

EVAPORATION OF DROPS OF BINARY LIQUID MIXTURES IN AIR UNDER FREE-CONVECTION CONDITIONS

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The evaporation of drops of mixtures of tetrafluorodibromomethane with benzene, toluene, and xylene is studied at room temperature in air at rest.

Sprayed liquid mixtures are widely used in energetics, the food industry, agriculture, etc., so that a study of the evaporation of drops of liquid mixtures is of practical as well as theoretical importance. This research began with a study of binary mixtures of liquids having approximately equal boiling points [1-3]. A natural second step is to study binary mixtures in which the boiling points are very different.

We report here a study of the evaporation of drops of mixtures of tetrafluorodibromomethane (Freon 114-C-2), which boils at 46.2°C, with benzene, toluene, and xylene, whose boiling points are 80, 111, and 141°C, respectively. Part of the motivation for choosing these mixtures is that it thus becomes possible to study several questions involving the suppression of the combustion of liquid fuels and questions which are of economic importance.

In the experiments we measured the mass m , diameter d , and temperature ϑ of the evaporating drops. We separately determined the composition of the vapor phase.

The mass measurements were carried out with a microbalance [4] having a sensitivity of $1.8 \cdot 10^{-5}$ g per scale division. The drops were suspended on a glass filament at whose end there was a ball 1 mm in diameter. The diameter of the evaporating drop was measured with a microscope with an ocular. The drop temperature was determined with a manganese-Constantan thermocouple, with wire diameters of 30 and 100 μ .

The initial drop diameter varied from 1.4 to 1.8 mm.

The composition of the vapor phase was determined in the following manner: a weak nitrogen stream was passed through a Drechsel bottle containing the test solution. The stream, saturated with the vapor of the mixture, then entered a U-shaped glass tube in a Dewar with liquid nitrogen, from which it escaped into the atmosphere. The vapor condensed in the U-shaped tube. A refractometer was used to determine the refractive index of the condensate, and then the composition of the condensed liquid was found from a calibration curve. The flow rate of the nitrogen in the determination of the composition of the vapor phase did not exceed 1 liter/min and was chosen empirically, such that a further reduction of the flow rate did not affect the condensate composition. The pressure in the system was atmospheric.

We first carried out experiments with the liquids used as components in the mixtures. The change in the drop mass during the evaporation can be described well by the equation from [4, 5]:

$$m = m_0 - at + bt^2, \quad (1)$$

where a and b are coefficients which depend on the nature of the liquid.

The agreement of Eq. (1) with experiment can be judged on the basis of Fig. 1, which shows experimental data for Freon and toluene; the solid curves are drawn from Eq. (1).

The drop diameter falls off essentially linearly over the range studied.

Some experimental data obtained in a study of the evaporation of the mixtures are shown in Fig. 1. We see that the $m(t)$ curves for the mixture differ from the corresponding curves for the pure liquids. Analysis of the experimental data reveals that when the initial weight fraction of the Freon in the mixture, x_0 , is no

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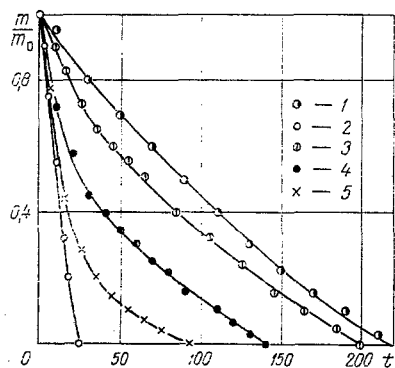


Fig. 1

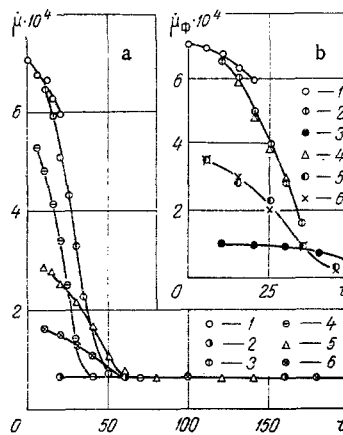


Fig. 2

Fig. 1. Time dependence of the drop mass during evaporation. 1) Toluene; 2) Freon; 3-5) mixtures of Freon with toluene. The weight fraction of Freon is: 3) 0.38; 4) 0.72; 5) 0.86. Here t is in seconds.

