3. Physical transformations

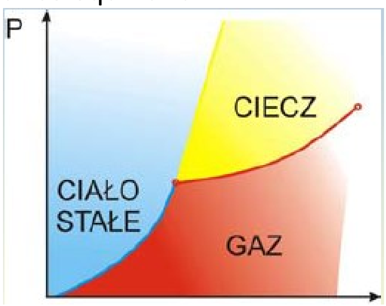
3.1. Gibbs's Phase Rule

3.1.-1.

Interpret the operation of a pressure cooker, the physicochemical mechanism of ice sheet movement, sliding on ice skates,

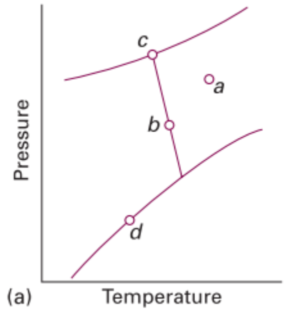
3.1.-2.

Interpret the meaning of the slope angle of the liquid-ice equilibrium



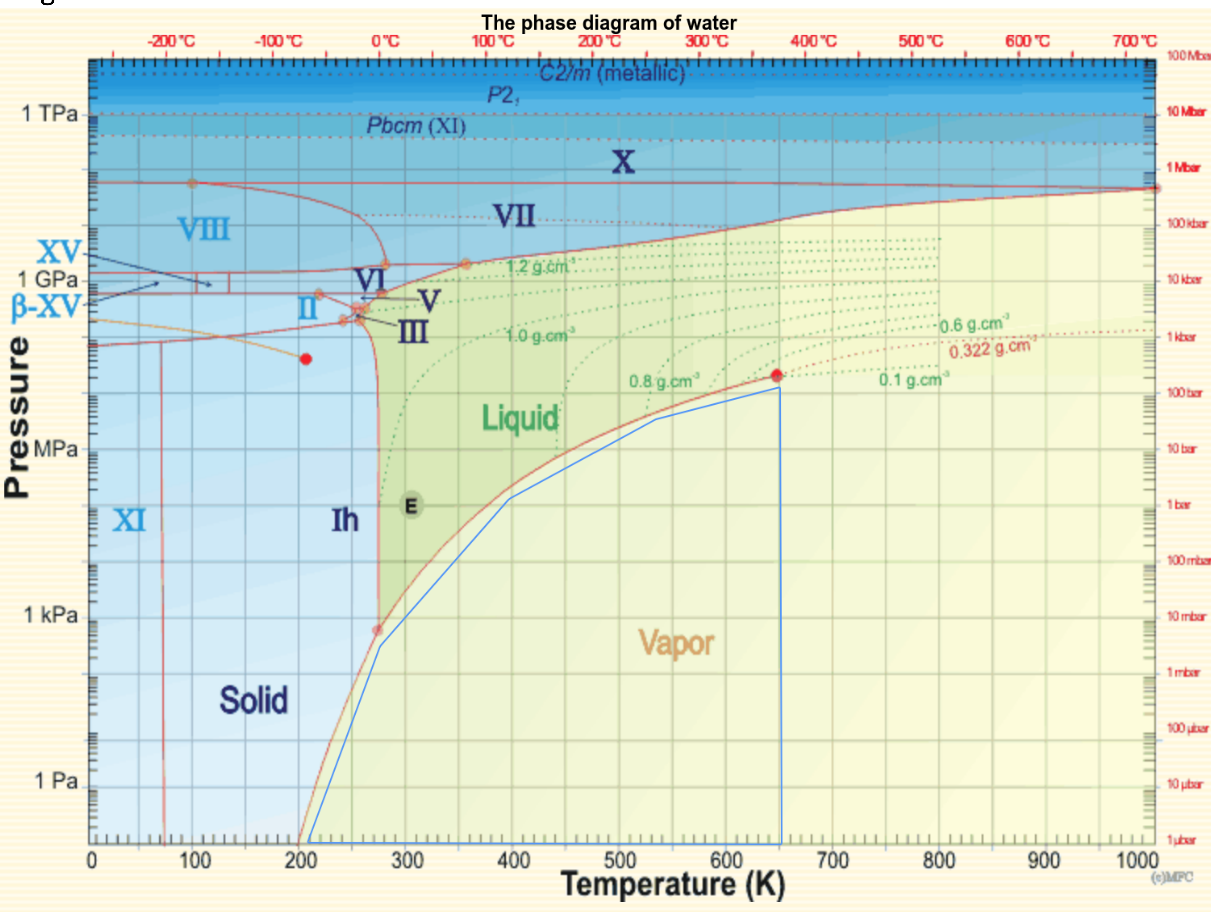
3.1.-3.

