

DIFFUSION OF METAL VAPORS IN GASES AND THE TRANSPORT PROPERTIES
OF VAPORS

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Test data on the diffusion of metal vapors in gases and on the viscosity of the vapors are generalized. The ionization energies and the polarizabilities are chosen as the scales.

The results of measurements of the coefficients of diffusion of monatomic vapors of metals in gases can be approximated with the power-law formula

$$PD_{12} = C(T/1000)^n. \quad (1)$$

Values of the constant C and the exponent n for a number of mixtures are presented in Table 1 (with an indication of the literature sources). Test values of PD_{12} established by the Stefan method (from the rate of vaporization of the metal through the gas) were used.

For the generalization of data on coefficients of diffusion it is convenient to use a modified method of thermodynamic similarity [3, 4], in which the ionization energies I_1 and I_2 and the polarizabilities α_1 and α_2 of the metal and gas, which determine the exchange and dispersion interactions [5, 6] and, hence, the diffusion cross section $Q_{12}^{(1,1)}$, are chosen as the scales. The value of the cross section $Q_{12}^{(1,1)}$ (\AA^2) can be established from the value of PD_{12} (N/sec) using the formula (from the first approximation of the theory of Enskog and Chapman [7])

$$Q_{12}^{(1,1)} = 0.0266 \sqrt{T^3(M_1 + M_2)/(2M_1M_2)}/PD_{12}. \quad (2)$$

The quantities I_1 , I_2 , α_1 , and α_2 , expressed in atomic units, for example, can be treated as dimensionless. Introducing the dimensionless cross section $\bar{Q}_{12}^{(1,1)}$, we can write

$$\bar{Q}_{12}^{(1,1)} \equiv Q_{12}^{(1,1)} (kT/I_2)^m / \alpha_2^{2/3} = f(I_1, I_2, \alpha_1, \alpha_2), \quad (3)$$

where $m = n - 1.5$.

Within the limits of subgroups of D. I. Mendeleev's periodic system there exists one-to-one dependences between the polarizabilities and the ionization energies [4]. Therefore, it is sufficient to retain the quantities I_1 and I_2 as the arguments on the right side of (3). An analysis of the test data of Table 1 with $Q_{12}^{(1,1)}$ determined from Eq. (2) showed that the dimensionless cross section satisfies the relation

$$\bar{Q}_{12}^{(1,1)} = a \exp(bI_2/I_1), \quad (4)$$

where the coefficients a and b depend on I_1 (with the coefficient a varying little). The exponent m in (3) also depends on I_1 . Equation (4) proved to be valid (with a single dependence of b and m on I_1) for mixtures of vapors of metals of different subgroups with inert gases — helium and argon — as well with nitrogen. The dependence of b and m on I_1 (Fig. 1) can be expressed through the formulas

$$\left. \begin{aligned} b = 0.55, \quad m = 0.15 \quad \text{for} \quad 0.14 \text{ a.e.} \leq I_1 \leq 0.16 \text{ a.e.}, \\ b = 3.2I_1 + 0.045, \quad m = 0.65I_1 + 0.045 \quad \text{for} \quad 0.16 \text{ a.e.} < I_1 < 0.33 \text{ a.e.}, \\ b = 1.05, \quad m = 0.25 \quad \text{for} \quad 0.33 \text{ a.e.} \leq I_1 \leq 0.39 \text{ a.e.} \end{aligned} \right\} \quad (5)$$

Here $\alpha = 0.35$ in the case of $I_1 = 0.14-0.19$ a.u. and $\alpha = 0.32$ in the case of $I_1 > 0.19$ a.u.

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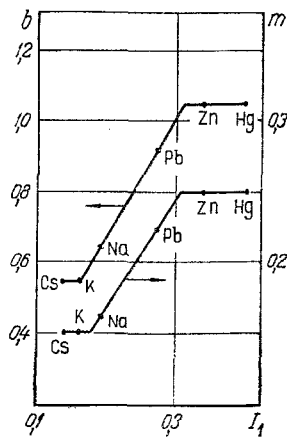


Fig. 1. Coefficient b in Eq. (4) and exponent m in Eq. (3) as functions of the ionization energy I_1 of the metal.

