

Transport Properties of Gaseous He³ and He⁴†

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(Received 22 March 1965)

A complete quantum phase-shift calculation of several transport coefficients of gaseous He³, He⁴, and He³-He⁴ mixtures has been carried out from 0.2 to 300°K for a Lennard-Jones (12-6) potential model. Emphasis was placed on those properties for which new experimental data had become available, which included the viscosity of He⁴, the thermal conductivity of He³ and He⁴, the spin diffusion of He³, and ordinary diffusion and thermal diffusion of He³-He⁴ mixtures. Agreement was in general surprisingly good for a potential as simple as this. A rather more elaborate potential may be required to obtain agreement over the full range of experimental measurements of transport properties and equation-of-state properties of the helium isotopes, which extends from less than 1°K to over 1000°K.

I. INTRODUCTION

THE transport properties of helium are of particular interest because large quantum effects are to be expected. These include both diffraction and symmetry effects. Because of the small mass of helium a complete quantum-mechanical calculation of the transport cross sections and collision integrals requires the evaluation of a large number of scattered-wave phase shifts in ranges where the semiclassical approximation is not sufficient. The present calculations are based on the Lennard-Jones (12-6) potential,

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (1)$$

where ϵ is the well depth and $\varphi(\sigma) = 0$. This simple two-constant potential turns out to be quite successful in describing the properties of helium at low temperatures. Although somewhat better results might have been obtained with the three-constant (exp-6) potential,¹ especially at higher temperatures, the extra computation necessary did not seem worth while.

Similar calculations with the (12-6) potential have been carried out previously on He⁴ by de Boer,² on He³ by de Boer and Cohen,³ and on He³-He⁴ mixtures by Cohen, Offerhaus, and de Boer.⁴ These calculations, coming before the ready availability of high-speed computing machines, were limited to temperatures

below 5°K. Subsequent machine calculations⁵ showed that the phase shifts calculated by de Boer and co-workers had some systematic errors, and Keller⁶ later used the newer phase shifts to calculate the viscosity of He³ and He⁴ up to 40°K.

A number of experimental and theoretical advances have occurred since the publication of these earlier calculations. In particular, Keller's reservations⁶ about the theoretical basis of the transport equations for quantum gases have been met by careful studies of the derivation of the quantum-mechanical analog of the Boltzmann transport equation.⁷ Measurements on the viscosity of He⁴ between 20 and 80°K have now been reported,⁸ as have new measurements on the heat conductivity of both He³ and He⁴ in the neighborhood of 1°K.⁹ The mutual diffusion coefficient for He³-He⁴ has been measured between 1.74 and 296°K,¹⁰ and the spin-diffusion coefficient of He³ between 1.7 and 4.2°K,¹¹ the latter leading to further theoretical work concerning the relation between spin-diffusion and self-diffusion.¹² Studies on thermal diffusion in He³-He⁴ mixtures are now being carried out at temperatures low enough for quantum effects to appear,^{13,14} and these effects are

⁵ J. E. Kilpatrick, W. E. Keller, E. F. Hammel, and N. Metro-
poli, *Phys. Rev.* **94**, 1103 (1954).

⁶ W. E. Keller, *Phys. Rev.* **105**, 41 (1957).

⁷ H. Mori and J. Ross, *Phys. Rev.* **109**, 1877 (1958), and references to other papers contained therein. A general review is given by H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962).

⁸ J. M. J. Coremans, A. van Itterbeek, J. J. M. Beenakker, H. F. P. Knaap, and P. Zandbergen, *Physica* **24**, 557 (1958).
⁹ K. Fokkens, K. W. Taconis, and R. de Bruyn Ouboter, *Proceeding of the Eighth International Conference on Low-Temperature Physics* (Butterworths Scientific Research Publications, Ltd., London, 1963), pp. 34-36.

¹⁰ P. J. Bendt, *Phys. Rev.* **110**, 85 (1958).

¹¹ (a) K. Luszczynski, R. E. Norberg, and J. E. Opfer, *Phys. Rev.* **128**, 186 (1962); (b) private communication.

¹² V. J. Emery, *Phys. Rev.* **133**, A661 (1964).

¹³ W. W. Watson, A. J. Howard, N. E. Miller, and R. M. Shiffrin, *Z. Naturforsch.* **18a**, 242 (1963).

¹⁴ F. van der Valk, thesis, Amsterdam University, 1963 (unpublished).

† Supported in part by the Bureau of Naval Weapons (The Johns Hopkins University), and by the U. S. Atomic Energy Commission (University of Maryland).

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¹ (a) E. A. Mason and W. E. Rice, *J. Chem. Phys.* **22**, 522 (1954); (b) J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, *Phys. Rev.* **97**, 9 (1955).

² J. de Boer, *Physica* **10**, 348 (1943).

³ J. de Boer and E. G. D. Cohen, *Physica* **17**, 993 (1951).

⁴ E. G. D. Cohen, M. J. Offerhaus, and J. de Boer, *Physica* **20**, 501 (1954).

expected to be especially large for thermal diffusion.^{4,15}

Because of these developments it seemed worthwhile to carry through a complete quantum phase-shift calculation of the transport coefficients of gaseous He³, He⁴, and He³-He⁴ mixtures from low temperatures up to room temperature, where the transport coefficients are essentially classical. A straightforward phase shift calculation is now relatively easy because of the availability of high-speed computing machines and the development of efficient programs for the numerical calculations of phase shifts and collision integrals.¹⁶ We feel that the present calculations are at least as accurate as any previously available, and considerably more extensive than the calculations by de Boer and co-workers²⁻⁴ and by Keller.⁶

II. PROCEDURE

The (12-6) potential parameters used were those originally determined by de Boer and Michels¹⁷ from the high-temperature second virial coefficient of He⁴, and used by de Boer and co-workers²⁻⁴ in all their subsequent calculations:

$$\epsilon/k = 10.22^\circ\text{K}, \quad \sigma = 2.556 \text{ \AA}. \quad (2)$$

These particular values do not give perfect agreement with experiment, as will be seen, but the agreement is sufficiently good to make it seem not worthwhile trying adjustments to produce some "best fit." A two-constant model of this sort is too simplified to represent the helium potential accurately, as has been clearly shown by analysis of the high-temperature properties.^{1a} Similarly, the present agreement did not justify altering the assumption that the same potential parameters describe the interaction of any pair of helium atoms regardless of their masses. Much finer experimental measurements would be required to investigate this point.

