Neutron Thermalization Theory Applied to Hot Atom Chemical Reactions: Consideration of Isotropic and Asymmetric Scattering

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The application of neutron thermalization theory to hot atom chemical reactions is discussed with emphasis on the possible errors involved. The assumption of isotropic scattering symmetry is specifically considered, and methods which have previously been proposed for the handling of hot atom data are evaluated. It is concluded that, at present, the use of hot atom data in calculating absolute values of the average energy losses and reaction probability integrals is severely limited if not impossible owing to the lack of scattering cross-section data in the range 1–30 e.v. However, since fewer assumptions are required, it may be possible to obtain some qualitative information about the ratios of these variables from inert gas moderated data and from systems of low total reactivity.

Introduction

Neutron thermalization (n.t.) processes and hot atom chemical reactions in homogeneous media appear to be similar in that the high-energy particles (neutrons or hot atoms) are degraded energetically by colliding with thermal-energy particles. In the process of becoming thermalized the neutrons may be absorbed by nuclei whereas the hot atoms may react chemically. The two processes, however, are not identical. For example, in the thermalization of neutrons it may be reasonable to assume that scattering is elastic and isotropic; the thermalization of hot atoms can involve appreciable scattering asymmetry and inelasticity. The n.t. model involving, among the assumptions, elastic and isotropic scattering has served partially as a basis for hot atom reaction models developed by Libby and co-workers,[1-3] Miller, Gryder, and Dodson,[4] Capron and Oshima,[5] Estrup and Wolfgang,[6] and Frère.[7]

Presented in this paper is an evaluation of the n.t. model as the various assumptions are introduced. Scattering asymmetry and inelastic collisions are discussed and methods of handling experimental data are proposed. The notation has been kept as consistent as possible with that of ref. 6.

Assumptions

For most gas phase hot atom reactions activated by nuclear processes we may safely assume that (a) a steady state will be valid in the calculation of the hot atom energy distribution function; (b) the system is homogeneous; (c) the hot atoms lose energy in collisions and mathematically these collisions can be treated as if they are between hot atoms of energy E and particles of zero energy; this implies that the activation energies of the reactions being studied are not of the same order of magnitude as thermal energies; (d) the hot atoms are produced at energies greater than the energies at which appreciable reaction takes place; photochemical, α-, or β-decay activation processes are therefore excluded from consideration; (e) no hot atoms are lost due to recoil to the walls of the container; if, experimentally, any recoil loss occurs the data must be corrected for the loss before the data are analyzed in terms of the equations to be derived.

Seven assumptions which, in various combinations, will be used to evaluate the hot atom reaction yields are given below.

1. Collisional Probability Is Not a Function of Energy.—The collisional probability is

$$f_i(E) = \frac{Q_i(E)X_i}{\sum\limits_{k} Q_k(E)X_k} = \frac{X_i}{\sum\limits_{k}[Q_k(E)/Q_i(E)]X_k} \quad (1)$$

where X_i is the mole fraction of substance i and $Q_i(E) = \pi(r_i + r_H)^2$ is the total viscosity cross section between i and the hot atom, H, and r is the collisional radius. The quantity $Q_i(E)$ for purposes of these calculations can be considered as the viscosity cross section (denoted by $Q^{(2)}$ in ref. 8). At the energies involved in the hot atom reactions (frequently >1 e.v.), the ratio of the two cross sections, based on Lennard-Jones potentials, $Q_1^{(2)}(E)/Q_2^{(2)}(E)$, may not vary by more than $\pm 10\%$.[8] If a Lennard-Jones potential of interaction is assumed, then the ratio of the squares of the distance at the classical turning point, $(r_{1m}/r_{2m})^2$, should be a constant (Appendix I). The quantity r_m is defined by

$$V(r_m) = \mu g^2/2 \quad (2)$$

where $V(r_m)$ is the interaction potential at r_m, μ is the reduced mass, and g is the relative velocity of the two particles. If the energy, E, of one of the interacting particles (of mass m_1) is much greater than the other particle, then $g = (2E/m_1)^{1/2}$. Although $2\pi r_m^2/3$ may differ from the actual viscosity cross section Q by as much as 20%,[3] the ratio $(r_{1m}/r_{2m})^2$ may not be different from $Q_1^{(2)}/Q_2^{(2)}$ by more than $\pm 5\%$. However, Fallon, Mason, and Vanderslice[9] suggested that a Lennard-Jones potential may not be completely valid. Using experimental data they present, $[r_{m,H-H_2}(E)/r_{m,H-He}(E)]^2$ was calculated at different energies and found to decrease from 1.04 to 0.44 in the range 1–5 e.v. (Appendix I). Unfortunately, very few atomic beam data are as yet available in this energy range and different potential functions yield different results.

2. The Energy Distribution Function in Nonreactive Collisions Is the Asymptotic Solution.—The distribution function, $F(E)$, is determined by solving the Boltzmann transport equation. For an infinite number of nonreactive collisions the solution is the asymptotic form[10]

(1) W. F. Libby, *J. Am. Chem. Soc.*, **69**, 2523 (1947).

(2) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

(3) M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

(4) J. M. Miller, J. W. Gryder, and R. W. Dodson, *ibid.*, **18**, 579 (1950).

(5) P. C. Capron and T. Oshima, *ibid.*, **20**, 1403 (1952).

(6) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2665 (1960).

(7) R. Frère, *Bull. Classe Sci., Acad. Roy. Belg.*, **49**, 216, 296 (1962).

(8) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquid," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 558.

(9) R. J. Fallon, E. A. Mason, and J. T. Vanderslice, *Astrophys. J.*, **131**, 12 (1960).

$$F(E) = 1/\alpha E \tag{3}$$

where α is the average logarithmic hot atom energy decrease in nonreactive collisions. It is

$$\alpha_i = \overline{\ln \frac{E'}{E}} = \frac{\int_{r_iE'}^{E'} k(E,E') \ln (E'/E) \, dE}{\int_{r_iE'}^{E'} k(E,E') \, dE} \tag{4}$$

where E' is the hot atom energy prior to a collision and E the energy following the collision. The minimum final hot atom energy which is possible in a collision is
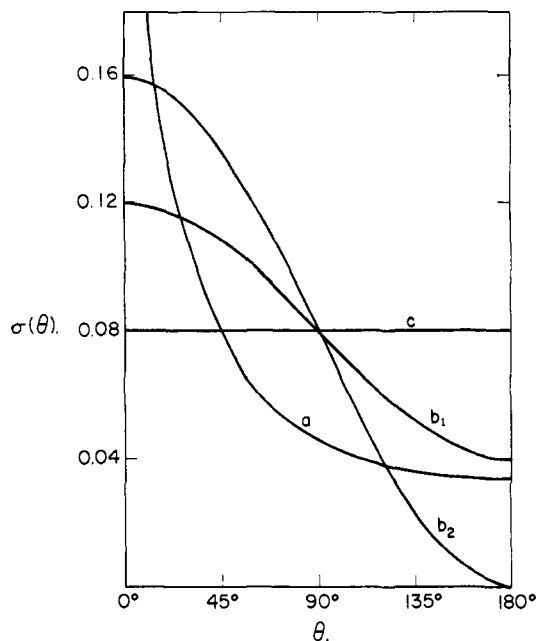

