

Binary Gaseous Diffusion Coefficients for Iodine in Helium and in Argon

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The binary gaseous diffusion coefficients at 1 atm of pressure for the systems iodine + helium and iodine + argon have been determined from 301 to 445 K using the modified entrainment method. The results are discussed in terms of the Lennard-Jones and Maitland-Smith intermolecular potentials.

Introduction

The binary gaseous diffusion coefficients of Zn and of Hg in H₂, He, Ar, N₂, and CO₂ have been reported recently (1). These systems are nonpolar, in some cases monoatomic, and the Lennard-Jones potential proved surprisingly inadequate in the interpretation of the numerical results. Interpretation using the Maitland-Smith potential (2) was far more successful, particularly for the systems including mercury. We have extended this work to include the gas pairs iodine + helium and iodine + argon, where the mass disparity of the interdiffusing components is very large. Such systems have been treated theoretically (3, 4), and experimentalists have been encouraged (5) to provide reliable data.

Experimental Section

The apparatus has been described before (1, 6-8). Briefly, the iodine is contained in a spherical silica capsule equipped with a vertical cylindrical orifice (the diffusion channel, ca. 20 mm long × 1 mm in diameter) that is inset (ca. 2 mm) into the capsule. A controlled stream of the second component (He or Ar) flows downward over the capsule, flushing away the evaporating iodine. The capsule, suspended on one arm of a recording microbalance, is positioned in the temperature plateau of a vertically-mounted tube furnace. Experimental temperatures were measured with a thermocouple (type K, ±0.5 K), and the experimental temperature ranges were from 301 to 358 K, a range where iodine is solid ($T_m = 387$ K), and from 392 to 445 K where iodine is liquid ($T_b = 485$ K). The experimental parameter is the rate of mass loss at a preset temperature. The technique is a modification of the capillary leak (or evaporation tube) method, pioneered by Stefan (9). The rates of mass loss varied from 1.5×10^{-11} kg s⁻¹ (at 301 K) to 7.7×10^{-9} kg s⁻¹ (at 445 K), and the maximum mole fractions of iodine were 0.67 and 0.72 for the He + I₂ and Ar + I₂ systems, respectively. The operating pressure was just in excess of atmospheric pressure, and the diffusive resistance of the channel (length over cross-sectional area) was $14\,760 \pm 360$ m⁻¹ for the experiments with I₂(c) and $20\,350 \pm 370$ m⁻¹ for the experiments with I₂(liq).

The iodine was sublimed (BDH Aristar grade), and the He and Ar (both BOC) were purified with a commercial rare gas purifier (BOC, model RGP-4).

Results

Solving the flux equation for one-dimensional transport in the capsule diffusion channel gives

$$p^\circ = P(1 - e^{-\xi}) \quad (1)$$

where

$$\xi = \frac{\dot{w}RTl}{\mathcal{D}_{12}M_1PA} \quad (2)$$

Combining and rearranging yield

$$\mathcal{D}_{12} = \frac{-\dot{w}RTl}{AM_1P} \left[\frac{1}{\ln(1 - p^\circ/P)} \right] \quad (3)$$

In these equations \dot{w} and p° are the rate of mass loss and the equilibrium vapor pressure of I₂, respectively, at the temperature T . The operating pressure is P , and the diffusive resistance of the channel is l/A (length over cross-sectional area); M_1 is the molecular mass of I₂, and \mathcal{D}_{12} is the binary diffusion coefficient. The experimental rates of mass loss, $\dot{w}(T)$, were used with Hultgren's recommended (10) vapor pressure of I₂(c), eq 4, in eq 3 to give \mathcal{D}_{12} . Corresponding

$$\log(p^\circ/\text{atm}) = 13.3740 - 3518.2/(T/\text{K}) - 2.018 \log(T/\text{K}) \quad (4)$$

results for \mathcal{D}_{12} were obtained from the experiments with I₂(liq) using Sako et al.'s (11) vapor pressures for liquid iodine. Sako et al.'s data in our temperature range were regressed to yield eq 5.

