

Energy Exchange between Inert Gas Atoms and a Solid Surface.

By J. M. JACKSON, Department of Mathematics, University of Manchester,
and N. F. MOTT, M.A., Gonville and Caius College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received July 19, 1932).

§ 1. *Introduction.*—If gas atoms, having energy corresponding to a temperature T_2 , are incident on a solid surface at a temperature T_1 , then the reflected atoms will have a mean energy corresponding to some new temperature T_2' , which is a function of T_1 and T_2 . For simplicity it is convenient to define Knudsen's thermal accommodation coefficient as

$$\alpha = \lim_{T_1 \rightarrow T_2 \rightarrow T} \frac{T_2' - T_2}{T_1 - T_2}.$$

The accommodation coefficient depends on the nature of the gas atom, the nature of the solid surface, and the temperature T .

Accommodation coefficients have been measured by various workers, and the present paper is an attempt to give a theoretical explanation of the results of Roberts,* who has measured the accommodation coefficient for helium on tungsten at various temperatures, taking particular precautions to obtain a clean surface.

The first step in the calculation of the accommodation coefficient is the calculation of the probability that when a gas atom with energy W hits an atom of the solid in the quantum state i , a transition will take place to the state n . We denote this probability by $p_i^n(W)$. One must then assume some energy distribution for the vibrating solid atoms. We assume that they are all independent, so that the number in the state with energy W_n is proportional to $\exp.(-W_n/KT)$, as in the Einstein specific heat theory. The accommodation coefficient is then found by averaging p_i^n for all W and all i, n .

A theory of the accommodation coefficient has already been given by one of us,† the interaction energy between the solid and the gas being taken to be of the form $V = C$ for $r > 0$, $V = 0$ for $r < 0$, where r denotes the distance between the two atoms. With a suitable choice of C it was possible to obtain a fairly good fit with the experimental curve. This type of field has, however, little resemblance to the actual field between the gas atom and the solid surface.

* 'Proc. Roy. Soc.,' A, vol. 129, p. 146 (1930); vol. 135, p. 192 (1932).

† J. M. Jackson, 'Proc. Camb. Phil. Soc.,' vol. 28, p. 136 (1932).

The method of calculating the accommodation coefficient given in this paper will be followed, except that we shall take the interaction energy between the gas atom and the solid atom to be of the form

$$C \exp. (-ar).$$

Zener* has calculated the accommodation coefficient using a field of this type, but in calculating the transition probabilities he approximates to the exponential by means of an inverse square term $A(r - b)^{-2}$ adjusted to fit on smoothly to the exponential at the classical distance of closest approach. This approximation appears to affect the answer by a factor of about 6. Good agreement with experiment was only obtained by giving a the somewhat large value $65 \times 10^8 \text{ cm.}^{-1}$.

In the present paper we have been able to evaluate the integrals involved in the transition probabilities exactly without making any approximations. Quite a simple formula is obtained, and good agreement with experiment, with a more reasonable value of a ($8 \times 10^8 \text{ cm.}^{-1}$). We also discuss the validity of the perturbation method used, and come to the conclusion that this is almost the only collision problem in which the terms neglected in a first order perturbation theory are certainly small.

§ 2. *The Probabilities of Energy Transfer.*—In this section we shall treat the solid surface as consisting of an assembly of independent atoms each free to vibrate about a position of equilibrium with the same frequency ν . The problem is to calculate the probability that, when a gas atom of given energy collides with an atom of the solid vibrating in the n th stationary state, the solid atom will make a transition to the n' th state. The model used is one dimensional, both atoms being supposed to move only at right angles to the surface of the solid.

Let X denote the displacement at any time of the solid atom from its mean position. The Schrödinger equation for the unperturbed solid atom is then

$$(H - W_n) \psi_n(X) = 0, \quad (1)$$

where H denotes

$$-\frac{\hbar^2}{8\pi^2M} \frac{d^2}{dX^2} + 2\pi^2M\nu^2X^2,$$

M being the mass of the solid atom. Equation (1) has the usual series of oscillator eigenfunctions $\psi_n(X)$ and eigenvalues $W_n = (n + \frac{1}{2})\hbar\nu$. We assume that the oscillator wave functions $\psi_n(X)$ are normalised to unity.

* 'Phys. Rev.', vol. 37, p. 557 (1931); vol. 40, pp. 178, 335 (1932).

Let us denote by ψ_i the wave function of the initial state and ψ_n the wave function of the final state of the solid atom. Let m denote the mass of the gas atom and x its distance from the mean position of the solid atom.

