Chemistry 217

Problem set 5 solution

4.2.

step 1: Isothermal Expansion

$$dw = -pdV$$

$$w = -\int pdV = -RT_1\int_{V_1}^{V_2}\frac{dV}{V-b} + a\int_{V_1}^{V_2}\frac{dV}{V^2}$$

$$\Rightarrow w_1 = -RT_1\ln\left(\frac{V_2-b}{V_1-b}\right) - a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$dE = dQ + dw \Rightarrow dQ = dE - dw = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV$$

$$\Rightarrow dQ = \frac{a}{V^2}dV + \left(\frac{RT_1}{V-b} - \frac{a}{V^2}\right)dV = \frac{RT_1}{V-b}$$

$$\Rightarrow Q_1 = RT_1\ln\left(\frac{V_2-b}{V_1-b}\right)$$

step 2: Adiabatic Expansion

$$Q_2 = 0$$

$$dw = dE = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV = C_v dT + \frac{a}{V^2}dV \Rightarrow w_2 = C_v\int_{T_1}^{T_2}dT + \int_{V_2}^{V_3}\frac{a}{V^2}dV$$

$$\Rightarrow w_2 = C_v\left(T_2 - T_1\right) - a\left(\frac{1}{V_3} - \frac{1}{V_2}\right)$$

step 3: Isothermal Compression

$$w_3 = -RT_2\ln\left(\frac{V_4-b}{V_3-b}\right) - a\left(\frac{1}{V_4}-\frac{1}{V_3}\right)$$

$$Q_3 = RT_2\ln\left(\frac{V_4-b}{V_3-b}\right)$$

step 4: Adiabatic Compression

$$Q_4 = 0$$

$$w_4 = C_v(T_1 - T_2) - a\left(\frac{1}{V_1} - \frac{1}{V_4}\right)$$

Total work: $w = w_1 + w_2 + w_3 + w_4$

$$w = -RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + C_v(T_2 - T_1) - a\left(\frac{1}{V_3} - \frac{1}{V_2}\right) - RT_2 \ln\left(\frac{V_4 - b}{V_3 - b}\right) - a\left(\frac{1}{V_4} - \frac{1}{V_3}\right) + C_v(T_1 - T_2)$$
$$- a\left(\frac{1}{V_1} - \frac{1}{V_4}\right)$$

$$\Rightarrow w = -RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right) - RT_2 \ln\left(\frac{V_4 - b}{V_3 - b}\right)$$

$$Q_1 = RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right)$$

$$y = \frac{-w}{Q_1} = 1 + \frac{T_2}{T_1}\frac{\ln\left(\frac{V_4 - b}{V_3 - b}\right)}{\ln\left(\frac{V_2 - b}{V_1 - b}\right)}$$

Find a relation between $\frac{V_4 - b}{V_3 - b}$ and $\frac{V_2 - b}{V_1 - b}$ from adiabatic steps:

$$dw = dE \Rightarrow -pdV = C_v dT + \frac{a}{V^2} dV = \left(\frac{-RT}{V-b} + \frac{a}{V^2} \right) dV$$

$$\Rightarrow C_v dT = \frac{-RT}{V-b} dV \Rightarrow \frac{C_v}{T} dT = -R \frac{dV}{V-b} \Rightarrow C_v d \ln T = -Rd \ln(V-b)$$

From step 2: $C_v \ln \frac{T_2}{T_1} = -R \ln\left(\frac{V_3 - b}{V_2 - b} \right) = R \ln\left(\frac{V_2 - b}{V_3 - b} \right)$

From step 4: $C_v \ln \frac{T_2}{T_1} = -R \ln\left(\frac{V_1 - b}{V_4 - b} \right)$

which means that $\frac{V_1 - b}{V_4 - b} = \frac{V_2 - b}{V_3 - b} \Rightarrow \frac{V_3 - b}{V_4 - b} = \frac{V_2 - b}{V_1 - b}$

$$\Rightarrow \eta = 1 + \frac{T_2 \ln\left(\frac{V_4 - b}{V_3 - b} \right)}{T_1 \ln\left(\frac{V_2 - b}{V_1 - b} \right)} = 1 - \frac{T_2 \ln\left(\frac{V_3 - b}{V_4 - b} \right)}{T_1 \ln\left(\frac{V_2 - b}{V_1 - b} \right)} = 1 - \frac{T_2}{T_1}$$

4.4.

a.