$$\ln(p^\circ/\text{mmHg}) = (18.15 \pm 0.11) - (5268.5 \pm 45.6)/(T/\text{K}) \quad (5)$$

Nesmeyanov (12), in an independent critical review of experimental vapor pressures, recommends an equation for the vapor pressure of I₂(c) that yields pressures that are ~10% higher than those from Hultgren's equation (eq 4). If our results are processed using Nesmeyanov's equation for the vapor pressure of I₂(c), we obtain results for D_0 and $1 + s$ (see below) that are significantly different from those obtained from the experiments with liquid iodine; this lends support for Hultgren's equation which generates contiguous results. It has been suggested (12, 13) that the evaporation coefficient for solid iodine is not unity. If this were so, then our results for D_0 and $1 + s$ obtained from experiments with liquid iodine would not be the same as those from experiments with the solid iodine. We conclude that the reports for the hindered vaporization of solid iodine are in error.

The temperature dependence of diffusion coefficients was taken into account by fitting the results to an expression (14) of the form $\mathcal{D}_{12} = D_0(T/T_0)^{1+s}$ where the reference temperature (T_0) was 273.15 K; as in previous work (1), the pressure dependence was ignored as the results were obtained at approximately constant pressure (atmospheric pressure plus 3-4 mmHg). Values for D_0 and $1 + s$ are collected in Table I, and the raw data are plotted in Figure 1, which also includes

Table I. Constants for $D_{12} = D_0(T/T_0)^{1+s}$ Obtained by Linear Regression ($T_0 = 273.15$ K)

system	$10^6 D_0 / (\text{m}^2 \text{s}^{-1})$	$1 + s$	T/K
$\text{I}_2 + \text{He}$	36.31 ± 0.09^a	1.551 ± 0.008	301–442
$\text{I}_2 + \text{Ar}$	7.444 ± 0.024	1.735 ± 0.010	329–445

^a The uncertainty intervals are ± 1 standard deviation of the regression coefficients.

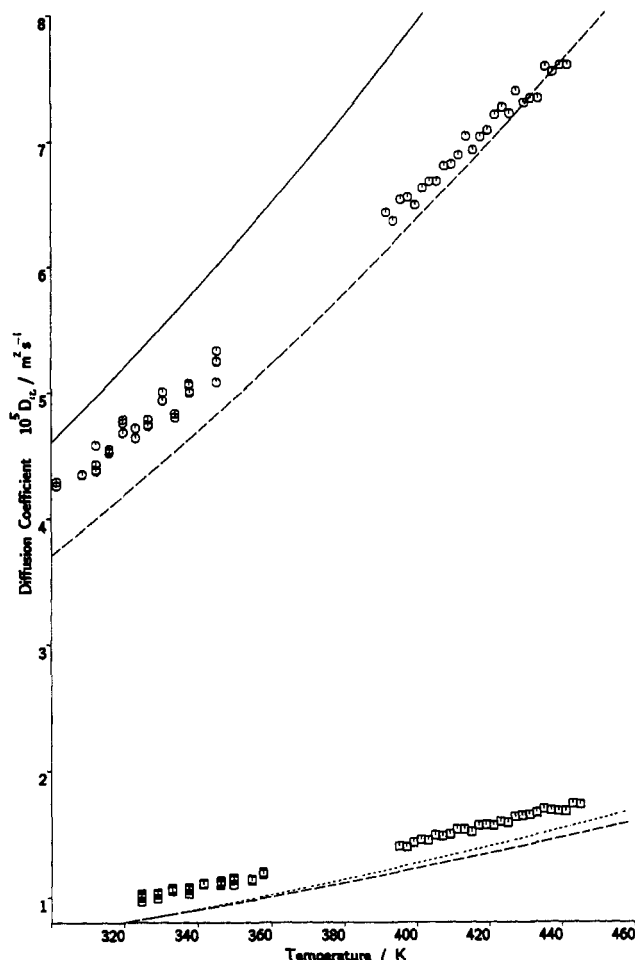


Figure 1. Experimental results for the binary diffusion coefficients of the $\text{I}_2 + \text{He}$ (○) and the $\text{I}_2 + \text{Ar}$ (□) systems. The corresponding calculated values from different intermolecular potentials (MS and LJ, see text) are $\text{I}_2 + \text{He}$ (—, MS; - - -, LJ) and $\text{I}_2 + \text{Ar}$ (· · ·, MS; - - -, LJ).

