The Many Footprints of Henry Eyring

Pallavi Bhattacharyya

Henry Eyring is most well-known as the proponent of the activated complex (transition state) theory for chemical reactions. He was also the one to construct the first Potential Energy Surface along with Michael Polanyi. Apart from his exemplary work in chemical kinetics, the plethora of problems he engaged in establish his versatile genius. Evaluation of dipole moments in complex molecules, one-electron theory for optical activity, conformation changes in proteins, deformation kinetics in materials are some of the fields where his contributions have been immensely significant. He was a prolific writer and authored more than 600 articles and 10 scientific volumes. This article will discuss the contributions of Henry Eyring.

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Chemistry as a science was known even to ancient civilizations, but a systematic study of the physics behind chemical reactions began much later. It was as late as 1850 that the rate of a chemical reaction was first measured by Lugwig Wilhelmy [1]. He used a polarimeter to study the acid-catalysed conversion of sucrose into a 1 : 1 mixture of fructose and glucose. Soon after, in 1889, Svante Arrhenius proposed the concept of an activation energy – the energy threshold which the molecules must overcome in order to undergo a reaction. The famous Arrhenius equation, based on empirical observations, for chemical equations is given as $\ln k = B - A/T$, (k is the reaction rate, A and B are parameters for a given reaction and T is the absolute temperature). This apparently simple expression became the master equation of reaction kinetics and physical chemists around the world were mobilized in their attempts to rationalize the observations of Arrhenius.

Steady contributions from researchers helped sustain a gradual evolution towards more sophisticated treatments and several new concepts were born, including that of the entropy of activation of a reaction proposed in 1911 by Scheffer in collaboration with Kohnstamm. In their formulation, in addition to the energies, they incorporated entropy terms for the reactant molecules as well as for an intermediate state which could be thought of as the activated state. The subsequent important development came in 1918: the calculations of W C McC Lewis where he formulated that the rate of a bimolecular reaction equals the number of activated collisions, i.e., molecules reacting = molecules colliding $\times\ e^{-E_a/k_\mathrm{B}T}$, where E_a is the difference in energy between the reactants and the activated state and k_B is the Boltzmann constant. There were a host of exciting studies which followed suit, notably those on unimolecular reaction rates by Lindemann, Hinshelwood, Rice and Rampsberger, and Kassel. However, the study of reaction dynamics achieved a giant leap in 1929 when a young researcher Henry Eyring and his advisor, Michael Polanyi, at the Kaiser Wilhelm Institute in Berlin, proposed the potential energy surface (PES) formalism for reaction dynamics.

1. Potential Energy Surface (PES)

Eyring's pursuit in the Polanyi laboratory was based on the experimental findings of Bonhoffer and Harteck on the conversion of para to ortho hydrogen. In the well documented reports by Bonhoffer and Harteck, Eyring saw the possibility of discovering a new approach to reaction dynamics. Thus was born the potential energy surface formalism and Eyring and Polanyi [2] constructed the first potential energy surface for the reaction: $H + H_2 \rightarrow H_2 + H$. The genesis of this formalism and a simplified construct is provided here.

Henry Eyring and Michael Polanyi constructed the first Potential Energy Surface.

A surface which gives the potential energy of reacting molecules as a function of their position, orientation and

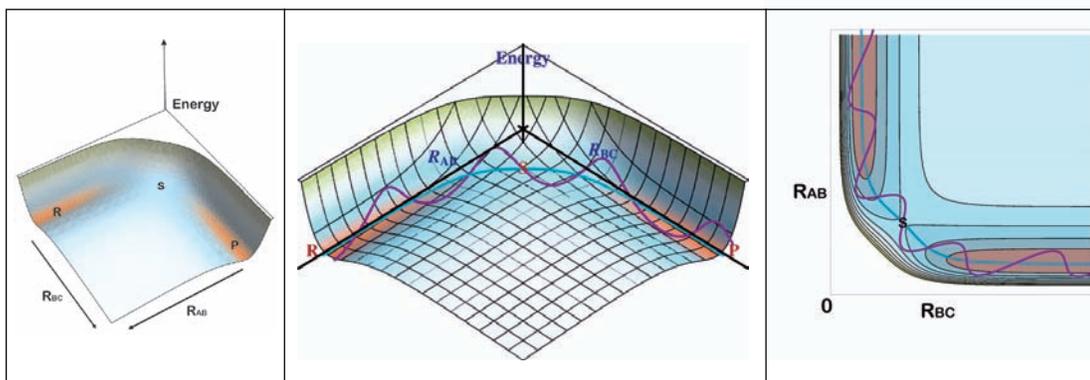**Figure 1 (left).** PES for the reaction $H + H_2 \rightarrow H_2 + H$; R denotes reactants and P denotes products. S stands for saddlepoint.

