Exam Physical Chemistry 1: Thermodynamics
15 January 2020

Please, hand in your answers to problems 1, 2, 3 and 4 on separate sheets.
Put your name and student number on each sheet.

The examination time is 8:30 until 11:30, so **three hours**
There are 4 problems, with each 4 subproblems, a list of constants and a formula sheet,
5 pages in total.
All 16 subproblems have equal weight for the final grade. [†]

Problem 1

a) Give a definition and/or *short* description of the following concepts

- standard hydrogen electrode
- biological standard state
- isochoric process
- activity coefficient
- Boltzmann entropy

b) Indicate for each of the following quantities whether we are dealing with a state function; answer using only yes or no:

- the temperature T,
- the difference of the Gibbs free energy and and the enthalpy $G - H$,
- the Helmholtz free energy A,
- the natural logarithm of the volume $\ln V$,
- the quotient of heat and temperature $\frac{Q}{T}$.

c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

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

d) A certain molecule has a doubly degenerate ground state and a first non-degenerate excited state ϵ_1.
All higher excited states have such a high energy that their occupation can be neglected.
At 300 K 95% of the molecules are present in the ground state.
Calculate the difference in energy between the ground state and the excited state in eV.

[†] **Do not forget to fill in the online survey to the course.**

Problem 2

Consider an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) with a molality of 0.300 mol/kg the molarity is 0.282 mol/dm^3 at 20 °C and 1 bar.
For pure H_2O the following data are given
$\rho = 0.998$ g/cm^3 at 20 °C and 1 bar
$M = 18.015$ g/mol
$T_{fus} = 273.15$ K
$\Delta_{fus}H = 6.008$ kJ/mol.

a) Determine the osmotic pressure in bar, using the van 't Hoff expression for very diluted ideal solutions.

b) Show that the osmotic pressure of a real (non-ideal) solution is given by

$$\Pi = -\frac{RT}{V_{m,A}} \ln a_A.$$

c) The measured osmotic pressure for this solution turns out to be 7.71 bar.
Determine the activity and the activity coefficient of the solvent.

d) Estimate the crystallization temperature of the solvent, assuming that the solute does not enter the ice.

Problem 3

Fuel cells deliver electrical energy through a chemical reaction at the electrodes. The "fuel" for this reaction can be supplied to the cell continuously. Such cells are a possible environmentally friendly alternative for the traditional combustion engine in cars, where the electrical energy from the fuel cell drives an electrical motor.
In the design of a fuel cell with H_2(g) and O_2(g) as fuels, O_2 is fed to the cathode and H_2 to the anode; the product H_2O is withdrawn on the side of the cathode.
By choosing a porous membrane only permeable to H^+-ions, and not permeable to gases, the current between the electrodes is carried by the H^+-ions.
At 298 K $\Delta_f G^\ominus(H_2O(l)) = -237.13$ kJ/mol.

a) Give the relevant chemical equations for the half reactions at the electrodes as well as the total cell reaction in case the reaction product is withdrawn in its liquid state.

b) Determine the EMF (terminal voltage, E(lectro)M(otive) F(orce)) for a fuel cell fed with 0.5 bar oxygen and 1.0 bar hydrogen as fuel at 298 K. Assume that the reactants are present as perfect gases.

c) A definition of the efficiency η of a fuel cell could be

$$\eta = \frac{W_e}{\Delta_r G}$$

in which W_e is the electrical work done on an external resistance.
Calculate the efficiency in case the internal resistance of the fuel cell is equal to $R_i = 0.5\ \Omega$ and the external resistance is $R_L = 10\ \Omega$.

d) Calculate the pressure of an almost empty H_2(g) tank, for which zero current flows through R_L, when the cell is fed with air containing 21 % O_2(g).

Problem 4

The process of protein unfolding generally involves a strong temperature dependence of the thermodynamic parameters.
We study the equilibrium between the folded, N, and unfolded, D, at $P = P^{\ominus}$, of λ-repressor, a protein from λ phage that binds to DNA and regulates transcription.
Some of the thermodynamic parameters for the unfolding of λ-repressor are
$\Delta G^{\ominus}$ 17.7 kJ/mol at $T = 298$ K,
$\Delta H^{\ominus}$ 90.4 kJ/mol at $T = 298$ K.
In Figure 1 the fraction, f_{D}, of D(enatured) (unfolded) protein is plotted as a function of temperature for λ-repressor.
In this problem we approximate activitites by concentrations, unless mentioned otherwise and we suppress the label r by writing $\Delta_r G$ as ΔG, etc.

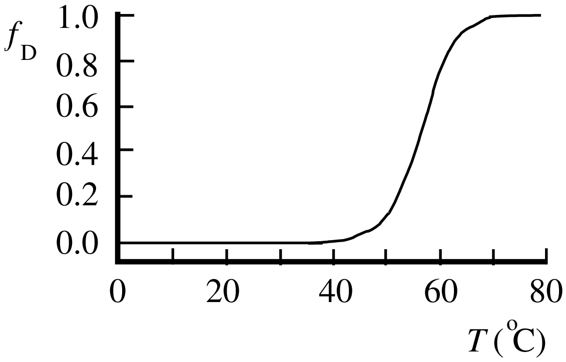

Figure 1: Fraction, f_{D}, of denatured protein *vs* temperature for λ-repressor.

a) Show that the fraction, f_{D}, of denatured (unfolded) protein can be written in terms of the thermodynamic equilibrium constant, K, of the equilibrium, according to

$$f_{\mathrm{D}} = \frac{[D]}{[D]+[N]} = \frac{K}{1+K}.$$

b) Estimate the so-called melting temperature, T_m, of the protein, for which half of the proteins is unfolded using the thermodynamic data at $T = 298$ K and compare your value with the graph in Figure 1.

