

Phase-space theory of electron detachment in slow atomic collisions*

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A classical phase-space theory for the excitation of electrons in slow atomic collisions is presented. An equation which governs the energy transfer between the electron and the heavy particles is derived for slow collisions (adiabatic approximation). This equation is analogous to the first law of thermodynamics for an open system. The theory contains only one adjustable parameter and gives excellent correlation for existing experimental measurements of detachment rate coefficients of $F^- + (Ar, N_2, CO)$ and $Br^- + Ar$. Possible modifications to the present theory are summarized. It is anticipated that the theory should be applicable to other electronic rate processes such as ionization and charge transfer.

I. INTRODUCTION

The process of electron detachment from negative ions in heavy particle collisions is of fundamental importance in the theory of atomic collisions. It also has numerous practical applications to problems in atmospheric physics, plasma physics, and hypersonic aerodynamics.

Research on this problem has been growing ever since the appearance, in 1950, of the second edition of the book *Negative Ions* by Massey.¹ The advances made between 1950 and 1956 have been reviewed by Branscomb,² and experimental results prior to 1964 have been summarized by Hasted.³ In addition, Massey and Burhop have devoted considerable attention to this topic in their books.⁴

The interest of the present paper is primarily in the thermal detachment process described by the reaction



where X^- is an atomic negative ion, M is a relatively inert heavy collision partner, and k_d is the detachment rate coefficient defined by

$$d[X^-]/dt = -k_d[X^-][M], \quad (1.2)$$

where t is the time and quantities in brackets represent concentrations. Under steady state conditions the inverse three-body attachment coefficient k_r , defined by

$$d[X^-]/dt = k_r[X][e][M], \quad (1.3)$$

is related to k_d by the detailed balancing condition

$$k_d/k_r = [X]_e[e]_e/[X^-]_e, \quad (1.4)$$

where the subscript e denotes equilibrium.

Measurements of detachment cross sections for reactions of this type have been reported⁵ for a large number of combinations of X^- and M . Typical ones include H^- , C^- , O^- , and halogen ions in collision with inert gases. These measurements were generally made at relative kinetic energies of col-

lision above about 10 eV, and practically nothing is known about the behavior of these cross sections near the threshold, which generally lies⁵ between a few tenths of an electron volt and nearly 4 eV. Recently, measurements of detachment rate coefficients for $Br^- + Ar$ and $F^- + (Ar, N_2, CO)$ have been reported by Ewing, Milstein, and Berry,⁶ Mandl, Kivel, and Evans,⁷ and Mandl,^{8,9} over the temperature range 3000–6000°K. No satisfactory theoretical description of such processes has been reported so far, however.

This paper presents a model for the $X^- + M$ collision process which permits one to calculate detachment rate coefficients in a relatively simple manner. The model is based on a classical phase-space theory described in Sec. III, following some general considerations which are presented in Sec. II. Section IV will contain the mathematical developments which lead to expressions for the electron detachment cross sections and rate coefficients. Numerical results for selected systems will be summarized and compared with experimental measurements in Sec. V. Finally, Sec. VI will contain our concluding remarks.

II. GENERAL CONSIDERATIONS

A. The Adiabatic Criterion

The theory of low-energy collisions between ions and neutral atoms is particularly difficult because the approximations which are valid at high energies (e.g., the impulse approximation) no longer apply when the interaction time is longer than or of the same order as the time characteristic of the electronic motion in the colliding systems. On the other hand, the general dependence of the inelastic collision cross section on relative collision energy for a large number of collision processes may be interpreted in terms of the extent to which the process approximates to the adiabatic condition,¹⁰ which applies when the colliding particles are approaching so slowly that the state of internal motion is able to adjust itself to the perturbation

without a transition taking place, even though the incident particle had sufficient energy to cause a transition. In this region the cross section will be small. The conditions may be taken as nearly adiabatic when

$$a\Delta E/hv > 1, \quad (2.1)$$

where a is a length of the order of the atomic dimensions involved, ΔE is the energy of transition, h is the Planck's constant, and v is the relative velocity. It is thus expected¹¹ that the inelastic cross section rises in the near adiabatic region until it reaches a maximum, after which it falls slowly. Data compiled by Hasted¹² showed that this simple "adiabatic criterion" was valid for many situations. For collisional detachment, however, it is now well known that cross sections remain large down to energies much less than 100 eV, in violation of the adiabatic criterion. [The adiabaticity factor, Eq. (2.1), is on the order of 20 for most collisional detachment reactions at thermal energies.]

A new criterion or model is therefore needed in order to explain and/or predict the threshold behavior and thereby to estimate the detachment rate coefficients at thermal energies.

B. Classical Monte Carlo Trajectory Calculations

Renewed interest in classical theories of atomic excitation was aroused by Gryzinski¹³ in 1959. Later developments have been reviewed by Burgess and Percival,¹⁴ Vriens,¹⁵ and Flannery.¹⁶ Of particular interest here are the works of Abrines, Percival, and Valentine,¹⁷ and Mansbach and Keck,¹⁸ who used Monte Carlo trajectory calculations to calculate rates of atomic excitation and ionization by electrons. At the same time, the present authors have demonstrated that these methods can be used successfully to calculate three-body recombination and dissociation rate coefficients of diatomic molecules.^{19,20} An attempt was, therefore, made to apply these methods to the calculation of detachment rate coefficients, k_d of Eq. (1.1).

The colliding system was considered to consist of three particles: an atom X with a loosely bound electron e , forming the negative ion X^- , and a collision partner (third body) M. Although it was anticipated that due to the very small mass of the electrons, the detachment process would be highly "adiabatic" in the sense that the electron would make many orbits about X during a single collision between M and X, the extremely large number of such orbits which might occur was not fully appreciated and, in fact, it was not considered practical with our existing computer facilities to complete even a single collision. A valuable lesson

was learned, however, since it became clear that with so many orbits involved the exact specification of the electron motion was unnecessary for the determination of the momentum transfer to the heavy particles provided the electron was more or less uniformly distributed over the available phase space. The numerical approach was therefore abandoned in favor of the phase-space theory described in the following section.

