Exercise 4.8(b): A sample consisting of 2.0 mol of a diatomic gas perfect gas at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{v,m} = 27.5 \text{ J-K}^{-1}\text{-mol}^{-1}$, calculate $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$.

$q = 0 \text{ J for adiabatic process.}$

$\Delta U = C_{v,m} \Delta T = 2.0 \text{ mol} * 27.5 \text{ J-K}^{-1}\text{-mol}^{-1} * 50 \text{ K} = 2,750 \text{ J}$

$w = \Delta U - q = 2,750 \text{ J} - 0 \text{ J} = 2,750 \text{ J}$

$\Delta H = C_{p,m} \Delta T$; $C_{p,m} = C_{v,m} + R$;

$C_{p,m} = C_{v,m} + R = 27.5 \text{ J-K}^{-1}\text{-mol}^{-1} + 8.314 \text{ J-K}^{-1}\text{-mol}^{-1} = 35.81 \text{ J-K}^{-1}\text{-mol}^{-1}$

$\Delta H = 2.0 \text{ mol} * 35.81 \text{ J-K}^{-1}\text{-mol}^{-1} * 50 \text{ K} = 3,581 \text{ J}$

$\Delta S = q/T = 0 \text{ J-K}^{-1} \text{ since reversible adiabatic process, } \Delta S > 0 \text{ for real processes.}$

Exercise 4.10(b): A system undergoes a process in which the entropy change is +5.51 J-K$^{-1}$. During the process, 1.50 kJ of heat is added to the system at 350 K. Is the process thermodynamically reversible? Explain your reasoning.

$\Delta S = q_{\text{reversible}}/T$

$q_{\text{reversible}} = T \Delta S = 350 \text{ K} * 5.51 \text{ J/K} = 1.9 \text{ kJ}$

Since $q > q_{\text{reversible}}$ the process is not reversible and $\Delta S_{\text{universe}} > 0$.

Exercise 4.11(b): A sample of copper of mass 2.75 kg is cooled at constant pressure from 330 K to 275 K. Calculate a) the energy that must be removed as heat and b) the change in entropy of the sample.

$\Delta H = m C_{p,m} \Delta T = 2750 \text{ g} * (63.5 \text{ g/mole})^{-1} * 24.4 \text{ J/K-mol}(275 \text{ K} - 330 \text{ K}) = -58.11 \text{ kJ}$

$\Delta S = q_{\text{reversible}}/T = m C_{p,m} \Delta T/T$

$\Delta S = m C_{p,m} \ln(T) = 2750 \text{ g} * (63.5 \text{ g/mole})^{-1} * 24.4 \text{ J/K-mol} \ln(275/330) = -192.7 \text{ J/K}$

Problem 4.1: Calculate the difference in molar entropy a) between water and ice at –5 °C, b) between liquid water and its vapor at 95 °C and 1 atm. The differences in heat capacities on melting and on vaporization are 37.3 J/K-mol and –41.9 J/K-mol, respectively. Distinguish between the entropy changes of the sample, the surroundings and the total system and discuss the spontaneity of the transitions at the two temperatures.

a) a thermodynamic cycle is needed to solve for the molar entropy

water(-5 °C) __________ ice(-5 °C)

<p>| |</p>
<table>
<thead>
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<tbody>
<tr>
<td>water(0°C)</td>
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</table>

We can find the quantity that we want by taking the detour.

$\Delta S_{\text{transition}} = m C_{p,\text{water}} \ln(273/268) + m \Delta H_{\text{fusion}}/T + m C_{p,\text{ice}} \ln(268/273)$

$= -m C_{p,\text{water}} \ln(268/273) + m \Delta H_{\text{fusion}}/273 + m C_{p,\text{ice}} \ln(268/273)$

$= -m \Delta C_{p,\text{water/ice}} \ln(268/273) + m \Delta H_{\text{fusion}}/273$ ; $m = 1 \text{ mole,}$

$= -37.3 \text{ J/K} \ln(268/273) + -6008 \text{ J/273 K} = -21.3 \text{ J/K}$ entropy decreases water $\rightarrow$ ice

We can do the same trick for $\Delta H$
\[ \Delta H_{\text{transition}} = mC_{p,\text{water}} (273-268) + m\Delta H_{\text{fusion}} + mC_{p,\text{ice}} (268-273) \]
\[ = -mC_{p,\text{water}} (268-273) + m\Delta H_{\text{fusion}} + mC_{p,\text{ice}} (268-273) \]
\[ = -m\Delta C_{p, \text{water/ice}} (268-273) + m\Delta H_{\text{fusion}} ; m = 1 \text{ mole}, \]
\[ = -37.3 \text{ J/K (268-273 K)} + 6008 \text{ J} = -5821.5 \text{ J} \text{ enthalpy decreases water} \rightarrow \text{ ice} \]

