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Modification of the Devonshire Formula for the Thermal Accommodation Coefficient of Helium on Tungsten

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The thermal accommodation coefficients (a.c.) of ^3He and of ^4He on clean tungsten were calculated using the Devonshire formula for temperatures between 70 and 600°K using "realistic" Morse potential parameters. The calculated a.c. values for ^3He and ^4He and the calculated ratios of the ^4He to ^3He values are compared with experimental data. The agreement is satisfactory if allowance is made for the error in the transition probability calculation used in the Devonshire formula.

I. INTRODUCTION

The extent of energy transfer between a gas and a solid surface is indicated by the thermal or energy accommodation coefficient (hereafter abbreviated as a.c.), defined as

$$\text{a.c.} = (E_R - E_i) / (E_S - E_i),$$

where E_i is the average energy-flux density of gas beam incident on a solid, E_R is the average energy-flux density of the reflected beam, and E_S is the average energy-flux density that would exist if the stream of molecules were to come into equilibrium with the solid surface at temperature T_S before being re-emitted. The theoretical investigations of energy exchange between gas atoms and a solid surface have employed both classical mechanics¹⁻⁴ and quantum mechanics.⁵⁻¹² Reliable experimental a.c. values are now available for rare-gas-clean-metal surface systems¹³ and the success of existing a.c. theories are tested by comparison with those data. For rare gases of small mass interacting with a tungsten surface, the a.c. behavior as a function of temperature is adequately described by either the classical mechanical theory of Goodman¹ or the quantum-mechanical theory of Devonshire,¹⁴

both of which use a Morse potential interaction between the atom and the surface. However, the values of the potential parameters required to give adequate agreement are significantly different for the two theories.

A further test of the theories is provided by comparison of predicted with experimental values of the ratio of the a.c. of ^4He to the a.c. of ^3He on clean tungsten determined as a function of temperature.¹⁵ These data provide a particularly good test of theory as the only parameter in the theoretical treatment which varies between ^4He -W and ^3He -W systems is the mass of the gas atom. Although neither the Goodman nor the Devonshire theory, using the Morse parameters obtained by best fit of the experimental a.c.-vs-temperature data, provides adequate agreement with experimental ^4He - ^3He ratio values, the Devonshire theory predicts the ratio to be less than unity over a large temperature range, in disagreement with experimental data.

Recently exact quantum-mechanical calculations of the transition probability of vibrational energy transfer between a harmonic oscillator and an atom have been reported.¹⁶ The reported values are much smaller than the approximate values calculated by Jackson and Mott and Devonshire for a repulsive exponential interaction. Recent work^{17,18} indicates that the ratio of the energy transfer calculated by the Jackson-Mott approximation (for single-phonon transitions between the zero and first vibrational states) to the exact energy transfer (for transitions between the zero and all other states) is nearly constant over the energy spectrum examined. The ratio increases from 3.19 to 3.40 as the energy increases from 6 to 20 zero-point energy units. The transition probability and the magnitude of the error caused by the Jackson-Mott approximation in calculation of the probability are

¹ F. O. Goodman and H. Y. Wachman, *J. Chem. Phys.* **46**, 2376 (1967).

² F. O. Goodman, *J. Phys. Chem. Solids* **24**, 1451 (1963).

³ F. O. Goodman, *Proc. Intern. Symp. Rarefied Gas Dyn.* 4th 1964, 366 (1966).

⁴ C. M. Chambers and E. T. Kinzer, *Surface Sci.* **4**, 33 (1966).

⁵ J. M. Jackson, *Proc. Cambridge Phil. Soc.* **28**, 136 (1931).

⁶ J. M. Jackson and N. F. Mott, *Proc. Roy. Soc. (London)* **A137**, 703 (1932).

⁷ A. F. Devonshire, *Proc. Roy. Soc. (London)* **A158**, 269 (1937).

⁸ P. Feuer, *J. Chem. Phys.* **39**, 1311 (1963).

⁹ P. Feuer, *Bull. Am. Phys. Soc.* **12**, 380 (1967).