III. PHASE-SPACE THEORY OF ELECTRONIC EXCITATION

Consider a collision between a pair of heavy particles X and M interacting with an orbiting electron e . The Hamiltonian corresponding to the energy in the center of mass of such a system can be written as

$$H_T(\mathbf{p}_{XM}, \mathbf{r}_{XM}, \mathbf{p}_e, \mathbf{r}_e) = H_{XM}(\mathbf{p}_{XM}, \mathbf{r}_{XM}) + H_e(\mathbf{p}_e, \mathbf{r}_e, \mathbf{r}_{XM}), \quad (3.1)$$

where

$$H_{XM} = \mathbf{p}_{XM}^2/2\mu_{XM} + V_{XM}(\mathbf{r}_{XM}) \quad (3.2)$$

is the Hamiltonian for the bare particles,

$$H_e = \mathbf{p}_e^2/2\mu_e + V_e(\mathbf{r}_e, \mathbf{r}_{XM}) \quad (3.3)$$

is the Hamiltonian for the electron,

$$V_e = V(\mathbf{r}_e, \mathbf{r}_{XM}) - V_{XM}(\mathbf{r}_{XM}) \quad (3.4)$$

is the interactional potential for the electron,

$$\mu_{XM} = m_X m_M / (m_X + m_M) \quad (3.5)$$

is the reduced mass of X and M,

$$\mu_e = m_e (m_X + m_M) / (m_e + m_X + m_M) \quad (3.6)$$

is the reduced mass of e and XM, \mathbf{r}_{XM} is the position of M relative to X, \mathbf{r}_e is the position of the electron relative to the center of mass of XM, and \mathbf{p}_{XM} and \mathbf{p}_e are the momenta conjugate to \mathbf{r}_{XM} and \mathbf{r}_e , respectively.

We now assume that the state of the heavy particles at any time t during the course of the collision is determined by the values of $\mathbf{p}_{XM}(t)$ and $\mathbf{r}_{XM}(t)$ while the state of the orbiting electron is determined by a distribution function in phase space $\rho_e(\mathbf{p}_e, \mathbf{r}_e, t)$. Then the probability of finding the electron inside a given volume $\Omega_e(\mathbf{r}_{XM})$ in phase space is

$$n_e(t) = \int_{\Omega_e} \rho_e d\Omega_e \quad (3.7)$$

and the corresponding electron energy is

$$U_e(t) = \int_{\Omega_e} \rho_e H_e d\Omega_e. \quad (3.8)$$

Differentiating (3.7) and (3.8) with respect to time we obtain

$$\dot{n}_e = \int_{\Omega_e} (\partial \rho_e / \partial t) d\Omega_e + \int_S \rho_e \mathbf{v}_e \cdot \mathbf{n}_s dS_e \quad (3.9)$$

and

$$\dot{U}_e = \int_{\Omega_e} (\partial \rho_e H_e / \partial t) d\Omega_e + \int_{S_e} \rho_e H_e \mathbf{v}_s \cdot \mathbf{n}_s dS_e, \quad (3.10)$$

where dS_e is an element of the surface S_e bounding Ω_e , \mathbf{n}_s in the unit outward normal to dS_e , and \mathbf{v}_s is the generalized velocity of dS_e . Introducing the continuity equation

$$\partial \rho_e / \partial t + \nabla_e \cdot \rho_e \mathbf{v}_e = 0 \quad (3.11)$$

into (3.9) and (3.10) and using Gauss' theorem to transform volume integrals into surface integrals we find

$$\dot{n}_e = - \int_{S_e} \rho_e (\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s dS_e \quad (3.12)$$

and

$$\dot{U}_e = \int_{\Omega_e} \rho_e (\partial H_e / \partial t) d\Omega_e - \int_{S_e} \rho_e H_e (\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s dS_e, \quad (3.13)$$

where \mathbf{v}_e is the generalized velocity of the electron in phase space and ∇_e is the generalized divergence. Equation (3.12) simply states that the rate of change of the probability n_e of finding the electron in Ω_e is just the negative of the probability flux across the boundary S_e . Equation (3.13) states that changes in the mean energy of the electron may occur either as a result of the explicit time dependence of the electron Hamiltonian within Ω_e or as a result of interactions on the boundary of Ω_e . In the absence of radiation interactions, which we have not considered, the term in (3.13) involving $\partial H_e / \partial t$ represents the work done by body forces acting on the electron. The term involving $(\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s$ is more complicated, however, and may represent changes in energy due to (1) the flux of electrons across S_e , (2) work interactions associated with a boundary displacement, or (3) heat interaction for which the boundary displacement is zero. Thus Eq. (3.13) is equivalent to the first law of thermodynamics for an open system in phase space.

An important special case of Eq. (3.13) with which we shall be concerned later is that in which $\partial H_e / \partial t = 0$ and the electrons are elastically reflected from a moving boundary in configuration space. Under these conditions the velocity \mathbf{v}'_e of the reflected particles will be related to the velocity \mathbf{v}_e of the incident particles by

$$\mathbf{v}'_e = -\mathbf{v}_e + 2\mathbf{n}_s (\mathbf{v}_e \cdot \mathbf{n}_s) \quad (3.14)$$

and the corresponding change in electron energy will be

$$H'_e - H_e = -2m_e (\mathbf{v}_s \cdot \mathbf{n}_s) (\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s. \quad (3.15)$$

Substituting (3.15) into (3.13) we obtain

$$\dot{U}_e = -2m_e \int_{S_e^*} \rho_e [(\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s]^2 \mathbf{v}_s \cdot \mathbf{n}_s dS_e, \quad (3.16)$$

where S_e^* is that part of S_e on which $(\mathbf{v}_e - \mathbf{v}_s) \cdot \mathbf{n}_s \geq 0$.

Note that the right side of Eq. (3.16) is just the work per unit time done by the pressure of the electron on the moving surface.

