

On the Saha Ionization Equation

Sushanta Dattagupta

We revisit the Saha Ionization Equation in order to highlight the rich interdisciplinary content of the equation that straddles distinct areas of spectroscopy, thermodynamics and chemical reactions. In a self-contained discussion, relegated to an appendix, we delve further into the hidden message of the equation in terms of rate theory. We employ a pedagogical style appropriate for a course in equilibrium and nonequilibrium statistical mechanics.

1. Introduction

In a couple of years, we are going to observe the centenary of a remarkable equation known as the Saha Ionization Equation (SIA), also referred to as the Saha Ionization Formula (SIF) written down by Meghnad Saha [1]. At that time Saha was about twenty-six, exactly the same age as another great Bengali physicist and a close friend – Satyendra Nath Bose. About the celebrated equation, Bose is quoted to have remarked to a gathering of his students: “Do you know what Meghnad did? Sitting at home, he measured the temperature of stars!” [2]. The originality and the far-reaching consequences of the SIA are so remarkable that the said theory is said to be the harbinger of modern astrophysics [3]. Saha’s work created a stir in then-Calcutta which was, at that time, arguably the centre of not just physics but all forms of intellectual pursuits of India. An example of the societal impact of the famous equation can be discerned in a popular book on science in Bengali written by Asia’s first Nobel Laureate Rabindranath Tagore, in the mid nineteen thirties, named *Viswa-Parichay (An Introduction to the Universe)*. Tagore wrote and we translate: “It is expected that the ninety-two elements that have been found on the Earth must have had their traces in the Sun too. Only thirty-six of these were however discovered in preliminary



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Keywords

Ionization, astrophysics, spectroscopy, chemical reaction, transition state.



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investigations. It is the Bengali scientist Meghnad Saha who has unearthed (the pun is mine) the puzzle of the missing elements in the Sun” [4].

Much has been written about the history of physics preceding Saha’s pioneering research, the West’s grudging acceptance of his equation and how the latter had influenced and spurred subsequent activities in astrophysics [5]. A detailed biography along with a lucid account of the SIA has also been presented in a form readily available to university students [6]. Our aim in this article is not to delve into history but to offer a critical assessment of how Saha moulded and integrated the just-evolved quantum model of Bohr and the consequent spectroscopy of atoms, the extant knowledge of thermodynamics, and what is also significant – the theory of chemical rate processes. Indeed our emphasis is to put Saha’s work in the modern context of equilibrium and non-equilibrium statistical mechanics, in a fairly nontechnical format. Hopefully, our relook at this nearly hundred-year-old equation would illustrate to today’s young students the importance of interdisciplinary research.

An outline of the paper is as follows. In Section 2 we indicate what spectroscopic considerations led Saha to formulate his simplified model of the ionized stellar atmosphere, and inter alia, introduce an important parameter called the ionization potential denoted by U , by way of the specific case of sodium [6]. This part of the discussion relates to Saha’s use of the Bohr model of the atom and measurement of the spectral line that yields U . Section 3 is the core of the paper which describes how Saha ingeniously took recourse to the notion of thermodynamic equilibrium in the context of chemical reactions. The fascinating simile that Saha employed between ionization and chemical reactions allowed him to relate the concentrations of species involved in the ionization (dissociation) process to the exponential of a parameter ($-U/k_B T$), k_B being the Boltzmann constant and T the temperature. Now comes another startling cross-border foray – Saha wrote the said concentrations in terms of ratios of partition functions – a key concept of Gibbs’ statistical mechanics.



