Additional Exercises Physical Chemistry 1 2021/2022

Exercise add_1

Consider the formation of gaseous formaldehyde from CO(g) and H_2(g) according to

$$\mathrm{CO(g)} + \mathrm{H_2(g)} \leftrightharpoons \mathrm{H_2CO(g)}.$$

For the production of *liquid* formaldehyde from CO and H_2 the reaction Gibbs free energy is $\Delta_r G^\ominus = 28.95$ kJ/mol at 298 K. The vapour pressure of formaldehyde at 298 K is equal to 1500 Torr.
(1 bar = 10^5 Nm^{-2} = 0.9869 atm = 750 Torr).
Calculate the equilibrium constant for the above reaction.
Hint: The reaction consists of two equilibria, the reaction between the gaseous reactants that results in liquid formaldehyde and the equilibrium between the liquid reaction product and its vapour.
Assume that for the activity of a fluid $a(l) \approx 1$ holds and that we are dealing with ideal gases.

Exercise add_2

Estimate the temperature at which calcite ($CaCO_3$) dissociates completely into CaO(s) and CO_2(g) at $P = P^\ominus$, assuming that the temperature dependence of the enthalpy and entropy is negligible and the product gas pressure is $P(CO_2) = P^\ominus$.

Exercise add_3

We compare an isobaric heating process and an alternative isochoric process for the non-perfect gas of exercise 4, for which

$$PV = nRT\left(1 + \frac{B}{V_m}\right).$$

We consider the case of 2 mol argon for which $B = -21.7$ cm^{3}mol^{-1} can be considered constant.
We compare two processes, both with a starting volume of 1.0 L. For the first process we heat the gas isochorically and reversibly from 27 °C to 77 °C. For the second process we heat the gas isobarically and reversibly between the same two temperatures.

a) Determine the pressure at the start of the processes.

b) Determine the change in the difference of the enthalpy and internal energy, $\Delta H - \Delta U$, for the two processes.

c) Compare the results of the former parts with the case of a perfect gas.

Exercise add_4

Electrical work is given by $\mathrm{d}W = E\mathrm{d}q$, in which E represents the potential difference (i.e. the voltage) across the terminals of for example a battery. In case the battery delivers no electrical current, the voltage is referred to as the electromotive force (EMF). When a resistance R is connected between the terminals of the battery, the voltage in principle becomes smaller because the current that flows results in a voltage drop over the internal resistance R_i of the battery (see figure 1). $\mathrm{d}q$ is the amount of charge that passes through the electrical load during the process.
In a reversible process this charge flow is so small that $E_{term} = E_{EMF}$; you could also say that in a reversible process the internal resistance of the battery is negligibly small compared to the external resistance.
The EMF of a battery is 20 V. If one connects a resistance R between the terminals of the battery the potential difference becomes 19 V at a current of $I = 2.5$ A.
Choose the battery as the system.

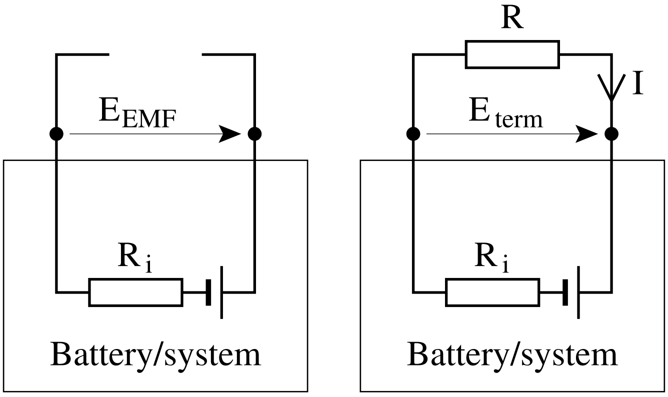


Figure 1: The battery is the system; if there is no external resistance, then the terminal voltage is equal to the maximum voltage of the battery E_{EMF}; if an external resistance R is connected the terminal voltage drops with an amount of $E_i = IR_i$ to the value E_{term}.

a) Calculate the external resistance by using Ohm's law: $E = IR = \left(\frac{\mathrm{d}q}{\mathrm{d}t}\right) R$.

b) Calculate the internal resistance of the battery.

c) We let the battery, with the resistance R connected, deliver current isothermally and isochorically for a while. The total charge transfer in this process is 1.0 Faraday.
Calculate the work done by the battery.

d) Calculate the work done by the battery if we let this battery produce 1.0 Faraday of charge isochorically, isothermally and reversibly by loading it with an infinitely high resistance, or during an infinite amount of time.

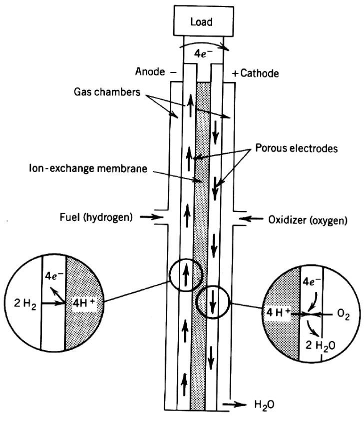
e) What is the maximum work the battery can do per mole of transferred electrons?

