UNDERGRADUATE CHEMISTRY RESEARCH REPORT

Joel Goldberg

10 May 1967

C O N T E N T S

The work herein described covers two independent, but related, projects involving methods of numerical solution of integral equations arising out of theoretical studies of the experimental work of John M. White. He investigated yields of HD and D_2 in a system of H_2 and hot, monoenergetic D atoms in an effort to determine minimum energies for the reaction

$$D^* + H_2 \longrightarrow HD + H$$

and the HD yield as a function of D* energy. While the work here described is formulated in terms of this system, the methods are applicable to any system of the same general nature.

I

Relative Yields and the Energy Distribution Function

Under a not-overly-stringent set of assumptions, the relative yields of HD and D_2 in the system under consideration are functions of the initial energy at which D^* is created (actually a particular distribution of D^* over a range of energy), and the elastic and inelastic cross-sections for D on H_2. For a given narrow initial D^* distribution about a mean energy, the plot of relative yield as a function of that energy is itself a function of the cross-sedtions only. And this plot of relative yield <u>versus</u> initial energy is an experimentally measurable fundtion. The entire process, therefore, can be used to gain an insight into the effect of the shape of the cross-section functions on the relative yield funetion; and, working backwards, an idea of the limitations on the cross-section functions themselves.

The complete reaction scheme for the system is taken to be

1)	$D^* + H_2$	⟶	$HD + H$	(reaction)
2)	$D^* + H_2$	⟶	$D^{*'} + H_2$	(scattering)
3)	$D^* + H_2$	⟶	$D + H_2$	(scattering)
4)	D	⇝	D_2	(cold rxn)

Here D^* (hot D atom) is a D atom at an energy above the threshold energy for reaction 1), while D (cold D atom) is one below that energy. In the work of John White,

where D^* was created by photolysis of DI, the condition of D^* effectively not reacting with DI to form D_2 required the initial condition,

$$5) \qquad \frac{(H_2)}{(DI)} \gg 1 \quad .$$

The kinetic energy of the H_2 itself was ignored in this initial investigation because it was felt and hoped that its effect on the results would be of a low enough order not to warrant the large amount of programming and machine time that would have been required to include it. This means that the calculations are in effect being run at an ambient temperature of 0° Kelvin. Under this condition of no H_2 energy, the cross-sections become functions only of D atom energy.

For a steady D^* source, there exists a steady-state distribution of D^* energies from the highest energy created by the source down to the reaction threshold energy. (The distribution obviously continues below threshold, but this region is of no interest since all cold D atoms are known to form D_2.) This distribution is the "energy distribution function," f(E)

$$6) \qquad f(E)\, dE. = \frac{1}{N_D} \frac{d}{dE} (N_D(E))$$

where N_D is the total number of D atoms, and $N_D(E)$ is the number at or below energy E.

The existence of this steady-state distribution implies the equilibrium,

$$7) \quad 0 = S(F)\,dt + \int_{F}^{F_\infty} \{X_s(F',F)\cdot dE\cdot f(F')\cdot v(F')\}\, dF'\cdot dt - \int_{0}^{E} \{X_s(F,F'')\cdot f(F)\cdot v(F)\cdot dF\}\, dF''\cdot dt - X_r(F)\cdot f(F)\cdot v(F)\cdot dE\cdot dt ,$$

where S(E) is the source distribution spectrum for initial D^* energies; F_∞ is the highest D energy involved; $X_s(E,F')$ is the differential scattering cross-section from energy E to energy F'; $X_r(F)$ is the reactive cross-section for energy E; and v(E) is the velocity of a D atom of energy F.

If we let $h(E) = f(F)\cdot F^{1/2}$, to take care of the velocity term, 7) becomes

$$8) \quad h(E) = \frac{S(E) + \int_{E}^{F_\infty} X_s(F',E)\cdot h(F')\cdot dF'}{X_r(F) + \int_{0}^{E} X_s(F,E'')\cdot dF''}$$

where a few constants have been absorbed into the source term. Equation 8) is a standard steady-state equation: the numerator is the rate at which D atoms of a given energy are being "created," while the denominator multiplied by h(E) is the rate at which D atoms are being lost from this range.

Under the steady-state distribution defined by 8), the yield of HD is

$$9) \quad G_{HD} = \int_{E_t}^{F_\infty} X_r(E)\cdot h(E)\cdot dE$$

and the yield of D_2 (of cold D atoms) is

$$10) \quad G_D = \int_{F_t}^{E_\infty} dE \int_{0}^{E_t} X_s(E,F')\cdot h(F)\cdot dE'$$

where E_t is the reaction threshold energy.

A computer program to find numerical values for the distribution function, f(E), over the range E_t to E_∞, the yields, G_{HD} and G_D, and the relative yield, G_{HD}/G_D, for any values of the three independent functions was written utilizing subroutines for the three functions.

The first two computational series run on the computer tested the validity of the assumption made initially that the effect of the H_2 thermal energy (at room temperature) is negligible. Using the same cross-sections for both series, the sourceesterm was varied so that the second had a primitive correction for H_2 energy. The first seriesus used a delta-function source,

11) $$S(E) = \delta(E_0) \quad .$$

E_0 is the energy at which the D^* are produced. The second series used a source which is the result of adding a source of the type of 11) to a normal Boltzmann distribution,

12) $$S(E) = \frac{1}{(kTE_0)^{1/2}} \left\{ e^{-\frac{m}{u}\left[(E_0')^{1/2}-(E')^{1/2}\right]^2} - e^{-\frac{m}{u}\left[(E_0')^{1/2}+(E')^{1/2}\right]^2} \right\}$$

where E' is the dimensionless E/kT; m is the mass of H_2; and u is the reduced mass of D and H_2. This initial source function allows for the energy of H_2 at time zero in the life of a D atom, but not during the degradation process, where it would have an effect of about the same order.

