ChemE 2200 - Physical Chemistry II for Engineers – Spring 2025

Solution to Homework Assignment 6

1.(A) For a process at constant pressure, $\Delta H = q$. Start with the definition of $\overline{C}_{\mathrm{P}}$.

$$\left(\frac{\partial H}{\partial T}\right)_P = n\overline{C}_{\mathrm{P}}$$

$$dH = n\overline{C}_{\mathrm{P}}dT \qquad \text{at constant } P$$

$$\int_{H_1}^{H_2} dH = n\int_{T_1}^{T_2} \overline{C}_{\mathrm{P}}dT$$

$$H_2 - H_1 = n\int_{T_1}^{T_2}\left[44.28 + 0.0601T - 1.11\times10^{-5}T^2 - \frac{1.68\times10^6}{T^2}\right]dT$$

$$q = n\left[44.28T + \frac{0.0601}{2}T^2 - \frac{1.11\times10^{-5}}{3}T^3 + \frac{1.68\times10^6}{T}\right]\Bigg|_{T_1}^{T_2}$$

Substitute values for q, n, and T_1. Note that $q/n = 85.0/6.16 = 13.80$ kJ/mol.

$$13.80 = 44.28(T_2 - 298) + \frac{0.0601}{2}(T_2^2 - 298^2) - \frac{1.11\times10^{-5}}{3}(T_2^3 - 298^3) + 1.68\times10^6\left(\frac{1}{T_2} - \frac{1}{298}\right)$$

It is not possible to solve for T_2. Solve by whatever means you prefer. For example, try different values of T_2 until the equation yields 13.80.

guess	q/n
400	5.079531
500	11.14633
550	14.47941
525	12.79046
530	13.12474
540	13.79861

The final temperature is 540 K.

(B) For this estimate, assume ethylene is an ideal gas at 1 atm and 300 to 600 K. Thus we use the relation $\overline{C}_{\mathrm{P}} = \overline{C}_{\mathrm{V}} + R$.

$$\overline{C}_{\mathrm{V}} = \overline{C}_{\mathrm{P}} - R = \left[44.28 + 0.0601T - 1.11\times10^{-5}T^2 - \frac{1.68\times10^6}{T^2}\right] - 8.314$$

$$\overline{C}_{\mathrm{V}} = 35.97 + 0.0601T - 1.11\times10^{-5}T^2 - \frac{1.68\times10^6}{T^2}$$

For a process at constant volume, $\Delta U = q$. Start with the definition of $\overline{C}_{\mathrm{V}}$.

$$\left(\frac{\partial U}{\partial T}\right)_V = n\overline{C}_{\mathrm{V}}$$

$$dU = n\overline{C}_{\mathrm{V}}dT \qquad \text{at constant } V$$

$$\int_{U_1}^{U_2} dU = n\int_{T_1}^{T_2} \overline{C}_{\mathrm{V}}dT$$

$$U_2 - U_1 = n\int_{T_1}^{T_2}\left[35.97 + 0.0601T - 1.11\times10^{-5}T^2 - \frac{1.68\times10^6}{T^2}\right]dT$$

$$13.80 = 35.97(T_2 - 298) + \frac{0.0601}{2}(T_2^2 - 298^2) - \frac{1.11\times10^{-5}}{3}(T_2^3 - 298^3) + 1.68\times10^6\left(\frac{1}{T_2} - \frac{1}{298}\right)$$

Again it is not possible to solve for T_2. Again I try different values of T_2.

guess	q/n
500	9.467711
600	15.47351
550	12.38529
570	13.60101
580	14.21877
573	13.78565
573.2	13.79799

The final temperature is 573 K.

(C) Heating at constant pressure has a lower final temperature because the volume increases and thus the gas does PV work on its surroundings. Some of the heat delivered to the gas is used to do this PV work and thus there is less heat available to increase the temperature.