Fig. 1.—Differential scattering cross section vs. scattering angle for isotropic, curve c, and asymmetric scattering, curves b, given by eq. 8 with positive b values. Curve b_1 is $b = \frac{1}{2}(1 - r)^{-2}$, curve b_2 is $b = 1/(1 - r)^2$ as used in eq. 8. Curve a is of the type found experimentally. These curves have been normalized to $Q = 1$.

r_iE'. The quantity $(1 - r_i)$, therefore, is the maximum fractional energy loss; r_i is limited to the range 0 to 1.0. If the collisions are elastic, e, then

$$r_{ie} = (m_i - m_H)^2/(m_i + m_H)^2 \tag{5}$$

where m_i and m_H are, respectively, the masses of molecule i and the hot atom H.

The quantity $k(E,E')$ is a scattering function given in terms of energy and is related to the differential scattering cross section.

If scattering is isotropic, then all collision angles are equally probable (Fig. 1, curve c) and, as a result, all energies between E' and $r_{ie}E'$(Fig. 2, curve c) are equally probable. (The conversion between the cross-section scattering angle relationship, Fig. 1, and the scattering function–energy relationship, Fig. 2, is given in Appendix II.) For elastic atom–atom and atom–molecule interactions, it has been demonstrated[11] that appreciable scattering asymmetry exists with small angle

(10) We are in the process of evaluating, using a computer approach, the applicability of eq. 3 for the particular case of $He^3(n,p)$ — activated T. Preliminary data suggest that eq. 3 is a reasonably valid approximation. In addition, if α is energy-dependent, the calculations suggest that energy averaged α-values may, in some cases, be reasonable approximations.

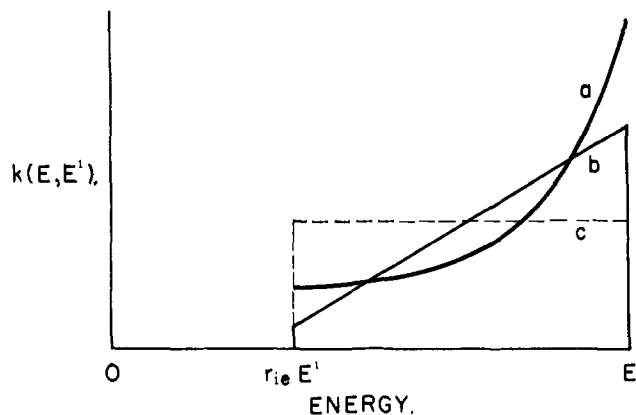(11) R. B. Bernstein, J. Chem. Phys., **33**, 795 (1960).

Fig. 2.—Scattering function vs. energy for scattering characteristic of the elastic contribution to collisions; refer to text for discussion of curves.

(glancing) being more probable than large angle (approaching head-on) collisions (Fig. 1 and 2, curve a). In some of the calculations which follow we will approximate such asymmetry by a linear function (Fig. 2, curve b). Curve b of Fig. 1 corresponds to this linear approximation.

Inelastic collisions involve a value of $r_i < r_{ie}$ since a head-on collision can result in the transfer of energy greater than that possible in an elastic collision.

Figure 3 contains various fictitious forms of the inelastic contribution to the scattering probability function. Curve a is of the type found in chemical reactions.[12,13]
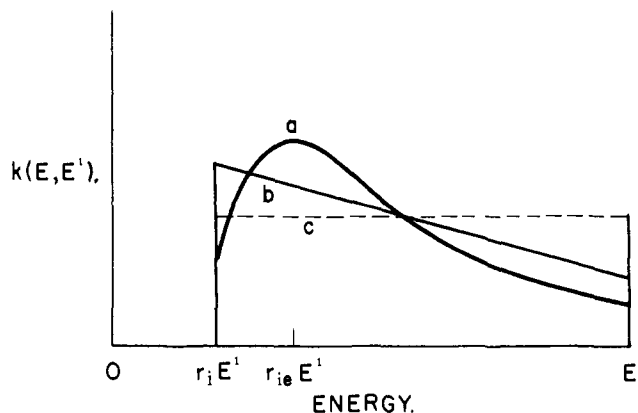

Fig. 3.—Scattering function vs. energy for scattering characteristic of inelastic contribution to collisions; refer to text for discussion of curves.

Evaluation of α.—If the collisions are isotropic, then $k(E,E') = a$ (a constant)[14] in the range E' to r_iE' and zero elsewhere. Since the total probability must be normalized to unity according to

$$\int_{r_iE'}^{E'} k(E,E') \, dE = 1 \tag{6}$$

there results $a = 1/E'(1 - r_i)$. The solution of eq. 4 for isotropic scattering, α_{iI}, is

$$\alpha_{iI} = 1 + \frac{r_i}{1 - r_i} \ln r_i \tag{7}$$

This term is energy independent.

(12) D. R. Hershbach, G. H. Kwei, and J. A. Norris, ibid., **34**, 1842 (1961).

(13) D. Beck, E. F. Greene, and J. Ross, ibid., **37**, 2895 (1962).

(14) See, for example. S. Glasstone and M. C. Edlund, "The Elements of Nuclear Reactor Theory." D. Van Nostrand Co., Inc., New York, N. Y., 1952, p. 164.
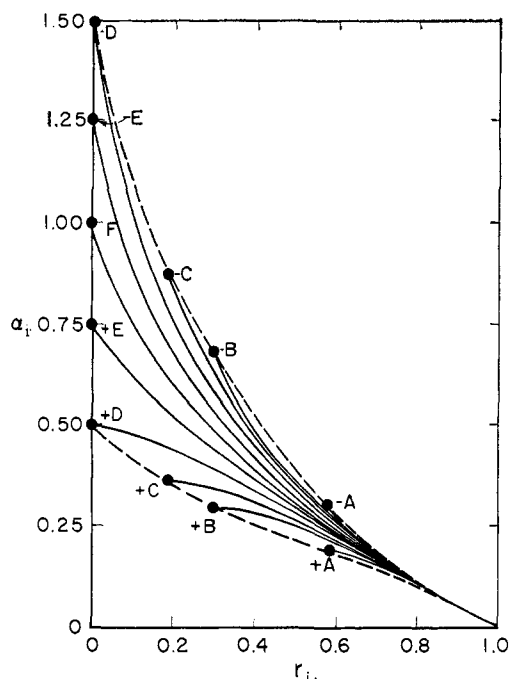
Fig. 4.—Average logarithmic energy decrease as a function of r for various values of b as defined by eq. 8. The solid circles define the maximum value of α_1 for each curve: curves $\pm$A $(b = \pm 3)$, $\pm$B $(b = \pm 2)$, $\pm$C $(b = \pm 1.5)$, $\pm$D $(b = \pm 1.0)$, $\pm$E $(b = \pm 0.5)$, and F $(b = 0)$.

