Low Temperature Transport Properties of Gases. II. Neon, Argon, Krypton, and Xenon

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Values are computed for the viscosity, thermal conductivity, and coefficient of self-diffusion, as functions of temperature, for the following gases: neon (60°–200°K), argon (110°–290°K), krypton (150°–370°K), and xenon (210°–550°K). The method of calculation is the same as that previously developed for gaseous helium and involves the use of classical scattering theory within angular regions where diffraction effects are absent, to obtain appropriate classical transport cross sections for insertion into the exact formulas of Chapman and Enskog.

The average absolute deviations between calculated and experimental values are 5.5 percent for viscosity and 5.9 percent for thermal conductivity. In the case of self-diffusion, only two experimental values are available for comparison with calculated values, one each for krypton and xenon. The absolute deviations are 9.7 and 10.3 percent, respectively.

A procedure is suggested for obtaining approximate values of the mutual diffusion coefficient of a binary gas mixture from the self-diffusion coefficients of the constituents.

IN a recent publication[1] (hereafter referred to as the helium paper), the transport properties of gaseous helium were computed by a combination of classical scattering theory and the theory of transport properties as developed by Chapman[2] and Enskog.[3] The results agreed well with experiment in the temperature range for which the calculations were valid, 14°–200°K. Since the method should be of general applicability, it seemed advisable to extend the calculations to other rare gases to test further the generality of the method and to obtain calculated values of the transport properties in temperature regions where experimental values are unavailable. In the present paper, appropriate formulas will be given without derivation since the procedure and derivations were presented in detail in the helium paper.

As indicated in the helium paper, the success of the calculations depends upon accurate knowledge of the interaction potential between two rare gas atoms. The potential functions used in the present case were obtained by combining expressions involving a single exponential repulsive term and a dipole-dipole interaction attractive term deduced by Kane[4] from properties of frozen inert gases, with ratios of the constants in the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole terms derived from calculations of Margenau.[5]

Kane used a potential energy function of the form

$$V(r) = A e^{-ar} - (c/r^6), \tag{1}$$

where r is the separation distance between two atoms, and adjusted the constants to reproduce the total energy at the absolute zero at the observed lattice distance r_l, which, in every case, was very close to the potential minimum. It will be assumed that a more accurate function can be obtained by allowing for dipole-quadrupole and quadrupole-quadrupole interactions as follows:

At r_l the attractive energy may be written

$$\frac{c}{r_l^6} = \frac{C}{r_l^6} \frac{D}{r_l^8} \frac{E}{r_l^{10}} = \frac{C}{r_l^6}\left(1 + \frac{p}{r_l^2} + \frac{q}{r_l^4}\right), \tag{2}$$

TABLE I. Constants of potential energy functions.

	Neon	Argon	Krypton	Xenon
p	1.48	2.17	2.57	3.05
q	1.13	2.45	3.46	4.81
c $(10^{-10}\,\mathrm{erg}\,A^6)$	0.140	0.874	1.48	3.54
A $(10^{-10}\,\mathrm{erg})$	0.966	8.30×10^3	2.18×10^4	1.84×10^5
a (A^{-1})	2.90	4.782	4.782	4.782
C $(10^{-10}\,\mathrm{erg}\,A^6)$	0.121	0.755	1.26	3.01
D $(10^{-10}\,\mathrm{erg}\,A^8)$	0.179	1.64	3.24	9.18
E $(10^{-10}\,\mathrm{erg}\,A^{10})$	0.137	1.85	4.36	14.5

[1] I. Amdur, J. Chem. Phys. 15, 482 (1947).

[2] S. Chapman, Phil. Trans. Roy. Soc. A211, 433 (1912); A216, 279 (1915); A217, 115 (1917).

[3] D. Enskog, "Kinetische Theorie der Vorgänge in massig verdünnten Gasen," Inaug. Diss., Upsala, 1917.

[4] G. Kane, J. Chem. Phys. 7, 603 (1939).