Figure 2 (center). Two possible paths for the reaction $H + H_2 \rightarrow H_2 + H$. The orange line shows the path that needs the minimum amount of energy and thus determines the activation energy. It is not necessary that the system should follow this path. If it has enough energy it may follow the purple (or a similar) path; R denotes reactants and P denotes products. Saddlepoint is denoted by S.

Figure 3 (right). It is difficult to draw PES in the fashion shown in *Figures* 1 and 2. An alternative is to draw contour plots where each line connects points of the same potential energy. The two paths in *Figure* 2 too are shown in this figure; saddlepoint is denoted by S.

interatomic distances is referred to as the potential energy surface (PES) (see *Figures* 1 and 2). As surfaces are difficult to draw, the same information is usually represented as a contour plot (see *Figure* 3).

We know that a molecule system with N atoms has $3N$ degrees of freedom. Out of these, 3 are translational and the rotational degrees of freedom are 3 for a non-linear molecule and 2 for a linear molecule. Consequently we have $3N - 6$ vibrational degrees of freedom for a non-linear molecule and if it is a linear molecule we are dealing with, then there will be $3N - 5$ vibrational degrees of freedom. The potential energy of a system is essentially independent of the translation of the system as a whole. It also does not change if one rotates the whole system. Therefore the number of coordinates required to define the potential energy of a system of N atoms will be $3N - 5$ for a linear system and $3N - 6$ if it is

non-linear. *Figure* 1 is the PES for a three-atom reaction:

$$H_A + H_B H_C \rightarrow H_A H_B + H_C.$$
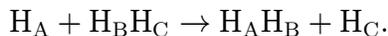
For our three atom system we have made things simpler by assuming that the system has a linear geometry in which all the atoms are constrained to be along a line, as $H - H - H$. Assumption of a linear geometry means that we do not include possible effects of bending on the reaction dynamics. It is certainly possible that the reaction occurs via a non-linear geometry but that would entail a more involved and difficult analysis. Two parameters are important for the linear geometry: i) $H_A - H_B$ separation, denoted as R_{AB}, and ii) $H_B - H_C$ separation, denoted as R_{BC}. A plot of the potential energy of the system as a function of the two variables R_{AB} and R_{BC} is shown in *Figures* 1 and 2 and is the PES for this system. The reason why this is referred to as the PES is that the kinetic energy of the atoms are not considered in making the plot.