2.(A) Path F: P_1, V_1, T_1 to P_2, V_1, T_5. Because the volume is constant, $w_F = 0$ and thus

$$\delta q_{\text{rev, F}} = dU = C_V dT$$

$$q_{\text{rev, F}} = \int_{T_1}^{T_5} C_V dT$$

To calculate ΔS for path F, start with the first equation above and divide by T.

$$\frac{\delta q_{\text{rev}}}{T} = \frac{dU}{T} dU = \frac{C_V}{T} dT$$

$$\Delta S_F = \int \frac{\delta q_{\text{rev}}}{T} = \int_{T_1}^{T_5} \frac{C_V}{T} dT$$

(B) Path G: P_2, V_1, T_5 to P_2, V_2, T_1. From the 1st law we have

$$\delta q_{\text{rev, G}} = dU - \delta w_{\text{rev}} = C_V dT + PdV$$

$$q_{\text{rev, G}} = \int_{T_5}^{T_1} C_V dT + \int_{V_1}^{V_2} PdV$$

Because the pressure is constant along Path G, we have

$$q_{\text{rev, G}} = \int_{T_5}^{T_1} C_V dT + P_2 \int_{V_1}^{V_2} dV = \int_{T_5}^{T_1} C_V dT + P_2 (V_2 - V_1)$$

To calculate ΔS for path G, start with the equation for $\delta q_{\text{rev, G}}$ above and divide by T.

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_V}{T} dT + \frac{P}{T} dV$$

$$\Delta S_G = \int \frac{\delta q_{\text{rev}}}{T} = \int_{T_5}^{T_1} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{P}{T} dV$$

Because the gas is ideal, $P/T = R/V$ for 1 mole.

$$\Delta S_G = \int_{T_5}^{T_1} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{R}{V} dV$$

$$= \int_{T_5}^{T_1} \frac{C_V}{T} dT + R \ln \frac{V_2}{V_1}$$

Here is an alternative derivation for Path G. Because the pressure is constant,

$$\delta q_{\text{rev, G}} = dH = C_P dT$$

$$q_{\text{rev, G}} = \int_{T_1}^{T_5} C_P dT$$

This simpler relation is equivalent to the expression derived from *dU* above, as follows. Use the relation $\overline{C}_\mathrm{P} = \overline{C}_\mathrm{V} + R$, or $C_\mathrm{P} = C_\mathrm{V} + nR$ to substitute into the previous equation.

$$q_{\mathrm{rev,\,G}} \;=\; \int_{T_1}^{T_5} C_\mathrm{P}\,dT \;=\; \int_{T_1}^{T_5} (C_\mathrm{V} + nR)\,dT \;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT \;+\; nR\int_{T_1}^{T_5} dT$$

Use the ideal gas law, $PV = nRT$, to derive an expression for *dT*.

$$\frac{dT}{dV} \;=\; \frac{d}{dV}\left(\frac{PV}{nR}\right) \;=\; \frac{dV}{nR}$$

$$dT \;=\; \frac{dV}{nR}$$

Use the previous expression to change the variable of integration to obtain the same expression derived from *dU* above.

$$q_{\mathrm{rev,\,G}} \;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT \;+\; nR\int_{T_1}^{T_5} dT \;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT \;+\; nR\int_{T_1}^{T_5} \frac{dV}{nR}$$

$$q_{\mathrm{rev,\,G}} \;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT + \int_{V_1}^{V_2} P\,dV$$

To calculate ΔS for path G using *dH* start with the equation for $q_{\mathrm{rev,G}}$ and divide by *T*.

$$\frac{\delta q_\mathrm{rev}}{T} \;=\; \frac{dH}{T}\,dH \;=\; \frac{C_\mathrm{P}}{T}\,dT$$

$$\Delta S_\mathrm{G} \;=\; \int \frac{\delta q_\mathrm{rev}}{T} \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{P}}{T}\,dT$$

Again substitute $C_\mathrm{P} = C_\mathrm{V} + nR$.

$$\Delta S_\mathrm{G} \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{P}}{T}\,dT \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V} + nR}{T}\,dT \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT \;+\; \int_{T_1}^{T_5} \frac{nR}{T}\,dT$$

$$\;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT \;+\; nR\ln\frac{T_5}{T_1}$$

Use the ideal gas law to substitute $T = PV/R$ for 1 mol.

$$\Delta S_\mathrm{G} \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT \;+\; R\ln\frac{P_2V_2/nR}{P_2V_1/nR}$$

$$\Delta S_\mathrm{G} \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT \;+\; R\ln\frac{V_2}{V_1}$$

Thus the same expression derived from *dU* for 1 mol of an ideal gas.