In general the evaluation of $\rho_e(\mathbf{p}_e, \mathbf{r}_e, t)$ for any given initial condition will involve the solution of the time dependent Liouville equation

$$\partial \rho_e / \partial t + \mathbf{v}_e \cdot \nabla \rho_e = 0 \quad (3.17)$$

for the electron in conjunction with the equations of motion for the heavy particles. However, if the characteristic period of the electron orbits about XM is very much smaller than the duration of the collisions between X and M, then it will be a reasonable approximation to assume that if the electron is initially uniformly distributed on the energy shell, it will remain so throughout the collision. This is equivalent to the assumption that the electron is always in the state of maximum entropy allowed by the volume (Ω_e) and energy (U_e) constraints, i. e., the equilibrium state. Under these conditions we have

$$\rho_e(\mathbf{p}_e, \mathbf{r}_e, t) = \rho_e(H_e, \mathbf{r}_{\text{XM}}) = Q_e^{-1} \delta(H_e - U_e), \quad (3.18)$$

where

$$Q_e(U_e, \mathbf{r}_{\text{XM}}) = \int_{\Omega_e} \delta(H_e - U_e) d\mathbf{p}_e d\mathbf{r}_e \quad (3.19)$$

is the partition function for the electron and $\delta(x)$ is the Dirac δ function of x so normalized that

$$\int_{-\infty}^{\infty} \delta(x) dx = 1. \quad (3.20)$$

Using the distribution function (3.18) we may evaluate Eqs. (3.12) and (3.13) to obtain \dot{n}_e and \dot{U}_e as functions of U_e and \mathbf{r}_{XM} .

The equation of motion for the heavy particles X and M may now be obtained by multiplying Eq. (3.1) by ρ_e and integrating over $d\Omega_e$. This gives

$$H_T = H_{\text{XM}} + U_e \quad (3.21)$$

and from Hamilton's equations we find

$$\begin{aligned} \dot{\mathbf{p}}_{\text{XM}} &= -\partial H_T / \partial \mathbf{r}_{\text{XM}} = -dV_{\text{XM}} / d\mathbf{r}_{\text{XM}} - \dot{U}_e / \dot{\mathbf{r}}_{\text{XM}}, \\ \dot{l}_{\text{XM}} &= -\partial H_T / \partial \omega_{\text{XM}} = 0, \end{aligned} \quad (3.22)$$

and

$$\dot{m}_{\text{XM}} = -\partial H_T / \partial \phi_{\text{XM}} = 0,$$

where l_{XM} is the angular momentum of XM, m_{XM} is the z component of l_{XM} , and ω_{XM} and ϕ_{XM} are the Euler angles conjugate to l_{XM} and m_{XM} , respectively. Given the interaction potential $V_e(\mathbf{r}_e, \mathbf{r}_{\text{XM}})$ for the electron, Eqs. (3.22) may easily be integrated to obtain the trajectories of the heavy particles and the energy of the electron as a function of time. Note that the theory described in this section can be used to describe either charge transfer or detachment. A detailed treatment of the latter process will be presented in the following sections.

IV. APPLICATION TO ELECTRON DETACHMENT COLLISIONS

A. Forces of Interaction

The motion of the three particles X, e , and M is governed by the appropriate full three-body interaction potential. In general, however, we do not have sufficiently accurate potentials for the systems under investigation. We must, therefore, resort to simpler representations of the forces of interaction, at the same time, of course, preserving important features of the actual forces.

We shall first carry out analysis and calculations based on a very simple set of interaction potentials. Effects of modifying the potentials will then be considered, based on the characteristics of the results and comparisons with experiment. On the other hand, when the present model is sufficiently well developed and more experimental data become available, it is hoped that something about the interaction potentials may be deduced from comparisons between theory and experiment.

The full three-body interaction potential is assumed to be given by the superposition of three pairwise potentials, i. e. ,

$$V = V_{eX}(r_{eX}) + V_{eM}(r_{eM}) + V_{XM}(r_{XM}), \quad (4.1)$$

where V_{eX} , V_{eM} , and V_{XM} are the effective pairwise potentials for e -X, e -M, and X-M, respectively.

For V_{eX} , we can use the Hartree-Fock-Slater potentials which have been computed and tabulated by Herman and Skillman.²¹ However, for the present purpose, it is sufficiently accurate to use the approximation

$$V_{eX}(r) \approx -\alpha r^{-4}, \quad (4.2)$$

where α is a parameter which can be obtained by

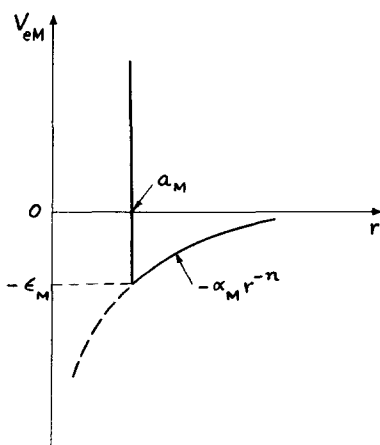


FIG. 1. Potential-energy diagram for the interaction between the electron and the third body, showing a hard core of radius a_M .

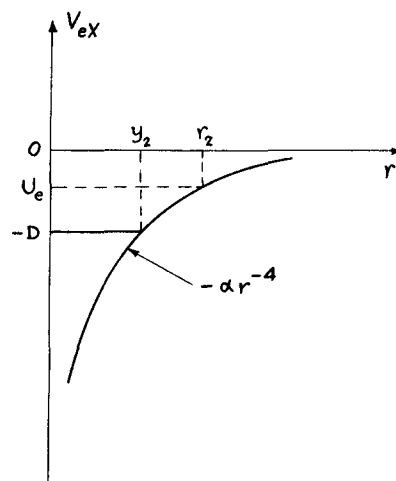


FIG. 2. Potential-energy diagram for X^- . D is the electron affinity of X.

fitting V_{eX} to the tabulated values in an appropriate range of r . It turns out that α is approximately given by the static dipole polarizability of the atom X (in appropriate units).

