

# Chemistry 2740 Spring 2011 Test 2 Solutions

1. Any of the following would be acceptable:

- Allows us to define an absolute entropy scale
- Implies that it is impossible to cool an object to absolute zero

2. (a)

$$\eta^* = \frac{T_l}{T_h - T_l} = \frac{187.15 \text{ K}}{293.15 - 187.15 \text{ K}} = 1.77 = \frac{q_{\text{removed}}}{w}.$$
$$\therefore q_{\text{removed}} = \eta^* w = 1.77(31 \text{ MJ}) = 55 \text{ MJ}.$$

This is the heat removed from the freezer compartment. This heat, plus the work, are equal to the heat that must be dumped into the room:

$$q_{\text{dumped}} = -(q_{\text{removed}} + w) = -(55 + 31 \text{ MJ}) = -86 \text{ MJ}.$$

(b) A real (irreversible) refrigerator must be less efficient than a reversible refrigerator. Therefore, if it consumes 31 MJ of work, it cannot extract as much heat from the freezer. The total heat dumped into the room will therefore be less than the 86 MJ calculated above. If this seems paradoxical, it is because a reversible refrigerator would actually consume less electricity to extract the same amount of heat to the room. To put it another way, by treating the freezer as ideal, we overestimated the amount of heat removed as a result of doing 31 MJ of electrical work.

3. (a)

$$\begin{aligned}\Delta_{r(1)} G_m^\circ &= -RT \ln K_1 \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(294.65 \text{ K}) \ln(9.32 \times 10^3) \\ &= -22.4 \text{ kJ/mol}\end{aligned}$$

(b) i.

$$\begin{aligned}\Delta_{r(2)} G_m^\circ &= -RT \ln K_2 \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(294.65 \text{ K}) \ln(2.10 \times 10^5) \\ &= -30.0 \text{ kJ/mol} \\ \therefore \Delta_{r(i)} G_m^\circ &= \Delta_{r(1)} G_m^\circ + \Delta_{r(2)} G_m^\circ \\ &= -22.4 + (-30.0) \text{ kJ/mol} = -52.4 \text{ kJ/mol}.\end{aligned}$$

$$\text{ii. } \Delta_{r(ii)} G_m^\circ = 2\Delta_{r(1)} G_m^\circ = 2(-22.4 \text{ kJ/mol}) = -44.8 \text{ kJ/mol}$$

$$\text{iii. } \Delta_{\text{coop}} G_m^\circ = \Delta_{r(i)} G_m^\circ - \Delta_{r(ii)} G_m^\circ = -52.4 - (-44.8) \text{ kJ/mol} = -7.6 \text{ kJ/mol}$$

(c) The activity of oxygen in this solution is

$$a_{\text{O}_2} = \frac{300 \times 10^{-6} \text{ mol/L}}{1 \text{ mol/L}} = 3 \times 10^{-4}.$$

From the equilibrium relationships, we have

$$\begin{aligned}\frac{[\text{HbO}_2]}{[\text{Hb}]} &= K_1 a_{\text{O}_2} = (9.32 \times 10^3)(3 \times 10^{-4}) = 2.8 \\ \frac{[\text{Hb}(\text{O}_2)_2]}{[\text{HbO}_2]} &= K_2 a_{\text{O}_2} = (2.10 \times 10^5)(3 \times 10^{-4}) = 63 \\ \frac{[\text{Hb}(\text{O}_2)_3]}{[\text{Hb}(\text{O}_2)_2]} &= K_3 a_{\text{O}_2} = (9.07 \times 10^3)(3 \times 10^{-4}) = 2.7 \\ \frac{[\text{Hb}(\text{O}_2)_4]}{[\text{Hb}(\text{O}_2)_3]} &= K_4 a_{\text{O}_2} = (6.60 \times 10^5)(3 \times 10^{-4}) = 198\end{aligned}$$

At this oxygen concentration, there is more of each form than of the previous, and there is almost 200 times more  $\text{Hb}(\text{O}_2)_4$  than of  $\text{Hb}(\text{O}_2)_3$ . The fully oxygenated form must therefore make up about 99.5% of the total haemoglobin.

If you prefer a more quantitative approach, here it is:

$$\begin{aligned}[\text{HbO}_2] &= 2.8[\text{Hb}]. \\ [\text{Hb}(\text{O}_2)_2] &= 63[\text{HbO}_2] &= 63(2.8[\text{Hb}]) &= 176[\text{Hb}]. \\ [\text{Hb}(\text{O}_2)_3] &= 2.7[\text{Hb}(\text{O}_2)_2] &= 2.7(176[\text{Hb}]) &= 479[\text{Hb}]. \\ [\text{Hb}(\text{O}_2)_4] &= 198[\text{Hb}(\text{O}_2)_3] &= 198(479[\text{Hb}]) &= 9.49 \times 10^4[\text{Hb}].\end{aligned}$$

$$\begin{aligned}\therefore \frac{[\text{Hb}(\text{O}_2)_4]}{[\text{Hb}]_{\text{total}}} &= \frac{[\text{Hb}(\text{O}_2)_4]}{[\text{Hb}] + [\text{HbO}_2] + [\text{Hb}(\text{O}_2)_2] + [\text{Hb}(\text{O}_2)_3] + [\text{Hb}(\text{O}_2)_4]} \\ &= \frac{9.49 \times 10^4[\text{Hb}]}{[\text{Hb}] + 2.8[\text{Hb}] + 176[\text{Hb}] + 479[\text{Hb}] + 9.49 \times 10^4[\text{Hb}]} \\ &= \frac{9.49 \times 10^4}{1 + 2.8 + 176 + 479 + 9.49 \times 10^4} \\ &= 0.993.\end{aligned}$$

(My hand-waving estimate of 99.5% was pretty close!)

- (d) If there were no cooperativity, then each form would only be more abundant than the previous by a factor of about 2.8. Many of the states of haemoglobin would in fact coexist under the stated conditions. (If you repeat the calculation above assuming that all the equilibrium constants are equal to  $K_1$ , you find that the fully oxygenated form only accounts for 64.6% of the total haemoglobin if binding is not cooperative.)