J. Condensed Matter Nucl. Sci. 31 (2020) 49–52

Research Article

The Eyring Rate Theory Applied to Cold Fusion

Melvin H. Miles* and Iraj Parchamazed

Department of Chemistry, University of LaVerne, LaVerne, CA 91750, USA

Abstract

The Eyring Absolute Rate Theory is generally applied to chemical reactions where bonds between atoms are broken and new bonds formed to give a transition state or activated complex. This theory has also been applied to physical rate processes such as diffusion and the viscosity of liquids. The activation parameters obtained from the Eyring theory when applied to cold fusion are all suggestive of a deuterium fusion rate controlled by the diffusion of deuterons within the palladium lattice. The D+D fusion process in the Pd/D system is apparently a zero-ordered reaction where only a small fraction of the reactants are in a location in which they are able to react.

Keywords: Activation energy, Activation entropy, Deuterium, Diffusion, Palladium, Reaction zones

---

1. Introduction

The Eyring Rate Theory can yield theoretical rate constants for chemical reactions by calculations involving the energy contours of the transition state and then using the lowest energy pathway in going from reactants to products [1,2]. It is claimed that this Eyring theory is not simply for chemical reactions, but it can be applied to any rate process [1]. This Eyring theory also treats the possibility of quantum mechanical tunneling [1]. The application of the Eyring theory to the D+D fusion reaction shows that the reaction rate would be extremely slow outside the palladium lattice due to the coulombic barrier. The catalysis of a chemical reaction, which greatly increases the reaction rate by providing a more favorable reaction pathway, is well known in chemistry. Apparently, a much more favorable pathway for D+D fusion is provided by the palladium lattice.

2. Thermodynamic Definitions

The Eyring theory involves thermodynamic activation parameters, therefore, a few definitions are required. The internal energy (U) can be expressed by

$$U = q + w, \tag{1}$$

---

*Corresponding author. E-mail: mhmiles1937@gmail.com.

where q is energy in the form of heat and w is energy in the form of work. Equation (1) is a statement of the First Law of Thermodynamics. The enthalpy (H) is defined by

$$H = U + PV, \tag{2}$$

where P and V are the pressure and volume, respectively, for a system. The Gibbs energy (G) is defined by

$$G = U + PV - TS = H - TS, \tag{3}$$

where T is the thermodynamic temperature in Kelvin (K) and S in the entropy introduced by the Second Law of Thermodynamics. At constant temperature, any changes in G is given by

$$\Delta G = \Delta H - T\Delta S. \tag{4}$$

At constant pressure with only $P - V$ work, the change in H is given by

$$\Delta H = \Delta U + P\Delta V = (q - P\Delta V) + P\Delta V = q. \tag{5}$$

Therefore, at constant pressure with only $P - V$ work, the change in the enthalpy is simply the heat involved in such changes. For typical laboratory conditions of constant temperature and pressure, it can be shown that spontaneous reactions require the change in the Gibbs energy to be less than zero (negative) as expressed by Eq. (6).

$$(\Delta G)_{T,P} < 0. \tag{6}$$

3. Thermodynamics For The D+D → He-4 Fusion Reaction

At $T = 298.15$ K and $P = 10^5$ Pa (approximately room conditions) it was shown previously [3] for D+D fusion to form helium-4 that

$$\Delta H = q = -23.846478 \times 10^6 \text{ eV} = -2.30084 \times 10^{12} \text{ J mol}^{-1}, \tag{7}$$

$$\Delta S = S^\circ(\text{He-4}) - 2S^\circ(\text{D}) = -120.548 \text{ J mol}^{-1}\text{K}^{-1}, \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \approx \Delta H = -2.30084 \times 10^{12} \text{ J mol}^{-1}. \tag{9}$$

Therefore, D+D fusion to form He-4 is certainly thermodynamically possible at room temperature [3]. However, thermodynamics provides no information on reaction rates or the coulombic barrier. Nevertheless, the favorable thermodynamics at room temperatures allows the possibility of catalysis or new reaction pathways that can increase the rate of this reaction.

