inapplicable if conductivity in the semiconducting phase could be described by a hopping model such as has been proposed for V_2O_3.[36] The pressure dependence of the conductivity of both VO_2 and V_2O_3 in the metallic state is $(d/dp) \ln\sigma \simeq 10^{-5}$/bar implying $(d/dp \ln\sigma \simeq 10^{-5}$/bar. In semiconducting V_2O_3 the pressure dependence of σ is given by $(d/dp) \ln\sigma \simeq 10^{-4}$/bar; so neglecting the effect of pressure on the mobility in Eq. (6) should cause an error of about 10% in $(d/dp) \ln E$. Such a calculation on Austin's data for the pressure dependence of the resistance at 125°K [23] shows $dE/dp = 4.6 \times 10^{-6}$ eV/bar. The value calculated from the pressure dependence of the slope of the $\ln\sigma$ vs $1/T$ curve[23] is $dE/dp = 5 \times 10^{-6}$ eV/bar. Although one might expect the value from Eq. (6) to be larger, the agreement is within experimental accuracy and the use of Eq. (6) neglecting $(d/dp) \ln\mu$ seems justified for V_2O_3. The pressure dependence of the conductivity of semiconducting VO_2 is given by $(d/dp) \ln\sigma \simeq 10^{-5}$/bar. The difference between $(d/dp) \ln\sigma$ in metallic VO_2 and $(d/dp) \ln\sigma$ in semiconducting VO_2, as shown in Fig. 4,

is no more than about 10%; so the value of dE/dp is no more than about 10^{-7} eV/bar, consistent with Eq. (4). The small values measured for dE/dp and dT_c/dp then limit the decrease in ϵ with pressure to $(d/dp) \ln\epsilon = -2 \times 10^{-6}$/bar.

VI. SUMMARY

In VO_2 the relationship between the pressure dependence of the resistance and the pressure dependence of the transition temperature is consistent with Mott's[16] model for the onset of metallic conductivity. The values dR/dp and dT_c/dp are small compared to those expected on the basis of Mott's argument that the electrical properties of such materials should vary strongly with interionic spacing. None of the other theories of the electrical and magnetic properties of the transition metal oxides explain the small pressure dependence of the properties of VO_2, and the matter warrants some attention. If the difference in the two oxides is related to the fact that VO_2 has only one $3d$ electron per cation, similar small pressure effects would be observed in Ti_2O_3.

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[36] G. A. Acket and J. Volger, Physica **28**, 277 (1962).

Energy-Distribution Function for Hot Atoms Produced by Nuclear Transformations*

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The energy-distribution function for hot atoms produced by nuclear transformations is examined in terms of the fraction of the initial hot-atom energy. Energy dependent and independent asymmetric scattering is specifically considered. For gaseous tritium generated by the ^{3}He(n, p) process, the asymptotic solution probably can serve as a reasonable approximation of the distribution function in the energy range 2–20 eV. For hot atoms produced with an initial distribution of energies, such as ^{79}Br(n, γ)-produced ^{80}Br, the asymptotic solution will be less valid than for tritium, but may still be a valid approximation.

INTRODUCTION

HOT atoms generated by nuclear processes undergo moderation and chemical reaction in a manner which appears to be similar in some respects to neutron thermalization (NT) and absorption processes. Mathematical descriptions of hot-atom reactions, therefore, have been given in terms of simplified neutron-thermalization theory, although some of the assumptions required in the use of the theory may not be applicable to hot-atom reactions.[1] As discussed in Ref. 1, the least number of assumptions will be needed when applying NT theory to hot-atom systems of very low chemical yields or those involving a large amount of

inert-gas additive. For such systems, where the hot atoms are formed at an energy E_0 which is appreciably larger than the energies at which most reaction occurs (perhaps about 1–20 eV), NT theory can be directly applied if an analytic form of the hot-atom energy distribution function is available.

