DIFFUSION OF MERCURY VAPOR IN GASES

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The results of experimental investigation of diffusion of the vapor of mercury and other metals in gases and a correlation of the data are given.

The literature gives contradictory information about the coefficients of diffusion of mercury vapor in gases. According to some data [1], the coefficient of diffusion of mercury vapor in nitrogen is low — at 273°K and atmospheric pressure $D_{12} = 0.119 \cdot 10^{-4}$ m²/sec, whereas according to other data [2], it is much higher — at the close temperature 292°K and atmospheric pressure $D_{12} = 0.325 \cdot 10^{-4}$ m²/sec.* At the same time, available data [3] on the diffusion of vapor of zinc (a metal of the same subgroup of the periodic table) in inert gases and nitrogen can be used to correlate and assess the reliability of the various data on the diffusion of mercury vapor in gases. For the correlation we use the method of thermodynamic similarity, developed in [4]. The diffusion cross section of molecular interaction $Q_{12}^{(1,1)}$ (Å²), which is connected with the diffusion coefficient D_{12} (m²/sec) by the first-approximation relation of the Enskog and Chapman theory [5],

$$Q_{12}^{(1,1)} = 0{,}0266 \sqrt{T^3(M_1+M_2)/2M_1M_2}/PD_{12}, \tag{1}$$

will, in the case of monotypical mixtures of metal vapors with inert gases or nitrogen,† be a function of the ionization energy of the metal (I_1) and gas (I_2), and also a function of the polarizability of the metal (α_1) and gas (α_2). This follows from the fact that the potential energies of exchange and dispersion interatomic interactions, which determine the cross section, depend primarily, according to quantum-mechanical ideas [6, 7], on I_1, I_2, α_1, and α_2. The polarizabilities, in turn, within the subgroups of the periodic table are also functions of the ionization energies. Thus, for mixtures of vapors of metals of the same subgroup with gases,

$$Q_{12}^{(1,1)} = f(I_1,\ I_2). \tag{2}$$

In this case the ionization energies (expressed in atomic units, for instance) can, as the quantum-mechanical relations indicate, be regarded as dimensionless quantities. As a dimensionless quantity, including the diffusion cross section, we take the complex

$$\bar{Q}_{12}^{(1,1)} = \frac{Q_{12}^{(1,1)}(kT/I_2)^m}{\alpha_2^{2/3}},$$

where m is the index of the temperature relation $Q_{12}^{(1,1)} \sim T^{-m}$. From the relation $D_{12} \sim T^n$, using (1), we obtain $m = n - 1.5$. The polarizability α_2 is 0.207 Å³ for helium, 1.63 Å³ for argon, and 1.74 Å³ for nitrogen N_2 [8].

Taking the above into account we can rewrite relation (2) in the following form:

$$\bar{Q}_{12}^{(1,1)} = f_1\left(\frac{I_2}{I_1},\ I_1\right). \tag{3}$$

We use the data of [3] for the diffusion of zinc vapor in helium, argon, and nitrogen. For all three mixtures in the experimental temperature range (820-1130°K) the index m = 0.25. The spread of the experimental values of D_{12} was 14 to 22% in experiments with different mixtures.

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*In [2] a value 100 times greater was erroneously reported.

†Metal vapors at low pressures are practically monatomic; inert gases are also monatomic. The N_2 molecules is similar to the argon atom in the structure of the outer electron shell.

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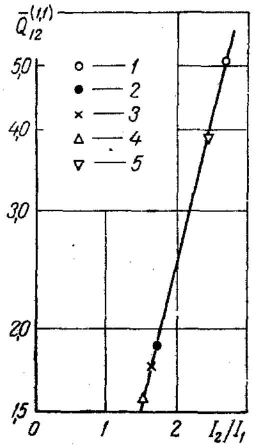

Fig. 1. Plot of dimensionless diffusion cross section against ratio of ionization energies: 1) Zn–He (data of [3]); 2) Zn–Ar (data of [3]); 3) Zn–N_2 (data of [3]); 4) Hg–N_2 (data of [2]); 5) Hg–He (our data).

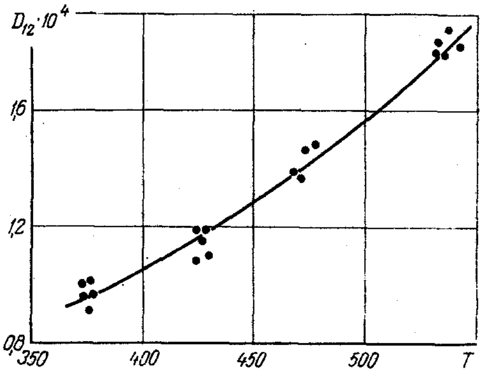

Fig. 2. Experimental plot of coefficient of diffusion of mercury vapor in helium against temperature (the values of D_{12} are given for pressure $P = 9.81\cdot 10^4$ N/m^2). D_{12}, m^2/sec; T, °K.