¹⁰ P. Feuer and C. Osburn, *Proc. Intern. Symp. Rarefied Gas Dyn.* 6th 1968 (to be published).

¹¹ R. T. Allen and P. Feuer, *Proc. Intern. Sym. Rarefied Gas Dyn.* 5th 1966, 109 (1967).

¹² J. W. Gadzuk, *Phys. Rev.* **153**, 759 (1967).

¹³ L. B. Thomas, Ref. 11, p. 155.

¹⁴ Robert E. Brown, Ph.D. thesis, University of Missouri—Columbia, Columbia, Mo. (1958).

¹⁵ L. B. Thomas, C. L. Krueger, and R. E. Harris, Ref. 10.

¹⁶ D. Secrest and B. R. Johnson, *J. Chem. Phys.* **45**, 4556 (1966).

¹⁷ D. Secrest, *J. Chem. Phys.* **49**, 2880 (1968).

¹⁸ R. E. Roberts, *J. Chem. Phys.* **49**, 2880 (1968).

dependent on the relative masses of the atom and the vibrator as well as on the repulsive potential parameter. The transition probability enters into the quantum-mechanical a.c. calculation in an integral over incident gas energies. Since this transition probability is in error by a factor nearly constant over the energy spectrum, the calculated a.c. may be in error by nearly the same factor at all temperatures. At the present time it appears unfeasible to extend the exact probability calculations to the higher energies necessary for evaluation of the energy integral in the Devonshire a.c. formula. The work reported here was undertaken to: (1) examine the ^4He a.c. on tungsten computed from the Devonshire formula (with parameters derived from the classical treatment) for a constant factor which would bring the calculated values into agreement with experimental values, and (2) to compute the ratio of ^4He and ^3He a.c. values, using the same parameters, for comparison with experimental values.

II. RESULTS AND DISCUSSION

The accommodation coefficients of ^4He and of ^3He on a tungsten surface (Debye temperature is 380°K) were calculated using the Devonshire formula⁷ for the two combinations of Morse parameters utilized in the classical calculations of Goodman¹⁹: (1) $D=320$ cal mole⁻¹, $\kappa=1.3 \text{ \AA}^{-1}$ and (2) $D=190$ cal mole⁻¹, $\kappa=1.3 \text{ \AA}^{-1}$. The calculated values for ^4He for the two combinations of Morse parameters were adjusted so that the calculated values at 302°K equalled the experimental value at 302°K ,¹³ a particularly reliable experimental value. To obtain this agreement, the

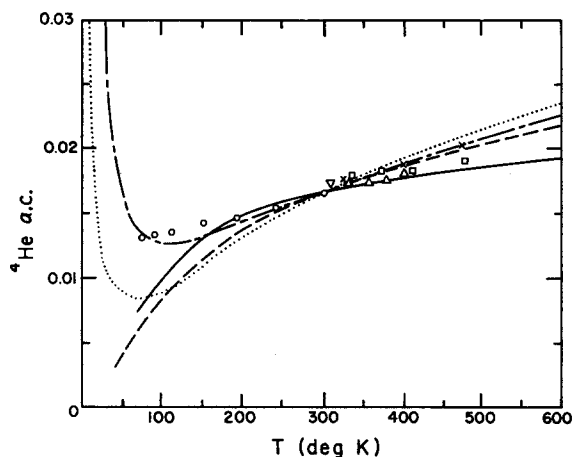


FIG. 1. Experimental data on the a.c. of ^4He on tungsten and the corresponding theoretical curves. O, Thomas and Silvernail (Ref. 13); Δ and \square , Roach and Thomas (Ref. 21); ∇ , Harris (Ref. 22); \times , Wachman (Ref. 20); —, present calculations with $D=190$ cal/mole; - - -, present calculations with $D=320$ cal/mole; ···, calculations by Goodman (Ref. 19) with $D=190$ cal/mole; - · - ·, calculations by Goodman (Ref. 19) with $D=320$ cal/mole.

