

1. N identical, ideal Carnot refrigerators are in series. In each cycle, the n -th refrigerator absorbs heat Q_n at temperature T_n , and emits heat Q_{n+1} at temperature T_{n+1} . The emitted heat Q_{n+1} is then absorbed by the $(n+1)$ -th refrigerator, and so on. Each refrigerator requires 3 J of work to run, per cycle. You are given that $Q_1 = 1$ J, and $T_1 = 1$ K. Express the answers below in the appropriate units (J or K). (i) What is Q_n , for all $n \geq 1$? (ii) What is T_n , for all $n \geq 1$?

Solution: (i) For each cycle, $|W_n| = |Q_{n+1}| - |Q_n|$ and so $|Q_{n+1}| = |W_n| + |Q_n| = n|W| + |Q_1| = 3n \text{ J} + 1 \text{ J} = (3n + 1) \text{ J}$. Therefore $|Q_n| = (3n - 2) \text{ J}$. (ii) For the n -th cycle $\frac{T_{n+1} - T_n}{T_n} = \frac{|W_n|}{|Q_n|} = \frac{3 \text{ J}}{3(n-1) \text{ J} + 1 \text{ J}}$ which implies $\frac{T_{n+1}}{T_n} - 1 = \frac{3}{3n-2}$ and so $\frac{T_{n+1}}{T_n} = \frac{3n+1}{3n-2}$. This leads to $T_{n+1} = \frac{3n+1}{3n-2} T_n = \prod_{i=1}^n \left[\frac{3i+1}{3i-2} \right] T_1 = (3n+1)T_1 = (3n+1) \text{ K}$, yielding $T_n = (3n-2) \text{ K}$.

2. A Carnot engine operates on 1 kg of methane (CH_4), which we will consider to be an ideal gas. Take $\gamma = 1.35$. The ratio of the maximum volume to the minimum volume is 4 and the cycle efficiency is 25%. Find the entropy increase of the methane during the isothermal expansion.

Solution: For reversible processes, $Tds = du + Pdv$. For the isothermal expansion, $dU = 0$ and therefore $Tds = Pdv$. For the ideal gas, $ds = Pdv/T = nRdv/v$ and so $\Delta s = nR \ln(v_b/v_a)$. What is v_b/v_a ? During the adiabatic expansion, $b \rightarrow c$, you can write $T_b v_b^{\gamma-1} = T_c v_c^{\gamma-1}$ and so $\frac{v_b}{v_c} = \left(\frac{T_c}{T_b}\right)^{1/(\gamma-1)} = \left(\frac{T_1}{T_2}\right)^{1/(\gamma-1)}$. The relationship between T_1 and T_2 can be found from the efficiency of the engine $\eta = 1 - T_1/T_2 = 25\%$, hence $T_1/T_2 = 3/4$. Putting everything together, you get $\Delta s = nR \ln(v_b/v_a) = nR \ln\left(\frac{v_b v_c}{v_c v_a}\right) = nR \ln\left[\left(\frac{T_1}{T_2}\right)^{1/(\gamma-1)} \frac{v_c}{v_a}\right] = nR \ln\left[\left(\frac{3}{4}\right)^{1/(1.35-1)} \times 4\right] = 293 \text{ J/K}$.

3. The low temperature specific heat of a diamond varies with temperature according to

$$c_v = 1.88 \times 10^6 \left(\frac{T}{\theta}\right)^3 \text{ J kilomole}^{-1} \text{ K}^{-1},$$

where $\theta = 2230 \text{ K}$. What is the entropy change of 1 kg of diamond when it is heated at constant volume from 4 K to 300 K.

Solution: Start with the main thermodynamic identity: $dU = TdS - PdV$. For a diamond in the air, P and V are almost constant at room temperature under 1 atm, thus $ds \simeq du/T$. This leads to $\Delta S \simeq n \int_4^{300} \text{K} c_v \frac{dT}{T} = \frac{1}{12} \int_4^{300} \text{K} 1.88 \times 10^6 \left(\frac{T}{\theta}\right)^3 \frac{dT}{T} \text{ JK}^{-1} = 127 \text{ JK}^{-1}$.

