Solution

PART A

The liquid boils when the pressure of its saturated vapor is equal to the external pressure. Thus, in order to find the boiling temperature of the liquid i (i - A or B), one should determine such a temperature T_{bi} (or t_{bi}) for which $p_i/p_0 = 1$.

Then $\ln(p_i / p_0) = 0$, and we have:

$$T_{bi} = -\frac{\alpha_i}{\beta_i}.$$

The coefficients α_i and β_i are not given explicitly. However, they can be calculated from the formula given in the text of the problem. For this purpose one should make use of the numerical data given in the Tab. 1.1.

For the liquid A, we have:

$$\ln 0.284 = \frac{\alpha_A}{(40 + 273.15)\text{K}} + \beta_A,$$

$$\ln 1.476 = \frac{\alpha_A}{(90 + 273.15)\text{K}} + \beta_A.$$

After subtraction of these equations, we get:

$$\ln 0.284 - \ln 1.476 = \alpha_A \left(\frac{1}{40 + 273.15} - \frac{1}{90 + 273.15} \right) \text{K}^{-1}.$$

$$\alpha_A = \frac{\ln \frac{0.284}{1.476}}{\frac{1}{40 + 273.15} - \frac{1}{90 + 273.15}} \text{K} \approx -3748.49\text{K}.$$

Hence,

$$\beta_A = \ln 0.284 - \frac{\alpha_A}{(40 + 273.15)\text{K}} \approx 10.711.$$

Thus, the boiling temperature of the liquid A is equal to

$$T_{bA} = 3748.49\text{K}/10.711 \approx 349.95 \text{ K}.$$

In the Celsius scale the boiling temperature of the liquid A is

$$t_{bA} = (349.95 - 273.15)°\text{C} = 76.80°\text{C} \approx 77°\text{C}.$$

For the liquid B, in the same way, we obtain:

$$\alpha_B \approx -5121.64 \text{ K},$$
$$\beta_B \approx 13.735,$$
$$T_{bB} \approx 372\text{-}89 \text{ K},$$
$$t_{bB} \approx 99.74°\text{C} \approx 100°\text{C}.$$

PART B

As the liquids are in thermal contact with each other, their temperatures increase in time in the same way.

At the beginning of the heating, what corresponds to the left sloped part of the diagram, no evaporation can occur. The free evaporation from the upper surface of the liquid B cannot occur - it is impossible due to the layer of the non-volatile liquid C. The evaporation from the inside of the system is considered below.

Let us consider a bubble formed in the liquid A or in the liquid B or on the surface that separates these liquids. Such a bubble can be formed due to fluctuations or for many other reasons, which will not be analyzed here.

The bubble can get out of the system only when the pressure inside it equals to the external pressure p_0 (or when it is a little bit higher than p_0). Otherwise, the bubble will collapse.

The pressure inside the bubble formed in the volume of the liquid A or in the volume of the liquid B equals to the pressure of the saturated vapor of the liquid A or B, respectively. However, the pressure inside the bubble formed on the surface separating the liquids A and B is equal to the sum of the pressures of the saturated vapors of both these liquids, as then the bubble is in a contact with the liquids A and B at the same time. In the case considered the pressure inside the bubble is greater than the pressures of the saturated vapors of each of the liquids A and B (at the same temperature).

Therefore, when the system is heated, the pressure p_0 is reached first in the bubbles that were formed on the surface separating the liquids. Thus, the temperature t_1 corresponds to a kind of common boiling of both liquids that occurs in the region of their direct contact. The temperature t_1 is for sure lower than the boiling temperatures of the liquids A and B as then the pressures of the saturated vapors of the liquids A and B are less then p_0 (their sum equals to p_0 and each of them is greater than zero).

In order to determine the value of t_1 with required accuracy, we can calculate the values of the sum of the saturated vapors of the liquids A and B for several values of the temperature *t* and look when one gets the value p_0.

From the formula given in the text of the problem, we have:

$$\frac{p_A}{p_0} = e^{\frac{\alpha_A}{T}+\beta_A}, \qquad (1)$$

$$\frac{p_B}{p_0} = e^{\frac{\alpha_B}{T}+\beta_B}. \qquad (2)$$

$p_A + p_B$ equals to p_0 if

$$\frac{p_A}{p_0} + \frac{p_B}{p_0} = 1.$$

Thus, we have to calculate the values of the following function:

$$y(x) = e^{\frac{\alpha_A}{t+t_0}+\beta_A} + e^{\frac{\alpha_B}{t+t_0}+\beta_B},$$

(where $t_0 = 273.15$ °C) and to determine the temperature $t = t_1$, at which $y(t)$ equals to 1. When calculating the values of the function $y(t)$ we can divide the intervals of the temperatures t by 2 (approximately) and look whether the results are greater or less than 1.