For asymmetric scattering approximated by the linear relationship (curves b, Fig. 2 and 3) we have

$$k(E,E') = a + 2bE/(E')^2 \qquad (8a)$$

in the range E' to $r_i E'$ and zero elsewhere. The slope is a constant equal to $2b/(E')^2$. Using eq. 6, it is possible to eliminate the constant a in eq. 8a. The result is

$$k(E,E') = -b(1 + r_i)/E' + 1/(1 - r_i)E' + 2bE/(E')^2 \qquad (8b)$$

For scattering given by eq. 8b, the solution of eq. 4 is

$$\alpha_i = \alpha_{iI} - b \left[\frac{1 - r_i^2}{2} + r_i \ln r_i \right] \qquad (9)$$

where α_{iI} is the isotropic scattering value as given by eq. 7. This expression for α_i is also energy independent.

Given in Fig. 4 are plots of α_i as a function of r_i for various values of b as given by eq. 9. The solid points represent the maximum value of α_i for a given value of b and are determined on the basis that $k(E,E')$ cannot be less than zero in the range E' to $r_i E'$. For this figure, curves A and $-$A correspond to $b = +3$ and -3, respectively. Similar $\pm$ identification applies to curves $\pm$B $(b = \pm 2)$, $\pm$C $(b = \pm 1.5)$, $\pm$D $(b = \pm 1.0)$, and $\pm$E $(b = \pm 0.5)$. Curve F is for $b = 0$, the isotropic scattering result. The dashed curves define the limits of α_i and r_i. It should be stressed that these limits apply only to the linear scattering probability function, eq. 8b.

Positive values of b are appropriate approximations for atom–atom elastic scattering, such as T + inert gases. As a result, the relationship between α and r is limited to the region defined by curve F $(b = 0)$ and the lower dashed curve in Fig. 4. By analogy, for
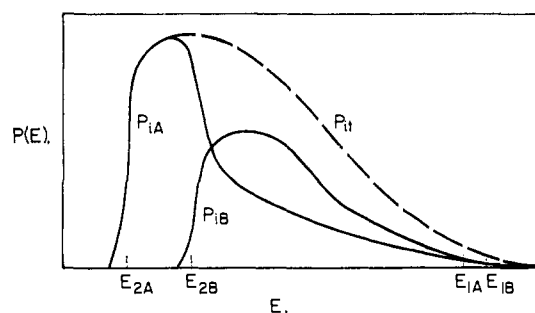
elastic scattering curves such as curve a, Fig. 1, the relationship between α_i and r_i will be limited to a region bounded by curve F and a dashed curve which lies below curve F, and has an intercept at $r_i = 0$ of $\alpha_i < 1.0$. Consider, for purposes of comparison T + He^4 collisions where $(r_{He})_e = 0.02$ and $(\alpha_{He})_{Ie} = 0.919$. If the asymmetric curve is approximated as a linear function of positive slope with $k(E,E') = 0$ at $r = 0.02$, then according to eq. 8b, $b = 1.042$ and $(\alpha_{He})_e = 0.479$; the ratio $(\alpha_{He})_{Ie}/(\alpha_{He})_e = 1.91$. If T + Xe collisions are considered, then $(r_{Xe})_e = 0.913$ and $(\alpha_{Xe})_{Ie} = 0.0450$. If $b = 1.042$ as before, then $(\alpha_{Xe})_e = 0.0449$, in very good agreement with the isotropic value. However, this value of b does not describe the same asymmetry function as was used for the T–He collisions. If $k(E,E') = 0$ at $r = 0.913$, then $b = 131.0$ and $(\alpha_{Xe})_e = 0.0293$. The ratio $(\alpha_{Xe})_{Ie}/(\alpha_{Xe})_e$ is 1.53. Therefore, it would appear that the use of isotropic scattering values of α for T–inert gas collisions could be considerably in error and the error would decrease in going from T–He to T–Xe.

For a mixture[14]

$$\alpha = \sum_i f_i \alpha_i \qquad (10)$$

If the collision fractions, f_i, are functions of energy, then α as defined by eq. 10 would also be a function of energy and α in eq. 3 should probably be treated as an energy-averaged value.[10]

Individual values of α also may be energy dependent in which case the α quantity in eq. 3 would represent the average value over the energy range of interest.[10]

3. Total Scattering Is Isotropic in Center of Mass System.—For high-energy neutrons this assumption is frequently a valid approximation. For chemical reactions this assumption is clearly in error.

4. Collisions Are Elastic.—This approximation has frequently been incorporated in n.t. theory in order to evaluate numerically one of the parameters. This assumption is undoubtedly valid for hot atom–inert gas collisions which do not involve electronic interactions. The assumption is invalid for hot atom–molecule collisions.

5. Head-on Collisions Result in Total Energy Transfer.—This assumption, that $r = 0$, can in some cases lead to a simple expression for the hot atom reaction yield.

6. Reaction Probability Is Very Small.—$P_{ij}(E)$ is the reaction probability per collision for the formation of product j. For the reaction between a hot atom and a thermal-energy molecule i, $P_{ij}(E)$ will be zero for hot atom energies less than an energy related to the activation energy of the reaction. With increasing

Fig. 5.—Fictitious reaction probabilities as a function of energy.

hot atom energy, the reaction probability per collision will increase and eventually decrease and approach zero. Illustrated in Fig. 5 are hypothetical reaction probability curves for a reaction of hot atoms with substance i where two products, A and B, can be formed. The total reaction probability, $P_{it}(E) = \Sigma P_{ij}(E)$. The lower energy thresholds, related to the activation energies of the two reactions, are E_{2A} and E_{2B}. The upper thresholds may be infinity but, for purposes of computation, we can consider them to be some finite energies above which is contained less than 1%, for example, of the total area under the $P_{ij}(E)$ curve. These pseudo-upper energy limits of reaction are labeled E_{1A} and E_{2A}. No direct information is available about these upper-energy values although crude approximations[15] and indirect evidence[16a] suggest that these energies may be of the order of 5–30 e.v. depending on the reaction. The reaction probability of a mixture can be made to approach zero by diluting the reactive substance with a large amount of an inert gas.