TABLE 1. Values of the Coefficient C and the Exponent n in Eq. (1) for Mixtures of Metal Vapors and Gases

Mixture	$C, N/sec$	n	Temperature range of tests, °K	Test error (scatter of values of PD_{12}), %
Cs—He [1]	34,5	1,65	600—820	±15
Cs—Ar [1]	11,5	1,65	630—840	±15
K—He [1]	51,0	1,65	723—830	±15
K—Ar [1]	17,7	1,65	723—830	±15
Pb—He [2]	37,9	1,72	1100—1320	±15
Pb—Ar [2]	10,9	1,72	1100—1300	±16
Pb—N ₂ [2]	11,7	1,72	1130—1330	±13
Zn—He [2]	45,3	1,75	830—1100	±22
Zn—Ar [2]	12,8	1,75	820—1100	±14
Zn—N ₂ [2]	15,7	1,75	830—1140	±16
Hg—He [3]	52,0	1,75	373—550	±5

A calculation using Eqs. (2)–(5) leads to values of PD_{12} differing by no more than 5–10% from the average test data used in the generalization; the corresponding data are presented in Table 2. Test values of PD_{12} for mixtures of sodium vapor with helium, argon, and nitrogen [8] and for mixtures of chromium, iron, manganese, cobalt, and nickel vapors with argon [9] and those calculated from Eqs. (2)–(5) are also compared in the same table. The deviations of the calculated values from the average test data also do not exceed 10% and do not go beyond the limits of the test accuracy.

In the literature there are also series of data on the coefficients of diffusion of metal vapors in inert gases established by different methods: For example, from the time of relaxation of excited Zeeman levels of alkali metals in atmospheres of inert gases (review [10]), from the time variation of the concentration of metal atoms, vaporized by an electric discharge, in gases, established using the atomic-absorption method [11 and others], from the velocity of diffusion of metal (mercury, cadmium) vaporized from a needle in a laminar gas stream [12, 13], by the Stefan method and its modifications [14, 15], and from the rate of condensation of a metal (potassium) from a mixture with an inert gas [16]. Some of these data agree with the generalization obtained, but there are also deviations (up to ±20% and more), which is possibly connected with inaccuracies in the treatment of the initial data when determining the coefficients of diffusion (owing to the complicated conditions of diffusion). The deviations pertain, for example, to data obtained with the atomic-absorption method. Deviations are also observed when the coefficients of diffusion are determined from the time of relaxation of excited Zeeman levels. In this case the measurement results for different series of tests can diverge twofold or more. And yet some of the data agree with the generalization. The results on diffusion of mercury vapor in argon and nitrogen [12, 13, 15] agree with the generalization,* but the test values of the coefficient of diffusion of cadmium vapor

*As shown by the refinements which were made, the test values of the coefficient of diffusion of mercury vapors in nitrogen of [14], in contrast to the results of [3], are about 15% lower than those calculated from the generalization. Also, the data given in [17] are strongly overstated.

TABLE 2. Calculated (from the generalization) and Test Values of $PD_{1,2}$ and Their Ratio d for Mixtures of Metal Vapors with Gases

Mixture	T, °K	$PD_{1,2}$ (calculated), N/sec	$PD_{1,2}$ (test), N/sec	d
Cs—He [1]	723	19,3	20,3	0,95
Cs—Ar [1]	723	6,4	6,8	0,94
K—He [1]	723	28,6	30,0	0,95
K—Ar [1]	723	10,0	10,4	1,01
Na—He [8]	655	22,7	22	1,03
Na—Ar [8]	655	9,0	8,9	1,01
Na—Ar	1000	18,2	17,6	1,03
Na—N ₂ [8]	655	10,0	9,2	1,09
Pb—He [2]	1000	38,0	37,9	1,003
Pb—Ar [2]	1000	10,3	10,9	0,945
Pb—N ₂ [2]	1000	12,2	11,7	1,04
Cr—Ar [9]	1873	39,6	40,5	0,98
Mn—Ar [9]	1873	37,9	39,4	0,96
Fe—Ar [9]	1873	36,0	33,3	1,08
Co—Ar [9]	1873	35,4	36,4	0,97
Ni—Ar [9]	1873	36,0	34,3	1,05
Zn—He [2]	1000	41,3	45,3	0,91
Zn—Ar [2]	1000	12,3	12,8	0,96
Zn—N ₂ [2]	1000	14,0	15,7	0,89
Hg—He [3]	1000	56,8	52,8	1,08
Hg—Ar	543	4,2	3,9	1,08
Hg—N ₂	1000	14,5	13,2	1,10

in nitrogen of [13] are more than 30% higher than those calculated from the generalization. In these tests the cadmium vapor, in contrast to the mercury vapor in the tests of [13] on the same installation, were supersaturated to a very high degree (because of the extremely low saturation pressure for cadmium at the test temperature of about 300°K), which might affect the concentration profile of the metal atoms (owing to the possible formation of aggregates of atoms and volumetric condensation) and serve as a source of errors in the determination of the coefficient of diffusion.

In the literature there are also data on the coefficients of diffusion of metal vapors in gases established from the results of measurements of the concentration distribution of the metal after vaporization in an arc discharge. These results cannot be used for comparisons, however, because of their gross inaccuracy, since the treatment of the test data is incorrect in connection with ignoring the influence of the convection currents which arise and the large temperature gradient.