We take for the interaction energy $V(x, X)$ between the two atoms

$$V(x, X) = C \exp[-a(x - X)]. \tag{2}$$

Let $\Psi(x, X)$ be the wave function which describes the collision and satisfies the wave equation

$$\left[-H + \frac{\hbar^2}{8\pi^2m} \frac{d^2}{dx^2} + \frac{8\pi^2m}{\hbar^2} (W - Ce^{-a(x-X)}) \right] \Psi = 0. \tag{3}$$

We require a solution with the following property; if it is expanded in a series

$$\Psi(x, X) = \sum_n \psi_n(X) f_n(x) \tag{4}$$

then for large x we must have

$$\begin{aligned} f_i(x) &\sim \exp(-ik_i x) + A_i \exp(ik_i x) \\ f_n(x) &\sim A_n \exp(ik_n x) \quad n \neq i. \end{aligned} \tag{5}$$

Here

$$k_i = 2\pi m v_i / \hbar, \quad k_n = 2\pi m v_n / \hbar,$$

v_i being the velocity of the gas atom before collision, and v_n its velocity after it has excited the solid atom to the state n .

The solution (5) represents a wave of unit amplitude falling on the solid atom together with a number of reflected waves. The probability per collision that the transition $i \rightarrow n$ will take place is

$$p_i^n = \frac{k_n}{k_i} |A_n|^2. \tag{6}$$

The method appropriate to the solution of equation (3) depends on the value of the constant a in the expression (2) for the interaction energy. If a^{-1} is small compared with the amplitude of oscillations of the solid atom, the atoms may be treated as rigid elastic spheres. In § 3 a method of solution suited to this case is given. If a^{-1} is large compared with this amplitude, the method employed by Zener is appropriate. This is discussed in § 4.

From the two formulæ one can obtain transition probabilities for all values of a by interpolation. We may remark here that if a^{-1} is large compared to the wave-length of the incident atoms, the collision is adiabatic and no energy transfer takes place.

§ 3. *Rigid Elastic Spheres as a Model for the Atoms.*—In this section the atoms are treated as rigid elastic spheres; that is to say, we write the interaction energy in the form

$$V(x, X) = C' e^{-a(x-X-\xi)} \quad (7)$$

and let $a \rightarrow \infty$. ξ may be interpreted as the sum of the radii of the spheres. Then

$$\begin{aligned} V(x, X) &= 0 & x - X > \xi \\ &= \infty & x - X < \xi \end{aligned}$$

We have therefore to find a solution of

$$\left[-H + \frac{\hbar^2}{8\pi^2m} \frac{d^2}{dx^2} + W \right] \Psi(x, X) = 0,$$

which vanishes along the line $x - X = \xi$. Such a solution, having the asymptotic form required in (4) and (5), is

$$\Psi(x, X) = \psi_i(X) 2i \sin k_i(x - \xi) + \sum_n A_n \psi_n(X) \exp[ik_n x],$$

the A_n being chosen in such a way that

$$\psi_i(X) 2i \sin k_i X + \sum_n A_n \psi_n(X) \exp[ik_n(X + \xi)] = 0 \quad (8)$$

for all values of X .

Now the wave-length of the incident helium atoms is large compared with the amplitude through which the solid atoms vibrate; hence $\psi_n(X)$ is only finite in a region in which $k_i X$, $k_n X$, etc., are small. We may therefore replace $\exp ik_n X$ in (8) by unity. We obtain

$$\psi_i(X) 2ik_i X + \sum_n A_n \psi_n(X) \exp[ik_n \xi] = 0$$

for all X .

Hence multiplying by $\psi_n(X)$ and integrating over all X , we obtain

$$A_n = -2ik_i X_{in} \exp(-ik_n \xi),$$

where

$$X_{in} = \int_{-\infty}^{\infty} X \psi_i \psi_n dX. \quad (9)$$

Hence from (6) the probability that the transition will take place is

$$p_i^n = 4k_i k_n |X_{in}|^2. \quad (10)$$

§ 4. In this section we suppose that a^{-1} is large compared with the amplitude of vibrations of the solid atom. (This is in fact the case, since for tungsten at ordinary temperatures this amplitude is of order 2×10^{-10} cm.) The method

is that used by Zener. It is similar to the Born method in collision problems, differing from it in that distorted zero order wave functions must be used.

We substitute the solution (4) in equation (3) and obtain

$$\sum_n \left[\frac{d^2}{dx^2} + k_n^2 - \frac{8\pi^2 m C}{h^2} e^{-a(x-X)} \right] f_n(x) \psi_n(X) = 0. \quad (11)$$

We now write

$$V_{ns}(x) = \frac{8\pi^2 m C}{h^2} \int_{-\infty}^{\infty} e^{-a(x-X)} \psi_n(X) \psi_s(X) dX,$$

which is equal to

$$U(x) Y_{ns},$$

where

$$U(x) = 8\pi^2 m C e^{-ax} / h^2, \quad (11.1)$$

$$Y_{ns} = \int e^{aX} \psi_n(X) \psi_s(X) dX. \quad (11.2)$$

Expanding e^{aX} , and remembering that aX is small in the region* (denoted by τ) where ψ_n is finite, we have to a very good approximation

$$Y_{nn} = 1.$$

We thus have approximately

$$V_{nn}(x) = U(x). \quad (12)$$

Further, we see that

$$Y_{n, n \pm 1} \text{ is of order } a\tau,$$

$$Y_{n, n \pm 2} \text{ is of order } (a\tau)^2.$$

From equation (11), multiplying by $\psi_s(X)$ and integrating with respect to X from $-\infty$ to $+\infty$,

$$\left(\frac{d^2}{dx^2} + k_s^2 \right) f_s(x) + \sum_n V_{sn}(x) f_n(x) = 0. \quad (13)$$

This equation is exact.