How many phases are present at each of the points marked in Fig.



3.1.-4.

Using Gibbs' phase rule, interpret the indicated equilibrium points and lines on the phase diagram of water.



3.1.-5.

Determine the number of independent components in the following systems: NaH_2PO_4 in water in equilibrium with water vapor, without taking into account salt dissociation, b) for the same system, taking into account salt dissociation.

3.1.-6.

Blue crystals of $CuSO_4 \cdot 5H_2O$ lose water of hydration when heated. How many phases and independent components are present if we heat this substance in an empty container?

3.1.-7.

The difference in chemical potential between two regions of a system is $-8.3\ \mathrm{kJ\ mol^{-1}}$. By how much does the Gibbs energy change when 0.15 mmol of a substance is transferred from one region to the other?

3.1.-8.

Estimate the difference between the normal and standard boiling points of water.

3.2. Claussius-Clapeyron equation

3.2.-1.

The molar volume of a certain solid is $142.0\ \mathrm{cm^3\ mol^{-1}}$ at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is $152.6\ \mathrm{cm^3\ mol^{-1}}$. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

3.2.-2.

The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\mathrm{Torr}) = 18.361 - 3036.8/(T/\mathrm{K})$. What is the enthalpy of vaporization of the liquid?

3.2.-3.

The vapour pressure of a liquid between 15°C and 35°C fits the expression $\log(p/\mathrm{Torr}) = 8.750 - 1625/(T/\mathrm{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of the liquid.

3.2.-4.

When a certain liquid of molar mass $46.1\ \mathrm{g\ mol^{-1}}$ freezes at -3.65°C its density changes from $0.789\ \mathrm{g\ cm^{-3}}$ to $0.801\ \mathrm{g\ cm^{-3}}$. Its enthalpy of fusion is $8.68\ \mathrm{kJ\ mol^{-1}}$. Estimate the freezing point of the liquid at 100 MPa.

3.2.-5.

The vapor pressure of dichloromethane at 24.1°C is 400 Torr, and the enthalpy of vaporization of this substance is 28.7 kJ/mol. At what temperature is the vapor pressure 500 Torr?

3.2.-6.
Calculate the freezing point of 250 cm^3 of water in which 7.5 g of sucrose has been dissolved. The cryoscopic constant is 1.86 K·kg/mol.

3.2.-7.
Calculate the cryoscopic and ebullioscopic constants of tetrachloromethane, knowing that: boiling point = 349.9 K, melting point = 250.3 K, enthalpy of vaporization = 30 kJ/mol, enthalpy of fusion = 2.47 kJ/mol, molar mass = 153.82 g/mol.

3.2.-8.
Calculate the change in boiling point and freezing point if 20 g of glucose with a molar mass of 180.18 g/mol is dissolved in 130 g of water. The enthalpy of vaporization of water at the boiling point is 43.66 kJ/mol, and the enthalpy of fusion of ice is 6 kJ/mol.

3.3. Phase diagrams

3.3.-1.

Using an example of your choice, explain the course of thermal and pressure distillation, indicating the course of the boiling curve and the dew curve.

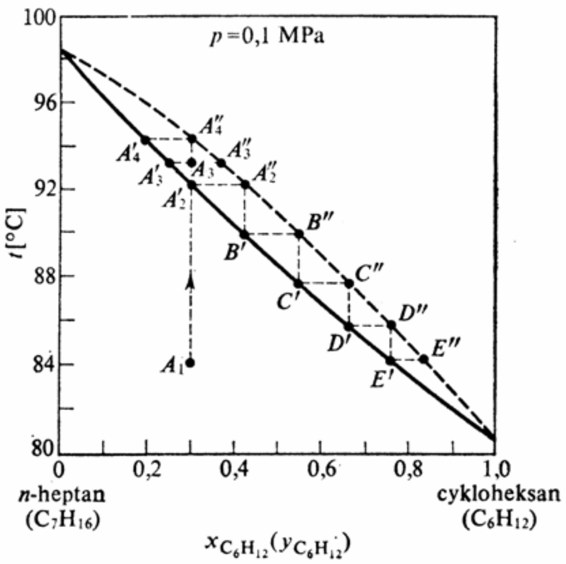
a) for a system that satisfies Roula's law

