

HENRY EYRING: QUANTUM CHEMISTRY, STATISTICAL MECHANICS, THEORY OF LIQUIDS, AND SIGNIFICANT STRUCTURE THEORY*

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Introduction

The author is pleased and honored to have a part in a symposium honoring Eyring that was part of an American Chemical Society Meeting in Salt Lake City in March, 2009. Earlier reminiscences and biographies, including one by Henry Eyring, the scientist, and one by his grandson, Henry J. Eyring, have been published earlier (1-6). Jan Hayes, the organizer of the symposium, pointed out that I am a coauthor of the last of Henry's publications. This is somewhat accidental as my book with him was the second edition of *Statistical Mechanics and Dynamics*, the first edition having appeared nearly twenty years earlier. Because of competing commitments, the production of the camera ready copy took five years. Had the preparation proceeded more quickly, I would not have occupied this position.

Recently, one of Henry's sons told me that Henry loved me. This is no great distinction as Henry thought positively of everyone. However, perhaps he loved some people more than others. He was a very warm and generous person. My parents were nervous when they were to meet such an eminent person. He immediately put them at ease. In any case, my truthful reply to his son was that I loved him. Henry treated me as an honorary son. The two scientists of whom I am most fond, Henry Eyring and John Barker, both treated me as an honorary family member. For this I am deeply grateful.

Early Years

Henry Eyring was grandson of Henry Eyring and Mary Brommeli, who came to America from Germany and Switzerland, respectively. His grandparents met as they traveled across the plains to Utah in 1860. They settled first in St. George in southern Utah and later were sent to northern Mexico to help establish a Mormon settlement. His grandfather was widely respected for his integrity. His grandmother spent some time in Berlin, where she

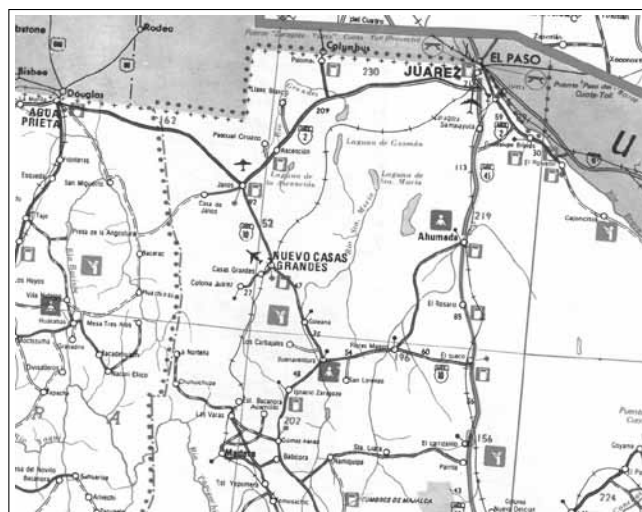


Figure 1. Map of the region of Northern Mexico where Henry Eyring was born. Colonia Juarez is southwest of Nuevos Casas Grandes, at the end of a secondary road. Distances in Mexico are in kilometers.

was jailed briefly because she refused to compromise her religious beliefs. His parents were Edward Eyring and Caroline Romney. Their son, Henry the scientist, was born in Colonia Juarez. Grandfather Henry Eyring owned a store, and his father, Edward Eyring, was a prosperous rancher with several hundred head of cattle. From this point, when I use the names, Henry Eyring and Henry, I refer to the grandson, the scientist.

Colonia Juarez is a small town located in the Mexican state of Chihuahua and is southwest of El Paso and southeast of the Arizona border crossings. A map of this region of Mexico is shown in Fig. 1. Several Mormon settlements were established in the late nineteenth century. Only two remain, Colonia Dublan and Colonia Juarez. The former does not appear on the map as it is now a suburb of Nuevos Casas Grandes.

The main industry of the region is fruit orchards. Today, Colonia Dublan / Nuevos Casas Grandes is the economic center of the region because there is more flat land and a railroad. However, Colonia Juarez is the religious/cultural center of the Mormon community and looks like a typical small town in Utah. The bilingual school, Academia Juarez, which Henry attended, is shown in Fig. 2 (a photograph taken by the author in 2007). It is in the foreground at the bottom of the hill. The building on the right dates back to Henry's time.

