determines most stable phase?

[Answer here?]

How does $\mu$ in three phases depends on $T$?

$$d\mu(T, P) = -S_m dT + V_m dP = -S_m dT$$

$$0 < S_{m, solid}(T) < S_{m, liquid}(T) < S_{m, gas}(T)$$

Assuming $S_m$ is constant,

$$\mu(T, P) = \mu(0, P) - S_m T$$

Q1. Where is the melting point?

Q2. Which line represents $\mu_{solid}(T)$?

Q3. How do you explain the phase transition from solid to liquid using the figure?
$\mu(T)$ plot when $P$ is increased

- How are $T_m$ and $T_b$ affected by $P$?

$\mu(T, P + \Delta P) \approx \{\mu(0, P) + V_m \Delta P\} - S_m T$

$V_m^{\text{Gas}} > V_m^{\text{Liquid}} > V_m^{\text{Solid}}$

$V_m^{\text{Gas}} > V_m^{\text{Solid}} > V_m^{\text{Liquid}}$

---

Sublimation and Triple Point

Sublimation Temp

$\text{Solid} \rightarrow \text{Gas}$

Solid, Gas, and Liquid Coexist

Triple Point

---

Triple Point Temp
### 7.2 The Pressure-Temperature Phase Diagram

**Isobar T Increases**
- S $\rightarrow$ L $\rightarrow$ G  
  (P higher than triple point Pressure)
- b) S $\rightarrow$ G  
  (P lower than triple point P)

**Isotherm; P Increases**
- c) G $\rightarrow$ L $\rightarrow$ S  
  (T higher than triple point T)

**L-G coexists above critical point**
(T $\geq T_c$, P $\geq P_c$)

---

**P7.3**) Within what range can you restrict the values of $P$ and $T$ if the following information is known about CO$_2$? Use Figure 7.8 to answer this problem.

**a.** As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.

**b.** As the pressure on a cylinder containing pure CO$_2$ is increased from 65 to 80 atm, no interface delineating liquid and gaseous phases is observed.

**c.** Solid, liquid, and gas phases coexist at equilibrium.

**a.** $5.11$ atm $< P < 73.75$ atm
7.4 Providing a Theoretical Basis for the P-T Phase Diagram

- When two phase \( \alpha \) and \( \beta \) are in equilibrium at a constant \( P \) and \( T \),
  \[ \mu_\alpha(P, T) = \mu_\beta(P, T) \]
  When \( (P,T) \) is changed by \( (dP,dT) \) while keeping the equilibrium,
  \[ \mu_\alpha(P, T) + d\mu_\alpha = \mu_\beta(P, T) + d\mu_\beta \]
  Thus,
  \[ d\mu_\alpha = d\mu_\beta \]
  \[ -S_{m\alpha}dT + V_{m\alpha}dP = -S_{m\beta}dT + V_{m\beta}dP \]
  \[ 0 = (S_{m\beta} - S_{m\alpha})dT - (V_{m\beta} - V_{m\alpha})dP = \Delta S_m dT - \Delta V_m dP \]

Clapeyron equation

\[ \frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \]

d\( P/dT \) for fusion and vaporization

For Fusion

Average of \( \Delta S_m \) and \( \Delta V_m \) for Ag, AgCl, Ca, CaCl\(_2\), KCl, Na, NaCl

\[ \left( \frac{dP}{dT} \right)_{\text{fusion}} = \frac{\Delta S_{m\text{fusion}}}{\Delta V_{m\text{fusion}}} \sim 22 \text{ J mol}^{-1} \text{ K}^{-1} \]
\[ \pm 4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \]
\[ = \pm 5.5 \times 10^6 \text{ Pa K}^{-1} \]

\( (dT/dP)_{\text{fusion}} \sim 0.05 \text{ K bar}^{-1} \)

Negative sign only for \( H_2O \)

For Vaporization

Average of \( \Delta S_m \) and \( \Delta V_m \) in Table 7.3

\[ \left( \frac{dP}{dT} \right)_{\text{vap}} = \frac{\Delta S_{m\text{vap}}}{\Delta V_{m\text{vap}}} \sim 95 \text{ J mol}^{-1} \text{ K}^{-1} \]
\[ 2 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} \]
\[ = 5.0 \times 10^3 \text{ Pa K}^{-1} = 5 \times 10^2 \text{ bar K}^{-1} \]

\( (dT/dP)_{\text{vap}} \sim 20 \text{ K bar}^{-1} \)
7.5 Using the Clapeyron Equation to Calculate Vapor Pressure as a Function of \( T \)

**For Vaporization**

\[
\left( \frac{dP}{dT} \right)_{vap} = \frac{\Delta S_{m}^{vap}}{\Delta V_{m}^{vap}} = \frac{\Delta H_{m}^{vap}}{\Delta V_{m}^{vap}T} = \frac{\Delta H_{m}^{vap}}{V_{m,\text{gas}}T} = \frac{P \Delta H_{m}^{vap}}{RT^{2}}
\]

\[
\frac{1}{P} dP = \frac{\Delta H_{m}^{vap}}{nR} \frac{1}{T^{2}} dT
\]