The potential $V_{XM}(r)$ is predominantly repulsive and is generally represented by expressions such as

$$A \exp(-r/L) \text{ or } Br^{-n}, \quad (4.3)$$

where A , L , B , and n are parameters.

The potential V_{eM} is approximated by

$$V_{eM}(r) = \infty \quad r < a_M \\ = -\alpha_M r^{-n} \quad r \geq a_M, \quad (4.4)$$

which consists of a repulsive core (radius a_M) and an attractive tail (Fig. 1). At large separations, the tail is characterized by the polarization potential (αr^{-4}), the ion-quadrupole potential (αr^{-3}), or the ion-dipole potential (αr^{-2}), corresponding to M being monatomic, homonuclear diatomic, or heteronuclear diatomic, respectively.

B. Mathematical Development

It is now well known that most atomic negative ions have only one stable state—the ground state. Figure 2 shows the potential-energy curve for X^- , where the ground state is indicated as having an energy $U_e = -D$. The energy required to detach an electron from X^- is thus equal to D , the electron affinity of the atom X.

The geometry of the collision complex is sketched in Fig. 3, where a sphere of radius a_M , which represents the core of the third body M, is shown to overlap the electron cloud, which is confined by the potential V_{eX} to within a spherical volume of radius r_2 (the classical turning point, see Fig. 2).

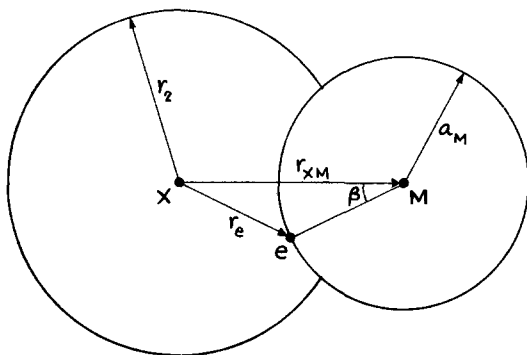


FIG. 3. Geometry of the collision complex $X + e + M$. A sphere of radius a_M , which represents the core of M , is shown to overlap the electron cloud, which is confined by the potential V_{eX} to within a spherical volume of radius r_2 (the classical turning point, see Fig. 2). The angle between \overline{XM} and \overline{eM} is denoted by β .

Under conditions such that the adiabatic approximation is valid we have $v_s \ll v_e$, and Eq. (3.16) becomes

$$\dot{U}_e = -2m_e \int \rho_e (\mathbf{v}_s \cdot \mathbf{n}_s) d\mathbf{p}_e dA, \quad \mathbf{v}_e \cdot \mathbf{n}_s > 0, \quad (4.5)$$

where \mathbf{p}_e is the momentum of the electron and A is now a surface in configuration space. Substituting Eq. (3.18) into Eq. (4.5), integrations over $d\mathbf{p}_e$ can be carried out exactly to yield

$$\dot{U}_e = -(4\pi/3) \int (\mathbf{v}_s \cdot \mathbf{n}_s) Q_e^{-1} [2m_e (U_e - V_e)]^{3/2} dA. \quad (4.6)$$

The surface A is taken as the surface of the hard sphere representing the core of the collision partner M . The effect of the weakly attractive tail of V_{eM} (see Fig. 1) is neglected in the present calculations. Thus the surface A is defined by the equation

$$r_{XM}^2 + a_M^2 - 2r_{XM}a_M \cos\beta - r_e^2 = 0, \quad (4.7)$$

where β is the angle between \overline{XM} and \overline{eM} . Equation (4.6) can then be written as

$$-dU_e/dr_{XM} = (8\pi^2 a_M^2 / 3Q_e) \int [2m_e (U_e - V_e)]^{3/2} \times \cos\beta d(\cos\beta). \quad (4.8)$$

Changing the variable to u , such that $u \equiv r_e^2 (-U_e/\alpha)^{1/2}$, and approximating V_e by $V_e = -\alpha r_e^{-4}$, Eq. (4.8) can be transformed to

$$-dU_e/dr_{XM} = (4\pi^2 a_M / 3r_{XM} Q_e) (-U_e) \alpha^{1/2} \times (2m_e)^{3/2} \int_w^1 u^{-3} (1-u^2)^{3/2} \cos\beta du, \quad (4.9)$$

where $w = (r_{XM} - a_M)^2 (-U_e/\alpha)^{1/2}$. For $w \ll 1$, u^{-3} has a strong maximum at $u = w$, corresponding to $\cos\beta = 1$, and the integral can be evaluated approximately as

$$\int_w^1 u^{-3} (1-u^2)^{3/2} \cos\beta du \approx 1/(2w^2), \quad w \ll 1. \quad (4.10)$$

Substitution of (4.10) into (4.9) yields

$$-dU_e/dr_{XM} = 2\pi^2 a_M (2m_e \alpha)^{3/2} / 3Q_e r_{XM} (r_{XM} - a_M)^4. \quad (4.11)$$

The partition function Q_e , Eq. (3.19) cannot be evaluated exactly in closed form since the accessible phase-space volume Ω_e depends on the instantaneous position of the surface S_e . For systems under consideration, however, the reduction in the accessible phase-space volume due to the presence of S_e is generally insignificant compared with the total volume allowed by the energy of the system. Thus Eq. (3.19) is integrated as if S_e were removed, giving the result

$$Q_e = 8\pi^2 (2m_e)^{3/2} \alpha^{3/4} (-U_e)^{-1/4} C_Q, \quad (4.12)$$

where

$$C_Q = \int_0^1 (1-x^4)^{1/2} dx = 0.876 \quad (4.13)$$

is a definite integral.