As we mentioned at the outset, our objective here is not merely a recounting of what Saha did but, more importantly perhaps, what he had anticipated and what he had implied but did not spell out! Recall that the enunciation of the SIA had preceded by almost fifteen years Eyring's 'Transition State Theory' of chemical reactions, which very craftily connected the rate of chemical reactions to the statistical mechanics of partition sums (see [8] and accompanying articles on p.11 and p.103 in this issue). While making this analysis of post-Saha developments we wish to point out that a concept like a rate that connotes to 'a change of something with respect to time', is outside the realm of thermodynamics and statistical mechanics, as the latter deals with phenomena in thermal equilibrium. The key hidden idea of Saha, and indeed also of Eyring, is that the rate is actually a 'steady-state rate', and hence, the underlying 'chemical equilibrium', in point of fact pertains to a stationary or a steady state which must be the culmination of a dynamical process that describes the approach to equilibrium. The latter process has to be described by going beyond equilibrium statistical mechanics and by writing time-dependent rate equations that explicitly violate time-reversal invariance and incorporate dissipation – ingredients which are outside the scope of the formulation of Gibbs and indeed that of Saha. The steady-state rate has to be extracted from the asymptotic (i.e., time t going to infinity) limit of the rate equations in terms of ratio of partition functions, as anticipated by Saha. Such a theory is attributed to the path-breaking work of Kramers which, in the language of chemical reactions – the language employed by Saha – analyzes a diffusion equation of a Fokker–Planck structure that builds-in, through the so-called 'drift' term, a thermodynamic 'free' energy as a function of reaction coordinates [9]. How the Kramers rate gets linked to the ratio of partition functions of the 'products' and 'reactants', as in the SIA, is relegated to the Appendix (which is intended for the more advanced and curious reader). Finally, Section 4 offers a few concluding remarks.

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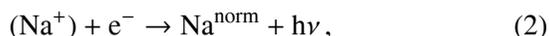
2. The Ionization Potential

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Clearly, the emitted electron would possess a kinetic energy that would be governed by the temperature of the gas via the classical equipartition theorem. The reverse process of association, in which an ionized sodium atom captures an itinerant electron, would yield a neutral atom but in an excited state, concomitant with the release of energy in the form of emission of a photon of frequency ν :



h being the Planck constant. Within the theories of Eyring and Kramers the process in (2) can be diagrammatically represented by *Figure 1*, in which the transition state is an activated 'complex' – Na^{exc} , in the present case. It is interesting also to write the



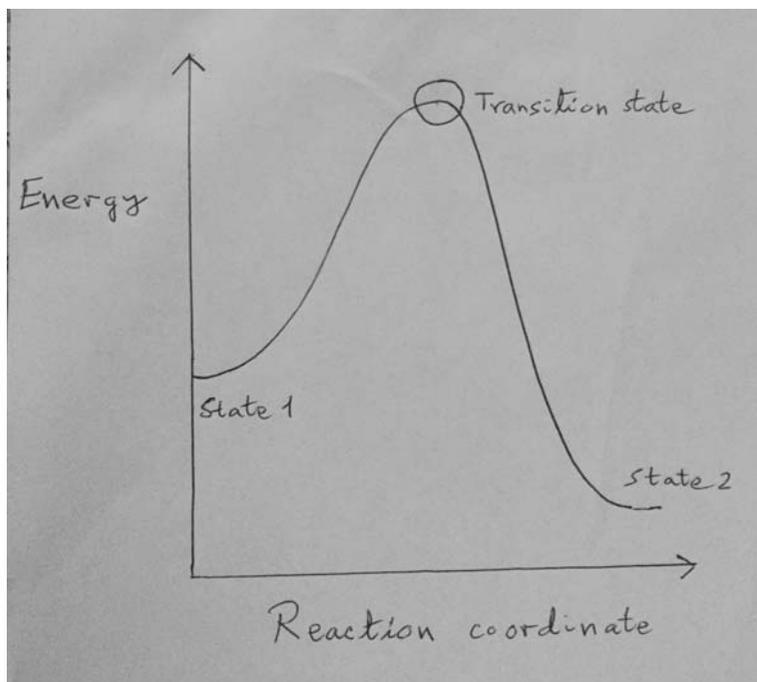


Figure 1. Energy versus reaction coordinate, in which State 1 corresponds to the ‘reactants’ – in this case Na ion and electron, and State 2 corresponds to the ‘products’, that is normal Na. The transition state is a saddle point that describes an activated complex in the form of Na in the excited state, in the present scenario.

energy balance akin to the so-called ‘photo-ionization’ process, in the light of *Figure 1*:

$$\text{Na}^{\text{norm}} + h\nu = \text{Na}^+ + e^- + h\nu_K, \quad (3)$$

where $h\nu_K$ is the energy corresponding to the kinetic energy of the ejected electron. Photo-ionization is then exactly akin to the photoelectric effect in which an electron is emitted by a metal upon being impinged by an incident electron. Evidently,

$$U = h(\nu - \nu_K). \quad (4)$$

In the context of photoelectric effect, U is called the work function of the metal.

