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Abstract

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ON A POSSIBLE CAUSE OF DISCREPANCIES

IN THE RESULTS OF MEASUREMENTS OF RATIOS

OF EQUILIBRIUM VAPOR PRESSURES OF ISOTOPES

BY THE DIFFERENTIAL AND RAYLEIGH METHODS

(Presented by Academician N. M. Zhavoronkov, 27 X 1962)

The separation coefficient of a binary isotopic mixture in the equilibrium system vapor—condensed phase is equal to the ratio of the saturated vapor pressures of the pure isotopes: $\alpha = p_{01}/p_{02}$.

In the presence of enriched isotopes this quantity can be determined by direct measurement of the ratio of the vapor pressures of two samples differing in their isotopic composition. In the absence of enriched materials, the separation coefficient is often determined by the indirect method of quasi-equilibrium evaporation of a large amount of a mixture of isotopes to a small residue, followed by calculation of α from the formula proposed by Rayleigh (1).

Comparison of the values of α obtained by these two methods has shown that in a number of cases: $[p_{\mathrm{B}^{10}\mathrm{F}_3}/p_{\mathrm{B}^{11}\mathrm{F}_3}]$ (2,4), $[p_{\mathrm{C}^{12}\mathrm{H}_4}/p_{\mathrm{C}^{13}\mathrm{H}_4}]$ (3,5,9), $[p_{\mathrm{N}^{14}\mathrm{O}}/p_{\mathrm{N}^{15}\mathrm{O}}]$ (6,7), $[p_{\mathrm{O}2^{16}}/p_{\mathrm{O}2^{18}}]$ (8,9), considerable discrepancies are observed. The present work is devoted to clarifying the causes of such a discrepancy for boron trifluoride (Fig. 1a) and methane (Fig. 1b).

As is seen from Fig. 1, for these substances the difference in the values of the enrichment coefficients $\varepsilon = \alpha - 1$, measured by the indicated methods, is very large. In the case of boron trifluoride, according to data obtained by direct measurements (2), ε decreases with increasing temperature, whereas according to data obtained by the Rayleigh method (4), it increases.

Fig. 1. Enrichment coefficients for $B^{10}F_3$—$B^{11}F_3$ (a) and $C^{12}H_4$—$C^{13}H_4$ (b), measured by the differential method (I) and by the Rayleigh method (II)

Figure 1: Fig. 1. Enrichment coefficients for $B^{10}F_3$—$B^{11}F_3$ (a) and $C^{12}H_4$—$C^{13}H_4$ (b), measured by the differential method (I) and by the Rayleigh method (II)

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One of the causes of the discrepancies noted above may be an error connected with the nonequilibrium conduct of the evaporation process during Rayleigh distillation. The influence of evaporation kinetics on the separation coefficient of isotopic mixtures was theoretically estimated in (^{10}), where the equation was obtained:

$$\alpha = \frac{p_{01}}{p_{02}}(1+\delta), \tag{1}$$

where the kinetic correction δ is determined by the formula:

$$\delta = \frac{2-\alpha}{4} \cdot \frac{\tau_p}{\tau_B} \cdot \frac{m_2 - m_1}{m_1}.$$

For $a \ll 1$

$$\delta = \frac{1}{2} \cdot \frac{\tau_p}{\tau_B} \cdot \frac{m_2 - m_1}{m_1}.$$

Here: τ_p is the evaporation rate in the experiment, $\tau_B = \dfrac{a p_{\text{n}}}{\sqrt{2\pi m k T}}$ is the limiting evaporation rate, equal to the evaporation rate in vacuum, m_1, m_2 are the isotope masses, a is the evaporation coefficient, k is Boltzmann' s constant, and p_{n} is the saturated vapor pressure at temperature T.

According to (1), the condition of quasi-equilibrium during the evaporation of isotopic mixtures is the inequality

$$\varepsilon \gg \delta. \tag{2}$$

As is seen from equation (1), if the more volatile isotope is the light isotope (for example, methane), the separation coefficient increases when the evaporation process is conducted under nonequilibrium conditions; whereas when the more volatile isotope is the heavy isotope (for example, boron trifluoride), it decreases.

In order to determine the kinetic correction experimentally, we measured the evaporation coefficients of a number of liquids. In particular, the evaporation coefficients of BF_3 (170° K) and CH_4 (113.5° K) are, respectively, $4.8 \cdot 10^{-4}$ and $3.3 \cdot 10^{-4}$ (^{11}). Using these data, the kinetic corrections were calculated for the experiments described in (^{4,5,9}). In doing so, we assumed that the evaporation rate of liquid boron trifluoride in work (^{4}) was 0.7 $cm^3/cm^2 \cdot h$, and that the evaporation rate of methane in work (^{5}) may be taken as 0.4 $g/cm^2 \cdot h$ (from a vessel filled with liquid methane, of capacity 1 cm^3, evaporation proceeds for about one hour). It is easy to see that under these conditions inequality (2) is not satisfied. The results of the calculation are given in Table 1.

Table 1

Isotopic system	T, °K	P, mm Hg	τ_p, $g/cm^2 \cdot s$	τ_B, $g/cm^2 \cdot s$	$\delta = \frac{\tau_p \cdot \Delta m}{2\tau_B \cdot \Delta m}$
$B^{10}F_3$—$B^{11}F_3$	168.2	600	$3.1 \cdot 10^{-4}$	$1.06 \cdot 10^{-2}$	$-2.1 \cdot 10^{-4}$
$B^{10}F_3$—$B^{11}F_3$	157.2	200	$3.1 \cdot 10^{-4}$	$3.7 \cdot 10^{-3}$	$-6 \cdot 10^{-4}$
$C^{12}H_4$—$C^{13}H_4$	111.5	760	$1.1 \cdot 10^{-4}$	$5.54 \cdot 10^{-3}$	$6 \cdot 10^{-4}$
$C^{12}H_4$—$C^{13}H_4$	100.5	269.13	$1.1 \cdot 10^{-4}$	$2.07 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$

At a constant evaporation rate, the kinetic corrections increase as the temperature is lowered and reach, in order of magnitude, the values of the enrichment coefficients. These results qualitatively explain the low values and the inverse dependence of ε on temperature for $B^{10}F_3$—$B^{11}F_3$, and the high values of ε for $C^{12}H_4$—$C^{13}H_4$, obtained by the Rayleigh method (^{4,5,9}), as compared with direct measurements of vapor pressures (^{2,3}).

The kinetic corrections calculated in the present communication are minimal. In experiments using Rayleigh distillation, a decrease in the limiting evaporation rate τ_B may also occur as a result of contamination of the residue by nonvolatile impurities (especially in the final stage of evaporation), which may lead to a considerable increase in the calculated value of the kinetic correction.

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