Initially, we have the reactants: H_A, the hydrogen atom and $H_B H_C$ the hydrogen molecule, at a large separation. Consequently, R_{AB} is large. R_{BC} is the H_2 equilibrium bond length. In the PES, this corresponds to the valley shown in orange in the region marked R in *Figures* 1 and 2. The products have large value for R_{BC}, and equilibrium value for R_{AB}, and correspond to the valley shown in orange in the region marked P in the *Figures*. The two valleys are separated by regions of higher potential energy (the mountainous region) in the vicinity of the point S in *Figures* 1 and 2. In order to go from the reactant valley R to the product valley P, it is easiest if one follows the blue path in *Figure* 2. Then the energy will increase at first, reach its maximum value at the point S (usually referred to as the saddle point) and then decrease. The blue path is unique in that it is the one that has the smallest value for its slope. If one follows this path from R to S, the climbing up will
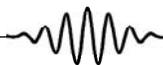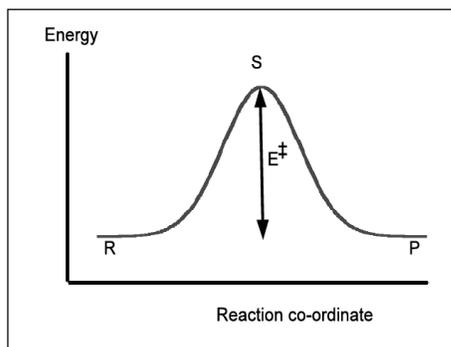
be easiest along this path. Similarly as one goes from S to P too, the slope will have the least value. The distance travelled from R along this path may be referred to as the reaction co-ordinate. If one plots the energy as a function of the reaction co-ordinate, then the energy steadily increases until one reaches S and then it decreases (see *Figure* 4). If one starts at S and moves along the reaction co-ordinate (the blue curve) in the direction of products or in the direction of reactants, the energy will decrease. But if one moves away from S, in a direction that is perpendicular to the reaction co-ordinate, the energy will increase! Thus the shape of the PES in the vicinity of the point S reminds one of a saddle and hence S is referred to as the saddle point. Imagine a marble sitting at S. If you displace it slightly along the reaction co-ordinate it will roll off, never to return and hence we say that this direction is an unstable mode. On the other hand, if you displace in the perpendicular direction it will come back and execute oscillations in that direction, implying that it is a stable mode. This is universal – a saddle always has one unstable direction and motion in all the other directions are stable.

It is not necessary that the system should follow the blue path for the reaction to occur. It may follow the pink path shown in *Figures* 2 and 3 or an infinity of similar possible paths. But it is obvious that the system should at least have enough energy to go over the saddle point

– only then reaction will occur. Thus the energy that the reactants should possess to reach the saddle point is the minimum energy needed to go from the reactant to the product side, and hence this energy is referred to as the activation energy $E^\ddagger$. Drawing a surface like the one in *Figure* 2 is tedious. However, the information contained in this figure can be condensed and represented by the contour plot as shown in *Figure* 3. In a contour plot, the potential energy has the same value along any contour.

2. The Activated Complex and the Rate Constants

After his stay at Berlin, Eyring returned to the University of California at Berkeley. Subsequently, he worked rigorously on PES with interesting results. In one of his studies, he explored why iodine is the only halogen which forms a four-atom activated complex in hydrogen–halogen reactions whereas all others form three-atom complexes. After this work surfaced, he received an invitation to move to Princeton University where he would be engaged in highly successful research for the next fifteen years. It was at Princeton that he worked with activated complexes and specific rate constants for reactions.

The usual procedure then for computing rate constants for bimolecular reactions employed the concept of collision theory. Here one estimates the number of collisions from a cross-sectional area evaluated from momentum transfer measurements. The drawbacks are several, the most profound being that the cross-sectional area doesn't relate clearly the steric orientation required to exchange mass as that would be one of the factors to determine the violence of the collisions. This is generally bypassed by introducing an empirical steric factor which takes care of the discrepancy between the observed and the computed chemical reaction rates. The steric factor usually has a value between 1 and 10^{-1} but might be

In one of his initial studies using PES, Eyring explored why iodine is the only halogen to form a four-atom activated complex in hydrogen–halogen reactions whereas all others form three-atom complexes.

as small as 10^{-8}. Eyring propounded a theory which gave a means of evaluating reaction rates to better accuracy [3]. Eyring and Polyani had already constructed potential energy surfaces for reactions employing London's idea that most reactions proceed adiabatically, i.e., only the lowest electronic state of the reactant is involved. The potential energy surface provided information which Eyring used to compute rates. In Eyring's calculations, statistical mechanics gives the probability of the activated state, which when multiplied with the rate of decomposition gives the rate.