The results of treatment of the data of [3] are shown in Fig. 1 in the form of a plot (in semilogarithmic coordinates) of the complex $\bar{Q}_{12}^{(1,1)}$ against the ratio I_2/I_1. Since one metal (zinc) is taken, the value of I_1 is constant. The line in Fig. 1 connecting the experimental points is given by the relation [4]

$$\bar{Q}_{12}^{(1,1)} = a \exp\left(b\,\frac{I_2}{I_1}\right), \tag{4}$$

where $a = 0.31$, $b = 1.06$.

This equation, as shown in [4], is valid also for the values of $\bar{Q}_{12}^{(1,1)}$ corresponding to the data of [3] for the diffusion of lead vapor in helium, argon, and nitrogen, and also to the data of [9] for the diffusion of vapor of two alkali metals with similar ionization energies — cesium ($I_1 = 0.143$ amu) and potassium ($I_1 = 0.159$ amu) in helium and argon. For the case of diffusion of lead vapor we can take $m = 0.22$, $a = 0.31$, and $b = 0.92$. In the experiments with lead in [3] the temperature varied from 1100 to 1300°K, and the spread of the experimental values of D_{12} did not exceed 14-16%. For the case of diffusion of cesium and potassium vapor $m = 0.15$, $a = 0.34$, and $b = 0.54$. The temperature range in the experiments in [9] was 630-840°K for cesium and 723-830°K for potassium, and the spread of the experimental values of D_{12} did not exceed ±15%.

We compare the values of $\bar{Q}_{12}^{(1,1)}$ found from the data of [1, 2] for the diffusion of mercury vapor in nitrogen with the values calculated from Eq. (4). The ionization energy I_1 on changeover from zinc to mercury is not greatly altered (for zinc $I_1 = 0.345$ amu, and for mercury $I_1 = 0.384$ amu). For this reason we retain only the ratio I_2/I_1 as a characteristic quantity and test if relation (4) with the values of a and b found for zinc can be applied to the data for mercury. We find that the data of [1] lead to greatly overestimated values of $\bar{Q}_{12}^{(1,1)}$ (by a factor of 2.3). The data of [2], however, correspond fairly well with the correlation. If we use $m = 0.3$, the experimental value of $\bar{Q}_{12}^{(1,1)}$ exceeds that calculated from Eq. (4) by only 5%.

For a more reliable test of the applicability of relation (4) for calculation of the diffusion coefficients for mercury vapor in gases, we carried out special experiments.

We determined the diffusion coefficient of mercury vapor in helium. As in [3, 9], we used Stefan's method; i.e., we found the diffusion coefficient from the rate of evaporation of metal through a column of gas in a diffusion tube. The experimental apparatus, designed for experiments with mercury, included a thermostat, which contained a stainless steel diffusion tube 79 mm high and 12 mm in diameter with an appropriate directing device for admission of the gas. The open top end of the diffusion tube was closed with a ground steel stopper,

TABLE 1. Experimental Values of Coefficient of Diffusion of Mercury Vapor in Helium, Referred to Pressure $9.81 \cdot 10^4$ N/m²

T, °K	$D_{12} \cdot 10^4$, m²/sec	T, °K	$D_{12} \cdot 10^4$, m²/sec	T, °K	$D_{12} \cdot 10^4$, m²/sec
375	1,04	423	1,17	471	1,51
374	0,97	422	1,20	540	1,89
373	0,96	421	1,10	545	1,83
374	0,89	464	1,39	539	1,81
373	1,01	465	1,38	538	1,82
424	1,19	468	1,49	539	1,84
424	1,20				

which could be removed, after the prescribed temperature was attained, by means of a special device with a Wilson seal (without admission of air to the apparatus). The rate of helium flow past the open end of the diffusion tube was about 30 liter/h (for cold gas at atmospheric pressure). This ensured a more than hundredfold dilution of the vapor at the outlet of the tube. With this gas flow rate, however, the vorticity at the mouth of the diffusion tube did not have any appreciable effect on the determined values of the diffusion coefficient. This was confirmed in similar conditions in experiments on the diffusion of vapors of cesium [9], zinc and lead [3], and of mercury in our experiments. The use of diffusion tubes of different heights did not lead to any change in the values of the diffusion coefficient.