calculated diffusion coefficients for comparison (see below for details of calculation). For hard spheres, $1 + s$ is exactly 1.5 (14, 15), and for real systems it usually lies in the range 1.5–2; this is observed for our results.

Discussion

In the dilute gas limit (15) the Chapman–Enskog formula, eq 6, gives the binary diffusion coefficient in terms of molecular parameters. In this equation μ_{12} is the reduced mass, σ_{12} is

$$[D_{12}]_1 = \frac{3}{16} \left(\frac{2\pi kT}{\mu_{12}} \right)^{1/2} \frac{1}{n\pi\sigma_{12}^2 \Omega_{12}^{*(1,1)}} \quad (6)$$

the collision diameter, k is the Boltzmann constant, n is the total number density, and $\Omega_{12}^{*(1,1)}$ is a reduced collision integral which is a function of T^* ($=kT/\epsilon_{12}$) where ϵ_{12} is the well depth that characterizes the intermolecular potential of the interdiffusing species. Equation 6 is the result of a first-order approximation and contains no concentration-dependent terms. The only physical situation when concentration dependence is of the order of more than a few percent is in

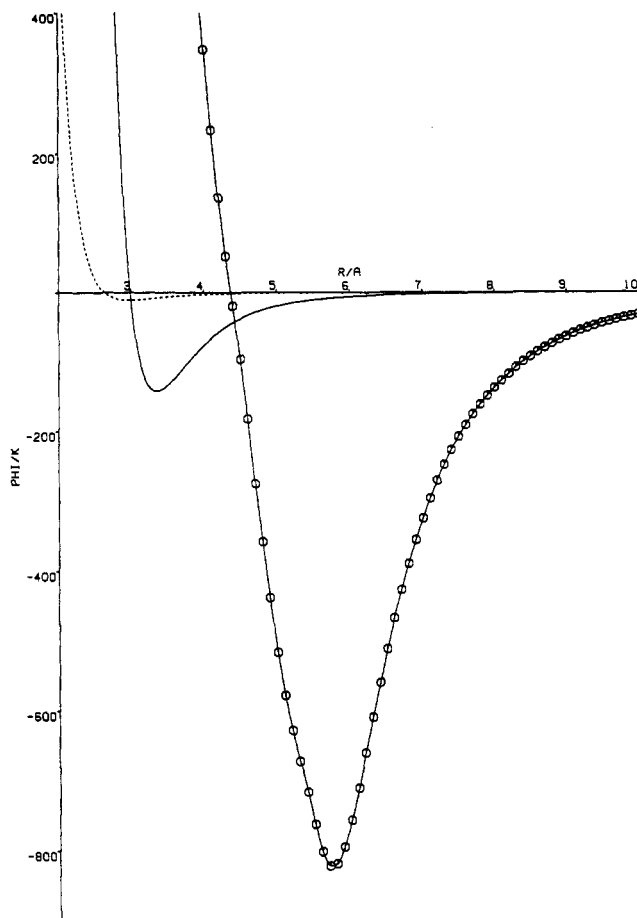


Figure 2. Intermolecular potentials for He (---), Ar (—), and I_2 (○); the He and Ar potentials are analytic Maitland–Smith potentials, and the I_2 potential is a RAM potential from eq 12.

