Problem Set 2

CH2-5

The greatest amount of work is done in a reversible expansion. The work is given by

$$w_{reversible} = -nRT\ln\frac{V_f}{V_i} = -nRT\ln\frac{P_i}{P_f} = -5.25\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 450\text{ K}\times\ln\frac{15.0\text{ bar}}{3.50\text{ bar}}$$

$$= -28.6\times 10^3\text{J}$$

The least amount of work is done in a single stage expansion at constant pressure with the external pressure equal to the final pressure. The work is given by

$$w = -P_{external}\left(V_f - V_i\right) = -nRTP_{external}\left(\frac{1}{P_f} - \frac{1}{P_i}\right)$$

$$= -5.25\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 450\text{ K}\times 3.50\text{ bar}\times\left(\frac{1}{3.50\text{ bar}} - \frac{1}{15.0\text{ bar}}\right) = -15.1\times 10^3\text{J}$$

The least amount of work done without restrictions on the pressure is zero, which occurs when $P_{external} = 0$.

CH2-7

$$w_{ad} = -\Delta U = n\left(C_{P,m} - R\right)\Delta T = -\frac{3}{2}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 150\text{ K} = -1.87\times 10^3\text{J}$$

$$w_{reversible} = -nRT\ln\frac{P_i}{P_f};\ \ln\frac{P_i}{P_f} = \frac{-w_{reversible}}{nRT}$$

$$\ln\frac{P_i}{P_f} = \frac{nRT}{w_{reversible}} = \frac{1.87\times 10^3\text{J}}{1\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 300\text{ K}} = 0.7497$$

$$P_f = 0.472P_i = 0.944\text{ bar}$$

CH2-10

because $q = 0$, $\Delta U = w$

$$nC_{V,m}\left(T_f - T_i\right) = -P_{ext}\left(V_f - V_i\right)$$

$$nC_{V,m}\left(T_f - T_i\right) = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

The factor n cancels out. Rearranging the equation

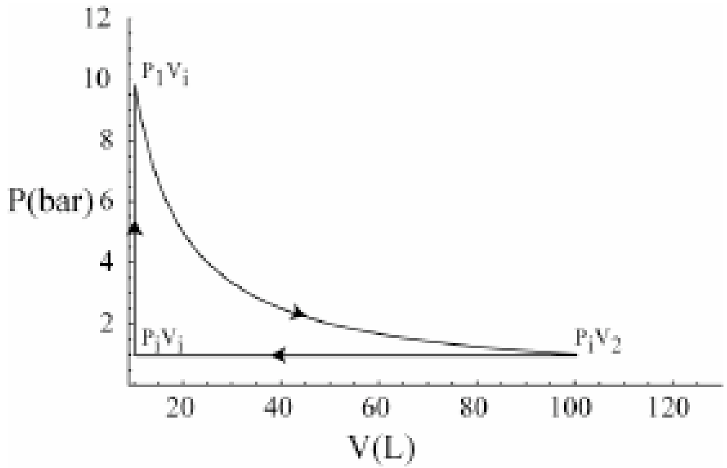
$$\left(C_{V,m} + \frac{RP_{ext}}{P_f}\right)T_f = \left(C_{V,m} + \frac{RP_{ext}}{P_i}\right)T_i$$

$$\frac{T_f}{T_i} = \frac{C_{V,m} + \frac{RP_{ext}}{P_i}}{C_{V,m} + \frac{RP_{ext}}{P_f}}$$

$$= \frac{2.5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} + \frac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 10^5\,\text{Pa}}{3.20 \times 10^5\,\text{Pa}}}{2.5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} + \frac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 10^5\,\text{Pa}}{10^5\,\text{Pa}}}$$

$T_f = 0.804T_i \quad T_f = 235\ \text{K}$

CH2 12



$$n = \frac{P_iV_i}{RT_i} = \frac{1.00 \text{ bar} \times 10.0 \text{ L}}{8.3145 \times 10^{-2} \text{L bar mol}^{-1}\text{K}^{-1} \times 300 \text{ K}} = 0.401 \text{ mol}$$

The process can be described by
step 1: $P_i,V_i,T_i \rightarrow P_1 = 10.0$ bar,V_i, T_1
step 2: P_1,V_i, $T_1 \rightarrow P_i,V_2$ T_1
step 3: P_i, V_2, $T_1 \rightarrow$ P_i,V_i,T_i.