(C) Calculate the sums for paths F +G.

$$q_\mathrm{rev} \;=\; q_{\mathrm{rev,\,F}} + q_{\mathrm{rev,\,G}} \;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT + \int_{T_5}^{T_1} C_\mathrm{V}\,dT + P_2(V_2 - V_1)$$

$$\;=\; \int_{T_1}^{T_5} C_\mathrm{V}\,dT - \int_{T_1}^{T_5} C_\mathrm{V}\,dT + P_2(V_2 - V_1)$$

$$\;=\; P_2(V_2 - V_1)$$

$$\Delta S_{\mathrm{F+G}} \;=\; \Delta S_\mathrm{F} + \Delta S_\mathrm{G} \;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT + \int_{T_5}^{T_1} \frac{C_\mathrm{V}}{T}\,dT + R\ln\frac{V_2}{V_1}$$

$$\;=\; \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT - \int_{T_1}^{T_5} \frac{C_\mathrm{V}}{T}\,dT + R\ln\frac{V_2}{V_1}$$

$$\;=\; R\ln\frac{V_2}{V_1}$$

The entropy change is the same as calculated for the other three paths. The heat, however, is different from any of the other paths.

Adapted from *Problems & Solutions to Accompany McQuarrie - Simon Physical Chemistry: A Molecular Approach*, Heather Cox (University Science Books, 1997), exercise 20-6.

3.(A) Because the path is reversible and isothermal, and because the gas is ideal,

$$\Delta S_{\text{gas}} = nR\ln\frac{V_2}{V_1} = (1\text{ mol})(8.314\text{ J/K}\cdot\text{mol})\ln\frac{10\text{ atm}}{1\text{ atm}} = 19.1\text{ J/K}$$

A reversible process is a succession of equilibrium states. Thus the 2nd law says that for the overall process (system plus surroundings), $\Delta S_{\text{total}} = 0$.

$$\Delta S_{\text{surroundings}} = -\Delta S_{\text{gas}} = -19.1\text{ J/K}$$

(B) This is a free expansion of an ideal gas into a vacuum. Note that because $q = 0$ (adiabatic) and $w = 0$, the 1st law says $\Delta U = q + w = 0$. Because this is an ideal gas, $\Delta U = 0$ requires $\Delta T = 0$; this is an isothermal process. The final state in part (B) is the same as the final state in part (A), so $\Delta S_{\text{gas}} = 19.1$ J/K. Because no heat flows to the surroundings, $\Delta S_{\text{surroundings}} = 0$.

(C) To calculate ΔS_{gas} we must devise reversible paths that connect the initial and final states. We need to determine the final state. Because the system did work on the surroundings, but no heat flowed, the temperature of the gas decreased.

$$w = \Delta U = n\overline{C}_{\text{V}}\Delta T = n\frac{3}{2}R(T_2 - T_1)$$

$$T_2 = T_1 + \frac{2w}{3nR} = 298\text{ K} + \frac{2(-810\text{ J})}{3(1\text{ mol})(8.314\text{ J/K}\cdot\text{mol})} = 298\text{ K} - 65\text{ K} = 233\text{ K}$$

We can now devise reversible paths to the final state. Path 1 - reversible and isothermal expansion to 10. L. Path 2 - reversible and isochoric cooling to 233 K. The entropy change for the first path is the same as in part (A). Calculate the entropy change for path 2.

$$\delta q_{\text{rev}} = C_{\text{V}}dT$$

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_{\text{V}}}{T}dT$$

$$\Delta S_2 = \int\frac{\delta q_{\text{rev}}}{T} = \int_{T_1}^{T_2}\frac{C_{\text{V}}}{T}dT = C_{\text{V}}\ln\frac{T_2}{T_1} = n\overline{C}_{\text{V}}\ln\frac{T_2}{T_1} = n\frac{3}{2}R\ln\frac{T_2}{T_1}$$

$$= (1\text{ mol})\frac{3}{2}(8.314\text{ J/K}\cdot\text{mol})\ln\frac{233\text{ K}}{298\text{ K}} = -3.07\text{ J/K}$$

Calculate the total entropy change.

$$\Delta S_{\text{gas}} = \Delta S_1 + \Delta S_2 = 19.1\text{ J/K} - 3.07\text{ J/K}\cdot\text{mol} = 16.0\text{ J/K}$$

Because no heat transferred to the surroundings in the actual process, $\Delta S_{\text{surroundings}} = 0$.

Adapted from K. J. Laidler and J. H. Meiser, *Physical Chemistry*, 3rd ed, 1999.

