

### TOPIC 3.A. Molecular-Kinetic Theory. Ideal and Real Gases

Molecular physics studies the physical properties, structure and state of aggregation of matter on the basis of molecular-kinetic conceptions.

The state of gas is defined in terms of certain parameters (unit of measurement should be added):

- *Volume*  $V$  is measured in [...];
- *Pressure*  $P$  is the force applied perpendicular to the surface of an object per unit area over which that force is distributed, it is measured in [...];
- *Temperature*  $T$  is a measure of the mean kinetic energy of molecules.

It is measured with a thermometer calibrated in one or more temperature scales. The most commonly used scales are the Celsius scale (formerly called centigrade) (denoted  $^{\circ}\text{C}$ ), and Kelvin scale (denoted  $\text{K}$ ). The temperature measured in the Kelvin scale is called *absolute* or *thermodynamic temperature*. It is measured in [.....].

Write down the relationship between Celsius and Kelvin scales:  $T = \dots\dots\dots$  (3.1a)

*The equation of state* relates the pressure  $P$ , volume  $V$  and temperature  $T$  of a physically homogeneous system.

*The number of molecules*  $N$  in a given mass of gas is (name the parameters in the relationship):

$$N = \dots\dots\dots \quad (3.2a)$$

- $v$  is \_\_\_\_\_
- $m$  is \_\_\_\_\_
- $N_A$  is \_\_\_\_\_
- $M$  is \_\_\_\_\_
- $n$  is \_\_\_\_\_
- $V$  is \_\_\_\_\_

#### **Example of problem solution.**

How many atoms are in 1 kg of helium? Determine the mass of a single atom of helium.

**Data:**

$$m = 1 \text{ kg}$$

$$M = 4 \times 10^{-3} \text{ kg/mol}$$

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$$N = ?$$

$$m_1 = ?$$

**Solution:**

According to the relationship (3.2a) we can find the number of molecules  $N$  in a given mass of gas. The molecule of helium is monatomic, so the number of atoms is equal to the number of molecules:

$$N = \frac{1 \cdot 6.02 \times 10^{23}}{4 \times 10^{-3}} \text{ atoms} = 1.50 \times 10^{26} \text{ atoms}.$$

In order to determine the mass of a single atom  $m_1$ , it is sufficient to divide the total mass of the gas by the number of atoms contained therein:  $m_1 = \frac{m}{N}$ .

After substitution we have:  $m_1 = \frac{1}{1.50 \times 10^{26}} = 6.67 \times 10^{-27} \text{ kg}.$

**Answer:** In 1 kg of helium are  $1.50 \times 10^{26}$  atoms, the mass of a single atom of helium is  $m_1 = 6.67 \times 10^{-27}$  kg .

*Amount of substance*  $\nu$  is a standard-defined quantity that measures the size of an ensemble of particles, such as atoms, molecules, electrons, and other particles. The International System of Units (SI) defines the amount of substance to be proportional to the number of particles present. The SI unit for amount of substance is the mole. It has the unit symbol *mol*. The proportionality constant is the inverse of the Avogadro number. The mole is defined as the amount of substance that contains an equal number of particles as there are atoms in 12g of the isotope carbon-12. (name the parameters in the relationship):

$$\nu = \dots\dots\dots (3.3a)$$

$C$  is \_\_\_\_\_

$V_M$  is \_\_\_\_\_

**Exercise 3.1a.** Define the following terms:

*Ideal gas* is \_\_\_\_\_  
 \_\_\_\_\_

Ideal gas law : \_\_\_\_\_ (3.4a)

*Real gas* is \_\_\_\_\_  
 \_\_\_\_\_

Van der Waals equation: \_\_\_\_\_ (3.5a)

$a$  is \_\_\_\_\_

$b$  is \_\_\_\_\_

*The internal energy of an ideal gas* is the sum of the kinetic energies of the particles in the gas and depends entirely on nature of the gas and thermodynamic temperature. (name the parameters in the equation):

$$U = \frac{i}{2} \cdot \frac{m}{M} RT (3.6a)$$

$i$  is \_\_\_\_\_

$R$  is \_\_\_\_\_

*Number of degrees of freedom* of a mechanical system is a number of independent variables, by means of which the system's configuration can be described.

$$i = i_{trans} + i_{rot} + 2i_{vib} (3.7a)$$

It is the sum of number of translational, rotational and double number of vibrational degrees of freedom.