a mixture of components of very unequal molecular masses and where the lighter component is present in trace amounts. Such effects could be significant in this work, and the second-order approximation is usually written as

$$[D_{12}]_2 = [D_{12}]_1 (1 + \Delta_{12}) \quad (7)$$

where Δ_{12} is a complicated dimensionless function of concentration and like and unlike collision integrals of higher order, e.g. $\Omega_{11}^{*(2,2)}$, $\Omega_{12}^{*(2,3)}$, etc.; these formulas are listed in ref 14. Using practical units for molecular mass (g mol^{-1}), pressure (atm), and collision diameter (\AA), eq 6 reduces to

$$[D_{12}]_1 / (\text{m}^2 \text{s}^{-1}) = 1.858 \times 10^{-7} \frac{((M_1 + M_2)/M_1 M_2)^{1/2} T^{8/2}}{P \sigma_{12}^2 \Omega_{12}^{*(1,1)}} \quad (8)$$

Two intermolecular potentials were explored to interpret the results, the Lennard–Jones (LJ) and the Maitland–Smith $n(r) - 6$ potentials (MS, eqs 9 and 10). In these equations ϵ

$$\Phi(r) = \epsilon \left(\frac{6}{n-6} \left(\frac{r_m}{r} \right)^n - \frac{n}{(n-6)} \left(\frac{r_m}{r} \right)^6 \right) \quad (9)$$

$$n = m + \gamma \left(\frac{r}{r_m} - 1 \right) \quad (10)$$

is the well depth, r_m is the separation at $\Phi = \epsilon$, and m and γ are constants; the MS potential reduces to the LJ potential when $m = 12$ and $\gamma = 0$. The MS potential has enjoyed considerable success in the prediction of properties of inert gas pairs (16). Intermolecular parameters (σ , ϵ) for the LJ (12, 6) potential have been tabulated by Reid et al. (17) for

Table II. Molecular Parameters for the MS and LJ Potentials and Comparison of Calculated and Experimental Diffusion Coefficients

	(I ₂) ₂	He ₂	Ar ₂	I ₂ + He	I ₂ + Ar
$\epsilon^a/k(\text{LJ})/\text{K}$	474.2	10.22	93.3	69.6	210.3
$\sigma^a(\text{LJ})/\text{\AA}$	5.16	2.551	3.54	3.85	4.35
$\epsilon^b/k(\text{MS})/\text{K}$	822.4	10.9	141.5	94.7	341.1
$\sigma^b(\text{MS})/\text{\AA}$	4.37	2.633	3.35	3.50	3.86
$m^b(\text{MS})$	2.9	12	13	7.45 ^c	7.95 ^c
$\gamma^b(\text{MS})$	5.0	6.0	7.5	5.5 ^c	6.25 ^c
$T^*{}^d$				3-6	1-2
$D_0(\text{LJ})/(\text{m}^2 \text{s}^{-1})$				3.11×10^{-5}	5.95×10^{-6}
(1 + s)(LJ)				1.873	1.893
$\Delta^e(\text{LJ})/\%$				5.5	16
$D_0(\text{MS})/(\text{m}^2 \text{s}^{-1})$				3.86×10^{-5}	5.78×10^{-6}
(1 + s)(MS)				1.883	2.053
$\Delta^e(\text{MS})/\%$				-18	13
$(\Delta_{12})^f$				0.02	0.003

^a From ref 17 and using Lorentz-Berthelot (16) combining rules.

^b (I₂)₂ data from RAM potential (see text); other data from ref 16.

^c In the absence of specific literature recommendation, arithmetic means were used for γ_{12} and m_{12} . ^d $T^* = kT/\epsilon$. ^e $\Delta = 100(\mathcal{D}(\text{exp}) - \mathcal{D}(\text{calc}))/\mathcal{D}(\text{exp})$; a mean value is quoted. ^f See eq 7, a mean value.

over 70 molecular species including I₂, Ar, and He. Consequently the relevant collision integrals may be calculated, and a theoretical value of the diffusion coefficient may be obtained from eqs 7 and 8.