¹⁹ F. O. Goodman J. Chem. Phys. 50, 3855 (1969).

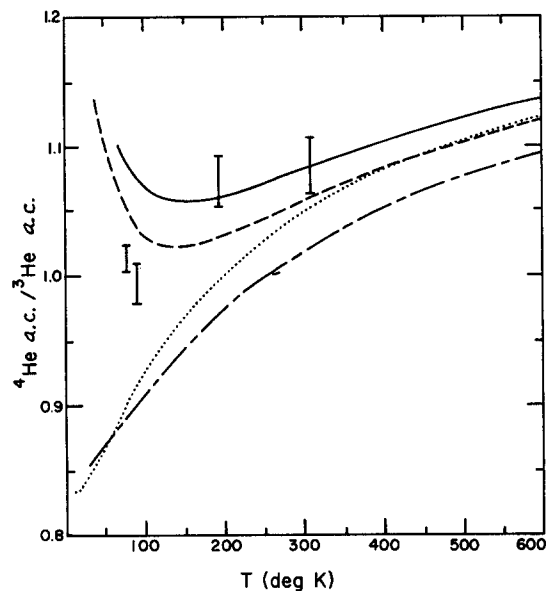


FIG. 2. Experimental data on the ratio ^4He a.c./ ^3He a.c. and the corresponding theoretical curves. |, experimental data of Thomas Krueger and Harris (Ref. 15); - - -, present calculations with $D=190$ cal/mole; —, present calculations with $D=320$ cal/mole; ···, calculations by Goodman (Ref. 19) with $D=190$ cal/mole; - · - ·, calculations by Goodman (Ref. 19) with $D=320$ cal/mole.

results with $D=320$ cal mole⁻¹, $\kappa=1.3 \text{ \AA}^{-1}$ were divided by 3.00 and those with $D=190$ cal mole⁻¹, $\kappa=1.3 \text{ \AA}^{-1}$ were divided by 2.14. These adjusted results are shown in Fig. 1, where the solid curve is for $D=320$ cal mole⁻¹, the dashed curve for $D=190$ cal mole⁻¹, and experimental results are shown for comparison.²⁰⁻²² The results of the classical calculations of Goodman¹⁹ are also shown in Fig. 1. The adjusted calculated results using the Devonshire formula agree well for temperatures above 200°K . The lack of agreement at lower temperatures may result from either or both of two causes: (1) The factor used for adjustment is dependent on temperature as indicated by the calculations of Secret and Johnson and becomes smaller as the temperature decreases, hence the low-temperature calculated values are over-corrected, and (2) the Devonshire formula is applicable only for single phonon transfers. The effect on the a.c. of ^4He caused by adsorption of ^4He at low temperatures has not been adequately treated with quantum theory, however, the classical model of Goodman does account for such a process and is shown in Fig. 1 as an increase in the calculated a.c. at low temperatures, a result qualitatively supported by experimental results.²³

The ratio of the calculated unadjusted values of the a.c. of ^4He to the a.c. of ^3He are shown in Fig. 2, where values calculated with the Devonshire formula with

²⁰ H. Y. Wachman, J. Chem. Phys. 45, 1532 (1966).

²¹ D. V. Roach and L. B. Thomas, Ref. 11, p. 163.

²² R. E. Harris, J. Chem. Phys. 46, 3217 (1967).

²³ L. B. Thomas and D. V. Roach (unpublished data).

$D=320$ cal mole⁻¹ are shown as a solid curve and those with $D=190$ cal mole⁻¹ are shown as a dashed curve. If the errors in the probability function for the two helium isotopes on a tungsten surface are nearly the same at each temperature, the ratio of the calculated unadjusted a.c. of the two isotopes should then agree with the experimental values. Over the temperature range where experimental results are available, the agreement of the calculated results using the Devonshire formula is satisfactory for either set of parameters. The large increase of the calculated ratio at low temperatures is particularly interesting and more experimental data in that temperature range are obviously desirable and of considerable importance to discern whether the effect is real or whether the ratio is influenced also by one or both of the factors discussed above in regard to Fig. 1. The behavior is particularly interesting when compared with that predicted by the results of the classical calculation of Goodman,¹⁹ which are shown in Fig. 2.