We have just seen that the non diagonal terms V_{ns} are small compared with the diagonal terms V_{nn} . We may therefore solve (13) by the method of successive approximations. We set for the waves representing the incident and elastically reflected particles

$$f_i(x) = f_i^{(0)} + f_i^{(1)} + \dots, \quad (14.1)$$

and for the particles reflected after causing a transition

$$f_n(x) = f_n^{(1)} + \dots. \quad (14.2)$$

* τ is equal to about 10^{-10} cm.

Substituting in (13) we obtain

$$\left[\frac{d^2}{dx^2} + k_i^2 - V_{ii} \right] f_i^{(0)} = 0, \quad (15)$$

$$\left[\frac{d^2}{dx^2} + k_n^2 - V_{nn} \right] f_n^{(1)} = Y_{in} U(x) f_i^{(0)}(x), \quad n \neq i. \quad (16)$$

We note that $V_{ii} = V_{nn} = U(x)$.

Let now $F_n(x)$ denote that solution of the equation

$$\left[\frac{d^2}{dx^2} + k_n^2 - U(x) \right] F_n(x) = 0, \quad (17)$$

which tends to zero as $x \rightarrow -\infty$, and is normalised so as to have the asymptotic form

$$F_n \sim \cos(k_n x + \eta) \quad x \rightarrow +\infty, \quad (18)$$

where η is a constant. Then we must take

$$f_i^{(0)} = 2F_i(x), \quad (18.1)$$

representing an incident and reflected wave each of unit amplitude, as demanded by (5).

We may solve (16) by the substitution

$$f_n^{(1)}(x) = y F_n(x).$$

This gives

$$\frac{d}{dx} \left(F_n^2 \frac{dy}{dx} \right) = 2Y_{in} U(x) F_n F_i.$$

Integrating, and remembering that f_n must vanish as $x \rightarrow -\infty$ we have

$$F_n^2 \frac{dy}{dx} = 2Y_{in} \int_{-\infty}^x U(x) F_n F_i dx.$$

Integrating this equation, we have, for large values of x ,

$$y \sim \left[\frac{1}{k_n} \tan(k_n x + \eta) + \text{const} \right] 2Y_{in} \int_{-\infty}^{\infty} U(x) F_n F_i dx.$$

Choosing the constant so that f_n shall have the asymptotic form (5), we find

$$f_n^{(1)} \sim \exp[-i(k_n x + \eta)] \frac{2Y_{in}}{k_n} \int_{-\infty}^{+\infty} U(x) F_n F_i dx.$$

Hence we have (cf. equation (5))

$$|A_n| = \frac{2Y_{in}}{k_n} \int_{-\infty}^{\infty} U(x) F_n F_i dx,$$

and from (6) the probability per collision that the solid atom of energy W will make a transition from the state i to the state n is

$$p_i^n = \frac{4(Y_{in})^2}{k_i k_n} \left[\frac{8\pi^2 m C}{h^2} \int_{-\infty}^{\infty} e^{-ax} F_i F_n dx \right]^2. \tag{19}$$

Zener obtains the result (19) without the factor 4. This is due to the omission of a factor 2 in the equation corresponding to (18.1).

§ 5. We now require the exact solutions of (17) which tend to zero as $x \rightarrow -\infty$, and which have the asymptotic form (18) as $x \rightarrow \infty$. Writing

$$U(x) = B^2 e^{-ax},$$

we can transform (17) by means of the substitution

$$y = 2B/a \cdot \exp(-\frac{1}{2}ax);$$

we obtain

$$F''_n + y^{-1} F'_n + (q_n^2 y^{-2} - 1) F_n = 0,$$

where the dashes denote differentiation with respect to y , and

$$q_n = 2k_n/a.$$

This is Bessel's equation of imaginary order $i q_n$ and imaginary argument iy . In the usual notation of Bessel functions* the solution of this equation which tends to zero as x tends to $-\infty$ is

$$K_{iq}(y), \quad q = q_n.$$

This function can be represented by the integral*

$$K_{iq}(y) = \int_0^{\infty} e^{-y \cosh u} \cos q_n u du. \tag{20}$$

It is clear from (20) that as $x \rightarrow -\infty$ and $y \rightarrow +\infty$, $K_{iq}(y) \rightarrow 0$. In order to show that it behaves like $\cos(kx + \eta)$ as $x \rightarrow +\infty$, $y \rightarrow 0$, we proceed as follows. Making the substitution $q \cosh u = x$, and assuming that y is small, the integral (20) becomes