Combining Eqs. (4.11), (4.12), and (4.13) we obtain a simple differential equation for U_e and r_{XM} :

$$-dU_e/dr_{XM} = a_M \alpha^{3/4} (-U_e)^{1/4} / 12C_Q r_{XM} (r_{XM} - a_M)^4, \quad (4.14)$$

which can be integrated to yield the internal energy U_e of the negative ion as a function of r_1 , the minimum distance between X and the surface of M ($r_1 = r_{XM} - a_M$). The result, valid for $(r_{XM} - a_M) \lesssim a_M$, is

$$\left(\frac{-U_e}{D} \right)^{3/4} = \frac{48C_Q + 1 - (y_2/r_1)^3}{(48C_Q)}, \quad (4.15)$$

where $y_2 = (\alpha/D)^{1/4}$ is the radius of the classical turning point of the ground-state negative ion (see Fig. 2).

The condition for detachment to occur is $U_e = 0$, corresponding to $r_1 = y_1$, which is given by

$$y_1/y_2 \cong (43)^{-1/3} \approx 0.28. \quad (4.16)$$

This assumes that when $U_e = 0$ the electron becomes detached and moves away from the reaction zone, i. e., the probability of reattachment is assumed to be zero, and further interactions between the heavy particles are considered to be inconsequential to the detachment of the electron.

The dimensionless electron energy U_e/D is plotted in Fig. 4 (solid curve) as a function of r_1/y_2 [Eq. (4.15)]. It shows that the internal energy of the negative ion increases slowly at the beginning of the collision but rises sharply when r_1/y_2 decreases further and approaches y_1/y_2 . The slope

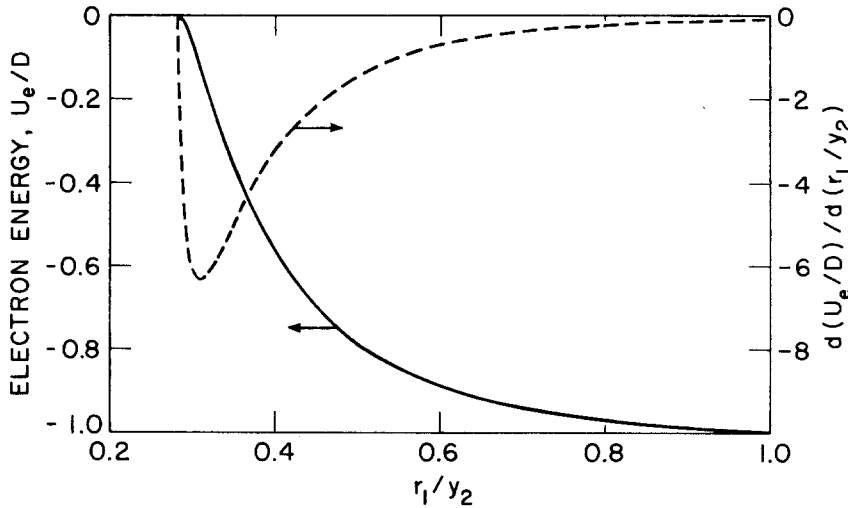


FIG. 4. Dependence of electron energy on internuclear distance. Solid curve: dimensionless electron energy (U_e/D) vs dimensionless distance (r_1/y_2). Broken curve: slope of the solid curve vs r_1/y_2 , which is a measure of the electron pressure. (See text, Sec. IV. B.)

of this curve, i. e., the quantity $d(U_e/D)/[d(r_1/y_2)^{-1}]$, is a measure of the pressure exerted by the electron on the third body, and thus should have two zeros. The first zero, at $r_1/y_2=1$, corresponds to the beginning of the collision ($r_{XM}=y_2+a_M$) when there is no overlap between the electron and M, i. e., the electron pressure on M is still zero. The second zero, at $r_1/y_2=y_1/y_2$ and $U_e=0$, exists because we have allowed the partition function to grow without limit when U_e approaches zero. In actual cases, of course, the phase space available to free electrons, although large, is still finite, so that attachment can occur at a nonzero rate which can be estimated from detailed balancing, Eq. (1.4). The quantity $d(U_e/D)[d(r_1/y_2)]^{-1}$, from Eqs. (4.14) and (4.15), is also plotted vs r_1/y_2 in Fig. 4 (dashed curve). It shows the behavior just described, except that its value at $r_1/y_2=1$ is not exactly zero. This small discrepancy is caused by the approximation used in evaluating the integral Eq. (4.10), and has negligible effect on our results. Also it may be pointed out here that the adiabatic approximation becomes invalid in two regions. One such region is near the beginning of the collision, when $U_e < -D[1 - (m_e/\mu_3)^{3/4}]$. The other is near the end of the collision, when $U_e > -D(m_e/\mu_3)^2$. Since $m_e/\mu_3 \ll 1$, their effect on detachment is negligible. But the electron can be regarded as detached when $U_e = -D(m_e/\mu_3)^2$ and its partition function remains finite. A detailed analysis leading to the above results is included in the Appendix.

C. Detachment Cross Section and Rate Coefficient

Equation (4.16) gives the value of y_1 at which the energy transfer from M to X^- is equal to the electron affinity D . The energy requirement which must be imposed on the collision is that the relative collision energy along the line XM must exceed the energy required for detachment. Conservation of

angular momentum requires that

$$E_3 b^2 = (E_3 - E_{XM} - D)(a_M + y_1)^2, \quad (4.17)$$

where E_3 is the relative kinetic energy of X and M at infinite separation, b is the impact parameter, and E_{XM} is the potential energy for X and M when detachment occurs, i. e., at $r_{XM} = a_M + y_1$. Thus the detachment cross section (πb^2) is given by^{21a}

$$\begin{aligned} \sigma(E_3) &= 0 & E_3 - E_{XM} < D \\ &= \pi(a_M + y_1)^2 [(E_3 - E_{XM} - D)/E_3] & E_3 - E_{XM} \geq D. \end{aligned} \quad (4.18)$$

The ratio $\sigma(E_3)/[\pi(a_M + y_1)^2]$ is plotted in Fig. 5 vs $(E_3 - E_{XM})/D$.