The purpose of this paper is to evaluate the conditions under which a particular form of the energy distribution function, the asymptotic solution, can be used in hot-atom reactions. The variables we will consider include the hot-atom energy relative to its initial energy E/E_0, asymmetric scattering, and the energy dependences of the scattering asymmetry.

We will frequently evaluate the distribution function with reference to tritium hot atoms generated by the ^{3}He$(n, p)^3$T reaction. For this process $E_0 = 2 \times 10^5$ eV.

The energy distribution of neutrons which have been degraded energetically by successive collisions with par

[1] C. Hsiung and A. A. Gordus, J. Am. Chem. Soc. **86**, 2782 (1964). The notation used in the present paper is consistent with this reference.

ticles of low thermal energy is calculated using the Boltzmann transport equation.

$$F(E) = \sum_i f_i(E_0) k_i(E, E_0)$$

$$+ \int_E^{E_0} \sum_i f_i(E') k_i(E, E')[1 - \sum_i P_{ij}(E')] F(E') dE,$$

$$(1)$$

where P_{ij} is the probability, per collision with Component i, that the hot atom of energy E' will react to form the product j. For most calculations which follow, $P_{ij}(E')$ is assumed equal to zero since we will be interested in evaluating $F(E)$ under conditions such that very little hot-atom reaction occurs.

$f_i(E)$ is the collision fraction. This quantity is the mole fraction X_i corrected for relative collisional cross sections,

$$f_i(E) = X_i / \sum_h \{ X_h[Q_h(E)/Q_i(E)] \}. \quad (2)$$

$k_i(E, E')$ is the scattering function which indicates the probability that a hot atom of energy E' will be reduced to an energy E upon collision with a (thermal-energy) component i. This function is related to the differential scattering cross section.[1] If scattering is isotropic, then

$$k_i(E, E') = 1/E'(1 - r_i). \quad (3)$$

We frequently approximate asymmetric scattering by the expression[1]

$$k_i(E, E') = \frac{-b(1 + r_i)}{E'} + \frac{1}{(1 - r_i) E'} + \frac{2bE}{(E')^2}. \quad (4)$$

A plot of Eq. (4) vs E will be a straight line of slope $2b/(E')^2$. It will be zero for all values less than $r_i E'$ or greater than E'. Positive values of b will be chosen; as a result, $k_i(E, E')$ will be a linear increasing function in the range $r_i E'$ to E'. Such positive values of b, when converted to the differential scattering cross section, indicate that low angle scattering (glancing collisions) are more probable than large angle scattering (head-on collisions) and thus serve as an approximation of the experimentally observed scattering behavior.[1]

Various analytical solutions of Eq. (1) are given by Boffi.[2] For the particular case where isotropic scattering is assumed, Placzek[3a] has calculated, as a function of the fraction of the initial neutron energy, the deviation in the energy distribution function, $F(E)$, from the distribution function which exists after an infinite number of collisions (assuming no neutron absorption). This latter distribution function, the asymptotic solution of the Boltzmann transport equation,[3b] is

$$F(E)_\infty = 1/\alpha E, \quad (5)$$

where α is the average decrease per collision in the logarithmic energy range of the energetic particle

$$\alpha = \langle \ln(E'/E) \rangle_{Av}. \quad (6)$$

The quantity E' is the neutron energy prior to a collision and E is the energy following the collision.

