## Problem Set 3

### Problem 2

$$\left(\frac{\partial f}{\partial x}\right)_y = 5xy\cos 5x + y\sin 5x - 12xe^{-2x^2}\cos y + 2x\sqrt{y}\ln y$$

$$\left(\frac{\partial f}{\partial y}\right)_x = x\sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2\ln y}{2\sqrt{y}} - 3e^{-2x^2}\sin y$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = 10y\cos 5x - 25xy\sin 5x - 12e^{-2x^2}\cos y + 48e^{-2x^2}x^2\cos y + 2\sqrt{y}\ln y$$

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -3e^{2x^2}\cos y - \frac{x^2\ln y}{4y^{\frac{3}{2}}}$$

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \frac{2x}{\sqrt{y}} + \frac{x\ln y}{\sqrt{y}} + \sin 5x + 5x\cos 5x + 12e^{-2x^2}x\sin y$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 5x\cos 5x + 12e^{-2x^2}x\sin y + \frac{2x}{\sqrt{y}} + \frac{x\ln y}{\sqrt{y}} + \sin 5x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = \left(5xy\cos 5x + y\sin 5x - 12xe^{-2x^2}\cos y + 2x\sqrt{y}\ln y\right)dx$$

$$+\left(x\sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2\ln y}{2\sqrt{y}} - 3e^{-2x^2}\sin y\right)dy$$

### Problem 4

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{\rho}{m}\left(\frac{\partial \frac{m}{\rho}}{\partial T}\right)_P = \frac{\rho}{m}\left(\frac{\partial \frac{m}{\rho}}{\partial \rho}\right)_P\left(\frac{\partial \rho}{\partial T}\right)_P = \frac{\rho}{m}\left(-\frac{m}{\rho^2}\right)\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$$

### Problem 5

$$\Delta P = \int \frac{\beta_{water}}{\kappa}dT - \int \frac{1}{\kappa V}dV \approx \frac{\beta_{water}}{\kappa}\Delta T - \frac{1}{\kappa}\ln\frac{V_f}{V_i}$$

$$= \frac{\beta_{water}}{\kappa}\Delta T - \frac{1}{\kappa}\ln\frac{V_i\left(1+\beta_{vessel}\Delta T\right)}{V_i} \approx \frac{\beta_{water}}{\kappa}\Delta T - \frac{1}{\kappa}\frac{V_i\beta_{vessel}\Delta T}{V_i} = \frac{\left(\beta_{water} - \beta_{vessel}\right)}{\kappa}\Delta T$$

$$= \frac{(2.07 - 1.02)\times 10^{-4}\left({}^\circ\mathrm{C}\right)^{-1}}{4.59\times 10^{-5}\left(\mathrm{bar}\right)^{-1}}\times 60.0^\circ\mathrm{C} = 77.8\,\mathrm{bar}$$

$$P_i + \Delta P = 78.8\,\mathrm{bar}$$

**Problem 9**

$\frac{C_{P,m}}{R} = 3.093 + 6.967\times10^{-3}\frac{T}{\text{K}} - 45.81\times10^{-7}\frac{T^2}{\text{K}^2} + 1.035\times10^{-9}\frac{T^3}{\text{K}^3}$. In this equation, $T$ is the absolute temperature in Kelvin. The ratios $\frac{T^n}{\text{K}^n}$ 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 $SO_2(g)$ is heated from 75° to 1350°C at a constant pressure of 1 bar. Explain the sign of $w$.

$$\Delta H = q = n\int_{T_i}^{T_f} C_{P,m}dT = 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times\int_{348.15}^{1623.15}\left(\begin{array}{l}3.093 + 6.967\times10^{-3}\frac{T}{\text{K}} - 45.81\times10^{-7}\frac{T^2}{\text{K}^2}\\ +1.035\times10^{-9}\frac{T^3}{\text{K}^3}\end{array}\right)d\frac{T}{\text{K}}$$

$$= 1\ \text{mol}\times8.314\ \text{J mol}^{-1}\times\left[3.093\frac{T}{\text{K}} + 0.0034835\frac{T^2}{\text{K}^2} - 1.527\times10^{-6}\frac{T^3}{\text{K}^3} + 2.5875\times10^{-10}\frac{T^4}{\text{K}^4}\right]_{348.15}^{1623.15}$$

