Athiqur Rahman
Problem set 4

Analytical 1. $\Delta S = 0$ for the expansion process
$\int dS = \int dq/T$ Since it is a reversible adiabatic
process $dq = 0$ so ΔS is 0.

2a. $\Delta U, \Delta H,$ and ΔS is 0 for the entire cycle.
  b. $nR T_{hot} \ln (v_b/v_a)$. This step occurs from a to b,
     which is the isothermal expansion.
  c. $W_{total} = -nRT_{hot} \ln \frac{v_b}{v_a} - nRT_{cold} \frac{v_d}{v_c}$
     $W_{total} = -nRT \ln \frac{v_b}{v_a} + nRT_{cold} \ln \frac{v_b}{v_a}$
     $W_{total} = -nR \ln \frac{v_b}{v_a} (T_{hot} - T_{cold})$, work is negative
  d. $E = (nR \ln \frac{v_b}{v_a} (T_{hot} - T_{cold})) / (nR \ln \frac{v_b}{v_a} T_{hot})$
     $= 1 - T_{cold}/T_{hot}$
     The efficiency is greater than 1 because $T_{cold} < T_{hot}$.

3a. $dS = (\frac{\partial S}{\partial P}) dP + (\frac{\partial S}{\partial T})_P dT$
    $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\beta V$ $(\frac{\partial S}{\partial T})_P = \frac{C_p}{T}$
    $\beta = \frac{1}{V} (\frac{\partial V}{\partial T})_P$ $d = \frac{1}{V} (\frac{\partial V}{\partial P})_T$
  b. $dS = \frac{C_p}{T} dT - \beta v dp$

Numerical 1a. $\Delta H_{rxn} = (-1364 - 278 - 394) - (1273) = -763 \ kJ/mol$
    $\Delta S_{rxn} = (192 + 161 + 213) - (209) = 357 \ J/mol \ K$
    $\Delta S_{surr} = -\Delta H_{rxn}/T = (-763 \times 1000)/(298.15) = 2559.1 \ J/K$
    $\Delta S_{univ} = \Delta S_{rxn} + \Delta S_{surroundings} = 357 + 2559.1 = 2916.1 \ J/K$
    $\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = (-763000) - (298.15 \times 357) = -86.94 \ kJ/mol$
    The reaction is spontaneous because ΔG_{rxn} is less than 0.

2. $dH = C_p dT$ $\int dH = \int_{298}^{351.3} C_p dT = \int_{298}^{351.3} 69.6 + 2.38 \times 10^{-4} \frac{-112}{T \partial T}$
   $\Delta H = \int_{298}^{351.3} (-46.4 + 2.38 \times 10^{-4}) T dT$ After integrating the
   result is $-2.469 \ kJ/mol$ $\Delta_{vap} H_m (78.3 °C) =$

$$\Delta_{vap}H_m(25°C) + \int_{298}^{351.3} C_p \, dT = 42.3 - 2.469$$

$$\Delta_{vap}H_m(78.3°C) = 39.83 \text{ kJ/mol}$$

$$\Delta_{vap}S_m(78.3°C) = 39.83/351.3$$
$$= 111.02 \text{ J/mol K}$$

3. $S_m(T) = S_m(0K) + \int_0^{TP} \frac{C_{pm} \, dT}{T} \Big|^{solid I,II} + \frac{\Delta H_{fusion}}{TP} + \int_{TP}^{Tb} \frac{C_{pm} \, dT}{T} \Big|^{liquid} +$

$\Delta H_{vaporization}/T_b + \int_{Tb}^{T} \frac{C_{pm} \, dT}{T} \Big|^{gas}$

$S_m(70K) = \int_0^{23.66} \frac{C_{pm} \, dT}{T} \Big|^{solid III} + \frac{93.8 J}{23.66 K} + \int_{23.66}^{43.76} \frac{C_{pm} \, dT}{T} \Big|^{solid II} + \frac{7435}{43.76 K}$

$+ \int_{43.76}^{54.39} \frac{C_{pm} \, dT}{T} \Big|^{solid I} + \frac{445.0 J}{54.39 K} + \int_{54.39}^{70} \frac{C_{pm} \, dT}{T} \Big|^{liquid} =$

$8.182 + 3.964 + 19.61 + 16.98 + 10.13 + 8.181 + 16.23$

$= 83.277 \text{ J/mol K}$

$S_m(150K) = \int_0^{23.66} \frac{C_{pm} \, dT}{T} \Big|^{solid III} + \frac{93.8 J}{23.66 K} + \int_{23.66}^{43.76} \frac{C_{pm} \, dT}{T} \Big|^{solid II} +$

$\frac{7435}{43.76 K} + \int_{43.76}^{54.39} \frac{C_{pm} \, dT}{T} \Big|^{solid I} + \frac{445.0 J}{54.39 K} + \int_{54.39}^{90.20} \frac{C_{pm} \, dT}{T} \Big|^{liquid} +$

$\frac{6815 J}{90.20 K} + \int_{90.20}^{150} \frac{C_{pm} \, dT}{T} \Big|^{gas}$

$S_m(150K) = 8.182 + 3.964 + 19.61 + 16.98 + 10.13 + 8.181 +$

$27.06 + 75.59 + 15.13 = 184.76 \text{ J/mol K}$

$\Delta S_{70K \to 150K} = 184.76 \text{ J/mol K} - 83.28 \text{ J/mol K} = 101.48 \text{ J/mol K}$

The process is spontaneous because $\Delta S > 0$.