PHYSICS

1965

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICS

Yu. T. MAZURENKO

A NEW METHOD FOR INVESTIGATING THERMAL DIFFUSION IN GASES

(Presented by Academician A. N. Terenin on 23 X 1964)

Investigating the action of foreign gases on the characteristics of the photoluminescence of vapors of organic compounds, B. S. Neporent (1,2) discovered the following phenomenon. When relatively small amounts of foreign gases are added to vapors of luminescing molecules, the intensity of the glow, as the concentration of the added gas increases, at first decreases rather sharply, and then, over wide ranges of the concentration of the foreign gas, remains practically constant (see Fig. 1). B. S. Neporent pointed out the clear differences between this phenomenon and the quenching process and the effect of stabilization of luminescence discovered by him, and also determined the conditions for observing it in pure form. In these same works it was shown that the observed decrease in the intensity of the glow occurs as a result of a weakening of the absorption of the light exciting the luminescence. The following simple regularity of the phenomenon was found:

$$(F - F_\infty)/(F_0 - F) \sim n_1/n_2, \tag{1}$$

here n_1 is the concentration of luminescing molecules; F_0 is the absorption in the absence of a foreign gas; F is the absorption corresponding to the concentration of molecules of the foreign gas n_2; F_∞ is the absorption corresponding to $n_2 = \infty$. Studies carried out by B. S. Neporent and co-workers (1–6) also showed that the weakening of absorption is usually the more significant, the lighter the molecules of the added gas.

Fig. 1. Change in the luminescence intensity of β-naphthylamine vapor upon addition of helium. Vapor pressure 0.53 mm Hg, temperature of the lower vessel 375° K, temperature of the upper vessel: 1—407° K, 2—427° K, 3—446° K, 5—487° K.

The effect described is the experimental basis of the new method proposed in the present work for investigating thermodiffusion in gases. Let us consider the experimental conditions essential for us in studying the luminescence of molecular vapors. The cuvette containing the substance under study consists of two vacuum vessels connected to one another—the lower and the upper. The substance under study is placed in the lower vessel in the solid or liquid state in excess, so that the vapor pressure in the cuvette is the saturated one. The temperature maintained in this vessel corresponds to the desired vapor pressure. Optical measurements are made with the aid of the upper vessel, the temperature of which, in order to avoid condensation of the vapors, must necessarily be higher than the temperature of the lower vessel (in practice by not less than 20-30°). When a foreign gas is added to the cuvette, owing to the temperature difference between its parts, a process of thermal diffusion in the mixture of the two gases and the opposite process of concentration diffusion should occur (7–9). In the established state the vapor concentration of the substance under study in the upper vessel will change, and consequently the absorption of light will change correspondingly as well (the vapor concentration in the lower vessel will remain the same, since it is determined by the temperature of the condensed phase).

Thus, the relative change in the absorption or luminescence of molecular vapors in the system described is a measure of the thermodiffusion properties of the mixture (of course, possible accompanying effects of other origin must be excluded). Comparison of the results of the experiments described at the beginning of the article with qualitative ideas about thermodiffusion, concerning the direction of the effect, as well as the character of its dependences on concentration, mass and size of the molecules, and on the temperature difference between the lower and upper vessels, fully confirms the interpretation given here.

Let us turn to the quantitative aspect of the method. In a mixture of two gases with a nonuniform temperature distribution in the stationary state, owing to the action of the processes of thermal and concentration diffusion, a concentration gradient is established, written in the form (10)

$$\operatorname{grad} c_1 = -\alpha c_1 c_2 \operatorname{grad} \ln T. \tag{2}$$

Here c_1, c_2 are the mole fractions of the two components ($c_1 + c_2 = 1$); T is the absolute temperature; α is the thermodiffusion constant, determined in the first approximation of the kinetic theory of gases (7,10).

$$\alpha = -5(C-1)(c_1 S_1 - c_2 S_2)/(c_1^2 Q_1 + c_1 c_2 Q_{12} + c_2^2 Q_2), \tag{3}$$

where C, Q, S are quantities depending on the masses of the molecules, the characteristics of their interaction, and the temperature. Let c_1 refer to the vapor, and c_2 to the added gas. Since, under the conditions of the method under discussion, usually $c_1 < c_2$, higher powers of c_1 in the expression $\alpha c_1 c_2$ may be neglected. Integration of (2), taking into account (3) and the conditions of the experiment, makes it possible to obtain the dependence of the change in vapor concentration in the upper vessel on the concentration of the added gas. It indeed has the form of the curves in Fig. 1 and is characterized by relations connecting the experimentally determined quantities with the characteristics of thermodiffusion:

$$\ln \frac{n_{1\infty}}{n_{10}} = 5(C-1)\frac{S_2}{Q_2} \ln \frac{T}{T'} = -\alpha_\infty \ln \frac{T}{T'}. \tag{4}$$

(n_1 is the vapor concentration in the upper vessel; the subscripts 0 and ∞ denote the absence of added gas and its presence in an infinitely large amount (the saturation region); T and T' are, respectively, the temperatures of the upper and lower vessels),

$$\frac{n_1 - n_\infty}{n_{10} - n_1} \approx \left(\frac{S_1}{S_2} + \frac{Q_{12}}{Q_2}\right)\left(\frac{T}{T'}\right)^{-\alpha_\infty} \frac{n_1'}{n_2'}. \tag{5}$$