Henry lived in Colonia Juarez until 1912. Because of the turmoil of the Mexican Revolution, life became dangerous. The Eyring family and most, if not all, of the Mormons were evacuated by rail to El Paso. The expectation was that they would return soon, but the Eyring family decided not to return. The family settled in Arizona in considerably reduced circumstances. The family thought that Henry was an American by birth. It was not until



Figure 2. View from a hill overlooking Colonia Juarez.

the 1930s that he found that he was not. Thus, some of his most important and famous work was accomplished while he was a Mexican. It is reasonable to say that he is probably Mexico's most famous chemist.

Quantum Mechanics and Kinetics

Following the completion of B.S. and M.S. degrees at the University of Arizona and the Ph.D. at Berkeley in 1927, Henry spent two years engaged in teaching and research at the University of Wisconsin in Madison. In 1929 he was awarded a post doctoral fellowship to work at the Kaiser Wilhelm Institute in Dahlem in Berlin. Curiously, my parents lived in Dahlem for a time, as members of the diplomatic corps, while I was a doctoral student of Eyring. Eyring's original plan was to work with Bodenstein; but, perhaps fortunately, Bodenstein was away; and he collaborated with Michael Polanyi.

Quantum mechanics was in its infancy and there was much to be done. Quantum mechanics had not yet been applied to study reactions. Eyring and Polanyi (7) chose to study the simplest reaction, the replacement reaction, $H + H_2 \rightarrow H_2 + H$ by applying the Heitler-London method, including exchange. This was one of the first applications of quantum mechanics to obtain an energy surface for a reaction and, in my opinion, this was one of his most significant papers.

During his fifteen year tenure on the faculty at Princeton, where he stayed until 1946, Eyring produced many important results. He developed his famous reaction rate theory (8). A typical plot of the energy, say as calculated by the method of Eyring and Polanyi, that the reacting molecules must trace is plotted in Fig. 3. In this plot, the energy of the reactants is on the left and the energy of the products is on the right. As the incoming molecule approaches the molecule with which it will react, the energy increases. This energy barrier must be surmounted, rather like a hiker climbing up to and passing over a summit and then descending. The energy state of the products is on the right, and this energy state may be greater or lesser than or equal to that of the reactants. In Fig. 3, the products have a lower energy; this is irrelevant to our argument. The height of this barrier is ΔE^\ddagger . As would a hiker, the constituents of the reaction may hesitate briefly at the pass. Eyring coined the name *activated complex* for this chemically unstable species at the top of the barrier.

The Boltzmann or Gibbs factor, $\exp(-E/RT)$, where R is the gas constant and T is the temperature, is

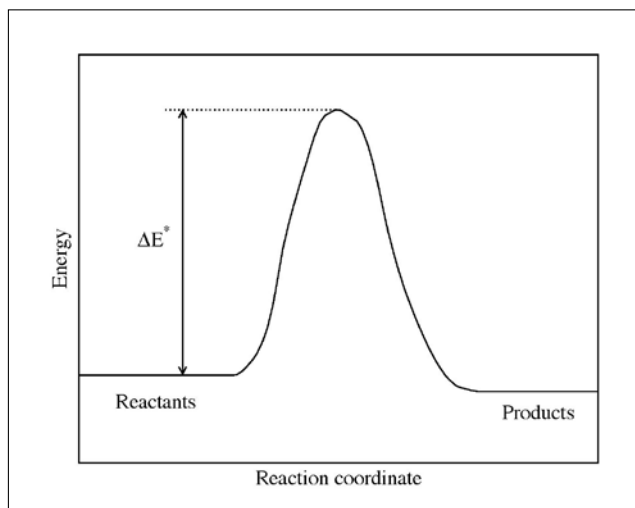


Figure 3. The energy of a reaction along the reaction path. The zero point energy is included. The reactants are on the left and the products are on the right and are separated by an energy barrier of height ΔE^\ddagger . At the pass over which the reactants must traverse for the reaction to proceed, the reacting molecules form a transient complex that Eyring called an activated complex.

