Chapter 4 Entropy and the Second Law of Thermodynamics

4.1. Reversible, Irreversible Processes and Entropy

4.2. The Second Law of Thermodynamics

Problem 1. Suppose 4.0 mol of an ideal gas undergoes a reversible isothermal expansion from volume V_1 to volume $V_2=2.0V_1$ at temperature T = 400K. Find (a) the work done by the gas and (b) the entropy change of the gas. (c) If the expansion is reversible and adiabatic instead of isothermal, what is the entropy change of the gas?

(a) $$W = nRT \ln\frac{V_2}{V_1} \quad \rightarrow W = 4.0 \times 8.31 \times 400 \times \ln\frac{2.0V_1}{V_1} = 9216\,(\mathrm{J})$$

(b) $$\Delta S = \int_i^f \frac{dQ}{T}$$

For an isothermal process: T=constant

$$\Delta S = \frac{Q}{T}; \Delta E_{\mathrm{int}} = Q - W = 0 \Rightarrow Q = W$$

$$\Delta S = \frac{W}{T} = \frac{9216}{400} = 23.0\,(\mathrm{J/K})$$

(c) $$Q = 0 \Rightarrow \Delta S = 0$$

Problem 2. An ideal gas undergoes a reversible isothermal expansion at 77.0^{0}C, increasing its volume from 1.30 L to 3.90 L. The entropy change of the gas is 22.0 J/K. How many moles of gas are present?

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} + nC_V \ln\frac{T_f}{T_i}$$

$$\Delta S = nR\ln\frac{V_f}{V_i} \Rightarrow n = \frac{\Delta S}{R\ln\frac{V_f}{V_i}} = \frac{22.0}{8.31\times\ln\frac{3.9}{1.3}}$$

$$n = 2.41\ \text{(mol)}$$

Problem 3. A 2.5 mol sample of an ideal gas expands reversibly and isothermally at 360 K until its volume is doubled. What is the increase in entropy of the gas?

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} + nC_V \ln\frac{T_f}{T_i}$$

For an isothermal process, T = constant:

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i}$$

$$\Delta S = 2.5\times 8.31\times \ln 2 = 14.4\ (\mathrm{J/K})$$

Problem 5. Find (a) the energy absorbed as heat and (b) the change in entropy of a 2.0 kg block of copper whose temperature is increased reversibly from 25.0^{0}C to 100^{0}C. The specific heat of copper is 386 J.kg^{-1}.K^{-1}.

(a) Energy absorbed as heat to increase the copper temperature:

$$Q = cm\Delta T$$

$$Q = 386 \times 2 \times 75 = 57900 \text{ (J)}$$

(b) The change in entropy:

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{cmdT}{T} = cm \ln \frac{T_2}{T_1}$$

$$T_1 = 25 + 273.15 = 298.15^0\text{K};$$

$$T_2 = 100 + 273.15 = 373.15^0\text{K}$$

$$\Delta S = 386 \times 2 \times \ln \frac{373.15}{298.15} = 173.2 \text{ (J/K)}$$

Problem 8. At very low temperatures, the molar specific heat C_V of many solids is approximately $C_V=AT^3$, where A depends of the particular substance. For aluminum, A = 3.15 x 10^{-5} J mol^{-1} K^{-4}. Find the entropy change for 4.0 mol of aluminum when its temperature is raised from 5.0 K to 10.0 K.

$$\Delta S = \int_i^f \frac{dQ}{T}$$

We assume that the volume change is negligible:

$$dQ = nC_V dT$$

$$\Delta S = \int_i^f \frac{nC_V dT}{T} = nA\int_{5.0}^{10.0} T^2 dT$$

$$\Delta S = \frac{1}{3}nAT^3\Big|_{5.0}^{10.0} = \frac{1}{3}\times 4.0\times 3.15\times 10^{-5}\left(10^3 - 5^3\right) = 0.037 \text{ (J/K)}$$

Problem 9. A 10 g ice cube at −10°C is placed in a lake whose temperature is 15°C. Calculate the change in entropy of the cube – lake system as the ice cube comes to thermal equilibrium with the lake. The specific heat of ice is 2220 J/kg · K. (*Hint:* Will the ice cube affect the lake temperature?)

