

## PROBLEM SET 5

### P3

$$\begin{aligned} a \rightarrow b & \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. & \quad q = -w = 7.62 \times 10^3 \text{ J} \\ b \rightarrow c & \quad \Delta U = w = -5.61 \times 10^3 \text{ J because } q = 0. & \quad \Delta H = \Delta H + nR\Delta T = -9.35 \times 10^3 \text{ J} \\ c \rightarrow d & \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. & \quad q = -w = -3.68 \times 10^3 \text{ J} \\ d \rightarrow a & \quad \Delta U = w = 5.61 \times 10^3 \text{ J because } q = 0. & \quad \Delta H = \Delta H + nR\Delta T = 9.35 \times 10^3 \text{ J} \\ q_{\text{total}} & = 7.62 \times 10^3 \text{ J} - 3.68 \times 10^3 \text{ J} = 3.94 \times 10^3 \text{ J} = -w_{\text{total}} \\ \Delta U_{\text{total}} & = \Delta H_{\text{total}} = 0 \end{aligned}$$

### P4

$$\begin{aligned} a \rightarrow b & \quad \Delta S = -\Delta S_{\text{surroundings}} = \frac{q_{\text{reversible}}}{T} = \frac{7.62 \times 10^3 \text{ J}}{873 \text{ K}} = 8.73 \text{ J K}^{-1} & \quad \Delta S_{\text{total}} = 0 \\ b \rightarrow c & \quad \Delta S = -\Delta S_{\text{surroundings}} = 0 \text{ because } q_{\text{reversible}} = 0 & \quad \Delta S_{\text{total}} = 0 \\ c \rightarrow d & \quad \Delta S = -\Delta S_{\text{surroundings}} = \frac{q_{\text{reversible}}}{T} = \frac{-3.68 \times 10^3 \text{ J}}{423 \text{ K}} = -8.70 \text{ J K}^{-1} & \quad \Delta S_{\text{total}} = 0 \\ d \rightarrow a & \quad \Delta S = -\Delta S_{\text{surroundings}} = 0 \text{ because } q_{\text{reversible}} = 0. & \quad \Delta S_{\text{total}} = 0 \text{ to within the} \\ & \quad \text{round-off error.} \end{aligned}$$

For the cycle,  $\Delta S = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$  to within the round-off error.

**P7**

$$V_i = \frac{nRT_i}{P_i} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}}{10^5 \text{ Pa}} = 2.49 \times 10^{-2} \text{ m}^3$$

$$V_f = \frac{T_f}{T_i} V_i = \frac{450 \text{ K}}{300 \text{ K}} \times 2.49 \times 10^{-2} \text{ m}^3 = 3.74 \times 10^{-2} \text{ m}^3$$

$$w = -P_{\text{external}} \Delta V = -10^5 \text{ Pa} \times (3.74 \times 10^{-2} \text{ m}^3 - 2.49 \times 10^{-2} \text{ m}^3) = -1.25 \times 10^3 \text{ J}$$

$$\Delta U = nC_{V,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J}$$

$$q = \Delta H = \Delta U - w = 1.87 \times 10^3 \text{ J} + 1.25 \times 10^3 \text{ J} = 3.12 \times 10^3 \text{ J}$$

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \left( \frac{3}{2} + 1 \right) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{450 \text{ K}}{300 \text{ K}} = 8.43 \text{ JK}^{-1}$$

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

$w = 0$  because  $\Delta V = 0$ .

$$\Delta U = q = nC_{V,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J}$$

$$\Delta H = nC_{P,m} \Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 3.12 \times 10^3 \text{ J}$$

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \left( \frac{3}{2} \right) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{450 \text{ K}}{300 \text{ K}} = 5.06 \text{ JK}^{-1}$$

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is hal of its initial value.

$\Delta U = \Delta H = 0$  because  $\Delta T = 0$ .

$$w_{\text{reversible}} = -q = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln 2 = -1.73 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{\text{reversible}}}{T} = \frac{1.73 \times 10^3 \text{ J}}{300 \text{ K}} = 5.76 \text{ JK}^{-1}$$

**P8**

a) 450 K, 1 bar

b) 450 K, 1 bar

c) 300 K, 0.500 bar

a) The gas is heated to 450 K at a constant pressure of 1.00 bar.

