EEN-E1030, Thermodynamics in Energy Technology, Fall 2020
Calculation problems 3

TEHTÄVÄ 1 ON TÄHTITEHTÄVÄ
PROBLEM 1 IS THE STAR PROBLEM

***PROBLEM 1.**

A) Define the vapor pressure of CO_2 at -20ºC by assuming that CO_2 behaves like an ideal gas. Use the triple point of CO_2 (-56.4ºC, 5.2bar) as reference/zero point for the enthalpy and entropy. Molar volume of liquid CO_2 can be ignored in the calculation (very small compared to molar volume of gaseous CO_2). Do not forget to take into account latent heat of vaporization when you define enthalpy and entropy values for gaseous CO_2. You can use the following thermodynamic values for CO_2 in the calculation.

Vaporization heat of CO_2 at triple point 15500 J/mol
Specific heat capacity of liquid CO_2 85.6 J/molK
Specific heat capacity of gaseous CO_2 34.2 J/molK

B) The measured vapor pressure of CO_2 at -20ºC is 19.7 bar. Why may the calculated pressure in Part A) differ from the measured one?

PROBLEM 2. a) Calculate the entropy of formation for water vapor at the standard state at 900K using the JANAF Tables. b) According to the JANAF Table the enthalpy of formation for water vapor is -247,185kJ/mol at 900K at the standard state. Define this enthalpy using enthalpies of formation at 298.15K and sensible enthalpies tabulated in JANAF Tables. c) Calculate the Gibbs free energy ΔG_f^o for water vapor at 900K on the basis of results that you have calculated at 1a) and 1b). Compare the value to the tabulated value.

TEHTÄVÄ 2. a) Laske vesihöyryn muodostumisentropia standarditilassa lämpötilassa 900K Janafin taulukokoiden perusteella. b) Janafin taulukon perusteella vesihöyryn muodostumisentalpia standarditilan lämpötilassa 900K on -247,185kJ/mol. Määritä tämä arvo lämpötilassa 298,15K määritettyjen muodostumisentalpioiden ja taulukkoon laskettujen tuntuvien entalpioiden avulla. c) Laske a) – ja b) -kohdan tulosten perusteella Gibbsin vapaa muodostumisenergia ΔG_f^o lämpötilassa 900K ja vertaa laskemaasi arvoa Janafin taulukkoarvoon.

SOLUTION

The chemical reaction for formation of water is

$H_2 + 1/2O_2 \rightarrow H_2O$

The absolute entropies for H_2, O_2 and H_2O at 900K are obtained from JANAF Tables

H_2 $S^o(900K) = 163.051 J/molK$
O_2 $S^o(900K) = 239.931 J/molK$
H_2O $S^o(900K) = 228.459 J/molK$

The entropy of formation ΔS_f^o for $H_2O(g)$ becomes

$\Delta S_f^o(900K) = S^o_{H2O} - S^o_{H2} - 1/2 S^o_{O2} = 228.459 - 163.051 - 1/2 \cdot 239.931 = \underline{-54.5575 J/molK}$

We have used the JANAF Table notation $S^o(T)$ for the entropy, even though the unit is kJ/mol (see JANAF Tables).

Enthalpies of formations for H_2, O_2 and H_2O at 298.15K are

H_2 ΔH_f^o (900K) = 0 kJ/mol
O_2 ΔH_f^o (900K) = 0 kJ/mol
H_2O ΔH_f^o (900K) = -241.826 kJ/mol

Sensible enthalpies for H_2, O_2 and H_2O between 298.15K and 900K are (see JANAF Tables)

H_2 $H^o(900K) - H^o(298.15K) = 17.676$ kJ/mol
O_2 $H^o(900K) - H^o(298.15K) = 19.241$ kJ/mol
H_2O $H^o(900K) - H^o(298.15K) = 21.938$ kJ/mol

We have used the JANAF Table notation $H^o(T) - H^o(T_r)$ for a sensible enthalpy, even though the unit is kJ/mol (see JANAF Tables).

The enthalpy of formation at 900K becomes

$$\Delta H^o_{f,H_2O}(900K) = \Delta H^o_{f,H_2O}(298.15K) + \left[H^o_{H_2O}(900K) - H^o_{H_2O}(298.15K)\right] -$$
$$\left[\Delta H^o_{f,H_2}(298.15K) + (H^o_{H_2}(900K) - H^o_{H_2}(298.15K)\right] - \frac{1}{2}\left[\Delta H^o_{f,O_2}(298.15K) + (H^o_{O_2}(900K) - H^o_{O_2}(298.15K)\right] =$$
$$-241.828 + 21.938 - 17.676 - \frac{1}{2} \cdot 19.241 = \underline{-247.187 kJ/mol}$$

The tabulated enthalpy is -247.185kJ/mol, which is practically the same as the calculated value in this problem.

The Gibbs free energy is

$\Delta G_f^o(900K) = \Delta H_f^o(900K) - T\Delta S_f^o(900K) = -247.187 - 900 \cdot (-54.5575) = -198.085 kJ/mol$

The tabulated ΔG_f^o at 900 is -198.087kJ/mol, which is practically the same as the calculated value in this problem.

Tabulated values for ΔH_f^o and ΔG_f^o at different temperatures at the standard state (p=1bar) can be defined like we have done in this problem. This requires that the enthalpy of formation ΔH_f^o at 298.15K and c_p^o as a function of temperature for each substance are known. These values can be defined experimentally.

PROBLEM 3. Define chemical potentials for $CH_4(g)$ and $O_2(g)$ at the standard state at 298.15 K and 600K using the JANAF Tables.

TEHTÄVÄ 3. Määritä Janafinin taulukoiden avulla kemialliset potentiaalit standarditilassa kaasuille $CH_4(g)$ ja $O_2(g)$ lämpötiloissa $T = T_o = 298.15$ K ja $T = 600$ K.

SOLUTION

The chemical potential is defined as follows

$$\mu^\circ(T) = h^\circ(T) - Ts^\circ(T)$$

Entropies and enthalpies are taken from JANAF Tables

CH_4:

$h^o(298.15K) = -74.873kJ/mol$
$s^o(298.15K) = 186.251J/molK$
$h^\circ(600K) = \Delta H_f^o(298.15K) + [H^\circ(600K) - H^\circ(298.15K)] = -74.873 + 13.130 = -61.743kJ/mol$
$s^o(600K) = 215.987J/molK$

O_2
$h^o(298.15K) = 0$ kJ/mol
$s^o(298.15K) = 205.147$ J/molK
$h^\circ(600K) = \Delta H_f^o(298.15K) + [H^\circ(600K) - H^\circ(298.15K)] = 0 + 9.244 = 9.244kJ/mol$
$s^o(600K) = 226.451$ J/molK

=> Chemical potentials become

CH_4: $\mu^o(298.15K) = -74.873\cdot1000-298.15\cdot186.251 = \underline{-130.40kJ/mol}$
$\mu^o(600K) = -61.743\cdot1000-600\cdot215.987 = \underline{-191.34kJ/mol}$

O_2 $\mu^o(298.15K) = 0-298.15\cdot205.147 = \underline{-61.16kJ/mol}$
$\mu^o(600K) = 9.244\cdot1000-600\cdot226.451 = \underline{-126.23kJ/mol}$