Here n_1' and n_2' are, respectively, the concentrations of the vapor molecules and of the added gas in the lower vessel. Formula (5) is valid in the region $n_2' \gg n_1'$. In this region practically $p_2' = p_2$. It is not difficult to see that formula (5) corresponds to the empirical dependence (1). A very favorable circumstance, making it possible to obtain the fairly simple relations (4) and (5) and relieving the experimenter of the need to know the volumes of the upper and lower vessels and to establish a sharp temperature boundary between them (in contrast to ordinary methods), is the fact that the vapor concentration near the condensed phase depends only on its temperature. (The change in the pressure of saturated vapors under the action of the pressure of a foreign gas by several millimeters of mercury is usually quite negligible (11).) Expressions (4) and (5) include only relative changes in the concentration n_1, proportional to relative changes in the coefficient of light absorption. Consequently, to determine the thermodiffusion characteristics appearing in (4) and (5), it is necessary, after establishing the temperatures of the upper and lower vessels, to measure only the relative change in absorption or in luminescence intensity as a function of the pressure of the added gas. In this connection, the "purely optical" investigations carried out by B. S. Neporent and his collaborators in works (1–6) contain all the neces-

···the necessary data for calculating the characteristics of thermal diffusion and are thus the material embodiment of the method described in the present work.

At a cursory examination of these experiments, attention is drawn first of all to the rather high values of the thermal-diffusion constant α following from the measurement results, usually amounting to several units, which exceeds the customary values by an order of magnitude (^{8}). This result is naturally explained by the great difference in the masses and sizes of the molecules of the mixtures (complex organic compounds and light gases). The record value $\alpha = 3.6$ is attained for a mixture of 9-diacetylaminoanthracene with helium (data of V. P. Klochkov (^{5})).

Table 1

T	407	427	446	465	487
T'	375	375	375	375	375
F_∞/F_0	0.77	0.67	0.60	0.55	0.48
α_∞	3.0	2.9	3.4	2.7	2.7

The linear dependence required by formula (4) is observed quite well in all cases. Over the not very broad temperature range of the experiments, no distinct temperature dependence of α was found. As an illustration we give the results of processing the data of B. S. Neporent (^{2}) for a mixture of β-naphthylamine with helium (these data are shown in Fig. 1). Table 1 gives the numerical results of the experiment and the determined values of α_∞. Application of the results of the theory of thermal diffusion for the molecular model of solid elastic smooth spheres (^{7,10}) makes it possible, from the value of the thermal-diffusion constant, to estimate the effective "hard" diameter of the β-naphthylamine molecule. Taking for the effective diameter of the He atom the value 2.1 Å, determined from the viscosity at 400° K, we obtain, for $\alpha_\infty = 3.0$, an effective diameter of 5.6 Å for the β-naphthylamine molecule. In view of the crudeness of the hard-sphere model, this value should be regarded as illustrative.

In conclusion, let us note some possibilities for the application of the method described, connected with its essential differences from the usual two-bulb method with analysis of the composition of the mixture. Owing to its selectivity with respect to one of the components and to the high sensitivity of concentration analysis by absorption or luminescence in the described device, measurements of the thermal-diffusion constant are possible at the edge of the concentration dependence ($c_1 \ll c_2$), including practically at the point $c_1 = 0$. In this region, and especially at $c_1 = 0$, the formulas of thermal diffusion, known for their complexity, are substantially simplified (^{10}). The described method considerably broadens the possibilities for investigating gaseous thermal diffusion and, consequently, intermolecular interactions for substances that are solid and liquid under ordinary conditions (including low-volatile ones). This is all the more valuable because the experimental material accumulated to date on thermal diffusion relates mainly to natural gases (^{8}). Among the most interesting normally solid or liquid objects in this respect are metals, as well as organic compounds with conjugated double bonds, a certain class of which possesses color and often bright luminescence.

The author expresses gratitude to his supervisor B. S. Neporent for proposing the study of the problem and for his interest and attention to the work.

Received
16 X 1964

REFERENCES

1. B. S. Neporent, Doctoral dissertation, State Optical Institute, 1945.
2. B. S. Neporent, DAN, **72**, 35 (1950).
3. B. S. Neporent, A. A. Solodovnikov, Optics and Spectroscopy, **1**, 951 (1956).
4. B. S. Neporent, V. P. Klochkov, Optics and Spectroscopy, **3**, 529 (1957).
5. V. P. Klochkov, Candidate dissertation, State Optical Institute, 1958.
6. S. O. Mirumyants, B. S. Neporent, Optics and Spectroscopy, **9**, 7 (1960).
7. S. Chapman, T. Cowling, *The Mathematical Theory of Non-uniform Gases*, IL, 1960.
8. K. E. Grew, T. L. Ibbs, *Thermal Diffusion in Gases*, Moscow, 1960.
9. J. Hirschfelder, Ch. Curtiss, R. Bird, *Molecular Theory of Gases and Liquids*, IL, 1961.
10. S. Chapman, Proc. Roy. Soc. London, A**177**, 38 (1940).
11. M. Kh. Karapetyants, *Chemical Thermodynamics*, Moscow–Leningrad, 1953.

Note: Figure translations are in progress. See original paper for figures.