The detachment rate coefficient k_d is obtained from $\sigma(E_3)$ by averaging over the thermal distribution of E_3 , i. e.,

$$k_d = (8kT/\pi\mu_3)^{1/2} \int \sigma(E_3) \epsilon_3 \exp(-\epsilon_3) d\epsilon_3, \quad (4.19)$$

where k is the Boltzmann's constant, T is the temperature, μ_3 is the reduced mass of the X^- -M collision, and $\epsilon_3 = E_3/kT$.

Since $D/kT \gg 1$ for all the cases of interest here, we obtain, by combining Eqs. (4.18) and (4.19), the approximate result

$$k_d = (8kT/\pi\mu_3)^{1/2} [\pi(a_M + y_1)^2] \exp(-E^*/kT), \quad (4.20)$$

where $E^* = D + E_{XM}$.

V. RESULTS

A. Choice of Parameters

Equation (4.20) indicates that the detachment rate coefficient k_d is determined by the parameters a_M , y_1 , E^* , and D , in addition to the given quantities μ_3 and T .

According to our model, y_1 is determined by D

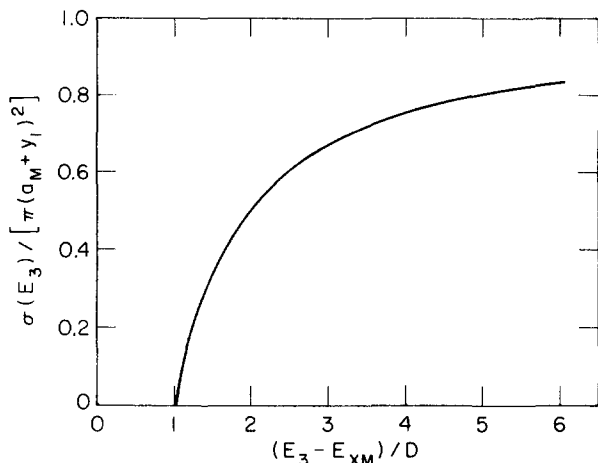


FIG. 5. Dependence of normalized detachment cross section on relative collision energy. The plot is based on the approximate result, Eq. (4.8), assuming $|E_{XM}|$ to be small compared with D .

and α [see Eq. (4.16) and Fig. 2]. Hence we must choose four parameters (D , α , a_M , E^*) in order to calculate k_d .

The parameter D is taken as the electron affinity of the atom X. Its values are now reasonably well known for many atoms and have been summarized in recent papers by Steiner⁵ and Zollweg.²²

The value of k_d is not very sensitive to reasonable variations in α . As was mentioned in Sec. IV.A, we have taken α to be given by the dipole polarizability of the atom X. Teachout and Pack²³ have collected and tabulated the values of α of all neutral atoms in their ground electronic states.

One source of information for choosing the parameter a_M is the data from transport properties of gases. However, it is expected that values of a_M deduced from these results are only valid for relatively low collision energies (thermal energies). In the present case, the e -M relative collision energy when detachment occurs (near $r_1 = \gamma_1$) is generally much higher than thermal energies. The electron e is thus expected to penetrate considerably into the region occupied by the outer electrons of M. A more reasonable value for a_M seems to be the radius (ρ_M) of the principal maximum in the radial distribution function for ground-state atom M, e.g., those calculated by Waber and Cromer.²⁴ When M is a diatomic molecule (AB), the value of a_{AB} is estimated as

$$a_{AB} = \frac{1}{2} r_e + \frac{1}{4} (\rho_A + \rho_B), \quad (5.1)$$

where r_e is the equilibrium internuclear separation of the diatomic molecule AB.

If we were to apply the superposition approxima-

tion for the interaction potentials [Eq. (4.1)] without modification, the remaining parameter E^* would be given by the pairwise interaction potential V_{XM} which may be estimated from semiempirical methods such as that of Mason and Vanderslice.²⁵ The existence of an electron gas located between X and M will undoubtedly screen the direct interaction between X and M, thereby making the estimation of E^* very difficult. On the other hand, the value of k_d is very sensitive to changes in E^* [see Eq. (4.20)]. Therefore, we have left E^* as the single adjustable parameter in our calculations which is to be determined by comparison between theory and experiment. This restriction can be removed when we know more about how to estimate the true interaction potentials, by quantum mechanical calculations or otherwise.

B. Comparison between Theory and Experiment

We have made calculations for the systems $F^- + (\text{CO}, \text{N}_2, \text{Ar})$ and $\text{Br}^- + \text{Ar}$ since detachment rate coefficients for these have been measured.⁶⁻⁹ The values of μ_3 and those of the parameters D , α , and a_M used in the calculations are summarized in Table I.

Figure 6 is an Arrhenius plot of k_d vs T^{-1} . The experimental measurements are plotted as point values²⁶: Δ : $F^- + \text{CO}$, \bullet : $F^- + \text{N}_2$, \circ : $F^- + \text{Ar}$. The three solid lines represent calculated values of k_d for the corresponding three systems, respectively. It can be seen from this comparison that excellent agreement is obtained between theory and experiment, the only adjustable parameter being E^* . The values of E^* used in generating these solid lines in Fig. 6 are also summarized in Table I. It shows that both $E^*(\text{CO})$ and $E^*(\text{N}_2)$ are very close to D , the electron affinity of fluorine, whereas, for $E^*(\text{Ar})$ the deviation from D is more significant. The over-all trend is $E^*(\text{Ar}) > E^*(\text{N}_2) > E^*(\text{CO})$. These features are in qualitative agreement with the observations that $a_M(\text{CO}) > a_M(\text{N}_2) > a_M(\text{Ar})$ which dictates the relative magnitudes of the X-M repulsive potential energy near detachment, and that $\alpha(\text{CO}) > \alpha(\text{N}_2) > \alpha(\text{Ar})$, which determines the relative magnitudes of the X^- -M attractive potential energy due to polarization.