The cross-section functions used in these two series were

13) $X_s(E,f) = 0.7\ E^{-1/3}\ f^{-7/6}$, $f = (E-E')/E$, the fractional energy loss, and

14) $X_r(E) = 2\ (1 - E_t/E)$ for $E > E_t$.

The first of these cross-sections is a classical small-angle approximation for a Lennard-Jones potential, extended to cover the entire range of fractional energy loss, and the second is a function invented for use in this trial, with E_t set at 0.3. (All energies are expressed in C.M. ev).

The results of these two series are given here only in terms of relative yields

E_0	Relative Yield S(E)=11)	S(E)=12)	
0.225	0	0.042	
.250	0	.060	
.275	0	.081	
.300	0	.106	$= E_t$
.325	0.029	.135	
..350	.070	.167	
.400	.167	.242	
.45	.277	.33	
.50	.39	.43	
.60	.64	..65	
.70	.90	.89	
.80	1.16	1.15	
.90	1.44	1.42	
1.00	1.72	1.70	
1.25	2.44	2.40	
1.50	3.18	3.14	
1.75	3.94	3.90	
2.0	4.72	4.68	

As can be seen, the effect of the Boltzmann distribution does disappear as the initial D energy gets farther away from threshold; but the effect of the thermal H_2 does extend surprisingly far (kT at room temperature is only 0.02 ev). Thus, especially in the crucial area near the threshold energy, it is obvious that the full effect of H_2 thermal energy on the D atom degradation and the relative yield cannot be ignored.

The primary conclusion to be drawn from these two series is that this method of determining relative yields through the energy distribution function is unrealistic as long as the H_2 thermal energy is ignored, unless one is ready to compare these calculations with experimental work on this type of system done at a temperature near absolute zero.

Unfortunately, the inclusion of the full H_2 energy effect would make the computation time involved at least an order of magnitude longer. As far as I have worked it out, the full effect involves constant.conversion back and forth between the lab energy D distribution and the center of mass energy between the D distribution and the H_2 Boltzmann distribution. I can't see the problem being handled in less than a four dimensional numerical integration, instead of the current one dimensional.

Extensive.work beyond the beginnings described here has been carried on by Patricia O'Keefe; .I would suggest consulting her for.information on the current status of this work on energy distribution functions.

II

J W K B Phase Shifts

The semi-classical elastic cross-section, as needed for the work on energy distribution functions, can be obtained from the JWKB approximation to the phase shifts for D on H_2.[1] The formula for the JWKB phase shift approximation is

$$1)\quad \delta_l = k \lim_{R\to\infty}\left[\int_{r_m}^{R} F(r)\,dr - \int_{b}^{R} (1 - b^2/r^2)^{1/2}\,dr\right]$$

$k = (2\cdot u\cdot E)^{1/2}$, the wavenumber

$b = (l + 1/2)/k$

l is the angular momentum quantum number

$F(r) = (1 - \varphi(r)/E - b^2/r^2)^{1/2}$

r_m is the outermost zero of $F(r)$

$\varphi(r)$ is the potential function, and

δ_l is the phase shift.

Here again, a Lennard-Jones potential was used,

$$2)\quad \varphi(r) = 4\cdot e\left\{(s/r)^{12}-(s/r)^{6}\right\}$$

For this case, $e = 33.0^{\circ}$ K, and $s = 2.93$ Å.

In his same article, Smith gives two Gaussian-Mehler quadrature formulae for obtaining numerical solutions to the phase shifts with very rapid convergence to any desired accuracy. The Lennard-Jones potential met the requirements he cited on the potential for applicability of the quadrature formulae.[2] Yet each of the two formulae had been programmed by Chris Parr, and found not to converge at all for this

case.

At this point I decided to drop the quadrature formulae and use a direct approach to the integrals. The method of solution which finally evolved divided the range of r into three sections, each of which was handled differently:

3) $b, r_m < R_1 < R_2 < \infty$

In the first section, b, r_m to R_1, which contains an infinite slope in both integrands, three separate terms were summed to evaluate the integrals. The function,

4) $g(r) = (1 - r_m^2/r^2)^{1/2}$

was subtracted from F(r) in the first integrand in order to "soften" the infinite slope. The remainder was integrated using standard Simpson approximation methods until the desired accuracy had been reached. The second integrand and the function g(r) are both analytically integrable, and their integrals were added.

The second section, R_1 to R_2, was evaluated through Simpson integration of the difference between the two integrands.

The last section, R_2 to ∞, was handled through the expansion of the difference of the integrands into an infinite series, which then was summed until the desired convergence was reached.

The points R_1 and R_2, both of which were functions of l, the quantum number, were located in positions which gave a reasonably good efficiency. All three sections used one convergence formulation, so that any shift of the R's

would improve the rate of convergence in one section at the expense of another.

The overall efficiency of the final method, while far worse than that claimed by Smith for the quadrature methods, was nevertheless tolerable. For moderate relative kinetic energies (> 0.2 ev), a set of 400 phase shifts took about twenty seconds. At lower energies, the computation time was markedly worse.

The elastic cross-sections computed from this JWKB approximation to the phase shift were never used in the energy distribution function work (or in anything else, for that matter) because the more accurate Karpluss-Porter function became available soon after this work was completed.

References

(1) Smith, F J, & Munn, R J, "Automatic Calculation of the Transport Collision Integrals ..." JCP,41:11,p 3560

(2) Smith, F J, "numerical Evaluation of the Classical Angle of Deflection and of the JWKB Phase Shift" Physica,30,p 497(1964)