

## Perspective

# Reaction rates in condensed phases. Perspective on “Brownian motion in a field of force and the diffusion model of chemical reactions”

Kramers HA (1940) *Physica* 7:284

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**Abstract.** The key concepts from H.A. Kramers’ influential work on noise-assisted escape of a particle bound in a potential well are summarized, as is the extensive impact that these ideas have had on the development of condensed-phase reaction-rate theories in the twentieth century.

**Key words:** Kramers theory – Reaction dynamics – Solvent effects – Stochastic processes – Escape over a potential barrier

In April 1940, H.A. Kramers published his work entitled “Brownian motion in a field of force and the diffusion model of chemical reactions” [1]. This work, which appears to have generated little activity at the time [2], was, many years later, to become one of the most influential contributions to reaction-rate theory in the twentieth century. The prominence of Kramers’ work is reflected in the titles of two recent reviews on the current status of condensed-phase reaction-rate theory: “Reaction-rate theory: fifty years after Kramers” and “New trends in Kramers’ reaction-rate theory”.

In his seminal work (as it is frequently called), Kramers treated the escape over a potential barrier by a particle undergoing Brownian motion, i.e. thermal noise-assisted escape [1]. Hence, his focus was on the effect of the medium – solvent or bath gas – on the solute reaction rate. While much of the physical chemistry community was at the time focused on the rate of reaction of an isolated molecule – and would remain so occupied for many years to come, Kramers’ work was not completed in a vacuum. Indeed, Lindemann, Rice and Ramsperger, Kassel, Slater, Christiansen, and others had already published their collision-rate-based theories of the role of the bath gas in promoting chemical reactions in low-density gases [3, 4]. Thus, one must ask,

what is it that distinguishes Kramers’ article? What new ideas and new results within his article have given his work such a prominent place in modern rate theory?

First, Kramers recognized that the motion of the solvent molecules could be modeled according to the theory of Brownian motion, i.e. according to the Langevin equation, within which the solvent is described by its viscosity and a random force term. Such a stochastic equation for the solute variables ( $p, q$ ) can be reformulated as either a diffusion or a master equation for the probability distribution of the solute variables [ $\mathcal{P}(p, q)$ ], leaving open many routes to the solution of the reaction problem [5]. Indeed, Kramers himself chose the diffusion-equation approach, devising a specific Fokker–Planck equation, now known as the Kramers–Klein equation, for the purpose. Yet, Kramers’ choice of a Brownian description for the reacting solute had much more far-reaching consequences in that it enabled Kramers to describe the effect of the solvent over a broad range of conditions, from the very low viscosities expected in low-density gases to the high viscosities expected in liquids. This description stands in contrast to the earlier collision theories, which are applicable only under the single-collision conditions of low-density gases. Kramers’ work thus introduced into the reaction dynamics community the novel idea that solvent motion, i.e. thermal noise, could affect solute reaction rates in high-density solvents, as well as in low-density gases.

Although Kramers’ description applies to all viscosity regimes, Kramers was only able to solve for the reaction rate in the limits of very low and very high viscosities (which, in itself, was no small feat). Kramers found that at low viscosities the reaction rate is controlled by the rate of energy diffusion (consistent with collision theories) and rises as  $k \propto \eta$ , where  $k$  is the rate constant and  $\eta$  is the viscosity. At high viscosities, Kramers indeed uncovered a thermal-noise effect, finding that the rate is controlled by spatial diffusion of the particle (i.e. of the reaction coordinate) and falls off as  $k \propto \eta^{-1}$  with increasing viscosity. These two findings comprise the main,

and far-reaching, result of Kramers' paper. They suggest that with increasing solvent viscosity the reaction rate should first increase (energy-diffusion-limited regime), pass through a turnover, and then subsequently decrease with further increases in viscosity (spatial-diffusion-limited regime), a behavior which has been verified via experiment and simulation, and is now referred to as the "Kramers turnover" [3, 6, 7].

Kramers final coup d'état in this work was a recasting of his rate expressions in terms of the then newly developed transition-state theory [8, 9], which has since become the most prominent rate theory in chemistry. In both limits Kramers was able to cast his result in terms of a multiplicative prefactor to the transition-state theory result. I note that the "transition-state method" to which Kramers compared takes only the solute degrees of freedom into consideration. Only some 40 years later was it recognized that multidimensional variational-transition-state theory [10], inclusive of all the solvent degrees of freedom, can reproduce the Kramers result in the high-viscosity, spatial-diffusion-limited regime [11–13].

In spite of, or perhaps because of, the novel, far-reaching conclusions of Kramers' work, it was largely neglected for 30–40 years. Indeed, authoritative books on chemical reaction dynamics, such as that by Moore and Pearson [4], make no mention of Kramers' work or the ideas contained therein. An important exception to this neglect was Chandrasekhar's application of Kramers' work to the astrophysical problem of star clusters in 1943 [14], as much of Chandrasekhar's work was, in turn, to later influence the chemical dynamics community. The works of Bak in the 1960s, pursuing Kramers' idea of applying diffusion equations to activated chemical reactions, also appear to have been influential [15, 16]. Yet, during the period 1940–1970, most chemical studies of reactions in low-density gases concentrated on the aforementioned strong-collision models and the development of important extensions thereof, most importantly RRKM theory [4, 17]. It was only much later that Kramers' "weak collision" energy-diffusion model was considered and the relationship between the strong- and weak-collision models was elucidated [18]. Similarly, in the high-viscosity, solution-phase limit, the chemical community (with the exception of Brinkman [19] and Takeyama [20]) primarily concerned itself with the effect of solvation free energies on the reaction activation barrier, an effect which, the astute reader will notice, is completely absent from the treatment of Kramers. Within Kramers' formalism, such solvation-induced changes in the barrier height would be hidden within the simple transition-state-theory rate to which Kramers' results provide a prefactor correction. However, it was many years before it was recognized that solvation effects on solute reaction rates can be formally separated into activation free-energy (potential of mean force) and dynamical (thermal-noise induced) effects [21], both of which will typically vary with changing solvent viscosity.