4.(A) First calculate the number of moles of each gas.

$$n_{\mathrm{A}} = \frac{P_{\mathrm{A}}V_{\mathrm{A}}}{RT_{\mathrm{A}}} = \frac{(2.5\ \mathrm{atm})(3.7\ \mathrm{L})}{(0.08206\ \mathrm{L\cdot atm/K\cdot mol})(300\ \mathrm{K})} = 0.376\ \mathrm{mol}$$

$$n_{\mathrm{B}} = \frac{P_{\mathrm{B}}V_{\mathrm{B}}}{RT_{\mathrm{B}}} = \frac{(2.5\ \mathrm{atm})(7.5\ \mathrm{L})}{(0.08206\ \mathrm{L\cdot atm/K\cdot mol})(400\ \mathrm{K})} = 0.571\ \mathrm{mol}$$

Because the process is adiabatic, the 1st Law of Thermodynamics requires that the energy gained by Gas A equals the energy lost by Gas B. The temperature is a state function and thus does not depend on path. For convenience, assume the following path: the gases first reach thermal equilibrium then they are mixed. Thus Gas A is heated at constant volume and Gas B is cooled at constant volume.

$$\Delta U_{\mathrm{A}} = -\Delta U_{\mathrm{B}}$$

$$n_{\mathrm{A}}\overline{C}_{\mathrm{V,A}}(T - T_{\mathrm{A}}) = -n_{\mathrm{B}}\overline{C}_{\mathrm{V,B}}(T - T_{\mathrm{B}})$$

$$T = \frac{n_{\mathrm{A}}\overline{C}_{\mathrm{V,A}}T_{\mathrm{A}} + n_{\mathrm{B}}\overline{C}_{\mathrm{V,B}}T_{\mathrm{B}}}{n_{\mathrm{A}}\overline{C}_{\mathrm{V,A}} + n_{\mathrm{B}}\overline{C}_{\mathrm{V,B}}}$$

Substitute the numerical values and calculate.

$$T = \frac{(0.376\ \mathrm{mol})(13.7\ \mathrm{J/K\cdot mol})(300\ \mathrm{K}) + (0.571\ \mathrm{mol})(21.7\ \mathrm{J/K\cdot mol})(400\ \mathrm{K})}{(0.376\ \mathrm{mol})(13.7\ \mathrm{J/K\cdot mol}) + (0.571\ \mathrm{mol})(21.7\ \mathrm{J/K\cdot mol})}$$

$$T = 371\ \mathrm{K}$$

(B) Calculate the entropy change along two reversible paths. First, each gas is reversibly heated (or cooled) to 371 K at constant *V*. Second, the gases are mixed.

$$\begin{aligned}\Delta S &= \Delta S_{\mathrm{A,\,path\,1}} + \Delta S_{\mathrm{B,\,path\,1}} + \Delta S_{\mathrm{mixing}} \\ &= n_{\mathrm{A}}\overline{C}_{\mathrm{V,A}}\ln\frac{T}{T_{\mathrm{A}}} + n_{\mathrm{B}}\overline{C}_{\mathrm{V,B}}\ln\frac{T}{T_{\mathrm{B}}} - R\left[n_{\mathrm{A}}\ln\frac{n_{\mathrm{A}}}{n_{\mathrm{A}}+n_{\mathrm{B}}} + n_{\mathrm{B}}\ln\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}+n_{\mathrm{B}}}\right] \\ &= (0.376\ \mathrm{mol})(13.7\ \mathrm{J/K\cdot mol})\ln\frac{371\ \mathrm{K}}{300\ \mathrm{K}} + (0.571\ \mathrm{mol})(21.7\ \mathrm{J/K\cdot mol})\ln\frac{371\ \mathrm{K}}{400\ \mathrm{K}} \\ &\qquad - (8.314\ \mathrm{J/K\cdot mol})\left[(0.376\ \mathrm{mol})\ln\frac{0.376\ \mathrm{mol}}{0.376+0.571} + (0.571\ \mathrm{mol})\ln\frac{0.571\ \mathrm{mol}}{0.376+0.571}\right] \\ &= 1.080 - 0.945 + 5.289\ \mathrm{J/K} \\ &= 5.42\ \mathrm{J/K}\end{aligned}$$

From J. H. Noggle, *Physical Chemistry*, 3rd ed, 1996.