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-3.12 \times 10^3 \text{ J}}{450 \text{ K}} = -6.93 \text{ JK}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 8.43 \text{ JK}^{-1} - 6.93 \text{ JK}^{-1} = 1.50 \text{ JK}^{-1}$$

The process is spontaneous.

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-1.87 \times 10^3 \text{ J}}{450 \text{ K}} = -4.16 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 5.06 \text{ J K}^{-1} - 4.16 \text{ J K}^{-1} = 0.90 \text{ J K}^{-1}$$

The process is spontaneous.

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

$$\Delta S_{\text{surroundings}} = \frac{q}{T} = \frac{-1.73 \times 10^3 \text{ J}}{300 \text{ K}} = -5.76 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 5.76 \text{ J K}^{-1} - 5.76 \text{ J K}^{-1} = 0$$

There is no natural direction of change in this process because it is reversible.

## P12

a)  $S_m^\circ(\text{Pb}, l, 773 \text{ K}) = S_m^\circ(\text{Pb}, s, 298.15 \text{ K})$

$$+ \int_{298.15}^{600.55} \frac{C_{P,m}}{[T/\text{K}]} d[T/\text{K}] + \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} + \int_{600.55}^{773.15} \frac{C_{P,m}}{[T/\text{K}]} d[T/\text{K}]$$

$$= 64.80 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$+ \int_{298.15}^{600.55} \frac{22.13 + 0.01172[T/\text{K}] + 1.00 \times 10^{-5}[T/\text{K}]^2}{[T/\text{K}]} d[T/\text{K}]$$

$$+ \frac{4770 \text{ J mol}^{-1}}{600.55 \text{ K}}$$

$$+ \int_{600.55}^{773.15} \frac{32.51 - 0.00301[T/\text{K}]}{[T/\text{K}]} d[T/\text{K}]$$

$$= 64.80 \text{ J mol}^{-1} \text{ K}^{-1} + 20.40 \text{ J mol}^{-1} \text{ K}^{-1} + 7.94 \text{ J mol}^{-1} \text{ K}^{-1} + 7.69 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 100.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

b)  $\Delta H_{\text{total}} = \int_{298.15}^{600.55} C_{P,m}^{\text{solid}} d[T/\text{K}] + \Delta H_{\text{fusion}} + \int_{600.55}^{773.15} C_{P,m}^{\text{liquid}} d[T/\text{K}]$

$$= 8918 \text{ J mol}^{-1} + 4770 \text{ J mol}^{-1} + 5254 \text{ J mol}^{-1}$$

$$= 18.94 \times 10^3 \text{ J mol}^{-1}$$

**P14**

$$\Delta U = \int_{V_i}^{V_f} \left( \frac{\partial U}{\partial V} \right)_T dV$$

for a van der Waals gas

$$\Delta U = a \left( \frac{1}{V_{m,i}} - \frac{1}{V_{m,f}} \right)$$

as shown in Example Problem 3.5

$$\Delta U = 0.556 \text{ Pa m}^6 \text{ mol}^{-2} \left( \frac{1}{0.020 \text{ m}^3} - \frac{1}{0.060 \text{ m}^3} \right) \times 1 \text{ mol} = 18.5 \text{ J}$$

$$w = - \int_{V_i}^{V_f} P dV = -RT \int_{V_i}^{V_f} \frac{dV}{V_m - b} + a \int_{V_i}^{V_f} \frac{dV}{V^2}$$

$$= -RT \ln \frac{(V_f - b)}{(V_i - b)} - a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

$$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K} \ln \frac{0.059936}{0.019936}$$

$$- 0.556 \text{ Pa m}^6 \text{ mol}^{-2} \left( \frac{1}{0.060 \text{ m}^3} - \frac{1}{0.020 \text{ m}^3} \right) = -2.73 \times 10^3 \text{ J}$$