For the specific case of isotropic, I, scattering,

$$\alpha_I = 1 + [r_i/(1 - r_i)] \ln r_i, \quad (7)$$

where r_i, the energy degradation factor, represents the smallest fraction of the initial energy which can be retained by a neutron following a collision with a particle of zero energy. For isotropic collisions involving a mixture of i substances,

$$\alpha = \sum_i f_i(E) \alpha_{Ii}. \quad (8)$$

Although it is possible to obtain analytical solutions for Eq. (1) for any energy range, the calculations are frequently extremely tedious. We therefore have resorted to the evaluation of Eq. (1) by numerical integration using a computer. We define

$$G(E) = EF(E), \quad (9a)$$

$$K_i(E, E') = Ek_i(E, E'), \quad (9b)$$

and assign

$$\sum_i P_{ij}(E) = 0.$$

The problem reduces to an evaluation of $G(E)$. Since the asymptotic solution of $G(E)$, according to Eq. (10) is $1/\alpha$, it is necessary only to determine $G(E)$ as a function of E/E_0. As E/E_0 becomes smaller, $G(E)$ approaches $1/\alpha$. The method of evaluating Eq. (12) is described in Appendix I.

RESULTS

Given in Fig. 1 are typical data for various asymmetry functions as given by Eq. (4). [For Curves a, d, e, and f, $k_i(E, E')$ was set equal to zero at $E = r_i E'$. Therefore, according to Eq. (4), $b = 1/(1 - r_i)^2$.] As noted in Ref. 1, the expression for α_i based on Eq. (4) is

$$\alpha_i = \alpha_{iI} - b[(1 - r_i^2)/2 + r_i \ln r_i], \quad (10)$$

where α_{iI} is given by Eq. (7).

Curve a, for example, is based on $r_i = 0.521$ ($b = 4.36$). According to Eqs. (7) and (10), $\alpha_i = 0.184$. This corresponds to $G(E)_\infty = 1/\alpha = 5.43$, the value of $G(E)$ computed (within $< \pm 0.1\%$ after correcting for a systematic deviation, see Appendix I) for $E/E_0 < 0.2$. Similar calculations can be made for the other curves of Fig. 1 to confirm that the level portions of the $G(E)$ curves at $E/E_0 < \sim 0.2$ are each $1/\alpha$.

If the scattering function, $k_i(E, E')$, is discontinuous at $r_i E'$ then a discontinuity will exist in $G(E)$ at $E/E_0 = r_i$. For example, isotropic scattering results in such discontinuity, as seen in Curves c and g of Fig. 1 for which $r_i = 0.521$ and 0.02, respectively.

From Fig. 1 it is seen that the greatest difference between $G(E)$ and $1/\alpha$ exists in the range $E/E_0 > r_i$. This difference, however, decreases as r_i decreases

[2] V. C. Boffi, Nuovo Cimento **21**, 935 (1961).

[3] (a) G. Placzek, Phys. Rev. **69**, 423 (1946); (b) S. Glasstone and M. C. Edlund, *The Elements of Nuclear Reactor Theory* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1952), Chap. 6.

(Curves a, d, e, and f, for example) and $G(E) \to 1/\alpha$ as $r_i \to 0$ for all values of E/E_0 as Placzek noted for the particular case of isotropic scattering.

Curves a, c, f, and g indicate the variation resulting from constant r_i but different b values. For example, Curve a corresponds to $r_i = 0.521$, $b = 4.358$ whereas Curve c corresponds to isotropic scattering with $r_i = 0.521$, $b = 0$. Curve f is $r_i = 0.02$, $b = 1.041$ whereas Curve g corresponds to isotropic scattering with $r_i = 0.02$, $b = 0$. In these two sets it is seen that the asymmetric scattering function results in $G(E)$ values which are more in accord with $1/\alpha$ (especially at $E/E_0 > r_i$) than does the isotropic scattering function. For an asymmetric scattering function which statistically weights the low-angle (small-energy-loss) collisions, a larger number of collisions are required, on the average, to decrease to a given value of E/E_0, than are required if isotropic scattering prevails. Thus, the asymptotic solution (which requires an infinite number of collisions) is approximated more closely using the positive-slope asymmetric function than using the isotropic scattering function.