fundamental in statistical mechanics. Thus, it is not surprising that such a factor is central in Eyring's famous rate equation. However, in the above form, the Boltzmann-Gibbs factor is appropriate for the canonical ensemble that is defined by volume and number of particles. In a reaction it is the pressure and chemical potential that are constant. Hence, it is the Gibbs free energy, G , rather than the energy, E , that should appear. The result that Eyring obtained for the reaction rate constant is

$$k' = \frac{kT}{h} \exp(-\Delta G^\ddagger / RT) \quad (1)$$

where k is Boltzmann constant, the gas constant per molecule, and h is Planck's constant. The prefactor, kT/h , is formally the frequency of oscillation, ν , of a soft spring that represents the mode of the activated complex that takes part in the reaction. This mode is soft, with a negative spring constant, because the activated complex is unstable. Using equipartition of energy, this frequency is given by $h\nu = kT$. A rigorous derivation of Eq. (1) is given in Laidler's text (9).

Of course, the reactants, on reaching the pass and forming an activated complex, may not cross the pass and form the products. They may fall back. Hence, it is often convenient to multiply the left hand side of Eq. (1) by a factor, k , that is called the transmission coefficient.

Although there is no general method of calculating k , Eyring's rate theory has been very illuminating and has been used in a wide variety of chemical and biological applications. Eyring was awarded the National Medal of Science, the Berzelius Medal, the Wolf Prize, and many other prestigious awards for this work but, alas, not a Nobel Prize.

At Princeton, he started writing his famous book, *Quantum Chemistry* (10). This may have been the first book in English with this title. The writing took a decade. Eyring told me that Kimball and Walter never met. In any case, the book became a standard text and was translated into several languages. It was the book from which I first studied quantum mechanics. Of course, I had encountered quantum mechanics but not as the exclusive subject of a course. Not only is quantum mechanics covered in this book, but it is an excellent reference for special functions and group theory.

Theory of Liquids; Significant Structure Theory

In 1946, with his wife's encouragement, he accepted the position of Dean of the Graduate School at the University of Utah. The University of Utah, a long established institution, planned to inaugurate a doctoral program; Henry found the chance to help build this program an irresistible temptation. In this he was highly successful. The University of Utah has a very prestigious graduate program.

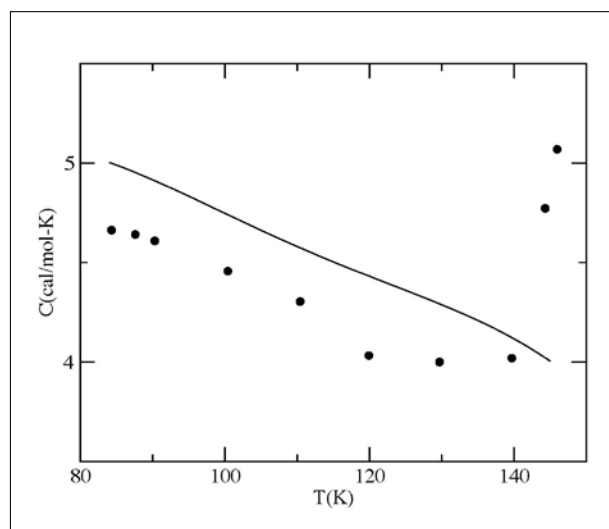


Figure 4. Heat capacity of argon, as obtained from Eq. (3), compared with experiment.

Earlier he had developed an interest in the theory of liquids. This, I assume, resulted from a desire to extend reaction rate theory from gas phase reactions to reactions in condensed phases. At the time it was thought that in contrast to gases and solids, there was no satisfactory theory of the liquid state. It is interesting that this is not true. The van der Waals theory did provide the basis of a satisfactory theory of liquids, but this was not understood until recently. In any case, until the 1960s the thinking was, since the density of a liquid is not too different from that of a solid, a theory of the solid state would be a promising starting point. Eyring, and others, developed the cell or lattice theory of liquids.