The *mean energy* of each degree of freedom is equal to:  $\varepsilon = \frac{1}{2}kT$ , (3.8a)

$k$  is \_\_\_\_\_

The *basic equation of molecular-kinetic theory of gases* establishes a relationship between macro parameter (gas pressure) and micro parameter (mean kinetic energy of translational motion of a single molecule of  $\langle \varepsilon \rangle$ ):

..... (3.9a)

**Problem 3.2a.** Carbon dioxide with mass of 6.6 kg under pressure of 0.1 MPa has a volume of 3.75 m<sup>3</sup>. Determine the gas temperature if we consider the gas as: 1) the ideal gas; 2) the real gas with constants  $a = 0.361 \text{ N}\cdot\text{m}^4/\text{mol}^2$  and  $b = 42.84 \text{ cm}^3/\text{mol}$ .

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

As a result of the continuous random motion the speed of the gas molecules continuously vary at collisions Maxwell deduced the law of distribution of speed of molecules (Fig. 3.1a).

$$f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left( -\frac{mv^2}{2kT} \right) \quad (3.10a)$$

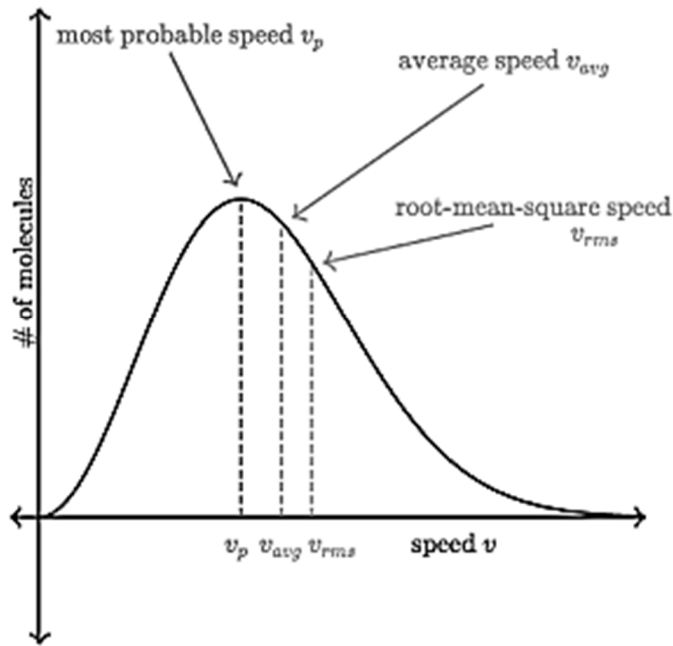


Fig. 3.1a. The function of distribution of speeds for gas molecules

**Exercise 3.3a.** Specify arrows the accordance between the physical quantity and the formula for its calculation:

Root mean square speed of molecules
Average (mean) speed of molecules
The most probable speed of the molecules

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} \quad (3.11a)$$

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \quad (3.12a)$$

$$v_{avg} = \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad (3.13a)$$

Write down the relationship between speeds:

.....  $v_p : \langle v \rangle : v_{rms} = \dots\dots\dots$  (3.14a)

**Problem 3.4a.** Calculate the most probable, the average and the root mean square speed of molecules of carbon dioxide (CO<sub>2</sub>) at 20°C. Make a conclusion.