We now give a simplified version of the theory due to Eyring. His calculations involved the following basic ideas: First one computes the PES for the system comprising of reactants leading on to the formation of products. The PES would be a surface of $3N-6$ dimensions. The low-lying regions correspond to stable configurations. A reaction involves passage from one low-lying region to another over the saddle. However, there could be several such pathways and the reaction is most likely to occur via the pathway which requires the minimum energy. The system possesses kinetic energy which gets distributed and quantized amongst the degrees of freedom corresponding to coordinates of the system in the potential energy surface. For instance, consider the following reaction:

$$A + B \rightarrow P.$$

Eyring postulated that the reactant molecules, A and B must form an 'activated complex', $AB^{\ddagger}$ in order to react. In the light of our earlier discussion, we say that the activated complex is formed if the system manages to reach the region of the saddle. The activated complex has a fleeting existence and whether $AB^{\ddagger}$ would proceed in the forward direction to form P or return in the backward direction to decompose into A and B is determined by the geometry and configuration of $AB^{\ddagger}$. Only those $AB^{\ddagger}$ complexes which correspond to the geometry and

Eyring was the proponent of the Activated Complex Theory which says that for the reactant molecules to undergo a reaction, they must first form an activated complex. The theory assumes that the activated complex will be in equilibrium with the reactants.

The decomposition of the activated complex into product occurs via a high-amplitude, low-frequency vibrational mode. However, not all activated complexes lead to products.

energy of the top of the free energy barrier are the ones which would actually react. To perform the calculations, the activated complex is assumed to be in equilibrium with the reactants, despite its slow unimolecular decomposition into products. This is a questionable assumption and has to be considered as the weakness of the Eyring approach. However, it was the best possible, as it made the calculation possible! The decomposition of the activated complex into products occurs via a high-amplitude, low-frequency unstable mode that we discussed earlier. It is possible that the activated complex may return without decomposing which reduces the reaction rate. This is usually taken care of by introducing a multiplicative factor κ, referred to as the transmission coefficient, though usually one assumes it to be unity. We shall use this value. Thus we have

$$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} AB^\ddagger \overset{\nu}{\rightarrow} P.$$
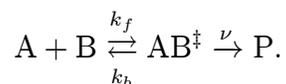
Here, k_f is the rate of the forward reaction leading to the production of $AB^\ddagger$ and k_b is the rate of backward decomposition of $AB^\ddagger$ into A and B. Now, at equilibrium, we have $k_f[A][B] = k_b[AB^\ddagger]$. Thus the assumption of equilibrium between the reactants and activated complex leads to

$$K^\ddagger = \frac{k_f}{k_b} = \frac{[AB^\ddagger]}{[A][B]}.$$

Here, $K^\ddagger$ is the equilibrium constant. Thus, the rate of the reaction can be given as:

$$v = \nu[AB^\ddagger] = \nu K^\ddagger [A][B],$$

where ν is the frequency with which the activated complex dissociates. As the rate constant k is defined by $v = k[A][B]$, we get

$$k = \nu\, K^\ddagger.$$

According to statistical mechanical theory of equilibrium processes, any equilibrium constant can be written

in terms of partition functions. Thus,

$$K^{\ddagger} = \frac{Q_{AB^{\ddagger}}}{Q_A Q_B} e^{-E^{\ddagger}/k_B T},$$

where $E^{\ddagger}$ is the activation energy, $Q_{AB^{\ddagger}}$ is the partition function for the activated complex including all the modes, and Q_A and Q_B are the partition functions for the reactants A and B. We now take the frequency associated with the reaction coordinate to be the frequency of dissociation. This mode contributes to the partition function $Q_{AB^{\ddagger}}$ too, so that one can write $Q_{AB^{\ddagger}}$ as the product of the partition function for this mode and that for the rest of the system. Thus we have $Q_{AB^{\ddagger}} = Q_{\text{reaction coordinate}} \, Q^{\ddagger}$. Thinking of the reaction coordinate as a low frequency vibrational mode, $Q_{\text{reaction coordinate}} = k_B T/h\nu$. Hence

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E^{\ddagger}/k_B T}.$$

It is to be noted that $Q^{\ddagger}$ is the partition function for the activated complex with the reaction coordinate omitted. The calculation of rate constant can now be done as one has well-developed methods for calculating the partition functions, once the molecular structures are known. The theory is the most successful theory for the calculation of rate constants.