4. (a) Derive an expression for the entropy of an ideal gas: (i) as a function of T and V ; (ii) as a function of T and P . Assume that the specific heats of the gas are constants. (b) An ideal monatomic gas undergoes a reversible expansion from specific volume v_1 to specific volume v_2 .

(i) Calculate the change in specific entropy Δs if the expansion is isobaric. (ii) Calculate Δs if the process is isothermal. (iii) Which is larger? By how much?

Solution: (a) (i) Start with the main thermodynamic identity: $du = Tds - Pdv$. It follows that $ds = \frac{P}{T}dv + \frac{du}{T} = \frac{R}{v}dv + c_v \frac{dT}{T}$, and hence $\Delta s = R \ln\left(\frac{v_2}{v_1}\right) + c_v \ln\left(\frac{T_2}{T_1}\right)$. (ii) Likewise, $ds = \frac{1}{T}Pdv + c_v \frac{dT}{T}$. Use the equation of state, $Pv = RT$, to obtain $Pdv + vdP = RdT$. Substitute this expression to obtain $ds = \frac{1}{T}(RdT - vdP) + c_v \frac{dT}{T} = (R + c_v) \frac{dT}{T} - \frac{v}{T}dP = c_P \frac{dT}{T} - R \frac{dP}{P}$. Integrate this expression to obtain $\Delta s = c_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$. (b) (i) For an ideal monoatomic gas which undergoes isobaric expansion, it follows that $ds = \frac{1}{T}(du + Pdv) = \frac{c_v}{T}dT + \frac{P}{T}dv = c_v \frac{dT}{T} + \frac{P}{Pv/R}dv = c_v \frac{dT}{T} + R \frac{dv}{v}$. Thus, $\Delta s_1 = c_v \int \frac{dT}{T} + R \int \frac{dv}{v} = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) = c_v \ln\left(\frac{v_2}{v_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) = c_P \ln\left(\frac{v_2}{v_1}\right)$. (ii) For an ideal monoatomic gas which undergoes isothermal expansion, it follows that $ds = \frac{P}{T}dv = R \frac{dv}{v}$ and so $\Delta s_2 = R \ln\left(\frac{v_2}{v_1}\right)$. (iii) $\Delta s_1 - \Delta s_2 = c_P - R \ln\left(\frac{v_2}{v_1}\right) = c_v \ln\left(\frac{v_2}{v_1}\right)$, which implies $\Delta s_1 > \Delta s_2$.

5. A kilomole of an ideal gas undergoes a reversible isothermal expansion from a volume of 5 liters to a volume of 10 liters at a temperature of 20° C. (i) What is the change in the entropy of the gas? Of the universe? (ii) What are the corresponding changes of energy if the process is a free expansion?

(i) A kilomole ($n = 1$) of an ideal gas undergoes isothermal expansion from $V_1 = 5$ liters to $V_2 = 10$ liters. For isothermal processes $dU = 0$ and hence $dS = dQ/T = dW/T$, yielding $dS = \frac{P}{T}dV$. This means that the entropy change in the system is $\Delta S_{\text{gas}} = \int \frac{P}{T}dV = \int \frac{nR}{V}dV = nR \ln\left(\frac{V_2}{V_1}\right) = R \ln 2 = 5.76 \times 10^3 \text{ J K}^{-1}$. On the other hand, $\Delta Q_{\text{gas}} = -\Delta Q_{\text{env}}$; this entails $\Delta S_{\text{env}} = -\int \frac{P}{T}dV = -\int \frac{nR}{V}dV = -nR \ln\left(\frac{V_2}{V_1}\right) = -R \ln 2$. Therefore $\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{env}} = 0$. (ii) For the same initial and final states the entropy change in the gas is the same so $\Delta S_{\text{gas}} = 5 \times 10^3 \text{ J K}^{-1}$. While the ideal gas undergoes free expansion, no heat enters or leaves the surroundings, so for the environment surrounding the system, $\Delta Q_{\text{env}} = 0$ and $\Delta S_{\text{env}} = 0$. In this case the total change of entropy in the universe is $\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{env}} = \Delta S_{\text{gas}} = 5 \times 10^3 \text{ J K}^{-1}$.