**Data:**

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**Solution:**

**Answer:** \_\_\_\_\_

**Exercise 3.5a.** Define the following terms:

The quantity of heat is \_\_\_\_\_

\_\_\_\_\_

Heat capacity is \_\_\_\_\_

\_\_\_\_\_

Molar heat capacity ( $C_\mu$ ) is the amount of heat energy required to increase the temperature of 1 mole

of a substance by 1 degree (or 1 K) is  $C_\mu = C_m \cdot M \left[ \frac{J}{K \cdot mol} \right]$ . (3.15a)

**Exercise 3.6a.** Define the following terms and write down the appropriate formula:

Specific heat capacity is \_\_\_\_\_

\_\_\_\_\_

..... (3.16a)

Heat capacity at the constant volume is \_\_\_\_\_

\_\_\_\_\_

..... (3.17a)

Heat capacity at the constant pressure is \_\_\_\_\_

\_\_\_\_\_

..... (3.18a)

The Mayer's relationship: ..... (3.19a)

**Problem 3.7a.** Calculate the specific heat capacity at the constant pressure  $C_P$  and at the constant volume  $C_V$  of a diatomic gas, if its density under normal conditions is equal to  $1.43 \text{ kg/m}^3$ .

**Data:**

\_\_\_\_\_

**Solution:**

|

**Answer:** \_\_\_\_\_

Exercise 3.8a. Fill in the table 3.1a:

Table 3.1a.

Gas laws

Constant parameter	Process name	Law (name)	Picture	Quantity of heat	Work	Internal energy
<b>V = const</b>	Isochoric process	<i>Charles's law</i> ..... (3.20a)		Q = .....	W = .....	U = .....
<b>P = const</b>	Isobaric process	<i>Gay-Lussac's Law</i> ..... (3.21a)		Q = .....	W = .....	U = .....
<b>T = const</b>	Isothermal process	<i>Boyle's law</i> ..... (3.22a)		Q = .....	W = .....	U = .....
<b>Q = const</b>	Adiabatic process	<i>Poisson's law</i> ..... (3.23a) where $\gamma = \dots\dots\dots$ (3.24a)		Q = .....	W = .....	U = .....

**Problem 3.9a.** The oxygen bag contains 9.93 g of the gas under certain pressure. Calculate the work done by the gas if it changes its volume from 2 to 6 liters. The process occurs at the constant temperature of 20 °C.

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

**Problem 3.10a.** 5 mol of the ideal monatomic gas adiabatically expands. The initial pressure equals 1 MPa. The temperature of the gas decreases from 320 to 275 K. What work is done?

**Data:**

**Solution:**

**Answer:** \_\_\_\_\_

### ***Control questions***

1. What is thermodynamic parameters? What thermodynamic parameters do you know?
2. What is the physical meaning of Maxwell's distribution?
3. What is the physical meaning of Avogadro number?
4. Write down the gas constant? What units of measurement it has?
5. Define the term "normal conditions".

### ***Individual assignments***

1. The mass of  $N = 2.15 \times 10^{27}$  molecules of certain gas is equal to 1 kg. Determine which is the gas.
2. Calculate the concentration of nitrogen molecules, if at a pressure of 0.1 MPa the root mean square speed of these molecules is 480 m/s.
3. How many hydrogen molecules are in volume of 1 m<sup>3</sup> under the normal conditions?
4. Which gas has the lowest most probable speed of the molecules: H<sub>2</sub>; CO<sub>2</sub> or CH<sub>4</sub>? ( $t = 15^\circ\text{C}$ ).
5. 15 liter tank contains the nitrogen gas under pressure of 100 kPa at the temperature  $t_1 = 27^\circ\text{C}$ . After 14 g of nitrogen gas has been released the temperature of gas has become equal to  $t_2 = 17^\circ\text{C}$ . Calculate the pressure of nitrogen gas remaining in the tank.
6. At what temperature the mean speed of oxygen gas molecules equals to 500 m/s?
7. What work is done at isobaric expansion of 1 mole of an ideal gas if it is heated at 1 K?
8. Carbon dioxide with a mass of 2.2 kg is at 290 K in 30 liters vessel. Find the gas pressure if it is: 1) the ideal gas; 2) the real gas with constants  $a = 0.361 \text{ N}\cdot\text{m}^4/\text{mol}^2$  and  $b = 4.28 \text{ m}^3/\text{mol}$ .
9. The greenhouse contains  $4.25 \times 10^{27}$  molecules of air at a temperature of  $27^\circ\text{C}$  and at a pressure of  $1.013 \times 10^5 \text{ Pa}$ . Find the volume of greenhouse.