$$\int_0^{\infty} e^{-z \frac{1}{2}} \left[\left(\frac{2z}{y} \right)^{iq} + \left(\frac{2z}{y} \right)^{-iq} \right] \frac{dz}{z},$$

which reduces to

$$\left(\frac{\pi}{q \sinh \pi q} \right)^{\frac{1}{2}} \cos(kx + \eta).$$

Thus for $F_n(x)$ we must take

$$F_n(x) = \left(\frac{q \sinh \pi q}{\pi} \right)^{\frac{1}{2}} K_{iq}(x). \tag{21}$$

* G. N. Watson, "Bessel Functions," pp. 73, 181.

§ 6. *Calculation of the Transition Probabilities.*—In §§ 3 and 4, equations (10) and (19), we have obtained expressions for the transition probabilities per collisions for gas atoms incident on the solid with definite energy. It is readily found that*

$$Y_{n, n \pm 1} = a \left(\frac{n + \frac{1}{2} \pm \frac{1}{2}}{8\pi^2 M h \nu / h^2} \right)^{\frac{1}{2}} \quad (22)$$

$$Y_{n, n \pm 2} = a^2 \frac{[(n + 1 \pm 1)(n \pm 1)]^{\frac{1}{2}}}{16\pi^2 M h \nu / h^2}. \quad (23)$$

We have further

$$\begin{aligned} X_{in} &= 0 & i &\neq n \pm 1 \\ &= Y_{in}/a & i &= n \pm 1. \end{aligned}$$

From (10) we have, therefore, for elastic spheres,

$$p_n^{n \pm 1} = 4 \frac{m}{M} (n + \frac{1}{2} \pm \frac{1}{2}) [E(E \mp 1)]^{\frac{1}{2}} \quad (24)$$

where

$$E = W/h\nu.$$

The evaluation of (19) depends on the integral

$$\int_{-\infty}^{\infty} e^{-ax} F_i F_n dx.$$

Changing the variable of integration to y as before we find for this integral

$$\frac{ah^2}{16\pi^2 m C} \frac{(qq' \sinh \pi q' \sinh \pi q)^{\frac{1}{2}}}{\pi} \int_0^{\infty} K_{iq} K_{iq'} y dy,$$

here q is written for q_i , q' for q_n .

Using (20) we can write the integral on the right as a repeated integral, namely

$$\int_0^{\infty} \int_0^{\infty} \int_0^{\infty} y e^{-y(\cosh t + \cosh u)} \cos qu \cos q't du dt dy.$$

Putting the lower limit of the y integration equal to y_0 , and interchanging the order of integration so that the y integration is performed first, afterwards allowing y_0 to tend to zero, we find that this integral reduces to

$$\frac{1}{4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\cos q't \cos qt}{(\cosh t + \cosh u)^2} du dt.$$

* Sommerfeld, 'Wellenmechanik,' p. 61.

Making the substitution* $t + u = 2T$, $t - u = 2U$, we find that this integral becomes

$$\frac{1}{2} \int_0^\infty \frac{\cos(q+q')T}{\cosh^2 T} dT \int_0^\infty \frac{\cos(q'-q)U}{\cosh^2 U} dU.$$

By integrating $e^{i p z} / \cosh^2 z$ round the closed rectangular contour $-\infty, +\infty, +\infty + \pi i, -\infty + \pi i$, enclosing the point $z = \frac{1}{2}i\pi$, we find that

$$\int_0^\infty \frac{\cos px}{\cosh^2 x} dx = \frac{1}{2}\pi p / \sinh \frac{1}{2}\pi p.$$

Therefore we have

$$\int_0^\infty y dy K_{iq} K_{iq'} = \frac{1}{4}\pi^2 (q'^2 - q^2) / (\cosh \pi q' - \cosh \pi q).$$

The transition probability p_i^n is therefore

$$p_i^n = \frac{a^2 Y_{in}^2}{\pi^2 K_i K_n} q q' \left[\frac{\frac{1}{4}\pi^2 (q'^2 - q^2)}{\cosh \pi q' - \cosh \pi q} \right]^2 \sinh \pi q \sinh \pi q'. \quad (25)$$

In particular

$$p_n^{n \pm 1} = \frac{32\pi^4 m}{h^2} \frac{m h \nu}{M a^2} \left(n + \frac{1}{2} \pm \frac{1}{2} \right) \frac{\sinh q \sinh q'}{(\cosh \pi q - \cosh \pi q')^2} \quad (25.1)$$

and

$$p_n^{n \pm 2} = 4\pi^2 \left(\frac{m}{M} \right)^2 (n + 1 \pm 1) (n \pm 1) \frac{\sinh \pi q' \sinh \pi q}{(\cosh \pi q - \cosh \pi q')^2} \quad (25.2)$$

etc.