The SIA, in this case of sodium, can then be simply written as:

$$[(x^+) \cdot (x^-)]/x = [2\pi m_e (k_B T)/h^2]^{3/2} \cdot \exp[-(U/k_B T)], \quad (5)$$



U being the ionization potential. The lower case x 's denote the respective concentrations of positive ions, electrons, and neutral atoms. The left-hand side of (5) is often referred to as 'equilibrium constant' or 'chemical constant', in the literature on chemical reactions. Saha further expressed the left hand side of (5) in terms of dimensionless concentrations and the pressure of the stellar gas with the aid of the ideal gas law. The derivation of (5) is provided below, in Section 3, and more elaborately, in Appendix 1.

If the excited state corresponds to the outer electron being in the $4p$ state ($n = 4, l = 1$) with the total angular momentum $j = 1/2$, the photon would have a wavelength of 5896 Angstrom, while a $4p$ - excited state ($n = 4, l = 1$) with $j = 3/2$ would lead to a photon of wavelength 5890 Angstrom, as illustrated in [1]. These two spectral lines form the familiar doublet, with a wavelength difference of 6 Angstrom due to spin-orbit interaction, that can be viewed in a sodium vapour lamp in an undergraduate physics laboratory. Of course, depending on the kinetic energy of the electron prior to its capture, the excited state is not just limited by the ones associated with the familiar doublet but indeed is one of a whole lot of states of the S-, P-, D-series (and $n = 3, 4, 5, \dots$ and others, going into the continuum). Besides, there can be multiple ionizations involving more than one electron. Now comes the crucial link with the Bohr quantum theory of atom. Saha surmised that the emitted photon must be the result of a transition from one discrete level to the 'normal' $3s$ -level (lower in energy) such that the energy of the photon would be related to the ionization potential U by (4). However, it may be pointed out that the transition from a discrete level to the ground level can have an energy less than U - e.g., in hydrogen, $2p$ to $1s$ transition would yield 10 eV as opposed to 13.6 eV for U . As we had explained, there would be not just one U but a series of them, which were all measured by Saha. He also looked at the spectrograph of numerous other stellar gases data from Harvard University and extracted U for all of them. Note that quantum mechanics enters into consideration only with regard to the identification of U while the rest of the theory simply



hinges on the classical kinetic theory of gases.

In order to get an idea of the numbers involved, it is best to look at a simpler dissociation process, that of neutral hydrogen into a hydrogen ion and an electron, like in (1), and treated in [11]. In this case, there is a solitary ionization potential U whose magnitude is 13.6 eV, of the order of the Coulomb energy, if we take the atomic radius to be about 1 Angstrom. Converting it to wavelength λ we obtain $\lambda \sim 10^3$ Angstroms, and a temperature $T \sim 1.6 \times 10^5$ K. Hence, the transition state theory works well for interstellar temperatures even somewhat higher than 10^4 K, and of course at lower temperatures.

3. Theory of Chemical Reactions

As has been stressed earlier, Saha's goal was to determine the temperature of stars from spectroscopic data. Clearly, therefore, he needed a theory in which the ionization energy U and the thermal energy $k_B T$ ought to enter on an equal footing. To this end, we can imagine à la Saha, the association process of (2) to be akin to a chemical reaction of two species (Na^+) and (e^-) resulting into neutral Na [11].

Onset of chemical equilibrium implies that the net free energy in the above process must vanish. Recall that the differential change in the free energy F , from thermodynamics, is given by:

$$dF = -PdV - SdT + \mu dN, \quad (6)$$

where P is the pressure, V is the volume, S is the entropy, T is the temperature, μ is the chemical potential, and N is the number of species. If the reaction takes place at constant volume and constant temperature, the first two terms on the right of (6) are zero, and hence, equilibrium ($dF = 0$) means the net μdN must vanish [12]. Because the magnitude of dN is unity, for all the three species in (2),

$$(\mu^+) + (\mu^-) = (\mu), \quad (7)$$



where, by (+) we mean (Na^+), by (–) we mean (e^-), and μ without superscript is meant for neutral Na. Combining (4) and (5),

$$(\partial F/\partial N)_{V,T}^+ + (\partial F/\partial N)_{V,T}^- = (\partial F/\partial N)_{V,T}. \quad (8)$$