Heat leaving system (-) enters surroundings (+).
\[ \Delta S_{\text{surroundings}} = 5821.5 \text{ J/ 268 K} = +21.7 \text{ J/K} \]
\[ \Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{transition}} = +21.7 \text{ J/K} -21.3 \text{ J/K} = +0.4 \text{ J/K} \]
processes is spontaneous.

b) a thermodynamic cycle is needed to solve for the molar entropy

Water freezes at temperatures below 0 °C and boils above 100 °C
Both are spontaneous according to 2nd Law.

Problem 4.5: A Carnot cycle uses 1.0 mole of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.0 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3), and then an adiabatic expansion (Step 4) back to the initial state. Determine the values of q, w, \( \Delta U \), \( \Delta H \), \( \Delta S \), and \( \Delta G \) for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

**Step 1**
\[ w = nRT \ln (P_b/P_a) = 1.0 \text{ mole} \times 8.314 \text{ J/mole-K} \times 600 \text{ K} \times \ln(1 \text{ atm/10 atm}) = -11.5 \text{ kJ} \]
\[ \Delta U = 0 \text{ ideal gas & isothermal process} \]
\[ q = -w = 11.5 \text{ kJ} \]
\[ \Delta H = \Delta U + \Delta PV = 0 \text{ kJ} + (P_a * nRT/P_a - P_b * nRT/P_b) = 0 \text{ kJ} \]
\[ \Delta S = q/T = 11.5 \text{ kJ}/600 \text{ K} = 19.17 \text{ J/K} \]
\[ \Delta G = \Delta H - T\Delta S = 0 - 600 * (19.17) = -11.5 \text{ kJ} \]
Step 2
\[ \Delta U = C_v \Delta T = \frac{3}{2} R (300-600 \text{ K}) = -3.7 \text{ kJ} \]
\[ w = \Delta U = -3.7 \text{ kJ} \]
\[ q = 0 \text{ adiabatic process} \]
\[ \Delta H = \Delta U + \Delta PV = \Delta U + nR \Delta T = -3.7 \text{ kJ} + 1.0 \text{ mole} \cdot 8.314 \text{ J/mole} \cdot \text{K} (300-600 \text{ K}) = -6.2 \text{ kJ} \]
\[ \Delta S = q/T = 0 \]
\[ \Delta G = \Delta H - T \Delta S = -6.2 \text{ kJ} \]

Step 3
\[ w = nRT \ln(P_c/P_d) = 1.0 \text{ mole} \cdot 8.314 \text{ J/mole} \cdot \text{K} \cdot 300 \text{ K} \cdot \ln(10 \text{ atm}/1 \text{ atm}) = 5.7 \text{ kJ} \]
\[ \Delta U = 0 \text{ ideal gas & isothermal process} \]
\[ q = -w = -5.7 \text{ kJ} \]
\[ \Delta H = 0 \text{ kJ ideal gas & isothermal process} \]
\[ \Delta S = q/T = -5.7 \text{ kJ}/300 \text{ K} = -19.17 \text{ J/K} \]
\[ \Delta G = \Delta H - T \Delta S = 0 - 300(-19.17) = +5.7 \text{ kJ} \]

Step 4
\[ \Delta U = C_v \Delta T = \frac{3}{2} R (600-300 \text{ K}) = +3.7 \text{ kJ} \]
\[ w = \Delta U = 3.7 \text{ kJ} \]
\[ q = 0 \text{ adiabatic process} \]
\[ \Delta H = \Delta U + \Delta PV = \Delta U + nR \Delta T = -3.7 \text{ kJ} + 1.0 \text{ mole} \cdot 8.314 \text{ J/mole} \cdot \text{K} (300-600 \text{ K}) = +6.2 \text{ kJ} \]
\[ \Delta S = q/T = 0 \]
\[ \Delta G = \Delta H - T \Delta S = +6.2 \text{ kJ} \]