The reason for the deviation in temperature is due to the strong temperature dependence of the thermodynamic parameters, mentioned above. In Figure 2 this temperature dependence for λ-repressor is presented.
The following values were found for these plots
$\Delta G^{\ominus}_{max} = 4.8$ kcal/mol at $T = 288$ K,
$\Delta H^{\ominus} =$ -88 kcal/mol at $T = 233$ K,
$\Delta H^{\ominus} = 100$ kcal/mol at $T = 353$ K,
$T\Delta S^{\ominus} =$ -80 kcal/mol at $T = 233$ K,
$T\Delta S^{\ominus} = 100$ kcal/mol at $T = 353$ K.

c) Use the data to Figure 2 to determine the temperature dependence of the difference in heat capacity $\Delta C_P = C_{D,P} - C_{N,P}$ between the unfolded and folded state. Assume that the relevant plot can be considered as a linear function.

d) Calculate the ratio of activity coefficients $\frac{\gamma_D}{\gamma_N}$ on the concentration scale in the most stable state of the folded protein. In this most stable state $f_D = 1.000 \cdot 10^{-3}$.

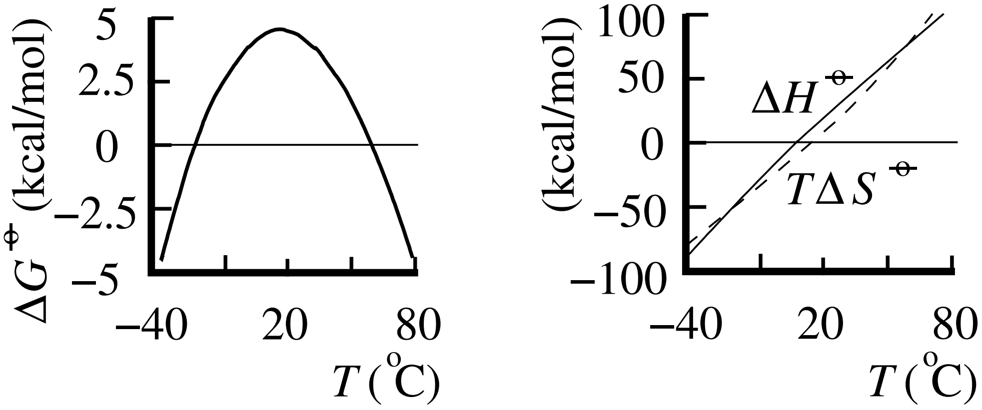

Figure 2: Temperature dependence of $\Delta G^{\ominus}$, and $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for λ-repressor.

List of constants

Elementary charge	e	$1.602 \cdot 10^{-19}$ C
Faraday's constant	F	$9.648 \cdot 10^{4}$ Cmol^{-1}
Boltzmann's constant	k	$1.381 \cdot 10^{-23}$ JK^{-1}
Planck's constant	h	$6.626 \cdot 10^{-34}$ Js
Bohr Magneton	μ_B	$9.274 \cdot 10^{-24}$ JT^{-1}
Atomic mass constant	m_u	$1.661 \cdot 10^{-27}$ kg
Amadeo Avogadro di Quaregna e Ceretto's constant	N_A	$6.022 \cdot 10^{23}$ mol^{-1}
Gas constant	R	8.314 JK^{-1}mol^{-1}
Free fall acceleration	g	9.807 ms^{-2}
Unit of energy		1 cal = 4.184 J
Standard pressure	$P^{\ominus}$	1 bar = 10^{5} Nm^{-2} = 0.9869 atm = 750 Torr

Formulae

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W' \quad \text{and} \quad \mathrm{d}W'_{max} = (\mathrm{d}G)_{P,T}$$

$$\mathrm{d}Q|_P = C_P\mathrm{d}T \quad \text{and} \quad \mathrm{d}Q|_V = C_V\mathrm{d}T$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{omg} \geq 0$$

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$H = U + PV$$

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT\ln Q, \quad \text{where} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT\ln K = -\Delta_r G^{\ominus}$$

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q, \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q \quad \text{and} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^{\ominus} + RT\ln a_i = \mu_i^{\ominus} + RT\ln\frac{P_i}{P^{\ominus}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}}H}\right) x_B$$

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

$$\Pi = [B]RT = \frac{n_B}{V}RT$$

$$S = k\ln W$$

$$\frac{n_i}{N} = \frac{\exp\frac{-\epsilon_i}{kT}}{q}, \quad \text{where} \quad q = \sum_i \exp\frac{-\epsilon_i}{kT} \quad \text{and} \quad <X> = N<x> = N\sum_i x_i\frac{n_i}{N}$$