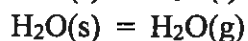
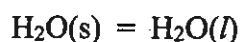


1. A coal-fired steam turbine operating with $T_C = 300$ K and $T_H = 500$ K does $-w = 2.5 \times 10^{13}$ J work per day. Calculate the minimum amount of heat q_H required per day to run the turbine. [2]
2. One mole of helium at 1.00 bar and 300 K is compressed reversibly and adiabatically to a final pressure of 32.0 bar. (Assume helium is an ideal gas with $C_{V,m} = 3R/2$ and $C_{p,m} = 5R/2$.) [6]
- a) Show that the final temperature of the compressed helium is 1200 K. *Hint: $T_f/T_i = (p_f/p_i)^{R/C_{p,m}}$*
- b) Calculate w , q , ΔU , ΔH and ΔS .
3. One mole of helium (assumed to be an ideal gas with $C_{V,m} = 3R/2$ and $C_{p,m} = 5R/2$) initially at 1.00 bar and 300 K undergoes a two-step process: [4]
- Step 1. heating from 300 K to 1200 K at 1.00 bar
- Step 2. isothermal compression from 1.00 bar to 32.0 bar at 1200 K
- a) Calculate ΔS_1 for step 1. b) Calculate ΔS_2 for step 2.
- c) Calculate the entropy change $\Delta S = \Delta S_1 + \Delta S_2$ for the overall process.
- [A helpful equation for answering this question is: $dS = (C_p/T)dT - (nR/p)dp$]
4. Questions 2 and 3 illustrate that the entropy is a state function. Explain. [1]
5. After tidying up a messy room, one of your classmates claims the decrease in disorder and the resulting decrease in the entropy of the room violates the Second Law of Thermodynamics which states that the entropy can never decrease. Why is this argument incorrect? [1]
6. A question on the last test asked you to use $dq_{\text{rev}} = C_V dT + p dV$ for an ideal gas to show the state function $q_{\text{rev}}(T, V)$ does not exist. Dividing by T gives $dq_{\text{rev}}/T = dS$ and [3]
- $$dS = (C_V/T)dT + (p/T)dV$$
- Use this expression for dS for an ideal gas to show the state function $S(T, V)$ does exist.
7. a) Calculate ΔS for the melting of 5.00 moles of ice at 0.00 °C and 1.00 bar. [3]
- b) Calculate ΔS for the sublimation of 5.00 moles of ice at 0.00 °C and 1.00 bar.
- c) Give a qualitative molecular explanation for the fact the entropy change for sublimation is much larger than that for fusion.

Data at 0.00 °C:



$$\Delta H_{\text{fus},m}^{\circ} = 6.00 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub},m}^{\circ} = 40.63 \text{ kJ mol}^{-1}$$

- Q1) A heat engine operating with $T_H = 500$ (from burning coal) and $T_C = 300$ K does 2.5×10^{13} J work on the surroundings per day. Minimum amount of heat q_H per day required?

reversible engine efficiency

$$\epsilon = \frac{-W}{q_H} = 1 - \frac{T_C}{T_H} \quad \left(\begin{array}{l} \text{"best" efficiency} \\ \text{possible} \end{array} \right)$$

work done on surroundings (per day) = $-W = 2.5 \times 10^{13}$ J

$$\epsilon = 1 - \frac{300 \text{ K}}{500 \text{ K}} = \boxed{0.40} \quad \left(40\% \text{ max. efficiency} \right)$$

minimum heat required

$$= q_H = \frac{-W}{\epsilon} = \frac{2.5 \times 10^{13} \text{ J}}{0.40} = \boxed{6.25 \times 10^{13} \text{ J (per day)}}$$

This is the minimum heat required (for a reversible engine). A real engine would be less efficient ($\epsilon < 0.40$), requiring more heat.

- Q2) 1.00 mol of helium ($C_{vm} = 3R/2$, $C_{pm} = 5R/2$) compressed reversibly and adiabatically from 1.00 bar, 300 K to a final pressure of 32.0 bar.

Useful equations (assuming ideal gas behavior and constant C_{vm}):

$$P_i V_i^{C_{pm}/C_{vm}} = P_f V_f^{C_{pm}/C_{vm}}$$

$$T_f/T_i = (P_f/P_i)^{R/C_{pm}} \quad \left(\text{more convenient here} \right)$$

(Q2 cont.)

a) $T_i = 300 \text{ K}$, $p_i = 1.00 \text{ bar}$, $C_{vm} = \frac{3}{2}R$, $C_{pm} = \frac{5}{2}R$
 $p_f = 32.0 \text{ bar}$

$$T_f / T_i = (p_f / p_i)^{R/C_{pm}} = (32.0 \text{ bar} / 1.00 \text{ bar})^{R / \frac{5}{2}R} = (32)^{\frac{2}{5}}$$

$$T_f / T_i = 4.00 \quad T_f = 4T_i = 4(300 \text{ K}) = \boxed{1200 \text{ K}}$$

b) $q = 0$ (adiabatic process)

$$\Delta S = \int \frac{dq_{rev}}{T} = 0 \quad (\text{reversible adiabatic process})$$