Curves a, b, and d serve to illustrate the behavior of $G(E)$ for a mixture of two substances. Curves a and d are for pure substances and Curve b is for a mixture of the two such that the f values, Eq. (2), are each equal to 0.5. In calculating Curve b it was assumed that the f values were energy-independent; therefore, according to Eq. (8), $\alpha = (0.5)(0.184) + (0.5)(0.308) = 0.246$ and $G(E)_\infty = 4.07$. It should be noted that at $E/E_0 > 0.2$, Curve b is more in accord with $G(E)_\infty$ than either Curves a or d,[4] rather than being a simple weighted average of the percentage deviations from the respective $G(E)_\infty$ values. This is due to the fact that a mixture of two scattering functions, in effect, results in greater energy "mixing" as the hot atoms decrease
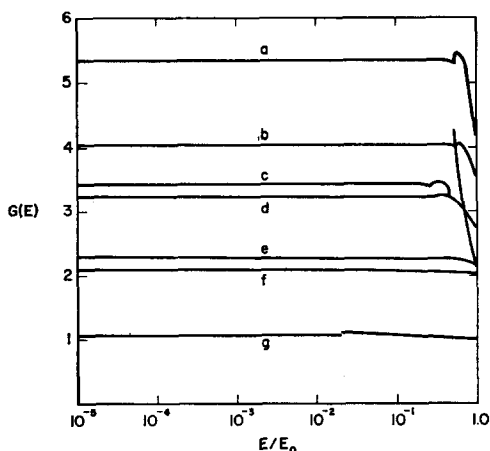

FIG. 1. Energy distribution function. Curves $a(r_i = 0.521)$, $d(r_i = 0.271)$, $e(r_i = 0.074)$, and $f(r_i = 0.020)$ are for positive-slope asymmetric scattering functions with $b = 1/(1-r_i)^2$. Curve b: equal collision-fraction mixture of substances of Curves a and d. Curve c: $r_i = 0.521$, $b = 0$. Curve g: $r_i = 0.020$, $b = 0$.

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[4] For example, at $E/E_0 \to 1.0$, $G(E)/G(E)_\infty = 0.767$, 0.852, and 0.847 for Curves a, b, and d, respectively.
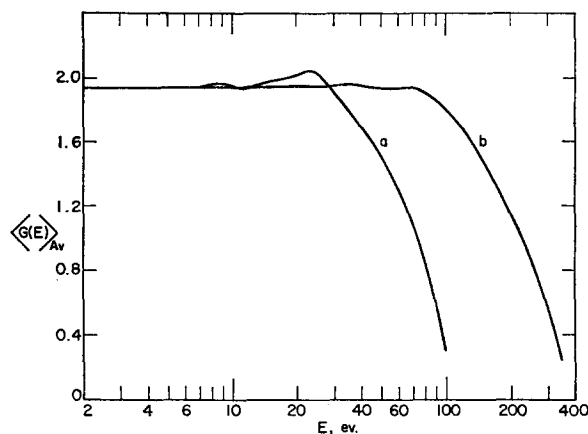

FIG. 2. Energy distribution function for hot atoms produced with variable E_0: $r_i = 0.271$, $b = 0$. E_0 assumed to increase linearly in the range: curve a, 20 to 100 eV, curve b, 20 to 350 eV.

in energy. Hence, the asymptotic solution is approximated within a smaller average number of collisions.

Variable E_0

For hot atoms generated by (n, γ) processes, where the nuclear binding energy may be released as a gamma-ray cascade, partial cancellation of gamma-ray momenta would result in a distribution of E_0 values.[5] For example, the $^{79}Br(n, \gamma)^{80}Br$ activation process will impart to the ^{80}Br initial energies which may vary from 0 to about 350 eV.[6] Presented in Fig. 2 are curves for $\langle G(E) \rangle_{Av}$ based on E_0 distributions which increase linearly[7] from 20 eV to either 100 eV (Curve a) or 350 eV (Curve b). Isotropic scattering with $r_i = 0.271$ was used; this results in $G(E)_\infty = 1.94$. As seen in Fig. 2, the average $G(E)$ value below 20 eV is in reasonable agreement with $G(E)_\infty$.

