

# Solutions Exam Physical Chemistry 1: Thermodynamics

## 15 January 2020

All 16 subproblems have equal weight for the final grade.

Sometimes a **NOTE** is added, just meant as an explanation or advise.

a) Note, that the answers below to part a) are not unique, in some cases overcomplete and are meant to be indicative.

– standard hydrogen electrode:

The standard hydrogen electrode is based on the reaction  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  and consists of  $\text{H}_2(\text{g})$  bubbling at 1 bar on a Pt-electrode with an activity  $a_{\text{H}^+} = 1$ . Its standard electric potential is defined as  $E^\ominus \equiv 0$  and the standard potential of all other redox couples are determined relative to this electrode.

– biological standard state:

$P^\oplus = P^\ominus = 1$  bar,  $a_i^\oplus = a_i^\ominus = 1$  for all components  $i$  except for  $a_{\text{H}^+}^\oplus$ , which is set to be in accordance with  $\text{pH}^\oplus = 7$ , so  $a_{\text{H}^+}^\oplus = 10^{-7}$ .

– isochoric process:

A process running at constant volume,  $dV = 0$ .

– activity coefficient:

The activity coefficient  $\gamma_i$  of component  $i$  in a mixture is determined by  $a_i = \gamma_i x_i$  when referenced to the mole fraction  $x_i$ , or  $a_i = \gamma_i b_i$  when referenced to the molality  $b_i$  and  $a_i = \gamma_i c_i$  if referenced to the concentration  $c_i$ , where  $a_i$  is the activity of component  $i$ .

– Boltzmann entropy:

$S = k \ln W$ , where  $W$  is the number of possible micro states for a macro state; used in statistical thermodynamics.

b) – the temperature  $T$ : yes (**NOTE**: all state variables are state functions)

– the difference of the Gibbs free energy and the enthalpy  $G - H$ : yes

– the Helmholtz free energy  $A$ : yes

– the natural logarithm of the volume  $\ln V$ : yes (**NOTE**: all state variables are state functions, so  $V$  and therefore also  $\ln V$ )

– the quotient of heat and temperature  $\frac{Q}{T}$ : no (**NOTE**: this looks like the entropy, but the entropy is defined for  $Q^{\text{rev}}$ )

c)

$$\Delta S = -nR(x_A \ln x_A + x_B \ln x_B) :$$

–  $S$ : the entropy

–  $R$ : the gas constant

–  $n$ : the total number of moles in the system

–  $x_A$ : the mole fraction of component A

–  $x_B$ : the mole fraction of component B

The formula is used to determine the mixing entropy of an *ideal* mixture of components A and B.

d) Use the Boltzmann distribution  $\frac{n_i}{N} = \frac{[-\epsilon_i/kT]}{q}$  including the degeneracy  $g_i$  of energy level  $i$ :

$$\frac{n_1}{n_0} = \frac{g_1 \exp\left[-\frac{\epsilon_1}{kT}\right]}{g_0 \exp\left[-\frac{\epsilon_0}{kT}\right]} = \frac{\exp\left[-\frac{\epsilon_1}{kT}\right]}{2 \exp\left[-\frac{\epsilon_0}{kT}\right]}.$$

Setting  $\epsilon_0 = 0$  we get

$$\frac{n_1}{n_0} = \frac{\exp\left[-\frac{\epsilon_1}{kT}\right]}{2} = \frac{0.05}{0.95} = 0.0526, \quad \text{or} \quad \frac{\epsilon_1}{kT} = -\ln(2 \cdot 0.0526) \quad \text{so}$$

$$\epsilon_1 = -1.38 \cdot 10^{-23} \cdot 300 \ln(2 \cdot 0.0526) = 9.32 \cdot 10^{-21} \text{ J}, \quad \text{so}$$

$$\epsilon_1 = \frac{9.32 \cdot 10^{-21}}{1.60 \cdot 10^{-19}} = 0.058 \text{ eV}.$$

(NOTE: Alternatively you could substitute the partition function  $q = 2 \exp\left[-\frac{\epsilon_0}{kT}\right] + \exp\left[-\frac{\epsilon_1}{kT}\right]$  in the Boltzmann distribution and use  $0.05 = \frac{n_1}{N} = \frac{\exp\left[-\frac{\epsilon_1}{kT}\right]}{q}$ .)