Extensive interest in Kramers' work by the chemical community had to wait until the late 1970s, early 1980s, when technological advances – fast pulsed lasers and

computers – provided the ability to probe the microscopic details of solution-phase reaction dynamics, thus enabling the study of noise-induced "dynamical" effects in liquids. A key paper in stimulating this renewed interest was that of Grote and Hynes [16], in which the Kramers result in the high-viscosity limit was rederived (along with an extension to time-dependent friction).

Once Kramers' work returned to the public eye, the approximations and restrictions inherent in Kramers theory came under close scrutiny. These are

1. An assumption that the microscopic friction  $\gamma(t)$ , exerted by the solvent on the solute reaction coordinate, can be approximated by the viscosity of the bulk fluid,  $\eta$ .
2. An assumption that the solvent moves rapidly with respect to the solute, such that the solvent friction acts effectively instantaneously, i.e.  $\gamma(t) = \eta\delta(t)$ , with  $\delta(t)$  the Dirac delta function.
3. The neglect of anharmonic terms in the solute potential of mean force (also known as nonlinearity and finite-barrier effects).
4. The restriction to a 1-dimensional (1D) solute.
5. The lack of a solution to the rate expression in the intermediate-viscosity "turnover" region.
6. The neglect of quantum effects.

By the late 1980s, development of theoretical extensions of Kramers' result, along with numerical (via computer simulation) and experimental tests, had become a cottage industry, as is evidenced by the 700-plus references cited in the review in Ref. [3]. These extensions came from both the chemistry and the physics communities and were developed from an extremely broad arsenal of formalisms [2, 3, 7].

Here I list just a small sample from the number of things about condensed-phase rate theory that have been learned from the past two decades of intense activity on this problem (I give only representative references, as there are far too many to list here). From studies of 1D model solutes coupled to a solvent bath, for example, we have learned that at intermediate viscosities, the spatial-diffusion effect typically becomes important before the energy-diffusion effect becomes negligible, a behavior which is greatly magnified in slowly relaxing solvents [22]. Consequently, the simple 1D transition-state-theory estimate of the rate is rarely, if ever, accurate for these model systems, even at intermediate viscosities [22]. Additionally, new methods have been developed for predicting rates in the difficult intermediate-viscosity regime [23, 24], where simple interpolation schemes have been shown to fail [25]. We now know that the viscosity of the bulk fluid is often a poor approximation to the microscopic friction [26], although how to determine the microscopic friction without resorting to computer simulation [27] remains an open question. We have also learned that Kramers' delta-function friction, which assumes rapid solvent motion, is a poor approximation for many chemical systems [28, 29], and that a slow solvent relaxation can greatly reduce the effect of the solvent, either in promoting (low viscosity) [22, 33] or hindering (high viscosity) [16, 30] the reaction. Numerous methods have

been developed for the incorporation of nonlinear, finite-barrier effects [3, 31], as have been methods to enable the microscopic friction to depend upon the reaction coordinate [32]. The effect of strongly coupled solute degrees of freedom has been examined, demonstrating that such strongly coupled modes enhance the rapidity with which the energy-diffusion-limited rate increases with increasing solvent friction [18] and can also lead to interesting spatial diffusion behaviors, such as saddle-point avoidance [33]. The transition from weakly to strongly coupled solute modes is an area of current investigation [34, 35], as is the incorporation of quantum effects, even though this latter topic has already seen extensive attention for well over a decade [36]. Finally, on a more practical note, it has become clear that only the spatial-diffusion regime is accessed in liquids, whereas only energy-diffusion behavior is typically found in gases; it is only in intermediate-density supercritical fluids that the turnover behavior is observed [26, 37]. Another hard-earned lesson has been that uncharacterized changes in the activation barrier, which generally occur simultaneously with changes in the viscosity (be they due to density changes or to changed chemical interactions), almost always inexorably cloud the extraction of dynamic solvent effects from the data. Indeed, spatial-diffusion effects in liquids typically alter the rate by a factor less than 10, whereas (at 298K) activation-energy changes alter the rate by an order of magnitude per kilocalorie/mole. Yet, if a factor of 2 accuracy is to be achieved in the prediction of reaction rates in condensed phases [7] such Kramers effects will require proper evaluation.

Given the successes of the past two decades, what does the future hold for Kramers' reaction-rate theories? In addition to continued work on the difficult problem of quantum effects in condensed media, I believe that the need to understand reactivity in a broad range of complex systems will drive the development of new extensions to the Kramers' method. In fact, such application-driven extensions have already begun to appear, such as the extension to nonstationary friction kernels,  $\gamma[(t' + \tau) - (t + \tau)] \neq \gamma(t' - t)$ , for thermosetting polymers [38], to multiple correlated barrier crossings for surface reactions in the energy-transfer-limited regime [39, 40], and to fluctuating barriers for modeling the kinetics of ion channels [41]. Thus, the ideas of Kramers are likely to be moved forward into the next century like a coat of many colors, being continually directed into new dimensions which have not yet entered our thoughts, but will arise naturally from new and varied complex applications.

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