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 $2H^+ + 2e^- \rightarrow H_2$ and consists of $H_2(g)$ bubbling at 1 bar on a Pt-electrode with an activity $a_{H^+} = 1$. 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 $a_{H^+}^{\oplus}$, which is set to be in accordance with $\mathrm{pH}^{\oplus} = 7$, so $a_{H^+}^{\oplus} = 10^{-7}$.
- isochoric process:
  A process running at constant volume, $dV = 0$.
- activity coefficient:
  The activity coefficient γ_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 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^{rev})

c)

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

- 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 Bolzmann 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)

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

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

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

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

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

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

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

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

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

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

$$V^*_{\text{m},\text{H}_2\text{O}} = \frac{M}{\rho} = \frac{18.015}{0.998} = 18.05\ \text{cm}^3\text{mol}^{-1} = 18.05 \cdot 10^{-6}\ \text{m}^3\text{mol}^{-1}, \quad \text{so}$$

$$\ln a_A = -\frac{\Pi V^*_{\text{m},\text{H}_2\text{O}}}{RT} = -\frac{7.71 \cdot 10^5 \cdot 18.05 \cdot 10^{-6}}{8.314 \cdot 293.15} = -5.71 \cdot 10^{-3}, \quad \text{so} \quad a_A = 0.994.$$

The activity coefficient γ_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:

$$H_2(g) \leftrightharpoons 2H^+(aq) + 2e^-,$$

$$2H^+(aq) + \frac{1}{2}O_2(g) + 2e^- \leftrightharpoons H_2O(l).$$

Total reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \leftrightharpoons H_2O(l).$$

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 $\Delta_f G^\ominus(H_2(g)) = \Delta_f G^\ominus(O_2(g)) = 0$):

$$\Delta_r G^\ominus = \Delta_f G^\ominus(H_2O(l)) - 2\Delta_f G^\ominus(H_2(g)) - \frac{1}{2}\Delta_f G^\ominus(O_2(g)) = \Delta_f G^\ominus(H_2O(l)) = -237.13 \text{ kJ/mol}.$$

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

In this reaction two electrons are transferred ($\nu = 2$ becomes clear from the half reaction $H_2(g) \leftrightharpoons 2H^+(aq) + 2e^-$).
The reaction quotient Q is given by ($P(O_2(g)) = 0.5P^\ominus$, $P(H_2(g)) = P^\ominus$ and $a(H_2O(l)) = 1$)

$$Q = \frac{a(H_2O(l))}{a(H_2)\cdot(a(O_2))^{\frac{1}{2}}} = \frac{a(H_2O(l))}{\left(\frac{P(H_2)}{P^\ominus}\right)\left(\frac{P(O_2)}{P^\ominus}\right)^{\frac{1}{2}}} = \frac{1}{1\cdot(0.5)^{\frac{1}{2}}} = 1.414, \quad \text{resulting in}$$

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

c) As $\Delta_r G = -237.13$ 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 (ν), 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:

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

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

(**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

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

$$Q = \frac{a(\mathrm{H_2O(l)})}{\left(\frac{P(\mathrm{H_2})}{P^\ominus}\right)\left(\frac{P(\mathrm{O_2})}{P^\ominus}\right)^{\frac{1}{2}}} = \frac{1}{\left(\frac{P(\mathrm{H_2})}{P^\ominus}\right)\cdot(0.21)^{\frac{1}{2}}} = 3.69\cdot 10^{41}, \quad \text{resulting in}$$

$$P(\mathrm{H_2}) = \frac{1}{(0.21)^{\frac{1}{2}}\cdot 3.69\cdot 10^{41}} P^\ominus = 5.9\cdot 10^{-42}\ \text{bar}.$$

Problem 4

a) The denaturation reaction is

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

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

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

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

At $T = 298K$ 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

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

This result is quite higher than 60 °C as estimated from Figure 1.

c)

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

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 $\Delta G^\ominus_\mathrm{max} = 4.8$ kcal/mol at $T = 288$ K, so (use the fact that $f_\mathrm{D} \ll 1$; **NOTE**: 1 cal = 4.184 J)

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

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