7. Reaction Probability Ratios Are Constant for Two-Component Reactive Mixtures. Hot Atom Yields.

—The fractional yields of product j, Y_{ij}, resulting from the reaction of hot atoms with molecule i can be given as

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

$F(E)dE$ is the probability that the hot atoms have an energy between E and $E + dE$. The quantity $F(E)$ is the energy distribution of hot atoms at any energy, E, below the maximum initial energy at which the hot atoms are formed. Thus, the calculation of $F(E)$ must take into account the perturbation in the energy distribution of the hot atoms which occurs at energies corresponding to the reactive energy range, $E_{1j}-E_{2j}$.

The above variables are of the type which are contained in n.t. theory. The only difference is that in n.t. theory the product, $f_i(E)P_{ij}(E)$, as given in eq. 11, is handled as an energy-dependent cross-section term.

As indicated below, under some circumstances it may be possible to determine, using hot atom data, reaction integrals defined as

$$I_{ij} = \int_{E_{2j}}^{E_{1j}} P_{ij}(E) \, d \ln E \qquad (12)$$

Inert Gas Moderated Reaction Systems.—Consider a reaction system composed of a reactive gas, R, an inert gas, G, a small amount of He³, and a small amount of a thermal-energy tritium scavenger. The yields of products can be determined as a function of the mole fraction of the inert gas, X_G. As $X_G \rightarrow 1.0$, the yields $\rightarrow 0$, and α, as given by eq. 10, $\rightarrow \alpha_G$ of the inert gas. Since very little reaction occurs, this is equivalent to $P_{it} \rightarrow 0$, and eq. 3 can be used. Therefore, for $X_G \rightarrow 1.0$ and assumptions 1 and 2, eq. 11 becomes

$$(Y_{Rj})_{X_G \rightarrow 1} = \frac{f_R}{\alpha_G} \int_{E_{2j}}^{E_{1j}} P_{Rj}(E) \, d \ln E \qquad (13)$$

Using eq. 1 and 12

$$(Y_{Rj})_{X_G \rightarrow 1} = X_R I_{Rj} / \alpha_G(Q_G/Q_R) \qquad (14)$$

(15) C. Hsiung, Ph.D. Dissertation, The University of Michigan, 1962 pp. 106, 107.

(16) (a) R. J. Cross, Jr., and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961); (b) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661 (1960).

A plot of Y_{Rj}/X_R vs. X_R has an intercept at $X_G \rightarrow 1$ of $I_{Rj}/\alpha_G(Q_G/Q_R)$.

The calculation of absolute values of I using eq. 14 of course requires additional assumptions. Thus Wolfgang and co-workers[6,16a] have assumed α_{He} is the isotropic elastic collision value, 0.919 (assumptions 3 and 4), and have used rigid-sphere radii in combination with the Bohr radius of hydrogen to determine I_{CH_3T} and I_{CD_3T} using a method of plotting inert gas moderated data based on a series expansion of eq. 15. If rigid-sphere or Lennard-Jones radii are used (Appendix I) the I-values would be about 29 or 66% greater, respectively. The recognition of asymmetric T + He scattering, on the other hand, might result in I-values which are very much smaller than those reported in ref. 6 and 16a. Until more information is available regarding total and differential cross sections, it appears impossible to determine quantitatively absolute values of I.

On the other hand, it may be possible to obtain some information from certain intercept ratios. For example, if the moderation of a reaction is studied using different inert gases then, for any two sets of data, according to eq. 14, the intercept ratios are inversely proportional to the $\alpha_G Q_G$ ratios since Q_R and I_{Rj} should be the same irrespective of the inert gas.

If isotopic reactions such as T + $CH_4 \rightarrow CH_3T$ + H and T + $CD_4 \rightarrow CD_3T$ + D are studied using the same inert gas, He, for example, $(Y_{CH_3T}/X_{CH_4})_{X_{He} \rightarrow 1}/(Y_{CD_3T}/X_{CD_4})_{X_{He} \rightarrow 1}$, according to eq. 14, is I_{CH_3T}/I_{CD_3T}. Cross and Wolfgang,[16a] using a different method of plotting experimental data, found this intercept ratio to be approximately unity. (It would be of interest to determine if the same ratio is found for xenon which possesses an ionization potential less than that of tritium since in highly moderated systems helium may not be completely effective in neutralizing tritium ions.[17])

If more than one product is formed in a reaction and data are available for inert gas moderation of the reaction, then additional ratios can be determined. Estrup and Wolfgang[16b] present data for the He⁴-moderated, halogen-scavenged T + CH_4 reaction; the yields of CH_3T, HT, and CH_2TX (X = Br or I) were determined. The plot of Y_{CH_3T}/Y_{CH_2TX} vs. X_{CH_4} (Fig. 6) has an intercept, according to eq 14, $I_{CH_3T}/I_{CH_2TX} \sim 5$, the value found by Estrup and Wolfgang[6] from separate plots of a different type.

The decrease in the yield ratio (or specific activity ratio) with increasing inert gas suggest that $(P_{CH_3T}/P_{CH_2TX})(E)$ is not a constant. The reasoning is: As $X_{CH_4} \rightarrow 1$ a large fraction of the tritium could react at energies corresponding to the upper energy portions of the $P(E)$ curves. As a result, the lower portions of the $P(E)$ curves would not influence the total observed yields to as great an extent since the tritium population is partially depleted before reaching these lower energies. In the highly inert gas moderated systems, the full ranges of the $P(E)$ curves are available to the tritium since very little reaction occurs and the tritium has equal opportunity to react in any portion of the $P(E)$ curve. If the $P(E)$ ratios are constant with energy, then the yield ratios will be constant

(17) F. S. Rowland, J. K. Lee, B. Musgrave, and R. M. White, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961, p. 67.
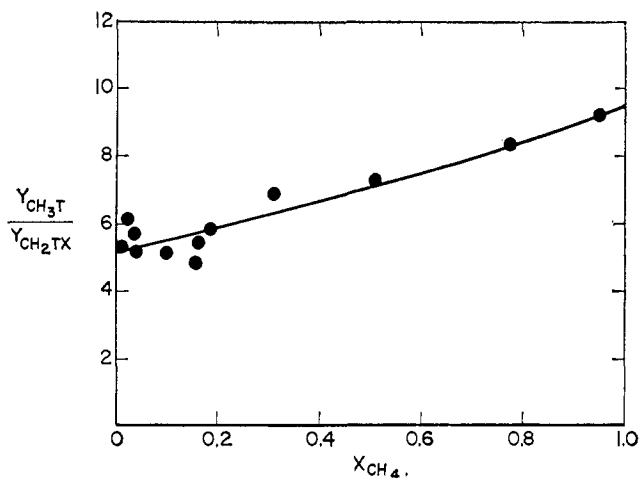
Fig. 6.—Plot of CH_3T/CH_2TX data of ref. 16b.

for all mole fractions.[18] The apparent decrease in the Y ratio of Fig. 6 suggests[19] that, on the average, the $P(E)$ curve for CH_3T lies at higher energies than the $P(E)$ curve for CH_2TX. Unlike the data of Fig. 6, data for a single yield are subject to any error involved in correcting[16b] the original experimental data for recoil loss.