In step 1, $P_i,V_i,T_i \rightarrow P_1,V_i$, T_1, $w = 0$ because V is constant.

In step 2, P_1,V_i, $T_1 \rightarrow P_i$, V_2, T_1
Before calculating the work in step 2, we first calculate T_1.

$$T_1 = T_i\frac{P_1}{P_i} = 300 \text{ K} \times \frac{10.0 \text{ bar}}{1.00 \text{ bar}} = 3000 \text{ K}$$

$$w = -nRT_1 \ln\frac{V_f}{V_i} = -nRT_1 \ln\frac{P_i}{P_f}$$

$$= -0.401 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 3000 \text{ K} \times \ln\frac{10.0 \text{ bar}}{1.00 \text{ bar}} = -23.0 \times 10^3 \text{J}$$

In step 3,

$$P_1V_i = P_iV_2; \quad V_2 = \frac{P_1V_i}{P_i} = 10V_i = 100 \text{ L}$$

$$w = -P_{external}\Delta V = -1.00 \text{ bar} \times \frac{10^5 \text{Pa}}{\text{bar}} \times (10 \text{ L} - 100 \text{ L}) \times \frac{10^{-3}\text{m}^3}{\text{L}} = 9.00 \times 10^3 \text{J}$$

$$w_{cycle} = 0 - 23.0 \times 10^3 \text{J} + 9.00 \times 10^3 \text{J} = -14.0 \times 10^3 \text{J}$$

If the cycle were traversed in the opposite direction, the magnitude of each work term would be unchanged, but all signs would change.

CH2 14

In this adiabatic expansion, $\Delta U = w$

$$nC_{V,m}\left(T_f - T_i\right) = -P_{ext}\left(V_f - V_i\right)$$

$$nC_{V,m}\left(T_f - T_i\right) = -P_{ext}\left(\frac{nRT}{V_f} - \frac{nRT}{V_i}\right)$$

$$\left(C_{V,m} + \frac{RP_{ext}}{P_f}\right)T_f = \left(C_{V,m} + \frac{RP_{ext}}{P_i}\right)T_i$$

$$\frac{T_f}{T_i} = \frac{C_{V,m} + \frac{RP_{ext}}{P_i}}{C_{V,m} + \frac{RP_{ext}}{P_f}}$$

$$= \frac{1.5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} + \frac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 101.9 \times 10^3\ \text{Pa}}{126.4 \times 10^3\ \text{Pa}}}{1.5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} + \frac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 101.9 \times 10^3\ \text{Pa}}{101.9 \times 10^3\ \text{Pa}}}$$

$$\frac{T_f}{T_i} = 0.923\ , \quad T_f = 271\ \text{K}$$

Once the stopper is put in place, the gas makes a transformation from

$T_i = 214\ \text{K},\ P_i = 101.9 \times 10^3\ \text{Pa}$ to $T_f = 294\ \text{K}$ and P_f

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}, \quad \text{but } V_i = V_f$$

$$P_f = \frac{T_f}{T_i} P_i = \frac{294\ \text{K}}{271\ \text{K}} \times 101.9 \times 10^3\ \text{Pa} = 110.5 \times 10^3\ \text{Pa}$$

The same calculation carried out for $C_{V,m} = \frac{5}{2}R$ gives

$$\frac{T_f}{T_i} = 0.945, \quad T_f = 278\ \text{K}$$

$$P_f = 107.8 \times 10^3\ \text{Pa}$$

CH2 17

a) $P_2 = \frac{P_1 V_1}{V_2} = \frac{P_1}{2} = 0.500\times10^6\,\text{Pa}$

$w = -nRT\ \ln\frac{V_2}{V_1} = -8.314\ \text{J mol}^{-1}\text{K}^{-1}\times\ln 2 = -1.69\times10^3\,\text{J}$

$\Delta U = 0$ and $\Delta H = 0$ because $\Delta T = 0$

$q = -w = 1.69\times10^3\,\text{J}$

b) $\frac{T_1}{P_1} = \frac{T_2}{P_2};\ P_2 = \frac{T_2 P_1}{T_1} = \frac{353\ \text{K}\times 0.500\times10^6\text{Pa}}{293\ \text{K}} = 6.02\times10^5\text{Pa}$