The phase shifts were calculated by direct numerical integration of the radial wave equation; the details of the procedure have been described previously.¹⁶ The phase shifts were then combined to form the first three transport cross sections, $S^{(1)}$, $S^{(2)}$, and $S^{(3)}$, which then were integrated over velocity distribution functions to obtain the reduced collision integrals $\Omega^{(1,1)*}$, $\Omega^{(1,2)*}$, $\Omega^{(1,3)*}$, $\Omega^{(2,2)*}$, $\Omega^{(2,3)*}$, and $\Omega^{(3,3)*}$. Only the integrals $\Omega^{(2,2)*}$ and $\Omega^{(2,3)*}$ for He³ and He⁴ refer to indistinguishable particles, for which symmetry effects must be taken into account; all the other integrals must refer to distinguishable particles in order to describe observable processes. To obtain the cross sections for collisions between distinguishable particles,

the sums over phase shifts are taken over all integral values of the angular-momentum quantum number l ; for indistinguishable He⁴ atoms having spin $s=0$, the sum runs over only even integral values of l ; for indistinguishable He³ atoms having spin $s=\frac{1}{2}$, a weighted mean is taken consisting of $\frac{3}{4}$ the sum over odd values of l and $\frac{1}{4}$ the sum over even values of l . The formulas and numerical methods used have already been described.¹⁸ The notation used here is a standard one in which the collision integrals are made dimensionless in such a way that they equal unity for classical rigid spheres of diameter σ .¹⁹ The collision integrals are conveniently given as functions of temperature and of a reduced de Broglie wavelength, $\Lambda^* = h/[\sigma(2\mu\epsilon)^{1/2}]$, sometimes called the de Boer parameter. The larger the value of Λ^* , the more important are the quantum effects; Λ^* is 2.67 for He⁴, 3.08 for He³, and 2.88 for He³-He⁴.

Values of the collision integrals are given in Tables I-III as functions of temperature for He³, He⁴, and He³-He⁴; $\Omega^{(1,1)*}$ is the collision integral for diffusion, and $\Omega^{(2,2)*}$ is the collision integral for viscosity and thermal conductivity in the first Chapman-Enskog

TABLE I. Quantal collision integrals for He³ ($\Lambda^*=3.08$).

T, °K	$\Omega_{33}^{(1,1)*}$	$\Omega_{33}^{(2,2)*}$	$\Omega_{33}^{(2,3)*}$	A_{33}^*	B_{33}^*	C_{33}^*	F_{33}^*
0.20	2.63364	1.71327	1.52739	0.90335	1.28471	0.61882	0.60523
0.40	1.38956	1.43383	1.37452	0.95781	0.80113	0.82070	0.94078
0.60	1.23566	1.32146	1.23599	0.93172	0.83335	0.96932	1.04270
0.80	1.22679	1.20908	1.10165	0.96336	0.95485	1.00466	1.03118
1.00	1.23123	1.11143	1.00329	0.98953	1.02841	1.00350	1.01379
1.20	1.23089	1.03718	0.94420	1.01809	1.06381	0.99495	1.00679
1.40	1.22564	0.98675	0.91771	1.04348	1.07923	0.98659	1.00760
1.60	1.21741	0.95692	0.91504	1.06424	1.08518	0.97993	1.01128
1.80	1.20771	0.94341	0.92813	1.08057	1.08687	0.97492	1.01681
2.00	1.19745	0.94202	0.95054	1.09318	1.08672	0.97123	1.02243
2.40	1.17711	0.96181	1.00580	1.11026	1.08486	0.96645	1.03195
2.80	1.15821	0.99545	1.05854	1.12029	1.08298	0.96374	1.03861
3.20	1.14112	1.03123	1.10046	1.12622	1.08157	0.96212	1.04292
3.60	1.12573	1.06352	1.13019	1.12971	1.08059	0.96110	1.04558
4.00	1.11185	1.09016	1.14915	1.13173	1.07992	0.96043	1.04713
4.50	1.09630	1.11505	1.16115	1.13303	1.07938	0.95988	1.04808
5.00	1.08242	1.13164	1.16408	1.13352	1.07905	0.95951	1.04835
5.50	1.06992	1.14157	1.16125	1.13355	1.07886	0.95926	1.04823
6.00	1.05857	1.14646	1.15500	1.13332	1.07877	0.95907	1.04787
7.00	1.03866	1.14629	1.13790	1.13248	1.07879	0.95881	1.04679
8.00	1.02163	1.13874	1.11950	1.13148	1.07895	0.95862	1.04555
9.00	1.00677	1.12801	1.10214	1.13049	1.07920	0.95847	1.04430
10.00	0.99362	1.11622	1.08643	1.12957	1.07949	0.95833	1.04311
12.00	0.97116	1.09300	1.05969	1.12802	1.08012	0.95807	1.04098
14.00	0.95246	1.07210	1.03783	1.12682	1.08075	0.95782	1.03919
16.00	0.93645	1.05375	1.01941	1.12590	1.08135	0.95758	1.03768
20.00	0.91009	1.02331	0.98954	1.12465	1.08245	0.95712	1.03531
25.00	0.88419	0.99354	0.96061	1.12379	1.08361	0.95660	1.03319
30.00	0.86334	0.96978	0.93756	1.12337	1.08458	0.95613	1.03165
35.00	0.84592	0.95009	0.91844	1.12320	1.08541	0.95572	1.03050
40.00	0.83098	0.93331	0.90211	1.12317	1.08612	0.95535	1.02960
50.00	0.80634	0.90578	0.87526	1.12333	1.08729	0.95472	1.02826
60.00	0.78650	0.88369	0.85362	1.12357	1.08822	0.95419	1.02724
70.00	0.76994	0.86524	0.83547	1.12378	1.08898	0.95374	1.02638
80.00	0.75574	0.84940	0.81984	1.12391	1.08963	0.95336	1.02561
100.00	0.73236	0.82318	0.79400	1.12399	1.09068	0.95272	1.02432
120.00	0.71356	0.80204	0.77328	1.12396	1.09149	0.95221	1.02336
140.00	0.69789	0.78445	0.75614	1.12395	1.09211	0.95179	1.02268
160.00	0.68450	0.76945	0.74161	1.12404	1.09260	0.95144	1.02222
180.00	0.67282	0.75644	0.72904	1.12420	1.09300	0.95115	1.02191
200.00	0.66248	0.74498	0.71799	1.12444	1.09335	0.95089	1.02171
225.00	0.65106	0.73237	0.70582	1.12481	1.09372	0.95062	1.02156
250.00	0.64095	0.72126	0.69510	1.12523	1.09406	0.95038	1.02149
275.00	0.63190	0.71135	0.68551	1.12566	1.09437	0.95018	1.02147
300.00	0.62372	0.70241	0.67685	1.12609	1.09465	0.94999	1.02147