3. Other Contributions

Eyring worked on a diverse range of topics. Interestingly, for his master's degree in 1924, his thesis was on 'The Separation of Heavy Sulfide Ores by Selective Flotation'. Prior to this, he was working as a mining engineer. His PhD thesis was entitled 'A Comparison of the Ionization by, and Stopping Power for, Alpha Particles of Elements and Compounds'. Initially, the problem he worked on involved studying the emitted radiation when the protons hit a beryllium target after

Interestingly, Eyring's master's thesis was based on a topic far removed from chemical kinetics and was entitled 'The Separation of Heavy Sulfide Ores by Selective Flotation'.

bombarding a long vacuum tube filled with hydrogen at low pressures. However, it did not work out too well and he later conducted studies on alpha particles from polonium – the amount of ionization induced by them in various gases and the extent to which they could be stopped in these gases. The deduction was that for the gas molecules to stop the alpha particles, it required the transfer of a large amount of kinetic energy of the alpha particles to the gas molecules. The transfer itself was independent of the subsequent ionization in the gas molecules. Thus the transfer did not depend on how strongly the atoms were bound in the molecules. However, the secondary process of ionization, induced owing to the presence of a large amount of energy, depended on the bond strengths between atoms in the gas molecules as it was only during ionization that the bonds dissociated.

3.1 *Effective Resultant Dipole Moment of Complex Molecules*

In 1932, at Princeton, Eyring worked on a problem of a different nature: the calculation of effective resultant dipoles of large molecules [4]. Dipole moment is an important molecular attribute that influences several physical properties such as solubility, conductivity, spectroscopic behaviors and also chemical properties including inductive effect and molecular reactivity. While dipole moments for small/rigid molecules can be easily evaluated from individual bond moment vectors, the calculation of dipole moments for flexible molecules is not as straightforward. Large molecules can adopt several conformations, each having a different resultant dipole moment. Thus, to find the effective dipole moment of the large molecule, the resultant dipole moment for each conformation and the relative abundance of the given conformation have to be taken into account. In other words a weighted average of the dipole moments for the molecule is needed. Eyring termed this weighted aver-

Eyring proposed a treatment for calculation of effective resultant dipole moment of complex molecules which could be extrapolated to calculate mean lengths and partition functions for polymers.

age as effective resultant dipole moment, and offered a tractable method for estimating it from the individual bond moments. His simplification relied on reducing the various bond moments in the molecule and expressing them in terms of the bond moment of a particular bond. Eyring's method was later used extensively for polymers, and extrapolated to calculate their mean lengths as well as partition functions.

3.2 *Heavy Water and Reaction Rate Theory of Isotopes*

James Chadwick discovered the neutron in 1930. Shortly afterwards, heavy water was discovered by Harold Urey at the University of Chicago. Both Chadwick and Urey received the Nobel Prize for their work. The discovery of heavy water caused considerable excitement among the scientific community and Eyring was not indifferent as well. Employing quantum mechanical calculations, Eyring could explain the observation of Urey and Chadwick of normal water being ionized in preference to heavy water on electrolysis. Eyring's calculations also suggested that salts are less soluble in heavy water compared to ordinary water and that reaction rates usually decelerate in heavy water. Consequently, when there are high concentrations of heavy water, there are chances that living organisms would die as the life-sustaining reactions are slowed down. Eyring's calculations formed the basis for the reaction rate theory of isotopes [5]. He was invited to present his findings at the American Philosophical Society in Philadelphia in 1933 where he came across Irving Langmuir, a recent Nobel laureate then. Langmuir was keenly interested in Eyring's work on heavy water and their meeting was an incident Eyring fondly recollected later.

In 1933, Eyring started his famous book *Quantum Chemistry* with George Kimball. Interestingly, the book was not published until 1944 and in the intervening decade,

After the discovery of heavy water, Eyring performed calculations to explain why normal water was ionized in preference to heavy water on electrolysis.

Eyring's famous book *Quantum Chemistry* was co-authored by George Kimball and John Walter. Interestingly, Kimball and Walter never met each other.

