Chapter 3 – New Exercises and Solutions

E3.2(c) Calculate the molar entropy of a constant-volume sample of nitrogen, N_2, at 350 K given that it is 191.61 J K^{-1} mol^{-1} at 298 K.

E3.2(c)   If we assume that neon is a perfect gas then $C_{V,m}$ may be taken to be constant and given by

$$C_{V,m} = C_{p,m} - R; \qquad C_{p,m} = 29.125 \, \text{J K}^{-1} \, \text{mol}^{-1} \, [\text{Table 2.6}]$$

$$= (29.125 - 8.314) \, \text{J K}^{-1} \, \text{mol}^{-1}$$

$$= 20.811 \, \text{J K}^{-1} \, \text{mol}^{-1}$$

Integrating, we obtain

$$S_m(500\,\text{K}) = S_m(298\,\text{K}) + C_{V,m} \ln\frac{T_f}{T_i}$$

$$= (191.61\,\text{J K}^{-1}\,\text{mol}^{-1}) + (20.811\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{350\,\text{K}}{298\,\text{K}}\right)$$

$$= (191.61 + 3.35)\,\text{J K}^{-1}\,\text{mol}^{-1} = \boxed{194.96\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E3.3(c) Calculate ΔS (for the system) when the state of 2.50 mol nitrogen, assumed to be a perfect gas, is changed from 25°C and 2.00 atm to 125°C and 8.00 atm. How do you rationalize the sign of ΔS?

E3.3(c)   However the change occurred ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2)

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

For the first step

$$\Delta S_1 = \int \frac{\mathrm{d}q_{rev}}{T} = \int \frac{C_{p,m}\,\mathrm{d}T}{T} = C_{p,m}\ln\frac{T_f}{T_i}$$

$$\Delta S_1 = (2.50\,\text{mol}) \times \left(\frac{7}{2}\right) \times (8.3145 \, \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\frac{(125+273)\,\text{K}}{(25+273)\,\text{K}} = 21.0\bar{5} \, \text{J K}^{-1}$$

and for the second

$$\Delta S_2 = \int \frac{\mathrm{d}q_{rev}}{T} = \frac{q_{rev}}{T}$$

where $q_{rev} = -w = \int p\,\mathrm{d}V = nRT\ln\frac{V_f}{V_i} = nRT\ln\frac{p_i}{p_f}$

so $\Delta S_2 = nR\ln\frac{p_i}{p_f} = (2.50\,\text{mol}) \times (8.3145 \, \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\frac{2.00 \text{ atm}}{8.00 \text{ atm}} = -28.8\bar{1} \, \text{J K}^{-1}$

$$\Delta S = (21.0\bar{5} - 28.8\bar{1})\,\text{J K}^{-1} = \boxed{-7.8 \text{ J K}^{-1}}$$

The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Or the ordering represented by confining the sample to a smaller volume in step 2 overcame the disordering represented by the temperature rise in step 1. A negative entropy change is allowed for a system as long as an increase in entropy elsewhere results in $\Delta S_{total} > 0$.

E3.6(c) Consider a system consisting of 3.0 mol $CO_2(g)$, initially at 35°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2. The sample is allowed to expand adiabatically against an external pressure of 2.5 atm until the piston has moved outwards through 25 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m}$ = 28.8 J K^{-1} mol^{-1}, and calculate (a) q, (b) w, (c) ΔU, (d) ΔT, (e) ΔS.

E3.6(c) (a) $q = 0$ [adiabatic]

(b) $w = -p_{ex}\Delta V = -(2.5\,\text{atm}) \times \left(\dfrac{1.01 \times 10^5\,\text{Pa}}{\text{atm}}\right) \times (100.0\,\text{cm}^2) \times (25\,\text{cm}) \times \left(\dfrac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right)$

$$= -51\overline{7.6}\,\text{J} = \boxed{-51\overline{8}\,\text{J}}$$

(c) $\Delta U = q + w = 0 - 51\overline{8}\,\text{J} = \boxed{-51\overline{8}\,\text{J}}$