## Problem 2

(NOTE: This is a copy of Exercise 17, up to subproblem d)

a)

$$\Pi = [BRT] = 0.282 \cdot 8.314 \cdot 293.15 = 687 \text{ mol dm}^{-3} \text{ J mol}^{-1} \text{ K}^{-1} \text{ K} = 687 \text{ J dm}^{-3}$$

(NOTE: Advise: always first convert all values to SI-units)

$$\Pi = 687 \text{ J dm}^{-3} = 687 \cdot 10^3 \text{ Nm} \cdot \text{m}^{-3} = 6.87 \cdot 10^5 \text{ N m}^{-2} = 6.87 \cdot 10^5 \text{ Pa} = 6.87 \text{ bar}.$$

b) One could use 'back engineering' and the approximations for ideal solutions and low concentrations [B], used in the original derivation:

$$\Pi = -\frac{RT}{V_{m,A}} \ln a_A; \quad \text{use the approximation of an ideal solution :}$$

$$\Pi \approx -\frac{RT}{V_{m,A}} \ln x_A, \quad \text{so}$$

$$\Pi \approx -\frac{RT}{V_{m,A}} \ln(1 - x_B); \quad \text{use that for } x \ll 1, \text{ so for small [B]: } \ln(1 - x) \approx -x :$$

$$\Pi \approx \frac{RT}{V_{m,A}} x_B = \frac{RT}{V_{m,A}} \frac{n_B}{n_A + n_B}, \quad \text{so for low concentrations [B]:}$$

$$\Pi \approx \frac{RT}{V_{m,A}} \frac{n_B}{n_A} \approx \frac{RT}{V_A} n_B \approx \frac{RT}{V} n_B \approx [B] RT.$$

c) (NOTE: Advise: check the units to find out whether to use  $\frac{M}{\rho}$  or  $\frac{\rho}{M}$ .)

$$V_{m,H_2O}^* = \frac{M}{\rho} = \frac{18.015}{0.998} = 18.05 \text{ cm}^3 \text{ mol}^{-1} = 18.05 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \quad \text{so}$$

$$\ln a_A = -\frac{\Pi V_{m,H_2O}^*}{RT} = -\frac{7.71 \cdot 10^5 \cdot 18.05 \cdot 10^{-6}}{8.314 \cdot 293.15} = -5.71 \cdot 10^{-3}, \quad \text{so} \quad a_A = 0.994.$$

The activity coefficient  $\gamma_A$  follows from  $a_A = \gamma_A x_A$ .

$$x_A = \frac{n_A}{n_A + n_B} = \frac{b_A}{b_A + b_B} = \frac{\frac{10^3}{18.015}}{\frac{10^3}{18.015} + 0.300} = 0.9946, \quad \text{so}$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.994}{0.995} = 0.999.$$

(NOTE: alternatively you could use  $a_i = \gamma_i b_i$  when referenced to the molality  $b_i$  or  $a_i = \gamma_i c_i$  when referenced to the concentration  $c_i$  (see problem 1a); the result will not be very different).

- d) Use the expression for freezing point depression:  
 (NOTE: The variables with an \* refer to the solvent)

$$\Delta T = \frac{R \left( T_{fus,A}^* \right)^2}{\Delta_{fus} H_A^*} x_B = \frac{R \left( T_{fus,A}^* \right)^2}{\Delta_{fus} H_A^*} (1 - x_A) = \frac{8.314 \cdot (273.15)^2}{6.008 \cdot 10^3} (1 - 0.9946) = 0.558 \text{ K.}$$

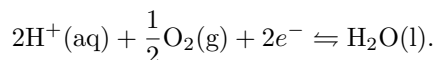
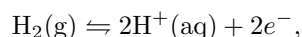
So the fusion temperature is

$$T_{fus} = T_{cryst} = 273.15 - 0.558 = 272.59 \text{ K.}$$

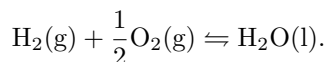
### Problem 3

(NOTE: This problem is partly similar to Exercise add.5 in Additional Exercises)