<table>
<thead>
<tr>
<th></th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta U )</td>
<td>0</td>
<td>-3.7 kJ</td>
<td>0</td>
<td>+3.7 kJ</td>
<td>0</td>
</tr>
<tr>
<td>( w )</td>
<td>-11.5 kJ</td>
<td>-3.7 kJ</td>
<td>+5.7 kJ</td>
<td>+3.7 kJ</td>
<td>-5.8 kJ</td>
</tr>
<tr>
<td>( q )</td>
<td>11.5 kJ</td>
<td>0</td>
<td>-5.7 kJ</td>
<td>0</td>
<td>5.8 kJ</td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>0</td>
<td>-6.2 kJ</td>
<td>0</td>
<td>+6.2 kJ</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>19.17 J/K</td>
<td>0</td>
<td>-19.17 J/K</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta G )</td>
<td>-5.7 kJ</td>
<td>-6.2 kJ</td>
<td>+5.7 kJ</td>
<td>+6.2 kJ</td>
<td>0</td>
</tr>
</tbody>
</table>

Note that all state functions are 0 for the cycle. No net change in a state function with a cyclic path. Net results are heat is absorbed and work is released by our cycle.
Problem 4.20: Show that the integral of $\frac{dq_{rev}}{T}$ round a Carnot cycle is zero. Then show that the integral is negative if the isothermal reversible expansion is replaced by an isothermal irreversible expansion.

$$\delta S = \delta q/T(\text{isothermal}) + \delta q/T(\text{adiabatic}) + \delta q/T(\text{isothermal}) + \delta q/T(\text{adiabatic})$$

$$= \delta q/T(\text{isothermal expansion}) + \delta q/T(\text{isothermal compression})$$

as $dq = 0$ for adiabatic processes.

$$= nRT_H \ln(V_b/V_a)/T_H + nRT_C \ln(V_c/V_d)/T_C$$

since $\delta q = \delta dV = nRT \delta V/V$ for a reversible isothermal process with an ideal gas as shown in class $V_b/V_a = V_d/V_c$

$$= nR \ln(V_b/V_a) - nR \ln(V_b/V_a) = 0$$

$$\delta S = \delta q/T(\text{isothermal}) + \delta q/T(\text{adiabatic}) + \delta q/T(\text{isothermal}) + \delta q/T(\text{adiabatic})$$

$$= \delta q/T(\text{isothermal expansion}) + \delta q/T(\text{isothermal compression})$$

as $dq = 0$ for adiabatic processes.

$$= nRT_H \ln(V_b/V_a)/T_H + nRT_C \ln(V_c/V_d)/T_C$$

since $\delta q = \delta dV = nRT \delta V/V$ for a reversible isothermal process with an ideal gas

since $\delta q = \delta p dV = p_{ex}(V_b-V_a)$ for an irreversible isothermal process with an ideal gas

$$= p_{ex}(V_b-V_a)/T_H - nR \ln(V_b/V_a) < 0$$

For ideal gases undergoing an isothermal process $\Delta U = 0$ so $q = -w$

Work is a maximum for a reversible process. The work produced by an irreversible process is less than the work produced by the reversible process.

Therefore our new cycle has an integral that is equal to a value that is less than zero.

Problem 4.24: A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1 + Bp)$. Initially at 373 K it undergoes a Joule-Thomson expansion from 100 atm to 1.0 atm. Given that $C_{p,m} = 5/2 R$, $\mu = 0.21$ K-atm$^{-1}$, $B = 0.525$ (K/T) atm$^{-1}$ and that these values are constant over the temperature range involved calculate $\Delta T$ and $\Delta S$ for the gas.

$$\mu = (\partial T/\partial p)_H$$

$$\Delta T = \mu \Delta p = 0.21 \text{ K/atm} \times (1 - 100 \text{ atm}) = -20.79 \text{ K}$$

$$dS = (\partial S/\partial T)_P dT + (\partial S/\partial P)_T dp$$

$$(\partial S/\partial T)_P = C_p/T$$

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P = (R/p)(1 + Bp) = (R/p + BR)$$

$$dS = C_p/T dT - (R/p + BR) dp$$

$$\Delta S = \int \left( C_p/T - \frac{\gamma R}{p + BR} \right) dp$$

$$\Delta S = C_p \ln(T) - R \ln(p) - BR p$$

$$= 5/2 \times 8.314 \text{ J/mole-K} \times \ln(352K/373K) - 8.314 \text{ J/mole-K} \times \ln(1.0 \text{ atm/100 atm})$$

$$= 8.314 \text{ J/mole-K} 	imes 0.525 \text{ K/363 K} \times (1 \text{ atm} - 100 \text{ atm})$$

$$= +38.3 \text{ J/K/mole}$$
Problem 4.31

Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is -5512 kJ/mol and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000 °C and the exit temperature is 800 °C?