The gas was withdrawn from the apparatus by a forepump (through a receiver), which enabled us to conduct experiments at reduced pressures (from 100 to 500 mm Hg). Before the pump the gas was passed through a cooler and a throttle for removal of the mercury vapor. After the pump the gas was passed through absorbing vessels, where it was bubbled through a solution of ferric chloride. This ensured the removal of all the mercury vapor from the gas.

The experiments were conducted in the temperature range 375-548°K.

In the treatment of the experimental results we used the data given in [10] for the saturated vapor pressure of mercury. The obtained values of the diffusion coefficient, referred to a pressure of $9.81 \cdot 10^4$ N/m², are given in Table 1 and are plotted against temperature in Fig. 2.

The spread of the experimental values of D_{12} did not exceed ±5%. The index of the power in the temperature dependence of the diffusion coefficient was $n = 1.75$, i.e., $m = 0.25$. The value of $\overline{Q}_{12}^{(1,1)}$ corresponds well with relation (4). The corresponding points are marked in Fig. 1. Thus, relation (4) is suitable for determination of the diffusion coefficients for zinc vapor and mercury vapor in the considered gases. It is quite certain also that the obtained correlation can be used for calculations of the diffusion coefficients of the vapor of cadmium (which is in the same subgroup of the periodic table) in helium, argon, and nitrogen. The value of the ionization energy for cadmium ($I_1 = 0.330$ amu) did not differ greatly from the value for zinc. We can also assert that Eq. (4) with the values of m, a, and b corresponding to the diffusion of lead vapor can be used to calculate $\overline{Q}_{12}^{(1,1)}$ for the case of diffusion of the vapor of tin, which belongs to the same subgroup as lead. The ionization energies I_1 for lead and tin are close (0.273 and 0.268 amu, respectively).

It should be noted that the index m and coefficients a and b are monotonic functions of the ionization potential I_1 of the metal (the values of m and b increase with increase in I_1, and the value of a decreases slightly). Small changes in I_1 have little effect (within the limits of accuracy of the correlation). The appreciable change of I_1 on changeover from potassium to sodium (for which $I_1 = 0.189$ amu) leads to a significant increase in $\overline{Q}_{12}^{(1,1)}$ (owing to the increase in coefficient b by a factor of 1.2). The available data on the diffusion of sodium vapor in gases [11] confirm this.

The method of calculating the diffusion coefficient by means of the obtained correlation is as follows. Assigning the values of m, a, and b appropriate to the particular subgroup of the periodic system we find from relation (4) the value of $\overline{Q}_{12}^{(1,1)}$ and then the value of $Q_{12}^{(1,1)} = (\alpha_2^{2/3}\overline{Q}_{12}^{(1,1)})/(kT/I_2)^m$ (Å²) for the prescribed temperature. We then use Eq. (1) to determine the value of the diffusion coefficient D_{12} for the prescribed temperature and pressure. The error of determination of the diffusion coefficient will not exceed the error of the experimental data used in the correlation (not more than 15-18% on the average).

The previously cited values of the index m correspond to the temperature ranges of the conducted experiments. For reliable extension beyond this temperature range we can use the results of the following more thorough correlation for the parameters of the potential function determining the cross section $Q_{12}^{(1,1)} = \sigma_{12}^2\Omega_{12}^{(1,1)*}$. The depth of the potential well on the curves representing the metal—gas interaction energy does not exceed in temperature units a few hundred degrees Kelvin for mixtures of zinc, mercury, and lead with gases, or a few tens or even a few degrees for mixtures of alkali metals with gases [12, 13]. Hence, for the relatively high temperatures of interest to us we can confine ourselves to the near branch of the interaction curve, corresponding to repulsion. The potential energy can be approximated by the function

$$\varphi = A\exp(-r/\rho). \tag{5}$$

Each specific mixture of metal vapor and gas has its own values of parameters A and ρ.

We calculated the collision integrals for the potential function (5), including the collision integral determining the cross section $Q_{12}^{(1,1)}$. The corresponding equations and tables are given in [14]. From the experimental values of the diffusion coefficients for mercury vapor in helium (from the data in this paper), and for vapors of zinc and lead [3], cesium and potassium [9], and sodium [11] in gases we selected the parameters A and ρ. We found that for metals of all the considered subgroups the dimensional quantities A/I_2 and $\rho/\alpha_2^{1/3}$ can be expressed as functions of I_2/I_1 by means of the equations

$$\frac{A}{I_2} = \beta\exp\left(-\gamma\frac{I_2}{I_1}\right), \tag{6}$$

$$\frac{\rho}{\alpha_2^{1/3}} = \delta\exp\left(\varkappa\frac{I_2}{I_1}\right), \tag{7}$$

where for mercury $\beta = 25$, $\gamma = 0.5$, $\delta = 0.15$, and $\varkappa = 0.55$.