Intermolecular parameters (σ , ϵ , m , and γ) for the MS potential have been tabulated (2, 16) for the inert gases but not for I₂, nor to our knowledge has a gas-phase intermolecular potential been reported for I₂. There is, however, a literature report (18) of a condensed-phase potential for iodine which is, of course, dependent on the relative orientation of the two molecules and which reproduces satisfactorily the limited physical data for condensed-phase iodine: crystal structure at 110 K, lattice frequencies, and structure factors from neutron scattering with liquid iodine. There is an element of risk in using a condensed-phase potential to predict gas-phase data, but this has been done satisfactorily for both argon (16) and chlorine (19). Consequently the condensed-phase (I₂)₂ potential of Rodger et al. (18) (ϕ_R) was Boltzmann-weighted and summed over all possible relative orientations according to eq 11, where Ω is the angle set (θ , α , β); θ is the

$$\Phi_B(r) = \langle \phi_R(r, \Omega) \sin \beta \exp(-\phi_R/kT) \rangle_{\Omega} \quad (11)$$

polar angle with the reference axis of the vector joining the molecular centers (the corresponding azimuthal angle is redundant), β is the polar angle of the interatomic vector of the nonfixed I₂ molecule with the reference axis, and α is the azimuthal angle of this iodine molecule. Coordinate systems for two linear molecules have been discussed by Streett and Tildesley (20) and, for the general case, by Goldstein (21). The potential (Φ_B) obtained by this route displayed clear discontinuities in the region $\sigma < r < r_m$, probably reflecting its origin in the condensed phase, and was abandoned. An alternative generation procedure (22) via the reference-average-Mayer potential (Φ_{RAM} , eq 12) gave a more regular

$$\Phi_{\text{RAM}}(r) = -kT \ln \left\langle \frac{\exp(-\phi_R(r, \Omega))}{kT} \right\rangle_{\Omega} \quad (12)$$

form; numerical integration for both procedures used 40-point Gaussian quadrature (23, 24), and T was taken as the mean temperature (380 K) of the experimental ranges. The (I₂)₂ potential generated from eq 12 is compared with analytic Maitland-Smith (MS) potentials for He₂ and Ar₂ in Figure 2. The (I₂)₂ potential was fitted by multivariate regression with m and γ as disposable parameters to the MS form, eqs 9 and 10; data points were selected at equal energy intervals rather than equal intermolecular distance intervals so as to

weight preferentially the repulsive limb of the potential curve. The experimental temperatures were in the range where T^* ($=kT/\epsilon$) > 1 and where the attractive component of the intermolecular potential is relatively unimportant. Values of the diffusion coefficient were calculated from eqs 7 and 8 using the LJ and MS potentials and are compared with the experimental values from Table I in Table II.

Reid et al. (17), using the Lennard-Jones potential, have calculated diffusion coefficients for 9 binary systems containing Ar and for 13 systems containing He; the average deviations are 7.6% and 6.5%, respectively. Only our result for I₂ + He falls within these limits. Results obtained from the MS potential are disappointing particularly in view of the improvement noted when using this potential for Hg + inert gas and Zn + inert gas (1) systems.

A significant problem in this work is the validity of the Lorentz-Berthelot (16) combining rules. A potentially attractive route for generating I₂ + inert gas (MS) potentials which avoids the use of combining rules is to simulate I₂ as Xe₂ with the known iodine molecular bond length. MS potential parameters are available (16) for the Xe + He and Xe + Ar pairs, and it is a simple matter to generate directly potentials for I₂(Xe₂) + He and I₂(Xe₂) + Ar using eq 12 in which ϕ_R is now an MS potential. Using this procedure, and comparing calculated with experimental results, the error function, Δ (see Table II), is -3% for I₂ + Ar but +65% for I₂ + He. It is clear from this work that, for systems where the mass difference of the components is marked, simple potentials such as LJ and MS are inadequate.

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Registry No. He, 7440-59-7; Ar, 7440-37-1; iodine, 7553-56-2.