[5] H. Margenau, J. Chem. Phys. 6, 896 (1938).

where p and q are the ratios computed from Margenau's results. Since Margenau's calculations are valid for distances near the minimum, the above method should correct satisfactorily for dipole-quadrupole and quadrupole-quadrupole interactions near the minimum, the region of interest in the present case, particularly since the inclusion of the higher order terms produced a *maximum* increase in the attractive energy of only 4.3 percent. Since Margenau[6] has shown that the effect of second-order exchange forces is negligible for all the inert gases except helium, the form of the complete potential function for neon, argon, krypton, and xenon will be taken as

$$V(r) = A e^{-ar} - \frac{C}{r^6} - \frac{D}{r^8} - \frac{E}{r^{10}}. \qquad (3)$$

Although most of the interaction potentials suggested in the literature were investigated, certain functions suggested by Kane and corrected as indicated gave the best results. Table I gives the Margenau ratios, the original constants of Kane, and the constants in the final potential function, Eq. (3).

Values of the classical total collision cross section, S, as a function of the relative velocity, v, are required for evaluation of the classical cross sections for viscosity and thermal conductivity, $Q_{\eta, K}$, and for self-diffusion, $Q_{D(1, 1)}$, as functions of temperature. Now

$$S = \pi [b(\Theta_c)]^2, \qquad (4)$$

where $b(\Theta_c)$, the impact parameter for the critical relative scattering angle sufficiently large to eliminate diffraction, is defined by

$$\left[1 - \frac{V(r_0)}{\frac{1}{2}\mu v^2}\right] r_0^2 = [b(\Theta_c)]^2, \qquad (5)$$

in which μ is the reduced mass of the colliding system, and r_0, the distance of closest approach of the two particles. The velocity dependence of S results from the velocity dependence of r_0. For a potential function of the form of Eq. (3), this latter dependence, for the critical scattering

[6] H. Margenau, Phys. Rev. **56**, 1000 (1939).

TABLE II. Classical total collision cross sections.

Gas	a' (A^2)	b' ($\frac{A^2\,cm}{sec.}$)	c' ($\frac{A^2\,cm^2}{sec.^2}$)	r_0 (A)	v ($\frac{10^5\,cm}{sec.}$)	$b(\Theta_c)$ (A)	S (A^2)
Ne	23.45	1.87×10^5	0.763×10^{10}	2.80	1.540	2.81	24.80
				2.83	1.242	2.85	25.51
				2.85	1.057	2.88	26.08
				2.88	0.793	2.94	27.25
				2.90	0.626	3.01	28.52
				2.93	0.392	3.24	33.01
A	39.85	2.05×10^5	3.40×10^{10}	3.6340	1.148	3.76	44.35
				3.6370	0.913	3.83	46.12
				3.6400	0.679	3.99	49.97
				3.6410	0.601	4.08	52.32
				3.6420	0.529	4.20	55.46
				3.6425	0.492	4.29	57.75
Kr	44.94	0.00	2.83×10^{10}	3.7860	0.716	4.01	50.42
				3.7865	0.662	4.04	51.36
				3.7870	0.612	4.09	52.54
				3.7875	0.557	4.14	54.02
				3.7880	0.504	4.23	56.08
				3.7890	0.397	4.47	62.91
Xe	55.14	0.00	3.05×10^{10}	4.1910	0.714	4.41	61.10
				4.1915	0.634	4.47	62.74
				4.1920	0.554	4.55	65.09
				4.1925	0.474	4.68	68.75
				4.1927	0.442	4.75	70.79
				4.1930	0.393	4.88	74.90
				4.1931	0.375	4.95	76.83

angle, Θ_c, is given by

$$v = \left(\frac{\pi r_0}{8a}\right)^{\frac{1}{4}} \frac{A}{h} (8ar_0 - 1)e^{-ar_0}$$
$$- \frac{11.78C}{h(r_0)^5} - \frac{13.74D}{h(r_0)^7} - \frac{15.46E}{h(r_0)^9}, \qquad (6)$$

where h is Planck's constant. Results of classical total collision cross section calculations are summarized in Table II. The general equation

$$S = a' + \frac{b'}{v} + \frac{c'}{v^2} \qquad (7)$$

was found capable of representing the velocity dependence of S in form suitable for evaluation of $Q_{\eta, K}$ and $Q_{D(1, 1)}$. Values of S calculated from Eq. (7) using the constants in Table II show the following absolute deviations from the recorded values: neon-maximum, 0.84 percent; average, 0.60 percent: argon-maximum, 0.72 percent; average, 0.48 percent: krypton-maximum, 0.11 percent; average, 0.06 percent: xenon-maximum, 0.08 percent; average, 0.04 percent.

