

Exam Physical Chemistry 1: Thermodynamics

13 January 2021

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,
4 pages in total.

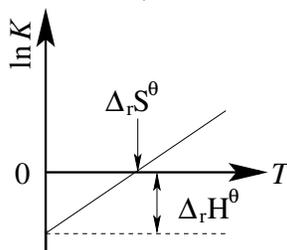
All 16 subproblems have equal weight for the final grade. †

Problem 1

- a) Give a definition and/or *short* description of the following concepts
- ideal solution
 - thermodynamic standard state
 - irreversible process
 - chemical potential
 - activity coefficient
- b) Indicate for each of the following quantities whether we are dealing with a state function; answer using only yes or no:
- the work W ,
 - the enthalpy minus the product of temperature and entropy $H - TS$,
 - the entropy S ,
 - the heat minus the work $Q - W$,
 - the product of entropy and volume SV .
- c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

- d) In the figure below the temperature dependence of the equilibrium constant of an endothermic reaction at constant pressure with $\Delta_r S^\ominus > 0$ is given. We can assume that both the reaction enthalpy and the reaction entropy are independent of the temperature. There are, however, 5 errors in the figure. Describe these 5 errors and draw the correct figure; Further explanation is not necessary.



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

Problem 2

We study the occupation of the two electron spin states in a magnetic field H using the Boltzmann distribution. In the presence of a magnetic field the otherwise degenerate levels ($\epsilon = 0$) split up into two levels with energies $\epsilon_0 = -\frac{1}{2}\mu_B H$ and $\epsilon_1 = +\frac{1}{2}\mu_B H$, in which $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24}$ J/Tesla is the so-called Bohr magneton. We only take into account the electron spin levels since we can consider them to a good approximation as independent of all other energy states.

The temperature is $T = 300$ K and the magnetic field strength $H = 10$ T.

We set the lowest level of our energy scale to 0.

- Show that the partition function is given by $q = 1 + \exp(-\beta\mu_B H)$.
- Calculate the fraction of electrons in the highest energy level.
- Calculate the average internal energy per electron.

The Shannon definition of entropy in statistical thermodynamics for a system of N particles is given by

$$S = -Nk \sum_i P_i \ln P_i,$$

where P_i represents the chance of a particle occupying the energy level with label i .

- Calculate the Shannon entropy per mole electrons.

Problem 3

An adiabatic container is made up of two compartments separated by an adiabatic removable wall. The two compartments are filled with 1kg water at a temperature of 298 K and 1 kg ethanol at a temperature of 348 K, respectively. At time zero the separating wall is removed such that the liquids can mix, until equilibrium is reached.

We can assume that ethanol and water form an ideal mixture.

$c_P(\text{CH}_3\text{CH}_2\text{OH}) = 2.38$ J/gK can be considered as constant,

$c_P(\text{H}_2\text{O}) = 4.184$ J/gK can be considered as constant,

$M(\text{CH}_3\text{CH}_2\text{OH}) = 46.07$ g/mol,

$M(\text{H}_2\text{O}) = 18.02$ g/mol.

- Determine the equilibrium temperature of the system.
- Determine the total entropy change ΔS during the process.
Hint: Consider an alternative process for which first only heat is exchanged between the compartments and subsequently the liquids mix.
- Determine the enthalpy of mixing $\Delta_{mix}H$ of the second (mixing) process mentioned in the hint above.
- Discuss whether the process fulfills the demands of the second law of thermodynamics.

Problem 4

A Daniell cell is an electrochemical cell consisting of a half cell with a copper electrode in a copper(II) solution and a half cell with a zinc electrode in a zinc solution.

We consider a Daniell cell at $P = P^\ominus$, with initially a 0.200 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution and a 0.010 M $\text{Zn}(\text{NO}_3)_2$ aqueous solution.

We connect an external (load) resistance, $R_L = 100 \Omega$, to this cell and keep the cell at constant temperature, $T = 298 \text{ K}$.

The cell voltage will decrease until the cell is in equilibrium. During this discharging process of the cell, the NO_3^- ions will migrate through the semipermeable membrane separating the two half cells to keep the net charge in the half cells equal to zero. The electrodes can be considered as large enough to never become depleted.

The internal resistance of the cell is $R_{int} = 20.0 \Omega$ and can be considered to represent all internal losses in the cell during discharge; R_{int} can be considered as constant.

The following data can be used

$$E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = +0.34 \text{ V at } T = 298 \text{ K,}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^\ominus = -0.76 \text{ V at } T = 298 \text{ K.}$$

$$\Delta_{fus}H(\text{H}_2\text{O}) = 6.008 \text{ kJ/mol at } T = 273.15 \text{ K.}$$

Assume that all activities can be approximated by the molarities.

- Give the chemical equation for the net cell reaction and determine the cell voltage at time zero, $E(t = 0)$, the moment just before the load resistance is attached.
- Calculate the concentrations in the two half cells at the end of the discharge process.
- Calculate the efficiency of the process.
- Next, we want to use the cell during winter time.

Assuming that all parameters are independent of the temperature, estimate the lowest temperature, which allows the cell to be used without the solution of one of the half cells to solidify; Do this both for $t = 0$ and the final equilibrium state.

List of constants

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

Formulae

$$PV = nRT = NkT$$

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

$$\Delta U = W + Q$$

$$dW = -P_{ext}.dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

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

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{omg} \geq 0$$

$$dU = -PdV + TdS + \sum_i \mu_i dn_i$$

$$H = U + PV$$

$$dH = VdP + TdS + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

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

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

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q, \quad \text{and} \quad dW' = Edq \quad \text{and} \quad E = IR \quad \text{and} \quad P = EI$$

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

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

$$\sum_j n_j d\mu_j = 0$$

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

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

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

$$S = k \ln W$$

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