3.8 The Joule-Thomson coefficient for air at temperatures near 298 K and pressures in the range 0 to 50 bar is relatively constant at 0.2 K bar\(^{-1}\). Estimate the final temperature if 58 g of air at 298 K and 50 bar undergoes Joule-Thomson expansion to a final pressure of 1 bar.

**Solution**

The Joule-Thomson coefficient relates the temperature change associated with constant enthalpy expansion:

\[ \mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H \]

Since we're told that \( \mu_{JT} \) is independent of temperature and pressure, we can easily integrate this:

\[ \int_{T_1}^{T_2} dT = \mu_{JT} \int_{P_1}^{P_2} dP \Rightarrow T_2 - T_1 = \mu_{JT}(P_2 - P_1) \]

We are given \( T_1, P_1, \) and \( P_2 \) so all we have to do is solve for \( T_2 \):

\[ T_2 = (P_2 - P_1) \mu_{JT} + T_1 \]

\[ = (1 \text{bar} - 50 \text{bar})(0.2 \text{Kbar}^{-1}) + 298 \text{K} \]

\[ = 288.2 \text{K} \]

3.9 (a) Derive the expression

\[ \left( \frac{\partial H}{\partial P} \right)_T = -C_p \mu_{JT} \]

(b) Show that

\[ \mu_{JT} = \frac{V}{C_p} (\kappa P - \mu_{JT} \kappa - 1) \]

where \( \kappa \) is defined by

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

**Solution**

a. Use the cyclic rule,

\[ \left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_\mu \left( \frac{\partial T}{\partial H} \right)_P = -1 \]

and solve for the desired derivative (the one in red):

\[ \left( \frac{\partial H}{\partial P} \right)_T = -\left( \frac{\partial T}{\partial P} \right)_\mu \left( \frac{\partial H}{\partial T} \right)_P \]

\[ = -\mu_{JT} C_p \]

b. Solve the expression derived in (a) for the Joule-Thomson coefficient:

\[ \mu_{JT} = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T \]

Now, substitute \( H = U + PV \) and differentiate:

\[ \mu_{JT} = -\frac{1}{C_p} \left( \frac{\partial (U + PV)}{\partial P} \right)_T \]

\[ = -\frac{1}{C_p} \left[ \frac{\partial U}{\partial P} \right]_T + P \left( \frac{\partial V}{\partial P} \right)_T + V \left( \frac{\partial P}{\partial P} \right)_T \]

\[ \downarrow \quad \text{the red derivative is} \quad \left( \frac{\partial V}{\partial P} \right)_T = -\kappa V \]

\[ = -\frac{1}{C_p} \left[ \frac{\partial U}{\partial P} \right]_T - \kappa PV + V \]

\[ = \frac{1}{C_p} \kappa PV - \left( \frac{\partial U}{\partial P} \right)_T - V \]

The remaining derivative (in blue) can be written as:

(continued on next page)
\[ \left( \frac{\partial U}{\partial P} \right)_T = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \]

\[ = -\left( \frac{\partial U}{\partial V} \right)_T \kappa V \]

(This is found by writing the total differential of \( U = U(T, V) \), then dividing through both sides by \( dP \) and imposing constant \( T \).) Substitute this into the expression for \( \mu_{JT} \) and continue:

\[ \mu_{JT} = \frac{1}{C_p} \left[ \kappa PV + \left( \frac{\partial U}{\partial V} \right)_T \kappa V - V \right] \]

\[ \downarrow \]

use the cyclic rule to express the derivative as:

\[ \frac{\partial U}{\partial V} = -\left( \frac{\partial T}{\partial P} \right)_V \frac{\partial U}{\partial T} \]

\[ = -\mu_c V \]

4.1 From the following data, determine \( \Delta_f H^\circ \) for diborane, \( B_2H_6(g) \) at 298 K:

- \( \Delta_f H^\circ(B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)) = -1941 \text{kJ mol}^{-1} \)
- \( \Delta_f H^\circ(2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)) = -2368 \text{kJ mol}^{-1} \)
- \( \Delta_f H^\circ(H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)) = -241.8 \text{kJ mol}^{-1} \)

