2. Thermodynamics impulses (stimuli)

2.1. Second law of thermodynamics

2.1-1.
Calculate the change in entropy of 9 g of ice when it melts at 273 K. The latent heat of fusion of ice is 333.6 J/g.

2.1-2.
Calculate the increase in entropy when 1.00 mol of a monatomic ideal gas with $C_{p,m} = \frac{5}{2}R$ is heated from 300 K to 600 K while expanding from 30.0 L to 50.0 L.

2.1-3.
Calculate the entropy change when 50 g of water at 80°C is mixed with 100 g of water at 10°C in a thermally insulated container ($C_{p,m}$ of water is 75.5 J·K·mol⁻¹).

2.1-4.
The molar heat capacity of hydrogen at constant pressure is given by the equation $C_p = 27.2 + 0.0037\,T$. Calculate the change in entropy during the expansion of 1 mole of hydrogen as the temperature changes from $T_1 = 233$ K do $T_2 = 523$ K.

2.1-5.
What final volume does an entropy change of 38.28 J/(mol·K) correspond to if 1 mole of an ideal gas occupying 0.02 m³ initially undergoes an isothermal expansion?

2.1-6.
After heating 4 dm³ of argon at a pressure of 2 atmospheres, the volume of the gas increased to 12 dm³. The initial temperature was 320 K. Calculate the change in entropy, assuming that the gas behaves as an ideal gas.

2.1-7.
The entropy of liquid ethanol at 298 K is 160.7 J/(mol·K). The vapor pressure of ethanol is $7.87 \cdot 10^3$ Pa. The heat of vaporization of ethanol at 298 K is 42.6 kJ/mol. Calculate the entropy of 1 mole of ethanol vapor at a pressure of $9.5 \cdot 10^3$ Pa and a temperature of 313 K. The molar heat capacity of ethanol vapor is 145 J/(mol·K).

2.1-8.
A tank with a volume of 30 dm³ was divided into two parts with volumes of 20 dm³ and 10 dm³. 2 moles of helium were introduced into the larger part of the tank, and 1 mole of oxygen into the smaller part. The temperature was 298 K. Calculate the entropy change that occurs when the partition dividing the two parts of the tank is removed and the system is heated to 450 K.

2.1-9.
To 6 moles of water at 323 K are added 1.5 moles of water in the form of ice at 263 K. Calculate the entropy change associated with the processes occurring if the final temperature is 296 K. The molar heat capacity of ice is 36.4 J/(mol·K); of water 75.3 J/(mol·K); the enthalpy of fusion of ice is 6007 J/mol.

2.2. Gibbs free energy

2.2-1.
Calculate the change in free energy of the reaction $C_2H_4 + H_2 = C_2H_6$ taking place in gaseous form and under standard conditions, given the standard free energy of formation of the reactants: C_2H_4 = 68,1 kJ/mol ; C_2H_6 = -32,9 kJ/mol.

2.2-2.
Calculate the change in free enthalpy of the combustion reaction of ethane, given the standard values of the free enthalpies of formation of the reactants:
CO_2 = -394,95 kJ/mol ; H_2O = -237,53 kJ/mol ; C_2H_6 = -32,93 kJ/mol.

2.2-3.
Calculate the free energy of the reaction $CO_2 + 4 H_2 = CH_4 + 2 H_2O$ taking place in the gas phase under standard conditions, given the standard enthalpies and entropies of the reactants.
standard enthalpies: CH_4 = -74,8 kJ/mol; H_2O = -241,8 kJ/mol; CO_2 = -393,5 kJ/mol
standard entropies: CH_4 = 186,1 J/(mol·K); H_2O = 188,7 J/(mol·K) CO_2 = 213,6 J/(mol·K); H_2 = 130,6 J/(mol·K).

2.2-4.
Using the information below, determine the standard free energy of the reaction:
$B_2H_6 + 3 O_2 = B_2O_3 + 3 H_2O$
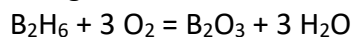
	B_2H_6	O_2	B_2O_3	H_2O
ΔH_{tw} [kJ/mol]	35,6	0	-1273,5	-285,8
S^{ϕ} [J/(mol·K)]	232,1	205,2	54,0	70,0

2.2-5.
Determine the temperature at which calcite decomposes according to the reaction
$CaCO_3 = CaO + CO_2$
standard enthalpies: $CaCO_3$ = -1206,9 kJ/mol; CaO = -635,9 kJ/mol; CO_2 = -393,51 kJ/mol
standard entropies: $CaCO_3$ = 92,9 J/(mol·K); CaO = 39,75 J/(mol·K) CO_2 = 213,74 J/(mol·K).

2.2-6.
Which allotrope of carbon, graphite or diamond, is more durable under standard conditions?
Combustion enthalpies: graphite = -393 514 J/mol ; diamond = -395 405 J/mol
Molar entropies: graphite = 5,69 J/(mol·K) ; diamond = 2,439 J/(mol·K).

2.2-7.
By how much does the chemical potential of benzene change when the pressure exerted on a sample is increased from 100 kPa to 10 MPa?

2.3. Equilibrium and equilibrium constant

2.3-1.

Consider the reaction $2 A \rightarrow B$. Initially 1.75 mol A and 0.12 mol B are present. What are the amounts of A and B when the extent of reaction is 0.30 mol?