We have:

Table 1.2

t	$y(t)$
40°C	< 1 (see Tab. 1.1)
77°C	> 1 (as t_1 is less than t_{bA})
59°C	0.749 < 1
70°C	1.113 > 1
66°C	0.966 < 1
67°C	1.001 > 1
66.5°C	0.983 < 1

Therefore, $t_1 \approx$ 67° C (with required accuracy).

Now we calculate the pressures of the saturated vapors of the liquids A and B at the temperature $t_1 \approx$ 67°C, i.e. the pressures of the saturated vapors of the liquids A and B in each bubble formed on the surface separating the liquids. From the equations (1) and (2), we get:

$$p_A \approx 0.734\, p_0,$$
$$p_B \approx 0.267\, p_0,$$
$$(p_A + p_B = 1.001 p_0 \approx p_0).$$

These pressures depend only on the temperature and, therefore, they remain constant during the motion of the bubbles through the liquid B. The volume of the bubbles during this motion also cannot be changed without violation of the relation $p_A + p_B = p_0$. It follows from the above remarks that the mass ratio of the saturated vapors of the liquids A and B in each bubble is the same. This conclusion remains valid as long as both liquids are in the system. After total evaporation of one of the liquids the temperature of the system will increase again (second sloped part of the diagram). Then, however, the mass of the system remains constant until the temperature reaches the value t_2 at which the boiling of the liquid (remained in the vessel) starts. Therefore, the temperature t_2 (the higher horizontal part of the diagram) corresponds to the boiling of the liquid remained in the vessel.

The mass ratio m_A / m_B of the saturated vapors of the liquids A and B in each bubble leaving the system at the temperature t_1 is equal to the ratio of the densities of these vapors ρ_A / ρ_B. According to the assumption 2, stating that the vapors can be treated as ideal gases, the last ratio equals to the ratio of the products of the pressures of the saturated vapors by the molecular masses:

$$\frac{m_A}{m_B} = \frac{\rho_A}{\rho_B} = \frac{p_A \mu_A}{p_B \mu_B} = \frac{p_A}{p_B} \mu .$$

Thus,

$$\frac{m_A}{m_B} \approx 22.0 .$$

We see that the liquid A evaporates 22 times faster than the liquid B. The evaporation of 100 g of the liquid A during the "surface boiling" at the temperature t_1 is associated with the evaporation of 100 g / 22 $\approx$4.5 g of the liquid B. Thus, at the time τ_1 the vessel contains 95.5 g of the liquid B (and no liquid A). The temperature t_2 is equal to the boiling temperature of the liquid B: $t_2 = 100°\text{C}$.

Marking Scheme

1.	physical condition for boiling	1 point
2.	boiling temperature of the liquid A (numerical value)	1 point
3.	boiling temperature of the liquid B (numerical value)	1 point
4.	analysis of the phenomena at the temperature t_1	3 points
5.	numerical value of t_1	1 point
6.	numerical value of the mass ratio of the saturated vapors in the bubble	1 point
7.	masses of the liquids at the time τ_1	1 point
8.	determination of the temperature t_2	1 point

REMARK: As the sum of the logarithms is not equal to the logarithm of the sum, the formula given in the text of the problem should not be applied to the mixture of the saturated vapors in the bubbles formed on the surface separating the liquids. However, the numerical data have been chosen in such a way that even such incorrect solution of the problem gives the correct value of the temperature t_1 (within required accuracy). The purpose of that was to allow the pupils to solve the part B of the problem even if they determined the temperature t_1 in a wrong way. Of course, one cannot receive any points for an incorrect determination of the temperature t_1 even if its numerical value is correct.

Typical mistakes in the pupils' solutions

Nobody has received the maximum possible number of points for this problem, although several solutions came close. Only two participants tried to analyze proportion of pressures of the vapors during the upward movement of the bubble trough the liquid B. Part of the students confused Celsius degrees with Kelvins. Many participants did not take into account the boiling on the surface separating the liquids A and B, although this effect was the essence of the problem. Part of the students, who did notice this effect, assumed a priori that the liquid with lower boiling temperature "must" be the first to evaporate. In general, this need not be true: if γ were, for example, 1/8 instead 8, then liquid A rather than B would remain in the vessel. As regards the boiling temperatures, practically nobody had any essential difficulties.