
**Answer**

(a) We first evaluate the standard free energy change and thus the equilibrium constant for \( \text{Br}_2(g) \rightleftharpoons 2\text{Br}(g) \) from the data provided:

\[
\Delta_r G^\circ = 2 \text{ mol} \times 82.396 \text{ kJ mol}^{-1} - 1 \text{ mol} \times 3.110 \text{ kJ mol}^{-1} = 161.682 \text{ kJ per mole of Br}_2(g)
\]

\[
K_p = \frac{(p_{\text{Br}}/p^\circ)^2}{(p_{\text{Br}_2}/p^\circ)} = \exp(-\Delta_r G^\circ / RT) = 4.728 \times 10^{-29}
\]

where we recognize that the equilibrium constant is the \( K_p \) from the standard state used (100 kPa or 1 bar pressure, 298.15 K). There are two ways to proceed at this point - in terms of partial pressures, or in terms of moles (making use of the ideal gas law). In each case, we can make the assumption that the total pressure of 1 bar is almost all due to bromine molecules. This assumption is justified on the basis of the extremely small value of the equilibrium constant. We will use partial pressures since it is simpler.

\[
(4.728 \times 10^{-29})^{1/2} = 6.87605 \times 10^{-15}
\]

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

\[
1 - p_{\text{Br}} \quad p_{\text{Br}}
\]

Therefore,

\[
K_p = \frac{p_{\text{Br}}^2}{(1 - p_{\text{Br}})} \simeq \frac{p_{\text{Br}}^2}{1 \text{ bar} \times p^\circ}
\]

\[
p_{\text{Br}} = (4.728 \times 10^{-29})^{1/2} = 6.87605 \times 10^{-15} \text{ bar}.
\]

We can also solve a quadratic from the expression for \( K_p \), as

\[
p_{\text{Br}}^2 + K_p p_{\text{Br}} - K_p = 0
\]

for which the physically meaningful solution is \( p_{\text{Br}} = 6.87605 \times 10^{-15} \text{ bar} \). It is clear now that the assumption \((1 - p_{\text{Br}}) \text{ bar} \simeq 1 \text{ bar} \) is a good one. Now we obtain

\[
N_{\text{Br}} = \frac{p_{\text{Br}} V}{RT} N_A
\]

\[
= \frac{6.87605 \times 10^{-15} \text{ bar} \times 1.00 \text{ dm}^3}{0.083145 \text{ dm}^3 \text{ bar}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \times 6.022 \times 10^{23} \text{ atoms mol}^{-1} = 1.67036 \times 10^8 \text{ atoms}
\]

An alternate approach is to assume that we start with \( n \) moles of \( \text{Br}_2(g) \). Then

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

\[
n - x \quad 2x
\]
so that the total number of moles at equilibrium is \((n + x)\) and the total pressure is calculated as

\[ p_T = (n + x)\frac{RT}{V}. \]  

We can also write the equilibrium expression using Dalton’s law of partial pressures \((p_i = y_i p_T)\) as

\[ K_p = \left(\frac{2x p_T}{n + x p^o}\right)^2 \left/ \left(\frac{n - x p_T}{n + x p^o}\right)\right. \].

Now Eqs. (1) and (2) can be solved for the two unknowns \(n\) and \(x\). However, this is unnecessary since we can assume that \(n + x \approx n\) and \(n - x \approx n\), which reduces this approach to the one shown above.

(b) The equilibrium vapor pressure of \(\text{Br}_2(g)\) can be found from the free energy data since we are considering the process \(\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)\). Since the dissociation of the vapor to bromine atoms is found to be quite negligible at 298.15 K, we can ignore that process. Therefore, equilibrium constant is

\[ K = \frac{a_{\text{Br}_2(g)}}{a_{\text{Br}_2(l)}} = a_{\text{Br}_2(g)} \approx \frac{p_{\text{Br}_2}}{p^o}. \]

Therefore,

\[ \Delta_{\text{vap}} G^o = 3.110 - 0.000 \text{ kJ mol}^{-1} \]

\[ K = \exp(-\Delta_{\text{vap}} G^o / RT) \]

\[ = 0.2852 \]

Therefore, the vapor pressure of \(\text{Br}_2\) at 0.100 MPa pressure (1 bar) is 0.2852 bar. Since vapor pressure changes rather slowly with external pressure, the vapor pressure at 0.101 MPa pressure can be safely assumed to be 0.2852 bar.