Chain rule: $\left(\frac{\partial T}{\partial V} \right)_S = -\frac{\left(\frac{\partial S}{\partial V} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_V}$

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V \Rightarrow \left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T}$$

$$dA = -SdT - PdV$$

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

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

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

c.

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

$$dG = -SdT - VdP$$

$$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

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

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$So \quad \left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$$

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

f.

$$\left(\frac{\partial H}{\partial G}\right) = \frac{(\partial H/\partial T)_E}{(\partial G/\partial T)_E}$$

$$dH = C_p dT - C_p \mu_{JT} dp \Rightarrow \left(\frac{\partial H}{\partial T}\right)_E = C_p - C_p \mu_{JT}\left(\frac{\partial p}{\partial T}\right)_E$$

$$dG = -SdT + Vdp \Rightarrow \left(\frac{\partial G}{\partial T}\right)_E = -S + V\left(\frac{\partial p}{\partial T}\right)_E$$

$$\left(\frac{\partial H}{\partial G}\right)_E = \frac{C_p\left[1-\mu_{JT}\left(\frac{\partial p}{\partial T}\right)_E\right]}{-S+V\left(\frac{\partial p}{\partial T}\right)_E} = \frac{C_p\left[1-\frac{V(T\alpha-1)}{C_p}\cdot\left(-\frac{C_p-pV\alpha}{V(p\kappa-T\alpha)}\right)\right]}{-S+V\left[-\frac{C_p-pV\alpha}{V(p\kappa-T\alpha)}\right]}$$

$$= \frac{C_pV(p\kappa-T\alpha)+V(T\alpha-1)(C_p-pV\alpha)}{-SV(p\kappa-T\alpha)-V(C_p-pV\alpha)} = \frac{C_p(p\kappa-T\alpha)-(1-T\alpha)(C_p-pV\alpha)}{-S(p\kappa-T\alpha)-(C_p-pV\alpha)}$$

4.5.

a.

$$dE = TdS - PdV \Rightarrow \left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial V}{\partial S}\right)_P = T\left(1-\frac{P}{T}\left(\frac{\partial V}{\partial S}\right)_P\right)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$ (Maxwell's relation)

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

$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_P = T\left(1-\frac{P}{C_P}\left(\frac{\partial V}{\partial T}\right)_P\right)$$

b.

$$dG = -SdT - VdP \Rightarrow \left(\frac{\partial G}{\partial T}\right)_V = -S + V\left(\frac{\partial P}{\partial T}\right)_V$$

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

$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$ because $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

and $\left(\frac{\partial V}{\partial P}\right)_T = -\kappa V$ because $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\alpha V}{-\kappa V} = \frac{\alpha}{\kappa} \Rightarrow \left(\frac{\partial G}{\partial T}\right)_V = -S + \frac{\alpha V}{\kappa}$$

4.6.

dA = -SdT – PdV

dG= -SdT + VdP

$\Rightarrow$ dA = dG – PdV – VdP   where –VdP = 0 (isobaric)

dH = TdS + VdP = TdS

dE = TdS – PdV = 0 (isothermal)

$\Rightarrow$ TdS = PdV $\Rightarrow$ dA = dG – dH $\Rightarrow$ ΔA = ΔG - ΔH

$$\Delta H = 3\Delta H_{f(H_2O)} + 6\Delta H_{f(CO_2)} - \Delta H_{f(C_6H_6)}$$

= 3(-285.8) + 6(-303.5) – 49.1 = -2727.5 KJ/mol

ΔA = -3174.9 + 2727.5 = -447.4 KJ/mol.

4.8.

$$\left(\frac{\partial E}{\partial l}\right)_T = f - T\left(\frac{\partial f}{\partial T}\right)_l$$

$$dE = TdS + fdl$$

$$\left(\frac{\partial E}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + f$$

$$Where - \left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial f}{\partial T}\right)_l$$

$$\Rightarrow \left(\frac{\partial E}{\partial l}\right)_T = f - T\left(\frac{\partial f}{\partial T}\right)_l$$

$$\Rightarrow \oint dS_{Total} = 0$$

4.9.

$$\Delta S = S_{60} - S_0 = \int_0^{60} \frac{C_p}{T} dT$$

$$\Delta S = \int_0^{60} \left(0.23 + \left(2.5\times10^{-3} T\right) - \left(1.9\times10^{-5} T^2\right)\right) dT$$

$$\Delta S = \left[0.23T + \left(\frac{2.5\times10^{-3}}{2} T^2\right) - \left(\frac{1.9\times10^{-5}}{3} T^3\right)\right]_0^{60}$$

$$\Delta S = 16.9 J / mol.K$$

4.10.

