DETERMINING THE DIFFUSIVITY OF NITROGEN TETROXIDE

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The diffusivity of nitrogen tetroxide evaporating into a nitrogen or a helium atmosphere has been determined by calculation and test.

The molecular diffusivity D is a kinetic parameter associated with static and dynamic conditions of a process. All the complexity and unwieldiness of many calculations is, indeed, connected with the determination of this quantity. There are no test data available in the technical literature on the diffusivity of nitrogen tetroxide N_2O_4.

Theoretical formulas for calculating the diffusivity have been derived by Maxwell, Boltzmann, Sutherland, et al., from the kinetic theory of gases [1, 2]. These formulas account for the fundamental relations (for instance, the inverse proportionality between diffusivity and pressure as well as the temperature dependence of diffusivity and the decrease of the latter with increasing molecular weight of the diffusing gases), but their accuracy is poor. Those theoretical relations constitute the basis of various semi-empirical formulas which are used when the physicochemical properties are known. Among the most widely used are the Gilliland formula and Andrusov formula [2, 3].

Examining the values of diffusivity given here in Table 1 and in other published sources [1, 3, 4], we see that both the Gilliland formula and the Andrusov formula yield values which are lower than those obtained in tests. The reason for this is, apparently, that the effects of the mixture concentration and composition on the diffusivity have been disregarded here, and yet these effects are significant in the case of nitrogen tetroxide. One would expect the following values of diffusivity: 0.094 cm^2/sec for the N_2O_4–air (nitrogen) system and 0.38 cm^2/sec for the N_2O_4–helium system.

The test values for the diffusivity of nitrogen tetroxide were obtained by two methods. The apparatus for both had been described earlier in [2, 3]. The special features of our apparatus were dictated by the specific characteristics of nitrogen tetroxide. In the first method we observed the steady-state evaporation process in an open cylindrical vessel. This method had been proposed by Stefan and developed by Winkelmann, with the diffusivity then to be calculated according to the Stefan formula [3, 7].

TABLE 1. Values of Diffusivity for Benzene and Nitrogen Tetroxide

System A–B	D, cm^2/sec			
	calculated values		test values	
	according to the Gilliland formula	according to the Andrusov formula	obtained by the Stefan method	obtained by the Irisov method
Benzene–air	0,072	0,069	—	0,075
Benzene–nitrogen	—	—	0,083	0,0812
Nitrogen tetroxide nitrogen	0,084	0,078	0,101	0,0985
Nitrogen tetroxide helium	0,374	0,352	0,415	0,398

According to the second method, which had been developed by A. S. Irisov [3], the diffusivity was determined from the evaporation kinetics in a closed vessel. It has been shown in [5] that evaluating the data as suggested in [3] would not necessarily yield reliable values for the diffusivity or accurate values for the vapor pressure in a closed vessel, because a certain coefficient here called the "instrument factor" appears as a constant. A theoretical relation has been derived in [6] for the case of isothermal evaporation in a closed volume, on the assumption that the diffusivity remains

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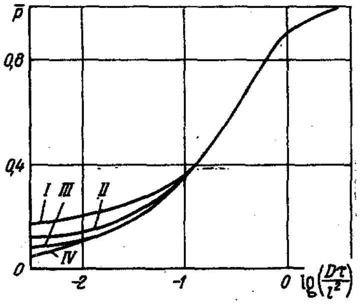

Fig. 1

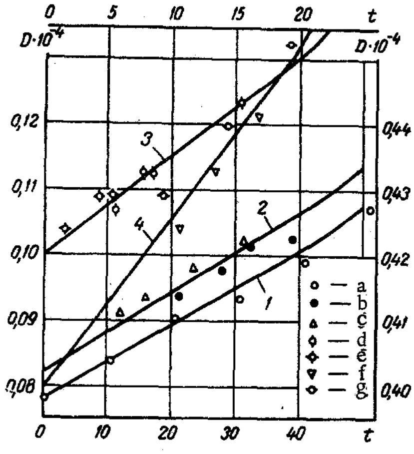

Fig. 2

Fig. 1. Relative pressure $\bar{P}$ as a function of log Fo_D. The numbers next to the curves indicate the number of terms retained in the series in expression (1).

Fig. 2. Relation D(t) for various systems: benzene-air (1), benzene-nitrogen (2), N_2O_4-nitrogen (3), N_2O_4-helium (4); test data in [1, 3] (a), Irisov method (b), Stefan method (c), Irisov method (d), Stefan method (e); for systems 1, 2, 3 the temperature scale is on the bottom and the diffusivity scale is on the left-hand side, for system 4 the temperature scale is on top and the diffusivity scale is on the right-hand side: t (°C), D (m^2/sec).

constant throughout the process. With the basic idea of the Irisov method and with our refinement of it [6], one can calculate the diffusivity for the case where the relative pressure $\bar{P} = P/P_s$ is a function of time. In our calculations we used the universal relation between the relative pressure $\bar{P}$ and the Fourier diffusion number $Fo_D = D\tau/l^2$ [6]:

$$\bar{P} = 1 - \frac{8(1-\bar{P}_0)}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\exp\{-[\pi(2n-1)]^2 Fo_D\} \tag{1}$$

shown in Fig. 1. A close confirmation of this universal relation was found in Irisov's test data [3] and in our test data [6] as regards the kinetics of N_2O_4 evaporation in a closed volume.

The values of diffusivity in Table 1, referred to 0°C, have been obtained as follows: experimentally by the Stefan–Winkelmann method and by the refined Irisov method, calculations according to the Gilliland formula and the Andrusov method. The diffusivity according to Irisov was calculated from the values of the Fourier diffusion number Fo_D, which in turn were found from the universal $\bar{P}(Fo_D)$ curve based on $\bar{P}(\tau)$ tests with T = const. and l = const.

The test values of diffusivity at the temperatures for which they have been calculated are shown in Fig. 2. Our test points agree closely with the Winkelmann relation

$$D_t = D_0\left(\frac{t+273}{273}\right)^n\cdot\frac{760}{P}.$$

The values of D_0 in Table 1 have been obtained by processing the test data on the basis of this relation. Here n = 1.75 for N_2O_4 evaporation in helium and n = 2 for all other cases.

A critical analysis of the methods used for calculation and testing yields, with satisfactory accuracy, the following values of diffusivity: 0.1 cm^2/sec for the N_2O_4-nitrogen (N_2) system and 0.4 cm^2/sec for the N_2O_4-helium (He) system.

NOTATION

P is the pressure;
P_s is the saturated-vapor pressure;

$\overline{P}$ is the relative pressure;
$\overline{P}_0$ is the initial relative pressure;
D_0, Dt is the diffusivity of vapor at 0°C and at t°C respectively.

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