Fig. 2. a: Time dependence of the drop evaporation rate: 1) Freon; 2) toluene; 3-6) mixtures of Freon with toluene. The weight fraction of the Freon is: 3) 0.91; 4) 0.86; 5) 0.72; 6) 0.38. b: Time dependence of the rate at which the Freon evaporates from the drop, μ_F . 1) Pure Freon; 2, 3) mixtures of Freon with toluene [the weight fraction of the Freon in the mixture is: 2) 0.91; 3) 0.83]; 4, 5) mixtures of Freon with benzene [the Freon fraction is: 4) 0.91; 5) 0.79]; 6) mixture of Freon with xylene with a Freon weight fraction of 0.72. Here t is in seconds.

higher than 0.2 the $m(t)$ curves are described satisfactorily by (1) if the coefficients a and b are approximately equal to the values of these coefficients for the second component. At $x_0 > 0.3$ the curves for the mixtures are not described completely by Eq. (1). Nevertheless, Eq. (1) does give a satisfactory description of the first, rapidly falling, and second, slowly falling, parts of the curves for various values of a and b , which, of course, depend on x_0 and the nature of the second component. This circumstance can be seen from Table 1, which shows the ratios of the coefficients a for the first parts of the curves for the mixtures to the coefficients for drops of pure Freon, benzene, toluene, and xylene (a_{1F} , a_{1b} , a_{1t} , and a_{1x} , respectively).

We see from this table that the values of a_{1F} increase with increasing x_0 , tending toward a value of unity; at a given value of x_0 , they are nearly the same for all the mixtures studied. The ratio of a_1 to the coefficient a for the second component is larger than one and increases rapidly in the series from benzene to toluene to xylene.

Analysis of the experimental data shows that the transition from the first to the second parts of the $m(t)$ curves occurs after the evaporation of that fraction of the drop for which the ratio of the mass m to the initial mass m_0 is essentially equal to the weight fraction of the Freon in the drop, x_0 .

Using these experimental data, we can find the rate of evaporation of the drops. For this purpose it is convenient to use the quantity $\dot{\mu}$, which is the ratio of the rate of change of the mass, \dot{m} , to the drop diameter at the given instant. The results calculated for mixtures of Freon and toluene are shown in Fig. 2a. We see that the evaporation rate $\dot{\mu}$ of the mixtures is initially high; it subsequently decreases, eventually becoming approx-

TABLE 1. Relative Values of the Coefficients a

Second component	x_0	0.38	0.71	0.79	0.85	0.91
Benzene	a_{1F}	0,4	0,75	0,72	—	1,0
	a_{1b}	2,2	3,8	3,7	—	5,4
Toluene	a_{1F}	0,3	0,5	—	0,86	0,93
	a_{1t}	2,6	4,2	—	7,2	7,8
Xylene	a_{1F}	—	0,61	—	—	0,8
	a_{1x}	—	14,5	—	—	18,0

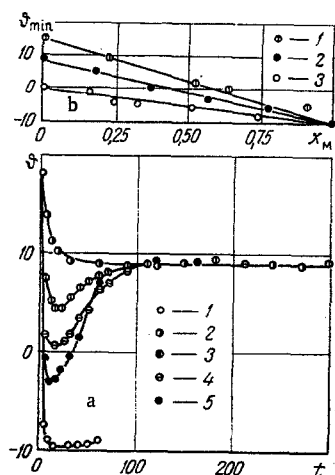


Fig. 3

Fig. 3. a: Time dependence of drop temperature. 1) Freon; 2) toluene; 3-5) mixtures of Freon with toluene [the weight fraction of the Freon is: 3) 0.38; 4) 0.63; 5) 0.79]. b: Minimum temperature ϑ_{\min} as a function of the mole fraction of Freon in the mixtures. The second component is: 1) xylene; 2) toluene; 3) benzene. Here ϑ is in Celsius degrees, and t is in seconds.

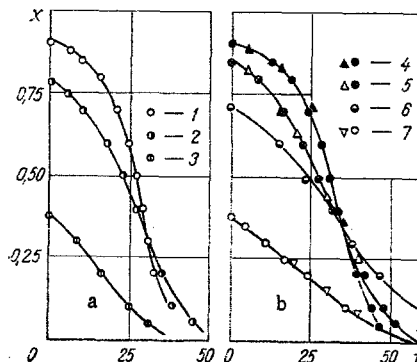


Fig. 4

Fig. 4. Time dependence of x during the drop evaporation. a) Mixtures of Freon with benzene with a Freon weight fraction of: 1) 0.91; 2) 0.79; 3) 0.38. b: The same, for mixtures of Freon with toluene with a Freon weight fraction of: 4) 0.91; 5) 0.86; 6) 0.71; 7) 0.38. Here t is in seconds, and x is expressed as a weight fraction.

imately equal to the evaporation rate of the second component. The initial rate, $\dot{\mu}_0$, increases with increasing x_0 ; at $x_0 = 0.9$ it is approximately equal to the value of μ for the pure Freon.

The shape of the $m(t)$ curves for the mixtures of Freon with benzene and of Freon with xylene is the same.

