Supporting Information

I. On the Empirical Nature of Chemical Kinetics

The rate of a general (uncatalyzed) reaction, r, for the process:

$$aA + bB \rightarrow cC + dD \tag{A1}$$

may be expressed as:

$$r = (-1/a)(d[A]/dt) = (-1/b)(d[B]/dt) = (1/c)(d[C]/dt) = (1/d)(d[D]/dt) \tag{A2}$$

From experimental observations, it is known that the rate of a reaction typically shows a dependence on the concentration of reagents in the system, at any time, t, as well as the temperature, T. In general terms, one can write, at constant T, the following expression for the rate of formation of product C (for example):

$$d[C]/dt = k[A]^a[B]^b \tag{A3}$$

where it is highlighted that a and b sometimes, but not always, match the stoichiometry in the balanced Eqn (A1). From Eqn (A3) one can see that the rate of the reaction is proportional to the reagent concentration(s) via the proportionality (i.e. rate) constant, k. Rate constants are determined experimentally, by measuring the dependence of the conversion rate on the concentrations of A and B (once the values of a and b have been

verified experimentally). Arrhenius showed that the rate constant has a temperature dependence due to the presence of an activation energy barrier, E_a, which must be overcome in order for reaction to occur. The Arrhenius equation, shown below, relates k in terms of E_a, T and $\Lambda*$ ($\Lambda*$ is considered here to be temperature-independent, though a temperature dependence is clearly supported by the author's earlier derivation of Eqn. (20) in the manuscript) where $\Lambda*$ describes the frequency of intermolecular collisions which have the correct geometry to lead to product(s):

$$k = \Lambda*\exp(E_a/RT) \tag{A4}$$

Together, $\Lambda*$ and the exponential term in Eqn (A4), describe the concentration-independent frequency of successful collisions (i.e. those forming products) at any given T; in other words, the number of colliding reagent molecules which have sufficient energy to overcome E_a. Combining Eqn (A3) and Eqn (A4) one obtains a more fundamental kinetic expression for the rate of formation of product C:

$$d[C]/dt = \{A*\exp(E_a/RT)\}[A]^a[B]^b \tag{A5}$$

Unfortunately, this result is not entirely satisfying, in a physical sense, in that it, too, is empirical.

Unlike thermodynamic (i.e. state) quantities, which can be readily predicted, the rates of chemical reactions are often obtained through experimentation. Two of the most

noteworthy attempts, to-date, to predict reaction rates based on thermodynamic quantities/concepts came from Eyring's Transition State Theory (discussed in the manuscript) and Marcus Theory (discussed later in this Supporting Information section). However, despite these theories, the fact that the study of chemical kinetics involves empirical manipulations of experimental data remains largely unchanged; in the majority of cases it remains impossible to predict reaction rates without some level of experimentation. (It is noted here that computer modeling of certain chemical reactions may be performed on a 'dimensionless time' scale in order to obtain apparent reaction rates, but experimentation is usually needed to correlate such values with absolute reaction rates.)

The underlying issue is that reaction rates are generally quantified using units of time (or 'dimensionless time', but the point is unchanged), in which the definition of time is quite arbitrary from a physical standpoint: the fundamental SI unit of time, the second, is based on the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine ground state levels of the ^{133}Cs atom. From this definition, time cannot be expressed in terms of any other physical parameters. Additionally, 'the arrow of time' that the scientific community is accustomed to is useful only in monitoring macroscopic changes in matter, since, on a molecular level, over a given period of time, any two molecules in an ensemble, with equivalent electronic, translational, vibrational and rotational energies, can move in opposite directions from their origin and, additionally, one may collide (and react) while the other may not. For these reasons, ultimately, time has not been successfully quantized to-date.