The agreement of the adjusted calculated values with experimental data as shown in Figs. 1 and 2 considered in light of the well-documented discrepancy in the Jackson-Mott transition probability leads us to conclude that the existing quantum-mechanical theory of thermal accommodation, if modified to account for the error in the probability calculation, would be in good agreement with experimental data under conditions such that the theory may be expected to yield meaningful results. Firm establishment of this conclusion awaits an exact calculation of the transition probability and the a.c. and subsequent comparison with reliable experimental data.

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Magnetic Resonance Study of the Dissociation of Peroxydisulfuryl Difluoride into Fluorosulfate Radicals

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Broadening of the NMR line of ¹⁹F in peroxydisulfuryl difluoride, S₂O₆F₂, was investigated between 40 and 100°C. The linewidth contribution from fluorine "exchanging" between the diamagnetic peroxide and paramagnetic SO₃F radicals was separated from other linewidth contributions by simultaneously observing stable, inert pyrosulfuryl fluoride, S₂O₆F₂. The concentration of fluorosulfate radicals as a function of temperature was obtained from EPR measurement by comparison of spectral intensity with that of a sample containing a known number of spins. The NMR chemical shift $\Delta\omega_R$ of the SO₃F radical was estimated from the isotropic hyperfine splitting constant $A=9.2$ G, which was determined by EPR from the peroxide at liquid-nitrogen temperature under uv irradiation. The activation energy $E_a=25.0$ kcal/mole for the reversible, thermally controlled reaction $S_2O_6F_2 \rightleftharpoons 2SO_3F$ was found from the temperature variation in width of the single fluorine NMR line observed. Equations developed by Swift and Connick and Luz and Meiboom were employed.

INTRODUCTION

NMR relaxation times in many paramagnetic solutions have been investigated for protons¹ and oxygen.² Few reports have appeared on fluorine or solutions of inorganic radicals.³

Most work has involved solutions of iron-group ions, where nuclei under investigation exist either as free solvent or coordinated to the paramagnetic ion. Coordinated nuclei undergo strong relaxation due to the $A\vec{I}\cdot\vec{S}$ scalar interaction. Rate constants are obtained which govern the exchange of solvent nuclei between the

uncoordinated (diamagnetic) and coordinated (paramagnetic) environments. Resonance in the coordinated site can be observed⁴ depending on the relative relaxation times of the paramagnetic electron and nuclei, and on the concentration of paramagnetic species. However, Swift and Connick developed modified McConnell equations in which only the relaxation time in the uncoordinated site need be determined in order to obtain the respective lifetimes.

$$T_{2\text{ ex}}^{-1} = T_{2\text{ obs}}^{-1} - T_{2\text{ oth}}^{-1} \\ = P_R \frac{T_{2R}^{-1}(T_{2R}^{-1} + \tau_R^{-1}) + (\Delta\omega_R)^2}{\tau_R(T_{2R}^{-1} + \tau_R^{-1})^2 + \tau_R(\Delta\omega_R)^2}, \quad (1)$$

* Research performed while a Research Fellow at the Department of Chemistry, University of Tokyo, Tokyo, Japan, 1968.

¹ N. Bloembergen and L. O. Morgan, J. Chem. Phys. **34**, 842 (1961); Z. Luz and S. Meiboom, *ibid.* **40**, 1066, 2686 (1963).

² T. J. Swift and R. E. Connick, J. Chem. Phys. **37**, 307 (1962).

³ H. S. Gutowsky and J. C. Tai, J. Chem. Phys. **39**, 208 (1963).

⁴ D. R. Eaton, W. D. Phillips, and D. J. Caldwell, J. Am. Chem. Soc. **85**, 397 (1963); W. D. Horrocks and G. N. LaMar, *ibid.* **85**, 3512 (1963).