

# Prediction of Gibbs Free Energy for Hydrogen

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## ABSTRACT

Hydrogen is an alternative renewable energy resource. We report a new efficient formulation representation for the Gibbs free energy of hydrogen. The present prediction model is related to experimental data of three molecular structure constants of hydrogen. The developed prediction model is effective from a comparison of the theoretically calculated values with the data from the National Institute of Standards and Technology (NIST) database.

**Keywords:** Gibbs free energy; Formulation representation; Hydrogen

## NONMENCLATURE

### Abbreviations

NIST National Institute of Standards and Technology

### Symbols

$r$	the internuclear distance
$r_e$	equilibrium bond length
$D_e$	dissociation energy
$c$	speed of light
$\mu$	reduced mass of a molecule
$\omega_e$	equilibrium vibrational frequency
$h$	Planck constant
$k$	Boltzmann constant
$T$	temperature
$R$	universal gas constant
$P$	gas pressure

## 1. INTRODUCTION

Hydrogen ( $H_2$ ) is often considered to be the most promising fuel for the future. An efficient formulation representation of the Gibbs free energy for hydrogen is useful for investigating operational conditions for thermochemical reaction processes [1] and chemical reaction equilibrium constants in hydrogen production from coal and biomass [2]. However, it is a formidable task to achieve an efficient formulation representation of the Gibbs free energy for hydrogen in chemical engineering and energy community. Based on a number of experimental and theoretical spectral data, the National Institute of Standards and Technology (NIST) database gives the temperature-dependent power series expressions at a standard pressure for the Gibbs free energy of hydrogen, but it includes 7 adjustable coefficients and their values are different in each temperature range of three temperature sections from 298 K to 1000K, 1000 K to 2500K, and 2500 K to 6000K [3]. Although Leachman et al. [4] proposed an empirical formulation representation with independent variables of temperature and density for the ideal-gas part of the Helmholtz energy of hydrogen, it contains 12 adjustable coefficients determined by fitting a number of calorimetric experimental data points. In view of this situation, it is necessary to explore an available formulation representation for the Gibbs free energy of hydrogen from the view of molecular structure.

The objective of this work is to establish an efficient formulation representation of the Gibbs free energy for hydrogen by the aid of experimental data of molecular structure constants of hydrogen. Applying the developed model, we predict the Gibbs free energy values for

hydrogen and compare those with the NIST data at different temperatures.

## 2. FORMULATION REPRESENTATION OF THE GIBBS FREE ENERGY FOR HYDROGEN

### 2.1 Methods and model

The improved five-parameter exponential-type oscillator is written as the following form [5, 6],

$$U(r) = D_e \left( 1 - \frac{e^{\alpha r_e} + q}{e^{\alpha r} + q} \right)^2 \quad (1)$$

where  $r$ ,  $r_e$ , and  $D_e$  denote the internuclear distance, equilibrium bond length, and dissociation energy, respectively. Dimensionless deformation parameter  $q$  is adjustable, and screening parameter  $\alpha$  is determined by

$$\alpha = \pi c \omega_e \sqrt{\frac{2\mu}{D_e}} + \frac{1}{r_e} \left( 1 - \frac{\ln(1 + \ln(1 + A))}{2 + \ln(1 + A)} \right) \ln(1 + A)$$

$$A = \pi c \omega_e r_e q \sqrt{\frac{2\mu}{D_e}} e^{-\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}}}$$

here,  $c$ ,  $\omega_e$ , and  $\mu$  stand

for the speed of light, equilibrium vibrational frequency, and reduced mass of a molecule, respectively. The improved five-parameter exponential-type oscillator is also known as Fu-Wang-Jia oscillator by Araújo and Ballester [7].

We use oscillator (1) to describe the internal vibration of  $H_2$  molecule, and take  $q=1$ . Through direct summation over all possible vibrational energies obtained by solving the Schrödinger equation with oscillator (1), we obtain the vibrational partition function of a hydrogen molecule [8],

$$Q^v = \frac{1}{2} e^{-\frac{D_e}{kT}} \left[ e^{\frac{\lambda a^2}{kT}} - e^{\frac{\lambda b^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left( \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} a \right) - \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} b \right) \right) \right. \\ \left. - e^{-\frac{2\lambda\delta}{kT}} \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} (2\delta + a^2) \right) + e^{\frac{2\lambda\delta}{kT}} \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} (2\delta + b^2) \right) \right] \quad (2)$$