The Wigner Equation.—For certain conditions, the Boltzmann equation and hence eq. 11 can be solved in closed form. If assumptions 1 to 3 plus 6 are valid, then for a mixture of substances, the result, which was first proposed by Wigner,[20,21] is

$$\ln (1 - Y_t) = -(\sum_i I_{ti} f_i)/\alpha_I \qquad (15)$$

Equation 15 will also be the solution for assumptions 1 to 3 + 5, all $r_i = 0$ (*i.e.*, all $\alpha_{iI} = 1.0$).

Equation 15 and a series expansion of eq. 15 have been used by Wolfgang and co-workers to evaluate tritium hot atom data.[6,16a,23] For this reason it is of importance to evaluate, if possible, the errors involved in the use of these equations.[24]

In evaluating the validity of their two-term series approximation of eq. 15, Estrup and Wolfgang[6] have

(18) It should be stressed that a constant specific activity ratio, however, does not necessarily imply a constant $P(E)$ ratio.

(19) This suggestion, however, should not be taken seriously since the change in the specific activity ratio with mole fraction might also result from other causes such as an energy dependence of f, and thus α, from partial lack of neutralization of T^* or greater radiation effects in the He^4 highly moderated systems, etc. The possible interpretation is presented here only because it differs from that given by Estrup and Wolfgang[6] and involves fewer assumptions than required for their conclusion. If the present suggestion is accepted, this implies that CH_2TX may possibly not be formed by the two-step process $T + CH_4 \rightarrow CH_3T + 2H$ followed by $CH_2T + X_2 \rightarrow CH_2TX + X$ since the first step requires more energy than that required for the direct formation of CH_3T.

(20) The narrow resonance equation was originally given by E. P. Wigner (unpublished). See, for example, ref. 14, pp. 166-168. The Wigner equation can also be obtained for the case of $P(E) \rightarrow 0$ or $r \rightarrow 0$ by neglecting second-order terms in the derivation.[7]

(21) By neglecting to include a term in their derivation, Estrup and Wolfgang[6] have derived the Wigner equation. Equation 5 of ref. 6 can be obtained by omitting the last term of eq. 53.2, p. 21 of ref. 22. As indicated in this paper, the expressions presented by Estrup and Wolfgang[6] require a larger number of assumptions than are stated in ref. 6.

(22) L. Dressner, "Resonance Absorption in Nuclear Reactors," Pergamon Press, New York, N. Y., 1960.

(23) H. C. Jurgeleit and R. Wolfgang, *J. Am. Chem. Soc.*, **85**, 1057 (1963).

(24) The series expansion of eq. 15 was also used to determine I-values for the $Br^{80} + CH_4$ and $I^{128} + CH_4$ reactions.[25,26] Because of the lack of knowledge of α-values and viscosity cross-section values, we do not consider these I-values and the corresponding slopes as significant.

(25) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).

(26) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961).

examined data for the inert gas moderated $T + CH_4$ reaction. They found, using isotropic scattering, elastic collision values of α_i, that plots of $Y_i \alpha / f_{CH_4}$ *vs.* f_{CH_4}/α were approximately linear for $i = CH_3T$ and CH_2TX in accord with the two-term expression, but nonlinear for the HT data. The latter curvature, they suggested, was due to the formation of HT by a spurious thermal reaction and was useful in "demonstrating that this model cannot be "adjusted" to provide a fit for thermal reactions."[6] However, it is open to question whether the linear plots serve as a basis for demonstrating the validity of the model as given by the two-term equation. In the first place, the linearity is, at least partially, a direct reflection of the apparent linearity in the specific activity of the original data. Secondly, it is, at least partially, the result of the particular α_{iI} and Q_i values used in their calculations. For example, if a value of the tritium radius of 1.2 Å. rather than the Bohr radius is used, then distinct curvature is seen.[27] Similarly, as noted by Jurgeleit and Wolfgang,[23] the use of a different value for α_{CH_4} results in a plot of a different shape.

In addition to the helium-moderated data, Estrup and Wolfgang also present four runs using other inert gases. These four points, if plotted as specific activity *vs.* X_{CH_4}, would lie considerably above the curve for the helium data. When plotted in terms of their two-term equation these points appear to fall, as predicted, on the same line as the helium-moderated data.[6] This was also taken[6] as an indication of the validity of the two-term equation. However, the use of different α_i and Q_i values can result in less agreement with the helium data although such displacement would probably never be as great as in the plots of specific activity *vs.* mole fraction.

The virtue, then, in the presentation of Estrup and Wolfgang is that they have illustrated convincingly that the main factors controlling the relative moderating efficiencies of inert gases are the difference in "sizes" and the average logarithmic energy-loss factors of the inert gases. Intuitively, one would probably compare the data in terms of collision fractions, eq. 1, rather than mole fractions but probably normalize the yields incorrectly in terms of weighted r factors (*e.g.*, $r_{total} = \sum_i f_i r_i$) rather than in terms of the weighted average logarithmic energy losses of the systems, eq. 10. In addition, their two-term equation indicates that the intercept at $f_R/\alpha \rightarrow 0$ is I_{Rj} in agreement with eq. 13.

Since we have, at present, no means of evaluating assumptions 1 and 2 except in terms of the qualitative discussions already presented, we will consider these assumptions as valid and attempt to determine the error due to assumptions 3 to 6 when applied to eq. 15 for the specific case of a pure system. For this case, eq. 15 becomes

$$\ln (1 - Y_t) = -I_t/\alpha_I \qquad (16)$$

For any given value of I and α_I the lowest value of Y_t is obtained when $P(E) \rightarrow 0$ since $E_1/E_2 \rightarrow \infty$ and the hot atoms are provided with the maximum opportunity to survive reaction. Thus, for assumption 1 to 3 + 6 the smallest possible value of Y_t is given

(27) A. A. Gordus, Progress Report No. 2, U. S. Atomic Energy Comm., *Nuclear Sci. Abstr.*, **16**, 13086 (1962), Fig. 2 and 4.

by eq. 15. For a given value of I and α_I the total yield will become greater for smaller values of E_1/E_2 and, therefore, correspondingly larger values of $P(E)$. The maximum yield for a given value of I is for $P(E) = 1.0$. If $P(E) = 1.0$ and $r = 0$ the yield is given by eq. 15. If $P(E) = 1.0$ and $r \geqslant E_2/E_1$, the atoms are not able to by-pass the reactive energy range; the yield is then 1.0. For assumptions 1 to 3, $P(E) = 1.0$, and $0 \leqslant r \leqslant (E_2/E_1)$, the solution of the Boltzmann equation and hence eq. 11, as indicated in Appendix III, is

$$Y_t = \frac{1}{\alpha_I(r-1)}\left[r \ln\left(\frac{E_1}{E_2}\right) - 1 + \frac{E_2}{E_1}\right] \quad (17)$$