b) in the case of positive azeotropy

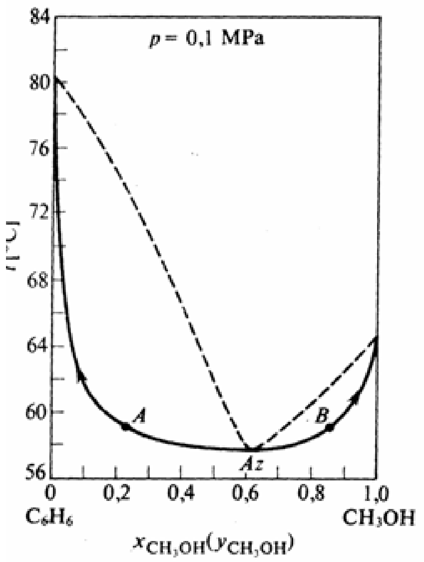
c) in the case of negative azeotropy

d) in the case of limited miscibility of liquids

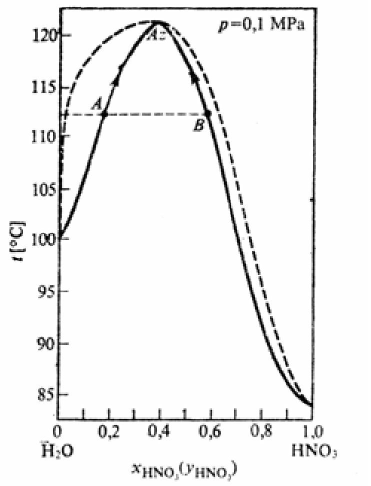
a



b



c



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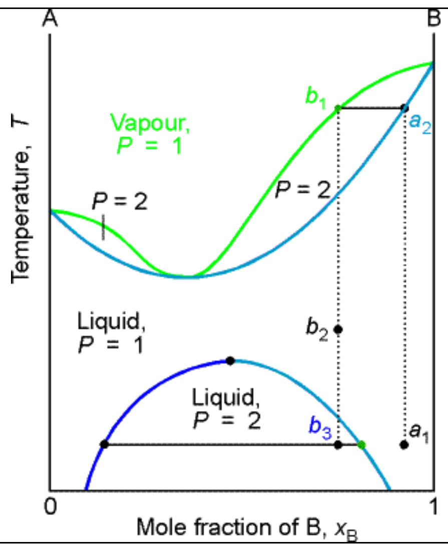