$dA = -SdT - PdT$ where $SdT = 0$ (isothermal)

$$\Rightarrow \Delta A = -\int PdV = -nRT \int_V^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$\Delta A = -(1)(8.314)(300.15)\ln 2 = -1730 J / mol$$

4.14.

$$dH = dQ + VdP = C_P dT + VdP$$

$$\Rightarrow \Delta H = \int C_P dT + \int VdP$$

$$\Delta H = \int_{T_1}^{T} \left(a + bT + cT^2\right) dT + \int_{P_1}^{P} \left(\frac{RT}{P} + B_2(T) + B_3(T)P\right) dP$$

$$\Delta H = a(T - T_1) + \frac{b}{2}\left(T^2 - T_1^2\right) + \frac{c}{3}\left(T^3 - T_1^3\right) + RT \ln P - RT_1 \ln P_1 + B_2 TP - B_2 T_1 P_1 + \frac{B_3}{2} TP^2 - \frac{B_3}{2} TP_1^2$$

$$\Delta S = \int_{T_1}^{T} \frac{C_P}{T} dT = \int_{T_1}^{T} \left(\frac{a}{T} + b + cT \right) dT = a\left[\ln T - \ln T_1\right] + b\left(T - T_1\right) + \frac{c}{2}\left(T^2 - T_1^2\right)$$

4.16.

a.

Prove that $\oint dE = 0$

Step 1 (isothermal) $\Rightarrow$ $dE = 0$

Step 2 (adiabatic) $\Rightarrow dE = dw = nC_V\left(T_2 - T_1\right)$

Step 3 (isothermal) $\Rightarrow dE = 0$

Step 4 (adiabatic) $\Rightarrow dE = nC_V\left(T_1 - T_2\right)$

$\Rightarrow \oint dE_{Total} = 0$

b.

Prove that $\oint dH = 0$

$dH = dE + d\left(PV\right)$

Step 1 : $dH = P_2V_2 - P_1V_1$

Step 2 : $dH = P_3V_3 - P_2V_2 + nC_V\left(T_2 - T_1\right)$

Step 3 : $dH = P_4V_4 - P_3V_3$

Step 4 : $dH = P_1V_1 - P_4V_4 + nC_V\left(T_1 - T_2\right)$

$\oint dH_{Total} = 0$

c.

Prove that $\oint dA = 0$

$dA = dE - d\left(TS\right) = dE - TdS - SdT$

Step 1 : $dA = 0 - T_1 dS - 0 = -T_1 dS$

Step 2 : $dA = nC_V \left(T_2 - T_1\right) - S\left(T_2 - T_1\right)$

Step 3 : $dA = -T_2 dS$

Step 4 : $dA = nC_V \left(T_1 - T_2\right) - S\left(T_1 - T_2\right)$

$\Rightarrow \oint dA = -T_1 dS - T_2 dS$ but $dS = \frac{C_P}{T} dT = 0$ (for isothermal process)

$\Rightarrow \oint dA_{Total} = 0$

d. Prove that $\oint dG = 0$

$dG = dH - d\left(TS\right) = dH - TdS - SdT$

Step 1 : $dG = dH_1 - T_1 dS$

Step 2 : $dG = dH_2 - S\left(T_2 - T_1\right)$

Step 3 : $dG = dH_3 - T_2 dS$

Step 4 : $dG = dH_4 - S\left(T_1 - T_2\right)$

$\Rightarrow \oint dG_{Total} = 0$

e.

Prove that $\oint dS = 0$

Step 1 : $dS = \frac{C_P}{T} dT = 0$

Step 2 : $dS = \frac{C_P}{T} dT \Rightarrow \Delta S = C_P \ln \frac{T_2}{T_1}$

Step 3 : $dS = \frac{C_P}{T} dT = 0$

Step 4 : $dS = \frac{C_P}{T} dT \Rightarrow \Delta S = C_P \ln \frac{T_1}{T_2}$

$$\Rightarrow \oint dS_{Total} = 0$$