For $r = 0$ ($\alpha_I = 1$) assumption 5 applies and eq. 17 reduces to eq. 16. For a given value of I, eq. 12 was used in combination with $P(E) = 1.0$ to calculate E_1/E_2. Then values of r (and therefore α_I) in the range 0 to E_2/E_1 were used to calculate Y_t according to eq. 17. For each Y_t value, $(I/\alpha_I)_{\text{Wigner}}$ was then calculated according to eq. 16. These data are depicted in Fig. 7 and serve as an indication of the maximum error in eq. 16. The maximum error for any value of Y is that given by the curve of $I = 0$. For a given value of I the I/α_I ratio will lie in the region under its curve. Thus, if $I = 0.1$ and $Y_t = 0.70$, the Wigner equation is in error by 30% if $P(E) = 1.0$, but in error by only a few per cent if $P(E)$ is very small.

We may consider next the error in eq. 16 introduced by assumption 3. Since eq. 16 has been used in conjunction with hot atom data obtained in nonmoderated systems it is important to consider the effects of both inelasticity and asymmetry. The appropriate scattering function might be some combination of curve a of Fig. 2 and curve a of Fig. 3. The actual shape is, as yet, unknown although the combined scattering function may appear similar to that of curve a of Fig. 2 except with a lower energy limit $r_i E' < r_{ie} E'$. Construction of a set of curves, of the type given in Fig. 7, for linear scattering asymmetry (curves b of Fig. 2 and 3) indicate features similar to those of Fig. 7.[28] The curve of $I = 0$ is the same as that of Fig. 7 since it is independent of the $k(E,E')$ function (Appendix III). The only difference is that whereas eq. 16 is valid for assumptions 1 to 3 + *either* 5 or 6, Fig. 7, eq. 16 is in agreement with the linear asymmetry collision calculations only for assumptions 1 and 2 + 5 *and* 6.

All such curves indicate that appreciable error could be introduced in the use of eq. 16, particularly for systems of large Y_t. Thus, conclusions which are based on the use of eq. 16, and especially when additional assumptions are introduced as in ref. 23, must be viewed as only approximations which may be considerably in error. These errors, as well as those involved in calculating numerical values of α according to eq. 10 and in calculating f_R, would affect the validity of some of the conclusions based on eq. 15 or the two-term series expansion of the equation as given in ref. 6.

If Y_t is small (*e.g.* <0.10) then, as noted in Fig. 7, deletion of assumption 3 (isotropic scattering) and assumption 5 or 6 will not introduce more than 6%

(28) These data, given in a supplement to this paper, Document No. 7774, may be obtained by remitting in advance $2.50 for photocopy or $1.75 for microfilm, payable to: Chief, Photoduplication Service, ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C.
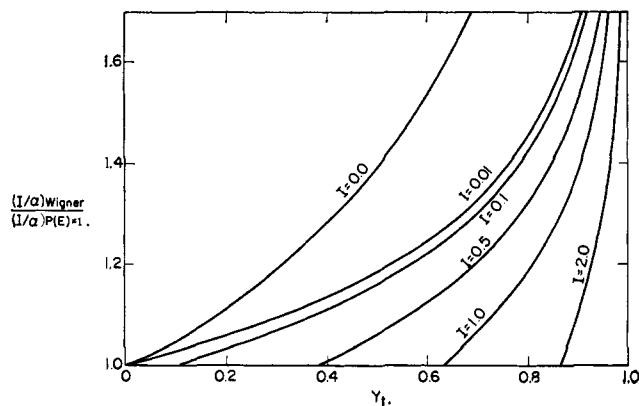

Fig. 7.—Comparison of I/α values calculated according to eq. 16 and 17. Isotropic scattering, eq. 6, is assumed; refer to Appendix III.

error in eq. 16 or, by analogy, eq. 15. Thus, for assumptions 1 and 2 and low Y_t, it may be possible to use experimental data to calculate additional variables. For example, for the inert gas, G, moderation of the reaction of hot atoms with a reactive gas, R, then, according to eq. 10 and 15

$$\alpha_R/I_t + (1 - f_R)\alpha_G/f_R I_t = -1/\ln(1 - Y_t) \quad (18)$$

or

$$\alpha_G/I_t + f_R(\alpha_R - \alpha_G)/I_t = -f_R/\ln(1 - Y_t) \quad (19)$$

Using eq. 1, eq. 19 can be rearranged as

$$\alpha_G Q_G/I_t Q_R + X_R(\alpha_R Q_R - \alpha_G Q_G)/I_t Q_R = \\ -X_R/\ln(1 - Y_t) \quad (20)$$

Since there may be doubt about the values of Q_G and Q_R to be used, it would seem preferable to use eq. 20. This expression indicates that a plot of $-X_R/\ln(1 - Y_t)$ *vs.* X_R should be a straight line. The intercept at $X_R = 0$ is $\alpha_G Q_G/I_t Q_R$ as indicated by eq. 14 since as $X_R \to 0$, $\ln(1 - Y_t) \to -Y_t$; the intercept at $X_R = 1.0$ is α_R/I_t as indicated by eq. 16. The ratio of the intercept at $X_R = 1.0$ to that at $X_R = 0$ is $\alpha_R Q_R/\alpha_G Q_G$. For reaction systems where Y_t is >0.10 for $X_R = 1.0$, eq. 20 may not be a good approximation over the full range of X_R. However, it should be possible to use only those data for low Y_t for which a plot of $-X_R/\ln(1 - Y_t)$ *vs.* X_R is linear. From this plot the slope and the intercept at $X_R = 0$ can be determined. According to eq. 20 the ratio of the slope of the intercept is $(\alpha_R Q_R/\alpha_G Q_G) - 1$.

For binary mixtures, A and B, with very small Y_t of both substances, Fig. 7 again suggests that eq. 15 may serve as a good approximation. According to eq. 16, for pure A, $-\ln(1 - Y_{At}°) = I_A/\alpha_A$, where $Y_{At}°$ is the total hot atom yield of A in pure A; a similar expression applies to B. Equation 15 may be rearranged[28] as

$$\frac{\alpha_A}{\alpha_B} = -\frac{f_B}{f_A}\left[\frac{(I_B/\alpha_B) + \ln(1 - Y_t)}{(I_A/\alpha_A) + \ln(1 - Y_t)}\right] \quad (21)$$

with $Y_t = Y_{At} + Y_{Bt}$.