Here q, q' are $4\pi m v / ah, 4\pi m v' / ah$ where v, v' are the velocities of the gas atom before and after the collision.

It is interesting to note that if we allow a to become very large in equation (25.1), the formula (25.1) tends to the form (24) obtained for hard spheres. Thus, although there is no theoretical justification for using this perturbation method for large a (as the non-diagonal elements are not small), the result obtained seems to be valid for all a .

§ 7. Calculation of the Thermal Accommodation Coefficient.—The thermal accommodation coefficient α is defined at the beginning of § 1. Using this definition it has been shown by one of us† that α can be expressed as a double series of partial accommodation coefficients $\alpha(n|n')$, one for each particular quantum transition $n \rightarrow n'$; it was found that

$$\alpha = \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \alpha(n|n'), \quad (26)$$

* G. N. Watson, *loc. cit.*, p. 440.

† Jackson, *loc. cit.*

where

$$\alpha(n|n') = \frac{2}{3} \mu^3 (1 - e^{-\mu}) (n - n')^2 e^{-n\mu} P_{n'}^{n'}(\mu). \quad (27)$$

In this expression $\mu = \Theta/T$ where Θ is the characteristic temperature of the solid, and

$$P_{n'}^{n'}(\mu) = \int_0^\infty p_{n'}^{n'}(E) e^{-\mu E} dE. \quad (28)$$

Expressions for $p_{n'}^{n'}$ have been given in the previous section (equations (25)). To calculate the accommodation coefficient we must therefore evaluate the integral (28).

We write

$$\alpha = \alpha(1) + \alpha(2) + \dots \quad (29)$$

where $\alpha(s)$ is a partial accommodation coefficient corresponding to change of quantum number by s .

We obtain, summing over all n, n' which differ by unity and by two

$$\alpha(1) = \frac{2}{3} \mu^3 (e^{-\mu} - 1)^{-1} P(1, \mu) \quad (30)$$

$$\alpha(2) = \frac{1}{3} \mu^3 (e^{\mu} - 1)^{-2} P(2, \mu), \quad (31)$$

where $P(1, \mu), P(2, \mu)$ are to be obtained from (28), for the cases $n' = n \pm 1, n' = n \pm 2$, by omitting the factor $(n + \frac{1}{2} \pm \frac{1}{2})$ from (25.1) and (24), and the factor $(n \pm 1)(n + \pm 1)$ from (25.2).

Further terms of the series (26) have not been investigated, as in the case of helium on tungsten $\alpha(2)$ is never more than 5 per cent. of $\alpha(1)$. The convergence seems sufficiently good to justify the neglect of further terms of the series.

Only in the case of rigid elastic spheres [§ 3 and § 6, equation (24)] is it possible to evaluate the integral (28) analytically. In this case, we have from (24)

$$P(1, \mu) = 4 \frac{m}{M} \int_0^\infty [E(E+1)]^\dagger e^{-\mu E} dE.$$

Changing the variable of integration to u , where $u = 2E + 1$, this integral reduces to

$$\frac{1}{2} \frac{m}{M} [K_2(\frac{1}{2}\mu) - K_0(\frac{1}{2}\mu)] e^{\frac{1}{2}\mu},$$

where K_2 and K_0 are Bessel functions of the third kind. We find from (29) and (30)

$$\alpha = \alpha(1) = \frac{1}{6} \mu^3 \frac{m}{M} \operatorname{cosech} \frac{1}{2}\mu \{K_2(\frac{1}{2}\mu) - K_0(\frac{1}{2}\mu)\}. \quad (32)$$

This is the result for a molecular model of rigid elastic spheres. With such a model the nature of the gas only enters into the result in the mass-ratio factor m/M and thus the accommodation coefficients of various monatomic gases at the same temperature on a clean tungsten surface would be proportional to their atomic weights.

With the exponential interaction energy Ce^{-ar} , the transition probabilities per collision are given by (25).

We obtain, from (25) and (30)

$$\alpha(1) = \frac{2}{3} \mu^3 (e^\mu - 1)^{-1} \frac{32\pi^4}{h^2} \frac{M}{m} \frac{mh\nu}{a^2} \int_0^\infty \frac{\sinh \frac{\gamma}{a} (E + 1)^\dagger \sinh \frac{\gamma}{a} E^\dagger \cdot e^{-\mu E} dE}{\left[\cosh \frac{\gamma}{a} (E + 1)^\dagger - \cosh \frac{\gamma}{a} E^\dagger \right]^2}$$

and

$$\alpha(2) = \frac{1.6}{3} \mu^3 (e^\mu - 1)^{-2} \cdot 4\pi^2 \left(\frac{m}{M} \right)^2 \int_0^\infty \frac{\sinh \frac{\gamma}{a} (E + 2)^\dagger \sinh \frac{\gamma}{a} E^\dagger \cdot e^{-\mu E} dE}{\left[\cosh \frac{\gamma}{a} (E + 2)^\dagger - \cosh \frac{\gamma}{a} E^\dagger \right]^2}$$

where $\gamma^2 = 32\pi^4 mh\nu/h^2$.