In reality this is a classical (as opposed to quantum) theory of a solid, due to the higher temperatures of most liquids. Eyring, and probably others, realized that the entropy of the cell theory lacked a factor of Nk . Eyring coined the term, *communal entropy*, and added the missing entropy arbitrarily. Although arbitrary, this is preferable to ignoring the issue and does give a liquid a different free energy from that of a solid. He went one step further and developed the idea that when a molecule evaporated, it left a hole or vacancy in the quasi-lattice of the liquid. Thus, for every molecule in the vapor phase, there would be a vacancy in the liquid that mirrored the gas molecule. If this were literally true the sum of the densities of the liquid and vapor would be a constant, equal to twice the critical density. This is not quite correct. The average density of the two phases is a linear function of the temperature but is not a constant and decreases somewhat as the temperature increases. Nonetheless, this reasoning provides a simple qualitative explanation of the law of rectilinear diameters.

He 'formalized' his reasoning into the *significant structure 'theory'* (11, 12) at Utah. Using the idea that a liquid is a mixture of molecules and vacancies that mimic the vapor molecules, the partition function, Z , could be written as

$$Z = Z_s^{V_s/V} Z_g^{(V-V_s)/V} \quad (2)$$

where Z_s and Z_g are the partition functions of the solid and vapor phases, respectively, and V and V_s are the volumes of the liquid and solid phases, respectively. Eyring used the Einstein theory and ideal gas theory for Z_s and Z_g . The Einstein parameter, θ_E , and V_s are taken from experiment. The significant structure theory is a description rather than a theory. Conventionally, a theory in statistical mechanics relates the properties of a system to the forces between the molecules, whereas

Eyring's description relates the properties of the liquid to those of the solid and vapor without obtaining either from the intermolecular forces. This said, Eyring by focusing on the volume as the important variable was on the right track and anticipated later developments, such as perturbation theory of liquids.

One consequence of Eq. (2) is that the heat capacity, C , of monatomic liquid, such as argon becomes

$$\frac{C}{Nk} = 3 \frac{V_s}{V} + \frac{3}{2} \frac{V - V_s}{V} \quad (3)$$

since, for argon, T greatly exceeds θ_E . As is seen in Fig. 4, Eq. (3) gives a reasonably good description of the heat capacity. The heat capacity is a second derivative of the free energy and is difficult to obtain accurately from theory. The experimental heat capacity becomes infinite at the critical point. Equation (3) does not predict this. Much has been made of this failure. However, it should be kept in mind that no simple theory predicts the singularity of the heat capacity at the critical point. Some are less successful than Eq. (3). For example, the augmented van der Waals theory (a widely accepted theory) gives the prediction $C = 3Nk/2$. Later Eyring grafted the renormalization group approach onto Eq. (2) to obtain the singularity. However, I find this artificial.

I collaborated with him in his study of liquids by applying the significant structure theory to liquid hydrogen. I also assisted in the writing of the book, *Statistical Mechanics and Dynamics* by Eyring, myself, Betsy Stover, and Ted Eyring (13). This book was an outgrowth of the lecture notes prepared by one of his first students at Utah, Marilyn Alder. These notes were mimeographed and bound with a yellow cover and referred to by students as the *yellow peril*. The book was rather unusual in that the first chapter covered the field in an informal way, and then the material was repeated more formally in the subsequent chapters. Needless to say, significant structure theory was included in one of the chapters. This book was moderately successful. With Jost, he and I collaborated on a multi-volume treatise on physical chemistry.

During his final years, he became interested in cancer both because of his wife's illness and because of the cancer that ultimately took his own life. Betsy Stover came to him with the observation that the mortality curves of the experimental animals that had been exposed to radiation that caused them to die of bone cancer were strikingly similar to a Fermi-Dirac distri-

bution. This suggested to Eyring that this was similar to saturation in adsorption and the rate of mutation that was responsible for the cancer was proportional to the product of the fraction of normal cells multiplied by the fraction of mutated cells. He and Stover wrote several papers under the general title of the *Dynamics of Life*, based on this idea.

