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CALCULATION OF INTERCHANGE REACTION RATES FROM TRANSITION TIMES

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Thermal energy gas reaction rates for exothermic processes of the type

$$X + YZ \rightarrow XY + Z \tag{1}$$

where both X and YZ may be neutral, but only one may be ionized, are well-known to differ from each other by orders of magnitude for not easily discernable reasons. In this letter we attempt, and compare with experiment, calculations, using approximations to a semiclassical impact parameter treatment [1] appropriate to the charge transfer process

$$A^+ + B \rightarrow A + B^+ \tag{2}$$

and depending essentially upon a comparison of the time $\tau_t = h/|\Delta E|$ of transition [2,3] between energy levels separated by energy ΔE and the time $\tau_c = a/v$ of collision. Here a is a collision length known as the adiabatic parameter and v is the velocity of impact. Only for $\tau_t \ll \tau_c$ is adiabatic adjustment of the collidant wavefunctions possible and the probability of transition between initial and final states small. The adiabatic criterion was found to hold in the form of a maximum rule [4] for atomic charge transfer processes, with $a = 7$ Å; the maximum cross section is when $\tau_t = \tau_c$. This rule is consistent [5] with the impact parameter calculations [1] which although relatively crude in that semi-empirical atomic orbitals are used, give surprisingly good agreement with experiment, even in the near-thermal energy region [6].

We propose that for low energy collisions in which rotational and vibrational energy levels are merely broadened and not made to overlap, the charge transfer, ion-atom interchange and atom-atom interchange processes are essentially similar. If this is the case, all will be dominated by "accidental resonance" conditions [7] in which $\tau_t \simeq \tau_c$. Since most thermal energy collisions take place with inward spiralling orbits [12] except at the largest impact parameters, τ_c is increased, so that for accidental resonance ΔE must be very small, probably only a few wavenumbers. In exothermic processes it is often possible when the products are formed in vibrationally and rotationally excited states to find an accidental near-resonance, but this is more likely when the nearest product rotational quantum number J is smallest, since the separation of levels increases with J. From a recent reactive scattering experiment [8] for $D + Br_2 \rightarrow DBr + Br$ it was concluded that "the bulk of the DBr observed ... is excited to the maximum attainable vibrational-rotational state".

Impact parameter calculations [1] show that as the impact velocity decreases from the value for which $\tau_t = \tau_c$, the cross section falls monotonically. An approximate expression for cross section σ has been found [9] to fit the experimental charge transfer data, and it may easily be shown that this expression is rather a crude approximation to the impact parameter calculations:

$$\sigma = A \exp\left(\frac{-k'a|\Delta E|}{hv}\right) \tag{3}$$

with A, k' constants. Since this expression is hardly justifiable theoretically, and in any case does not hold in the far adiabatic region, it has never been widely used, except for two-electron capture processes [10]. But it is particularly suitable for rough approximation to processes dominated by accidental resonance. The maximum value of the cross section, σ_m, may be calculated directly from ref. [1] and inserted in eq. (3):

$$\sigma_m = A \exp\left(\frac{-k'a\Delta E}{hv_m}\right), \tag{4}$$

where the velocity v_m at which maximum cross section is reached is given by $h/|\Delta E| = a/v_m$, with a determined empirically; but $a \gg 7$ Å on account of the spiralling orbits. For $v \geqslant v_m$,

$\sigma = \sigma_m$ is a sufficiently good approximation. For $v \leqslant v_m$, A is eliminated to give

$$k = \sigma v = v\sigma_m \exp k'\left(1-\frac{a|\Delta E|}{hv}\right). \qquad (5)$$

To calculate a thermal energy rate constant k eq. (5) is applied in the following manner. The six smallest possible exothermic energy defects are determined and the cross sections for these calculated and summed. Since the majority of transitions take place during a spiralling motion in which there is very little impact momentum available for exchange, endothermic processes energetically possible in the thermal energy experiment are precluded. The number six is an arbitrary choice, but the contributions from all except the smallest ΔE is usually not large, so that six is more than sufficient. At $T = 300^{\circ}$K the molecular collidants are in a distribution $f(J)$ of rotational states, and the rate must be summed over this distribution

$$k = \frac{\sum_J k_J f(J)}{\sum_J f(J)} . \qquad (6)$$

Certain processes can terminate in more than one electronic level; the computed rate is a summation of the rates for each*, calculated from eqs. (5), (6). Certain collidant levels possess fine structure; the components are equally weighted. Only the lowest collision product fine structure sub-levels are considered, since the formation of the higher energy sub-levels is sometimes precluded, for incompletely understood reasons [8,24].

A search has been made for available rate-constant data for which all the internal energy levels are known with sufficient accuracy. The most recently available spectroscopic data have been used. Rate constants have been computed for the processes and energies tabulated in table 1, and the results are compared with experimental data (13-23) graphically in fig. 1. The results are sufficiently encouraging for us to claim that accurate quantum calculations using molecular orbitals of the quasi-molecule of collision would be rewarding. Our calculations have been made for a number of different adiabatic parameters, and it is found that for ion-molecule reactions $a = 100$ Å is most suitable. Classical spiralling orbit calculations are in progress. For neutral processes we find $a = 200$ Å most suitable.

The constant k' is a measure of the "sharpness" of the maximum in the cross-section function. For high energy atomic charge transfer data $k' \simeq 1$ is appropriate, but $k' = \frac{1}{4}$ is sometimes incorrectly assumed. These calculations have been carried out for a number of different values of k', and the most appropriate is found to be $k' = 2$. Low energy charge transfer maxima are indeed "sharper" [25] than those at high energies, but no theoretical reason has been advanced.

In atomic charge transfer it is necessary [1] to multiply the calculated cross section by a statistical weight factor, equal to the ratio of number of configurations of the quasi-molecule of collision able to pass directly to the product states to the total number of configurations which can be formed from the collidant states [11]. We find that such a procedure does not weaken the importance of the adiabatic criterion in interpreting the experimental data, but it does lower nearly all the calculated rate constants until they are rather smaller than the experimental data. In fig. 1 no statistical weight factor has been included, in the belief that this is indirect evidence that transitions between different configurations of the quasi-molecule can occur in tri-nuclear systems.

It is arguable that processes 8, 10, 11, 13, 15, 17 are able to proceed in two ways, namely with interchange of either of the two atoms of the homologous molecular species; however, the calculated rates have not been multiplied by a factor of two in conformity with this argument.

One conclusion that can be drawn from a detailed examination of the calculations is that some of the spectroscopic data are insufficiently accurate for precise calculation of rate constants, so that the stimulus to accumulate more data is great.

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* Except where the statistical weight factor is zero, as is the case for certain excited products of processes 9, 13, 16.