Until now, only thermodynamic considerations have been employed. But, following Saha, in order to bring-in U , we now need to express the derivatives in (8) in terms of the partition function Z of statistical mechanics [12, 13]. Recall that Z and F are connected by [11–13]:

$$F = -k_B T \ln Z, \quad (9)$$

and Z is the product of two components, one for translational motion of the species (no rotational or vibrational component is relevant for (2)) and the other for the internal (quantum) variables [11]:

$$Z = [(Z)_{\text{tran}}(Z)_{\text{int}}]^N, \quad (10)$$

where the presence of the power N hinges on our assumption that the species N do not interact with one another. Evidently, the translational component relates to the kinetic energy of motion, and hence,

$$[(Z)_{\text{tran}}]^N = [1/(N!)]\{V(2m_e\pi k_B T)^{3/2}/[(h)^3]\}^N. \quad (11)$$

The mass m for Na and Na^+ can be taken to be nearly the same and hence, the respective translational contributions to Z are equal, leaving only the kinetics of the electron to reckon with, for which however, there is no internal contribution to Z ! The pre-factor ($N!$) takes care of the correct ‘Boltzmann counting’ in view of the indistinguishability of individual species. Using the Stirling approximation,

$$\ln(N!) \sim N[\ln(N) - 1],$$

(7–9) can be combined to yield for the chemical potential μ :



$$\mu = (\partial F/\partial N)_{V,T} = k_B T \ln(Z)_{\text{int}} + \ln[(V/N) \cdot (2m_e \pi k_B T)^{3/2} / h^3]. \quad (12)$$

Incidentally, (11), in combination with the Stirling formula, yields the Sackur–Tetrode equation for the entropy of an ideal gas at high temperatures, that Saha was quite aware of [13]. Balancing the chemical potentials as in (7) and writing the ratio N/V as the concentration x , we have:

$$[\ln(Z)_{\text{int}} - \ln(Z^+)_{\text{int}}] = \ln(x^+) + \ln(x^-) - \ln(x) - \ln\{[2\pi m_e (k_B T)/h^2]\}^{3/2}, \quad (13)$$

m_e being the electron mass. Rearranging terms,

$$[(x^+) \cdot (x^-)]/x = [2\pi m_e (k_B T)/h^2]^{3/2} \cdot [(Z_{\text{int}})]/[Z^+]_{\text{int}}. \quad (14)$$

Using (9) the ratio of the internal partition functions turns out to be the exponential of the difference of the respective free energy which, for internal dynamics, is precisely the ionization potential U . Thus, we are led to the SIA quoted earlier in (5). Couched though in the simplified scenario of Na atoms, (14), in essence, is the core thesis behind the SIA. As anticipated in the first paragraph of this section, what appears in the equation is the dimensionless ratio of the ionization energy and the thermal energy.

4. Epilogue

In conclusion, we go back to where we started. As we have emphasized in the introductory section, our motivation to write this pedagogical essay was to take stock, after nearly one hundred years, of the ionization equation, and to underscore the significance of interdisciplinary signatures behind Saha’s futuristic and far-reaching thoughts. Today, we have the advantage of hindsight – over nearly a century – but it is amazing to ponder on how a young Indian scientist, working under adverse conditions of colonial regime, dared to piece together a variety of phenomena, spread over different topics of science, to lay the foundation

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of a completely novel area – that of stellar atmosphere. Through this essay we wish to pay tribute to this great man, an institution-builder, a champion of research in universities, a planner of post-independent India – especially with regard to atomic energy and the river system [5, 6] – who is alas largely forgotten in the humdrum of today’s pursuit of cocooned, specialized research.

5. Acknowledgments

While carrying out this work I have benefitted from useful inputs by Profs. Mustansir Barma, Jayanta Bhattacharjee, Kumar Chitre, Naresh Dadhich, Partha Ghose, Harihara Subra Mani, and Narayanasami Sathyamurthy, to whom I am indebted. I am particularly grateful to Profs. Barma, Chitre, and Sathyamurthy for critical reading of the manuscript and invaluable comments which have led to improvement in the presentation. I am also thankful to the Senior Scientist scheme of the Indian National Science Academy, New Delhi, for supporting my research work at the Bose Institute. Finally, I record my gratitude to a referee for raising pertinent issues that have helped enhance the clarity of the paper.