Summary

As I have mentioned Henry had a warm personality. At times, he became annoyed with someone (including me) but never held a grudge. Despite his accomplishments, he never felt he was better than someone else. I found him to be very kind.

Many people have conjectured about why he never won a Nobel Prize. Henry J. Eyring (Ref. 5) wonders whether it was because he left Princeton for Utah. Certainly his cheering section of prominent people would have been greater had he stayed at Princeton. However, one person at the University of Utah has won a Nobel Prize, so it is not impossible to win that distinction at a 'provincial' university. Others have wondered whether the fact that Henry was religious played a role. Perhaps it was due to Henry's intuitive style of research that was more fashionable in the 1930s than later. Peter Debye called Henry's style, "the inductive-deductive method." Henry's description was that his method of finding the path through the forest was first to cut down all the trees in the forest. My feeling is that his not being awarded a Nobel Prize is part of the uncertainties of life. He won many prizes. He would not have won them if the above considerations were a factor. The other prizes are equally important. In any case, he was beloved by all who knew him.

At Henry's funeral, Neal Maxwell, a friend and neighbor, former university colleague, and church leader, said that Henry taught us how to live well and how to die well—not a bad epitaph.

REFERENCES AND NOTES

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1. H. Eyring, "Men, Mines, and Molecules," *Ann. Rev. Phys. Chem.*, **1977**, 28, 1-13.
2. W. Kauzmann, "Henry Eyring, February 20, 1901-December 26, 1981", *Biogr. Mem. Natl. Acad. Sci. USA*, available online at www.nasonline.org/memoirs.
3. D. Henderson, "My Friend, Henry Eyring," *J. Phys. Chem.*, **1983**, 87, 2638-2656.
4. S. H. Heath, "The Making of a Physical Chemist, The Education and Early Researches of Henry Eyring," *J. Chem. Educ.*, **1985**, 62, 93-98.
5. H. J. Eyring, *The Life and Faith of Henry Eyring*, Deseret Book Company, Salt Lake City, UT, 2007.
6. J. M. Hayes and P. L. Perez, "Henry Eyring: His Science and Legacy," *Chemistry*, **2009**, 18, 12-13.
7. H. Eyring and M. Polanyi, "Uber Einfache Gasreaktionen," *Z. Phys. Chem. B*, **1931**, 12, 279.
8. H. Eyring, "The Activated Complex in Chemical Reactions," *J. Chem. Phys.*, **1935**, 3, 107-115.
9. K. J. Laidler, *Chemical Kinetics*, Harper Collins, New York, 3rd ed., 1987; see Eq. 4.85 and related discussion.
10. H. Eyring, G. E. Kimball, and J. Walter, *Quantum Chemistry*, Wiley, New York, 1944.
11. H. Eyring, T. Ree, and N. Hirai, "Significant Structures in the Liquid State. I," *Proc. Natl. Acad. Sci. USA*, **1958**, 44, 683-691.
12. H. Eyring and M. S. Jhon, *Significant Liquid Structures*, Wiley, New York, 1969.
13. H. Eyring, D. Henderson, B. J. Stover, and E. M. Eyring, *Statistical Mechanics and Dynamics*, Wiley, New York, 1964; second ed., 1982.

ABOUT THE AUTHOR

Douglas Henderson obtained his Ph. D. at the University of Utah, under the direction of Henry Eyring, in 1961. He collaborated with Eyring on the writing of a book on statistical mechanics and in the editing of several other books. The bulk of his career was spent at the IBM Almaden Research Laboratory in San Jose, CA. Since 1995 he has been with the Department of Chemistry and Biochemistry of Brigham Young University, Provo, UT 84602, from which he retired in 2005. Email: doug@chem.byu.edu. In 1967 he helped develop the well-known perturbation theory of liquids. Subsequently, he worked on the theory of charged ions near charged electrodes and in physiological channels.