where

$$\lambda = \frac{h^2 \alpha^2}{8\pi^2 \mu}$$

$$a = \frac{\frac{8\pi^2 \mu D_e}{h^2 \alpha^2} (e^{2\alpha r_e} - 1)}{1 + \sqrt{1 + \frac{32\pi^2 \mu D_e (e^{\alpha r_e} + 1)^2}{h^2 \alpha^2}}} - \frac{1 + \sqrt{1 + \frac{32\pi^2 \mu D_e (e^{\alpha r_e} + 1)^2}{h^2 \alpha^2}}}{4}$$

$$b = \frac{\frac{8\pi^2 \mu D_e}{h^2 \alpha^2} (e^{2\alpha r_e} - 1)}{33 + \sqrt{1 + \frac{32\pi^2 \mu D_e (e^{\alpha r_e} + 1)^2}{h^2 \alpha^2}}} - \frac{33 + \sqrt{1 + \frac{32\pi^2 \mu D_e (e^{\alpha r_e} + 1)^2}{h^2 \alpha^2}}}{4}$$

$$\delta = \frac{4\pi^2 \mu D_e}{h^2 \alpha^2} (e^{2\alpha r_e} - 1)$$

here  $h$ ,  $k$ , and  $T$  represent the Planck constant, Boltzmann constant, and the absolute temperature, respectively, and the symbol  $\operatorname{erfi}$  denotes the imaginary error function. The translational and rotational partition functions for a hydrogen molecule with occupying the spatial volume  $V$ , are represented as, respectively [9, 10],

$$Q^t = \left( \frac{4\pi\mu kT}{h^2} \right)^{\frac{3}{2}} V \quad (3)$$

$$Q^r = \frac{T}{2\Theta_r} \left( 1 + \frac{1}{3} \frac{\Theta_r}{T} + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 \right) \quad (4)$$

where  $\Theta_r = \frac{h^2}{8\pi^2 \mu r_e^2 k}$ . Using the thermodynamic

formula,  $G = RTV \left( \frac{\partial \ln Q}{\partial V} \right)_T - RT \ln Q$ , and

considering the translational, rotational and vibrational contributions to the Gibbs free energy, we obtain a formulation representation of the molar Gibbs free energy for  $H_2$ ,

$$G = -RT \ln \left[ \frac{1}{2} e^{-\frac{D_e}{kT}} \left( e^{\frac{\lambda a^2}{kT}} - e^{\frac{\lambda b^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left( \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} a \right) - \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} b \right) \right) \right. \right. \\ \left. \left. - e^{-\frac{2\lambda\delta}{kT}} \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} (2\delta + a^2) \right) + e^{\frac{2\lambda\delta}{kT}} \operatorname{erfi} \left( \sqrt{\frac{\lambda}{kT}} (2\delta + b^2) \right) \right) \right] \\ - RT \ln \left[ \frac{(4\pi\mu)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3 P} \right] - RT \ln \left[ \frac{T}{2\Theta_r} \left( 1 + \frac{1}{3} \frac{\Theta_r}{T} + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 \right) \right] \quad (5)$$

where  $R$  denotes the universal gas constant, and  $P$  is gas pressure. In the above representation, two independent variables are temperature and pressure, and all the input parameters are only involved three molecular constants and the fundamental physical constants. Inputting the experimental values of three molecular constants into formulation expression (5), we can directly and conveniently determine the Gibbs free energy value in a given temperature and pressure for hydrogen.

### 2.2 Applications

The experimental data of three molecular constants for  $H_2$  molecule are taken from literature [11]:  $D_e = 4.7467$  eV,  $r_e = 0.74173$  Å,  $\omega_e = 4400.39$   $\text{cm}^{-1}$ . The reduced mass of  $H_2$  molecule is  $\mu = 8.36862 \times 10^{-28}$  kg. Taking into account the contributions of excited states of  $H_2$ , we add additional

term  $-\frac{2}{5}RT$  to the right hands of equation (5). With the help of representation (5), we predict the Gibbs free energy values in the temperature range from 298 to 6000 K and at the pressure of 0.1 MPa, and give the predicted values in Table 1, in which we also list the NIST data [3]. The predicted results are also graphically shown in Fig. 1, in which the NIST data are also depicted. The reduced molar Gibbs free energy is defined as  $G_r = -(G - H_{298.15})/T$ , here  $H_{298.15}$  represents the molar enthalpy value at temperature 298.15 K. The reduced molar Gibbs free energy of  $H_2$  is  $130.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  at 298 K from the NIST database [3]. The predicted molar Gibbs free energy from formulation (5) is  $-3952.5019 \text{ J}\cdot\text{mol}^{-1}$  at 298 K. Using these two values, the value of  $H_{298.15}$  is yielded with  $34996.098 \text{ J}\cdot\text{mol}^{-1}$ . From Table 1 and Fig. 1, we observe that the predicted results are in excellent agreement with the NIST data. The relative deviations of the predicted reduced molar Gibbs free energies from the NIST database is 0.126 % in the temperature range of 298 to 6000 K. This result indicates that the developed model performs well in predicting the Gibbs free energy for hydrogen.

