CHEM-E6100 FUNDAMENTALS OF CHEMICAL THERMODYNAMICS

EXAMINATION 22.2.2024, 9:00-13:00

All relevant calculation steps should be included in the responses. An equation sheet is provided at the end of the document. All questions give a maximum 5 points each, maximum score is 30 points.

Responsible teacher: Daniel Lindberg (Daniel.k.lindberg@aalto.fi)

Gas constant R = 8.314 J / (mol K)

Questions

1. Calculate the entropy of zinc at 800°C using the following information:

   The standard entropy ($S°_{298}$) at 25°C is 41.63 J/(mol K)

   Zinc melts at 420°C and melting enthalpy (ΔH_m) is 7280 J/mol

   The heat capacities of solid and molten zinc are:

   C_p (s) = $22.38 + 10.04 \cdot 10^{-3} \cdot T$ J/ (mol K)

   C_p (l) = 31.38 J/(mol K)

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2. Calculate the heat of formation of PbO from Pb and O_2 at 227°C from the following data:

   $\Delta H°_{298}$ (PbO) = -219.24 kJ/mol

   C_p (PbO) = $44.35 + 16.74 \cdot 10^{-3} \cdot T$ J/ (mol K)

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

   C_p (O_2) = $29.96 + 4.184 \cdot 10^{-3} \cdot T$ J/ (mol K)

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3. Calculate the temperature where the decomposition pressure of limestone ($CaCO_3$) is 0.8 atm. The following standard Gibbs energies of formation are known, when the substances are formed from their elements:

   $\Delta G°(CaO) = -633123 + 98.99 \cdot T$ J/mol

   $\Delta G°(CO_2(g)) = -394133 - 0.80 \cdot T$ J/mol

   $\Delta G°(CaCO_3) = -1202984 + 249.62 \cdot T$ J/mol

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4. A flame is produced by burning (igniting) the stoichiometric quantities of hydrogen (H_2) and fluorine (F_2) to hydrogen chloride (HF) at 25 °C. Calculate the adiabatic flame temperatures.

$\Delta H°_{formation,298.15}(HF) = -268.6$ kJ/mol

C_p (HF) = $26.9 + 3.43 \times 10^{-3}(T/K)$ J/(mol·K)

Comment: The calculated flame temperature in this assignment is much higher than in reality, as high-temperature decomposition of HF(g) to H(g) and F(g) is not considered. The decomposition or breaking of H-F bonds will consume heat and lower the real temperature.

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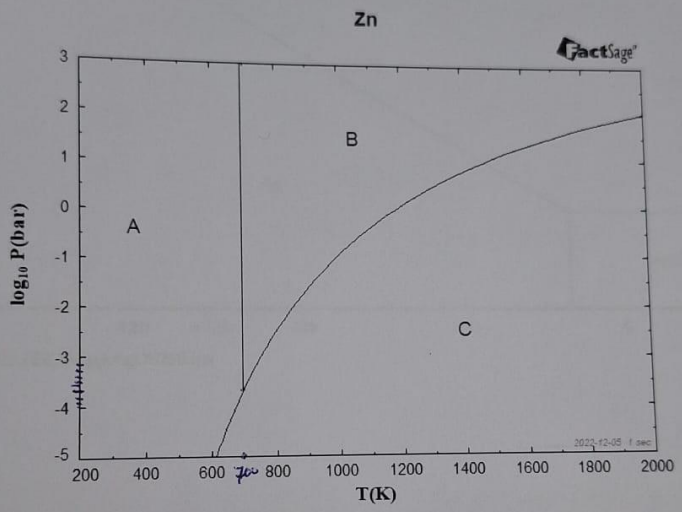
5. a) What is the Gibbs phase rule and the meaning of its variables?

b) Below is the P-T phase diagram of zinc.

(i) Identify the state of the phases A, B, and C in the phase diagram.

(ii) Identify the P-T-coordinates for the invariant point in the P-T phase diagram of zinc

(iii) Estimate from the phase diagram, the melting point and boiling point of zinc at total pressure of 1 bar.



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6. The included Kellogg diagram shows equilibria and the phase boundaries between pure substances and gas (limited to S_2 and O_2) at a constant temperature in system Ag-S-O.

a) Write the equilibrium reaction and the Gibbs energy of the reaction for the phase boundary between silver sulfide and silver sulphate.

b) Calculate the equilibrium pressure of oxygen at the silver sulfide and silver sulphate phase boundary using the Gibbs energy values given below.

c) What is the stable phase at 250 °C when sulphur pressure in the system is $P(S_2) = 10^{-100}$ atm and oxygen pressure is $P(O_2) = 10^{-20}$ atm?

Reactions	T = 523.15 K	ΔG° / J/mol
$2Ag + ½O_2(g) = Ag_2O$		3622
$2Ag + ½S_2(g) = Ag_2S$		-68903
$2Ag + ½S_2(g) + 2O_2(g) = Ag_2SO_4$		-567736