$$= \left(\begin{array}{r}1\ \text{mol}\times3.279\times10^4\ \text{J mol}^{-1} + 7.279\times10^4\ \text{J mol}^{-1} - 5.375\times10^4\ \text{J mol}^{-1}\\ +1.490\times10^4\ \text{J mol}^{-1}\text{K}^{-1}\end{array}\right)$$

$$= 6.67\times10^4\ \text{J}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - nR\Delta T$$

$$= 6.673\times10^4\text{J} - 1\ \text{mol}\times8.314\text{J mol}^{-1}\text{K}^{-1}\times(1623.15\ \text{K} - 348.15\ \text{K})$$

$$= 5.61\times10^4\text{J}$$

$$w = \Delta U - q = 5.613\times10^4\text{J} - 6.673\times10^4\text{J} = -1.06\times10^4\text{J}$$

**Problem 13**

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{nR}{P};\quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{nRT}{VP^2} = \frac{1}{P}$$

$$C_P - C_V = TV\frac{\beta^2}{\kappa} = TV\left(\frac{1}{V}\frac{nR}{P}\right)^2 P = TV\frac{n^2R^2}{V^2P} = nR$$

**Problem 19**

$$\Delta H_m = -\int_{P_i}^{P_f} C_{P,m}\mu_{J-T}dP \approx -C_{P,m}\mu_{J-T}(P_f - P_i)$$

$$= -C_{P,m}\,x\frac{1}{C_{P,m}}\left(\frac{2\times0.1355\ \text{m}^6\text{Pa mol}^{-2}}{8.314\ \text{J mol}^{-1}\text{K}^{-1}\times300\ \text{K}} - 0.03201\times10^{-3}\text{m}^3\text{mol}^{-1}\right)\times(1.00\times10^5\ \text{Pa} - 400\times10^5\text{Pa})$$

$$= 3.06\times10^3\text{J}$$

For an ideal gas, $\Delta H_m = 0$ because $\mu_{J-T}$ is zero for an ideal gas.

**Problem 22**

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = -T\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} - P = T\frac{V\beta}{V\kappa} - P = T\frac{\beta}{\kappa} - P$$

**Problem 23**

The internal pressure of a gas is given by

$$\left(\frac{\partial V}{\partial T}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Using the Redlich-Kwong equation of state,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m - b} + \frac{1}{2}\frac{a}{T^{3/2}V_m(V_m+b)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V_m - b} + \frac{1}{2}\frac{a}{\sqrt{T}\,V_m(V_m+b)} - \left(\frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m+b)}\right)$$

$$= \frac{1}{2}\frac{a}{\sqrt{T}\,V_m(V_m+b)} + \frac{a}{\sqrt{T}V_m(V_m+b)} = \frac{3a}{2\sqrt{T}V_m(V_m+b)}$$

**Problem 26**

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

The order of differentiation can be reversed because $U$ is a state function.

Using the equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)\right)_V$$

$$= \left(\frac{\partial P}{\partial T}\right)_V + T\left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

**Problem 29**

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial C_{P,m}}{\partial P}\right)_T$$

Equation 3.44 states that

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Therefore,

$$\left(\frac{\partial C_{P,m}}{\partial P}\right)_T = \left(\frac{\partial}{\partial T}\left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)\right)_P$$

$$= \left(\frac{\partial}{\partial T}\left((RT/P) + B(T) - T\left(\frac{\partial\left[(RT/P) + B(T)\right]}{\partial T}\right)_P\right)\right)_P$$

$$= \left(\frac{\partial}{\partial T}\left((RT/P) + B(T) - T\left(\frac{R}{P} + \frac{dB(T)}{dT}\right)_P\right)\right)_P$$

$$= \left(\frac{R}{P} + \frac{dB(T)}{dT} - \frac{R}{P} - \frac{dB(T)}{dT} + T\frac{d^2B(T)}{dT^2}\right)_P$$

$$= T\frac{d^2B(T)}{dT^2}$$