5.(A) Calculate the total work during a cycle. $w = 0$ for paths AB and CD because $\Delta V = 0$. For the adiabatic paths BC and DA, $q = 0$, and

$$w = \Delta U = \int C_{\mathrm{V}}\,dT$$

Thus the total work for the cycle is

$$w_{\mathrm{cycle}} = \int_{T_{\mathrm{B}}}^{T_{\mathrm{C}}} C_{\mathrm{V}}\,dT + \int_{T_{\mathrm{D}}}^{T_{\mathrm{A}}} C_{\mathrm{V}}\,dT$$

Because C_{V} may be assumed to be independent of temperature,

$$w_{\mathrm{cycle}} = C_{\mathrm{V}}(T_{\mathrm{C}} - T_{\mathrm{B}}) + C_{\mathrm{V}}(T_{\mathrm{A}} - T_{\mathrm{D}}) = C_{\mathrm{V}}(T_{\mathrm{A}} - T_{\mathrm{B}} + T_{\mathrm{C}} - T_{\mathrm{D}})$$

The system is heated along path AB.

$$q_{\mathrm{AB}} = \int_{T_\mathrm{A}}^{T_\mathrm{B}} C_\mathrm{V}\,dT = C_\mathrm{V}(T_\mathrm{B} - T_\mathrm{A})$$

To calculate the efficiency, note that the work done by the system is $-w_{\mathrm{cycle}}$ because of the convention for w; w is positive for work done by the surroundings on the system. The efficiency is therefore

$$\varepsilon = \frac{-w_{\mathrm{cycle}}}{q_{\mathrm{AB}}} = \frac{-C_\mathrm{V}(T_\mathrm{A} - T_\mathrm{B} + T_\mathrm{C} - T_\mathrm{D})}{C_\mathrm{V}(T_\mathrm{B} - T_\mathrm{A})} = \frac{-T_\mathrm{A} + T_\mathrm{B}}{T_\mathrm{B} - T_\mathrm{A}} + \frac{-T_\mathrm{C} + T_\mathrm{D}}{T_\mathrm{B} - T_\mathrm{A}} = 1 - \frac{T_\mathrm{C} - T_\mathrm{D}}{T_\mathrm{B} - T_\mathrm{A}}$$

(B) For the adiabatic change of a diatomic ideal gas,

$$\left(\frac{T_2}{T_1}\right)^{5/2} = \frac{V_1}{V_2}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{2/5}$$

For the adiabatic paths BC and DA,

$$T_\mathrm{C} = T_\mathrm{B}\left(\frac{V_\mathrm{B}}{V_\mathrm{C}}\right)^{2/5} \qquad \text{and} \qquad T_\mathrm{D} = T_\mathrm{A}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5}$$

Because $V_\mathrm{B} = V_\mathrm{A}$ and $V_\mathrm{C} = V_\mathrm{D}$,

$$T_\mathrm{C} = T_\mathrm{B}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5} \qquad \text{and} \qquad T_\mathrm{D} = T_\mathrm{A}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5}$$

Substitute these expressions into the efficiency equation derived in part (A).

$$\begin{aligned}
\varepsilon &= 1 - \frac{T_\mathrm{C} - T_\mathrm{D}}{T_\mathrm{B} - T_\mathrm{A}} \\
&= 1 - \frac{T_\mathrm{B}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5} - T_\mathrm{A}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5}}{T_\mathrm{B} - T_\mathrm{A}} \\
&= 1 - \frac{T_\mathrm{B} - T_\mathrm{A}}{T_\mathrm{B} - T_\mathrm{A}}\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5} \\
&= 1 - \left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/5}
\end{aligned}$$

$V_\mathrm{D}/V_\mathrm{A}$ is the compression ratio for the engine. Higher compression ratios yield higher efficiencies. The typical compression ratio for a car is about 9, so the typical maximum efficiency about 60%. For an irreversible engine with a compression ratio of about 9, the efficiency is about 30-35%. A nice description of the Otto cycle in the family car can be viewed at http://www.familycar.com/engine.htm.

Of course, the gas in the engine is not entirely N_2. For a gas mixture with heat capacities C_V and C_P, the general expression for efficiency is

$$\varepsilon = 1 - \left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{C_\mathrm{V}/(C_\mathrm{P}+C_\mathrm{V})}$$