$\Delta U = nC_{V,m}\Delta T = 1.5\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times(353\ \text{K} - 293\ \text{K}) = 748\ \text{J}$

$w = 0$ because $\Delta V = 0$

$q = \Delta U = 748\ \text{J}$

$\Delta H = nC_{P,m}\Delta T = n\left(C_{V,m} + R\right)\Delta T = \frac{3}{2}\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times(353\ \text{K} - 293\ \text{K})$

$= 1.25\times10^3\,\text{J}$

For the overall process,

$q = 1.69\times10^3\text{J} + 748\ \text{J} = 2.44\times10^3\text{J}$

$w = -1.69\times10^3\text{J} + 0 = -1.69\times10^3\text{J}$

$\Delta U = 0 + 748\ \text{J} = 748\ \text{J}$

$\Delta H = 0 + 1.25\times10^3\text{J} = 1.25\times10^3\text{J}$

CH2 18

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma};\ \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma};\ \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00\times10^5\text{Pa}}{1.00\times10^6\text{Pa}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = (0.100)^{-0.4} = 2.51$$

$T_f = 2.51\times 298\ \text{K} = 749\ \text{K}$

$q = 0$ because the process is adiabatic.

$w = \Delta U = nC_{V,m}\Delta T = 1\ \text{mol}\times\frac{3\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2}\times(749\ \text{K} - 298\ \text{K}) = 5.62\times10^3\text{J}$

$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T = 5.62\times10^3\text{J} + 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times(749\ \text{K} - 298\ \text{K})$

$\Delta H = 9.37\times10^3\text{J}$

CH2 22

The number of moles of gas in each part is given by

$$n = \frac{P_i V_i}{RT_i} = \frac{1.00\text{ bar} \times 50.0\text{ L}}{8.3145 \times 10^{-2}\text{L bar mol}^{-1}\text{K}^{-1} \times 298\text{ K}} = 2.02\text{ mol}$$

a) We first calculate the final temperature in the right side.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma};= \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma};\frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00\text{ bar}}{7.50\text{ bar}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = 2.24$$

$$T_f = 2.24 \times 298\text{ K} = 667\text{ K}$$

$$\Delta U = w = nC_{V,m}\Delta T = 2.02\text{ mol} \times \frac{3 \times 8.314\text{ J mol}^{-1}\text{K}^{-1}}{2} \times (667\text{ K} - 298\text{ K}) = 9.30 \times 10^3\text{ J}$$

b) We first calculate the final volume of the right part.

$$V_{rf} = \frac{RT_{rf}}{P_{rf}} = \frac{2.02\text{ mol} \times 8.314 \times 10^{-2}\text{L bar mol}^{-1}\text{K}^{-1} \times 667\text{ K}}{7.50\text{ bar}} = 14.9\text{ L}$$

Therefore, V_{lf} = 100.0 L – 14.9 L = 85.1 L.

$$T_{lf} = \frac{P_{lf} V_{lf}}{nR} = \frac{7.50\text{ bar} \times 85.1\text{ L}}{2.02\text{ mol} \times 8.314 \times 10^{-2}\text{L bar mol}^{-1}\text{K}^{-1}} = 3.80 \times 10^3\text{K}$$

$$\Delta U = nC_{V,m}\Delta T = 2.02\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times \left(3.80 \times 10^3\text{K} - 298\text{ K}\right) = 58.8 \times 10^3\text{J}$$

From part (a), $w = -9.30 \times 10^3$J

$q = \Delta U - w = 58.3 \times 10^3\text{ J} + 9.30 \times 10^3\text{ J} = 67.3 \times 10^3\text{ J}$