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¹⁷ J. de Boer and A. Michels, Physica 8, 409 (1939).

¹⁸ R. J. Munn, F. J. Smith, E. A. Mason, and L. Monchick, J. Chem. Phys. 42, 537 (1965).

¹⁹ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

TABLE II. Quantal collision integrals for He⁴ (Λ* = 2.67).

T, °K	Ω ₄₄ ^{(1,1)*}	Ω ₄₄ ^{(2,2)*}	Ω ₄₄ ^{(2,3)*}	A ₄₄ *	B ₄₄ *	C ₄₄ *	F ₄₄ *
0.20	10.02802	11.49374	6.68100	0.78305	1.21833	0.55441	0.52500
0.40	4.44410	3.28290	1.90518	0.88646	1.09372	0.68356	0.72832
0.60	3.18807	2.11226	1.92774	0.90236	1.15995	0.76373	0.77572
0.80	2.63968	2.15676	2.35101	0.92452	1.19712	0.79601	0.78978
1.00	2.31626	2.36004	2.58802	0.95390	1.20066	0.81285	0.80780
1.20	2.09792	2.49694	2.63083	0.98221	1.19151	0.82507	0.82961
1.40	1.93951	2.54251	2.55289	1.00612	1.17978	0.83543	0.85151
1.60	1.81910	2.51779	2.41587	1.02531	1.16875	0.84463	0.87152
1.80	1.72443	2.44850	2.25903	1.04045	1.15919	0.85286	0.88899
2.00	1.64799	2.35509	2.10440	1.05238	1.15106	0.86025	0.90396
2.40	1.53200	2.14731	1.83868	1.06944	1.13829	0.87281	0.92754
2.80	1.44791	1.95432	1.64345	1.08061	1.12890	0.88297	0.94477
3.20	1.38392	1.79400	1.50787	1.08819	1.12181	0.89127	0.95762
3.60	1.33339	1.66698	1.41521	1.09351	1.11631	0.89813	0.96744
4.00	1.29233	1.56818	1.35134	1.09735	1.11194	0.90387	0.97512
4.50	1.25050	1.47521	1.29696	1.10077	1.10763	0.90982	0.98257
5.00	1.21631	1.40677	1.25949	1.10318	1.10424	0.91471	0.98833
5.50	1.18771	1.35529	1.23180	1.10493	1.10152	0.91879	0.99288
6.00	1.16332	1.31553	1.20992	1.10622	1.09932	0.92223	0.99653
7.00	1.12368	1.25812	1.17584	1.10795	1.09598	0.92770	1.00199
8.00	1.09253	1.21795	1.14896	1.10901	1.09363	0.93182	1.00582
9.00	1.06713	1.18744	1.12643	1.10972	1.09192	0.93501	1.00860
10.00	1.04586	1.16287	1.10704	1.11022	1.09067	0.93753	1.01069
12.00	1.01179	1.12460	1.07506	1.11092	1.08900	0.94124	1.01357
14.00	0.98526	1.09528	1.04955	1.11142	1.08804	0.94378	1.01541
16.00	0.96369	1.07158	1.02849	1.11184	1.08748	0.94560	1.01667
20.00	0.93000	1.03477	0.99521	1.11261	1.08701	0.94797	1.01822
25.00	0.89870	1.00073	0.96391	1.11350	1.08699	0.94964	1.01928
30.00	0.87452	0.97455	0.93950	1.11434	1.08722	0.95058	1.01990
35.00	0.85488	0.95334	0.91954	1.11512	1.08755	0.95114	1.02030
40.00	0.83837	0.93554	0.90268	1.11585	1.08790	0.95148	1.02058
50.00	0.81168	0.90680	0.87521	1.11715	1.08859	0.95180	1.02092
60.00	0.79058	0.88407	0.85329	1.11822	1.08922	0.95188	1.02109
70.00	0.77318	0.86526	0.83502	1.11908	1.08977	0.95185	1.02113
80.00	0.75840	0.84922	0.81937	1.11976	1.09027	0.95177	1.02108
100.00	0.73425	0.82285	0.79360	1.12071	1.09112	0.95154	1.02088
120.00	0.71499	0.80170	0.77298	1.12136	1.09181	0.95129	1.02069
140.00	0.69903	0.78414	0.75592	1.12188	1.09237	0.95104	1.02056
160.00	0.68542	0.76920	0.74146	1.12236	1.09283	0.95082	1.02050
180.00	0.67359	0.75623	0.72893	1.12284	1.09321	0.95061	1.02049
200.00	0.66314	0.74481	0.71791	1.12332	1.09353	0.95043	1.02052
225.00	0.65160	0.73224	0.70577	1.12381	1.09390	0.95022	1.02058
250.00	0.64141	0.72116	0.69506	1.12449	1.09422	0.95003	1.02066
275.00	0.63229	0.71127	0.68549	1.12504	1.09451	0.94986	1.02076
300.00	0.62406	0.70234	0.67683	1.12557	1.09478	0.94971	1.02086

TABLE III. Quantal collision integrals for He³-He⁴ (Λ* = 2.88).