Using I_A/α_A and I_B/α_B as given by eq 16 and $f_B/f_A = X_B Q_B/X_A Q_A$ as given by eq. 1, there results

$$\alpha_A Q_A/\alpha_B Q_B = (X_B/X_A)\ln[(1 - Y_{Bt}°)/ \\ (1 - Y_t)]/\ln[(1 - Y_t)/(1 - Y_{At}°)] \quad (22)$$

Data for Y_t as a function of X_A, when substituted in eq. 22, should result in identical values of α_A/α_B if Y_t is low.[29]

Summary

From plots of specific activities *vs.* mole fractions for inert gas-moderated reactions it may be possible to obtain some information from the ratio of intercepts for data extrapolated to zero mole fraction of the reactive molecule. The lack of knowledge concerning differential and total scattering cross sections in the energy range 1–30 e.v. precludes obtaining quantitative information about absolute values of I. The Wigner equations can serve as a reasonable approximation for systems of very low total reactivity for which assumptions 1 and 2 apply.

Appendix I

Collision Cross Sections.—The collision cross section for an encounter between nonrigid atomic or molecular particles is usually a function of energy and depends on the interacting potential field. The general feature of such interacting potentials is that they indicate both attractive and repulsive effects. For those interactions where the relative kinetic energy is much less than the depth of the potential well, the dominating factor in the energy dependence of the collision cross section should be the attractive part of the potential. Conversely, for collisions where the relative kinetic energy is greater than the depth of the potential well the repulsive part of the potential should dominate. Nonreactive hot atom collisions involve energies which probably are greater than the depths of the wells.

For a purely repulsive field of the form A/r^n, where A and n are constants and r is the distance between the interacting particles, it has been shown[32] that the impact parameter, p, is related to the kinetic energy of the oncoming particle, E_0, and the scattering angle θ, by the expression

$$p(E_0,\theta) = E_0^{-1/n} f(\theta) \qquad (23)$$

Since the differential cross section, $\sigma(E_0,\theta)$, is defined as

$$\sigma(E_0,\theta) = [p(E_0,\theta)/\sin\theta] \,|\partial p(E_0,\theta)/\partial\theta| \qquad (24)$$

there results

$$\sigma(E_0,\theta) = [E_0^{-2/n} f(\theta)/\sin\theta](df(\theta)/d\theta) \qquad (25)$$

(29) If Y_t is large but r_A, r_B, $P_{At}(E)$, and $P_{Bt}(E)$ all approach zero, (assumptions 5 and 6) then eq. 22 should also be valid. The only tritium hot atom data available for a binary mixture are those for the $D_2 + CH_4$ mixture.[30] The values of $(\alpha Q)_{CH_4}/(\alpha Q)_{D_2}$ calculated using eq. 22 are very sensitive to the choice of $Y_{D_2t}^\circ$ and the manner in which correction is made for the HT formed by the reaction of T with HD impurity.[30] The $(\alpha Q)_{CH_4}/(\alpha Q)_{D_2}$ values we have calculated vary between about 0.8 and 5.0. Even if the data resulted in a consistent set of $\alpha_{CH_4}/\alpha_{D_2}$ values, we would hesitate to accept the value since it is possible such agreement could be fortuitous.

Recently, Wolfgang[31] used assumptions 1 and 2 + 5 to 7 to derive an expression which he used in conjunction with the data of Root and Rowland[18,30] to calculate $\alpha_{CH_4}/\alpha_{D_2} = 2.1 \pm 0.2$. Since it does not appear possible to use assumptions 1 and 2 + 5 and 6 to calculate unambiguously this α ratio, we are reluctant to accept a value based on expressions involving an additional assumption. However, the straight-line plots presented[31] appear to support the derivation. We have attempted to understand these plots by synthesizing data based on assumptions 1 to 3 and expressions similar to those given in the supplement. When plotted according to the method prescribed,[31] these data also described straight lines but yielded α_A/α_B ratios which frequently differed by up to a factor of two from the α_A/α_B ratios used in synthesizing the data.

(30) J. W. Root and F. S. Rowland, *J. Chem. Phys.*, **38**, 2030 (1963).

(31) R. Wolfgang, *ibid.*, **39**, 2983 (1963).

(32) L. D. Landau and E. M. Lifshitz, "Mechanics," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960, p. 51.

The total viscosity cross section becomes

$$Q(E_0) = 2\pi \int_0^\pi \sigma(E_0,\theta) \sin^3\theta \; d\theta \qquad (26a)$$

$$= \pi E_0^{-2/n} \int_0^\pi f(\theta) \sin^2\theta \; df(\theta) \qquad (26b)$$

or

$$Q(E_0) = C E_0^{-2/n} \qquad (27)$$

where C is a constant which characterizes the interaction potential of the pair.

The ratio of the viscosity cross sections of two interacting pairs, A–B and A–C, is then

$$Q_{AB}(E_0)/Q_{AC}(E_0) = \\ (C_{AB}/C_{AC})(E_0)^{-2[(1/n_{AB}) - (1/n_{AC})]} \qquad (28)$$

If the repulsive field is that given by the Lennard-Jones potential, then $n = 12$ and C_{AB} will be related to the Lennard-Jones radii of A and B, and C_{AC} to those of A and C.

Given in Table I are cross-section ratios calculated using various data.

TABLE I

CALCULATED CROSS-SECTION RATIOS

Source	$\left(\dfrac{Q_{H-CH_4}}{Q_{H-He}}\right)$	$\left(\dfrac{Q_{H-H_2}}{Q_{H-He}}\right)$	$\left(\dfrac{r_{m,H-H_2}}{r_{m,H-He}}\right)^2$
Rigid sphere[a]	2.0	1.2	..
Lennard-Jones[b]	1.56	1.1	..
Experimental			
0.3 e.v.	..	1.1[c]	..
1.0 e.v.	..	..	1.04 ⎫
2.0 e.v.	..	..	0.86 ⎪
3.0 e.v.	..	..	0.71 ⎬[d]
4.0 e.v.	..	..	0.57 ⎪
5.0 e.v.	..	..	0.44 ⎭

[a] The radii used were: H, 1.2; He, 1.1; H_2, 1.4; CH_4, 2.1 Å.; H radius from R. A. Buckingham and J. W. Fox, *Proc. Roy. Soc.* (London), **A267**, 102 (1962), others from S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge, 1939, p. 299. The values given are viscosity cross-section ratios. [b] From ref. 8, p. 1110; the values given are viscosity cross-section ratios. [c] H. Harrison, *J. Chem. Phys.*, **37**, 1164 (1962); the value is the total cross-section ratio. [d] H–He and H–H_2 potentials from: "Atomic and Molecular Processes," D. R. Bates, Ed. Academic Press, Inc., New York, N. Y., 1962, pp. 688, 689. The value is the ratio of the square of the distances at the classical turning point; refer to text.