VISCOSITY AND THERMAL CONDUCTIVITY

The classical expression for the viscosity of a single gas is

$$\eta = \frac{5}{16} \frac{(1+\epsilon)(\pi MRT)^{\frac{1}{2}}}{NQ_{\eta, K}}, \qquad (8)$$

TABLE III. Calculated and experimental† values of viscosity and thermal conductivity.

Gas	T (°K)	$Q_{\eta,K}$ (A^2)	$\eta_{exp.} \times 10^5$ $\left(\dfrac{g}{sec.\ cm}\right)$	$\eta_{cal.} \times 10^5$ $\left(\dfrac{g}{sec.\ cm}\right)$	$100\left\|\dfrac{\Delta\eta}{\eta_{exp.}}\right\|$ (%)	$K_{exp.} \times 10^5$ $\left(\dfrac{cal.}{sec.\ cm\ deg.}\right)$	$K_{cal.} \times 10^5$ $\left(\dfrac{cal.}{sec.\ cm\ deg.}\right)$	$100\left\|\dfrac{\Delta K}{K_{exp.}}\right\|$ (%)
Ne	200	26.03	23.755	20.85	12.2	8.82*	7.78	11.8
	180	26.21	22.040	19.62	11.0		7.32	
	160	26.44	20.255	18.33	9.4		6.84	
	140	26.71	18.405	16.97	7.8		6.33	
	120	27.07	16.460	15.50	5.8		5.78	
	100	27.55	14.345	13.91	3.0		5.19	
	90	27.86	13.200	13.04	1.2	4.93*	4.86	1.4
	80	28.24	11.980	12.14	1.3		4.53	
	70	28.71	11.17*	11.19	0.2		4.17	
	60	29.32	9.78*	10.15	3.8		3.79	
A	290	46.86	22.080	19.51	11.6		3.67	
	270	47.29	20.805	18.64	10.4	3.85*	3.50	9.1
	250	47.79	19.465	17.75	8.8		3.34	
	230	48.37	18.090	16.84	6.9		3.17	
	210	49.05	16.665	15.85	4.9		2.98	
	190	49.87	15.210	14.82	2.6	2.87*	2.79	2.8
	170	50.88	13.725	13.76	0.3		2.59	
	150	52.14	12.220	12.62	3.3		2.37	
	130	53.78	10.695	11.38	6.4		2.14	
	110	55.98	9.155	10.06	9.9		1.89	
Kr	370	51.29	30.49*	29.16	4.4		2.65	
	330	52.06		27.13			2.46	
	290	53.33	24.40*	24.96	2.3		2.27	
	270	53.64		23.81		2.10*	2.16	2.9
	250	54.34		22.62			2.05	
	230	55.16		21.39			1.94	
	210	56.13		20.06			1.82	
	190	57.31		18.69			1.70	
	170	58.76		17.25			1.57	
	150	60.61		15.72			1.43	
Xe	550	62.38	39.54	36.49	7.7		2.11	
	500	63.10	36.52	34.39	5.8		1.99	
	450	63.98	33.51	32.17	4.0		1.86	
	400	65.09	30.09	29.82	0.9		1.72	
	370	65.90	28.58*	28.33	0.9		1.64	
	340	66.85		26.77			1.55	
	310	67.98		25.13			1.45	
	290	68.86	22.52*	24.00	6.6		1.39	
	270	69.88		22.81		1.23*	1.32	7.3
	250	71.06		21.59			1.25	
	230	72.45		20.33			1.18	
	210	74.09		18.97			1.10	

† (a) Viscosity: neon (60° and 70°K), A. van Itterbeek and O. van Paemel, Physica **7**, 265 (1940); neon (80°–200°K) and argon, H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942); krypton and xenon (290° and 370°K), A. G. Nasini and C. Rossi, Gazz. chim. ital. **58**, 433 (1928); xenon (400°–550°K), M. Trautz and R. Heberling, Ann. d. Physik **20**, 118 (1934). (b) Thermal conductivity: neon, S. Weber, Commun. Leiden Suppl. No. 42b (1918); argon, A. Eucken, Physik. Zeits. **12**, 110 (1911); krypton and xenon, M. Curie and A. Lepape, J. d. phys. et rad. [7] **2**, 392 (1931).