## CONCLUSIONS

We propose a new formulation representation of the Gibbs free energy for hydrogen. The proposed representation involves only the dissociation energy, equilibrium bond length and equilibrium vibration frequency for the hydrogen molecule. The validity of the developed prediction model is verified by a comparison of the calculated values with the data reported in the NIST database.

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Table 1 A comparison of the predicted values of the reduced molar Gibbs free energy with the NIST data for hydrogen at different temperatures. The reduced Gibbs free energy and temperature are in units of  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and K, respectively.

Temperature	NIST value	Predicted value	Temperature	NIST value	Predicted value
298	130.7	130.69	3200	175.2	175.47
300	130.7	130.69	3300	176.2	176.39
400	131.8	131.45	3400	177.1	177.29
500	134.0	133.44	3500	178.0	178.17
600	136.4	135.80	3600	178.8	179.03
700	138.8	138.23	3700	179.7	179.87
800	141.2	140.61	3800	180.5	180.69
900	143.4	142.89	3900	181.3	181.49
1000	145.5	145.08	4000	182.1	182.28
1100	147.5	147.16	4100	182.9	183.05
1200	149.5	149.14	4200	183.7	183.79
1300	151.3	151.02	4300	184.4	184.53
1400	153.0	152.81	4400	185.2	185.26
1500	154.7	154.51	4500	185.9	185.97
1600	156.2	156.16	4600	186.6	186.66
1700	157.7	157.72	4700	187.3	187.35
1800	159.2	159.21	4800	188.0	188.02
1900	160.6	160.66	4900	188.7	188.68
2000	161.9	162.03	5000	189.4	189.33
2100	163.2	163.37	5100	190.1	189.97
2200	164.5	164.65	5200	190.7	190.60
2300	165.7	165.89	5300	191.3	191.21
2400	166.9	167.09	5400	192.0	191.82
2500	168.0	168.25	5500	192.6	192.41
2600	169.2	169.37	5600	193.2	193.01
2700	170.2	170.47	5700	193.8	193.59
2800	171.3	171.52	5800	194.4	194.16
2900	172.3	172.55	5900	195.0	194.71
3000	173.3	173.55	6000	195.6	195.28
3100	174.3	174.51			
Average deviation (%)			0.126		

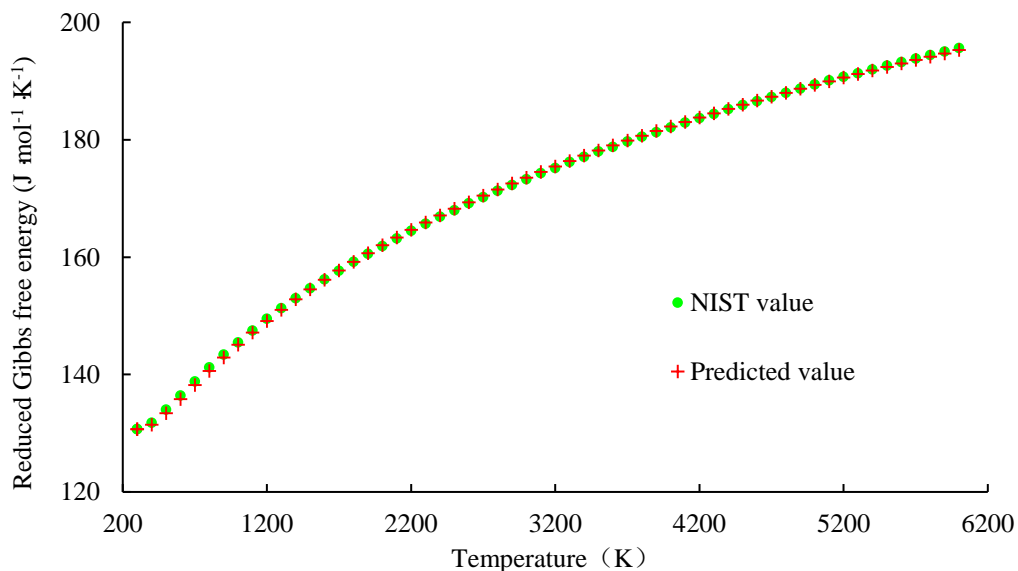


Fig.1. Temperature variation of the reduced molar Gibbs free energy for hydrogen.