T, °K	Ω ₃₄ ^{(1,1)*}	Ω ₃₄ ^{(2,2)*}	Ω ₃₄ ^{(2,3)*}	A ₃₄ *	B ₃₄ *	C ₃₄ *	F ₃₄ *
0.20	5.54464	4.55759	3.30099	0.82198	1.27630	0.57347	0.53457
0.40	2.55507	2.32666	1.88223	0.91060	0.97535	0.72187	0.79515
0.60	1.97430	1.82812	1.63529	0.92596	1.01512	0.84518	0.88677
0.80	1.76565	1.67025	1.57848	0.94597	1.08819	0.88984	0.90045
1.00	1.64922	1.60793	1.55482	0.97497	1.12261	0.90434	0.90759
1.20	1.56778	1.57422	1.53238	1.00411	1.13256	0.90994	0.91895
1.40	1.50496	1.54881	1.50721	1.02914	1.13207	0.91311	0.93261
1.60	1.45422	1.52578	1.48080	1.04921	1.12797	0.91565	0.94625
1.80	1.41209	1.50368	1.45478	1.06485	1.12303	0.91801	0.95867
2.00	1.37646	1.48234	1.43008	1.07693	1.11829	0.92027	0.96945
2.40	1.31921	1.44251	1.38592	1.09346	1.11040	0.92446	0.98622
2.80	1.27500	1.40698	1.34863	1.10352	1.10461	0.92811	0.99788
3.20	1.23958	1.37570	1.31707	1.10981	1.10036	0.93123	1.00601
3.60	1.21039	1.34817	1.29007	1.11383	1.09718	0.93388	1.01177
4.00	1.18579	1.32387	1.26670	1.11645	1.09474	0.93613	1.01593
4.50	1.15982	1.29725	1.24147	1.11850	1.09242	0.93849	1.01962
5.00	1.13784	1.27405	1.21973	1.11971	1.09066	0.94044	1.02219
5.50	1.11889	1.25361	1.20073	1.12040	1.08931	0.94208	1.02402
6.00	1.10230	1.23544	1.18391	1.12078	1.08824	0.94346	1.02534
7.00	1.07441	1.20441	1.15530	1.12100	1.08672	0.94564	1.02701
8.00	1.05162	1.17873	1.13167	1.12087	1.08573	0.94728	1.02790
9.00	1.03244	1.15697	1.11165	1.12062	1.08509	0.94853	1.02835
10.00	1.01594	1.13819	1.09434	1.12032	1.08467	0.94951	1.02856
12.00	0.98866	1.10709	1.06560	1.11978	1.08425	0.95090	1.02857
14.00	0.96668	1.08207	1.04237	1.11936	1.08415	0.95182	1.02835
16.00	0.94833	1.06124	1.02294	1.11906	1.08422	0.95245	1.02805
20.00	0.91886	1.02799	0.99173	1.11877	1.08459	0.95317	1.02741
25.00	0.89064	0.99640	0.96183	1.11876	1.08521	0.95358	1.02675
30.00	0.86834	0.97163	0.93822	1.11895	1.08585	0.95371	1.02614
35.00	0.84995	0.95130	0.91875	1.11924	1.08644	0.95371	1.02569
40.00	0.83433	0.93409	0.90220	1.11958	1.08699	0.95364	1.02532
50.00	0.80878	0.90606	0.87510	1.12028	1.08793	0.95342	1.02475
60.00	0.78837	0.88371	0.85335	1.12093	1.08871	0.95315	1.02428
70.00	0.77143	0.86512	0.83517	1.12145	1.08937	0.95289	1.02384
80.00	0.75697	0.84921	0.81956	1.12185	1.08994	0.95264	1.02341
100.00	0.73324	0.82295	0.79378	1.12235	1.09090	0.95218	1.02265
120.00	0.71423	0.80184	0.77313	1.12266	1.09165	0.95179	1.02206
140.00	0.69843	0.78428	0.75604	1.12292	1.09224	0.95145	1.02165
160.00	0.68494	0.76932	0.74155	1.12320	1.09271	0.95115	1.02138
180.00	0.67319	0.75634	0.72901	1.12352	1.09311	0.95090	1.02122
200.00	0.66279	0.74490	0.71797	1.12388	1.09344	0.95068	1.02113
225.00	0.65132	0.73231	0.70581	1.12436	1.09381	0.95043	1.02108
250.00	0.64117	0.72122	0.69509	1.12486	1.09414	0.95022	1.02109
275.00	0.63209	0.71132	0.68551	1.12535	1.09444	0.95003	1.02112
300.00	0.62388	0.70239	0.67685	1.12583	1.09472	0.94986	1.02118

approximation. Higher approximations for viscosity and thermal conductivity involve Ω^{(2,3)*} as well. The other collision integrals, which enter into higher diffusion approximations and other mixture formulas, are conveniently tabulated as ratios:

$$A_{ij}^* = \Omega_{ij}^{(2,2)*} / \Omega_{ij}^{(1,1)*}, \quad (3a)$$

$$B_{ij}^* = [5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}] / \Omega_{ij}^{(1,1)*}, \quad (3b)$$

$$C_{ij}^* = \Omega_{ij}^{(1,2)*} / \Omega_{ij}^{(1,1)*}, \quad (3c)$$

$$F_{ij}^* = \Omega_{ij}^{(3,3)*} / \Omega_{ij}^{(1,1)*}. \quad (3d)$$

The value of Ω_{ij}^{(2,2)*} appearing in A_{ij}^{*} is not the same as the value given directly in the tables; the one appearing in A_{ij}^{*} refers to distinguishable particles, the other to indistinguishable particles.