where ϵ is 0.016, M, the molecular weight, R, the gas constant per mole, N, Avagadro's number, and $Q_{\eta,K}$, the classical cross section for viscosity and thermal conductivity for a Maxwellian gas at temperature T. This cross section is defined by

$$Q_{\eta,K} = \frac{M^4}{512 R^4 T^4} \int_0^\infty v^7 S_{\eta,K} \exp[-Mv^2/(4RT)]dv, \quad (9)$$

where $S_{\eta,K} = 2S/3$. For the functional form of S given in Eq. (7), Eq. (9) reduces to

$$Q_{\eta,K} = a' + 3.04 \times 10^{-5} M^{\frac{1}{2}} b'/T^{\frac{1}{2}} + 1.00 \times 10^{-9} Mc'/T \ A^2, \quad (10)$$

and Eq. (8) to

$$\eta = \frac{8.52 \times 10^{-5} M^{\frac{1}{2}} T^{\frac{1}{2}}}{a' + 3.04 \times 10^{-5} M^{\frac{1}{2}} b'/T^{\frac{1}{2}} + 1.00 \times 10^{-9} Mc'/T} \times \frac{g}{sec.\ cm}. \quad (11)$$

For a monatomic gas, the thermal conductivity may be written

$$K = 2.5(1+\delta)\eta c_v, \qquad (12)$$

where δ is 0.01 and c_v is the specific heat at constant volume which may be set equal to $1.5R/M$. If η is expressed in cgs units, Eq. (12) becomes

$$K = 7.52\eta/M \frac{\text{cal.}}{\text{sec. cm deg}}. \qquad (13)$$

Values of $Q_{\eta,K}$ and η calculated from Eqs. (10) and (11), using the constants of Table II, and values of K calculated from Eq. (13) are shown in Table III as functions of temperature. Reliable experimental values have been included for comparison although viscosity determinations in the case of krypton and xenon, and thermal conductivity determinations in the case of all the gases, are relatively scarce. Starred values differ slightly from values cited in the literature because of correction to the rounded temperatures in the second column. As in the case of helium, the calculated values are terminated at the upper temperature limit because of decreasing accuracy of the potential energy functions at distances too far removed from the minimum, and at the lower temperature limit because the present development is demonstrably valid only for relatively

small values of the critical scattering angle, Θ_c.

The average absolute deviation between calculated and experimental values is 5.5 percent in the case of viscosity and 5.9 percent in the case of thermal conductivity.

COEFFICIENT OF SELF-DIFFUSION

The classical expression for the coefficient of self-diffusion, $D(1, 1)$, is

$$D(1, 1) = \frac{3}{8} \frac{(1+\epsilon)(\pi MRT)^{\frac{1}{2}}}{N\rho Q_{D(1,1)}}, \qquad (14)$$

where ρ is the density in grams per unit volume and $Q_{D(1,1)}$, the classical cross section for self-diffusion in a Maxwellian gas at temperature T defined by

$$Q_{D(1,1)} = \frac{M^3}{32R^3T^3} \int_0^\infty v^5 S_{D(1,1)}$$
$$\times \exp. [-Mv^2/(4RT)]dv, \qquad (15)$$

where $S_{D(1,1)} = S/2$. For the form of S in Eq. (7), Eq. (15) reduces to

$$Q_{D(1,1)} = a' + 3.65 \times 10^{-5} M^{\frac{1}{2}} b'/T^{\frac{1}{2}} + 1.50$$
$$\times 10^{-9} Mc'/T \ A^2, \qquad (16)$$

and Eq. (14) to

$$D(1, 1) = \frac{1.02 \times 10^{-4} M^{\frac{1}{2}} T^{\frac{1}{2}}}{\rho(a' + 3.65 \times 10^{-5} M^{\frac{1}{2}} b'/T^{\frac{1}{2}} + 1.50 \times 10^{-9} Mc'/T)} \frac{\text{cm}^2}{\text{sec.}}, \qquad (17)$$

where ρ is in g/cc, or

$$D(1, 1) = \frac{8.50 \times 10^3 T^{\frac{1}{2}}}{PM^{\frac{1}{2}}(a' + 3.65 \times 10^{-5} M^{\frac{1}{2}} b'/T^{\frac{1}{2}} + 1.50 \times 10^{-9} Mc'/T)} \frac{\text{cm}^2}{\text{sec.}}, \qquad (18)$$

where P is in dynes/cm², since $\rho = PM/(RT)$.