Appendix 1. Kinetics – Ionization Equation in a Post-Saha Perspective

A moment’s thought would reveal that the derivation of the ionization equation, as sketched in Section 3, is based on purely equilibrium considerations as extant in thermodynamics and exploits the fact that in equilibrium, the net chemical potential of the reacting species vanishes. By the same token, a non-zero net chemical potential ought to be the driving force to take the system out of equilibrium. We may then invert the question and ask: Can (14) be arrived at, as the end-product of a dynamic process when all time-dependent variables have reached their constant, equilibrium values? In other words, can we relate the left hand side of (14) to a rate constant, though Saha actually bypassed the concept of rate in his original papers? To find the answer to this poser the rate of production of (Na) from (Na⁺) and (e⁻) can be formulated in terms of a first order rate equation of the form:

$$(d/dt)[x(t)] = \gamma_1(T)[x^+(t)] \cdot [x^-(t)] - \gamma_2(T)[x(t)], \quad (\text{A.1})$$

Continued



Appendix 1. Continued.

where the γ 's are temperature-dependent terms which have the dimension of frequency $[(t)^{-1}]$ and are appropriately called rate constants. Such rate equations are frequently encountered in a variety of situations, such as radioactive decay, population dynamics of predators and preys, to name a few. Innocuous though they look, the rate equations of the kind (A.1) disobey time-symmetry as the left hand side changes sign when t is reversed to $-t$, an attribute that is absent in Newton's classical mechanics, Schrödinger's quantum mechanics or Gibbs' statistical mechanics! While (A.1) provides a description for a system out-of-equilibrium, a straightforward way of handling equilibrium would be to set the left side of (A.1) to zero, when $[x]$ reaches a constant value. In that case,

$$\{[x^+] \cdot [x^-]\}/[x] = [\gamma_2(T)]/[\gamma_1(T)]. \tag{A.2}$$

The condition (A.2) is often referred to as 'detailed balance'. If the right hand side of (A.2) is designated as a temperature-dependent constant $\Omega(T)$, the latter evidently equals, in the case of association/dissociation of sodium vapour, the right hand side of the SIA (5). As a matter of fact, Saha did introduce the concept of 'reaction rate' without however going through the subtleties discussed in this section [1, 7]. An exponential temperature dependence of $\Omega(T)$ on a parameter, like $(-U)/k_B T$, is not uncommon in evaporation of liquid into vapour, or thermal emission of an electron from a filament in a diode [14], etc. Just as evaporation of water, for instance, can take place at temperatures much lower than the normal boiling point – and at thermal energies smaller than the latent heat – so can ionization occur at temperatures substantially below that corresponding to the ionization potential [15]. Indeed, the entire validity of the concept of transition state hinges on the barrier height (*Figure 1*) being 'larger' than the thermal energy [16].

We wish to dispose of one red herring in the literature discussion – made almost in the same breath – of an 'equilibrium' state and a 'stationary' state. To expound on that issue, consider the familiar problem of electric current flow in a metallic wire when connected to a battery. The velocity $v(t)$ of the electron (assumed one-dimensional, for the sake of simplicity) obeys the equation [17]:

$$m_e(d/dt)v(t) = -m_e\gamma(T)v(t) + |e| \cdot E, \tag{A.3}$$

where $|e|$ is the magnitude of the electron's charge and E is the electric field intensity provided by the battery. The temperature-dependent term $\gamma(T)$, like the γ 's occurring in (A.3) is also a rate that incorporates the collision losses of the velocity due to scattering of the flowing electron. The presence of the term $\gamma(T)$ explicitly breaks the invariance of an otherwise time-reversal-invariant Newtonian equation. As before, we arrive at a time-independent solution of (A.3) as:

$$(v)_0 = |e| \cdot E/[m_e\gamma(T)]. \tag{A.4}$$

Writing (A.4) as a current density and relating it to E via Ohm's law immediately leads to the familiar Drude formula for electrical conductivity in which the inverse of $\gamma(T)$ is often referred to as the 'relaxation time'. What this facile derivation of the Drude law camouflages however is the fact that a 'dissipative' parameter

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Appendix 1. Continued.

like $\gamma(T)$ shows up in a steady-state property like the conductivity! Now comes the punch line: Equation (A.4) is the culmination of a transport process in the steady state (such as also in the onset of a terminal velocity of a ball falling under gravity through a Stokes medium of a viscous liquid); on the other hand, the dissipative rate parameter, which aids the process of reaching thermal equilibrium, is conspicuously absent in the end-product of the SIA (5)! It is important to bear in mind this distinction between a ‘driven’ steady state, such as electric conduction driven by a battery, as opposed to a thermal equilibrium state, such as prevailing in intrastellar ionization, albeit both are time-independent solutions of underlying rate equations.