The tabulated quantities are believed accurate to within 1 or 2 parts in 1000 down to 1°K, within 5 parts in 1000 to 0.5°K, and within about 10 parts in 1000 to 0.2°K.¹⁸ The subscripts on the tabulated collision integrals and integral ratios refer to the mass numbers of the isotopes, and a prime on a mass number means that it is a distinguishable particle; thus the subscript 33' refers to collisions between two He³ atoms which are distinguishable (e.g., because of different nuclear spin orientation), and the subscript 33 refers to collisions between two He³ atoms which are indistinguishable.

III. RESULTS

In this section we give the formulas used to calculate transport coefficients from the tabulated functions, and discuss the comparison with experiment. The formulas for the first approximations, denoted by the symbol []₁, are well known,¹⁹ and we give here only the correction terms used to compute the higher approximations.

A. Viscosity and Thermal Conductivity

The viscosity η is given by the expression

$$\frac{\eta}{[\eta]_1} = 1 + \frac{3}{196} \left[8 \frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}} - 7 \right]^2 + \dots, \quad (4)$$

and the thermal conductivity λ by

$$\frac{\lambda}{[\lambda]_1} = 1 + \frac{1}{42} \left[8 \frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}} - 7 \right]^2 + \dots, \quad (5)$$

in which the collision integrals refer to indistinguishable particles. The formulas for binary mixtures are not given here, inasmuch as no new experimental work has been reported since the discussion of Cohen, Offerhaus, and de Boer.⁴

The low-temperature viscosity of He³ and He⁴ has been discussed in detail by Keller.⁶ New measurements have since been reported by Coremans *et al.*⁸ on the

viscosity of He⁴ between 20 and 80°K, and they also give corrections to some earlier Leiden measurements at lower temperatures due to mirror damping. These results are shown in Fig. 1, together with some of the previous measurements.²⁰ The agreement seems reasonable, although not perfect, and no further discussion seems required beyond what has already been given.^{6,8} The agreement of our calculations with Keller's is very good, confirming his conclusion that there are fairly large systematic errors in the de Boer and Cohen calculations for He³. It is perhaps worth remarking that the correction given by Eq. (4) for the higher approximations is usually small, but is by no means negligible for these quantum gases. The maximum corrections in the temperature range shown in Fig. 1 are about 4% for He³ near 3°K, and about 5% for He⁴ near 1°K.

Fokkens, Taconis, and de Bruyn Ouboter⁹ have recently measured the thermal conductivity of He³ from 0.8 to 1.1°K and of He⁴ from 1.1 to 1.6°K. Their results are plotted in Fig. 2, together with those of Ubbink and de Haas²¹ which were taken from 1.6 to 3°K. The agreement with the present calculations seems fairly good. Some other calculations are also shown in the figure, corrected according to Eq. (5) with our calculated (12-6) correction terms. Keller's calculations are in good agreement with ours, as are de Boer's on He⁴, and any deviations do not even show on the scale of the figure. The de Boer-Cohen calculations on He³, however, clearly contain errors. The theoretical calculations of Buckingham and Scriven¹⁵ based on a Buckingham-Corner (exp-6-8) potential are also shown, corrected to a second approximation with our (12-6) correction term. The agreement with the present (12-6) results is perhaps closer than might have been anticipated for two such different potentials. The previous conclusion by Fokkens, Taconis, and de Bruyn Ouboter that the (exp-6-8) potential gave better agreement with their experimental results is not valid, and was due to numerical errors in de Boer and Cohen's He³ calculations.

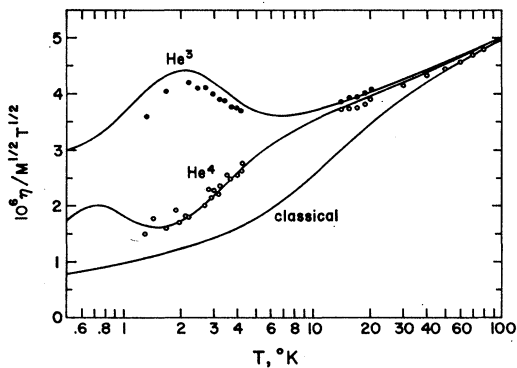


FIG. 1. Viscosity of helium.

²⁰ E. W. Becker, R. Misenta, and F. Schmeissner, *Z. Physik* **137**, 126 (1954); E. W. Becker and R. Misenta, *ibid.* **140**, 535 (1955).

²¹ J. B. Ubbink and W. J. de Haas, *Physica* **10**, 465 (1943).

Finally, it is worth remarking that the correction given by Eq. (5) is not negligible at these low temperatures, being about half again as large as the viscosity correction.

The large difference between the He³ and He⁴ curves in Figs. 1 and 2 is due to both diffraction and symmetry effects. The effect of symmetry for He³ is to de-emphasize *s*-wave scattering, which is large at low temperatures, and to emphasize it for He⁴. This is the main reason that the low-temperature collision cross sections are smaller for He³ than for He⁴. The maxima and points of inflection are the remnants of classical orbiting, which have been described elsewhere.^{16b} The classical (12-6) curves are also plotted in these figures, and it can be seen that quantum deviations are very large, especially for He³.