Values of $Q_{D(1,1)}$ and $D(1, 1)$ for $P = 1.01 \times 10^6$ dynes/cm² (1 atmosphere) have been computed from Eqs. (16) and (18) using the constants of Table II. The results appear in Table IV which does not include a column for experimental values since there are but two determinations at temperatures suitable for comparison with the calculated values. Groth and Harteck[7] find that at 1 atmosphere $D(1, 1)$ is 0.091 cm²/sec. for krypton at 293.96°K and 0.0443 cm²/sec. for

xenon at an average temperature of 292.31°K. These values, which have a probable error of 5 percent, become 0.089 and 0.0437 when corrected to 290°K and differ by 9.7 percent and 10.3 percent respectively from the corresponding calculated values in Table IV.

Lord Kelvin[8] has outlined a method, which Chapman and Cowling[9] feel is somewhat justified

[7] W. Groth and P. Harteck, Zeits. f. Elektrochemie **47**, 167 (1941).

[8] Lord Kelvin, *Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light* (C. J. Clay and Sons, London, England, 1904), p. 295.

[9] S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Teddington, England, 1939), pp. 250 and 251.

TABLE IV. Calculated values of the self-diffusion coefficient at 1 atmosphere.

Gas	T (°K)	$Q_{D(1,1)}$ (A^2)	$D(1,1)$ (cm²/ sec.)	Gas	T (°K)	$Q_{D(1,1)}$ (A^2)	$D(1,1)$ (cm²/ sec.)
Ne	200	26.78	0.199	Kr	370	54.48	0.122
	180	27.02	0.167		330	55.64	0.100
	160	27.32	0.138		290	57.11	0.0804
	140	27.70	0.112		270	58.02	0.0711
	120	28.18	0.0874		250	59.06	0.0623
	100	28.83	0.0652		230	60.29	0.0538
	90	29.26	0.0549		210	61.75	0.0458
	80	29.77	0.0451		190	63.52	0.0384
	70	30.42	0.0362		170	65.70	0.0314
	60	31.27	0.0279		150	68.47	0.0250
A	290	49.66	0.133	Xe	550	66.01	0.144
	270	50.28	0.118		500	67.10	0.123
	250	51.00	0.104		450	68.43	0.103
	230	51.83	0.0902		400	70.09	0.0843
	210	52.82	0.0772		370	71.30	0.0738
	190	53.69	0.0650		340	72.73	0.0637
	170	55.47	0.0537		310	74.43	0.0542
	150	57.30	0.0430		290	75.76	0.0482
	130	59.68	0.0333		270	77.29	0.0424
	110	62.90	0.0246		250	79.06	0.0369
					230	81.14	0.0318
					210	83.62	0.0269

by the self-consistency of the results, for calculating self-diffusion coefficients from suitable combinations of experimental mutual diffusion coefficients of binary mixtures. Since it appears possible to calculate values of the self-diffusion coefficient, it seems desirable to point out that Lord Kelvin's method may be readily inverted.

At a given temperature, a pair of values of $Q_{D(1,1)}$ may be used to compute an approximate value of the mutual diffusion coefficient, $D(1, 2)$, for a binary mixture from the formula

$$D(1, 2) = \frac{3}{8} \frac{(RT)^{\frac{1}{2}}}{PNQ_{D(1,2)}} \left[\frac{\pi(M_1+M_2)}{2M_1M_2} \right]^{\frac{1}{2}}, \quad (19)$$

where M_1 and M_2 are the molecular weights of the gases, and $Q_{D(1,2)}$, the classical equivalent mutual cross section for diffusion for a Maxwellian binary gas mixture at temperature T. If the self-diffusion cross sections for the individual gases at the temperature T are represented by $^1Q_{D(1,1)}$ and $^2Q_{D(1,1)}$, $Q_{D(1,2)}$ is given by

$$Q_{D(1,2)} = \frac{1}{4}\{ ^1Q_{D(1,1)} + 2[^1Q_{D(1,1)}{}^2Q_{D(1,1)}]^{\frac{1}{2}} + ^2Q_{D(1,1)}\}, \quad (20)$$

which states that the equivalent hard sphere diameter for the two molecule system is the average of the equivalent hard sphere diameters of the two single molecule systems.

Eq. (19) does not take into account a small variation of $D(1, 2)$ with composition and omits a small correction term, similar in character to the $(1+\epsilon)$ term in Eq. (14), which depends upon the law of force between the molecules. In spite of these limitations, the above method for estimating mutual diffusion coefficients may prove useful since, in most cases, insufficient information about interactions between unlike molecules is available for direct calculations of $D(1, 2)$ by the methods outlined in the helium paper.