Clausius-Clapeyron equation

\[
\int_{P_{\text{ini}}}^{P_{\text{fin}}} \frac{1}{P} dP = \int_{T_{\text{ini}}}^{T_{\text{fin}}} \frac{\Delta H_{m}^{vap}}{R} \frac{1}{T^{2}} dT
\]

\[
\ln \frac{P_{\text{fin}}}{P_{\text{ini}}} = -\frac{\Delta H_{m}^{vap}}{R} \left( \frac{1}{T_{\text{fin}}} - \frac{1}{T_{\text{ini}}} \right)
\]

---

**P6.17** If the reaction \( \text{Fe}_2\text{N}(s) + \frac{3}{2}\text{H}_2(g) \rightarrow 2\text{Fe}(s) + \text{NH}_3(g) \) comes to equilibrium at a total pressure of 1 bar, analysis of the gas shows that at 700 and 800 K, \( P_{\text{NH}_3}/P_{\text{H}_2} = 2.165 \) and 1.083, respectively, if only \( \text{H}_2(g) \) was initially present in the gas phase and \( \text{Fe}_2\text{N}(s) \) was in excess.  

a. Calculate \( K_p \) at 700 and 800 K.  
b. Calculate \( \Delta S_{\text{reaction}}^{0} \) at 700 and 800 K and \( \Delta H_{\text{reaction}}^{0} \) assuming that it is independent of temperature.  
c. Calculate \( \Delta G_{\text{reaction}}^{0} \) for this reaction at 298.15 K.

- \( \text{Fe}_2\text{N}(s) + \frac{3}{2}\text{H}_2(g) \rightarrow 2\text{Fe}(s) + \text{NH}_3(g) \)

  \[
  N_{\text{ini}} - \xi = n_{\text{ini}} - 3/2 \xi \rightarrow 2\xi - \xi
  \]

  a. \( K_p = \exp(-\Delta G^{0}/RT) = (P_{\text{NH}_3}/P_{\text{H}_2})/(P_{\text{H}_2}/P_{0})^{3/2} \)  

  \[
  P_{\text{NH}_3} = x_{\text{NH}_3} P_{0}; P_{\text{H}_2} = (1-x_{\text{NH}_3}) P_{0}
  \]

  \[
  P_{\text{NH}_3}/P_{\text{H}_2} = 2.165 = x_{\text{NH}_3}/(1-x_{\text{NH}_3}) \rightarrow x_{\text{NH}_3} @ 700K
  \]

  b. \( \ln(K_p(800K)) - \ln(K_p(700K)) = -(\Delta H/R)(1/800K - 1/700K) \)

  \[
  \Delta G = \Delta H - T \Delta S. \quad \text{From} \quad (*) \rightarrow \Delta G = -RT \ln(K_p)
  \]
P6.24) At $T = 298$ K and pH=3 chymotrypsinogen denatures with $\Delta G^\circ = 30.5 \text{ kJ mol}^{-1}$, $\Delta H^\circ = 163 \text{ kJ mol}^{-1}$, and $\Delta C_{P,m} = 8.36 \text{ kJ K}^{-1} \text{ mol}^{-1}$. Determine $\Delta G^\circ$ for the denaturation of chymotrypsinogen at $T = 320. \text{ K}$ and pH=3. Assume $\Delta C_{P,m}$ is constant between $T = 298 \text{ K}$ and $T = 320. \text{ K}$.

First, we calculate $\Delta S^0$ at $T = 298 \text{ K}$:

\[
\Delta S^0 = \frac{(\Delta G^0 - \Delta H^0)}{T} \rightarrow \Delta H(320K) = \Delta C_{P,m} \Delta T + \Delta H^0
\]

\[
\Delta S(320K) = \int_{T_{ini}}^{T_{fin}} \frac{\Delta H}{T} dT + \Delta S^0 = \Delta S^0 + \Delta C_{P,m} \ln \left(\frac{T_{fin}}{T_{ini}}\right)
\]

P6.30) You have containers of pure H$_2$ and He at 298 K and 1 atm pressure. Calculate $\Delta G_{mixing}$ relative to the unmixed gases of

a. a mixture of 10 mol of H$_2$ and 10 mol of He.

b. a mixture of 10 mol of H$_2$ and 20 mol of He.

$\Delta G_{mixing} = n_A RT \ln(x_A) + n_B RT \ln(x_B)$

c. Calculate $\Delta G_{mixing}$ if 10 mol of pure He are added to the mixture of 10 mol of H$_2$ and 10 mol of He.

$\Delta G_{mixing} = \Delta G_b - \Delta G_a$
• **P6.38** Consider the equilibrium in the reaction

\[ 3O_2 \leftrightarrow 2O_3 \] with \[ \Delta H_{\text{reaction}}^{\circ} = 285.4 \times 10^3 \text{ J mol}^{-1} \] at 298 K.

Assume that \[ \Delta H_{\text{reaction}}^{\circ} \] is independent of temperature.

• **a.** Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the pressure is increased.

• **b.** Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the temperature is increased.

• **c.** Calculate \( K_p \) at 550 K.

• **d.** Calculate \( K_x \) at 550 K and 0.500 bar.

\[ K_p(298K) = \exp(-\Delta G/RT) \]

\[ \text{Use } \ln(K_p(550K)) = \ln(K(298K)) - \Delta H\{1/T_2-1/T_1\}/R \]

\[ K_p = K_x(P/P_0)^{\Delta v} \quad K_x = (P/P_0)^{-\Delta v} K_p \]