4. Eyring Rate Equations

From the Eyring Absolute Rate Theory [1], the rate constant (k) for a reaction is given by

$$k = (k_\text{B}T/h) \exp(-\Delta G^\ddagger/RT), \tag{10}$$

where k_B is the Boltzman constant $(1.3806488 \times 10^{-23}$ JK$^{-1})$, h the Planck constant $(6.62606957 \times 10^{-34}$ Js), $\Delta G^\ddagger$ the activation Gibbs energy, R the molar gas constant (8.3144621 J mol^{-1} K^{-1}), and T is the thermodynamic temperature in Kelvin. This Eyring rate constant can also be written as

$$k = (k_\text{B}T/h) \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \tag{11}$$

by using the thermodynamic relationship, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta^{\ddagger}$ for the activation Gibbs energy, $\Delta G^{\ddagger}$. The Arrhenius rate equation is given by

$$k = A\exp(-E_{\mathrm{A}}/RT), \tag{12}$$

where E_{A} is the activation energy. Comparing the Eyring and Arrhenius equations, it can be shown [1] that

$$A = (ek_{\mathrm{B}}T/h)\exp(\Delta S^{\ddagger}/R) \tag{13}$$

and

$$E_{\mathrm{A}} = \Delta H^{\ddagger} + RT = \Delta G^{\ddagger} + T\Delta S^{\ddagger} + RT. \tag{14}$$

5. Application of the Eyring Rate Theory to Cold Fusion

For a typical cold fusion experiment using a palladium cathode volume of 0.1 cm^3, the expected excess power near room temperature would be about 0.100 W. The D+D fusion reaction yields 2.6174×10^{11} He-4 atoms per second per watt of excess power. Therefore, for 0.100 W of excess power, the rate of helium-4 production would be $k = 2.6174 \times 10^{10}$ He-4/s.

Rearranging Eq. (10) gives

$$\Delta G^{\ddagger} = -RT\ln(kh/k_{\mathrm{B}}T). \tag{15}$$

Therefore, at $T = 300$ K, $\Delta G^{\ddagger} = 13,700$ J mol^{-1}.

From Eq. (14), the $\Delta G^{\ddagger}$ value is found to be in good agreement with the reported activation energy of $E_{\mathrm{A}} = 0.206$ eV or 19,900 J mol^{-1} for the diffusion of deuterons in palladium [4]. In fact, from Eq. (14) and using $E_{\mathrm{A}} = 19,900$ J mol^{-1}, a reasonable value of $\Delta S^{\ddagger} = 12.3$ J mol^{-1} K^{-1} is obtained for the activation entropy. The Eyring theory applied to the diffusion of hydrogen in metals gives similar values for activation energies and entropies.

The assumption of different values of excess power for palladium cathodes in D$_2$O electrolysis experiments would give different values for $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ as shown in Table 1. However, the assumption of 0.100 W of excess power at 300 K for a palladium volume of 0.100 cm^3 seems to be the best assumption.

6. Eyring Theory For Diffusion

The Eyring Rate Theory for diffusion [1] is expressed by the equation

$$D = \lambda^2(k_{\mathrm{B}}T/h)\exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT), \tag{16}$$

where D is the diffusion constant (cm^{2}s^{-1}) and λ is the distance (cm) between successive diffusion positions. Using $\Delta H^{\ddagger} = E_{\mathrm{A}} - RT$, this equation becomes

$$D = e\lambda^2(k_{\mathrm{B}}T/h)\exp(\Delta S^{\ddagger}/R)\exp(-E_{\mathrm{A}}/RT). \tag{17}$$

Table 1. Different assumptions for excess power at 300 K.

P_{X}(W)	k (s^{-1})	$\Delta G^{\ddagger}$ (Jmol^{-1})$^{\mathrm{a}}$	$\Delta H^{\ddagger}$ (Jmol^{-1})$^{\mathrm{b}}$	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})$^{\mathrm{c}}$
0.050	1.3050×10^{10}	15,400	17,400	6.7
0.100	2.6174×10^{10}	13,700	17,400	12.3
0.200	5.2348×10^{10}	11,900	17,400	18.3

[a] $\Delta G^{\ddagger} = -RT\ln(kh/k_{\mathrm{B}}T)$.

