Homework 3 Solutions

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

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

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

(a) For reversible adiabatic expansion,

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

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

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

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

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

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

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

On the other hand, $p_f V_f = nRT_f$

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

Solving this equation for T_f gives $$T_f = \frac{p_{ex}V_i + nC_{V,m}T_i}{nC_{V,m} + \frac{p_{ex}nR}{p_f}}$$

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

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

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

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

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

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

(b) n = 1.4 g / 18.02 g = 0.078 mol

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

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

3. Adiabatic expansion: $q = 0$

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

$\Delta U = q + w$ = -3.2 kJ

$w = C_V\Delta T = nC_{V,m}\Delta T$ $\Delta T = w/(nC_{V,m})$

$C_{V,m}(O_2) = C_{p,m}(O_2) - R = 29.355 - 8.314 = 21.041$ J K^{-1} mol^{-1}

ΔT = -3.2 kJ / {(4.0 mol) × (21.041 J K^{-1} mol^{-1})} = -38 K

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

4. (a) at 25°C, $\Delta_{vap}H^{\varnothing}$ = 44.01 kJ mol^{-1} [Table 2.3]

(b) at 100°C, $\Delta_{vap}H^{\varnothing}$ = 40.7 kJ mol^{-1} [Table 2.3]

n = 1.00×10^3 g × 1 mol / 18.02 g = 55.5 mol

$q = n\Delta_{vap}H^{\varnothing}$

(a) at 25°C, q = 44.01 kJ mol^{-1} × 55.5 mol = 2.44×10^3 kJ

(b) at 100°C, q = 40.7 kJ mol^{-1} × 55.5 mol = 2.26×10^3 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: $\Delta U_c = 0$

$w_c = -nRT_i \ln(V_{cf}/V_{ci})$, 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 atm

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

(b) Initially, we have V_i, $2T_i$, and $p_{bi} = p_{af}$ = 2 atm

In adiabatic, reversible expansion: $V_{bf} = V_i(2T_i/T_i)^c$ with $c = C_{V,m}/R = 5/2$

$V_{bf} = 5.657V_i$ Also, $p_{bi}V_i^{\gamma} = p_{bf}V_{bf}^{\gamma}$ with $\gamma = C_{p,m}/C_{V,m} = 7/5 = 1.4$

$p_{bf} = p_{bi}(V_i/5.657V_i)^{1.4} = 0.088p_{bi} = 0.177$ atm

(c) Initially, we have $V_{ci} = V_{bf} = 5.657V_i$, T_i, and $p_{ci} = p_{bf} = 0.177$ atm

In isothermal compression, $p_{ci}V_{ci} = p_{cf}V_{cf}$ and $V_{cf}/V_{ci} = p_{ci}/p_{cf}$

Since p_{cf} = 1.0 atm, $V_{cf}/V_{ci} = 0.177$

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

$q_c = -w_c = -1.733RT_i$

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

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:

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

Overall values for the entire cycle are:

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

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

6. 3 C(s) + 3 H_2(g) + O_2(g) → CH_3COOCH_3(l) $\Delta_fH^{\varnothing}$ = -442 kJ mol^{-1}

$\Delta_fU^{\varnothing} = \Delta_fH^{\varnothing} - \Delta n_gRT$, Δn_g = -4 mol

$\Delta_f U^\varnothing$ = -442 kJ mol^{-1} – (-4 × 8.3145×10^{-3} kJ K^{-1} mol^{-1} × 298.15 K) = -432 kJ mol^{-1}

7. $C_{10}H_8(s) + 12\ O_2(g) \rightarrow 10\ CO_2(g) + 4\ H_2O(l)$ $\Delta_c H^\varnothing$ = -5157 kJ mol^{-1}

The reverse reaction is

$10\ CO_2(g) + 4\ H_2O(l) \rightarrow C_{10}H_8(s) + 12\ O_2(g)$ $\Delta H^\varnothing$ = 5157 kJ mol^{-1}

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 $\Delta_f H^\varnothing(CO_2)$ and $\Delta_f H^\varnothing(H_2O)$

$10\ C(s) + 10\ O_2(g) \rightarrow 10\ CO_2(g)$ $\Delta H^\varnothing = 10\times(-393.5$ kJ mol$^{-1})$

$4\ H_2(g) + 2\ O_2(g) \rightarrow 4\ H_2O(g)$ $\Delta H^\varnothing = 4\times(-285.8$ kJ mol$^{-1})$

Overall

$10\ C(s) + 4\ H_2(g) \rightarrow C_{10}H_8(s)$

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

8. $C_{10}H_8(s) + 12\ O_2(g) \rightarrow 10\ CO_2(g) + 4\ H_2O(l)$ $\Delta_c H^\varnothing$ = -5157 kJ mol^{-1}

$\Delta_c U^\varnothing = \Delta_c H^\varnothing - \Delta n_g RT$, Δn_g = -2 mol

$\Delta_c U^\varnothing$ = -5157 kJ mol^{-1} – (-2 × 8.3145×10^{-3} kJ K^{-1} mol^{-1} × 298.15 K) = -5152 kJ mol^{-1}

$q = n\Delta_c U^\varnothing$

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

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

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

$C_6H_6O(s) + 7\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$ $\Delta_c H^\varnothing$ = -3054 kJ mol^{-1}

$\Delta_c U^\varnothing = \Delta_c H^\varnothing - \Delta n_g RT$, Δn_g = -1 mol

$\Delta_c U^\varnothing$ = -3054 kJ mol^{-1} – (-1 × 8.3145×10^{-3} kJ K^{-1} mol^{-1} × 298.15 K) = -3051.5 kJ mol^{-1}

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

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

As one can see, the differences between $\Delta_c H^\varnothing$ and $\Delta_c U^\varnothing$ are actually rather small. Therefore, in these calculations one can use $\Delta_c H^\varnothing$ in place of $\Delta_c U^\varnothing$ without any significant loss in accuracy.

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

	$\Delta_r H^\varnothing$, kJ mol^{-1}
$N_2(g) + O_2(g) \rightarrow 2NO(g)$	+180.5
$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$	-114.1
$2\ NO_2(g) + (1/2)\ O_2(g) \rightarrow 2\ N_2O_5(g)$	(1/2) (-110.2)
$N_2(g) + 5/2\ O_2(g) \rightarrow N_2O_5(g)$	+11.3

Therefore, $\Delta_f H^\varnothing[N_2O_5(g)]$ = +11.3 kJ mol^{-1}

10. We use Kirchhoff's law:

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

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

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