(d) $\Delta U = nC_{V,m}\Delta T$

$$\Delta T = \frac{\Delta U}{nC_{V,m}} = \frac{-51\overline{8}\,\text{J}}{(2.5\,\text{mol}) \times (28.8\,\text{J\,K}^{-1}\,\text{mol}^{-1})}$$

$$= \boxed{-7.2\,\text{K}}$$

(e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_{V,m}\ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right) \quad \text{[3.19 \& 3.13]}$$

$$T_f = 308.\overline{2}\,\text{K} - 7.2\,\text{K} = 301.\overline{2}\,\text{K}$$

$$V_i = \frac{nRT}{p_i} = \frac{(2.5\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm\,K}^{-1}\,\text{mol}^{-1}) \times (308.\overline{2}\,\text{K})}{9.0\,\text{atm}}$$

$$= 7.0\overline{25}\,\text{dm}^3$$

$$V_f = 7.0\overline{25}\,\text{dm}^3 + (100\,\text{cm}^2) \times (15\,\text{cm}) \times \left(\frac{1\,\text{dm}^3}{1000\,\text{cm}^3}\right)$$

$$= 7.0\overline{25}\,\text{dm}^3 + 2.5\,\text{dm}^3 = 9.5\overline{3}\,\text{dm}^3$$

$$\Delta S = (2.5\,\text{mol}) \times \left\{(28.8\ \text{J\,K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{301}{308}\right)\right.$$

$$\left. + (8.314\,\text{J\,K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{9.5\overline{3}}{7.0\overline{25}}\right)\right\}$$

$$= 2.5\,\text{mol}(-0.662\overline{1}\ \text{J\,K}^{-1}\,\text{mol}^{-1} + 2.53\overline{6}\ \text{J\,K}^{-1}\,\text{mol}^{-1}) = \boxed{4.7\,\text{J\,K}^{-1}}$$
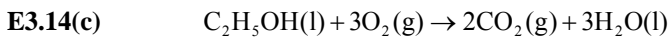
E3.7(c) The enthalpy of vaporization of ethanol is 43.5 kJ mol^{-1} at its normal boiling point of 352 K. Calculate (a) the entropy of vaporization of ethanol at this temperature and (b) the entropy change of the surroundings.

E3.7(c) (a) $\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T_b} = \dfrac{43.5 \times 10^3\,\text{J\,mol}^{-1}}{352\,\text{K}} = +123.\overline{6}\,\text{J\,K}^{-1} = \boxed{124\,\text{J\,K}^{-1}}$

(b) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{sys} + \Delta S_{sur} = 0 \quad \text{so} \quad \Delta S_{sur} = \boxed{-124\,\text{J K}^{-1}}$$

E3.14(c) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of ethanol at 298 K.

E3.14(c)
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$
$$\Delta_r G^{\ominus} = \sum_{\text{Products}} \nu \Delta_f G^{\ominus} - \sum_{\text{Rectants}} \nu \Delta_f G^{\ominus} [3.40]$$
$$\Delta_r G^{\ominus} = 2\Delta_f G^{\ominus}(CO_2,g) + 3\Delta_f G^{\ominus}(H_2O,l) - \Delta_f G^{\ominus}(C_2H_5OH,l)$$
$$= \{2\times(-394.36) + (3\times-237.13) - (-174.78)\}\,\text{kJ mol}^{-1} = -1325.33\,\text{kJ mol}^{-1}$$

Therefore, the maximum non-expansion work is $\boxed{1325.33\,\text{kJ mol}^{-1}}$ since $\left|w_{add}\right| = \left|\Delta G\right|$.

E3.15(c) (a) Calculate the Carnot efficiency of a primitive steam engine operating on steam at 180°C and discharging at 100°C. (b) Repeat the calculation for a modern steam turbine that operates with steam at 360°C and discharges at 100°C.

