1. In a thermochemical study of N\textsubscript{2}, the following heat capacity data were found:

\[ \int_{T_0}^{T_t} \frac{C_{p,m}}{T} dT = 27.2 J mol^{-1} K^{-1} \]

\[ \int_{T_t}^{T_f} \frac{C_{p,m}}{T} dT = 23.4 J mol^{-1} K^{-1} \]

\[ \int_{T_f}^{T_b} \frac{C_{p,m}}{T} dT = 11.4 J mol^{-1} K^{-1} \]

where \( T_t = 35.61 \) K, the enthalpy of transition is \( .229 \) kJ mol\(^{-1}\); \( T_f = 63.14 \) K, \( \Delta H_{melt,m} = .721 \) kJ mol\(^{-1}\); \( T_b = 77.321 \) K, \( \Delta H_{vap,m} = 5.58 \) kJ mol\(^{-1}\). Calculate the third law entropy of nitrogen vapor at the boiling point.

\textbf{Answer:}

\[ S = \int_{T_0}^{T_t} \frac{C_{p,m}dT}{T} + \frac{\Delta H_t}{T_t} + \int_{T_t}^{T_f} \frac{C_{p,m}dT}{T} \]

\[ + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} \]

\[ = 27.2 \text{ J mol}^{-1}\text{K}^{-1} + \frac{.229 \times 10^3 \text{ J mol}^{-1}}{35.61 \text{ K}} + 23.4 \text{ J mol}^{-1}\text{K}^{-1} \]

\[ + \frac{.721 \times 10^3 \text{ J mol}^{-1}}{63.14 \text{ K}} + 11.4 \text{ J mol}^{-1}\text{K}^{-1} + \frac{5.58 \times 10^3 \text{ J mol}^{-1}}{77.32 \text{ K}} \]

\[ = 152.02 \text{ J mol}^{-1}\text{K}^{-1} \]

2. A certain gas obeys the equation of state

\[ p(V_m - b) = RT \]
where b is a constant. Show that the partial molar enthalpy of the gas is given by

\[ H_i = \left( \frac{\partial H}{\partial n_i} \right)_{T,V,n_1,n_2,...} - b \left( \frac{\partial p}{\partial n_i} \right)_{T,V,n_1,n_2,...} \]

Answer:

\[ dH = \left( \frac{\partial H}{\partial T} \right)_{p,\{n_i\}} dT + \left( \frac{\partial H}{\partial p} \right)_{T,\{n_i\}} dp + \sum_i \left( \frac{\partial H}{\partial n_i} \right)_{T,p,\{n_j\} j \neq i} dn_i \]

\[ dH = TdS + Vdp + \sum_i \mu_i dn_i \]

\[ \left( \frac{\partial H}{\partial p} \right)_{T,\{n_i\}} = T \left( \frac{\partial S}{\partial p} \right)_{T,\{n_i\}} + V \]

\[ dG = -SdT + Vdp + \sum_i \mu_i dn_i \]

\[ \left( \frac{\partial S}{\partial p} \right)_{T,\{n_i\}} = - \left( \frac{\partial V}{\partial T} \right)_{p,\{n_i\}} \]

\[ \left( \frac{\partial V}{\partial T} \right)_{p,\{n_i\}} = \frac{RT}{p} + b \]

Then

\[ H_i = \left( \frac{\partial H}{\partial n_i} \right)_{T,V,\{n_j\} j \neq i} - b \left( \frac{\partial p}{\partial n_i} \right)_{T,V,\{n_j\} j \neq i} \]

3. At -5.0°C the vapor pressure of ice is 3.012 mm of Hg whereas the vapor pressure of of super-cooled liquid water at -5.0°C is 3.163 mm Hg. Calculate \( \Delta G_m \) for the transition water \( \rightarrow \) ice at -5.0°C.

Answer:

At equilibrium

\[ \mu_{ice} = \mu_{vapor} = \mu^o + RT \ln \frac{p_{ice}}{p^o} \]
\[ \mu_{\text{water}} = \mu_{\text{vapor}} = \mu^* + RT \ln \frac{p_{\text{water}}}{p^*} \]

\[ \Delta G_m = \mu_{\text{ice}} - \mu_{\text{water}} = RT \ln \frac{p_{\text{ice}}}{p_{\text{water}}} \]

\[ = (8.3144 \text{ J mol}^{-1} \text{K}^{-1})(268 \text{ K}) \ln \frac{3.012}{3.163} \]

\[ = -109 \text{ J} \]

4. The density of lithium metal is .53 g ml\(^{-1}\). Assuming lithium to be incompressible, calculate \(\Delta G\) when the pressure on 5.0 g of lithium is raised isothermally from 1.0 to 100.0 atmospheres.