Time is widely recognized as the fourth dimension in the universe, with the first three dimensions used to treat space. Following Einstein's development of the theory of special relativity, Minkowski, realizing the shortcomings of our current definition of time, treated space and time together. Today it is generally accepted that, in a relativistic sense, as speeds approach that of light, temporal and spatial dimensions may become 'warped'. Thus, by defining a new quantity, *spacetime* (*s*) as:

$$s^2 = r^2 - c^2 t^2 \qquad \text{(A6)}$$

where c is the speed of light and r defines spatial coordinates (using the Cartesian coordinate system x, y and z; i.e. $r^2 = x^2 + y^2 + z^2$), it is possible to more accurately relate changes in four-dimensional space under relativistic conditions. Note that s^2 can be positive, negative or zero, depending on whether a given event is more 'space-like', 'time-like' or 'light-like'. Additionally, spacetime, like energy, can be quantized (e.g. in String/M-Theory).

In the study of chemical kinetics, generally one needs not concern themselves with time-scales approaching the speed of light. However, the concept of combining time and distance to yield a parameter with a clearer physical significance (i.e. that may be quantized) is very attractive. In order to pursue this idea further, one can introduce the concept of temperature, a second fundamental parameter (which is independent of both

time and concentration) key to our current understanding of the rates of chemical
reactions.

Definitions of temperature exist based on both the Zeroth Law and Second Law of
thermodynamics. The Ideal Gas Law, which is a classical result which may also be
obtained from first principles using statistical thermodynamics, yields:

$$T = PV/nR \qquad\qquad (A7)$$

Where P and V are the pressure and volume occupied by the gas, respectively, and n is
the number of moles of gas present in the system. In this case, temperature is a measure
of the average kinetic energy of a system. For a given atom, the kinetic energy, ε_{KE}, is
described by: $\varepsilon_{KE} = \frac{1}{2}mv^2$, where m is the mass of the particle and v is its speed. In the
manuscript, it was mentioned that for an ideal gas, the distribution of kinetic energies,
and thus speeds, is described by the M-B distribution.

Rewriting the classical expression for kinetic energy, one obtains:

$$v = (2\varepsilon_{KE}/m)^{\frac{1}{2}} \qquad\qquad (A8)$$

and thus one can see that in using molecular speeds one obtains a direct measure of the
kinetic energy in both a *space-* and *time*-dependent fashion, since speed = distance/time.
As per relativistic spacetime, molecular speeds can be quantized (i.e. as per the M-B

distribution). Thus, the author's hypothesis is that molecular speeds may be useful in describing the reaction kinetics (e.g. of dispersive chemical systems), in a more physically meaningful fashion than using the time domain (alone).

Unfortunately, the measurement/calculation of 'kinetic energy distributions' for polyatomic molecules in the gas phase and for molecules in condensed phases is non-trivial. Thus, time-based (i.e. traditional) kinetic approaches provide a simpler and more convenient means of describing reaction rates. It turns out that the treatment of dispersive kinetics described in this work, using assumptions about the kinetic energies of the species defining the r.d.s. of the conversion (possessing the functional form of the M-B equation), in conjunction with the present-day convention of studying chemical conversions in the time domain, is able to yield *semi-empirical* model equations. These equations differ from traditional models in that they are not entirely phenomenological. Additionally, they have a broad range of applicability to various (dispersive) chemical reactions/phase transformations occurring on very different time-scales. Their success, to-date, may be attributable to the 'quantization of the activation energy barrier' that was able to be achieved, fundamentally, by starting with the hypothesis that molecular dynamics are important in modeling the reaction kinetics of dispersive systems.

II. Three-Dimensional Marcus Theory Supports Dispersive Kinetics

Marcus Theory (MT) provides a fairly good approximation for the activation energy of simple chemical reactions, such as redox and acid-base processes (in which either an

electron or proton is transferred, respectively, during the reaction), based solely on the change in free energy of the reaction, ΔG_r, the solvent reorganization energy, λ, and the work needed to move the reactants, w_r, in the following general reaction scheme