Equations (6) and (7) correspond also to the data of [3, 9, 11] for the diffusion of vapors of other metals. For lead $\beta = 29$, $\gamma = 0.37$, $\delta = 0.13$, $\varkappa = 0.49$; for cesium and potassium $\beta = 6.4\cdot10^3$, $\gamma = 0.20$, $\delta = 0.064$, $\varkappa = 0.33$; for sodium $\beta = 4.5\cdot10^3$, $\gamma = 0.20$, $\delta = 0.072$, $\varkappa = 0.33$. The change in the coefficients on changeover from cesium and potassium to sodium is due to the appreciable increase in I_1. The increase in I_1 on subsequent changeover to lead and zinc (mercury) leads to a sharp reduction of the coefficient β and an increase in coefficients γ, δ, and .

The error of the discussed correlation does not exceed the error of the previous correlation (which is determined by the accuracy of the initial data. For sodium Eqs. (6) and (7) and Eq. (4) (including the dependence of the coefficients on I_1) are confirmed also by the new data that we obtained. Using Stefan's method we determined, to an accuracy of ±10%, the values of the diffusion coefficients for sodium in argon at 810-880°K (as against 655°K in the experiments in [11]).

By using Eqs. (6) and (7), and also the equations and tables in [14], the cross section $Q_{12}^{(1,1)}$ can be calculated for mixtures of vapors of mercury, cadmium, zinc, and metals of other subgroups with helium, argon, and nitrogen with due allowance for temperature. The diffusion coefficients D_{12} can then be determined from Eq. (1). Outside the temperature ranges in which the experimental data were contained the temperature dependences of $Q_{12}^{(1,1)}$ and, hence, D_{12} are slightly altered (they become weaker with increase in temperature). This is taken into account in the considered calculations.

NOTATION

D_{12}, diffusion coefficient, m²/sec; T, absolute temperature, °K; M, molecular weight, kg/kmole; P, total pressure, N/m²; I, ionization energy (potential), J or amu; α, polarizability, Å³; k, Boltzmann constant, J/°K; σ, geometric parameter of molecular interation (mean diameter of molecules in rigid-sphere model), Å; $\Omega_{12}^{(1,1)*}$, reduced collision integral of molecules (for diffusion); φ, potential energy of molecular interaction, J; r, intermolecular spacing, Å; A, ρ, parameters in equation for potential energy of interaction, J, Å. Indices: 1, metal vapor; 2, gas; 12, mixture of metal vapor and gas.

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EFFECT OF LEADING EDGE ON FREE-CONVECTION HEAT TRANSFER

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The leading edge affects heat transfer at moderate values of the Grashof number. The results of calculations are compared with experimental results.

The experimental investigation of free-convection heat transfer shows that the experimental data for the heat-transfer coefficient deviate significantly and systematically from the curve determined by boundary-layer theory in the region $\mathrm{Gr} < 10^4$ [1]. This is consistent with general ideas on the nature of free-convection heat transfer, according to which there is an induced flow upstream of the leading edge, which causes intensification of heat transfer [2, 3]. It was shown in [4] by integral methods that in the case of an isothermal plate the leading edge affects the relative vertical position of the boundary layer on the plate, but not the velocity and temperature profiles.

The effect of the leading edge is manifested at moderate values of the Grashof number, when the interaction of the boundary layer with the external flow must be taken into account. This interaction is obtained by the method of matched asymptotic expansions, and for the local heat-transfer coefficient at $\mathrm{Pr} = 0.72$ we have [5]

$$\mathrm{Nu}_x = 0.356\,\mathrm{Gr}_x^{1/4} + c_1 0.072\,\mathrm{Gr}_x^{-1/12} + 0.891\,\mathrm{Gr}_x^{-1/4} + O(\mathrm{Gr}_x^{-1/2}), \tag{1}$$

where c_1 is an indeterminate constant in the characteristic solution. The obtained solution has a singularity on the leading edge and represents the flow only in the region $x > 0$. To shift the singularities in the direction of their true position, we deform the longitudinal coordinate x by the formula

$$x = X + \mathrm{Gr}^{-1/4} f(X,\ y\,\mathrm{Gr}^{1/4}). \tag{2}$$

The function f is determined from the conditions for conservation of the self-similar nature of the solution and the exponential decrease in vorticity on the outer boundary of the boundary layer.

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