### TOPIC 3.B. Basic Concepts and Laws of Thermodynamics

*Thermodynamics* considers the energy conversion in macroscopic systems without taking the objects microscopic structure into consideration.

**Exercise 3.1b.** Define the following terms:

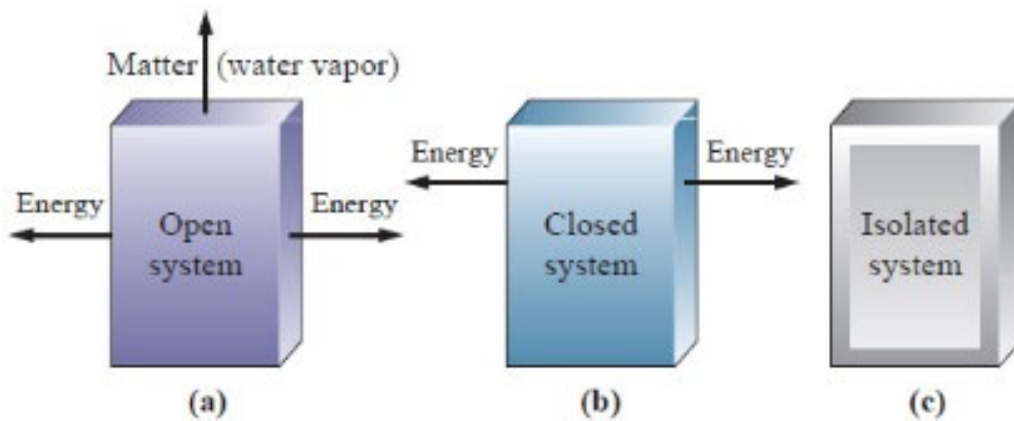
*Thermodynamic system* is \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

There are three types of thermodynamic systems (Fig. 3.1b.):

*Isolated system* is \_\_\_\_\_  
\_\_\_\_\_

*Closed system* is \_\_\_\_\_  
\_\_\_\_\_

*Open system* is \_\_\_\_\_  
\_\_\_\_\_



**Fig. 3.1b.** Different types of thermodynamic systems

The thermodynamic state of the system is \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

The thermodynamic state of the system can be:

*equilibrium* is such state in which \_\_\_\_\_  
\_\_\_\_\_

*nonequilibrium* is such state in which \_\_\_\_\_  
\_\_\_\_\_

*stationary* is such state in which \_\_\_\_\_  
\_\_\_\_\_

*Thermodynamic process* is \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_



Reversible process is \_\_\_\_\_

Irreversible process is \_\_\_\_\_

### The First and Second Laws of Thermodynamics

**Exercise 3.2b.** Mathematical notation of the *first law of thermodynamics* and definition of parameters involved:

(3.1b)

$dU$  is \_\_\_\_\_

$\delta Q$  is \_\_\_\_\_

$\delta W$  is \_\_\_\_\_

#### Example of problem solution.

Find the change in the internal energy of 1 kg ideal gas, that is cooled at the constant volume if its initial temperature is 423 K and as a result of the process the pressure decreased from 8.08 to 2.02 Pa.  $C_v = 700 \text{ J}/(\text{kg}\cdot\text{K})$

#### Data:

$$m = 1 \text{ kg}$$

$$T = 423 \text{ K}$$

$$P_1 = 8.08 \text{ Pa}$$

$$P_2 = 2.02 \text{ Pa}$$

$$C_v = 700 \text{ J}/(\text{kg}\cdot\text{K})$$

$$\Delta U = ?$$

#### Solution:

The amount of heat is  $Q = C_v m \Delta T$ . According to the first law of thermodynamics  $Q = \Delta U + W$ . Since the gas is at the constant volume, there is no work done  $W = 0$ , so the internal energy  $\Delta U = Q$ , and we have  $\Delta U = C_v m \Delta T$ .

