# Bimolecular Electron Transfer in Liquid Solution - Diffusion Matters (Obviously)

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Of all chemical reactions perhaps the simplest and most well studied is electron transfer. Research on intramolecular reactions has been successful in revealing many details but is limited to the number of systems that can be studied for synthetic reasons. However, in many instances the reaction between separated reactants is more relevant. In this case, the role of mutual diffusion needs to be taken into account, rendering the picture of these reactions in the condensed phase completely different from that in the gas phase.

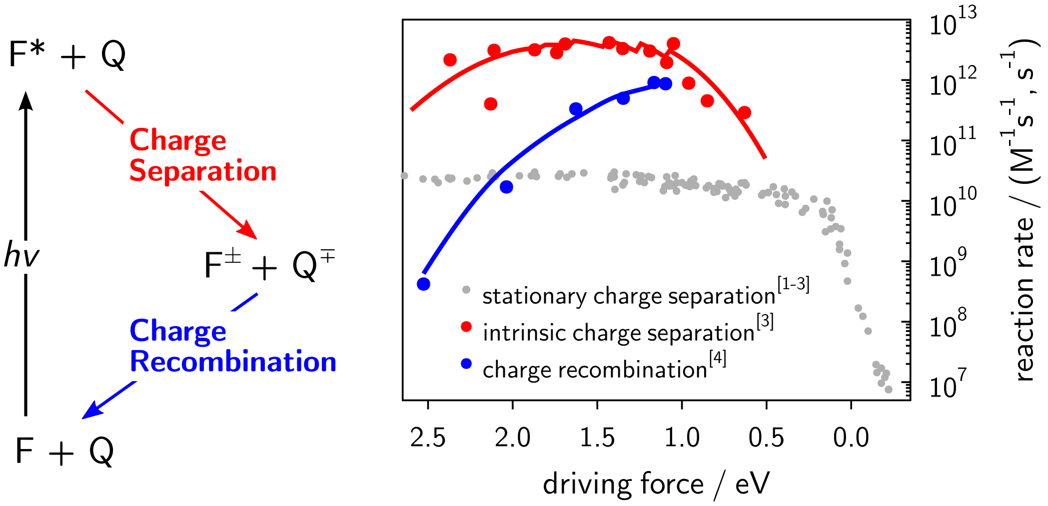

*Figure 1: Reaction scheme for the simplest photocycle of freely diffusing donor / acceptor pairs (left) and the ensuing driving force dependence of the observed reaction rates in liquid solution (right).*[1–4]

Despite being known since the groundbreaking work by Smoluchowski, so far bimolecular electron-transfer reactions have been - with few exceptions - in general badly described: either theory is not compared to experiments or experiments are not compared with the appropriate theories. We have shown that especially the latter practice leads to dangerous misconceptions for the advancement of our understanding of the dynamics of chemical reactions. Only a combination of a large number of experiments with adequate theoretical models can shine light on the subject. As a matter of fact, these insights may also be extremely beneficial for applications like photovoltaics, solar fuels, artificial photosynthesis, photocatalysis or optoelectronics. A sound theoretical basis will provide a more reliable way to choose substances, architectures and in general strategies for superior devices.

It is not surprising that various enigmas, such as the apparent absence of the Marcus inverted region for bimolecular charge separation or notable differences in the driving force dependence of bimolecular charge separation and recombination reactions have persisted until today (see Figure 1). The proper way to consider the influence of diffusion on an intrinsically non-contact reaction was developed only recently.[5] In this communication we will elaborate on how to overcome the difficulties of studying electron transfer in bimolecular reactions, and how to gain considerable new insight. We combine various time-resolved optical spectroscopies, which cover the sub-ps to sub-$\mu$s time-range, with theoretical models based on diffusion-reaction-equation (DRE) approaches.[5,6]

On the one hand, we will show how through assiduous experiments and thorough theoretical analysis, we could reconcile the findings of the Rehm-Weller experiment for charge separation and Marcus theory for electron transfer.[3] On the other hand, we will move one step further and show how a model-free approach to experimental excited-state populations based on broadband transient absorption spectroscopy in combination with - again - a DRE approach yields a quantitative description of the fate of radical ion pairs, which have been generated via bimolecular electron transfer.

**Funding:** University of Geneva

**References:**

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