EXPERIMENTAL DETERMINATION OF THE LATENT HEAT OF EVAPORATION OF ISOMER MIXTURES

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A method is proposed for determining the latent heat of evaporation of a mixture of isomers with the aid of a mass spectrometer by employing the Clapeyron equations for multicomponent systems.

A Clapeyron equation for multicomponent systems was obtained in [1] from the conditions of equilibrium for liquid–vapor systems:

$$\sum_i (x_i - y_i)\, d\ln f^m_{y_i} = \sum_i (x_i - y_i)\, d\ln f^l_{x_i} = \frac{\Delta H - \Delta H^0}{RT^2}\, dT + \frac{\Delta V}{RT}\, dP,$$

where

$$\Delta H = H^m_y - H^l_x; \quad \Delta H^0 = H^0_y - H^0_x = \sum_i y_i H^0_i - \sum_i x_i H^0_i;$$

$$\Delta V = V^m_y - V^l_x;$$

f is the fugacity of the system components, saturated at T and P; H, molar enthalpy; P, total pressure in the system; R, gas constant; T, absolute temperature; x, molar fraction of the saturated liquid; y, molar fraction of vapor in equilibrium with the liquid; V, molar volume; l, liquid phase; m, vapor; 0, ideal gas.

Assuming that the phase composition is constant, the equation takes the form

$$\left[d\ln f^m_{y_i} = \frac{H^0_i - H^l_{y_i}}{RT^2}\, dT + \frac{V^m_{y_i}}{RT}\, dP \right]_y,$$

$$\left[d\ln f^l_{x_i} = \frac{H^0_i - H^m_{x_i}}{RT^2}\, dT + \frac{V^l_{x_i}}{RT}\, dP \right]_x.$$

For multicomponent systems the Clapeyron equation can be written in the following form [1]:

$$\left(\frac{\partial P}{\partial T}\right)_y = \frac{\Delta H + \sum_i (x_i - y_i) H^m_{y_i}}{T\left[\Delta V + \sum_i (x_i - y_i) V^m_{y_i}\right]} = \frac{\sum_i x_i H^m_{y_i} - H^l_{x_i}}{T\left[\sum_i x_i V^m_{y_i} - V^l_x\right]},$$

$$\left(\frac{\partial P}{\partial T}\right)_x = \frac{\Delta H + \sum_i (x_i - y_i) H^l_{x_i}}{T\left[\Delta V + \sum_i (x_i - y_i) V^l_{x_i}\right]} = \frac{H^m_y - \sum_i y_i H^l_{x_i}}{T\left[V^m_y - \sum_i y_i V^l_{x_i}\right]}.$$

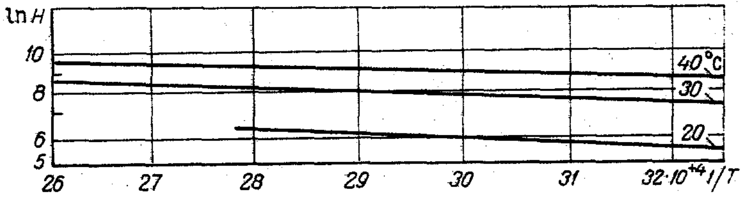

Fig. 1. Peak height of diethyl ketone–methylisopropyl ketone mixture vs inverse temperature.

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TABLE 1. Latent Heat of Evaporation of Diethyl Ketone-Methylisopropyl Ketone Isomer Mixture

t, °C	K, deg	L_x, kJ/kg
22	5350	513
30	5000	484
40	4800	463

The sum of the enthalpies is the difference between the latent heats of condensation and vapor formation. At low pressures it can be assumed that the vapor behaves as an ideal gas and the equation takes on the form

$$\left[\frac{\partial \ln P}{\partial (1/T)}\right]_x = \frac{H_y^m - \sum_i y_i H_{x_i}^l}{R}.$$

If we assume that the liquid solution is also ideal, the sum of the enthalpies is equal to the mean latent heat of evaporation of the mixture $\sum_i y_i \Delta H_i$, where ΔH_i is the latent heat of vapor formation of the pure component:

$$L_x = \sum_i y_i \Delta H_i = R\frac{d \ln P}{d(1/T)},$$

where L_x is the mean latent heat of evaporation.

Thus, in principle it is possible to measure the mean latent heat of evaporation from the slope of ln P as a function of inverse temperature. To do this the assumptions that phase composition does not change, that the liquid is ideal, and that the vapor behaves as an ideal gas must be satisfied.

A study was made of a mixture of the isomers diethyl ketone and methylisopropyl ketone, formed from chemically pure materials in a 1:1 weight ratio. An MKh-1304 mass spectrometer was used with the method described in [2].

A peculiarity of using the mass spectrometer to study materials is that the height of the mass spectrum peaks H is proportional to the partial pressures [3], so that it is sufficient to determine the slope of curves of ln H as a function of inverse temperature.

Calculations were performed with a molecular peak common to both materials. The error in determination of the latent heat of evaporation does not exceed 2%.

Figure 1 shows the dependence of mixture peak height on inverse temperature. Table 1 presents the results of the study, where K is the slope of the corresponding curves in Fig. 1.

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