Exercise add_5

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, where the electrical energy from the fuel cell drives an electrical motor.
In the design of a fuel cell with H_2 and O_2 as fuels, as in the accompanying drawing, the electrodes are porous to the gases and the cathode is also permeable to the formed water; O_2 is fed through the cathode and H_2 through the anode; the water 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. In this way it is prevented that the gases can react with each other to form water without the transfer of electrons through an external load. This guarantees a high efficiency of the cell doing electrical work on the external load.
At 298 K $\Delta_f G^\ominus(H_2O(l)) = -237.13$ kJ/mol.

a) Determine the EMF (terminal voltage, E(lectro)M(otive) F(orce)) of a fuel cell with 1.0 bar oxygen and 1.0 bar hydrogen as fuel at 298 K, via the reaction quotient Q and the number of electrons that is transferred in the reaction. Assume that the reaction product is formed in its liquid state and that the reactants are present as ideal gases.

b) Then determine the EMF at $T = 298$ K, for the case that the reaction product remains gaseous and all gases can be considered ideal. Assume that all partial pressures are held constant at $P^\ominus$; $\Delta_f G^\ominus(H_2O(g)) = -228.57$ kJ/mol.



c) Calculate the EMF in standard state for a fuel cell based on the combustion of 1 bar butane with oxygen at 1 bar and 298 K; use the same design as in the previous parts. Assume that in one of the half cells butane reacts with water to CO_2 and H^+. Assume that the water is present in liquid form.
$\Delta_f G^\ominus(\text{butane}) = -17.0$ kJ/mol and $\Delta_f G^\ominus(CO_2(g)) = -394$ kJ/mol.

d) The design of part a) is no longer usable since for the second half reaction water needs to flow through the membrane to the anode. Such a membrane would also be permeable to fuel gases, which would decrease the efficiency considerably.
An alternative design is an oxygen-ion electrolyte with as cathode reaction

$$13\ O_2 + 52\ e^- \rightarrow 26\ O^{2-}$$

and as anode reaction

$$8\ CO_2 + 10\ H_2O + 52\ e^- \rightarrow 2\ C_4H_{10} + 26\ O^{2-}.$$

Calculate the standard EMF for this fuel cell.

e) A definition of 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 for the cells in part b) and c) in the case the cell works reversibly at arbitrary temperature and pressure.

f) Repeat part e) for an irreversible process for which the internal resistance of the fuel cell is equal to $R_i = 1\ \Omega$. The external resistance is $R_L = 10\ \Omega$.
Investigate the cause of that internal resistance in practical situations.

Exercise add_6

The folded state of the protein lysozyme in a solution transforms to the unfolded state at 75°C with an enthalpy change equal to $\Delta_{unfold}H = 509$ kJ/mol. At this temperature the folded and unfolded states

are in equilibrium. The pressure change corresponding to that transition, in solution, is negligible. The difference between the isobaric heat capacity in unfolded and folded state is $\Delta c_P = c_P(unfolded) - c_P(folded) = 6.28$ kJ/molK.
Furthermore, we can consider both the c_P values to be independent of temperature.

a) Calculate the entropy change of the unfolding process at 75°C.

Next we consider the unfolding process of the protein starting in the metastable folded state at a higher temperature of 105°C.

b) Describe a reversible path as alternative for the irreversible unfolding process at 105 °C.
Hint: only use isobaric paths.

c) Calculate the enthalpy change of the unfolding process at 105°C.
Hint: Determine ΔH via the alternative reversible path and use the state function property of H.

d) Calculate the entropy change of the unfolding process at 105°C.

e) Use the second law of thermodynamics to verify whether the unfolding process proceeds spontaneously at 105°C.

Exercise add_7

We consider the temperature dependence of the equilibrium constant once more. For that, we assume that both the reaction enthalpy as well as the entropy change are independent of the temperature. Furthermore, we work at constant pressure.
Express the temperature dependence of the equilibrium constant in terms of the enthalpy and entropy change of the reaction. Make a scetch of the Van 't Hoff-plot ($\ln K$ vs. $\frac{1}{T}$) for the following four situations and indicate for all temperatures in which direction the reaction proceeds.

a) exothermic and $\Delta_r S^\ominus > 0$,

b) exothermic and $\Delta_r S^\ominus < 0$,

c) endothermic and $\Delta_r S^\ominus > 0$,

d) endothermic and $\Delta_r S^\ominus < 0$.

Exercise add_8

In this exercise we study the discharge of the NiCd battery of exercise 18. We take a cell with initial molalities $b_{\mathrm{OH}^-,k} = b_{\mathrm{OH}^-,a} = b_0 = 0.1$ mol/kg.
We connect an external (load) resistance, $R_L = 10\ \Omega$, to this cell and keep the cell at constant temperature. The cell voltage will decrease until the cell is in equilibrium.

a) Determine the molalities in the half cells at the moment the cell has reached equilibrium.

