

Homework 3 Solutions

1. We first determine the amount of molecules in the sample:

$$n = 65.0 \text{ g} / 131.29 \text{ g mol}^{-1} = 0.495 \text{ mol}$$

$$V_i = nRT_i/p_i = (0.495 \text{ mol}) \times (0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) / 2.00 \text{ atm} = 6.053 \text{ L}$$

(a) For reversible adiabatic expansion,

$$p_i V_i^\gamma = p_f V_f^\gamma \quad \gamma = C_{p,m}/C_{v,m}$$

For a perfect monoatomic gas, $C_{v,m} = (3/2)R$, $\gamma = 5/3$

$$V_f = (p_i/p_f)^{1/\gamma} V_i = (2.00 \text{ atm} / 1.00 \text{ atm})^{3/5} \times 6.053 \text{ L} = 9.175 \text{ L}$$

$$T_f = (V_i/V_f)^{1/\gamma} T_i = (V_i/V_f)^{\gamma-1} T_i = (6.053 \text{ L} / 9.175 \text{ L})^{2/3} \times (298 \text{ K}) = 225.8 \text{ K}$$

$$w = nC_{v,m}\Delta T = -448.4 \text{ J}$$

(b) For adiabatic expansion against a constant external pressure:

$$w_{\text{ad}} = -p_{\text{ex}}\Delta V = C_V\Delta T \quad -p_{\text{ex}}(V_f - V_i) = C_V(T_f - T_i)$$

On the other hand, $p_f V_f = nRT_f$

$$V_f = \frac{nRT_f}{p_f} \quad -p_{\text{ex}} \left(\frac{nRT_f}{p_f} - V_i \right) = nC_{v,m}(T_f - T_i)$$

Solving this equation for T_f gives

$$T_f = \frac{p_{\text{ex}} V_i + nC_{v,m} T_i}{nC_{v,m} + \frac{p_{\text{ex}} nR}{p_f}}$$

Since the expansion against a constant pressure will continue until the pressure of the gas becomes equal to the external pressure, $p_f = p_{\text{ex}} = 1 \text{ atm}$, the formula can be simplified as

$$T_f = \frac{p_{\text{ex}} V_i / n + C_{v,m} T_i}{C_{v,m} + R}$$

$$T_f = \{ (1 \text{ atm} \times 6.053 \text{ L} / 0.495 \text{ mol}) + (3/2) \times (0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \} / \{ (3/2) \times (0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}) + (0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}) \} = 238.4 \text{ K}$$

$$w = nC_{v,m}\Delta T = -369.4 \text{ J}$$

2. (a) $p_i V_i^\gamma = p_f V_f^\gamma \quad \gamma = 1.4$

$$p_f = (V_i/V_f)^\gamma p_i = (1.0 \text{ L} / 2.0 \text{ L})^{1.4} \times 57.4 \text{ kPa} = 21.75 \text{ kPa}$$

(b) $n = 1.4 \text{ g} / 18.02 \text{ g} = 0.078 \text{ mol}$

$$p_i = nRT_i/V_i = (0.078 \text{ mol}) \times (0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) / 1.0 \text{ L} = 1.913 \text{ atm}$$

$$p_f = (V_i/V_f)^\gamma p_i = (1.0 \text{ L} / 3.0 \text{ L})^{1.3} \times 1.913 \text{ atm} = 0.459 \text{ atm}$$

3. Adiabatic expansion: $q = 0$

$$w = -p_{\text{ex}}\Delta V = -p_{\text{ex}}(V_f - V_i) = -(600 \text{ Torr}) \times (60 \text{ L} - 20 \text{ L}) = -(600 \times 133.32 \text{ Pa}) \times (40 \times 10^{-3} \text{ m}^3) = -3.2 \text{ kJ}$$

$$\Delta U = q + w = -3.2 \text{ kJ}$$

$$w = C_V \Delta T = n C_{V,m} \Delta T \quad \Delta T = w / (n C_{V,m})$$

$$C_{V,m}(\text{O}_2) = C_{p,m}(\text{O}_2) - R = 29.355 - 8.314 = 21.041 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta T = -3.2 \text{ kJ} / \{(4.0 \text{ mol}) \times (21.041 \text{ J K}^{-1} \text{ mol}^{-1})\} = -38 \text{ K}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T = -3.2 \text{ kJ} + (4.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-38 \text{ K}) = -4.46 \text{ kJ}$$