On the basis of only Figs. 1 and 2 it would appear that the asymptotic solution for $F(E)$, Eq. (5), is a reasonable approximation to use in hot-atom calculations involving, for example, $^3He(n, p)$-produced tritium or (n, γ)-activated ^{80}Br. However, other factors, such as energy-dependent scattering asymmetry effects could modify this conclusion. Before evaluating these factors it is necessary to consider the manner in which the energy distribution function is to be used in applying neutron-thermalization theory to hot-atom reactions.

USE OF $F(E)$

The basic equation defining the fractional yield of a product j, Y_{ij}, resulting from the reaction of hot atoms with Molecule i is

$$Y_{ij} = \int_{E_{2j}}^{E_{1j}} f_i(E) P_{ij}(E) F(E) dE, \qquad (11)$$

[5] C. Hsiung, H. Hsiung, and A. A. Gordus, J. Chem. Phys. **34**, 535 (1961).
[6] C. Hsiung and A. A. Gordus, J. Chem. Phys. **36**, 847 (1962).
[7] Figure 7 of Ref. 5 suggests that such a linear dependence of E_0 may serve as a reasonable approximation.
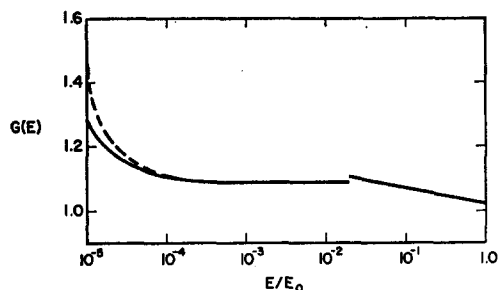
FIG. 3. Energy distribution function for an energy-dependent asymmetry factor, $b=1/E(1-r_i)^2$. $E_0=2\times10^5$, $r_i=0.020$. Dashed curve is a plot of the actual value of $1/\alpha$.

where E_{1j} and E_{2j} are probably of the order of 20 and 2 eV, respectively, and where $P_{ij}(E)$ is the probability of formation of Product j per collision of the hot atom with Molecule i.

For simplicity in evaluating any energy-dependent effects of $F(E)$, we only consider the portion of the integral of Eq. (11) containing $F(E)$ and equate it to the expression which results if the asymptotic form of $F(E)$, Eq. (5), is assumed valid. Thus

$$\int_{E_2}^{E_1} F(E)dE = \frac{\ln(E_1/E_2)}{\alpha_a}. \qquad (12)$$

It is then possible to calculate the apparent value α_a using Eq. (12) and compare this value to the actual value of α which exists in the range E_1 to E_2.

As noted in Fig. 1, if E_0 is 2×10^5 eV, then for the range 2–20 eV, α_a is (within $<\pm0.1$) the actual value of α. For the type of data given in Fig. 2, α_a is, between 2 and 20 eV, at the most, only a few percent less than the actual α value.

Energy-Dependent Scattering Function

Theoretical considerations of atomic scattering indicate that the asymmetry will be energy-dependent.[8] To investigate this effect we defined the parameter b of the asymmetry scattering function, Eq. (4), as

$$b=1/E(1-r_i)^2. \qquad (13)$$

For $r_i=0.020$, $b\rightarrow0$ as E increases and the asymmetry in the scattering becomes appreciable only for energies less than about 20 eV. Given in Fig. 3 is a plot of $G(E)$ for the energy-dependent asymmetric scattering using $r_i=0.020$. Since b in Eq. (4) is energy-dependent, α will also be energy-dependent and, using Eqs. (10) and (13), will be given by

$$\alpha(E)=0.920-0.438/E. \qquad (14)$$

The reciprocal of Eq. (14) is represented by the dashed curve in Fig. 3 using $E_0=2\times10^5$ eV.