The change in the cell voltage in time is rather complicated but can be approximated by the function

$$E(t) = E_0 \exp\left[-\frac{2RT}{F^2 R_{tot}}\frac{b^\ominus}{b_0}t\right],$$

in which R_{tot} is the total resistance, E_0 and b_0 the cell voltage and molality at time $t = 0$ respectively and t the time starting from the moment the external resistance was connected.

b) Calculate the total electrical work done by the cell.

c) Calculate the total heat that the battery has delivered to the surroundings.

d) Calculate the efficiency of the process.

Exercise add_9

In statistical thermodynamics the indistinguishability character of the particles in a system plays an important role, not for the internal energy or the enthalpy, but for the entropy and therefore also for the free energy. A perfect gas is a good example of a system, in which the particles are indistinguishable. In a crystal, however, the particles are distinguishable, because they are located at fixed positions.
We will consider the effect of the indistinguishability of atoms for a perfect gas. To that end, we use the so-called Sackur-Tetrode equation, that is based on quantum mechanics

$$S_{indistinguishable} = Nk \ln \left[\frac{kT}{P\Lambda^3} \mathrm{e}^{\frac{5}{2}} \right] \quad \text{with} \quad \Lambda = \frac{h}{\sqrt{2\pi m k T}},$$

and describes the entropy of a perfect atomic gas. In this expression m is the mass of the atoms, h is Planck's constant, $\mathrm{e} = \exp(1)$ and the other symbols have their usual meaning. If the indistinguishability character of the atoms were not taken into account, this equation would have the following form.

$$S_{distinguishable} = Nk \ln \left[\frac{NkT}{P\Lambda^3} \mathrm{e}^{\frac{3}{2}} \right] \quad \text{with} \quad \Lambda = \frac{h}{\sqrt{2\pi m k T}},$$

a) Discuss, without using formulas, whether the indistinguishability character of the atoms results in a larger or a smaller entropy.

b) Calculate the entropy of 1 mol helium at $T = 298$ K and $P = P^{\ominus}$.

c) Calculate the difference $S_{indistinguishable} - S_{distinguishable}$, and compare the answer with the result of part a).

d) In exercise 25 we found that for the isothermal expansion of n mol of a perfect mono-atomic gas from a volume V_1 to a volume $V_2 = 2V_1$, the entropy change is equal to $\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln 2$. Verify whether the same result is found with the Sackur-Tetrode equation; do this for both the distinguishable and the indistinguishable case.

Exercise add_10

The standard formation Gibbs free energy of NH_3(g) at 298 K is $\Delta_f G^{\ominus} = -16.45$ kJ/mol. Consider the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \leftrightharpoons NH_3(g)$, in which the partial pressures of N_2, H_2 and NH_3 are 3.0, 1.0 and 4.0 bar, respectively. Assume the gases to behave as perfect gases.

a) Calculate the standard reaction Gibbs free energy at 298 K.

b) Calculate the thermodynamic equilibrium constant K.

c) Calculate the reaction Gibbs free energy at 298 K.

d) In what direction does the reaction proceed spontaneously at 298 K?

Exercise add_11

The standard potentials of proteins are not easy to determine, since proteins often loose their structure and with that their functionality in reactions on the surface of electrodes. An alternative is to let the oxidized protein in solution react with a suitable electron donor (reductor). The standard potential of the protein is then determined using the Nernst-equation, in which all relevant concentrations (as approximation for the activities) in the solution and the standard potential of the reductor are substituted. As an example we consider the protein cytochrome c (cyt). In the redox reaction between cyt and 2,6-dichloroindophenol (D) one electron is transferred. The concentrations can be followed spectrophotometrically (in the solution) since each of the reaction components has a specific absorption spectrum. We denote the reaction components as cyt_o, D_r, cyt_r and D_o, in which the subscripts o and r represent the oxidized and reduced state, respectively.

a) Give the half reactions and express the standard cell potential $E^{\ominus}$ for the net reaction in terms of the standard potentials $E^{\ominus}_{cyt}$ and $E^{\ominus}_{D}$. Then express the cell potential E for arbitrary circumstances in T, $E^{\ominus}$ and the concentrations (assume that the activities can be replaced by the concentrations).

b) Show that in equilibrium a plot of $\ln \frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}}$ versus $\ln \frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}}$, is linear. Determine the slope and the intercept.

c) A measurement of the reaction between oxidized cytochrome c and reduced D in a buffer solution with pH = 6.5 at 298 K results in the following values.

$\frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$\frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

Use these data and the result of the previous part to calculate the standard potential of cytochrome c at 298 K and pH = 6.5. The standard potential of D is $E^{\ominus}_{D} = 0.237$ V.

Exercise add_12

The osmotic pressure of solutions of polystyrene in toluene at 25 °C is measured; see the table below (h is the pressure in terms of the height of a fluid column with density $\rho = 1.004$ g cm^{-3}).

c [g/L]	2.042	6.613	9.521	12.602
h [cm]	0.592	1.910	2.750	3.600

Determine the molar mass of the polymer.