Since the process is isochoric:  $\frac{p_1}{T_1} = \frac{p_2}{T_2} \Rightarrow T_2 = \frac{p_2 T_1}{p_1}$

$$\Delta T = T_2 - T_1 = \frac{(p_2 - p_1) T_1}{p_1}$$

$$\text{So we get: } \Delta U = C_v m \frac{(p_2 - p_1) T_1}{p_1},$$

Substituting the numerical values we have:

$$\Delta U = 700 \cdot 1 \frac{(2.02 - 8.08) \cdot 423}{8.08} = -2.2 \times 10^5 \text{ J}.$$

**Answer:**  $\Delta U = -2.2 \times 10^5 \text{ J}$ .

**Problem 3.3b.** After getting the amount of heat of 2.5 kJ, the internal energy of an ideal gas has increased by 1.5 kJ. Find the work done by the gas.

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

**Exercise 3.4b.** Mathematical notation of the *second law of thermodynamics* and definition of parameters involved:

(3.2b)

$dS$  is \_\_\_\_\_

$\delta Q$  is \_\_\_\_\_

$T$  is \_\_\_\_\_

The entropy  $S$  is \_\_\_\_\_

**Exercise 3.5b.** Boltzmann's relationship between thermodynamic probability  $W$  and entropy  $S$  has the form:

$$S = \quad (3.3b)$$

$k$  is \_\_\_\_\_

$W$  is \_\_\_\_\_

The change of entropy as a result of transition between two equilibrium states is:

$$\Delta S_{1 \rightarrow 2} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} = \int_1^2 \frac{dU + \delta A}{T} \quad (3.4b)$$

**Problem 3.6b.** In an open thermodynamic system, that is maintained at 25 °C as a result of a chemical reaction released heat of 3.2 MJ. The system exchanges of 2.76 MJ of heat with the environment. Find the entropy change of the system.

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

**Problem 3.7b.** Find the change of oxygen gas entropy, as a result of gas expansion from initial volume 10 L at temperature 80 °C to the final volume 40 L at 300 °C. Oxygen should be considered as an ideal gas with mass 8 g.

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

**Problem 3.8b.** The entropy of the thermodynamic system is 2.76 kJ/K. Find the number of real microstates  $W$  corresponding to the system' macrostate.

**Data:**

**Solution:**

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**Answer:** \_\_\_\_\_

### Thermodynamic Potentials

**Exercise 3.9b.** Define the following terms and specify arrows the accordance between the name and formula of the state function.

*Thermodynamic potential* is \_\_\_\_\_

*Enthalpy* is \_\_\_\_\_

1) Internal energy	a) $dH = dU + pdV$ (3.5b)
2) Enthalpy	b) $dU$
3) Helmholtz free energy	c) $dG = dU + rdV - TdS = dH - TdS$ (3.6b)
4) Gibbs free energy	d) $dF = dU - TdS$ (3.7b)

Gibbs free energy of one mole of a substance called *chemical potential*  $\mu$ , (in case of uncharged particles) or *electrochemical potential* (in case of charged particles)  $\bar{\mu}$ . Change in the chemical (electrochemical) potential is equal to:

$$\Delta\mu = \frac{\Delta G}{\nu}; \quad \Delta\bar{\mu} = \frac{\Delta G}{\nu}, \quad (3.8b)$$

where  $\nu$  is the number of moles.

If the system consists of several components, than the electrochemical potential of the  $i$ -th component

$\bar{\mu}_i$  is defined as:  $\Delta\bar{\mu}_i = \frac{\Delta G_i}{\nu_i}$ , where  $\nu_i$  - the number of moles of the  $i$ -th component  $\Delta G_i$  is the

change in the Gibbs free energy of the  $i$ -th component.