Given in Table I are data for α_a as determined from Eq. (12) using the computer data represented by the solid curve of Fig. 3. The actual (average) value of α

existing in these energy ranges is also given in Table I. This latter quantity was calculated using the expression

$$\langle\alpha\rangle_{Av} = \frac{0.920(\ln E_1/E_2)}{\ln[(0.920E_1-0.438)/(0.920E_2-0.438)]}. \qquad (15)$$

As seen in Fig. 3, the dashed curve does not differ appreciably from the $G(E)$ curve indicating that compensation for an energy-dependent scattering function is at least partially achieved in the energy distribution function. The actual degree to which compensation has not been achieved depends on the energy range of interest. However, as indicated in Table I, the error in the apparent α value is usually not more than a few percent.[9]

It seems unlikely that an energy dependence of the type discussed in this section would be appreciably greater than the fictitious dependence chosen for illustration. As a result, we would conclude that energy-dependent effects of this type probably do not introduce appreciable error in the use of the asymptotic distribution function for hot-atom tritium reactions activated by the n, p nuclear process. This conclusion, however, is limited to tritium reaction systems for which the value of α is determined principally by only one component. In systems where two or more components are present at appreciable concentrations, Eq. (8) indicates that the energy dependence of the collision fractions f_i will also affect the α term.

Reaction Moderating Collisions

Thus far we have assumed that collisions between a hot atom and thermal-energy atom or molecule lead to moderation of the hot atom by processes involving positive slope $(b>0)$ asymmetric scattering. However, it would appear possible, for example, for some of the hot atoms to react to form a short-lived molecular complex which then dissociates freeing the hot atom.[10] These hot atoms are also moderated, at least in the sense that the atoms can lose energy through such a reaction–dissociation process. In fact, the average energy loss by this process could conceivably be much larger than that achieved in moderating collisions. To

TABLE I. Average and apparent energy-dependent α values.[a]

E_1 (eV)	E_2 (eV)	α_a	$\langle\alpha\rangle_{Av}$
20	10	0.897	0.888
20	5	0.886	0.872
20	2	0.857	0.830
10	2	0.840	0.807

[a] For $E_0=2\times10^5$ eV, $r=0.020$, and b, as given in Eq. (10), equal to $1.04/E$; refer to Fig. 3.

[9] Other calculations were performed with $b=1/[(1-r_i)^2E^{\frac{1}{2}}]$ and also with $r_i=0.521$. The differences between α_a and $\langle\alpha\rangle_{Av}$ for this energy-dependent slope were of the same order of magnitude as those in Table I.

[10] E. K. C. Lee and F. S. Rowland, J. Am. Chem. Soc. **85**, 897 (1963).

[8] H. W. S. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 371.

investigate the effect on $G(E)$ of such reaction-moderating collisions we assumed that hot atoms of $E_0 = 2 \times 10^5$ eV are moderated initially by collisions for which $r = 0.271$ and $b = +1.500$. At 300 eV we assumed that a given percent of the hot atoms will then undergo collisions for which $r = 0.020$ and $b = -1.041$. These data are given in Fig. 4, where it is seen that $G(E)$ approximates the new distribution function at energies less than 60 eV $(E/E_0 = 3 \times 10^{-4})$.

The data of Fig. 4 serve further to confirm what is seen in Fig. 1, namely that, for energy-independent α values, the asymptotic solution is approximated within an energy range of $E/E_{\text{initial}} = \sim 0.2$. If a rapid change in moderation occurs principally in the reactive energy range, E_1 to E_2, then the distribution function which exists in that energy range could differ from the asymptotic distribution function by as much as 200%–300%. In the real hot-atom reaction systems any change in moderation is probably gradual over the energy range; as a result, the apparent α value in the reaction energy range will differ from the average asymptotic α value by what must certainly be less than 200%–300%.

