

## Thermal Accommodation of the Helium Isotopes on Clean Tungsten Surfaces

J. KOUPTSIDIS and D. MENZEL

Eduard-Zintl-Institut, Technische Hochschule Darmstadt, Germany

(Z. Naturforsch. **24** a, 479—480 [1969]; received 6 February 1969)

Using a previously described technique to insure extreme cleanliness, the accommodation coefficients (a.c.) of the helium isotopes have been measured on clean tungsten surfaces between 77 and 373 °K. It was found that the a.c. of  $^3\text{He}$  is about 10% smaller than that of  $^4\text{He}$  above 250 °K; at lower temperatures the difference becomes smaller.

In the last years considerable effort, especially from the theoretical side, has been invested to come to a better understanding of the energy and momentum exchange which takes place upon impact of gas particles on solid surfaces<sup>1</sup>. The examination of the proposed models is hampered by the fact that reliable experimental data are still scarce, which is mainly due to the very strong influence of surface contamination on these processes. We have recently described a system<sup>2</sup> which makes possible the exclusion of all contamination effects in the measurements of thermal accommodation coefficients (a.c.'s) by the hot filament method. In the measurements with this system, we aim at separating as clearly as possible the influence of different parameters on the value of the a.c. It would be of interest, for instance, to show directly the influence of the mass of the impinging particle on the a.c. This cannot be found by comparing the a.c.'s of different atoms, e.g. the rare gases, as a number of other important parameters change from one species to the other. This can be avoided, if the a.c.'s of different isotopes of the same chemical species are compared, the most convenient being the helium isotopes. The a.c.'s of  $^3\text{He}$  and  $^4\text{He}$  have therefore been measured as a function of the temperatures of gas and surface between 77 and about 400 °K. The only measurement of this kind known to us is a preliminary result of KRUEGER (reported by THOMAS<sup>3</sup>), who obtained a ratio

$$\alpha_4/\alpha_3 = 1,09 \text{ at } 308^\circ\text{K}.$$

The measurements have been carried out using the hot filament method, using potential leads; the results have been corrected for small errors (some percent) due to the change of the temperature distribution along the filament in vacuum and gas. The technique to obtain and control extreme cleanliness of the system and of the used rare gases, which comprises the use of a field emission microscope as integrating contamination monitor, has been described in detail previously<sup>2</sup>. A thermostat using mineral oil, ethyl alcohol, isopentane, and liquid nitrogen as coolants has been

used to establish a gas temperature constant to about 0,05 °K. The gases were cleaned by successive gettering as described in <sup>2</sup>. Mass spectrometric analysis showed the used  $^3\text{He}$  to contain 99,6%  $^3\text{He}$ , 0,2%  $^4\text{He}$ , all other contaminants being below 0,2% (mostly hydrogen) before cleaning. The pressure measurements were made with a bakeable McLeod; care was taken to eliminate errors caused by thermal transpiration and the mercury pumping effect.

On the same filament, the reproducibility of the measurements was better than 2%. On different filaments, the measured a.c. values differed up to about 6%, probably due to errors in the measurement of the pertinent constants of the filaments, and/or to small changes of the surface exposed by the filaments, e.g. roughness, exposed crystal faces etc. Absolute variations of this magnitude are of no importance; however, they disturb the comparison of the a.c. values of the two isotopes somewhat. They could be eliminated by measuring on one filament only; yet, because of the rather high tendency of the potential leads to break during the experiments, it was necessary to combine measurements on different filaments in order to cover the complete temperature range. To eliminate the systematic deviations between filaments for the comparison, the measurements were normalized: for each filament the a.c. of  $^4\text{He}$  at 298 °K was measured first; all other measurements on it were corrected by its deviation from the mean value for 8 filaments, which was  $\alpha_4(298) = 0,0167$  (in excellent agreement with <sup>4</sup>). This led to corrections of 0 to 5%. The results for the a.c. values of  $^4\text{He}$  and  $^3\text{He}$  obtained thus are shown in Fig. 1 as a function of the gas temperature. In agreement with findings reported before<sup>2,5</sup> for  $^4\text{He}$ , no dependence of

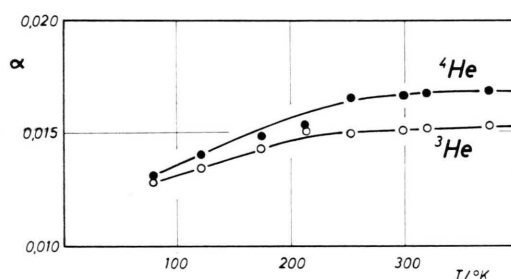


Fig. 1. Temperature dependence of the a.c.'s of the helium isotopes on clean tungsten.

the a.c.'s on the temperature difference between gas and surface,  $\Delta T$ , was found except at the lowest gas temperature, where the a.c. increased slightly with  $\Delta T$ ; the values given for these cases were obtained by extrapolation to  $\Delta T = 0$ .