$$P_i = \frac{RT}{V_i - b} - \frac{a}{V_i^2} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}}{0.019936 \text{ m}^3} - \frac{0.556 \text{ Pa m}^6 \text{ mol}^{-2}}{(0.020 \text{ m}^3)^2} = 1.237 \times 10^5 \text{ Pa}$$

$$P_f = \frac{RT}{V_f - b} - \frac{a}{V_f^2} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}}{0.059936 \text{ m}^3} - \frac{0.556 \text{ Pa m}^6 \text{ mol}^{-2}}{(0.060 \text{ m}^3)^2} = 4.146 \times 10^4 \text{ Pa}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i$$

$$= 18.5 \text{ J} + (4.146 \times 10^4 \text{ Pa} \times 0.060 \text{ m}^3 - 1.237 \times 10^5 \text{ Pa} \times 0.020 \text{ m}^3) = 32.1 \text{ J}$$

$$q = \Delta U - w \approx 2.73 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{\text{reversible}}}{T} = \frac{2.73 \times 10^3 \text{ J}}{300.13 \text{ K}} = 9.10 \text{ J K}^{-1}$$

**P18**

$$\Delta U = nC_{v,m}\Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (250 \text{ K} - 600 \text{ K}) = -4.36 \times 10^3 \text{ J}$$

$$\Delta H = nC_{p,m}\Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (250 \text{ K} - 600 \text{ K}) = -7.27 \times 10^3 \text{ J}$$

$$\begin{aligned} \Delta S &= -nR \ln \frac{P_f}{P_i} + nC_{p,m} \ln \frac{T_f}{T_i} \\ &= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{4.500 \text{ bar}}{1.00 \text{ bar}} + 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times \ln \frac{250 \text{ K}}{600 \text{ K}} \\ &= -12.5 \text{ J K}^{-1} - 18.2 \text{ J K}^{-1} = -30.7 \text{ J K}^{-1} \end{aligned}$$

**P22**

Assume that the final state is liquid water. If this is not the case, the calculated temperature will be greater than 373 K.

$$-n_{\text{steam}} \Delta H_{\text{vaporization}}^{H_2O} + n_{\text{steam}} C_{p,m}^{H_2O} (T_f - T_i^{\text{steam}}) + n_{H_2O} C_{p,m}^{H_2O} (T_f - T_i^{H_2O}) = 0$$

$$T_f = \frac{n_{\text{steam}} C_{p,m}^{H_2O} T_i^{\text{steam}} + n_{H_2O} C_{p,m}^{H_2O} T_i^{H_2O} + n_{\text{steam}} \Delta H_{\text{vaporization}}^{H_2O}}{n_{\text{steam}} C_{p,m}^{H_2O} + n_{H_2O} C_{p,m}^{H_2O}} =$$

$$\frac{\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1}\text{mol}^{-1} \times 373 \text{ K} + \frac{250 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K} + \frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 40650 \text{ J mol}^{-1}}{\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1}\text{mol}^{-1} + \frac{250 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ J K}^{-1}\text{mol}^{-1}}$$

$$T_f = 333 \text{ K}$$

$\Delta S$  is calculated for the steam. It consists of condensing the steam at 373 K and cooling the resulting water to 333 K.

$$\begin{aligned} \Delta S &= -n \frac{\Delta H_{\text{vaporization}}}{T_{\text{vaporization}}} + nC_{p,m} \ln \frac{T_f}{T_{\text{vaporization}}} \\ &= -\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times \frac{40650 \text{ J mol}^{-1}}{373 \text{ K}} + \frac{15.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.291 \text{ J K}^{-1}\text{mol}^{-1} \times \ln \frac{333 \text{ K}}{373 \text{ K}} \\ &= -90.7 \text{ J K}^{-1} - 7.11 \text{ J K}^{-1} = -97.8 \text{ J K}^{-1} \end{aligned}$$

$\Delta S$  is calculated for the water. It consists of heating the water from 298 K to 333 K.

$$\Delta S = nC_{p,m} \ln \frac{T_f}{T_{\text{fusion}}} = \frac{250.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{333 \text{ K}}{298 \text{ K}} = 116 \text{ J K}^{-1}$$

$\Delta S_{\text{total}} = 0 + 116 \text{ J K}^{-1} - 97.8 \text{ J K}^{-1} = 18.2 \text{ J K}^{-1}$ . The process is spontaneous.