With this preamble we now outline the theory of activated rate processes due to Kramers which subsumes Eyring’s earlier work on the transition state theory. The starting point of Kramers is essentially a diffusion equation for a probability density $P(r, t)$ in the phase space defined by generalized coordinates $\{r\}$ (referred to as reaction coordinates in chemical reactions) with however a drift term [9, 17]. The latter has its origin in a force field that can be viewed as the gradient of a potential energy $V(r)$, or in the more general thermodynamic setting, a free energy. It is written as

$$(\partial/\partial t)P(r, t) = (1/\omega) \cdot \{(k_B T)(\partial^2/\partial r^2)P(r, t) + (\partial/\partial r)[V(r) \cdot P(r, t)]\}, \quad (\text{A.5})$$

where ω is a constant that fixes the dimension of both sides of the equation. Note that if drift is absent such as in the continuum version of an unbiased random walk [18], we recover the ordinary diffusion equation:

$$(\partial/\partial t)P(r, t) = D(\partial^2/\partial r^2)P(r, t), \quad (\text{A.6})$$

where the diffusion constant D is given by the Einstein relation:

$$D = k_B T/\omega. \quad (\text{A.7})$$

Further, in the time-independent state, a form of $P(r)$ that is a solution of (A.5) is given by

$$P_{\text{eq}}(r) \sim \exp[-V(r)/(k_B T)], \quad (\text{A.8})$$

which is the Boltzmann–Gibbs measure (un-normalized) for a system in thermal equilibrium. Thus, the diffusion equation we wrote in (A.5) builds-in, at the outset, the thermal equilibrium state that can be reached asymptotically (as t goes to infinity). (Needless to say, if the situation so demands, we can also employ a diffusion equation of the same form as in (A.5) to describe a steady state that is not necessarily an equilibrium state, in the senses delineated above.) Like the Schrödinger equation, the diffusion equation (A.5) can be written as a continuity equation:

$$(\partial/\partial t)P(r, t) + (\partial/\partial r)J(r, t) = 0, \quad (\text{A.9})$$

where the current density is

Continued



Appendix 1. Continued.

$$J(r, t) = -(1/\omega)\{(\partial/\partial r)V(r) + k_B T(\partial/\partial r)\}P(r, t). \quad (\text{A.10})$$

As we have elaborated upon earlier, we are interested in the approach to equilibrium, in the quasi-stationary state, in which $P(r, t)$ is a slowly varying function of time. Correspondingly, as (A.9) suggests, that is also the state in which $J(r, t)$ is almost independent of r , and can be represented by:

$$J_{qs}(t) = -(1/\omega)\{(\partial/\partial r)V(r) + k_B T(\partial/\partial r)\}P_{qs}(r, t), \quad (\text{A.11})$$

wherein the right hand side containing the quasi-stationary probability P_{qs} and other r -dependent terms must conspire in such a manner as to render $J_{qs}(t)$ almost r -independent! The quasi-stationarity of $J_{qs}(t)$ is indeed the key idea of the transition state, i.e., the latter is a state of ‘no return’ [16]. Once the classical trajectories reach the saddle point in *Figure 1*, there is no looking back – the reaction ‘slides down’ to the reactant-state at a steady rate. Given this background to the form of quasi-stationary current we now specialize to the ionization reaction as depicted in (1). Adapting to the language of the transition state theory, the combination of (Na^+) and (e^-) can be dubbed as the ‘reactant’, localized in ‘State 1’, while (Na) is the ‘product’, localized in ‘State 2’ (see *Figure 1*).

State 1 and State 2 are separated by a large barrier in the space of $V(r)$ versus r where the top of the barrier is actually the transition state. In the more general setting of a molecular reaction, r represents a ‘reaction coordinate’ which could be a bond direction. Also, $V(r)$ versus r , in that case, is a free energy landscape. Once the ‘activated complex’ of the $(\text{Na}^+)-(e^-)$ pair reaches the transition state it proceeds to the product state of neutral Na . The rate equation (A.2) can now be transcribed to the form:

$$(d/dt)p_2(t) = -(d/dt)p_1(t) = J_{qs}(t), \quad (\text{A.12})$$

where

$$p_2(t) = [Na] = [x(t)], \quad (\text{A.13})$$

and similarly,

$$p_1(t) = [Na^+] \cdot [e^-] = [x^+(t)] \cdot [x^-(t)]. \quad (\text{A.14})$$

We now carry out the following steps in order to arrive at the desired structure of the rate equation.

