NTNU
Det skapende universitet

Institutt for materialteknologi
Institutt for kjemi

Eksamensoppgave i:
TMT4276 Grunnleggende termodynamikk
KJ1042 Grunnleggende termodynamikk med laboratorium

Faglig kontakt under eksamen:
Ragnhild E. Aune, Tlf.: 9189 7663
Nicholas Worth, Tlf.: 9804 8297

Eksamensdato: 27 may 2016
Eksamenstid (fra-til): 09:00-13:00
Hjelpemiddelkode/Tillatte hjelpemidler:
Vedlegg 1 – Formelark. Godkjent lommekalkulator.
Ingen andre trykte eller håndskrevne hjelpemidler er tillatt.

Målform/språk: Bokmål, nynorsk og engelsk
Antall sider: X
Antall sider vedlegg: XX

Kontrollert av:

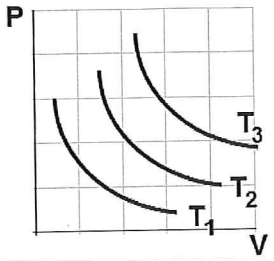
Dato Sign

KJ1042 Problem 1-4 should be solved. **TMT4276 Problem 1-3 and 5 should be solved.**

ENGLISH

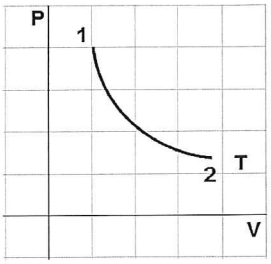
Problem 1 (KJ1042 and TMT4276)

a) The state of an ideal gas has been changed three times at three different temperatures. The figure to the right represents three different isothermal curves. What is the relationship between the temperatures of the gas, *i.e.* between T_1, T_2 and T_3? Justify your answer.



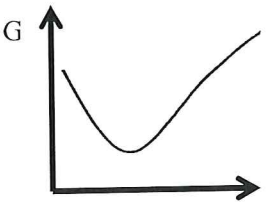
b) A container with rigid walls filled with a sample of ideal gas. What happens to the pressure of the gas when the absolute temperature of the gas is doubled? Justify your answer.

c) The state of an ideal gas is changed isothermally from position *1* to position *2* as shown in the figure to the right. What is the change in the internal energy of the gas during this process? Justify your answer.

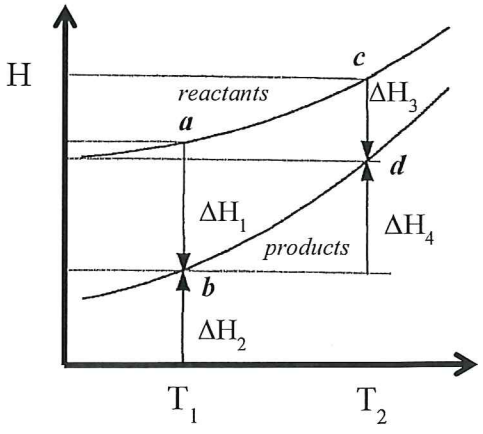


d) Substances usually expand with increase in temperature at constant pressure. Is C_p usually larger than C_v? Justify your answer.

e) The figure to the right schematically shows the relationship between the Gibbs free energy of the system and the reaction path. Identify the position on the graph that represents the equilibrium of the system at constant temperature and pressure. Justify your answer.



f) Consider a general reaction $aA + bB = cC + dD$. The figure to the right shows the change of the enthalpy of the reactants and the products with temperature. Answer the following questions:



i. Which point represents the sum of the enthalpies of the reactants at T_1?

ii. Which point represents the sum of the enthalpies of the products at T_2?

iii. Which of the enthalpy changes represents the enthalpy change of the products with the change in temperature from T_1 to T_2?

iv. Which of the enthalpy changes represents the heat of reaction at T_2?

v. Is the reaction endothermic or exothermic at T_2?

Problem 2 (KJ1042 and TMT4276)

At 473°C the Pb-Sn system exhibits regular solution behavior with the activity coefficient of Pb being given by:

$$\log \gamma_{Pb} = -0.32(1 - X_{Pb})^2$$

a) Write the corresponding equation for the variation of γ_{Sn} with composition $X_{Pb} = 0.5$ which is thermostated at 473°C.

b) If 1 mole of lead at 25°C is added to a large quantity of liquid alloy of composition $X_{Pb} = 0.5$ at 473°C:

   i. Calculate the heat flow from the thermostat into the liquid alloy.

   ii. Calculate the entropy increase in the surroundings resulting from the process.

   iii. Calculate the a_{Pb} in the $X_{Pb} = 0.5$ alloy at 746 K and 1000 K.