- a) Half reactions:



Total reaction:



- b) The EMF of the cell is

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q$$

$E^\ominus$  we find with  $\Delta_r G^\ominus = -\nu F E^\ominus$  (use  $\Delta_f G^\ominus(\text{H}_2(\text{g})) = \Delta_f G^\ominus(\text{O}_2(\text{g})) = 0$ ):

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}_2\text{O}(\text{l})) - 2\Delta_f G^\ominus(\text{H}_2(\text{g})) - \frac{1}{2}\Delta_f G^\ominus(\text{O}_2(\text{g})) = \Delta_f G^\ominus(\text{H}_2\text{O}(\text{l})) = -237.13 \text{ kJ/mol.}$$

$$E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} = -\frac{-237.13 \cdot 10^3}{2 \cdot 96485} = 1.2288 \text{ V.}$$

In this reaction two electrons are transferred ( $\nu = 2$  becomes clear from the half reaction  $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+(\text{aq}) + 2e^-$ ).

The reaction quotient  $Q$  is given by ( $P(\text{O}_2(\text{g})) = 0.5P^\ominus$ ,  $P(\text{H}_2(\text{g})) = P^\ominus$  and  $a(\text{H}_2\text{O}(\text{l})) = 1$ )

$$Q = \frac{a(\text{H}_2\text{O}(\text{l}))}{a(\text{H}_2) \cdot (a(\text{O}_2))^{\frac{1}{2}}} = \frac{a(\text{H}_2\text{O}(\text{l}))}{\left(\frac{P(\text{H}_2)}{P^\ominus}\right) \left(\frac{P(\text{O}_2)}{P^\ominus}\right)^{\frac{1}{2}}} = \frac{1}{1 \cdot (0.5)^{\frac{1}{2}}} = 1.414, \quad \text{resulting in}$$

$$E = 1.2288 - \frac{8.314 \cdot 298}{2 \cdot 96485} \ln 1.414 = 1.2288 - 0.0044 = 1.224 \text{ V.}$$

- c) As  $\Delta_r G = -237.13 \text{ kJ/mol}$  we determine the electrical work done on the external resistor also in J/mol, so we need once more the number of electrons per mol reaction progression ( $\nu$ ), so  $W_e = -\nu F E_L$ . The potential difference  $E_L$  across  $R_L$  we find by first determining the current  $I$  in the circuit:

$$I = \frac{E}{R_L + R_i}, \quad \text{so} \quad E_L = I R_L = \frac{E R_L}{R_L + R_i}, \quad \text{and we find}$$

$$\eta = \frac{W_e}{\Delta_r G} = \frac{-\nu F E_L}{\Delta_r G} = \frac{-\nu F E R_L}{\Delta_r G (R_L + R_i)} = \frac{R_L}{R_L + R_i} = \frac{10}{10 + 0.5} = 0.95 = 95 \text{ \%}.$$

(NOTE: This latter expression,  $\eta = \frac{R_L}{R_L + R_i}$ , was also deduced in the lecture (see also SG. p. 22), which could have been used also without the derivation).

d) A zero current implies  $E = 0$ , so  $\Delta_r G = 0$ , implying

$$\Delta_r G^\ominus = -RT \ln Q, \quad \text{so} \quad Q = \exp \left[ -\frac{\Delta_r G^\ominus}{RT} \right] = \exp \left[ \frac{237.13 \cdot 10^3}{8.314 \cdot 298} \right] = 3.69 \cdot 10^{41}, \quad \text{so}$$

$$Q = \frac{a(\text{H}_2\text{O}(l))}{\left( \frac{P(\text{H}_2)}{P^\ominus} \right) \left( \frac{P(\text{O}_2)}{P^\ominus} \right)^{\frac{1}{2}}} = \frac{1}{\left( \frac{P(\text{H}_2)}{P^\ominus} \right) \cdot (0.21)^{\frac{1}{2}}} = 3.69 \cdot 10^{41}, \quad \text{resulting in}$$

$$P(\text{H}_2) = \frac{1}{(0.21)^{\frac{1}{2}} \cdot 3.69 \cdot 10^{41}} P^\ominus = 5.9 \cdot 10^{-42} \text{ bar.}$$