[b] $\Delta H^{\ddagger} = E_{\mathrm{A}} - RT$, where $E_{\mathrm{A}} = 0.206$ eV (19,900 J mol^{-1}).

[c] $\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$.

The Arrhenius equation for the diffusion of deuterium in palladium [4] is given by

$$D = A\exp(-E_{\mathrm{A}}/RT), \tag{18}$$

where experimentally $A = 1.7 \times 10^{-3}\mathrm{cm}^2\mathrm{s}^{-1}$ [4]. Therefore,

$$\lambda^2 \exp(\Delta S^{\ddagger}/R) = Ah/ek_{\mathrm{B}}T = 1.00 \times 10^{-16}\mathrm{cm}^2 \tag{19}$$

at $T = 300$ K. For $\Delta S^{\ddagger} = 12.3$J mol^{-1}K^{-1}, $\lambda = 0.48 \times 10^{-8}$ cm, or 0.48 Å. For this cold fusion application, the diffusion distance of 0.48 Å is for a reacting deuteron just prior to undergoing the fusion reaction to form helium-4. This rather small distance may be related to the very small size of D$^+$ involving only the atomic nucleus. This small value also suggests a large concentration of D$^+$ ions for the location where the fusion reaction takes place.

7. Results and Discussion

The application of the Eyring Rate Theory to the D + D fusion reaction suggest that this reaction is controlled by the diffusion of deuterons within the palladium into some fusion reaction zones. Such reaction zones may also be called a nuclear active environment or NAE at the palladium surface as suggested by Storms [5]. However, other reaction zones within the palladium, especially near the electrochemical double layer, cannot be ruled out [3]. Vacancies in the palladium lattice are also possible fusion reaction zones as suggested by Hagelstein and others [6]. These reaction zones likely contain an unusually high concentration of deuterons and electrons. Proposed reaction zones were presented in a previous publication [3].

The small positive value for the entropy of activation obtained from the Eyring theory ($\Delta S^{\ddagger} = 12.3$ J mol^{-1}K^{-1}, see Table 1) is quite different from the large and negative entropy change for the D+D fusion reaction to form helium-4 ($\Delta S = -120.548$ J mol^{-1}K^{-1}, see Eq. 8). However, such small positive values for $\Delta S^{\ddagger}$ have been reported for the diffusion of hydrogen in metals and were explained by a transition state that is less ordered then the initial state. This is another indication that the rate of the D+D fusion reaction in palladium is controlled by the diffusion rate of deuterons within the palladium and not by the coulombic barrier.

Features of the D+D fusion reaction in palladium suggests that a zero-order reaction is involved. For a zero-order reaction, only a small fraction of the reacting species are in a location or state in which they are able to react. This small fraction is continually replenished from the larger pool. Furthermore, zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants. The D+D fusion reaction is possibly a pseudo-zero order reaction due to the fact that the concentration of deuterons remains relatively constant.

Acknowledgement

This work was supported from an anonymous fund at the Denver Foundation via Dixie State University and administered by “the Dixie Foundation”.

References

- [1] S. Glasstone, K.J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, NY, 1941.
- [2] K.S. Laidler and M.C. King, The development of transition-state theory, *J. Phys. Chem.* **87**, (1983) 2657–2664.
- [3] M.H. Miles, Thermodynamic and kinetic observations concerning the D+D fusion reaction for the Pd/D system, *J. Condensed Matter Nucl. Sci.* **16** (2015) 17–22.
- [4] Y. Fukai, *The Metal–Hydrogen System: Basic Bulk Properties*, Springer, Berlin, 1992, pp. 229–231.
- [5] E. Storms, *The Explanation of Low Energy Nuclear Reaction*, Infinite Energy Press, Concord, NH, USA, 2014, pp. 2–8.
- [6] D. Letts and P.L. Hagelstein, Modified Szpak protocol for excess heat, *J. Condensed Matter Nucl. Sci.* **6** (2012) 44–54.