4. (a) at 25°C , $\Delta_{\text{vap}}H^\circ = 44.01 \text{ kJ mol}^{-1}$ [Table 2.3]
 (b) at 100°C , $\Delta_{\text{vap}}H^\circ = 40.7 \text{ kJ mol}^{-1}$ [Table 2.3]
 $n = 1.00 \times 10^3 \text{ g} \times 1 \text{ mol} / 18.02 \text{ g} = 55.5 \text{ mol}$
 $q = n \Delta_{\text{vap}}H^\circ$
 (a) at 25°C , $q = 44.01 \text{ kJ mol}^{-1} \times 55.5 \text{ mol} = 2.44 \times 10^3 \text{ kJ}$
 (b) at 100°C , $q = 40.7 \text{ kJ mol}^{-1} \times 55.5 \text{ mol} = 2.26 \times 10^3 \text{ kJ}$

5. (a) constant-volume heating: $w_a = 0$,
 $q_a = C_V \Delta T = (5/2)RT_i$ because $C_{V,m} = C_{p,m} - R$ and $\Delta T = 2T_i - T_i = T_i$
 $\Delta U_a = w_a + q_a = (5/2)RT_i$ $\Delta H_a = \Delta U_a + nR\Delta T = (7/2)RT_i$
 (b) reversible adiabatic expansion: $q_b = 0$
 $w_b = -C_{V,m}\Delta T = -(5/2)RT_i$
 $\Delta U_b = w_b + q_b = -(5/2)RT_i$ $\Delta H_b = \Delta U_b + nR\Delta T = -(7/2)RT_i$
 (c) Reversible isothermal compression back to 1.0 atm: $\Delta U_c = 0$
 $w_c = -nRT_i \ln(V_{\text{cf}}/V_{\text{ci}})$, so we need to find how the volume changes in this step. So, we have to follow volume, pressure, and temperature changes along all the steps:

(a) Initially, we have V_i , T_i , and $p_i = 1 \text{ atm}$
 In the end, we have V_i , $2T_i$, and p_{af} . The latter can be found from the combined perfect gas equation: $p_i V_i / T_i = p_{\text{af}} V_i / (2T_i)$ $p_{\text{af}} = 2p_i = 2 \text{ atm}$

(b) Initially, we have V_i , $2T_i$, and $p_{\text{bi}} = p_{\text{af}} = 2 \text{ atm}$
 In adiabatic, reversible expansion: $V_{\text{bf}} = V_i (2T_i / T_i)^c$ with $c = C_{V,m} / R = 5/2$
 $V_{\text{bf}} = 5.657 V_i$ Also, $p_{\text{bi}} V_i^\gamma = p_{\text{bf}} V_{\text{bf}}^\gamma$ with $\gamma = C_{p,m} / C_{V,m} = 7/5 = 1.4$
 $p_{\text{bf}} = p_{\text{bi}} (V_i / 5.657 V_i)^{1.4} = 0.088 p_{\text{bi}} = 0.177 \text{ atm}$

(c) Initially, we have $V_{\text{ci}} = V_{\text{bf}} = 5.657 V_i$, T_i , and $p_{\text{ci}} = p_{\text{bf}} = 0.177 \text{ atm}$
 In isothermal compression, $p_{\text{ci}} V_{\text{ci}} = p_{\text{cf}} V_{\text{cf}}$ and $V_{\text{cf}} / V_{\text{ci}} = p_{\text{ci}} / p_{\text{cf}}$
 Since $p_{\text{cf}} = 1.0 \text{ atm}$, $V_{\text{cf}} / V_{\text{ci}} = 0.177$

$$w_c = -nRT_i \ln(V_{\text{cf}}/V_{\text{ci}}) = -RT_i \ln(0.177) = 1.733 RT_i$$

$$q_c = -w_c = -1.733 RT_i$$

$$\Delta H_c = \Delta U_c + nR\Delta T = 0$$

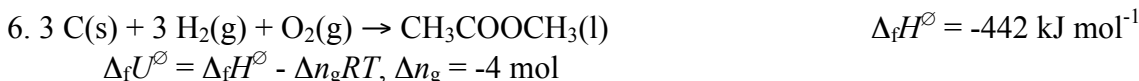
Or, a simpler way is to consider that the system in step c) returns to the same temperature and pressure as in the beginning and therefore to the same volume:

$$V_{\text{cf}} = V_i \quad V_{\text{ci}} = V_{\text{bf}} = 5.657 V_i \quad V_{\text{cf}} / V_{\text{ci}} = 0.177$$

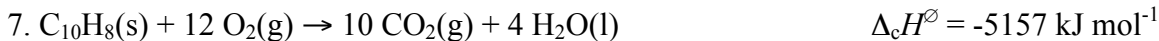
Overall values for the entire cycle are:

$$\Delta U = 0 \quad \Delta H = 0 \quad q = 0.767 RT_i \quad w = -0.767 RT_i$$

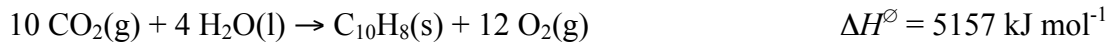
Pay attention that in this solution everything is done for arbitrary T_i . Numerical calculations can be carried out for $T_i = 298.15 \text{ K}$.