In addition, direct calculations of the diffusion cross sections $Q_{1,2}^{(1,1)}$ and the coefficients of diffusion $D_{1,2}$ have been made from theoretically obtained potentials of the interaction between atoms of an alkali metal and an inert gas [18, 20].

Potentials found by two methods were used in the calculations. These are the Hartree-Fock interaction functions for the pairs Li—He and Na—He calculated by the method of molecular orbitals with basis functions of the Slater type [18]. Interaction functions for all pairs of atoms of an alkali metal and an inert gas were also obtained in [19] using a semiempirical potential model. An improvement of this method made in [20] by increasing the number of states taken into account in the atomic basis led to an improvement of the results. And these more precise potentials for the ground states were used in calculating the coefficients of diffusion.

Since the depths of the wells (from several or tens of degrees up to, in the extreme case, one to two hundred degrees for heavy inert gases) are slight compared with the temperature level, in the region from 600 to 1600°K the potential curves are well approximated by the expression

$$\varphi(r) = A \exp(-r/\rho).$$

Consequently, according to [21],

$$Q_{1,2}^{(1,1)} \equiv \sigma^2 \Omega^{(1,1)*} = 4 \alpha^2 \rho^2 I(1,1),$$

where $I(1, 1)$ is the collision integral, tabulated in [21] as a function of $\alpha = \ln(A/kT)$. Thus, we find $PD_{1,2}$ from Eq. (2).

TABLE 3. Calculated (from the theoretical potential) Values of $PD_{1,2}$ for Mixtures of Vapors of Alkali Metals with Helium and Argon; d_1 is the Ratio of Calculated Values of $PD_{1,2}$ to Those Found from the Generalization

Mixture	T, °K	$PD_{1,2}$, N/sec	d_1
Cs—He	1000	37,5	1,14
Cs—He	723	23,4	1,21
Rb—He	1000	45,1	1,07
K—He	1000	41,8	0,86
K—He	723	25,8	0,90
Na—He	1000	42,6 (44,5)	0,93 (0,97)
Na—He	655	19,9 (19,6)	0,87 (0,86)
Li—He	1100	70,0 (72,9)	1,05 (1,09)
Cs—Ar	1000	10,0	0,92
Cs—Ar	723	5,8	0,90
Rb—Ar	1000	11,4	0,85
K—Ar	1000	13,5	0,79
K—Ar	723	7,9	0,79
Na—Ar	1000	16,7	0,92
Na—Ar	655	8,0	0,89
Li—Ar	1100	33,3	0,93

In Table 3 we present the results of calculations of $PD_{1,2}$ from the potentials of [20] for mixtures with He and Ar, and we also give the ratio d_1 of the values of $PD_{1,2}$ calculated from the theoretical potential and found from the generalization. The corresponding values obtained using the interaction curves from [18] are given in parentheses. It is seen that the disagreements basically do not go beyond the limits of the test accuracy. A similar picture is observed for mixtures with Kr and Xe. For certain K—Kr, K—Xe, Rb—Xe, and Cs—Xe mixtures, however, the departure of the calculated values of $PD_{1,2}$ from those found from the generalization increases to 19%, while for mixtures with Ne the error reaches 38%. This is possibly connected with inaccuracy of the potential curves used. An experimental test of the results for mixtures of vapors of alkali metals with heavy inert gases and with neon is desirable.

On the whole, the existing confirmations of the correctness of the proposed generalization allow one to use it, i.e., Eqs. (2)-(5), with confidence in calculations of the coefficients of diffusion of metal vapors in inert gases and nitrogen for cases which are still unstudied and difficult to subject to experiment.

A generalization was also made for the parameters of the interaction of metal atoms with each other. From data on the viscosity of monatomic metal vapors [22-27], using an equation of the first approximation of the theory of Enskog and Chapman [7],

$$\eta = 2,67 \cdot 10^{-2} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)*} (kT/\epsilon)},$$

we found the effective values of the parameters σ and ϵ of the Lennard-Jones potential

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

which are presented in Table 4. The accuracy in fitting the values of σ and ϵ was $\pm 1\%$ with respect to viscosities for alkali metals and $\pm 2\%$ for zinc, cadmium, and mercury (when the test accuracy is several percent). The values of σ and ϵ obtained for alkali metals were also checked against values of the coefficient of thermal conductivity of the vapors given in the literature, and convergence within the limits of the experimental accuracy was obtained.

Values of the parameters of the Lennard-Jones potential for inert gases [7] and the values of the ionization energies I and polarizabilities α are also presented in Table 4. For alkali metals and inert gases the values of the polarizabilities are taken from the data of [6, 28], while for cadmium, zinc, and mercury they were estimated from the presumed dependence $\alpha = \alpha(I)$ of [4].