$$\mathbf{A + BC \rightarrow AB + C},$$
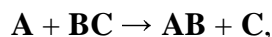
from their respective equilibrium positions along the reaction coordinate to some intermediate point where the Lennard-Jones (L-J) potential curves for the two reactant species intersect, defining the transition state (TS) [see Figure 9.10 in Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*.; John Wiley & Sons, Inc.: New York, 1996, pp.628-629.].   The power of the theory lays in the fact that it introduces the possibility of predicting the activation energy based on thermodynamic quantities. Practically, however, the Marcus Equation defines a correlation between the rates of simple chemical reactions and corresponding thermodynamic quantities such as equilibrium constants, the Gibbs free energy change or the applied potential. The Marcus Equation, which can be written as:

$$E_a = \lambda(1 + \Delta G_r/4\lambda)^2 + w_r \qquad\qquad\qquad (A9)$$

is elegant in its simplicity and its usefulness in describing kinetic trends. The equation predicts a linear dependence of E_a on ΔG_r over a limited range of ΔG_r, but a quadratic dependence over a wide range of free energy change (which is experimentally justified).

Following the derivation of the Marcus Equation given by Masel, one can approximate

the L-J potentials of species **BC** and **AB** using parabolas in the vicinity of the TS (this

approximation has a basis in the vibrational energies of a harmonic oscillator and it is

useful for simple molecules/reactions). Using the terminology of Masel, one can write:

$$E_{left}(r_x) = SS_1(r_x\text{-}r_1)^2 + E_1 \qquad\qquad\qquad\qquad (A10)$$

$$E_{right}(r_x) = SS_2(r_x\text{-}r_2)^2 + \Delta G_r + E_2 \qquad\qquad\qquad (A11)$$

for the energies of the **BC** and **AB** parabolas, respectively, as a function of the location

on the reaction coordinate, r_x. The constants SS_1, SS_2, r_1 and r_2 are 'fit parameters'.

Defining $r^{\ddagger}$ as the value of r_x where the two energy parabolas intersect (i.e. where $E_{left} =$

E_{right}) and using the Marcus simplifications $SS_1 = SS_2$ and $E_1 = E_2$, one can obtain the

following expression for $r^{\ddagger}$:

$$r^{\ddagger} = (r_1\text{+}r_2)/2 + \Delta G_r/[2SS_1(r_2\text{-}r_1)] \qquad\qquad\qquad (A12)$$

At this point, one may introduce the idea that $r^{\ddagger}$ does not have to be single-valued. If $r^{\ddagger}$ is

allowed the flexibility to vary with time (thus one may redefine the variable as $r^{\ddagger}(t)$), one

may conclude that SS_1 in Eqn (A12) must also be a function of the reaction time, t. This

makes sense as SS_1 is related to the vibrational frequency of the atom, **B**, being

transferred. If not all atoms are inherently transferred with the same frequency, one may

observe dispersion in the rate of reaction. Thus, one can rewrite Eqn (A12) as:

$$r^{\ddagger}(t) = (r_1+r_2)/2 + \Delta G_r/\{2[SS_1(t)][(r_2-r_1)]\} \tag{A13}$$

Inserting Eqn (A13) into Eqn (A10) and solving, one ultimately obtains an expression for a time-dependent activation energy, $E_a(t)$:

$$E_a(t) = \lambda(t)[1 + \Delta G_r/4\lambda(t)]^2 + w_r \tag{A14}$$

in which $\lambda(t) \equiv \{[SS_1(t)][r_2-r_1]^2\}/4$ (note that one can expect w_r to be nearly constant for a group of related reactions). Eqn (A14) provides a description of a reaction time-dependent activation energy, potentially useful for describing dispersive kinetics; the equation is referred to here as the '3-D Marcus Equation'. From this equation, one can see that the time-dependent reorganization energy, $\lambda(t)$, is fundamentally responsible for the variation in $E_a(t)$, which is entirely consistent with the idea that molecular motion is responsible for the 'dispersion in the activation energy' in the majority of dispersive kinetic systems. Returning to the earlier discussion of Eqn (A13), one may also conclude that the rate at which atom **B** is transferred from **C** to **A** may be limited, to a notable extent, by the time-scale of the reorganization (i.e. of molecules solvating the various species in the above reaction scheme).