It is seen that the a.c. of  $^4\text{He}$  is about 10% higher than that of  $^3\text{He}$  above 250 °K, in good agreement with <sup>3</sup>, while

<sup>1</sup> See e.g. Rarefied Gas Dynamics, 5th Sympos., Academic Press, New York 1967, Vol. I.

<sup>2</sup> D. MENZEL and J. KOUPTSIDIS, Fundamentals of Gas-Surface Interactions, Academic Press, New York 1967, p. 493. — J. KOUPTSIDIS and D. MENZEL, Ber. Bunsenges. Phys. Chem. **71**, 720 [1967].

<sup>3</sup> L. B. THOMAS, p. 162 of <sup>1</sup>.

<sup>4</sup> D. V. ROACH and L. B. THOMAS, p. 167 of <sup>1</sup>.

<sup>5</sup> L. B. THOMAS and E. B. SCHOFIELD, J. Chem. Phys. **23**, 861 [1955].



the difference diminishes to lower temperatures. As the latter finding was unexpected, and in order to exclude the possibility of this finding being caused by errors, a very careful comparison was made of the a.c.'s of the two isotopes on the same surface at 298 and at 77°K: at each temperature, three independent runs for each gas were made, each consisting of 10 measurements at different  $\Delta T$ -values; the final value was found by extrapolation to  $\Delta T = 0$ . The utmost care was taken to use identical procedures, so that all systematic errors would cancel in the comparison. Table 1 shows the results. It is seen that the results of Fig. 1 are confirmed. As the possible relative error is estimated to be about 1%, it is concluded that the a. c. of  $^4\text{He}$  is larger than that of  $^3\text{He}$  by 8 to 12% at 298°K, and by 1 to 5% at 77°K. The difference in these ratios is well outside the experimental error.

$T$ (°K)	$\alpha_4$	$\alpha_3$	$\gamma = 100 \left( \frac{\alpha_4}{\alpha_3} - 1 \right)$
298	0,0167	0,0153	10%
	0,0170	0,0154	
	0,0169	0,0153	
77	0,0133	0,0127	3%
	0,0133	0,0129	
	0,0130	0,0128	

Table 1. Comparison of the a.c. values of  $^4\text{He}$  and  $^3\text{He}$  on the same  $W$  surface at 77 and 298°K.

A first comparison with existing theories shows the following: The simple theory of BAULE<sup>6</sup> which is based on

collisions of isolated hard spheres leads to

$$\alpha \sim m \quad \text{for } m \ll M$$

( $m$ : mass of gas atom;  $M$  mass of isolated metal atom); BAULE's result is identical with the so-called "high temperature" or "hard spheres" limit of several treatments<sup>7,8</sup>. This prediction is disproven by the experimental result. An even stronger contradiction is found with the result of LANDAU's<sup>9</sup> continuum theory:  $\alpha \sim 1/\sqrt{m}$ , which even predicts the wrong direction of the change. The theory of TRILLING<sup>10</sup> postulates a dependence  $\alpha \sim \sqrt{m}$  for  $m \ll M$ , independent of temperature, i.e.

$$\gamma = 100 (\alpha_4/\alpha_3 - 1) = 15,5\%,$$

which is not far from the value measured for  $T > 250^\circ\text{K}$ . GOODMAN and WACHMAN<sup>11</sup> made a prediction for the a.c.'s of the helium isotopes using a semiempirical formula based on GOODMAN's classical lattice theory. From their Fig. 8 a value of  $\gamma$  of about 11,5%, practically independent of temperature, is derived. This is in excellent agreement with the measured value for  $T > 250^\circ\text{K}$ , while the decrease of  $\gamma$  with decreasing temperature remains unexplained. (The shape of the temperature dependence of the a.c.'s predicted in<sup>11</sup> is somewhat different from our results, especially above 250°K, but this is considered not too significant, as by a small adjustment of the constants used in the formula of<sup>11</sup> agreement with our results could probably be obtained).

An explanation of the change of  $\gamma$  with decreasing temperature will be attempted in a forthcoming publication.

Financial support by the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie is gratefully acknowledged.

<sup>6</sup> B. BAULE, Ann. Phys. **44**, 145 [1914].

<sup>7</sup> F. O. GOODMAN, J. Phys. Chem. Solids **23**, 1269 [1962].

<sup>8</sup> R. E. STICKNEY, Rarefied Gas Dynamics, 4th Sympos., Academic Press, New York 1966, Vol. II, p. 474.

<sup>9</sup> L. LANDAU, Physik. Z. Sowjetunion **8**, 487 [1935].

<sup>10</sup> L. TRILLING, p. 139 of<sup>1</sup>.

<sup>11</sup> F. O. GOODMAN and H. Y. WACHMAN, J. Chem. Phys. **46**, 2376 [1967].