Entropy change of the ice

$$\Delta S = \int \frac{dQ}{T} = mc_I \int_{T_i}^{T_f} \frac{dT}{T} = mc_I \ln\frac{T_f}{T_i} = (0.010\text{ kg})(2220\text{ J/kg}\cdot\text{K})\ln\left(\frac{273\text{ K}}{263\text{ K}}\right) = 0.828\text{ J/K}.$$

$$\Delta S = Q/T = mL_F/T = (0.010\text{ kg})(333\times10^3\text{ J/kg})/(273\text{ K}) = 12.20\text{ J/K}.$$

$$\Delta S = mc_w \ln\frac{T_f}{T_i}, \quad \Delta S = (0.010\text{ kg})(4190\text{ J/kg}\cdot\text{K})\ln\left(\frac{288\text{ K}}{273\text{ K}}\right) = 2.24\text{ J/K}.$$

$$\longrightarrow \quad \Delta S = 0.828\text{ J/K} + 12.20\text{ J/K} + 2.24\text{ J/K} = 15.27\text{ J/K}.$$

Entropy change of the lake

$$Q = -mc_I\left(T_f - T_i\right) = -(0.010\ \text{kg})(2220\ \text{J/kg}\cdot\ \text{K})(10\ \text{K}) = -222\ \text{J}.$$

$$Q = -mL_F = -(0.010\ \text{kg})\left(333\times 10^3\ \text{J}/\text{kg}\right) = -3.33\times 10^3\ \text{J}.$$

$$Q = -mc_w\left(T_f - T_i\right) = -(0.010\ \text{kg})(4190\ \text{J}/\text{kg}\cdot\ \text{K})(15\ \text{K}) = -629\ \text{J}.$$

$$\longrightarrow \quad Q = -222\ \text{J} - 3.33\times 10^3\ \text{J} - 6.29\times 10^2\ \text{J} = -4.18\times 10^3\ \text{J}.$$

$$\longrightarrow \quad \Delta S = -\frac{4.18\times 10^3\ \text{J}}{288\ \text{K}} = -14.51\ \text{J/K}.$$

Entropy change of the ice – lake system

$$\Delta S = (15.27 - 14.51)\ \text{J/K} = 0.76\ \text{J/K}.$$

Problem 16. An 8.0 g ice cube at −10°C is put into a Thermos flask containing 100 cm³ of water at 20°C. By how much has the entropy Of the cube–water system changed when equilibrium is reached? The specific heat of ice is 2220 J/kg.K.

c_w = 4190 J/kg.K L_F = 333000 J/kg

$$\sum Q = 0$$

$$Q_{\text{warm water cools}} + Q_{\text{ice warms to } 0^\circ} + Q_{\text{ice melts}} + Q_{\text{melted ice warms}} = 0$$

$$c_w m_w \left(T_f - 20^\circ\right) + c_i m_i \left(0^\circ - \left(-10^\circ\right)\right) + L_F m_i + c_w m_i \left(T_f - 0^\circ\right) = 0$$

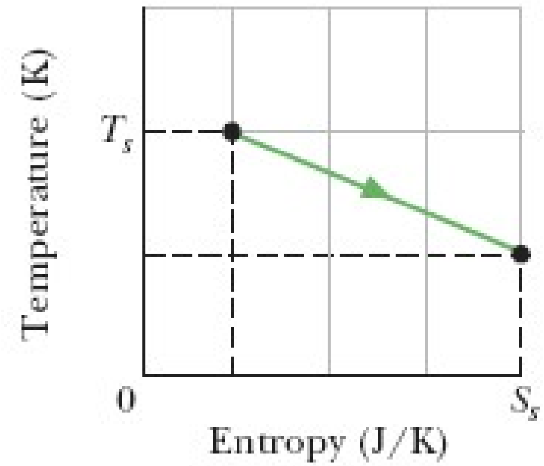
$\longrightarrow$ T_f = 12.24°C → T_f = 285.39 K

$$\Delta S_{\text{temp change}} = mc \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_{\text{system}} = m_w c_w \ln\left(\frac{285.39}{293.15}\right) + m_i c_i \ln\left(\frac{273.15}{263.15}\right) + m_i c_w \ln\left(\frac{285.39}{273.15}\right) + \frac{L_F\, m_i}{273.15}$$

$$= (-11.24 + 0.66 + 1.47 + 9.75)\,\text{J/K} = 0.64\ \text{J/K.}$$

Problem 18. A 2.0 mol sample of an ideal monatomic gas undergoes the reversible process shown in Fig. 20-26. The scale of the vertical axis is set by T_s = 400.0 K and the scale of the horizontal axis is set by S_s = 20.0 J/K. (a) How much energy is absorbed as heat by the gas? (b) What is the change in the internal energy of the gas? (c) How much work is done by the gas?



$$Q_{\text{straight}} = \left(\frac{T_i + T_f}{2}\right)\Delta S$$

$$Q = (300\text{ K})\,(15\text{ J/K}) = 4.5\times10^{3}\text{ J}$$

$$\Delta E_{\text{int}} = n\left(\frac{3}{2}R\right)\Delta T = (2.0\text{ mol})(8.31\text{ J/mol}\cdot\text{K})(200\text{ K} - 400\text{ K}) = -5.0\times10^{3}\text{ J.}$$

$$W = Q - \Delta E_{\text{int}} = 4.5\text{ kJ} - (-5.0\text{ kJ}) = 9.5\text{ kJ.}$$