Figure 3a shows some of the measured temperatures of the evaporating drops. We see that during the evaporation of the Freon-toluene drops the temperature ϑ initially decreases rapidly and then remains essentially constant throughout the experiment. A different situation is observed in the evaporation of drops of mixtures. In this case ϑ initially decreases rapidly, but after reaching some minimum value ϑ_{\min} it begins to rise again, tending toward the temperature of a drop of the second component (which is relatively involatile). The minimum temperature is lower, the higher the Freon concentration in the mixture, x_0 . Figure 3b shows ϑ_{\min} as a function of the mole fraction of Freon in the drop, x_M .

These results clearly imply that the composition of the drops of these mixtures changes during the evaporation. At $x_0 > 0.3$ the Freon evaporates from the drop rapidly; the Freon concentration decreases rapidly, and in the late stage of the evaporation the evaporation rate is essentially equal to that of the second component. The drops of mixtures with a low initial Freon concentration evaporate at a rate nearly equal to that of the less volatile component.

Using these experimental results we can easily determine the evaporation rates of the components. The equations required for these calculations can be easily derived in the following manner, after [4].

We clearly have

$$\dot{m}_d = \dot{m}_F + \dot{m}_2 \quad (2)$$

If the process is assumed quasisteady, we can write

$$\dot{m}_F L_F + \dot{m}_2 L_2 = \alpha (\vartheta_m - \vartheta) S = \pi d \lambda \text{Nu} (\vartheta_m - \vartheta) \quad (3)$$

Here \dot{m}_d , \dot{m}_F , and \dot{m}_2 are the evaporation rates of the drop, the Freon, and the second component, respectively; L_F and L_2 are the heats of vaporization of the Freon and the second component; and ϑ and ϑ_m are the temperatures of the drop and the medium.

TABLE 2. Values of A/x_0 , ε , τ , and τ/t_0 for Certain Mixtures

Component	x_0	A/x_0	ε	τ	τ/t_0	Component	x_0	A/x_0	ε	τ	τ/t_0
Benzene	0,22	0,67	0,08	8	0,06	Toluene	0,38	0,89	0,08	28	0,13
	0,39	0,90	0,12	15	0,17		0,72	0,90	0,07	31	0,19
	0,79	1,0	0,13	26	0,40		0,86	0,95	0,10	29	0,29
Xylene	0,91	1,0	0,17	27	0,78	0,91	1,0	0,15	32	0,43	
	0,91	1,0	0,12	36	0,19						

From Eqs. (2) and (3) we find

$$\dot{\mu}_F = \frac{\dot{m}_F}{d} = \frac{\pi \lambda \text{Nu} (\theta_m - \theta) - L_2 \dot{\mu}_d}{L_F - L_2} \quad (4)$$

According to the data of Ranz and Marshall [6], we have

$$\text{Nu} = 2 + 0.6 \text{Gr}^{1/4} \text{Pr}^{1/3} \quad (5)$$

Using Eqs. (4) and (5), we can easily find $\dot{\mu}_F$, the evaporation rate of the Freon from the drop; from Eq. (2) we can determine the evaporation rate of the second component.

Some of the results obtained in this manner are shown in Fig. 2b; we see that the evaporation rate of the Freon from the drop of mixture, $\dot{\mu}_F$, is a strong function of x_0 and falls off rapidly as time elapses. The initial value of $\dot{\mu}_F$ for the solution with a Freon concentration of 0.9 is nearly the same as the evaporation rate of a drop of pure Freon. Interestingly, the $\dot{\mu}_F(t)$ curves corresponding to solutions with the same values of x_0 and different second components essentially coincide.

The evaporation rate of the second component from drops in which there is a high initial Freon concentration is initially small; it increases as time elapses, approaching the values of $\dot{\mu}$ for the drop of the pure second component. During the evaporation of mixtures with a low Freon concentration, the rate $\dot{\mu}$ changes little over time and is approximately equal to the evaporation rate of a drop of the pure second component.

Since the mass and diameter of the drops are measured simultaneously in the experiments, it is possible to determine the drop density ρ ; using this value and a calibration curve, we can find the weight fraction of the Freon in the drop, x , during the evaporation. Since the drop diameter changes by no more than 1 mm during the experiment, we can use only the results of experiments which were carried out particularly carefully for this purpose. The results calculated for certain mixtures of Freon and toluene are shown by the triangles in Fig. 4b. We see that the composition of the drops of mixtures changes during the evaporation, and we can determine the time dependence of x .