$$\Delta_f U^\circ = -442 \text{ kJ mol}^{-1} - (-4 \times 8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) = -432 \text{ kJ mol}^{-1}$$



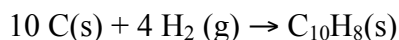
The reverse reaction is



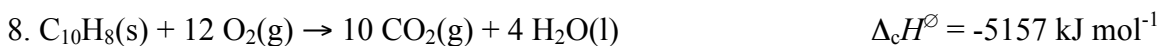
The CO_2 and H_2O can be replaced by adding the following two reactions and using data from Table 2.6 (Data Section) for $\Delta_f H^\circ(\text{CO}_2)$ and $\Delta_f H^\circ(\text{H}_2\text{O})$



Overall



$$\Delta_r H^\circ = (+5157 - 3935 - 1143) \text{ kJ mol}^{-1} = +79 \text{ kJ mol}^{-1}$$



$$\Delta_c U^\circ = \Delta_c H^\circ - \Delta n_g RT, \Delta n_g = -2 \text{ mol}$$

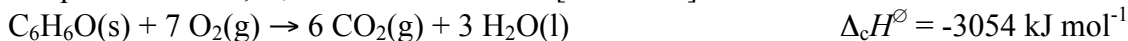
$$\Delta_c U^\circ = -5157 \text{ kJ mol}^{-1} - (-2 \times 8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) = -5152 \text{ kJ mol}^{-1}$$

$$q = n \Delta_c U^\circ$$

$$|q| = (120 \times 10^{-3} \text{ g} / 128.18 \text{ g mol}^{-1}) \times 5152 \text{ kJ mol}^{-1} = 4.82 \text{ kJ}$$

$$C = q/\Delta T = 4.82 \text{ kJ} / 3.05 \text{ K} = 1.58 \text{ kJ K}^{-1}$$

When phenol is used, $\Delta_c H^\circ = -3054 \text{ kJ mol}^{-1}$ [Table 2.5]



$$\Delta_c U^\circ = \Delta_c H^\circ - \Delta n_g RT, \Delta n_g = -1 \text{ mol}$$

$$\Delta_c U^\circ = -3054 \text{ kJ mol}^{-1} - (-1 \times 8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) = -3051.5 \text{ kJ mol}^{-1}$$

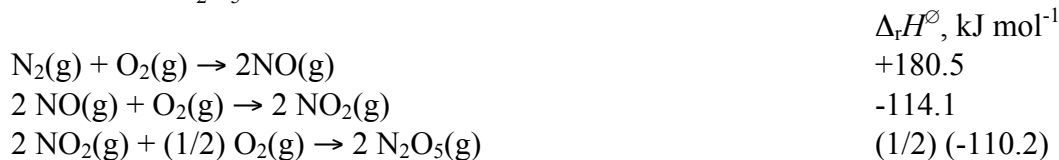
$$|q| = (100 \times 10^{-3} \text{ g} / 94.12 \text{ g mol}^{-1}) \times 3051.5 \text{ kJ mol}^{-1} = 3.242 \text{ kJ}$$

$$\Delta T = q/C = 3.242 \text{ kJ} / 1.58 \text{ kJ K}^{-1} = 0.205 \text{ K}$$

As one can see, the differences between $\Delta_c H^\circ$ and $\Delta_c U^\circ$ are actually rather small.

Therefore, in these calculations one can use $\Delta_c H^\circ$ in place of $\Delta_c U^\circ$ without any significant loss in accuracy.

9. The formation of N_2O_5 is the sum of the three reactions



Therefore, $\Delta_f H^\circ[\text{N}_2\text{O}_5(\text{g})] = +11.3 \text{ kJ mol}^{-1}$

10. We use Kirchhoff's law:

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \Delta_r C_p \Delta T$$

$$\Delta_r C_p = \sum \nu C_{p,m}(\text{products}) - \sum \nu C_{p,m}(\text{reactants}) = (77.28 - 2 \times 37.20) \text{ J K}^{-1} \text{ mol}^{-1} = +2.88 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r H^\circ(373 \text{ K}) = \Delta_r H^\circ(298 \text{ K}) + \Delta_r C_p \Delta T = (9.16 - 2 \times 33.18) \text{ kJ mol}^{-1} + (2.88 \text{ J K}^{-1} \text{ mol}^{-1} \times 75 \text{ K}) = (-57.20 + 0.22) \text{ kJ mol}^{-1} = -56.98 \text{ kJ mol}^{-1}$$