COMBINED ENERGY DEPENDENCIES

As indicated by Eq. (11) evaluation of apparent α values should be made in terms of

$$\int_{E_2}^{E_1} f_i(E) P_{ij}(E) F(E) dE = \frac{1}{\alpha_a} \int_{E_2}^{E_1} f_i(E) P_{ij}(E) d \ln E$$

(16)

rather than in terms of Eq. (12). For pure systems $(f_i = 1.0)$, an evaluation of α_a as performed above would require knowledge of $P_{ij}(E)$. Since the reaction probability will vary with energy, rather than be constant as was assumed above, this implies that certain portions of the energy range E_1 to E_2 would have less effect on α_a. However, the difference between α_a and $\langle \alpha \rangle_{\text{Av}}$ should still be less than 200%–300%.

In cases where a large amount of inert gas is present, such as in He-moderated T+CH$_4$ reactions, Eqs. (2), (8), and (11) will yield

$(Y_{\text{CH}_4,j}) x_{\text{CH}_4 \to 0}$

$$= X_{\text{CH}_4} \int_{E_{2j}}^{E_{1j}} \left[\frac{Q_{\text{CH}_4}}{Q_{\text{He}}} (E) \right] P_{\text{CH}_4,j}(E) F(E) dE, \quad (17)$$

with $\alpha \to \alpha_{\text{He}}$. For the example given by Eq. (17), the averaging process for determining α_a requires averaging in terms of both $P(E)$ and the energy-dependent cross-section ratio.

SUMMARY

On the basis of the data presented here it would appear that the use of the asymptotic energy distribution in ^{3}He(n, p) activated tritium hot-atom reactions would lead to an error in α_a which must be less than
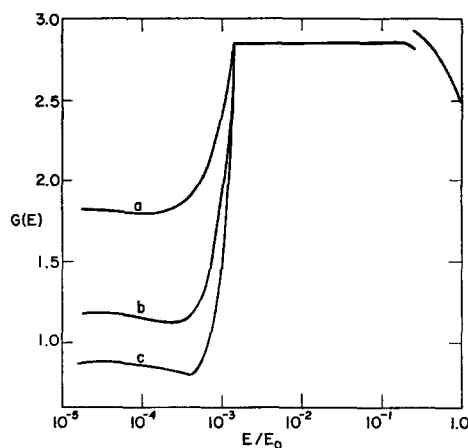

FIG. 4. Effect of reaction moderating collisions on the energy distribution function. Unperturbed scattering data: $r_i = 0.271$, $b = 1.500$; At $E/E_0 = 1.5 \times 10^{-3}$, 20% (Curve a), 50% (Curve b), or 80% (Curve c) of the atoms then undergo scattering with $r_i = 0.020$, $b = -1.041$.

200%–300%. In fact, it is perhaps not unreasonable to assign an upper limit to the error of $\pm 50\%$. For (n, γ) activated reactions such as those leading to ^{80}Br or ^{128}I, the upper error limit in α_a may be greater than $\pm 50\%$ since a large fraction of the hot atoms may be positively charged and the charge-transfer processes could contribute to pronounced energy dependent scattering functions.

Since the energy dependence of the cross-section ratios are as yet unknown, in cases where the collision cross-section ratio enters into the expression, such as Eq. (17), it would seem preferable to consider Eq. (17) in the form

$$(Y_{\text{CH}_4,j}) x_{\text{CH}_4 \to 0} = X_{\text{CH}_4} R \int_{E_{2j}}^{E_{1j}} P_{\text{CH}_4,j}(E) d \ln E, \quad (18)$$

where $R = (Q_{\text{CH}_4}/Q_{\text{He}} \alpha_{\text{He}})_a$ and is considered an apparent energy-averaged term.

It is evident from the figures presented in this paper that the asymptotic solution can be considerably in error for hot-atom reactions activated by processes where E_0, or the range of E_0 values, is in the region of 2–50 eV. Examples of such activation methods include photochemical and beta-decay processes.