In calculating the ratios $\sigma/\alpha^{1/3}$ and ϵ/I (Table 4) it was found that these ratios are one-to-one functions of the ionization energy I within the limits of subgroups of the periodic

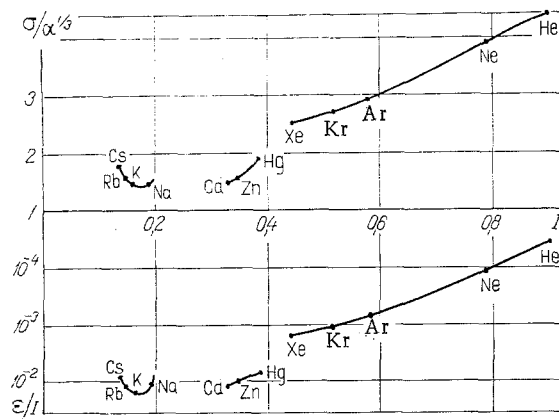


Fig. 2. The quantities $\sigma/\alpha^{1/3}$ and ϵ/I as functions of the ionization energy I , a.u.

TABLE 4. Values of α , I , σ , ϵ/k , $\sigma/\alpha^{1/3}$, and ϵ/I for Metal Vapors and Inert Gases

Gas (vapor)	Cs	Rb	K	Na	Li	Cd	Zn	Hg	Xe	Kr	Ar	Ne	He
α , Å ³	36	29(32)	29	18	15	4,6	4	3,1	4,03	2,46	1,63	0,39	0,207
I, a.u.	0,143	0,154	0,159	0,189	0,198	0,330	0,344	0,384	0,445	0,515	0,579	0,790	0,901
σ , Å	5,91	5,16	4,48	3,84	3,95	2,58	2,46	2,91	4,05	3,61	3,46	2,85	2,57
ϵ/k , °K	370	435	700	615	500	1260	1040	825	229	190	116	27,5	10,2
$\sigma/\alpha^{1/3}$	1,78	1,63	1,46	1,47	1,60	1,54	1,55	1,98	2,52	2,68	2,98	3,94	4,34
$(\epsilon/I) \cdot 10^4$	82	112	139	106,5	80	121	95,5	68,4	16,3	11,7	6,34	1,10	0,36

system (Fig. 2). The generalization obtained makes it possible, for example, to determine the effective parameters of the Lennard-Jones potential for lithium atoms (see Table 4) (test data on the transfer properties in lithium vapors are absent from the literature). If these values are used in calculations of the viscosity and thermal conductivity of monatomic lithium vapors, then for the temperature region of 800–2000°K we arrive at practically the same values as in detailed calculations based on kinetic theory [29], made using a computer. For $T = 800^\circ\text{K}$, for example, $\eta = 100 \cdot 10^{-7}$ kg/(m·sec) and $\lambda = 450 \cdot 10^{-4}$ W/(m·°K) according to our calculation, while $\eta = 103 \cdot 10^{-7}$ kg/(m·sec) and $\lambda = 463 \cdot 10^{-4}$ W/(m·°K) according to the calculations of [29]. For $T = 2000^\circ\text{K}$, correspondingly, $\eta = 208 \cdot 10^{-7}$ kg/(m·sec) and $\lambda = 930 \cdot 10^{-4}$ W/(m·°K) according to our calculation and $\eta = 209 \cdot 10^{-7}$ kg/(m·sec) and $\lambda = 938 \cdot 10^{-4}$ W/(m·°K) according to the calculation of [29]. The values of the viscosity and thermal conductivity of monatomic sodium vapor found using the effective values of the parameters of the Lennard-Jones potential presented in Table 4 also coincide exactly with those given in [29]. The agreement of the test and calculated values of the viscosity and thermal conductivity of potassium and sodium vapors is noted in [29], and we used the same test data in our initial determination of σ and ϵ for potassium and sodium vapors.

NOTATION

P , total pressure, Pa; $D_{1,2}$, coefficient of interdiffusion in a binary mixture, m²/sec; C , constant, N/sec; T , absolute temperature, °K; n , exponent; $Q_{1,2}^{(1,1)}$, diffusion cross section, Å²; M_1 and M_2 , molecular masses of the metal and gas, kg/kmole; $k = 1.38 \cdot 10^{-23}$, Boltzmann constant, J/°K; I_1 and I_2 , ionization energies of the metal and gas, J or a.u. (1 a.u. = $4.36 \cdot 10^{-18}$ J); α_1 and α_2 , polarizabilities of the metal and gas, Å³; η , coefficient of dynamic viscosity, kg/(m·sec); σ , Å³, and ϵ , J (or ϵ/k , °K), parameters of the Lennard-Jones potential for the metal; $\Omega^{(2,2)*}$, reduced interaction integral [6] ϕ , potential energy of the interaction of metal atoms; r , distance between atoms, Å; λ , coefficient of thermal conductivity, W/(cm·°K).

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