**Solution**

The reaction enthalpy for the first reaction in terms of the formation enthalpies of the reactants and products is:

\[ -1941 \text{kJ mol}^{-1} = \Delta_f H^\circ \]

\[ = 3\Delta_f H^\circ(H_2O,g) + \Delta_f H^\circ(B_2O_3,s) - 3\Delta_f H^\circ(O_2,g) - \Delta_f H^\circ(B_2H_6,g) \]

All of the remaining quantities are known except the formation enthalpy of diborane. So we just solve for it:

\[ \Delta_f H^\circ(B_2H_6,g) = 3\Delta_f H^\circ(H_2O,g) + \Delta_f H^\circ(B_2O_3,s) - \Delta_f H^\circ \]

\[ = 3(-241.8 \text{kJ mol}^{-1}) + (-2368 \text{kJ mol}^{-1}) - (-1941 \text{kJ mol}^{-1}) \]

\[ = -1152 \text{kJ mol}^{-1} \]

4.2 Given that the standard combustion enthalpy of graphite is \(-393.5 \text{kJ mol}^{-1} \) and that of diamond is \(-395.41 \text{kJ mol}^{-1} \), calculate the standard enthalpy of the graphite-to-diamond transition.

**Solution**

If you write the reaction for the combustions of graphite and the reverse reaction for the combustion of diamond you see that the two reactions combine to give the desired reaction:

\[ C(s, \text{graph.}) + O_2(g) \rightarrow CO_2(g) \quad \Delta_f H^\circ = -393.5 \text{kJ mol}^{-1} \]

\[ CO_2(g) \rightarrow C(s, \text{diam.}) + O_2(g) \quad \Delta_f H^\circ = -395.41 \text{kJ mol}^{-1} \]

\[ C(s, \text{graph.}) \rightarrow C(s, \text{diam.}) \quad \Delta_{\text{trs}} H^\circ = -395.41 \text{kJ mol}^{-1} + 395.41 \text{kJ mol}^{-1} \]

\[ = +1.99 \text{kJ mol}^{-1} \]

4.3 Set up a thermodynamic cycle for determining the enthalpy of hydration of \( \text{Ca}^{2+} \) ions, \( \Delta_{\text{hyd}} H^\circ(\text{Ca}^{2+}, g) \), using the following data: enthalpy of sublimation of \( \text{Ca}(s), \Delta_{\text{sub}} H^\circ(\text{Ca}, s) = +178.2 \text{kJ mol}^{-1} \); first ionization enthalpy of \( \text{Ca}(g), \Delta_{\text{ion}} H^\circ(\text{Ca}, g) = +589.7 \text{kJ mol}^{-1} \); second ionization enthalpy of \( \text{Ca}^+(g), \Delta_{\text{ion2}} H^\circ(\text{Ca}^+, g) = +1145 \text{kJ mol}^{-1} \); enthalpy of vaporization of \( \text{Br}_2(l), \Delta_{\text{vap}} H^\circ(\text{Br}_2) = +30.91 \text{kJ mol}^{-1} \); dissociation enthalpy of \( \text{Br}_2(g), \Delta_{\text{diss}} H^\circ(\text{Br}_2, g) = +192.9 \text{kJ mol}^{-1} \); electron gain enthalpy of \( \text{Br}^-(g), \Delta_{\text{e.g.}} H^\circ(\text{Br}, g) = +331.0 \text{kJ mol}^{-1} \); enthalpy of solution of \( \text{CaBr}_2(s), \Delta_{\text{soln}} H^\circ(\text{CaBr}_2, s) = -103.1 \text{kJ mol}^{-1} \); enthalpy of hydration of \( \text{Br}^-(g), \Delta_{\text{hyd}} H^\circ(\text{Br}^-, g) = -337 \text{kJ mol}^{-1} \); formation enthalpy of \( \text{CaBr}_2(s), \Delta_{\text{fH}}(\text{CaBr}_2, s) = -682.8 \text{kJ mol}^{-1} \).