John Walter joined as a co-author. Amusingly, Kimball and Walter never met each other. This book was a huge success and it contained Eyring's original contributions to quantum mechanical calculations. Another book titled *The Theory of Rate Processes* authored by Samuel Glasstone, K J Laidler and Eyring was published in 1941. This volume also was a giant pedagogical success.

3.3 *One-Electron Theory for Optical Activity*

The period 1930–1940 witnessed attempts by several researchers at understanding the molecular genesis of optical activity. Optical activity is a phenomenon whereby chiral molecules rotate the plane polarized light (PPL) and has classically been the single common test for chirality. However, the electronic origin of optical activity remained an enigma for decades, as neither the magnitude nor the direction of optical rotation exhibited by a chiral molecule could be predicted beforehand. However, a tool for correlating molecular structure with optical activity would have immensely helped scientists in assigning the exact (absolute) configuration of an enantiomer. Enantiomers of a chiral molecule are isomers (designated as R or S) that have identical bond connectivity, chemical and physical properties but differ in spatial orientation of the atoms and rotate PPL in opposite direction (clockwise/+ or counterclockwise/−). Since, the direction of optical rotation (+ or −) of a given enatiomer cannot be correlated to the absolute configuration (R or S), X-ray diffraction (XRD) studies is the only direct method for determining the absolute configuration of an enantiomer. However, all molecules are not solid and might not be available in crystalline forms suitable for XRD analysis. Therefore, chemists actively sought theories correlating molecular structure with the sign of optical rotation.

In 1937, Eyring along with E U Condon and W Alter

offered a single electron model for correlating the sign of optical rotation with the absolute configuration or conformation of a particular molecule [6]. In developing this theory they also provided a genesis for optical activity in molecules. It is known that the interaction of a molecule with UV/visible light causes electronic transitions in the molecule. The authors argued that optical activity is essentially an interaction between a chiral molecule and plane polarized light, and should have its origin in electronic transitions. Therefore, like any other electronic transition, optical activity was assumed to arise at electron-rich regions of the molecules called chromophores. These chromophores have electronic states which might suffer perturbation from neighbouring groups and get altered. Next it was argued that electronic transitions between these altered states should show optical activity provided the system has no plane or centre of symmetry as a whole. Although other methods for correlating molecular structure with optical activity also existed, some like the Rosenfeld Equation demanded rigorous quantum mechanics and were untenable for real purposes. Eyring's method was relatively simple and worked well for several systems including tris ethylenediamine cobalt(III) ion and became immensely popular. Eyring's contributions to this field continued in his book *Quantum Chemistry and The Theory of Optical Activity*, co-authored by Dennis Caldwell.

3.4 *Bioluminescence in Bacteria*

While at Princeton, in 1942, interactions with Newton Harvey, the then head of the biological department at Princeton, introduced him to the problem of bioluminescence of bacteria and the effects of temperature and pressure on it. He also had fruitful discussions with Frank Johnson in this regard. Bioluminescence refers to the production and emission of light by a living organism. It is essentially a form of chemiluminescence and involves the release of energy by a chemical reaction in

Eyring, along with E U Condon and W Alter, first proposed a one-electron model for correlating the sign of optical rotation with the absolute configuration of a particular molecule.

Eyring used the activated complex theory to explain various findings related to bioluminescence in bacteria.

the form of light emission. For instance, fireflies produce the chemicals luciferin (a pigment) and luciferase (an enzyme). Reaction of luciferin with oxygen creates light and luciferase acts as a catalyst, accelerating the reaction. The reaction is sometimes mediated by cofactors such as calcium ions or ATP. The chemical reaction can occur either inside or outside the cell. Now, bioluminescence in bacteria is absent at ice temperature. But, as one gradually increases the temperature, it increases and becomes maximal at about halfway the blood temperature. However, at the blood temperature, the intensity falls off to a very small value as a consequence of the inactivity of the enzyme at higher temperatures. However, Johnson found that when taken in a suitable solution, the bacteria, being subjected to a pressure of about 200 atm, showed a marked decrease in luminescence at lower temperatures but the intensity of luminescence rose at higher temperatures.