**Answer:**

\[ dG = -SdT + Vdp \]

\[ \left( \frac{\partial G}{\partial p} \right)_T = V \]

\[ \Delta G = \int_{p_1}^{p_2} Vdp \cong V\Delta p \]

\[ V = \frac{10^{-3}}{0.53 \text{ g}} \times 5.0 \text{ g} = 0.00943 \text{ L} \]

\[ \Delta G = (0.00943 \text{ L})(99 \text{ atm}) \left( \frac{8.3144 \text{ J}}{0.0821 \text{ L atm}} \right) = 94.6 \text{ J} \]

5. The element phosphorus occurs in two solid phases often called red and white phosphorus. At 25.\(^\circ\)C and 1.0 bar pressure, the process

\[ P_{(\text{red})} \rightarrow P_{(\text{white})} \]

has \(\Delta_r G_m^o=-12134.\) J mol\(^{-1}\) and \(\Delta_r H_m^o=-17573.\) J mol\(^{-1}\). Assuming the enthalpy change for the process to be temperature independent, at what temperature are the two phases in equilibrium at 1.0 bar pressure?

**Answer:**

\[ \frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

At equilibrium \(\Delta G(T_2) = 0\). Then

\[ \frac{1}{T_2} - \frac{1}{T_1} = \frac{-\Delta G(T_1)}{T_1 \Delta H} \]

\[ \frac{1}{T_2} = \frac{1}{298 \text{ K}} - \frac{12134}{(17573)(298 \text{ K})} \]

\[ T_2 = 963 \text{ K} \]
6. Consider the reaction between ideal gas molecules

\[ a \text{ A}_{(g)} + b \text{ B}_{(g)} \rightarrow e \text{ E}_{(g)} + d \text{ D}_{(g)} \]

Define equilibrium constants

\[ K_p = \frac{p_E p_D^d}{p_A p_B^b} \]

and

\[ K_C = \frac{C_E C_D^d}{C_A C_B^b} \]

where \( C_i \) is the concentration of species \( i \) in moles per unit volume.

(a) Show that

\[ K_C = K_p (RT)^{-\Delta \nu} \]

where

\[ \Delta \nu = e + d - a - b \]

Answer:

\[ p_i = \frac{n_i RT}{V} = C_i RT \]

where

\[ C_i = \frac{n_i}{V} \]

Then

\[ K_p = \frac{p_E p_D^d}{p_A p_B^b} = \frac{C_E C_D^d}{C_A C_B^b} (RT)^\Delta \nu \]

where

\[ \Delta \nu = e + d - a - b \]

and the concentrations are expressed in moles per liter with \( R \) having units consistent with the defined standard state. Then

\[ K_C = K_p (RT)^{-\Delta \nu} \]

with

\[ K_C = \frac{C_E C_D^d}{C_A C_B^b} \]
(b) Show that
\[
\frac{d \ln K_C}{dT} = \frac{\Delta U}{RT^2}
\]
where \(\Delta U\) is the change in the internal energy for the reaction.

**Answer:**
\[
\frac{d \ln K_C}{dT} = \frac{d}{dT} \ln \left[ K_p + \ln (RT)^{-\Delta \nu} \right]
\]
\[
= \frac{d \ln K_p}{dT} - \Delta \nu \frac{d \ln T}{dT}
\]
\[
= \frac{\Delta_r H_m^o}{RT^2} - \frac{\Delta \nu}{T}
\]
\[
= \frac{\Delta_r H_m^o - RT \Delta \nu}{RT^2}
\]

For a gas-phase reaction
\[
\Delta_r U_m^o = \Delta_r H_m^o - \Delta (pV)
\]
\[
= \Delta_r H_m^o - RT \Delta \nu
\]

Then
\[
\frac{d \ln K_C}{dT} = \frac{\Delta_r U_m^o}{RT^2}
\]

7. Consider the reaction
\[
\text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g)
\]

(a) Show that if one starts with pure PCl\(_5\) and a fraction, \(\alpha\), dissociates, the reaction quotient will be given by
\[
Q_p = \frac{\alpha^2}{(1 - \alpha^2)} \left( \frac{p}{p^0} \right)
\]

**Answer:**
Let \(n\) = the initial number of moles of PCl\(_5(g)\)
Then at equilibrium
\[
n_{\text{PCl}_5} = (1 - \alpha)n
\]
\[
n_{\text{PCl}_3} = n_{\text{Cl}_2} = \alpha n
\]
\[
n_{\text{total}} = 2\alpha n + (1 - \alpha)n = (1 + \alpha)n
\]
\[
p_{\text{PCl}_5} = x_{\text{PCl}_5} p = \frac{1 - \alpha}{1 + \alpha} p
\]
\[
p_{\text{PCl}_3} = p_{\text{Cl}_2} = x_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha} p
\]
Then
\[
Q_p = \frac{(p_{PCl_3}/p^o)(p_{Cl}_2/p^o)}{p_{PCl_5}/p^o}
\]
\[
= \frac{[(\alpha/(1 + \alpha))(p/p^o)]^2}{[(1 - \alpha)/(1 + \alpha)(p/p^o)]}
\]
\[
= \frac{\alpha^2 p}{1 - \alpha^2 p^o}
\]

(b) At 250.°C the equilibrium constant for the reaction is \(K_p = 1.78\). Calculate \(\alpha\) for \(p = 0.1\) bar and \(p = 1.0\) bar at equilibrium.