For dilute solutions of the uncharged particles the chemical potential is equal to:

$$\mu_i = \mu_{0i} + RT \ln C_i, \quad (3.9b)$$

where  $\mu_{0i}$  is the standard chemical potential which is numerically equal to the chemical potential of the component when its concentration in a solution is  $1 \text{ mol}\cdot\text{L}^{-1}$ , and  $C_i$  is molar concentration.

**Exercise 3.10b.** The change in the standard free energy during a chemical reaction (under standard conditions):

$$\Delta G^0 = \quad (3.10b)$$

$R$  is \_\_\_\_\_

$T$  is \_\_\_\_\_

$K$  is \_\_\_\_\_

### Example of problem solution

What amount of substance of non-polar compound was transferred from a non-polar solvent into water, if at  $20^\circ\text{C}$  enthalpy decreased by  $8 \text{ kJ}\cdot\text{mol}^{-1}$ , the entropy has decreased by  $67 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and total change in Gibbs energy is equal to  $+140 \text{ kJ}$ .

#### Data:

$$T = 20^\circ\text{C} = 293 \text{ K}$$

$$\Delta H = -8 \text{ kJ}\cdot\text{mol}^{-1} = -8 \times 10^3 \text{ J}\cdot\text{mol}^{-1}$$

$$\Delta S = -67 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta G = 140 \text{ kJ}$$

$\nu$  -?

#### Solution:

The change in Gibbs energy per mole:

$$\Delta G_v = \Delta H_v - T\Delta S_v.$$

Then the number of moles of the solution could be calculated by dividing the total change in Gibbs energy by  $\Delta G_v$ :

$$\nu = \frac{\Delta G}{\Delta G_v} = \frac{\Delta G}{\Delta H_v - T\Delta S_v} = \frac{14 \times 10^4}{-8 \times 10^3 + 293 \times 67} = 12 \text{ mol.}$$

**Answer:** 12 moles of nonpolar compound were transferred from a non-polar solvent into water.

**Problem 3.12b.** How does change the entropy of 4 moles nonpolar compound during its transfer from the organic solvent into the water if the enthalpy decreased by  $6.4 \text{ kJ}\cdot\text{mol}^{-1}$ , and Gibbs energy increased by  $9 \text{ kJ}\cdot\text{mol}^{-1}$ . The temperature of the solution is  $20^\circ\text{C}$ .

Data:

Solution:

Answer:

**Problem 3.13b.** Find the change in the standard free energy of reaction, which equilibrium constant is  $K = 10$ .

Data:

Solution:

Answer:

**Control questions**

1. Give examples of open thermodynamic systems
2. What is the statistical nature of entropy? Give its unit of measurement.
3. List the state functions.
4. What is the physical sense of the second law of thermodynamics.
5. What is the physical sense of the first law of thermodynamics.
6. What thermodynamic potentials do you know?

**Individual assignments**

1. Calculate the change in entropy in fusion of 1 mol of ice. The specific latent heat of fusion of ice is  $l_f = 335 \text{ kJ/kg}$ .
2. The entropy of thermodynamic system in some state is equal to  $2.5 \text{ kJ}\cdot\text{K}^{-1}$ . Calculate the thermodynamic probability  $W$  of this state?
3. The internal energy of an ideal gas increased by  $4.5 \text{ kJ}$  after the amount of heat  $7.5 \text{ kJ}$  was obtained. Calculate the work performed by the gas.
4. As a result of the isothermal expansion the volume of  $8 \text{ g}$  of the oxygen gas has increased twice. Determine the change in entropy of the gas.
5. Find the entropy change of  $6$  moles nonpolar compound during its transfer from the organic solvent into the water if the enthalpy decreased by  $6.4 \text{ kJ}\cdot\text{mol}^{-1}$ , and Gibbs energy increased by  $9 \text{ kJ}\cdot\text{mol}^{-1}$ . The temperature of the solution is  $37^\circ \text{C}$ .
6. Find the chemical equilibrium constant of the chemical reaction  $A \leftrightarrow B$  at  $t = 25^\circ \text{C}$  if  $\mu_A^0 = -16 \text{ kJ/mol}$ ,  $\mu_B^0 = -6 \text{ kJ/mol}$ .