E3.15(c)
$$\varepsilon_{rev} = 1 - \frac{T_c}{T_h} [3.10]$$
$$\varepsilon = 1 - \frac{373\,\text{K}}{353\,\text{K}} = \boxed{0.18} \qquad \text{(18 per cent efficiency for the old steam engine)}$$
$$\varepsilon = 1 - \frac{453\,\text{K}}{633\,\text{K}} = \boxed{0.41} \qquad \text{(41 per cent efficiency for the modern turbine)}$$

E3.16(c) Suppose that 2.5 mol Ar(g) occupies 72 dm^3 at 298 K and expands to 100 dm^3. Calculate ΔG for the process.

E3.16(c)
$$\Delta G = nRT \ln\left(\frac{p_f}{p_i}\right) [3.56] = nRT \ln\left(\frac{V_i}{V_f}\right) \quad [\text{Boyle's law}]$$
$$\Delta G = (2.5\ \text{mol}) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times \ln\left(\frac{72}{100}\right) = \boxed{-2.0\ \text{kJ}}$$

E3.17(c) The change in the Gibbs energy of a certain constant–pressure process was found to fit the expression $\Delta G/\text{J} = -85.40 + 42.8(T/\text{K})$. Calculate the value of ΔS for the process.

E3.17(c)
$$\left(\frac{\partial G}{\partial T}\right)_p = -S\ [3.50]; \quad \text{hence} \quad \left(\frac{\partial G_f}{\partial T}\right)_p = -S_f, \quad \text{and} \quad \left(\frac{\partial G_i}{\partial T}\right)_p = -S_i$$

$$\Delta S = S_f - S_i = -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p = -\left(\frac{\partial (G_f - G_i)}{\partial T}\right)_p$$

$$= -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\frac{\partial}{\partial T}\left(-85.40\,J + 42.8\,J \times \frac{T}{K}\right)$$

$$= \boxed{-42.8\,J\,K^{-1}}$$

E3.19(c) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 202.0 kPa to 352.0 kPa at 70°C.

E3.19(c)
$$\Delta G_m = G_{m,f} - G_{m,i} = RT \ln\left(\frac{p_f}{p_i}\right)\ [3.56]$$

$$= (8.314\,J\,K^{-1}\,mol^{-1}) \times (343\,K) \times \ln\left(\frac{352.0}{202.0}\right) = \boxed{1.58\,kJ\,mol^{-1}}$$

E3.20(c) The fugacity coefficient of a certain gas at 290 K and 3.1 MPa is 0.70. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

E3.20(c) For an ideal gas, $G_m^O = G_m^\ominus + RT \ln\left(\frac{p}{p^\ominus}\right)$ [3.56 with $G_m = G_m^O$]

But for a real gas, $G_m = G_m^\ominus + RT \ln\left(\frac{f}{p^\ominus}\right)$ [3.58]

So $G_m - G_m^O = RT \ln\frac{f}{p}$ [3.58 minus 3.56]; $\frac{f}{p} = \phi$

$$= RT \ln\phi = (8.314\,J\,K^{-1}\,mol^{-1}) \times (290\,K) \times (\ln 0.70) = \boxed{-0.86\,kJ\,mol^{-1}}$$

E3.21(c) Estimate the change in the Gibbs energy of 1.00 dm³ of ethanol when the pressure acting on it is increased from 101.3 kPa to 202.6 kPa.

E3.21(c) $\Delta G = nV_m \Delta p\ [3.55] = V\Delta p$

$$\Delta G = (1.0\ dm^3) \times \left(\frac{1m^3}{10^3\ dm^3}\right) \times (101.3 \times 10^3\,Pa) = 101.3\ Pa\ m^3 = \boxed{101\ J}$$

E3.22(c) Calculate the change in the molar Gibbs energy of methane when its pressure is increased isothermally from 101.3 kPa to 202.6 kPa at 500 K.

E3.22(c) $\Delta G_m = RT \ln\left(\frac{p_f}{p_i}\right)[3.56] = (8.314\,J\,K^{-1}\,mol^{-1}) \times (500\,K) \times \ln\left(\frac{202.6\ kPa}{101.3\ kPa}\right)$

$$= \boxed{+2.88\,kJ\,mol^{-1}}$$