Given:

$Cp_{Pb\,(s)} = 23.56 + 9.75 \cdot 10^{-3} \cdot T$ (J/mol K)

$Cp_{Pb\,(l)} = 32.43 - 3.10 \cdot 10^{-3} \cdot T$ (J/mol K)

$\Delta H_{melting\,(Pb)} = 4\,810$ J

$T_{melting\,(Pb)} = 600$ K

Problem 3 (KJ1042 and TMT4276)

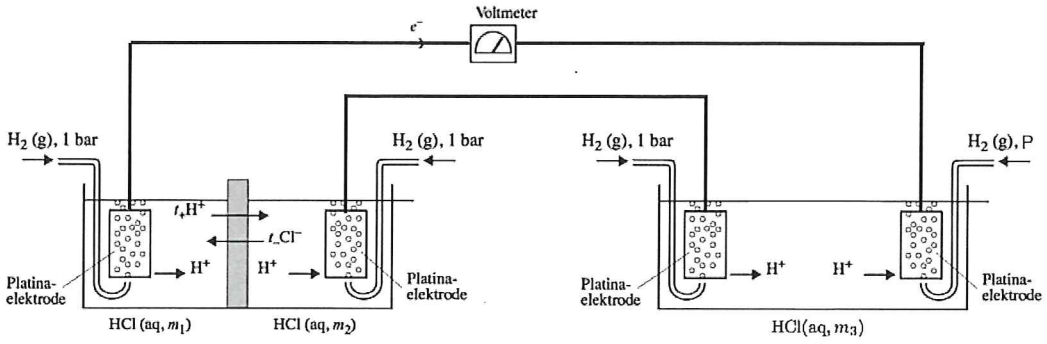
One mole of an ideal gas is subjected to the following sequence of steps:

1. Starting at 25°C and 1 atm, the gas expands freely into a vacuum to double its volume.
2. The gas is next heated to 125°C at constant volume.
3. The gas is reversibly expanded at constant temperature until its volume is again doubled.
4. The gas is finally reversibly cooled to 25°C at constant pressure.

Calculate ΔU, ΔH and ΔS in the gas.

Problem 4 (KJ1042)

Consider the double cell of the figure below. Both cells have hydrogen gas electrodes and diluted HCl as electrolyte solution. The left cell has a membrane that separates the anode and cathode electrolyte solutions, which have different HCl concentrations (m_1 and m_2). The membrane generates a transport number t_+ for H^+ ions and t_- for Cl^- ions. The gas electrodes are set at 1 bar. The right cell has a single compartment with an electrolyte solution with concentration m_3. The left gas electrode has again a pressure of 1 bar the right electrode has a different pressure P.



a) Write down the cell diagram of the double cell.

b) Write down the chemical reactions that occur at the anodes and cathodes of the left cell and the right cell.

c) What are the standard cell potentials (E^0) for each cell?

d) Write down the total overall reactions for each cell corresponding to the transfer of 1 mol of electrons in the outer circuit (include as well the diffusion of ions through the membrane).

e) Assume we have concentrations m_1 = 0.015 M, m_2 = 0.027 M, and m_3 = 0.040 M. Now, we tune the pressure P in the most right gas electrode such that the voltmeter shows 0 V. This occurs at P = 2.5 bar. At these concentrations and pressures, we can assume ideal behavior in which all activity coefficients are one and the fugacities are identical to the pressures. The temperature is 300 K. Calculate the transport numbers t_+ and t_- .

f) If we would replace the membrane with a salt-bridge filled with, *e.g.* KCl solution, what would be the new pressure P to get again 0 V for the overall cell potential of the double cell?

Problem 5 (TMT4276)

Liquid iron, contained in an $A1_2O_3$ crucible under a gaseous atmosphere of $P_{O_2} = 3 \cdot 10^{-12}$ atm at 1600°C, contains its equilibrium contents of dissolved oxygen and aluminum.

a) To what value must the P_{O_2} in the equilibrating gaseous atmosphere be raised in order to secure that solid hercynite ($FeO \cdot Al_2O_3$) appears in equilibrium with the melt and solid Al_2O_3?

b) What is the activity of Al (with respect to the 1 wt% in Fe standard state) in this state?

c) How many degrees of freedom does this equilibrium have at 1600°C?

Given:

$$\frac{1}{2}O_2(g) = O(1\ wt\%\ in\ Fe) \qquad \Delta G^0 = -111\,070 - 5.87 \cdot T \quad (J)$$

$$Al\ (l) = Al(1\ wt\%\ in\ Fe) \qquad \Delta G^0 = -43\,100 - 32.267 \cdot T \quad (J)$$

$$FeO \cdot Al_2O_3(s) = Fe(l) + O(1\ wt\%\ in\ Fe) + Al_2O_3 \qquad \Delta G^0 = 146\,230 - 54.35 \cdot T \quad (J)$$