$\Delta S = 0$

$$dU = C_v dT = n C_{vm} dT \quad (\text{ideal gas, } U \text{ depends on } T \text{ only})$$

$$\Delta U = \int n C_{vm} dT = n C_{vm} \int dT \quad (C_{vm} \text{ constant})$$

$= 3R/2$

$$\Delta U = (1.00 \text{ mol}) \frac{3}{2} (8.314 \frac{\text{J}}{\text{K mol}}) (1200 - 300 \text{ K})$$

$$\Delta U = 11,220 \text{ J} = w \quad (q = 0)$$

$$\left(C_{pm} = \frac{5}{2}R \right. \\ \left. (\text{constant}) \right)$$

$$\Delta H = \int C_p dT = \int n C_{pm} dT = n \frac{5}{2}R \int dT$$

$$\Delta H = (1.00 \text{ mol}) \frac{5}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta H = 18,710 \text{ J}$$

(could also use $p_i V_i^{C_{pm}/C_{vm}} = p_f V_f^{C_{pm}/C_{vm}}$
with $V_i = \frac{nRT_i}{p_i} = 24.94 \text{ L}$ to calculate $V_f = 3.118 \text{ L}$
and $T_f = (p_f V_f / nR) = 1200 \text{ K}$)

$$dS_p = \frac{C_p}{T} dT$$

$$\text{useful: } dS = \frac{C_p}{T} dT + \frac{nR}{V} dV$$

Q3 a) Step 1 Heat 1.00 mol helium from 300 K to 1200 K at constant pressure (1.00 bar):

take a reversible path (easiest calculation of ΔS !)

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{n C_{p,m} dT}{T} = n \frac{5}{2} R \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S_1 = (1.00 \text{ mol}) \frac{5}{2} (8.314 \frac{\text{J}}{\text{K mol}}) \ln \left(\frac{1200 \text{ K}}{300 \text{ K}} \right) = \boxed{28.81 \frac{\text{J}}{\text{K}}}$$

$$dS_T = \frac{nR}{V} dV$$

b) Step 2 Compress 1.00 mol helium from 1.00 bar to 32.0 bar at 1200 K. (isothermal ideal gas)
(isothermal) $\left(\begin{array}{l} dU = C_v dT = 0 = dq + dw \\ -dw = dq \end{array} \right)$

take a reversible path:
($P_{ext} = P$)

$$\Delta S_2 = \int \frac{dq_{rev}}{T} = - \int \frac{dw_{rev}}{T} = - \int \frac{(-P_{ext}) dV}{T} = \int \frac{P dV}{T}$$

$$\Delta S_2 = \int \frac{nR}{V} dV = nR \int \frac{dV}{V} = nR \ln \left(\frac{V_f}{V_i} \right)$$

$$\Delta S_2 = nR \ln \left(\frac{\frac{nRT_f}{P_f}}{\frac{nRT_i}{P_i}} \right) = nR \ln \left(\frac{P_i}{P_f} \right) \quad \left(\begin{array}{l} \text{here:} \\ T_f = T_i = 1200 \text{ K} \\ \text{isothermal} \end{array} \right)$$

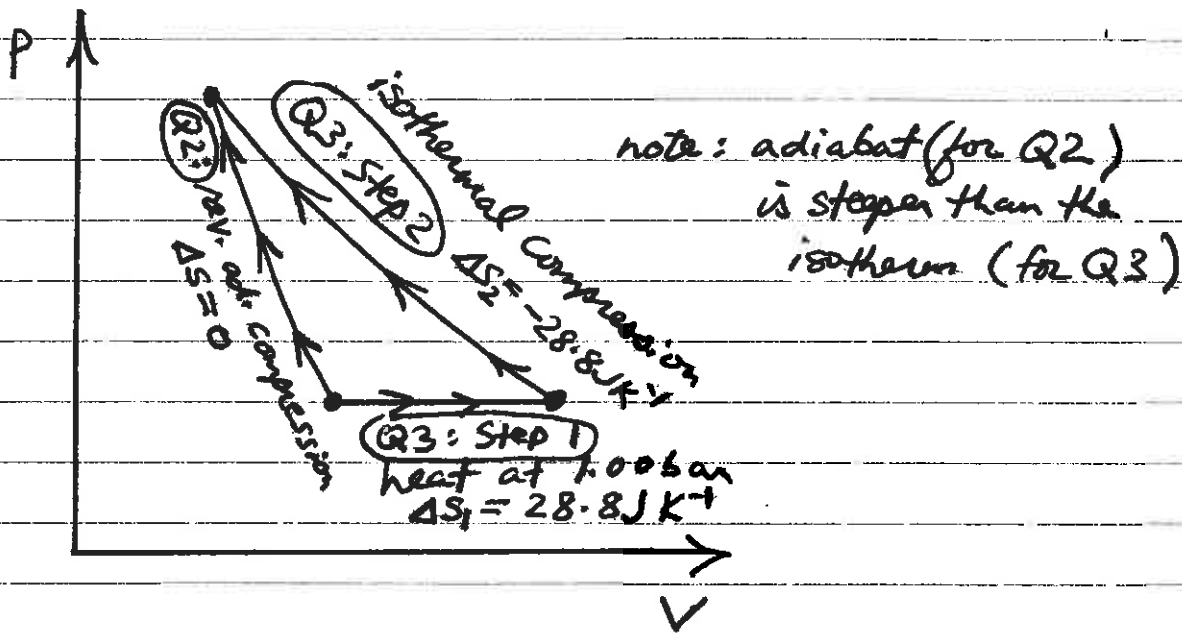
$$\Delta S_2 = (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{K mol}} \right) \ln \left(\frac{1.00 \text{ bar}}{32.0 \text{ bar}} \right)$$