**Answer:**
\[
K_p = \frac{\alpha^2 p}{1 - \alpha^2 p^o}
\]
\[
(1 - \alpha^2)K_p = \frac{\alpha^2 p}{p^o}
\]
\[
\alpha^2 \left(\frac{p}{p^o} + K_p\right) = K_p
\]
\[
\alpha = \left(\frac{K_p}{K_p + p/p^o}\right)^{1/2}
\]
\[
\alpha(0.1) = \left(\frac{1.78}{1 + 1.78}\right)^{1/2} = 0.973
\]
\[
\alpha(1.) = \left(\frac{1.78}{2.78}\right)^{1/2} = 0.800
\]

(c) Calculate \(\Delta_r G_m\) for an equimolar mixture at 1 bar pressure and 250.°C.

**Answer:**
\[
\Delta_r G_m = \Delta_r G_m^o + RT \ln Q_p
\]
\[
= RT \ln K_p + RT \ln Q_p
\]
\[
= -RT \ln K_p + RT \ln \frac{(p_{PCl_3}/p^o)(p_{Cl}_2/p^o)}{(p_{PCl_5}/p^o)}
\]
\[
= -RT \ln K_p + RT \ln \left(\frac{p}{p^o} \frac{(1/3)(1/3)}{1/3}\right)
\]
\[
= (-8.3144 \text{ J mol}^{-1}\text{K}^{-1})(523\text{K})[\ln 1.78 - \ln(1/3)] = -7285\text{J}
\]

(d) Calculate \(\Delta_r G_m\) for 20 per cent dissociation at 250.°C and 1 bar pressure.

**Answer:**
\[
Q_p = \frac{\alpha^2}{1 - \alpha^2} = 0.0417
\]
\[
\Delta_r G_m = (-8.3144 \text{ J mol}^{-1}\text{K}^{-1})(523\text{K})[\ln 1.78 - \ln 0.0417] = -16323\text{J}
\]
8. The following results were obtained for the degree of dissociation, $\alpha$, of CO$_2$ in the reaction

$$\text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g)$$

at a pressure of 1.0 bar:

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>2. $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>1400</td>
<td>1.27 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>2000</td>
<td>1.55 $\times$ 10$^{-2}$</td>
</tr>
</tbody>
</table>

Calculate $\Delta_rS_m^o$ for the reaction at 1400.°K.

**Answer:**

Let $n= \text{initial number of moles of CO}_2(g)$

$$n_{\text{CO}_2} = (1 - \alpha)n$$

$$n_{\text{CO}} = \alpha n$$

$$n_{\text{O}_2} = \frac{\alpha}{2} n$$

$$n_{\text{total}} = (1 - \alpha)n + \alpha n + \frac{1}{2} \alpha n = (1 + \frac{\alpha}{2})n$$

$$p_{\text{CO}_2} = \frac{2(1 - \alpha)}{2 + \alpha} p$$

$$p_{\text{CO}} = \frac{2\alpha}{2 + \alpha} p$$

$$p_{\text{O}_2} = \frac{(1/2)\alpha}{1 + (1/2)\alpha} p = \frac{\alpha}{2 + \alpha} p$$

Then

$$K_p = \frac{(p_{\text{CO}}/p^o)(p_{\text{O}_2}/p^o)^{1/2}}{p_{\text{CO}_2}/p^o}$$

$$= \frac{(2\alpha/[2 + \alpha])(\alpha/[2 + \alpha])^{1/2}}{2(1 - \alpha)/(2 + \alpha)} \left( \frac{p}{p^o} \right)^{1/2}$$

$$= \frac{\alpha^{3/2}}{(1 - \alpha)(2 + \alpha)^{1/2}} \left( \frac{p}{p^o} \right)^{1/2}$$