## P24

Consider the two pathways at 1 bar: (a)  $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$  and (b)  $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$ . Because  $S$  is a state function,  $\Delta S$  must be the same for both pathways.]

For pathway b)  $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$

$$\begin{aligned} \Delta S &= nC_{p,m}(l) \ln \frac{273.15 \text{ K}}{270.90 \text{ K}} - n \frac{\Delta H_{\text{fusion}}}{273.15 \text{ K}} + nC_{p,m}(s) \ln \frac{270.90 \text{ K}}{273.15 \text{ K}} \\ &= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{273.15 \text{ K}}{270.90 \text{ K}} - 1 \text{ mol} \times \frac{6008 \text{ J mol}^{-1}}{273.15 \text{ K}} \\ &\quad + 1 \text{ mol} \times 37.7 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{270.90 \text{ K}}{273.15 \text{ K}} \\ &= 0.608 \text{ J K}^{-1} - 22.0 \text{ J K}^{-1} - 0.312 \text{ J K}^{-1} = -21.7 \text{ J K}^{-1} \end{aligned}$$

To calculate  $\Delta S_{\text{surroundings}}$ , we first calculate  $\Delta H_p = q$ .

$$\Delta H(-2.25^\circ\text{C}) = \Delta H(0.00^\circ\text{C}) + (C_p(\text{solid}) - C_p(\text{liquid}))\Delta T$$

$$\begin{aligned} \Delta H(-2.25^\circ\text{C}) &= -6008 \text{ J mol}^{-1} + (37.7 \text{ J mol}^{-1} \text{ K}^{-1} - 73.15 \text{ J mol}^{-1} \text{ K}^{-1}) \times (-2.25 \text{ K}) \\ &= -5928 \text{ J mol}^{-1} = q \end{aligned}$$

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{5928 \text{ J mol}^{-1}}{270.90 \text{ K}} = 21.9 \text{ J K}^{-1}$$

$\Delta S_{\text{total}} = 21.9 \text{ J K}^{-1} - 21.7 \text{ J K}^{-1} = 0.2 \text{ J K}^{-1} > 0$ . The process is spontaneous.

**P27**

- a) What is the efficiency of a reversible Carnot engine operating under these conditions?
- b) If the efficiency of the boiler is 91.2%, the overall efficiency of the turbine, which includes the Carnot efficiency and its mechanical efficiency, is 46.7%, and the efficiency of the generator is 98.4%, what is the efficiency of the total generating unit? (Another 5% needs to be subtracted off for other plant losses.)
- c) One of the coal burning units produces 355 MW. How many metric tons (1 metric ton =  $1 \times 10^6$  g) of coal per hour are required to operate this unit at its peak output if the enthalpy of combustion of coal is  $29.0 \times 10^3$  kJ kg<sup>-1</sup>?

a) 
$$\epsilon = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{303 \text{ K}}{813 \text{ K}} = 0.627$$

- b) The efficiency of the generating plant is the product of the individual efficiencies.

$$\epsilon = 0.912 \times 0.467 \times 0.984 \times 0.95 = 0.398$$

- c) The energy output per hour is given by  $355 \text{ MW} \times \frac{3600 \text{ s}}{\text{hr}} = 1.278 \times 10^{12} \text{ J hr}^{-1}$

The heat required to output this energy is

$$q = \frac{E_{output}}{\epsilon} = \frac{1.278 \times 10^{12} \text{ J hr}^{-1}}{0.398} = 3.211 \times 10^{12} \text{ J hr}^{-1}$$

The number of tons of coal needed is  $\frac{3.211 \times 10^{12} \text{ J hr}^{-1}}{29.0 \times 10^9 \text{ J ton}^{-1}} = 110.7 \text{ ton hr}^{-1}$ .