The integrals were evaluated numerically for various values of μ , a . The results are given in § 8.

§ 8. *Modification of the Theory when an Attractive Potential is included in the Field of the Solid.*—In order to take some account of the possibility of adsorption it is interesting to include in some way the long range attractive field of the solid (van der Waals forces). The simplest method of doing this is to include a small attractive potential step of magnitude Φ situated at a constant distance d from the mean position of the oscillating surface atom. For d we have taken about 5 A.U.

With this very approximate representation of the attractive field of the solid, the only modifications* which must be made in the analysis of the preceding section are that instead of $P(1)$ one must write

$$P(1, \chi) = \int_\chi^\infty p(1) e^{-\mu E} dE, \quad \chi = \Phi/h\nu.$$

(1) and (2) must also be multiplied by the factor $\exp \Phi/kT$.

The expressions for $\alpha(1)$ and $\alpha(2)$ now become

$$\frac{2}{3} \mu^3 (e^\mu - 1)^{-1} e^{\mu\chi} P(1, \chi)$$

$$\frac{1.6}{3} \mu^3 (e^\mu - 1)^{-2} e^{\mu\chi} P(2, \chi).$$

* Jackson, *loc. cit.*, p. 156.

The factor $e^{\mu x}$ increases as the temperature decreases, but the integral $P(1, \chi)$ decreases with the temperature more rapidly than $P(1)$. The effect of the factor $e^{\mu x}$ is predominant, but the alterations in the integrals P are not negligible and are more marked for low temperatures.

§ 9. *Numerical Results.*—The experiments of Roberts (*loc. cit.*) provide the only available data with which the theory may be compared. The experimental results for tungsten and helium are

$$295^\circ \text{ K}, \alpha = 0.057; \quad 195^\circ \text{ K}, \alpha = 0.046; \quad 79^\circ \text{ K}, \alpha = 0.025.$$

Calculations have been made for values of a equal to 4.02, 8.05, $9.00 \times 10^8 \text{ cm.}^{-1}$, and also for the hard sphere model. The value of the characteristic temperature Θ of tungsten is 205° K , if we take the atomic frequency to be $4.3 \cdot 10^{12} \text{ sec.}^{-1}$. This frequency is determined from Lindemann's melting point formula, which gives good agreement with the values of Θ determined from specific heat data, particularly in the case of metals. The accommodation coefficient was computed for the above values of a , and for the following values of μ

$$\mu = 0.7, 1.0, 1.4, 2.0, 3.0$$

or

$$T = 293^\circ, 205^\circ, 147^\circ, 102.5^\circ, 68.4^\circ.$$

For the attractive potential step we have taken $\chi = 0.20, 0.25$, and also zero. The two former values correspond to $\Phi = 3.54$ and $4.43 \cdot 10^{-3}$ electron volts, or heats of adsorption* of helium on tungsten of the order of 80–100 cal./gm. atom. These are probably of the correct order of magnitude.

The variation of the accommodation coefficient with temperature for various values of a and Φ is shown in fig. 1. In fig. 2 the results are shown multiplied by an arbitrary factor to fit them to the experimental curve at $T = 205^\circ \text{ K}$. We do this for two reasons: firstly it is possible that the use of a one dimensional model may have introduced a constant factor in our results; and secondly the experimental values are probably too large, owing to the roughness of the solid surface. The best agreement is obtained with $a = 9 \times 10^8 \text{ cm.}^{-1}$, which is rather large.

The value $a = 4 \times 10^8 \text{ cm.}^{-1}$ is probably approximately correct. The theoretical curve for this value is shown in fig. 1. With this value of a one

* Lennard-Jones, 'Trans. Faraday Soc.', vol. 28, p. 340 (1932).

has to multiply the theoretical curve by 2 in order to fit it to the experimental curve. This factor 2 may well be accounted for by the roughness of the surface. The agreement, fig. 2, between the fitted curve and the experimental is not quite so good as for $a = 9 \times 10^8 \text{ cm.}^{-1}$, but is nevertheless satisfactory