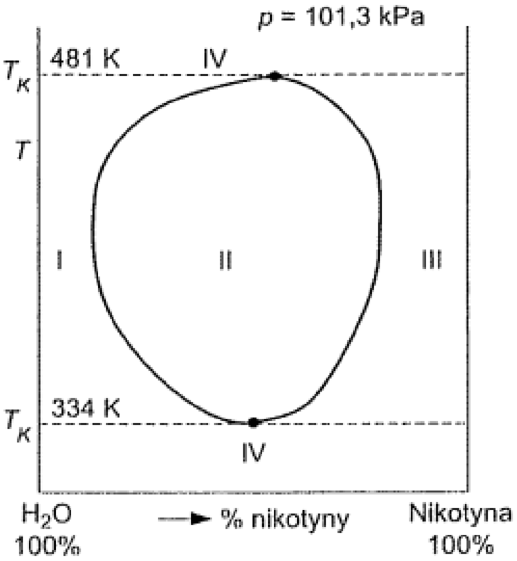
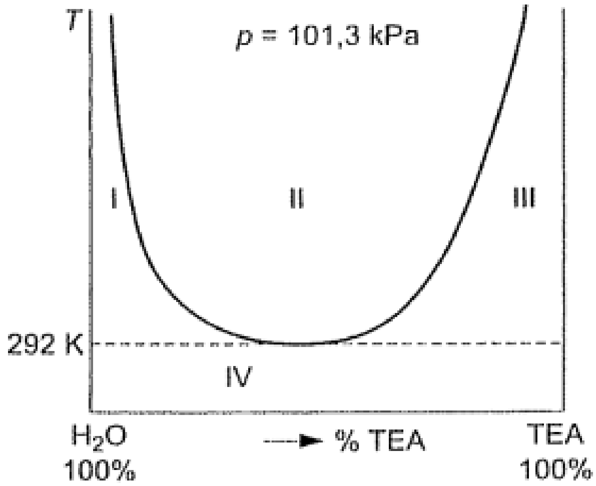
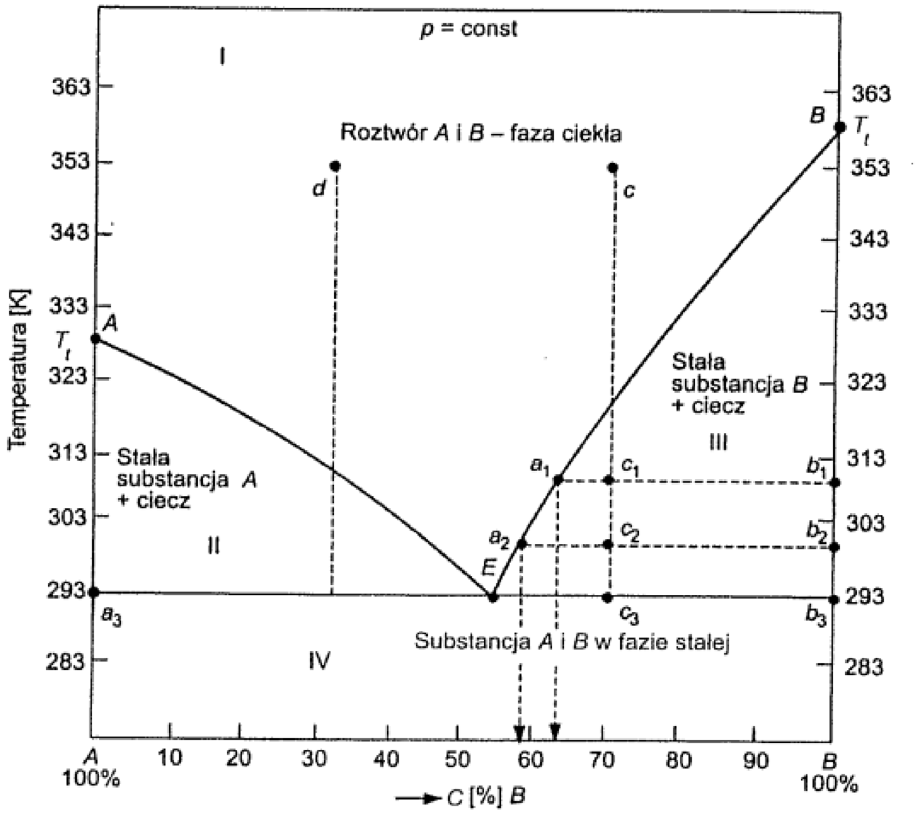


3.3.-2.
Interpret the following liquid-liquid equilibrium diagrams with a miscibility gap.

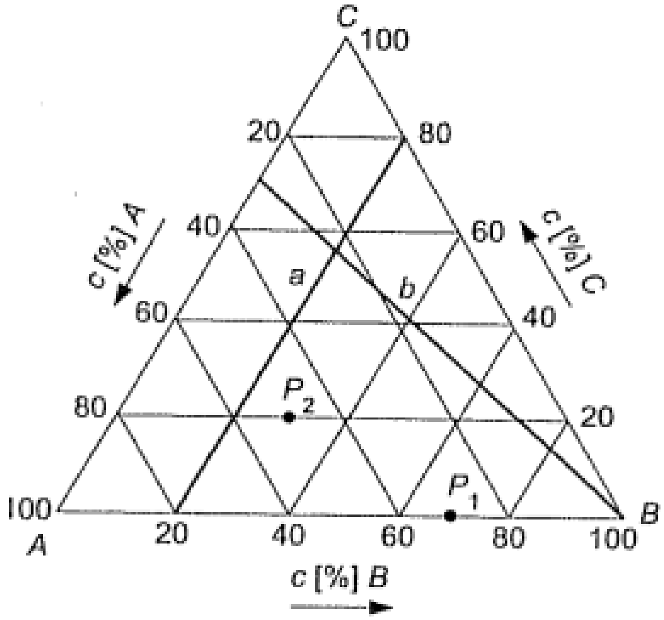




3.3.-3.
Interpret the following liquid-solid equilibrium diagrams.



