Chemistry 2740 Spring 2016 Test 1 solutions

1. The SI units of pressure and of volume are, respectively, Pa and m^3.

$$\begin{aligned}\Delta V &= \frac{0.5\,\mathrm{L}}{1000\,\mathrm{L\,m^{-3}}} = 5\times 10^{-4}\,\mathrm{m}^3.\\ w &= -p_{\mathrm{ext}}\,\Delta V\\ &= -(90\times 10^3\,\mathrm{Pa})(5\times 10^{-4}\,\mathrm{m}^3) = -45\,\mathrm{J}.\end{aligned}$$

This is the work done per breath. Over a day,

$$\begin{aligned}w_{\mathrm{total}} &= (-45\,\mathrm{J\,breath^{-1}})(15\,\mathrm{breaths\,min^{-1}})(60\,\mathrm{min\,h^{-1}})(24\,\mathrm{h})\\ &= -972\,\mathrm{kJ}.\end{aligned}$$

To put this number in perspective, it's roughly the amount of energy you would derive from eating two slices of bread. Note however that this is an overestimate. You probably use something much closer to 125 kJ per day to do the muscle work necessary to breathe. The reason for the discrepancy is that not all of the 0.5 L of gas taken in is accommodated by expanding the chest. A lot of the necessary space is made by expanding the alveoli within the lungs. There, you have to think in terms of the elastic properties of lung tissue rather than in terms of working against the external pressure.

2. (a)

$$\begin{aligned}\langle E\rangle &= \frac{k_BT^2}{q}\frac{\partial q}{\partial T}.\\ \frac{\partial q}{\partial T} &= \frac{2Ik_B}{\sigma\hbar^2}.\\ \therefore \langle E\rangle &= k_BT^2\frac{\sigma\hbar^2}{2Ik_BT}\frac{2Ik_B}{\sigma\hbar^2} = k_BT.\\ \therefore U_{m,\mathrm{rot}} &= L\langle E\rangle = Lk_BT = RT.\end{aligned}$$

(b)

$$\begin{aligned}U_m &= U_{m,\mathrm{trans}} + U_{m,\mathrm{rot}}\\ &= \frac{3}{2}RT + RT = \frac{5}{2}RT.\\ C_{V,m} &= \left.\frac{\partial U_m}{\partial T}\right|_V = \frac{5}{2}R.\\ C_{p,m} &= C_{V,m} + R\\ &= \frac{5}{2}R + R = \frac{7}{2}R\\ &= \frac{7}{2}\left(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}\right) = 29.100\,65\,\mathrm{J\,K^{-1}mol^{-1}}.\end{aligned}$$

This is just slightly less (by $0.25\,\mathrm{J\,K^{-1}mol^{-1}}$) than the experimental value for O_2. The difference is almost entirely due to the small vibrational contribution. Using the vibrational partition function, we can calculate that the vibrational contribution is $0.23\,\mathrm{J\,K^{-1}mol^{-1}}$. The rest of the difference is what we would call modeling error. The rotational and vibrational partition functions are both obtained from simplified models of a diatomic molecule. In particular, the vibrational partition function is based on the harmonic oscillator model (an exactly quadratic vibrational potential), and both models neglect coupling between rotation and vibration. Still, the simple model that includes only translation and rigid rotation does a remarkable job at predicting the heat capacity.

Bonus: Vibrational levels are widely spaced compared to k_BT. This means that excited vibrational states are mostly inaccessible. Since matter stores energy by moving molecules to higher energy levels, this makes vibrations in O_2 poor at storing energy, which is what heat capacities measure.