B. Diffusion

The mutual diffusion coefficient \mathfrak{D}_{ij} is given by the expression,

$$\mathfrak{D}_{ij} = [\mathfrak{D}_{ij}]_1 / (1 - \Delta_{ij} - \dots) = [\mathfrak{D}_{ij}]_1 (1 + \Delta_{ij} + \dots), \quad (6)$$

where $[\mathfrak{D}_{ij}]_1$ is independent of composition and the composition dependence is contained in the higher approximations, which are

$$\Delta_{ij} = \frac{1}{10} (6C_{ij}^* - 5) \left(\frac{x_i^2 P_i + x_j^2 P_j + x_i x_j P_{ij}}{x_i^2 Q_i + x_j^2 Q_j + x_i x_j Q_{ij}} \right), \quad (7a)$$

where

$$P_i = \frac{2M_i^2}{M_j(M_i + M_j)} \left(\frac{2M_j}{M_i + M_j} \right)^{1/2} \left[\frac{\Omega_{ii}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \right] \left(\frac{\sigma_{ii}}{\sigma_{ij}} \right)^2, \quad (7b)$$

$$P_{ij} = 15 \left(\frac{M_i - M_j}{M_i + M_j} \right)^2 + \frac{8M_i M_j A_{ij}^*}{(M_i + M_j)^2}, \quad (7c)$$

$$Q_i = \frac{2}{M_j(M_i + M_j)} \left(\frac{2M_j}{M_i + M_j} \right)^{1/2} \left[\frac{\Omega_{ii}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \right] \left(\frac{\sigma_{ii}}{\sigma_{ij}} \right)^2 \times \left[\left(\frac{5}{2} - \frac{6}{5} B_{ij}^* \right) M_i^2 + 3M_j^2 + \frac{8}{5} M_i M_j A_{ij}^* \right], \quad (7d)$$

$$Q_{ij} = \frac{15(M_i - M_j)^2}{(M_i + M_j)^2} + \frac{32M_i M_j A_{ij}^*}{(M_i + M_j)^2} + \frac{8(M_i + M_j)}{5(M_i M_j)^{1/2}} \times \left[\frac{\Omega_{ii}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \right] \left[\frac{\Omega_{jj}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \right] \left(\frac{\sigma_{ii} \sigma_{jj}}{\sigma_{ij}^2} \right)^2. \quad (7e)$$

The relations for P_j and Q_j are obtained from those for P_i and Q_i by an interchange of subscripts. These expressions are obtained using the Chapman-Cowling theory; the Kihara expressions can be obtained by setting $B_{ij}^* = 5/4$.²²

²² E. A. Mason, *J. Chem. Phys.* **27**, 75 (1957).

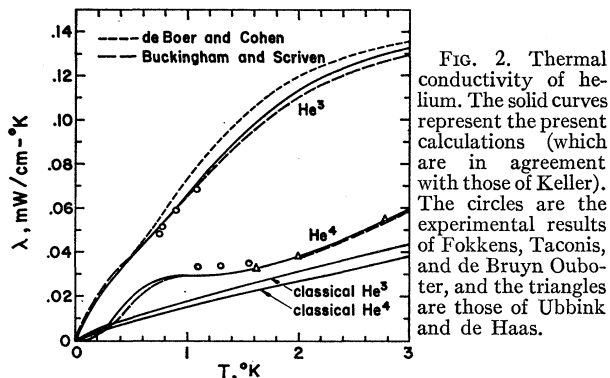


FIG. 2. Thermal conductivity of helium. The solid curves represent the present calculations (which are in agreement with those of Keller). The circles are the experimental results of Fokkens, Taconis, and de Bruyn Ouboter, and the triangles are those of Ubbink and de Haas.

The collision integrals $\Omega_{ii}^{(2,2)*}$ and $\Omega_{jj}^{(2,2)*}$ in Eqs. (7) refer to indistinguishable particles. These formulas therefore make precise the remark by Emery¹² that symmetry effects first appear only in the second approximation to \mathfrak{D}_{ij} , even if i and j are the same chemical species. Previous calculations of the "self-diffusion" coefficients of He³ and He⁴ have used collision integrals for indistinguishable particles to obtain the first approximation.⁴ That this is erroneous has been shown in detail by Emery¹²; it is almost obvious from the fact that distinguishable particles must be involved in order to conduct any diffusion experiment at all.

Bendt¹⁰ has measured \mathfrak{D}_{34} , for He³-He⁴ mixtures having an average composition of 7.94 mole % He³, from 1.74 to 296°K, with a quoted error of from 2 to 6%. His results are plotted in Fig. 3 together with the theoretical calculations. The disagreement of the present calculations and those of Cohen, Offerhaus, and de Boer⁴ can be due only to numerical error; presumably this is again due to the errors in the calculated He³ phase shifts, since Cohen, Offerhaus, and de Boer obtained the phase shifts for He³-He⁴ collisions by interpolation between phase shifts for He³ and He⁴.

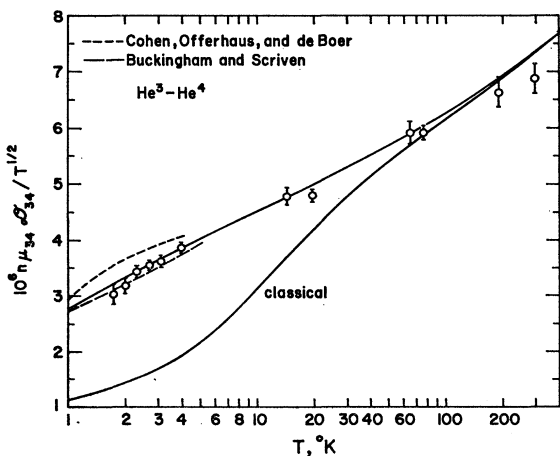


FIG. 3. Diffusion coefficient of He³-He⁴. The error limits indicated on the experimental points (Bendt) are the standard deviations of repeated measurements. n is the number density and μ_{34} is the reduced mass.

The calculations of Buckingham and Scriven¹⁵ are also shown, corrected to the second approximation by means of our (12-6) values of Δ_{34} . The correction due to Δ_{34} is only about 1%. The agreement between these calculations and ours is again rather good. The agreement with experiment seems to be within experimental error, except possibly at the highest temperature. The calculated classical curve is also plotted, and shows that the diffraction effects increase \mathfrak{D}_{34} by a factor of about 2 at low temperatures.