3.3.-4.
Determine the composition of the ternary system at point P2.



3.3.-5.
An aqueous solution of barbital containing 0.5 g of the drug in 50 cm^3 of water was extracted with chloroform. How much of the drug would remain in the aqueous solution if:
a) one extraction with 50 cm3 of chloroform was performed,
b) five extractions with 10 cm3 of chloroform were performed.
The partition coefficient of barbital between water and chloroform at 25°C is 0.7.

3.4. Raoult's law

3.4.-1.
Calculate the water vapour pressure above the solution if 12 grams of glucose are dissolved in 125 grams of water and the water vapour pressure above pure water is 21.78 kPa.

3.4.-2.
Calculate the vapor pressure of water above the solution if in 125 grams of water dissolved the boiling of a binary solution of substances A and B, in which the mole fraction of A is x_A = 0.6589, occurs at a pressure of 1 atm. The vapor pressures of the pure components are 957.0 Torr and 379.5 Torr, respectively. Is the solution ideal? What is the initial composition of the vapor above the solution? 12 grams of glucose, and the vapor pressure of water above pure water is 21.78 kPa.

3.4.-3.
The vapour pressure of a 500 g sample of benzene at 60.6°C is 400 Torr, and after dissolving 19 g of a non-volatile organic substance in it, the pressure drops to 386 Torr. Calculate the molar mass of the dissolved substance.

3.4.-4.
At 90°C the vapour pressure of methylbenzene is 400 Torr, and of 1,2-dimethylbenzene 150 Torr. What is the composition of the mixture of these liquids if it boils at this temperature under a pressure of 0.50 atm?

3.4.-5.

The vapour pressure of 2-propanol is 50.00 kPa at 338.8°C, but it fell to 49.62 kPa when 8.69 g of an involatile organic compound was dissolved in 250 g of 2-propanol. Calculate the molar mass of the compound.

3.4.-6.

At 310 K, the partial vapour pressures of a substance B dissolved in a liquid A are as follows:

x_B	0.010	0.015	0.020
p_B/kPa	82.0	122.0	166.1

Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 310 K.

3.4.-7.

Predict the partial vapour pressure of the component B above its solution in A in Exercise 5.3b when the molality of B is 0.25 mol kg^{-1}. The molar mass of A is 74.1 g mol^{-1}.

3.4.-8.

By measuring the equilibrium between liquid and vapour phases of a solution at 30°C at 1.00 atm, it was found that $x_A = 0.220$ when $y_A = 0.314$. Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^* = 73.0$ kPa and $p_B^* = 92.1$ kPa. (x_A is the mole fraction in the liquid and y_A the mole fraction in the vapour.)

3.4.-9.

At 90°C, the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 19 kPa? What is the composition of the vapour produced?

3.4.-10.

It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96°C. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 76.5 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

Assessment

A3.-1.

The molar volume of a certain solid at a melting point of 350.75 K and a pressure of 1 atm is 161 cm^3/mol. The molar volume of the liquid phase under the same conditions is 163.3cm^3/mol. The melting point at a pressure of 100 atm changes to 351.26 K. Calculate the molar entropy and enthalpy of fusion of this body.

A3.-2.

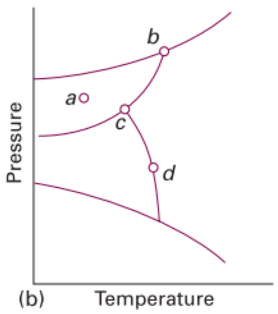
The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

A3.-3.

The molar volume of a certain solid is 142.0 $cm^3\ mol^{-1}$ at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 $cm^3\ mol^{-1}$. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

A3.-4.

How many phases are present at each of the points marked in Fig.



A3.-5.

The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.