Step 1

Note that for a ‘large’ barrier height the quasi-stationary probability is expected to be ‘peaked’ around r_1 and r_2 , hence

$$p_1(t) = \int_{r_1-dr_1}^{r_1+dr_1} P_{qs}(r, t) dr \sim P_{qs}(r_1, t) \left[\exp\left(\frac{V(r_1)}{k_B T}\right) \right] \cdot \int_{r_1-dr_1}^{r_1+dr_1} dr \left[\exp\left(-\frac{V(r)}{k_B T}\right) \right], \quad (\text{A.15})$$

Continued



Appendix 1. Continued.

dr_1 being a small region around r_1 . Here we have used the fact that near equilibrium,

$$P_{qs}(r, t)/[\exp(-V(r)/k_B T)] \sim P_{qs}(r_1, t)/[\exp(-V(r_1)/k_B T)]. \quad (\text{A.16})$$

Interchanging 1 and 2 we obtain a similar expression for $p_2(t)$.

Step 2

Using (A.15) and a similar one for $p_2(t)$ we plan to express $J_{qs}(t)$ in terms of $p_{1,2}(t)$. To this end, we rewrite $J_{qs}(t)$ in (A.11) as

$$J_{qs}(t) \cdot [\exp(V(r)/k_B T)] = -D \left(\frac{\partial}{\partial r} \right) \left\{ \exp \frac{V(r)}{k_B T} P_{qs}(r, t) \right\}, \quad (\text{A.17})$$

and integrate both sides over r from r_1 to r_2 to obtain

$$J_{qs}(t) = -[1/(DI_3)] \{ [\exp(V(r_2)/k_B T)] P_{qs}(r_2, t) - [\exp(V(r_1)/k_B T)] P_{qs}(r_1, t) \}, \quad (\text{A.18})$$

where

$$I_3 = \int_{r_1}^{r_2} \exp[(V(r)/k_B T)] dr. \quad (\text{A.19})$$

Further, from (A.15),

$$J_{qs}(t) = -[1/(DI_3)] \{ p_2(t)/I_2 - p_1(t)/I_1 \}, \quad (\text{A.20})$$

which was the desired goal of step 2. In (A.8),

$$I_1 = \int_{r_1-dr_1}^{r_1+dr_1} \exp \left[-\frac{V(r)}{k_B T} \right], \quad (\text{A.21})$$

and a similar expression holds for I_2 . We now have (A.12) in the coveted form of (A.1):

$$(d/dt)p_2(t) = [1/(DI_3)] \{ p_1(t)/I_1 - p_2(t)/I_2 \}. \quad (\text{A.22})$$

Comparing with (A.18) we can identify,

$$\gamma_1(T) = [1/(DI_1 I_3)], \gamma_2(T) = [1/(DI_2 I_3)], \gamma_1(T)/\gamma_2(T) = I_2/I_1. \quad (\text{A.23})$$

Continued



Appendix 1. Continued

Recalling that I_1 refers to the ‘reactant’ state, the integral over the Gibbs–Boltzmann measure in (A.21) is just the corresponding partition function that yields the Boltzmann factor for the internal state of (Na^+) ion apart from the partition function of the free motion of the electron (e^-), whereas I_2 is the corresponding Boltzmann factor associated with the internal (excited) state of neutral (Na). Thus, we recover the Saha equation (5) in the text! It is interesting to point out that though the Saha equation refers only to the ratio of the two rates, as in (A.23), and hence the said equation does not involve the rate explicitly, the more general kinetic formalism of Kramers allows one to estimate the individual rates as well, via the first two expressions in (A.23). Indeed Kramers calculated I_1 , I_2 and I_3 by the saddle-point approximation around the transition state [9, 18]. Further, it is fair to stress that the transition state theory of Eyring and Kramers, following the pioneering work of Wigner, is much richer in structure than what is needed to derive the ionization equation. Indeed Wigner’s work, which is the earliest in the field, already had considered various generalizations of the transition state theory, including corrections to the rate when the stipulation of ‘high barrier-weak thermal energy’ breaks down as well as when quantum effects are important [16]. Also, the basic assumption of the transition state that it is a point of no return allows the Kramers rate, or more accurately its inverse, to be related to what is called the ‘mean first passage time’ [19]. It is not surprising then that the ratio of ‘first passage times’ gets related to the ratio of partition functions, as is often invoked in sophisticated analyses of the random walk problem [20].

Suggested Reading

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