2. Exercise E9.3 (p. 492).

Answer

(a) The variation of equilibrium constant with temperature is given as

\[ \ln K = 18.854 - \frac{5331.6}{T} - 0.02360 T. \]

Therefore (see Eq. 9.54),

\[ \Delta_r H^o = RT^2 \left( \frac{\partial \ln K}{\partial T} \right)_p \]

\[ = RT^2 \left( \frac{5331.6}{T^2} - 0.02360 \right). \]

(b) The following relationship will be used to calculate the quantities requested in the question at 298.15 K:

\[ \Delta_r G^o = -RT \ln K = -(18.854RT - 5331.6R - 0.02360RT^2) \]

\[ \Delta_r H^o = RT^2 \left( \frac{\partial \ln K}{\partial T} \right)_p = RT^2 \left( \frac{5331.6}{T^2} - 0.02360 \right) \]

\[ = 5331.6R - 0.02360RT^2 \]

\[ \Delta_r S^o = \frac{\Delta_r H^o - \Delta_r G^o}{T} = \frac{10663.2R}{T} - 18.854R \]

\[ \Delta_r C_p^o = \left( \frac{\partial \Delta_r H^o}{\partial T} \right)_p = -0.04720RT \]
Now, substituting \( R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \) and \( T = 298.15 \text{ K} \), we get
\[
\Delta_r G^\circ = 15034.0 \text{ J mol}^{-1} \\
\Delta_r H^\circ = 26886.7 \text{ J mol}^{-1} \\
\Delta_r S^\circ = 140.603 \text{ J K}^{-1} \text{ mol}^{-1} \\
\Delta_r C_p^\circ = -117.007 \text{ J K}^{-1} \text{ mol}^{-1}
\]

3. The blue color of the Iodine-starch complex is due to the absorption of the linear \( I_3^- \) ion, which has the linear structure I-I...I^-...I-I (i.e., an iodide ion sandwiched between two \( I_2 \) molecules), enclosed in the \( \alpha \)-helix of the amylose form of starch. The absorption spectrum shows a maximum at \( \lambda = 600 \text{ nm} \). Let us assume that this absorption is due to the extra electron in \( I^- \) going from the ground to the first excited state. Adopting the one-dimensional infinite well model for the electron, calculate the range of motion of this electron.

**Answer**

The transition we are interested in is from the ground state \((n = 1)\) to the first excited state \((n = 2)\). The energy levels of the one-dimensional infinite well model are
\[
\varepsilon_n = \frac{n^2 \hbar^2}{8ma^2}
\]
where \( a \) is the length of the well, or the range of motion of the particle. Thus, from the data given, we have
\[
\Delta \varepsilon = \frac{hc}{\lambda} = (4 - 1) \frac{\hbar^2}{8ma^2}
\]
or
\[
a = \left( \frac{3\hbar\lambda}{8mc} \right)^{1/2}
\]
where \( m = m_e = 9.109 \times 10^{-31} \text{ kg} \). Thus we get
\[
a = \left( \frac{3 \times 6.626 \times 10^{-34} \text{ J s} \times 600 \times 10^{-9} \text{ m}}{8 \times 9.109 \times 10^{-31} \text{ kg} \times 2.998 \times 10^8 \text{ m s}^{-1}} \right)^{1/2} = 7.39 \times 10^{-10} \text{ m}
\]
or 7.39 Å.

4. Equation (10.19) can be factored as follows:
\[
\ln W = N \ln N - N + \sum_i n_i \left( 1 + \ln \frac{g_i}{n_i} \right).
\]
Show that
\[
\left( \frac{\partial \ln W}{\partial n_j} \right)_N = \ln \frac{g_j}{n_j}.
\]

**Answer**

Since \( N \) is a constant, we get
\[
\left( \frac{\partial \ln W}{\partial n_j} \right)_N = \frac{\partial}{\partial n_j} \sum_i n_i \left( 1 + \ln \frac{g_i}{n_i} \right).
\]
The derivatives of all the terms in the sum except for the \( i = j \) term will vanish. Recall that \( \frac{d(\ln u)}{dx} = \frac{1}{u} \frac{du}{dx} \). Therefore, the \( i = j \) term gives

\[
\left( \frac{\partial \ln W}{\partial n_j} \right)_N = \frac{\partial}{\partial n_j} \left[ n_j \left( 1 + \ln \frac{g_j}{n_j} \right) \right] \\
= \left( 1 + \ln \frac{g_j}{n_j} \right) + n_j \left( \frac{1}{g_j/n_j} \right) \left( -\frac{g_j}{n_j^2} \right) \\
= \ln \frac{g_j}{n_j}.
\]

Thus the relationship is proved.