$$\boxed{\Delta S_2 = -28.81 \frac{\text{J}}{\text{K}}}$$

$$c) \Delta S_1 + \Delta S_2 = 28.81 \frac{\text{J}}{\text{K}} + \left(-28.81 \frac{\text{J}}{\text{K}} \right)$$

$$\boxed{\Delta S_1 + \Delta S_2 = 0}$$

Q4 Indicator Diagram for Questions 2 and 3



ΔS is path independent

Q2:

$$1.00 \text{ bar}, 300 \text{ K} \longrightarrow 32.0 \text{ bar}, 1200 \text{ K}$$

$$\Delta S = 0$$

Q2:

$$1.00 \text{ bar}, 300 \text{ K} \xrightarrow{\text{Step 1}} 1.00 \text{ bar}, 1200 \text{ K} \xrightarrow{\text{Step 2}} 32.0 \text{ bar}, 1200 \text{ K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 0$$

Identical ΔS for different paths connecting states
1.00 bar, 300 K and 32.0 bar, 1200 K

Q5 The room is not an isolated system. (Work is done on it.)

The entropy change for a system that is not isolated can increase, decrease or remain constant.

The entropy of an isolated system can never decrease (from the Second Law).

Q6 (For an ideal gas: $p = \frac{nRT}{V}$ and $(\frac{\partial U}{\partial V})_T = 0$.)

$$dS = \frac{C_V}{T} dT + \frac{p}{T} dV \quad g(T,V) = \frac{C_V}{T}$$

$$dS = g(T,V) dT + h(T,V) dV \quad h(T,V) = \frac{p}{T}$$

The state function $S(T,V)$ exists if $(\frac{\partial g}{\partial V})_T \stackrel{?}{=} (\frac{\partial h}{\partial T})_V$

$$\begin{aligned} LS &= \left(\frac{\partial g}{\partial V}\right)_T = \left(\frac{\partial}{\partial V} \frac{C_V}{T}\right)_T = \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{1}{T} \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right]_T \\ &= \frac{1}{T} \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right]_V = \frac{1}{T} \left(\frac{\partial 0}{\partial T}\right)_V = 0 \end{aligned}$$

(reverse order)

$$RS = \left(\frac{\partial h}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \frac{p}{T}\right)_V = \left(\frac{\partial}{\partial T} \frac{nR}{V}\right)_V = \frac{1}{V} \left(\frac{\partial nR}{\partial T}\right)_V = \frac{1}{V} (0) = 0$$

$LS = RS = 0, \therefore S(T,V)$ exists

Q7 a) $\Delta S_{fus} = \frac{q_{rev}}{T} = \frac{n \Delta H_{fus,m}^\circ}{T_{fus}}$

$$= \frac{(5.00 \text{ mol})(6000 \text{ J mol}^{-1})}{273.15 \text{ K}} = \boxed{\Delta S_{fus} = 109.8 \frac{\text{J}}{\text{K}}}$$

b) $\Delta S_{sub} = \frac{q_{rev}}{T} = \frac{n \Delta H_{sub,m}^\circ}{T_{sub}}$

$$= \frac{(5.00 \text{ mol})(40630 \text{ J mol}^{-1})}{273.15 \text{ K}} = \boxed{\Delta S_{sub} = 743.7 \frac{\text{J}}{\text{K}}}$$

c) Entropy change for solid \rightarrow gas is much larger than the solid \rightarrow liquid entropy change because gases have significantly larger entropies than solids or liquids. Gases are the most "disordered" state.

$W_{gas} \gg W_{solid}$
 $W_{gas} \gg W_{liquid}$