Octane C₈H₁₈ FW = 114 g/mol
1 gal = 3 kg * 1 mol/114 g = 26.3 mol
ΔH = 26.3 mol * -5512 kJ/mol = -1.45 * 10⁵ kJ

ε = 1 - T_c/T_h = 1 - 1073/2273 = 0.472 the engine is less than 50% efficient at heat → work
w = ε * q_h = 0.472 * 1.45 * 10⁵ kJ = 6.84 * 10⁴ kJ

If this is changed into potential energy E = mgh or h = E/mg
h = 6.84 * 10⁷ J/1000 kg * 9.8 m/sec² = 6980 m

If we want to take into account the change in mass while burning the gasoline.

dh = dE/mg;

\[ dE = 0.472 * 4.83 * 10^7 \text{ J/kg} \times \text{dm} \text{(kg)} = 2.28 * 10^7 \text{ J/kg} \times \text{dm}_{\text{gas}} \text{(kg)} \]

\[ dh = \frac{2.28 * 10^7 \text{ J/kg} \times \text{dm}_{\text{gas}} \text{(kg)}}{(1003 - m_{\text{gas}} \text{(kg)})} \]

Integrate this expression for m_{gas} going from 3 to 0.

h = 6979 m for no real change as the gas is a small, small fraction of the total mass to be lifted.

Problem 4.32

The cycle involved in an internal combustion engine is called the Otto cycle. Air can be considered to be the working substance and can be assumed to be an ideal gas. The cycle consists of the following steps:

1) Reversible adiabatic compression from A to B.
2) Reversible constant volume pressure increase from B to C due to the combustion of a small amount of fuel.
3) Reversible adiabatic expansion from C to D
4) Reversible and constant volume pressure decrease back to state A.

Determine the change in entropy (of the system and surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle assuming that heat is supplied in step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A, V = 4.0 L, p = 1.0 atm, and T = 300 K, that V_A = 10 V_B, p_c/p_B = 5 and that C_{p,m} = 7/2 R.

n = 4.0 L * 1.0 atm/0.082 L atm/mol-K * 300 K = 0.163 mol or about 0.2 mol

Since Steps 1 & 3 are adiabatic q = 0; \( \Delta S_{\text{sur}} = 0; \) & reversible \( \Delta S_{\text{total}} = 0 \)

Since Steps 2 & 4 are constant volume \( w = 0 \).

Step 1 - \( w_1 = \Delta U \) as q = 0

\[ w_1 = C_d \Delta T = 5/2 R \Delta T \]

\[ T_i = T_c(V_i/V_o)^{1/c} \]

\[ c = C_{v,m}/R = 5/2 \]

\[ w_1 = 5/2 R (754 - 300 K) \]

\[ T_f = 300 K * (10/1)^{2/5} = 754 K \]

\[ w_1 = +9.4 \text{ kJ/mol} \]

\[ \Delta S = 0 \]
Step 2 - \( q_2 = \Delta U \) as \( w = 0 \)

\[
q_2 = C_v dT = \frac{5}{2} R \Delta T \\
q_2 = \frac{5}{2} R (3770 - 754) \\
q_2 = +62.69 \text{ kJ/mol}
\]

\[
\Delta S = \frac{\Delta q}{T} = \frac{\Delta C_v dT}{T} \\
\Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) \\
\Delta S = +33.45 \text{ J/K-mol}
\]

Since reversible \( \Delta S_{\text{surr}} = -33.45 \text{ J/K-mol} \)

Step 3 - \( w_3 = \Delta U \) as \( q = 0 \)

\[
w_3 = C_v dT = \frac{5}{2} R \Delta T \\
w_3 = \frac{5}{2} R (1501 - 3770) \\
w_3 = -47.16 \text{ kJ/mol}
\]

\[
\Delta S = \frac{\Delta q}{T} = \frac{\Delta C_v dT}{T} \\
\Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) \\
\Delta S = 0
\]

Step 4 - \( q_4 = \Delta U \) as \( w = 0 \)

\[
q_4 = C_v dT = \frac{5}{2} R \Delta T \\
q_4 = \frac{5}{2} R (300 - 1501) \\
q_4 = -24.96 \text{ kJ/mol}
\]

\[
\Delta S = \frac{\Delta q}{T} = \frac{\Delta C_v dT}{T} \\
\Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) \\
\Delta S = -33.47 \text{ J/K-mol}
\]

Since reversible \( \Delta S_{\text{surr}} = +33.47 \text{ J/K-mol} \)

Overall Entropy Change for System \( +33.45 \text{ J/K-mol} - 33.47 \text{ J/K-mol} = 0.0 \)

Round-off error causes slight deviation

Efficiency = \( \frac{\text{net work}}{q_h} = \frac{(47.16 - 9.4 \text{ kJ/mol})}{62.69 \text{ kJ/mol}} = 0.60 \)