Eyring's explanation was: From the transition state theory, one could say that the activated complex in this reaction would be in equilibrium with the reactants, and the activated complex would decompose unidirectionally into the products which exhibit luminescence. Consequently, higher the concentration of the activated complex, greater would be the rate of formation of the products. Again, from the Le-Chatelier principle, higher pressure shifts the equilibrated system to lower volumes. Consequently, considering an equilibrium between the activated complex and the reactants, decreased luminescence at low temperatures when the pressure is increased would suggest that the reactants become more voluminous compared to the activated complex. Thus the intensity of luminescence diminishes as the reactant molecules are incapable of luminescence. However, at high temperatures, the activated complex would acquire more volume than the reactants and hence the rate of formation of products would be enhanced leading to

increased luminescence [7]. These studies initiated a fruitful collaboration with Frank Johnson in the fields of biology and medicine.

3.5 *Stability of Detonation and Deformation Kinetics*

During the Second World War, Eyring actively worked with the Navy as a consultant on explosives. This led to an article 'The Stability of Detonations' which was co-authored by Richard Powell, George Duffy and Ransom Parlin [8]. In 1944, the Textile Research Institute was established at Princeton and Eyring was asked to design a program for the institute. Physical properties of fibres and fabrics got him interested and his work on deformation kinetics followed suit [9]. He was essentially concerned with the deformation of a number of essentially independent molecules or molecular segments distributed statistically with respect to the distance between the ends of the molecules. One would expect that they would be free to assume several configurations owing to thermal agitation. However, at certain points stabilized by chemical forces, they form more or less tightly held and hence well-defined ends.

3.6 *Structure Theory of Liquids*

Eyring was a scientist with a bold vision. To dare the pursuit of molecular problems, two decades before the invention of the first computer, is a courage that theoreticians can best appreciate. To approach such daunting problems Eyring relied on modeling, a tool that is popular among theoretician to this date. Thus, a complicated physical system is approached by decomposing it into a simplified, yet plausible picture. For Eyring, such approaches paid off well in most cases; however, in certain instances the model turned out to be over simplified. In 1946, Eyring joined the University of Utah as the dean of the graduate school and as a professor of chemistry. He was interested in designing a "complete

Eyring worked with the Navy during the Second World War as a consultant on explosives.

Eyring proposed a structure theory for liquids and considered a liquid to be a mixture of solid-like clusters interspersed with vapour molecules. However, this theory was not very well-received.

and consistent" model for liquids, a problem that bothered him for a while [10]. Ever since the discovery of 'critical point' in 1822, scientists came to realize that for a certain range of temperature and pressure, liquid and vapour coexist without a well-defined phase boundary. At critical temperature, the substance would exist as a gas at low pressures while at higher pressure, only the liquid phase is available. There is no sharp transition from gas to liquid upon increasing pressure at critical temperature. In other words, the liquid and gaseous phases form a continuity of states. Eyring also observed that several of the properties of liquids are analogous to those of solids too, including thermal expansion and short-range molecular ordering.

Following these observations, Eyring postulated liquid as an intermediate between the solid and the gaseous states of a substance, and treated the liquid state as a mixture of solid-like clusters interspersed with vapour molecules. Thus, he attempted to explain the properties of a liquid in terms of its solid and gaseous phases. Using this model, Eyring, along with T Ree and N Hirai, propounded the structure theory of liquids and used it to analyse the thermodynamic and kinetic transport properties of many liquids. However, as stated at the onset, this piece of work was not very well-received and generated a lot of controversy.

3.7 *Conformation Changes in Proteins*

At Utah, Eyring performed studies on proteins and their conformation changes [11]. The polypeptide chains in proteins fold upon themselves to form hydrogen-bonded secondary structures whereas interactions with amino acid side chains give them their rigid tertiary structure. Denaturation is defined as the change in conformation. Eyring studied the model using the activated complex theory and in terms of energy states available to the protein and the possibility of denaturation reactions. He

concluded that folding of proteins is spontaneous and is directed by the peptide amino acid residues. Reversible denaturation is a consequence of changes in arrangement of tertiary structure whereas changes in secondary structure lead to irreversible denaturation.