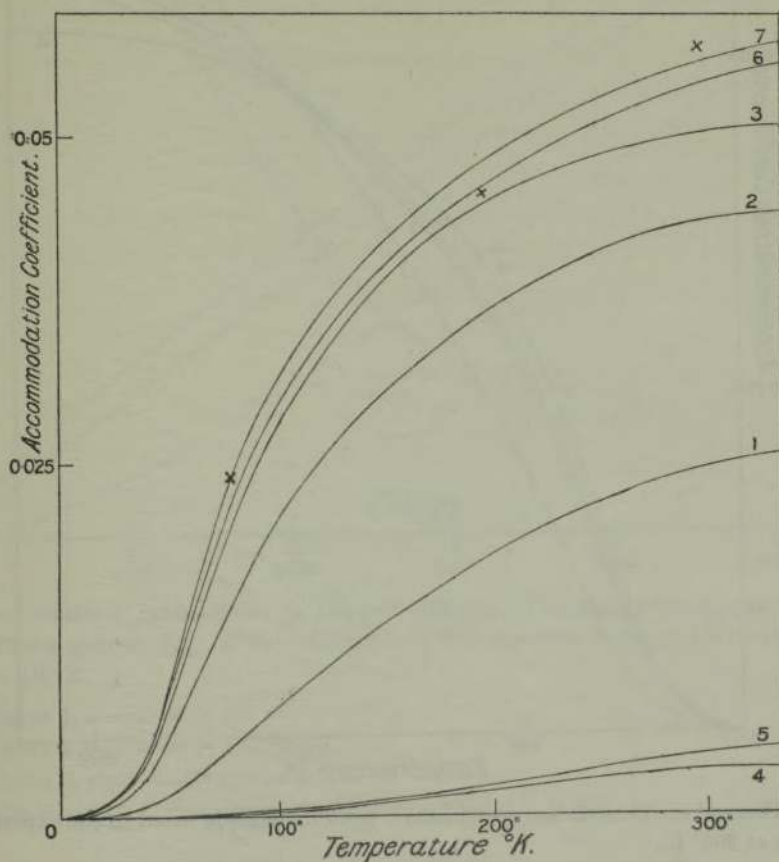


FIG. 1.—Calculated values of the thermal accommodation coefficient for tungsten/helium, with interaction energy e^{-ar} .

- | | |
|--|---------------------------------|
| Curve 1, $a = 4.02 \times 10^8 \text{ cm.}^{-1}$ | } One quantum transitions only. |
| Curve 2, $a = 9.0 \times 10^8 \text{ cm.}^{-1}$ | |
| Curve 3, rigid elastic sphere model | |
| Curve 4, $a = 9.0 \times 10^8 \text{ cm.}^{-1}$, two quantum transitions only. | |
| Curve 5, $a = 9.0 \times 10^8 \text{ cm.}^{-1}$, two quantum transitions only, but including an attractive potential step $\chi = 0.2$. [$\Phi = 3.54 \cdot 10^{-3}$ electron volts.] | |
| Curve 6, $a = 9.0 \times 10^8 \text{ cm.}^{-1}$, $\chi = 0.2$ including both one- and two-quantum transitions. | |
| Curve 7, $a = 9.0 \times 10^8 \text{ cm.}^{-1}$, $\chi = 0.25$ including both one- and two-quantum transitions. | |

The experimental values are marked with a cross.

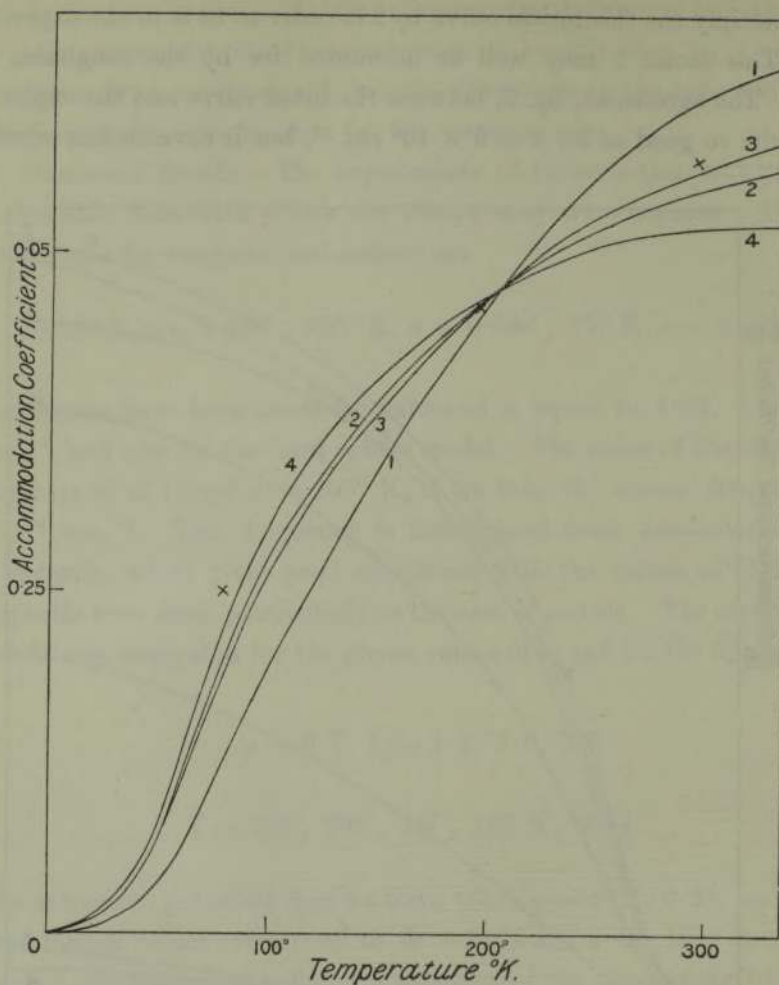


FIG. 2.—Thermal accommodation coefficients: helium/tungsten fitted to the experimental value at 205° K.