Ewing *et al.*⁶ reported that $k_d = 3.1 \times 10^{-15} \text{ cm}^3/\text{sec}$ for $\text{Br}^- + \text{Ar}$ at $T = 3960^\circ \text{K}$. This alone does

TABLE I. Parameters used in the calculation of k_d .

X	M	μ_3 (a. u.)	D (eV)	α ($\text{eV} \cdot \text{\AA}^4$)	a_M (\AA)	E^* (eV)
F	CO	11.3	3.47	8.2	0.82	3.2
F	N ₂	11.3	3.47	8.2	0.79	3.7
F	Ar	12.9	3.47	8.2	0.66	4.2
Br	Ar	26.7	3.37	52	0.66	...

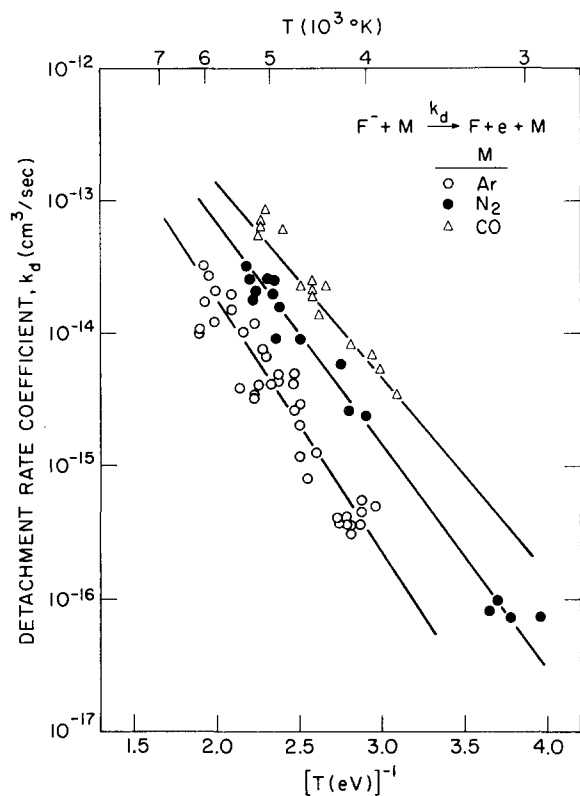


FIG. 6. Detachment rate coefficient k_d vs temperature. O: $F^- + \text{Ar}$,⁷ ●: $F^- + \text{N}_2$,⁸ Δ: $F^- + \text{CO}$.⁹ Solid lines are theoretical results obtained from Eq. (4.20) using the parameters listed in Table I.

not enable us to find the value of E^* . However, the calculated value of k_d for $E^* = D$ is 3.4×10^{-15} cm^3/sec at the same temperature. A deviation of E^* from D is expected to lower the value of k_d somewhat. Thus the agreement between theory and experiment is also very good in this case.

VI. DISCUSSION

Several comments may now be made based on the comparison between theory and experiment presented in the previous section:

(1) It appears that the model proposed in this paper adequately describes the important features of "adiabatic" collisional detachment of negative ions [Eq. (1.1)] near the threshold energy. For the first time, detachment rate coefficients can be estimated simply and with reasonable accuracy. In this connection it may be noted that in the present model the component of angular momentum parallel to the nuclear axis has been treated statistically in computing the electron distribution function. In fact it may be anticipated that this component of angular momentum will be an "adiabatic invariant" in slow collisions and should therefore be conserved. Although this can be easily done in principle, it leads to a somewhat more complicated

calculation and was not attempted in order to preserve the simplicity of the results. Thus the relation between the physics of the model and the final results can be more clearly seen and evaluated.

(2) Direct application of the superposition of potentials [Sec. IV. A, and Eq. (4.1)] is not a good approximation. In fact, the results provide evidence that direct interaction between X and M is strongly screened by the loosely bound electron in the negative ion so that for most cases the effective "activation energy" of reaction E^* does not deviate significantly from the electron affinity of the atom.

(3) For the purpose of calculating the detachment rate coefficient k_d , the behavior of the cross section $\sigma(E_3)$ at very high relative collision energies ($E_3 \gg D$) is unimportant since the contributions to k_d from these collisions are negligible due to the Boltzmann weighting factor $\exp(-E_3/kT)$.

(4) The model is not applicable to detachment processes at very high relative collision energies since the "adiabatic" assumption is invalid under such conditions. This is analogous to the restriction on the application of conventional quasiequilibrium kinetic theories in situations where boundaries move at supermolecular velocities.

(5) Rate coefficients for the reverse process of Eq. (1.1), three-body electron attachment, can be obtained by detailed balancing Eq. (1.4).

(6) Although the "phase-space theory of electron excitation" developed in this paper has been applied only to the attachment and detachment of electrons to atoms, Eq. (1.1), the theory should be applicable to other electronic rate processes such as ionization and charge transfer. These possibilities will be investigated in the near future.

(7) The simplicity of the present model leaves a number of places where improvements can be made. Most of these have already been alluded to in previous sections. Among the most important are (1) conservation of angular momentum along the nuclear axis, (2) use of more realistic potential functions, (3) consideration of the effect of the angular momentum barrier of the electron, and (4) calculation of the energy and angular distributions of detached electron.

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provided much of the background and inspiration required to complete the work. They would also like to thank Dr. B. Kivel and Dr. A. Mandl for a number of helpful suggestions and discussions related specifically to this paper.

APPENDIX: CONDITIONS FOR ADIABATIC APPROXIMATION TO BE VALID

Expansion of Eq. (3.16) shows that one condition for the adiabatic approximation to be valid is

$$I_1 > I_2, \quad (\text{A1})$$

where

$$I_1 = \left| 2m_e \int \rho_e (\mathbf{v}_e \cdot \mathbf{n}_s)^2 (\mathbf{v}_s \cdot \mathbf{n}_s) dS_e \right| \quad (\text{A2})$$

is the contribution to \dot{U}_e due to the momentum of the electron alone, and

$$I_2 = \left| 4m_e \int \rho_e (\mathbf{v}_e \cdot \mathbf{n}_s) (\mathbf{v}_s \cdot \mathbf{n}_s)^2 dS_e \right| \quad (\text{A3})$$

is the additional contribution to \dot{U}_e due to the momentum of the third body, higher order terms being neglected.