**Solution**

This is what we want:

\[ \text{Ca}^{2+} (g) \rightarrow \text{Ca}^{2+} (aq) \]

From the information given, the following cycle would allow you to determined the desired enthalpy:
To find the hydration enthalpy, we recognize that the sum of the enthalpies of the hydration step is equal to the algebraic sum of all the other enthalpies around the cycle:

\[
\Delta_{\text{hyd}} H(\text{Ca}^{2+},g) + 2\Delta_{\text{hyd}} H(\text{Br}^-,g) = -2 \Delta_{\text{e.g.}} H(\text{Br},g) - \Delta_{\text{ion}} H(\text{Ca}^+,g) - \Delta_{\text{diss}} H(\text{Br}_2,g) - \Delta_{\text{ion}} H(\text{Ca},g) - \Delta_{\text{vap}} H(\text{Br}_2,\ell) - \Delta_{\text{sub}} H(\text{Ca},s) + \Delta_{1} H(\text{CaBr}_2,s) + \Delta_{\text{soln}} H(\text{CaBr}_2,s) - 2\Delta_{\text{hyd}} H(\text{Br}^-,g)
\]

Solve for the hydration enthalpy of \( \text{Ca}^{2+} \):

\[
\Delta_{\text{hyd}} H(\text{Ca}^{2+},g) = -2 \Delta_{\text{e.g.}} H(\text{Br},g) - \Delta_{\text{ion}} H(\text{Ca}^+,g) - \Delta_{\text{diss}} H(\text{Br}_2,g) - \Delta_{\text{ion}} H(\text{Ca},g) - \Delta_{\text{vap}} H(\text{Br}_2,\ell) - \Delta_{\text{sub}} H(\text{Ca},s) + \Delta_{1} H(\text{CaBr}_2,s) + \Delta_{\text{soln}} H(\text{CaBr}_2,s) - 2\Delta_{\text{hyd}} H(\text{Br}^-,g)
\]

\[
= -1587 \text{kJmol}^{-1}
\]

4.4 Determine whether the differentials of the following functions are exact: (a) \( f(x, y) = x^2y + 3y^2 \), (b) \( f(x, y) = x \cos xy \), and (c) \( f(x, y) = x(x + e^y) + y \).

**Solution**

Use Euler’s test for exactness; if the mixed second partial derivatives are equal, then the differentials are exact.

a. Evaluate the first derivatives:

\[
\frac{\partial f}{\partial x} = 2xy \quad \text{and} \quad \frac{\partial f}{\partial y} = x^2 + 6y
\]

Evaluate the mixed second derivatives:

\[
\frac{\partial^2 f}{\partial y \partial x} = 2x \quad \text{and} \quad \frac{\partial^2 f}{\partial x \partial y} = 2x
\]

They are equal, so \( df \) is an exact differential.

b. Evaluate the first derivatives:

\[
\frac{\partial f}{\partial x} = \cos xy - xy \sin xy \quad \text{and} \quad \frac{\partial f}{\partial y} = -x^2 \sin xy
\]

Evaluate the mixed second derivatives:

\[
\frac{\partial^2 f}{\partial y \partial x} = -2x \sin xy - x^2 \cos xy \quad \text{and} \quad \frac{\partial^2 f}{\partial x \partial y} = -2x \sin xy - x^2 \cos xy
\]

They are equal, so \( df \) is exact.
We want this:

\[
\begin{align*}
\lambda_{2H_2O, 473K} \rightarrow H_2O(g, 473K) \\
\lambda_{2H_2O, 373K} \rightarrow H_2O(g, 373K) \\
\lambda_{coolH, 373K} \rightarrow \lambda_{heatH, 473K} \\
\lambda_{vapH_{373K}} \rightarrow H_2O(g, 373K)
\end{align*}
\]

Based on the data that is given, we can construct the following cycle:

\[
\begin{align*}
\Delta_{vapH_{473K}} = ? \\
\Delta_{vapH_{373K}} = ? \\
\Delta_{coolH(\ell)} \\
\Delta_{healH(g)} \\
\end{align*}
\]

The enthalpies for the heating and cooling steps are calculated using the heat capacities:

\[
\begin{align*}
\Delta_{coolH(\ell)} &= C_{p,m}(\ell)(373K - 473K) \\
\Delta_{heatH(g)} &= C_{p,m}(g)(473K - 373K)
\end{align*}
\]

The desired quantity is the sum of the enthalpies for each step around the cycle:

\[
\Delta_{vapH_{473K}} = \Delta_{coolH(\ell)} + \Delta_{vapH_{373K}} + \Delta_{heatH(g)}
\]

\[
= 36.5 \text{ kJ mol}^{-1}
\]

The answer makes sense—it should require less heat to vaporize water at a temperature well above its normal boiling point.