- Curve 1, $a = 4.02 \times 10^8 \text{ cm.}^{-1}$, one quantum transitions only.
 Curve 2, $a = 9.00 \times 10^8 \text{ cm.}^{-1}$, one quantum transitions only.
 Curve 3, $a = 9.00 \times 10^8 \text{ cm.}^{-1}$, including two quantum transitions.
 Curve 4, rigid elastic sphere model.

The experimental values are marked with a cross.

in view of the difficult nature of the experiments, and the simple model used in the theory.

In fig. 3 some transition probabilities are drawn plotted against $E = W/h\nu$, where W is the translational energy of a gas atom normal to the surface. They are also plotted against T , where $W = \frac{1}{2}KT$.

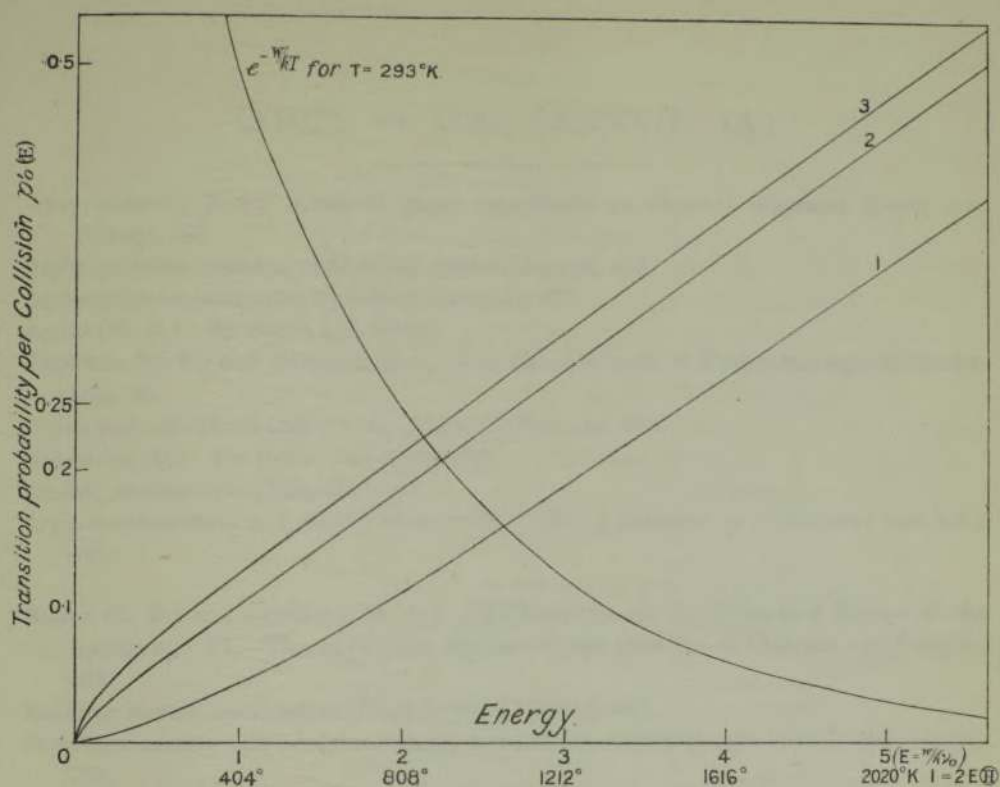


FIG. 3.—Transition probabilities $p_0'(E)$ per collision. The energy scale is in terms of oscillator quanta, $E = W/h\nu$; alternatively it is expressed in terms of the temperature $T = \frac{1}{2}W/K$.

Curve 1, $a = 4.02 \times 10^8 \text{ cm.}^{-1}$.

Curve 2, $a = 9.00 \times 10^8 \text{ cm.}^{-1}$.

Curve 3, rigid elastic sphere model.

The curve $e^{-W/kT}$ is drawn on the same scale for $T = 293^\circ \text{ K}$.

Summary.

A theory of the accommodation coefficient for helium on tungsten is given, using an exponential field between the gas atom and a surface atom of the solid. Good agreement is obtained with the experimental results of Roberts.

In conclusion, we would like to thank Mr. J. K. Roberts for his interest in this work.