## Problem 4

a) The denaturation reaction is

$$\text{N} \rightleftharpoons \text{D}, \quad \text{with equilibrium constant } K = \frac{a_{\text{D}}}{a_{\text{N}}} \approx \frac{[\text{D}]}{[\text{N}]}, \quad \text{so } f_{\text{D}} = \frac{[\text{D}]}{[\text{N}] + [\text{D}]} = \frac{[\text{N}]K}{[\text{N}] + [\text{N}]K} = \frac{1}{1 + K}.$$

b) At  $T = T_m$  (we choose to write  $\Delta_r G$  as  $\Delta G$ , etc. and use  $\Delta G = \Delta H - T\Delta S$  at constant  $T$ )

$$f_{\text{D}} = \frac{1}{2}, \quad \text{so } \frac{1}{1 + K} = \frac{1}{2} \quad \text{and therefore } K = 1, \quad \text{so } \Delta G^\ominus = -RT \ln 1 = 0 \quad \text{and therefore}$$

$$\Delta H^\ominus = T_m \Delta S^\ominus, \quad \text{so } T_m = \frac{\Delta H^\ominus}{\Delta S^\ominus}.$$

At  $T = 298\text{K}$  the data given result in

$$\Delta S^\ominus = \frac{\Delta H^\ominus - \Delta G^\ominus}{298} = \frac{90.4 \cdot 10^3 - 17.7 \cdot 10^3}{298} = 244 \text{ J/molK}$$

As an estimate we make the usual assumption that  $\Delta H^\ominus$  and  $\Delta S^\ominus$  are only weakly dependent on the temperature, so

$$T_m \approx \frac{\Delta H^\ominus(298 \text{ K})}{\Delta S^\ominus(298 \text{ K})} = \frac{90.4 \cdot 10^3}{244} = 370 \text{ K} \approx 97 \text{ }^\circ\text{C}.$$

This result is quite higher than  $60 \text{ }^\circ\text{C}$  as estimated from Figure 1.

c)

$$\Delta C_P = C_{\text{D},P} - C_{\text{N},P} = \left( \frac{\partial H_{\text{D}}}{\partial T} \right)_P - \left( \frac{\partial H_{\text{N}}}{\partial T} \right)_P = \left( \frac{\partial \Delta H}{\partial T} \right)_P,$$

the value of which can be read of directly from Figure 2b, assuming straight lines, which results in (**NOTE**: 1 cal = 4.184 J)

$$\Delta C_P = \frac{100 + 88}{80 - (-40)} = 1.57 \text{ kcal/molK} = 6.6 \text{ kJ/molK}.$$

d) The most stable state of the folded protein corresponds to the most unstable state of the unfolded protein, which is found at the maximum in Figure 2a, which has a reaction energy  $\Delta G_{\text{max}}^\ominus = 4.8 \text{ kcal/mol}$  at  $T = 288 \text{ K}$ , so (use the fact that  $f_{\text{D}} \ll 1$ ; **NOTE**: 1 cal = 4.184 J)

$$\Delta G_{\text{max}}^\ominus = -RT \ln Q = -RT \ln \left( \frac{a_{\text{D}}}{a_{\text{N}}} \right), \quad \text{and using } \frac{a_{\text{D}}}{a_{\text{N}}} = \frac{\gamma_{\text{D}}[\text{D}]}{\gamma_{\text{N}}[\text{N}]} \approx \frac{\gamma_{\text{D}}}{\gamma_{\text{N}}} \frac{[\text{D}]}{[\text{N}] + [\text{D}]} = \frac{\gamma_{\text{D}}}{\gamma_{\text{N}}} f_{\text{D}}$$

$$\frac{\gamma_{\text{D}}}{\gamma_{\text{N}}} = \frac{1}{f_{\text{D}}} \exp \left[ \frac{-\Delta G_{\text{max}}^\ominus}{RT} \right] = \frac{1}{10^{-3}} \exp \left[ -\frac{4.8 \cdot 10^3 \cdot 4.184}{8.314 \cdot 288} \right] = 0.228.$$