The quantity I_1 is actually the first order approximation for \dot{U}_e obtained in Sec. IV. B, and is given by [see Eq. (4.11)]

$$I_1 = 2\pi^2 a_M \dot{r}_{XM}^2 (2m_e \alpha)^{3/2} / 3 Q_e r_{XM} (r_{XM} - a_M)^4. \quad (\text{A4})$$

The quantity I_2 may be evaluated by the same procedure, giving

$$I_2 = 8\pi^2 a_M \dot{r}_{XM}^2 m_e^2 \alpha / Q_e r_{XM} (r_{XM} - a_M)^2 \quad (\text{A5})$$

By using the relationship $\mu_3 \dot{r}_{XM}^2 / 2 = E_3 \approx D$ and the first order solution for $(r_{XM} - a_M)$, i. e., Eq. (4.15), we substitute (A4) and (A5) into (A1) and obtain the approximate condition

$$(D + U_e) / D > (m_e / \mu_3)^{3/4}. \quad (\text{A6})$$

This means that the adiabatic approximation breaks down in an energy range $-D < U_e < -D[1 - (m_e / \mu_3)^{3/4}]$. Since $m_e / \mu_3 \ll 1$, this energy range is very small compared to D and its effect on the detachment process is negligible.

When U_e approaches zero the mean electron velocity becomes comparable to the relative velocity of the heavy particles (\dot{r}_{XM}). This provides another condition for adiabatic approximation to be valid:

$$\dot{r}_{XM} \bar{\tau} < r_{XM} - a_M, \quad (\text{A7})$$

where $\bar{\tau}$ is a mean period of the electron given by

$$\bar{\tau}^{-1} = \int \rho_e (\mathbf{v}_e \cdot \mathbf{n}_s) dS_e. \quad (\text{A8})$$

Evaluating the integral in (A8) and replacing \dot{r}_{XM}^2 by $(2/\mu_3)[b/(r_{XM} - a_M)]^2$, we obtain

$$-\frac{U_e}{D} > \left(\frac{m_e}{\mu_3}\right)^2 \left[(8C_Q)^4 \left(\frac{D(r_{XM} - a_M)^8}{\alpha r_{XM}^4}\right) \left(\frac{E_3}{D}\right)^2 \left(\frac{b}{r_{XM}}\right)^2 \right]. \quad (\text{A9})$$

For the cases under investigation, the quantity in brackets is very close to 1. Thus we obtain the second approximate adiabatic condition:

$$-U_e/D > (m_e/\mu_3)^2. \quad (\text{A10})$$

Again, its effect on detachment is negligible since $m_e/\mu_3 \ll 1$.

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¹H. S. W. Massey, *Negative Ions* (Cambridge U.P., London, 1950), 2nd ed.

²L. M. Branscomb, *Adv. Electron. Electron Phys.* **9**, 43 (1957).

³J. B. Hasted, *Physics of Atomic Collisions* (Butterworth, Washington, D. C., 1964).

⁴H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford U.P., Oxford, England, 1969), 2nd ed.

⁵See, e. g., B. Steiner, in *Case Studies in Atomic Collision Physics*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1972), Vol. 2.

⁶J. J. Ewing, R. Milstein, and R. S. Berry, 7th Shock Tube Symposium, Toronto, Canada, 1969 (unpublished).

⁷A. Mandl, B. Kivel, and E. W. Evans, *J. Chem. Phys.* **53**, 2363 (1970).

⁸A. Mandl, *J. Chem. Phys.* **54**, 4129 (1971).

⁹A. Mandl, *J. Chem. Phys.* **57**, 5617 (1972).

¹⁰H. S. W. Massey, *Rep. Prog. Phys.* **12**, 248 (1949).

¹¹J. B. Hasted, *Proc. R. Soc. A* **212**, 235 (1952).

¹²J. B. H. Stedford and J. B. Hasted, *Proc. R. Soc. A* **227**, 466 (1955).

¹³M. Gryzinski, *Phys. Rev.* **115**, 374 (1959); *Phys. Rev.* **138**, A305 (1965); *Phys. Rev.* **138**, A322 (1965).

¹⁴A. Burgess and I. C. Percival, *Adv. At. Mol. Phys.* **4**, 109 (1968).

¹⁵L. Vriens, *Case Studies At. Collision Phys.* **1**, 333 (1970).

¹⁶M. R. Flannery, *Case Studies At. Collision Phys.* **1**, 1 (1970).

¹⁷R. Abrines, I. C. Percival, and N. A. Valentine, *Proc. Phys. Soc. Lond.* **89**, 515 (1966).

¹⁸P. Mansbach and J. C. Keck, *Phys. Rev.* **181**, 275 (1969).

¹⁹V. H. Shui, J. P. Appleton, and J. C. Keck, *J. Chem. Phys.* **56**, 4266 (1972).

²⁰V. H. Shui, *J. Chem. Phys.* **58**, 4868 (1973).

²¹F. Herman and S. Skillman, *Atomic Structure Calculation* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

^{21a}Note added in proof: A similar expression has been obtained by E. A. Mason and J. T. Vanderslice, *J. Chem. Phys.* **28**, 253, 1070 (1958).

²²R. J. Zollweg, *J. Chem. Phys.* **50**, 4251 (1969).

²³R. R. Teachout and R. T. Pack, *At. Data* **3**, 195 (1971).

²⁴J. T. Waber and D. T. Cromer, *J. Chem. Phys.* **42**, 4116 (1965).

²⁵E. A. Mason and J. T. Vanderslice, *J. Chem. Phys.* **28**, 432 (1958).

²⁶Experimental results reported in Refs. 7-9. We thank A. Mandl for supplying us with full size plots of these measurements from which the point values in Fig. 6 were obtained.