Dobrynina [5] gave the following equation for the complete mixing of evaporating binary solutions:

$$\ln \frac{m}{m_0} = \int_{x_0}^x \frac{dx}{y-x} \quad (6)$$

As we mentioned earlier, in these experiments we studied the composition of the vapor from these mixtures. It turns out that x and y can be related satisfactorily by

$$\frac{y}{1-y} = \delta \frac{x}{1-x} \quad \text{or} \quad y = \frac{\delta x}{1 + (\delta - 1)x} \quad (7)$$

Here δ is a coefficient. For the Freon-benzene mixtures it turns out to be 6; for the Freon-toluene mixtures it is 16, and for the Freon-xylene mixtures it is 91.

Using empirical equation (7) we can easily calculate the integral on the right side of Eq. (6), finding

$$\frac{m}{m_0} = \left(\frac{x}{x_0} \right)^\beta \left(\frac{1-x_0}{1-x} \right)^{1-\beta} \quad (8)$$

where $\beta = 1/\delta$.

If we determine the times corresponding to various values of the ratio m/m_0 from the experimental curve, we can use Eq. (8) to find the values for the corresponding times if there is complete mixing in the drop.

Corresponding calculations were carried out for mixtures of Freon with benzene, toluene, and xylene. Some of the results are shown in Fig. 4a and 4b (circles). We see that the values of x determined from the

density and from Eq. (8) agree satisfactorily. The clear implication of this agreement is that total mixing occurs in the evaporating drop of solution* and that Eq. (8), along with the experimental data, can be used for reliable calculations of the quantity x , which is a measure of the composition of the evaporating drops. There is another way to determine x : we can use Eqs. (2) and (4) to find the evaporation rate of the Freon, $\dot{\mu}_F$, and that of the second, $\dot{\mu}_2$, from the drop of mixture, and we can use the $\vartheta(t)$ curve to find the drop temperature ϑ . Then, noting that the evaporation rate of pure Freon is proportional to the saturation vapor density of the drop, and knowing the dependence of the evaporation rate on the diameter d , we can easily calculate the evaporation rate of a drop of pure Freon, $\dot{\mu}_{pF}$ at a temperature ϑ and at a diameter equal to the diameter of the mixture drop. Assuming $\mu_F : \dot{\mu}_{pF} = c_{dF} : c_F$, where c_{dF} and c_F are the measured concentrations of Freon in the vapor phase near the surface of the mixture drop and near the surface of a drop of pure Freon (expressed in grams per cubic centimeter), we can find c_{dF} .

In the same manner we can calculate the vapor density of the second component, and then it is a simple matter to find y and then x , from the $y(x)$ curve.

The results calculated in this manner agree satisfactorily with the values of x found from Eq. (8). This agreement again confirms that there is a total mixing in the drop.

The dependence of x on the time t can be described well by the empirical equation

$$x = \frac{A}{\exp(z) + 1}, \quad z = \varepsilon(t - \tau). \quad (9)$$

Here A is a quantity approximately equal to x_0 , τ is the time at which we have $x = 0.5A$, and ε is a coefficient.

Figure 4 compares Eq. (9) with the experiment; the solid curves are drawn from this equation, with the appropriate values of A and ε . Some data on A/x_0 , ε , τ , and τ/t_0 , where t_0 is the time required for complete evaporation of the drop, are shown in Table 2.

This study has thus made it possible to determine the evaporation kinetics of drops of solutions in which the components have very different boiling points. It turns out that there is an initial rapid evaporation of the drops; then the evaporation rate $\dot{\mu}$ decreases and tends toward the evaporation rate of the drops of the pure second components. Using the laws of energy and mass conservation, we can find the rates at which the components evaporate from the mixture drops. We have found that there is a complete mixing in the drops and that Eq. (8) can be used to calculate x in an evaporating drop. It has been established that empirical equation (9) gives a good description of the time dependence of x .

NOTATION

m_0 , m , initial mass and instantaneous mass of evaporating drop (g); d , drop diameter (cm); ϑ , ϑ_{\min} , ϑ_m , temperatures of drop, minimum temperature, and temperature of medium; x_0 , initial weight fraction of Freon in mixture; x , weight fraction of Freon in the evaporation drop; x_M , initial mole fraction of Freon; y , weight fraction of Freon in vapor phase; $\dot{\mu} = m/d$ (g/sec · cm); \dot{m} , rate of change of drop mass; L , heat of vaporization; λ , thermal conductivity of air; S , surface area of drop; Nu , Gr , Pr , Nusselt, Grashof, and Prandtl numbers; α , heat-transfer coefficient; t_0 , time required for complete evaporation of drop; c , vapor concentration (g/cm³).

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*This conclusion was also verified by direct observations: In the evaporating drops we clearly observed an intense, ordered motion of dust particles which had entered the drops; this motion could occur only if there were a convective flow of the liquid, which would tend to equalize the concentration and temperature in the drop.