3.8 *Theory of Rate Processes in Biology*

It was in the year 1970 that Betsy Jones Stover came to Eyring with her studies on beagles whom she had irradiated with plutonium and radium, causing them to die of bone-cancer. Her data could be fitted using the equation:

$$S = \frac{1}{1 + e^{k(t-\tau)}}, \qquad (1)$$

$$-\frac{dS}{dt} = kS(1 - S) = \frac{d(1 - S)}{dt}. \qquad (2)$$

In the above equations, S is the fraction of population surviving, t stands for age and hence $1-S$ is the population not surviving. τ is the age at which the population reduces to $1/2$. Also, at $t = \tau$, the slope is $-k/4$. This rate equation resembles that for an autocatalytic reaction. Eyring and Stover related the above to the rate of mutation as well, where S was the probability that a gene was undamaged and $1 - S$ the probability that a neighbouring gene was damaged. The volume *The Theory of Rate Processes in Biology and Medicine* followed suit which was written jointly by Eyring, Stover and Johnson.

3.9 *Religious Volumes*

Eyring was a practising Mormon and spoke and wrote extensively about the compatibility of science and religion. He authored the following religious volumes: *Science and your Faith in God* (1958), *The Faith of a Scientist* (1967) and *Reflections of a Scientist* (1983).

Eyring was a practising Mormon. Interestingly, he had also authored some religious volumes.

4. Conclusion

Henry Eyring was undoubtedly a prolific scientist, his work on Activated Complex theory being one of the most potent ideas to have emerged in chemistry. Hugh Taylor, his colleague at Princeton, has said: "The golden decade of my life in Princeton was the period from 1929 to 1939. The Frick Chemical Laboratory was new and excellently excellently equipped for the researches then underway. But the richness of the decade came from the presence of Eyring and his co-workers, exploring the new absolute rate theory of chemical rate processes, complementing the active experimental studies underway in the laboratories. It was the immense range of the absolute rate theory, applicable not only to atom-molecule and molecule-molecule but alike to physical processes, conduction, transport number, viscosity, diffusion and biological processes of wide variety and scope."

Suggested Reading

[1]   L Wilhelmy, Ueber das gesetz, nach welchem die einwirkung der säurenauf den rohrzucker stattfindet, *Annal. der Phys.*, Vol.157, p.499, 1850.

[2]   H Eyring and M Polanyi, *Z. Phys. Chem. Abt. B*, Vol.12, p.279, 1931.

[3]   H Eyring, The activated complex in chemical reactions, *J. Chem. Phys.*, Vol.3, p.107, 1935.

[4]   H Eyring, The resultant electric moment of complex molecules, *Phys. Rev.*, Vol.39, p.746, 1932.

[5]   F W M Cagle Jr and H Eyring, The significants of isotopic reactions in rate theory, *J. Phys. Chem.*, Vol.56, p.889, 1952.

[6]   H Eyring, E U Condon and W Altar, One-electron rotatory power, *J. Chem. Phys.*, Vol.5, p.753, 1937.

[7]   R W Williams, F H Johnson and H Eyring, The nature of enzyme inhibitions in bacterial luminescence: Sulfanilamide, urethane, temperature and pressure, *J. Cell. Physiol.*, Vol.20, p.247, 1942.

[8]   G H Duffy, R B Parlin, H Eyring and R E Powell, The stability of detonation, *Chem. Rev.*, Vol.45, p.69, 1949.

[9]   H Eyring and A S Krausz, Chemical kinetics of plastic deformation., *J. Appl. Phys.*, Vol.42, p.2382, 1971.

[10] H Eyring, J Hirschfelder and D Stevenson, A theory of liquid structure, *J. Chem. Phys.*, Vol.5, p.896, 1937.

[11] H Eyring and R Lumry, Conformation changes of proteins. *J. Phys. Chem.*, Vol.58, p.110, 1954.

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