Appendix II

Relationship between the Differential Cross Section and the Scattering Function.—The scattering function, $k(E,E')dE$, is a statement of the probability that in a collision the energy of the hot atom changes from E' to an energy between E and $E + dE$. By momentum and energy balances the ratio of energy is[33]

$$E/E' = (1 + r)/2 + [(1 - r)\cos\theta]/2 \qquad (29)$$

where θ is the scattering angle in the center of mass system. Thus, $\theta \to 0°$ implies glancing collisions and $\theta = 180°$ is a head-on collision. It is seen that the energy E is directly related to the scattering angle θ thus permitting a direct change from the variable E to the variable θ.

The probability that, in a collision, the angle of deflection of the hot atoms will lie between $\Omega + d\Omega$ is

(33) I. Kaplan, "Nuclear Physics," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1955, p. 453.

$\sigma(E',\theta)d\Omega$, the differential cross section. The differential solid angle is $d\Omega = 2\pi \sin\theta\, d\theta$. Therefore

$$\sigma(E',\theta) = [k(E,E')/2\pi \sin\theta]Q(E')\, dE/d\theta \quad (30)$$

Solving eq. 29 for $dE/d\theta$ and combining with eq. 30, there results

$$\sigma(E',\theta) = E'(1 - r)k[E(\theta),E']Q(E')/4\pi \quad (31)$$

Substituting eq. 8 for $k[E(\theta),E']$ in eq. 31 and using eq. 29, then, for the scattering function given by eq. 8

$$\sigma(E',\theta) = [1 + b(1 - r)^2 \cos\theta]Q(E')/4\pi = \sigma(\theta) \quad (32)$$

Appendix III

Solution for Isotropic Scattering and $P(E)$ a Constant.—If assumption 1 applies, if assumption 2, eq. 3, applies at energies above E_1, and $k_i(E,E_0) = 0$ since $r_iE_0 > E_1$, then, for a one-component reactive system, $f_i = 1.0$, $\sum_j P_{ij}(E) = P_{it}$, a constant, the Boltzmann equation[22,34] becomes

$$F(E) = \int_E^{E/r} k(E,E')(1 - P_t)F(E')\, dE' \quad (33)$$

This equation is discontinuous and must be evaluated in segments. The segments are separated at energies related to the minimum number of collisions, n, required to traverse the reactive energy range E_1 to E_2. These energies are E_1, rE_1, r^2E_1, . . ., $r^nE_1 \leqslant E_2$. The integral is separated into two parts. As a result, for $r^{n-1}E_1 > E > r^nE_1$

$$F_n(E) = \int_{r^{n-1}E_1}^{E/r} k(E,E')(1 - P_t)F_{n-1}(E')dE' + \int_E^{r^{n-1}E_1} k(E,E')(1 - P_t)F_n(E')dE' \quad (34)$$

If $n = 1$, then $E_1 > E > E_2 \geqslant rE_1$. In the first integral of eq. 34, $P_t = 0$ and $F_0(E') = 1/\alpha E'$. If isotropic scattering exists, assumption 3, then $k(E,E')$ is $1/(1 - r)E'$, and eq. 34 and its derivative are

$$F_1(E) = \frac{1}{\alpha(1 - r)} \int_{E_1}^{E/r} \frac{dE'}{(E')^2} + \frac{1 - P_t}{1 - r} \int_E^{E_1} \frac{F_1(E')dE'}{E'} \quad (35)$$

$$\frac{dF_1(E)}{dE} = \frac{r}{\alpha(1 - r)E^2} - \left(\frac{1 - P_t}{1 - r}\right)\frac{F_1(E)}{E} \quad (36)$$

Equation 36 is a first-order differential equation; its solution is

(34) G. Placzek, *Phys. Rev.*, **69**, 423 (1946).

$$F_1(E)E^{(1 - P_t)/(1 - r)} \bigg|_E^{E_{1t}} = \frac{r}{\alpha(1 - r)} \int_E^{E_{1t}} E'^{\frac{1 - P_t}{1 - r} - 2}\, dE' \quad (37)$$

Since $F_1(E)$ at E_{1t} is equal to $1/\alpha E_{1t}$

$$\frac{1}{\alpha E_{1t}} E_{1t}^{(1 - P_t)/(1 - r)} - F_1(E)E^{(1 - P_t)/(1 - r)} = \frac{r}{\alpha(r - P_t)}\left[E_{1t}^{\left(\frac{r - P_t}{1 - r}\right)} - E^{\left(\frac{r - P_t}{1 - r}\right)}\right] \quad (38a)$$

$$F_1(E) = \frac{1}{\alpha E}\left[\frac{r}{r - P_t} - \frac{P_t}{r - P_t}\left(\frac{E_{1t}}{E}\right)^{\frac{r - P_t}{1 - r}}\right] \quad (38b)$$

The yield, $Y_{1j} = P_j \int_{E_{2i}}^{E_{1i}} F_1(E)\, dE$, is

$$Y_{1j} = \frac{P_j}{\alpha(r - P_t)}\left\{r \ln\left(\frac{E_1}{E_2}\right)_i + \frac{P_t(1 - r)}{(r - P_t)}\left[\left(\frac{E_{1t}}{E_{1j}}\right)^{\frac{r - P_t}{1 - r}} - \left(\frac{E_{1t}}{E_{2j}}\right)^{\frac{r - P_t}{1 - r}}\right]\right\} \quad (39)$$

The total yield, Y_{1t}, can be obtained by substituting t for the subscript j in eq. 39. If, in addition, $P_t = 1.0$, eq. 17 is the result.

If $E_{2j} = rE_{it}$, then

$$Y_{1j} = \frac{P_j}{\alpha(r - P_t)}\left\{r \ln\frac{E_{1j}}{rE_{1t}} + \frac{P_t(1 - r)}{(r - P_t)}\left[\left(\frac{E_{1t}}{E_{1j}}\right)^{\frac{r - P_t}{1 - r}} - \left(\frac{1}{r}\right)^{\frac{r - P_t}{1 - r}}\right]\right\} \quad (40)$$

If $E_{2t} = rE_{1t}$, then by substituting t for subscript j in eq. 36 there results Y_{1t}. Additional solutions for $n = 2$, 3, and 4 are given in the supplement.[28] These expressions all are based on assumptions 1 to 3 for $P(E) = $ constant, the assumptions used by Rowland in calculating Y-values using a computer approach.[35] Also contained in the supplement are expressions, based on these assumptions, for inert gas moderated mixtures, and two-component reactive mixtures.

It can be shown[14,22] that, as $I \rightarrow 0$, $Y_t \rightarrow I/\alpha$ for any shape of $P(E)$, any shape of $k(E,E')$, and any value of α. However, according to the Wigner equation, $Y_t \rightarrow I/\alpha$ only if $I/\alpha \rightarrow 0$. Thus the curve for $I = 0$, Fig. 7, was calculated as $- [\ln(1 - Y)]/Y$.

(35) F. S. Rowland, private communication.