CH2 24

$$\Delta H = n\int_{T_i}^{T_f} C_{p,m} dT$$

$$= \int_{500}^{300}\left(44.35+1.47\times10^{-3}\frac{T}{\mathrm{K}}\right)d\left(\frac{T}{\mathrm{K}}\right)$$

$$= 44.35\times(300\ \mathrm{K}-500\ \mathrm{K})$$

$$+\left[\frac{1.47\times10^{-3}}{2}\left(\frac{T}{\mathrm{K}}\right)^2\right]_{500\ \mathrm{K}}^{300\ \mathrm{K}}$$

$$= -8870\ \mathrm{J}-117\ \mathrm{J}$$

$$= -8.99\times10^3\ \mathrm{J}$$

CH2 25

a)

$$\frac{T_f}{T_i}=\left(\frac{V_f}{V_i}\right)^{1-\gamma}=\left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma};=\left(\frac{T_f}{T_i}\right)^{\gamma}=\left(\frac{P_i}{P_f}\right)^{1-\gamma};\frac{T_f}{T_i}=\left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i}=\left(\frac{3.25\,\mathrm{bar}}{1.00\ \mathrm{bar}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}}=0.626$$

$$T_f=0.626\times300\ \mathrm{K}=188\ \mathrm{K}$$

b)

$$\Delta U = nC_{V,m}\left(T_f-T_i\right)=-P_{external}\left(V_f-V_i\right)$$

$$nC_{V,m}\left(T_f-T_i\right)=-nRP_{external}\left(\frac{T_f}{P_f}-\frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{V,m}+\frac{nRP_{external}}{P_f}\right)=T_i\left(nC_{V,m}+\frac{nRP_{external}}{P_i}\right)$$

$$T_f=T_i\left(\frac{C_{V,m}+\frac{RP_{external}}{P_i}}{C_{V,m}+\frac{RP_{external}}{P_f}}\right)=300\ \mathrm{K}\times\left(\frac{1.5\times8.314\ \mathrm{J\ mol^{-1}K^{-1}}+\frac{8.314\ \mathrm{J\ mol^{-1}K^{-1}}\times1.00\,\mathrm{bar}}{3.25\,\mathrm{bar}}}{1.5\times8.314\ \mathrm{J\ mol^{-1}K^{-1}}+\frac{8.314\ \mathrm{J\ mol^{-1}K^{-1}}\times1.00\,\mathrm{bar}}{1.00\,\mathrm{bar}}}\right)$$

$$T_f=217\ \mathrm{K}$$

More work is done on the surroundings in the reversible expansion, and therefore ΔU and the temperature decrease more than for the irreversible expansion.

CH2 30

a) for the ideal gas

$$w_{reversible} = -nRT\ln\frac{V_f}{V_i} = -1\,\text{mol}\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times 300\ \text{K}\times\ln\frac{23.0\ \text{L}}{2.50\ \text{L}} = -5.54\times 10^3\,\text{J}$$

b) for the van der Waals gas

$$w = -\int_{V_i}^{V_f} P_{external}\,dV = -\int_{V_i}^{V_f}\left(\frac{RT}{V_m-b}-\frac{a}{V_m^2}\right)dV$$

$$= -\int_{V_i}^{V_f}\left(\frac{RT}{V_m-b}\right)dV + \int_{V_i}^{V_f}\left(\frac{a}{V_m^2}\right)dV$$

The first integral is solved by making the substitution $y = V_m - b$.

$$-\int_{V_i}^{V_f}\left(\frac{RT}{V_m-b}\right)dV = -\int_{y_i}^{y_f}\left(\frac{RT}{y}\right)dy = -RT\left[\ln\left(V_f+b\right)-\ln\left(V_i+b\right)\right]$$

Therefore, the work is given by

$$w = -nRT\ln\frac{\left(V_f-b\right)}{\left(V_i-b\right)} + a\left(\frac{1}{V_i}-\frac{1}{V_f}\right)$$

$$= -1\ \text{mol}\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times 300\ \text{K}\times\ln\frac{23.0\ \text{L}-0.0380\ \text{L}}{2.50\ \text{L}-0.0380\ \text{L}}$$

$$+1.366\ \text{L}^2\ \text{bar}\times\frac{10^5\text{Pa}}{\text{bar}}\times\frac{10^{-6}\text{m}^6}{\text{L}^2}\left(\frac{1}{2.50\times 10^{-3}\text{m}^3}-\frac{1}{23.0\times 10^{-3}\text{m}^3}\right)$$

$$w = -5.56\times 10^3\ \text{J} + 48.7\ \text{J} = -5.52\times 10^3\text{J}$$

$$\text{Percent error} = 100\times\frac{-5.52\times 10^3\text{J} + 5.54\times 10^3\text{J}}{-5.52\times 10^3\text{J}} = -0.4\%$$