The two orientations of a He³ nucleus in a magnetic field may be regarded as distinguishable because the probability of exchange on collision is very small. Luszczynski, Norberg, and Opfer^{11a} have described a spin-echo technique for measuring the spin-diffusion coefficient of He³. In Fig. 4 we have plotted the results of their newest measurements^{11b} together with our second Chapman-Cowling approximation for $\mathfrak{D}_{33'}$ and

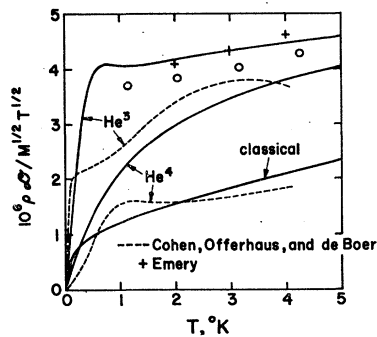


FIG. 4. "Self-diffusion" coefficients of He³ and He⁴. (These are really tracer diffusion coefficients). The circles are the spin-diffusion measurements on He³ by Luszczynski, Norberg, and Opfer.

the calculations of Cohen, Offerhaus and de Boer⁴ and of Emery.¹² The relatively large deviation of the Cohen, Offerhaus, and de Boer curve is caused by the erroneous symmetry effect already mentioned. The three points by Emery were recalculated from de Boer's tabulated phase shifts³ on the basis of distinguishable particles. The agreement with experiment seems satisfactory. The total correction due to Δ is 1-3% over most of the range shown, but the variation of Δ with composition amounts to a correction of 0.6% at most.

Although He⁴ has zero nuclear spin, it is still possible to imagine a measurement of $\mathfrak{D}_{44'}$ by means of an excited nuclear state of He⁴. Our calculated second Chapman-Cowling approximation for $\mathfrak{D}_{44'}$ is therefore also shown in Fig. 4, even though it may never actually be measured because the known excited nuclear states of He⁴ are unstable and break up into a proton and a triton.²³ The total correction due to Δ is at most 0.7%, essentially independent of composition.

The calculated classical curve for $\mathfrak{D}_{33'}$ and $\mathfrak{D}_{44'}$ is also shown in Fig. 4, and again shows the importance of the diffraction effects at low temperatures. The curves are scaled so that they merge at high temperatures.

²³ P. D. Parker, P. F. Donovan, J. V. Kane, and J. F. Mollenauer, Phys. Rev. Letters 14, 15 (1965).

It is interesting to note that spin or tracer diffusion provides a means of separating diffraction and symmetry effects, since the particles are regarded as distinguishable in diffusion. In this case only diffraction effects occur in the first Chapman-Enskog approximation. The symmetry effects which appear in the second approximation are of an altogether smaller order of magnitude.

C. Thermal Diffusion

The thermal diffusion factor α_T for a mixture of i and j is given by the expression,

$$\alpha_T = (6C_{ij}^* - 5) \left(\frac{x_i S_i - x_j S_j}{x_i^2 Q_i + x_j^2 Q_j + x_i x_j Q_{ij}} \right) (1 + \kappa_{ij}), \quad (8)$$

where all the Q 's are as given in Eq. (7), and

$$S_i = \frac{M_i}{M_j} \left(\frac{2M_j}{M_i + M_j} \right)^{1/2} \left[\frac{\Omega_{ii}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \right] \left(\frac{\sigma_{ii}}{\sigma_{ij}} \right)^2 - \frac{4M_i M_j A_{ij}^*}{(M_i + M_j)^2} + \frac{15M_j(M_i - M_j)}{2(M_i + M_j)^2}, \quad (9)$$

with the convention that $M_i > M_j$. The expression for S_j is obtained by interchanging the subscripts in the expression for S_i . The term κ_{ij} is a correction arising from higher approximations to the theory; the expression for κ_{ij} is very complicated²² and need not be given here. In magnitude κ_{ij} is usually small but not negligible, and for a given system it depends weakly on composition and temperature. The temperature dependence of α_T is given primarily by the factor $(6C_{ij}^* - 5)$, and the composition dependence primarily by the factor containing the S 's and Q 's.

The results for an equimolar mixture of He³ and He⁴ are shown in Fig. 5, calculated with the Kihara second approximation²² for κ_{ij} . The extreme variation of α_T with composition is less than 5% down to 10°K, rising to about 20% at 5°K, and to over 50% at 1°K. The

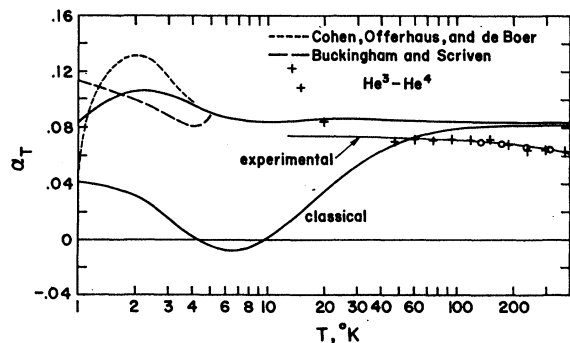


FIG. 5. Thermal diffusion factor of equimolar He³-He⁴. The circles are the experimental results of Watson, Howard, Miller, and Shiffrin, and the crosses are those of van der Valk. The curve marked "experimental" actually represents the measured separations within experimental uncertainty.

magnitude of κ_{ij} for an equimolar mixture amounts to a correction to α_T of about 5% down to 10°K, then rises to a maximum of about 9% near 4°K.

The thermal diffusion factor is much more sensitive to computational errors and to the intermolecular forces than are the other transport coefficients. The differences among the theoretical calculations shown in Fig. 5 are consistent with the corresponding differences in the calculations of \mathfrak{D}_{34} which were shown in Fig. 3. The experimental measurements shown in Fig. 5 were made on equimolar mixtures by Watson, Howard, Miller, and Shiffrin,¹³ and on mixtures containing 10 mole % of He³ by van der Valk.¹⁴ The discrepancy at higher temperatures, in which the measured α_T is smaller than the calculated α_T , is real, and is caused by too steep a repulsion in the 12-6 model. The discrepancy below 20°K is only apparent, however. The values of α_T at low temperatures were obtained experimentally from the slope of a logarithmic plot of the mixture separation factor against the temperature.²⁴ The value of the slope becomes very hard to determine when there is appreciable scatter in the separation measurements, as there was in van der Valk's low-temperature measurements. The α_T curve in Fig. 5 marked "experimental" was obtained by drawing a curve on the logarithmic separation plot of roughly the same shape as predicted by the (12-6) and (exp-6-8) calculations, but with its slope adjusted to fit the experimentally measured separations. This curve passes through the measured separation points within their probable uncertainty.