Then

$$K_p(1000K) = 6.32 \times 10^{-11}$$
\[ K_p(1400K) = 1.01 \times 10^{-6} \]
\[ K_p(2000K) = 1.38 \times 10^{-3} \]
\[ \Delta_r G_m^o (1400K) = -RT \ln K_p \]
\[ = -(8.3144 \text{ J mol}^{-1} \text{ K}^{-1})(1400K) \ln(1.01 \times 10^{-6}) = 160.7 \text{kJ mol}^{-1} \]
\[ \ln \frac{K_p(1400K)}{K_p(1000K)} = \frac{\Delta_r H_m^o}{RT} \left( \frac{1}{1000K} - \frac{1}{1400K} \right) \]
\[ \ln \frac{1.01 \times 10^{-6}}{6.32 \times 10^{-11}} = \frac{\Delta_r H_m^o}{8.3144 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{1000K} - \frac{1}{1400K} \right) \]
\[ \Delta_r H_m^o = 281.7 \text{kJ mol}^{-1} \]
\[ \Delta_r S_m^o = \frac{\Delta_r H_m^o - \Delta_r G_m^o}{T} \]
\[ = \frac{(281700 - 160700) \text{J mol}^{-1}}{1400K} = 86.43 \text{kJ mol}^{-1} \text{K}^{-1} \]

9. Hydrogen iodide gas dissociates according to the reaction

\[ \text{HI}(g) \rightarrow \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{I}_2(g) \]

At 0.°C and 1.0 bar pressure, the degree of dissociation is \( \alpha = 0.40 \), and at 100.°C, \( \alpha = 0.88 \). Assuming \( \Delta_r H_m^o \) to be independent of temperature, calculate \( \Delta_r H_m^o \), \( \Delta_r G_m^o \) and \( \Delta_r S_m^o \) for the reaction at 0.°C.

**Answer:**

Let \( n \) = initial number of moles of HI

\[ n_{HI} = (1 - \alpha)n \]
\[ n_{H_2} = n_{I_2} = \frac{\alpha n}{2} \]
\[ n_{total} = \alpha n + (1 - \alpha)n = n \]
\[ p_{HI} = (1 - \alpha)p \]
\[ p_{H_2} = p_{I_2} = \frac{\alpha}{2}p \]
\[ K_p = \frac{[(\alpha/2)^{1/2}]^2}{1 - \alpha} = \frac{\alpha}{2(1 - \alpha)} \]
\[ K_p(273K) = 0.333 \]
\[ K_p(373K) = 3.67 \]
\[ \Delta_r G_m^o (273K) = -RT \ln K_p(273K) \]
\[ = -(8.3144 \text{ J mol}^{-1} \text{ K}^{-1})(273K) \ln 0.333 = 2496 \text{kJ mol}^{-1} \]
\[ \ln \frac{K_p(T_2)}{K_p(T_1)} = \frac{\Delta_r H_m^o}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

\[ \ln \frac{3.67}{0.333} = \frac{\Delta_r H_m^o}{8.3144 \text{J mol}^{-1} \text{K}^{-1}} \left( \frac{1}{273 \text{K}} - \frac{1}{373 \text{K}} \right) \]

\[ \Delta_r H_m^o = 20318 \text{J mol}^{-1} \]

\[ \Delta_r S_m^o = \frac{\Delta_r H_m^o - \Delta_r G_m^o}{T} \]

\[ = \frac{(20318 - 2496) \text{J mol}^{-1}}{273 \text{K}} = 65.28 \text{J mol}^{-1} \text{K}^{-1} \]

10. Hydrogen bromide dissociates according to the reaction

\[ \text{HBr}(g) \rightarrow \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Br}_2(g) \]

Use Tables 4.2 and 7.2 of the text to find the degree of dissociation of HBr at 35°C and 2.0 bars pressure.

**Answer:**

\[ \Delta_r G_m^o = \left[ \frac{1}{2} (3.110) - (-53.45) \right] \text{kJ mol}^{-1} = 55.005 \text{kJ mol}^{-1} \]

\[ \Delta_r H_m^o = \left[ \frac{1}{2} (30.907) - (-36.40) \right] \text{kJ mol}^{-1} = 51.854 \text{kJ mol}^{-1} \]

\[ K_p(298K) = \exp\left[ -\frac{\Delta_r G_m^o}{RT} \right] \]

\[ = \exp\left[ -\frac{55005 \text{J mol}^{-1}}{(8.3144 \text{J mol}^{-1} \text{K}^{-1})(298 \text{K})} \right] = 2.28 \times 10^{-10} \]

\[ \ln \frac{K_p(308K)}{2.28 \times 10^{-10}} = \frac{51854 \text{J mol}^{-1}}{8.3144 \text{J mol}^{-1} \text{K}^{-1}} \left( \frac{1}{298 \text{K}} - \frac{1}{308 \text{K}} \right) \]

\[ K_p(308K) = 4.50 \times 10^{-10} \]

As in problem 9

\[ K_p = \frac{\alpha}{2(1 - \alpha)} \]

or

\[ \alpha = \frac{2K_p}{1 + 2K_p} = 9.0 \times 10^{-10} \]