3. (a) You have to start with a balanced reaction:

$$\mathrm{C_5H_{12}O_{(l)}} + \frac{15}{2}\mathrm{O_{2(g)}} \longrightarrow 5\,\mathrm{CO_{2(g)}} + 6\,\mathrm{H_2O_{(l)}}$$

Note that the enthalpy of combustion of a substance is the enthalpy change for the combustion of *one* equivalent of that substance, so you can't, for instance, double this reaction to avoid fractions.

$$\begin{aligned}\Delta_c H_m^\circ &= 5\Delta_f H^\circ(\mathrm{CO_2}) + 6\Delta_f H^\circ(\mathrm{H_2O,l}) - \Delta_f H^\circ(\mathrm{C_5H_{12}O}),\\ \therefore\ \Delta_f H^\circ(\mathrm{C_5H_{12}O}) &= 5\Delta_f H^\circ(\mathrm{CO_2}) + 6\Delta_f H^\circ(\mathrm{H_2O,l}) - \Delta_c H_m^\circ\\ &= 5(-393.51) + 6(-285.830) - (-3368.97)\,\mathrm{kJ\,mol^{-1}}\\ &= -313.56\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

(b) Again, you can't do anything without a balanced reaction:

$$\mathrm{C_4H_{8(l)}} + \mathrm{CH_3OH_{(l)}} \longrightarrow \mathrm{C_5H_{12}O_{(l)}}$$

$$\begin{aligned}\Delta_r H_m^\circ &= \Delta_f(\mathrm{C_5H_{12}O}) - [\Delta_f H^\circ(\mathrm{C_4H_8}) + \Delta_f H^\circ(\mathrm{CH_3OH})]\\ &= -313.56 - [6.1 + (-239.1)]\ \mathrm{kJ\,mol^{-1}} = -80.6\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

(c) We have the molar enthalpy of reaction, which is the heat at constant pressure. From the mass, we can calculate the number of moles:

$$n_{\mathrm{MMP}} = \frac{50\,000 \times 10^3\,\mathrm{g}}{88.15\,\mathrm{g\,mol^{-1}}} = 5.7 \times 10^5\,\mathrm{mol}.$$

The heat produced by the reaction is therefore

$$\Delta_r H = n_{\mathrm{MMP}}\Delta_r H_m^\circ = (5.7 \times 10^5\,\mathrm{mol})(-80.6 \times 10^3\,\mathrm{J\,mol^{-1}}) = -4.7 \times 10^{10}\,\mathrm{J}.$$

There are at least two ways to proceed from here, depending on what you consider to be the system.

i. Considering the water as the system, you would consider that heat is being added to the water in the amount

$$\begin{aligned} q &= 80\% \times (-\Delta_r H) \\ &= (0.80)(4.7 \times 10^{10}\,\mathrm{J}) \\ &= 3.7 \times 10^{10}\,\mathrm{J}. \end{aligned}$$

Then the heat balance is

$$q = m_{\mathrm{H_2O}} c_p(l)\Delta T_1 + m_{\mathrm{H_2O}}\Delta_{\mathrm{vap}} h + m_{\mathrm{H_2O}} c_p(g)\Delta T_2. \tag{1}$$

$$\begin{aligned} \therefore m_{\mathrm{H_2O}} &= \frac{q}{c_p(l)\Delta T_1 + \Delta_{\mathrm{vap}} h + c_p(g)\Delta T_2} \\ &= \frac{3.7 \times 10^{10}\,\mathrm{J}}{(4.184\,\mathrm{J\,K^{-1}g^{-1}})(10\,\mathrm{K} + 2257\,\mathrm{J\,g^{-1}} + (1.874\,\mathrm{J\,K^{-1}g^{-1}})(30\,\mathrm{K})} \\ &= 1.6 \times 10^{7}\,\mathrm{g} \equiv 1.6 \times 10^{4}\,\mathrm{kg} \equiv 16\,\mathrm{t}. \end{aligned}$$

ii. If we consider the system to consist of the reaction vessel as well as the steam pipes, then we would set it up slightly differently. In the heat balance, the heat of reaction would appear on the right-hand side. However, the system is not adiabatic since 20% of the heat is lost. We would therefore have

$$q = 20\% \times \Delta_r H = \Delta_r H + m_{\mathrm{H_2O}} c_p(l)\Delta T_1 + m_{\mathrm{H_2O}}\Delta_{\mathrm{vap}} h + m_{\mathrm{H_2O}} c_p(g)\Delta T_2.$$

After bringing the $\Delta_r H$ term from the right to the left-hand side, we get the same equation as (1).