APPENDIX

Since the analytical solution of $G(E)$ over the full range is tedious to calculate, we resorted to computer analysis. The range E/E_0 between 1 and 0.8×10^{-5} was divided into 90 equal segments on a logarithmic energy-ratio scale. The average value on a logarithmic energy scale of K_i in each interval was used in the calculation.

The value of $G(E)$ in an energy interval was assumed constant. This assumption results in a cumulative systematic error. As noted in Fig. 1, for example, a constant $G(E)$ value is a reasonable approximation for $E/E_0 < \sim 10^{-1}$. As a result, the principal contribution

to this systematic error will occur at higher values of E/E_0 and specifically at $E/E_0 > r$.

It is relatively easy to determine the analytical solution for $G(E)$ in the range E/E_0 of r to 1.0. Using such an expression we calculated the true value of $G(E)$ at $E/E_0 = r$ and assumed that the error in the computer result at $E/E_0 = r$ is not increased further at $E/E_0 < r$. The raw computer data for $G/(E)$ at $E/E_0 < r$

exhibit oscillations about a value of $G(E) \neq G(E)_\infty$.[11] When the correction at $E/E_0 = r$ is applied to all data for $E/E_0 < r$ the oscillations in $G(E)$ are then centered around $G(E)_\infty$, which implies, as we have assumed, that a negligible contribution to the systematic error occurs at $E/E_0 < r$.

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[11] The oscillations usually were centered about a value of $G(E)$ which did not differ from $G(E)_\infty$ by more than 0.2%.

Comparison of Experimental and Theoretical Vibrational Relaxation Times for Diatomic Gases

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A comparison of theoretical and experimental vibrational relaxation times has been carried out for the halogens, nitrogen, oxygen and carbon monoxide. Reasonably good agreement is obtained for all gases except oxygen. For oxygen the predicted variation of the vibrational collision number with temperature appears to be correct; however, experimental values at high temperatures appear to be low by a factor of 0.55. Values obtained at room temperature on the other hand agree well with theory. It would seem therefore that an anomalous decrease in the vibrational collision number takes place in the temperature range from 300° to 500°K.

Since data for carbon monoxide could be fitted very well by theory, it is apparent that the effect of radiation is negligible, at least in the temperature range above 1000°K. This is consistent with the value of 0.03 sec for the radiative lifetime of carbon monoxide in the first excited vibrational state.

An empirical relationship is established between the interaction constant α and the molecular diameter σ, which reproduces the experimentally derived values quite closely.

I. INTRODUCTION

EXISTING treatments of vibrational excitation during molecular collision can be related in one way or another to a series of papers published in the 1930's. Most prominent among these are the works of Zener,[1,2] who treated the problem of energy transfer both quantum mechanically and classically, Jackson and Mott,[3] who treated in analytical detail the case of a repulsive exponential interaction potential by means of quantum mechanics, and Landau and Teller,[4] who showed the dependence of the averaged vibrational excitation cross section on temperature.

Somewhat later Schwartz, Slawsky, and Herzfeld[5] using a one-dimensional approach, subsequently extended to three dimensions,[6] succeeded in establishing a fully quantum-mechanical description of the collision

process in an approximate, but reasonably accurate, form which could be used to calculate vibrational collision numbers. Such calculations have been made and the results compared with experimental data for many types of gas molecules.[7] Concurrent with the work of Schwartz, Slawsky, and Herzfeld were a series of papers by Takayanagi,[8] and Takayanagi and Kaneko,[9] who presented a more complete quantum-mechanical description of the collision process, and gave numerical estimates of transition probabilities for O_2–He and H_2–H_2 collisions. Unfortunately the results obtained by Takayanagi do not lend themselves to ready calculation as do those of Schwartz, Slawsky, and Herzfeld; however, quite recently[10,11] a series of papers has appeared in which are tabulated quantities used in calculating transition probabilities, and it is hoped that these will be used to correlate existing experimental

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