The most remarkable result in Fig. 5 is the way the quantum diffraction effects keep α_T nearly constant down to 1°K. The experimental results, despite their uncertainty, seem definitely to be more consistent with this behavior than with the behavior predicted classically.

IV. DISCUSSION

In summary, the quantum effects for He³ and He⁴ are generally large, and are rather well accounted for by the (12-6) model. We may now inquire whether the discrepancies noted between theory and experiment are to be regarded as significant or not. For pure He³ and He⁴ the only notable discrepancy appears to be viscosity of He³ between 1 and 4°K. This cannot definitely be blamed on the theoretical model, however, for then the heat conductivity of He³ should also show nearly the same discrepancies, and it does not. In other words, it appears that the experimental measurements of η and λ for He³ at low temperatures are discordant with each other, and this conclusion is almost independent of the nature of the intermolecular forces. This conclusion is reinforced by the observation that

²⁴ K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge University Press, London and New York, 1952), Chap. 3 and 4.

the model gives good agreement for the low-temperature second virial coefficients of both isotopes.^{5,25}

The calculated diffusion coefficients seem to be in agreement with experiment, as nearly as it is possible to assess the experimental uncertainties.

Thermal diffusion in He³-He⁴ shows a distinct discrepancy at higher temperatures, due to the steepness of the repulsion term in the (12-6) model. This is not surprising, since it has been known for some time^{1a} that the high-temperature viscosity clearly indicates that an r^{-12} repulsion is too "hard."

We conclude, therefore, that there is no justification for trying to improve the agreement between calculation and experiment at low temperatures by adjustment of the (12-6) potential parameters. However, it is known

that the (12-6) model is not as good at high temperatures, and it is then of interest to ask how the model should be altered to obtain agreement at high temperatures without spoiling the agreement at low temperatures. Although use of the (exp-6) or (exp-6-8) models will "soften" the repulsion and thereby improve matters at high temperatures, as well as improve the agreement for α_T , it has previously been shown,^{1(b),6} at least for the (exp-6) model, that the low-temperature agreement is then worse. The reason is that these particular three-parameter models are insufficiently flexible; that is, that the repulsive and attractive parts cannot be varied independently. It is not clear how to alter the usual models in other ways to achieve this without at the same time introducing more adjustable parameters and allowing the whole procedure to degenerate into physically meaningless curve fitting.

²⁵ W. E. Keller, *Phys. Rev.* **97**, 1 (1955); **98**, 1571 (1955).

Temperature and Frequency Dependence of Ultrasonic Absorption in Liquid Helium below 1°K*

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(Received 24 March 1965)

From measurements of the temperature dependence of the amplitude of ultrasonic pulses propagated over a fixed path in liquid helium, the attenuation coefficient has been determined at the six frequencies 1.00, 2.02, 3.91, 6.08, 10.2, and 11.7 Mc/sec, at temperatures extending down to 0.2°K. Below 0.6°K, the observed variation of the absorption coefficient α (cm⁻¹) with frequency f (Mc/sec) and temperature T (°K) can be represented by the empirical equation $\alpha = 0.11 f^{3/2} T^3$. This behavior differs from that predicted by several existing theories that are based upon the three-phonon or four-phonon interaction between longitudinal acoustic quanta and thermal phonons. Over the temperature interval 0.6–0.8°K, the measured attenuation is somewhat greater than would be expected from an extrapolation of the results below 0.6°K into this temperature region. A comparison of the data with some calculations by Khalatnikov suggests that the additional absorption arises from thermal conduction in the normal fluid. An equation that is analogous to the classical Kirchhoff expression adequately accounts for this contribution to the total absorption, even at temperatures for which the lifetime of the thermal phonons exceeds the period of the sound wave.

I. INTRODUCTION

AT temperatures just below 1°K, the absorption of ordinary sound in liquid helium goes through a maximum. The behavior of the absorption on the high-

temperature side of the peak has been quite well defined experimentally.¹ Chase² has made careful measurements of the (amplitude) attenuation coefficient α at the frequencies 2, 6, and 12 Mc/sec at temperatures above 0.85°K, and has established a close correspondence between his results and a microscopic theory of the absorption developed by Khalatnikov.³ The pressure dependence of the attenuation has been examined by Newell and Wilks.⁴ Although it is not feasible to make a detailed quantitative comparison with the

* This work was supported in part by the U. S. Army Signal Corps, the U. S. Air Force Office of Scientific Research, and the U. S. Office of Naval Research; additional support was received from the National Science Foundation. Concluding phases of the work were performed at the Jet Propulsion Laboratory, California Institute of Technology, supported by the National Aeronautics and Space Administration under Contract No. NAS 7-100. Some of the results described in the paper form the basis of a Ph.D. thesis submitted by W. A. Jeffers, Jr., to the Department of Physics, MIT, 1962. A preliminary account of the research has been given at a meeting of the American Physical Society [W. A. Jeffers, Jr., and W. M. Whitney, *Bull. Am. Phys. Soc.* **7**, 472 (1962)].

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¹ For accounts of previous studies of sound propagation in liquid helium, see the review article by J. Wilks, *Z. Physik. Chem.* **16**, 372 (1958); and K. R. Atkins, *Liquid Helium* (Cambridge University Press, Cambridge, England, 1959), Chap. 5.

² C. E. Chase, *Proc. Roy. Soc. (London)* **A220**, 116 (1953).

³ I. M. Khalatnikov, *Zh. Eksperim. i Teor. Fiz.* **20**, 243 (1950).

⁴ J. A. Newell and J. Wilks, *Phil. Mag.* **1**, 588 (1956).