Chapter 3

1) The function \( f(x,y) \) is given by \( f(x,y) = xy \sin(5x + x^2 \sqrt{y \ln y + 3e^{-2x^2}} \cos y) \). Determine \( \left( \frac{\partial^2 f}{\partial x \partial y} \right)_y \), \( \left( \frac{\partial^2 f}{\partial y \partial y} \right)_x \), \( \left( \frac{\partial^2 f}{\partial y \partial x} \right)_x \), \( \left( \frac{\partial f}{\partial x} \right)_y \) and \( \left( \frac{\partial f}{\partial y} \right)_x \).

Is \( \left( \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_y \right)_x = \left( \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y \)? Obtain an expression for the total differential \( df \).

2) The molar heat capacity \( C_{p,m} \) of \( \text{SO}_2(g) \) is described by the following equation over the range \( 300 \, \text{K} < T < 1700 \, \text{K} \).

\[
\frac{C_{p,m}}{R} = 3.093 + 6.967 \times 10^{-3} \frac{T}{K} - 45.81 \times 10^{-7} \frac{T^2}{K^2} + 1.035 \times 10^{-9} \frac{T^3}{K^3}.
\]

In this equation, \( T \) is the absolute temperature in Kelvin. The ratios \( \frac{T^n}{K^n} \) ensure that \( C_{p,m} \) has the correct dimension.

Assuming ideal gas behavior, calculate \( q \), \( w \), \( \Delta U \), and \( \Delta H \) if 1 mol of \( \text{SO}_2(g) \) is heated from 75\(^\circ\) to 1350 \(^\circ\)C at a constant pressure of 1 bar. Explain the sign of \( w \).

3) An 80.0-g piece of gold at 650 K is dropped into 100.0 g of \( \text{H}_2\text{O}(l) \) at 298 K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that \( C_{p,m} \) for \( \text{Au} \) and \( \text{H}_2\text{O} \) is constant at their values for 298 K throughout the temperature range of interest.

4) Approximating the van der Walls equation of state by the virial equation:

\[
Z = 1 + \frac{1}{RT} (b - \frac{a}{RT}) P,
\]

where \( Z = PV/nRT \), show that the Joule-Thomson coefficient \( \mu_{J-T} \) is given by:

\[
\mu_{J-T} = \frac{1}{C_{p,m}} \left( \frac{2a}{RT} - b \right)
\]

Note that because of the approximation used this expression is only valid in the limit of zero pressure.
5) Derive the following expression for calculating the isothermal change in the constant volume heat capacity:

\[
\left( \frac{\partial C_V}{\partial V} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_V.
\]

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

6) Methane can be described by the van der Walls equation of state, with \( a = 0.230 \text{ Pa m}^6 \text{ mol}^{-2} \) and \( b = 4.31 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \). Assume that the enthalpy is given by the formula:

\[
H = H_0 + (C_{V,m} + R)T + \left( b - \frac{2a}{RT} \right)P, \quad \text{with } H_0 \text{ a constant and } C_{V,m} = 27.0 \text{ J K}^{-1} \text{ mol}^{-1}.
\]

(a) Calculate \( \left( \frac{\partial H}{\partial T} \right)_P \) and \( \left( \frac{\partial H}{\partial P} \right)_T \). Compare to the values for an ideal gas.

(b) The gas, initially at \((P_1, T_1)\) is pushed through a throttle to a final state at \((P_2, T_2)\), with \( P_2 < P_1 \). Show that a cooling \((T_2 < T_1, \text{Joule-Thompson effect})\) of the gas can be obtained whatever the final pressure \( P_2 \), but there is a maximum initial temperature \( T_{\text{limit}} \) above which there is no cooling. Give its numerical value for methane.

(c) What should be the initial pressure \( P_1 \) of methane if we want to reach \( T_2 = 110 \text{ K} \) from \( T_1 = 300 \text{ K} \), with an output at atmospheric pressure?

Chapter 4

1) Calculate \( \Delta H^\circ_{\text{reaction}} \) and \( \Delta U^\circ_{\text{reaction}} \) at 298.15 K for the following reactions:

a) \( 4\text{NH}_3(g) + 6\text{NO}(g) \rightarrow 5\text{N}_2(g) + 6\text{H}_2\text{O}(g) \)

b) \( 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \)

c) \( \text{TiCl}_4(l) + 2\text{H}_2\text{O}(l) \rightarrow \text{TiO}_2(s) + 4\text{HCl}(g) \)

d) \( 2\text{NaOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(s) + 2\text{H}_2\text{O}(l) \)

e) \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \)

f) \( \text{CH}_3\text{OH}(g) + \text{CO}(g) \rightarrow \text{CH}_3\text{COOH}(l) \)

2) From the following data at 25 °C

<table>
<thead>
<tr>
<th>( \Delta H^\circ_{\text{reaction}} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_2\text{O}_3(s) + 3\text{C(graphite)} \rightarrow 2\text{Fe}(s) + 3\text{CO}(g) )</td>
</tr>
<tr>
<td>( \text{FeO}(s) + \text{C(graphite)} \rightarrow \text{Fe}(s) + \text{CO}(g) )</td>
</tr>
<tr>
<td>( \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) )</td>
</tr>
<tr>
<td>( \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) )</td>
</tr>
</tbody>
</table>
Calculate the standard enthalpy of formation of FeO(s) and of Fe₂O₃(s).

3) Calculate $\Delta H^\circ_{\text{reaction}}$ at 650 K for the reaction $4\text{NH}_3(g) + 6\text{NO}(g) \rightarrow 5\text{N}_2(g) + 6\text{H}_2\text{O}(g)$ using the temperature dependent heat capacities in the data tables.

4) From the following data at 25 °C

\[ \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{OH}(g) \quad \Delta H^\circ_{\text{reaction}} = 38.95 \text{ kJ mol}^{-1} \]
\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{reaction}} = -241.814 \text{ kJ mol}^{-1} \]
\[ \text{H}_2(g) \rightarrow 2\text{H}(g) \quad \Delta H^\circ_{\text{reaction}} = 435.994 \text{ kJ mol}^{-1} \]
\[ \text{O}_2(g) \rightarrow 2\text{O}(g) \quad \Delta H^\circ_{\text{reaction}} = 498.34 \text{ kJ mol}^{-1} \]

Calculate $\Delta H^\circ_{\text{reaction}}$ for
a) $\text{OH}(g) \rightarrow \text{H}(g) + \text{O}(g)$
b) $\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g)$
c) $\text{H}_2\text{O}(g) \rightarrow \text{H}(g) + \text{OH}(g)$

Assuming ideal gas behavior, calculate $\Delta H^\circ_{\text{reaction}}$ and $\Delta U^\circ_{\text{reaction}}$ for all three reactions.

5) Given the data in Table 4.3 and the Data Tables, calculate the average bond enthalpy and energy of

a) the C–H bond in CH₄
b) the C–C single bond in C₂H₆
c) the C=C double bond in C₂H₄

Use your result from part a) to solve the other parts of the problem.

6) A sample of Na₂SO₄(s) is dissolved in 225 g of water at 298 K such that the solution is 0.325 molar in Na₂SO₄. A temperature rise of 0.146 °C is observed. The calorimeter constant is 330 J K⁻¹. Calculate the enthalpy of solution of Na₂SO₄ in water at this concentration. Compare your result with that calculated using the data in Table 4.1 (Appendix B, Data Table).