2.3-2.

When the reaction $2 A \rightarrow B$ advances by 0.051 mol (that is, $\Delta\xi = +0.051$ mol) the Gibbs energy of the system changes by -2.41 kJ mol^{-1}. What is the Gibbs energy of reaction at this stage of the reaction?

2.3-3.

The standard Gibbs energy of the reaction $2 NO_2(g) \rightarrow N_2O_4(g)$ is -4.73 kJ mol^{-1} at 298 K. What is the value of $\Delta_r G$ when $Q =$ (a) 0.10, (b) 1.0, (c) 10, (d) 100? Estimate (by interpolation) the value of K from the values you calculate. What is the actual value of K?

2.3-4.

The mixture of gases obtained in the reaction: $2 SO_{2(g)} + O_{2(g)} = 2 SO_{3(g)}$ in equilibrium is placed in a vessel of volume of 1 liter at temperature of 600oC. The composition of the mixture is as follows: 0.5 moles of S O_2, 0.12 moles of O2 and 5 moles of S O_3. At the moment of starting the reaction, the vessel contained only SO_2 and O_2. Calculate the equilibrium concentration constant and how many moles of oxygen should be pumped into the vessel so that the number of moles of SO_3 in the equilibrium state increases to 5.2.

2.3-5.

At a temperature of 500 K and a pressure of 1 atmosphere, thermal dissociation of nitrosyl chloride occurs in the reaction: $2 NOCl_{(g)} = 2 NO_{(g)} + Cl_{2(g)}$. Calculate the equilibrium pressure constant if the pressure of NOCl at equilibrium is equal to $0.648 \cdot 10^5$ Pa.

2.3-6.

At 473 K and 1 atmosphere pressure, phosphorus pentachloride is 48.5% dissociated. Calculate the pressure equilibrium constant of the reaction: $PCl_{5(g)} = PCl_{3(g)} + Cl_{2(g)}$.

2.3-7.

Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2 Br(g)$. Calculate K at (a) 1600 K, (b) 2000 K given that $\Delta_r H^\ominus = +112$ kJ mol^{-1} over the temperature range.

2.3-8.

In the gas-phase reaction $A + B \rightleftharpoons C + 2 D$, it was found that, when 2.00 mol A, 1.00 mol B, and 3.00 mol D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.79 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^\ominus$.

2.3-9.

      The standard enthalpy of a certain reaction is approximately constant at +125 kJ mol^{-1} from 800 K up to 1500 K. The standard reaction Gibbs energy is +22 kJ mol^{-1} at 1120 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

2.3-10.

      The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^3$ between 400 K and 500 K with $A = -2.04$, $B = -1176$ K, and $C = 2.1 \times 10^7$ K^3. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.

2.3-11.

      Establish the relation between K and K_c for the reaction $3 \, N_2(g) + H_2(g) \rightleftharpoons 2 \, HN_3(g)$.

2.3-12.

The equilibrium constant of a certain reaction is 4500 at 298 K and 6000 at 273 K. Calculate the heat of the reaction.

2.3-13.

The equilibrium constant of a certain reaction is 1.6 at 273 K and 0.018 at 333 K. What is the equilibrium constant at 353 K and what is the value of the chemical affinity of the pure components at this temperature?

2.3-14.

What is the standard enthalpy of a reaction whose equilibrium constant a) doubles and b) decreases by half when the temperature increases by 10 K at 298 K?

2.3-15.

At temperatures above 750 K the reaction occurs: $2 \, MnO_{2(s)} = Mn_2O_{3(s)} + \frac{1}{2} \, O_{2(g)}$. The equilibrium pressures of oxygen are:

at 773 K $p_{O2} = 10^4$ Pa   at 873 K $p_{O2} = 10^5$ Pa

Calculate the average heat of reaction over this temperature range.

Assessment

A2-1.

Calculate the entropy change that occurs when 5 moles of hydrogen are cooled from 350 K to 270 K. The heat capacity of hydrogen at constant pressure is C_p = 28.9 J/(mol·K). Cooling occurs under: a) isobaric, b) isochoric conditions.

A2-2.

The change in free enthalpy for a certain process taking place at constant pressure can be expressed by the formula $\Delta G/J$ = -85.40 + 36.5 (T/K). Calculate the value of ΔS for this process.

A2-3.

At a temperature of 2257 K and a pressure of 1 atmosphere in equilibrium, water dissociates according to the reaction: $2H_2O_{(g)}$ = $2H_{2(g)}$ + $O_{2(g)}$ to a degree of 1.77%. Calculate the equilibrium pressure constant, the value of chemical affinity and the chemical affinity of the pure components.

A2-4.

The standard free energy of the isomerization reaction of cis-pent-2-ene to trans-pent-2-ene at 400 K is -3.67 kJ·mol^{-1}. Calculate the equilibrium constant of isomerization.

A2-5.

The standard free enthalpy of the reaction of a certain metal M(s) + H_2O(g) = M(s) + H_2(g) is approximately constant in the temperature range from 920 K to 1280 K and is +224 kJ·mol-1. At 1280 K the standard free enthalpy of this reaction is +33 kJ·mol^{-1}. Determine the temperature at which the equilibrium constant becomes greater than 1.