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Comments on the article 'Direct conflict of Marcus theory with the law of conservation of energy' by X.-Q. Zhu and J.-D. Yang

After a recent publication in the *JPOC* by Zhu and Yang,^[1] the journal received several unsolicited opinions from readers who disputed the conclusions and the reasoning behind the article. After these opinions were received the principal author was contacted and informed of the specific criticisms brought forth and his response was to fully reaffirm the content and conclusions of his article. In view of this response I decided to publish one of the comments, by Prof. Eric Vauthey, where he explains his reasons to disagree with the assumptions and conclusions presented in this article.

Luis Echegoyen
Editor-in-Chief

One of my coworkers recently drew my attention to an article by Zhu and Yang (ZY) which argues that Marcus electron transfer (ET) theory 'is erroneous', because it does not respect the principle of energy conservation.^[1] This is a strong statement, and I was first surprised that a more than 50-year-old theory that has been discussed, refined and put to the test for decades would have survived so long with such a fundamental flaw. After reading the ZY paper, I am of the opinion that this supposed violation of the law of energy conservation in Marcus theory is due to a misunderstanding of important parameters entering Marcus theory.

In my opinion, the major flaw in the reasoning of ZY resides in their definition of ΔG^0 : ' ΔG^0 is the potential energy difference between the solvent surrounding the reactants at the equilibrium state and the solvent surrounding the products at the equilibrium state'.^[1]

This is not how ΔG^0 is defined in Marcus theory. First, ΔG^0 is a free energy (or free enthalpy) difference and not a potential energy difference. More importantly, ΔG^0 is the standard free energy of the ET reaction,^[2] i.e. the free energy difference between the product and the reactant states. This quantity is not equal to the difference of solvation energy, although the latter can contribute, but it depends rather on the redox properties of the reactants. This makes a big difference with the definition of ZY, where ΔG^0 is associated with the solvent only and is not related to the reactants. The alleged violation of energy conservation of Marcus theory simply follows from this misunderstanding of ΔG^0 .

It is easy to see that if ΔG^0 were just the difference of solvation energy, charge recombination processes such as $D \cdot^- + A \cdot^+ \rightarrow D + A$ would never take place in a polar solvent, because the solvation energy of the neutral product state is always much smaller than that of the ionic reactant state.

As an example, ZY use the reaction $V^{2+} + Fe^{3+} \rightarrow V^{3+} + Fe^{2+}$. The experimental ΔG^0 value of this reaction is -23 kcal/mol. According to their definition of ΔG^0 , this -23 kcal/mol corresponds to the difference of solvation energies between $V^{3+} + Fe^{2+}$ and $V^{2+} + Fe^{3+}$. To make this possible, ZY invoke different curvatures of the reactant and product parabolas and thus different reorganisation

energies. However, such a trick is not necessary if the correct definition of ΔG^0 is used. The -23 kcal/mol comes simply from the fact that the electron affinity of Fe^{3+} is higher than that of V^{3+} .

One should also note that the different curvatures and reorganisation energies proposed by ZY to 'correct' Marcus theory point to some misunderstanding of the meaning of the solvent reorganisation energy, λ .

The solvation energy and λ are not directly related quantities. λ is a measure of how the solvent configuration around the product state differs from that around the reactant state. In terms of free energy parabolas, λ is a measure of the horizontal spacing of the reactant and product parabolas along the solvent coordinate. On the other hand, the solvation energy difference contributes to ΔG^0 , i.e. influences the vertical spacing between the two parabolas. For example, a substantial λ value but no change of solvation energy can be expected for the self-exchange reaction: $M \cdot^+ + M \rightarrow M + M \cdot^+$. The statement in Figs. 2 and 3 of the ZY paper that $\Delta G^0 = \lambda_R + \lambda_P$ is not correct.

Finally, I and the other authors of ref.13 of the ZY paper^[3] were surprised to see our paper cited as an experimental evidence of the supposed failure of Marcus theory. In this paper, we showed that several reports of the observation of the inverted region are spurious, not because of a flaw in Marcus theory, but only because of the neglect of non-equilibrium effects in the data analysis.^[3] In my opinion and that of my coauthors, our paper should not have been cited by ZY in this context.

In summary, the claim that Marcus theory is erroneous and not consistent with the principle of energy conservation is not correct, as it is based on a wrong definition of the driving force of ET. Furthermore, the approach proposed by ZY to circumvent this alleged problem is incorrect as well, as it is based on a wrong interpretation of the solvent reorganisation energy.

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