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Computation of Kinetics for the Hydrogen/Oxygen System Using the Thermodynamic Method

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Abstract

A new method for predicting chemical rate constants using thermodynamics has been applied to the hydrogen/oxygen system. This method is based on using the gradient of the Gibbs free energy and a single proportionality constant D to determine the kinetic rate constants. Using this method the rate constants for any gas phase reaction can be computed from thermodynamic properties. A modified reaction set for the H/O system is determined. All of the third body efficiencies M are taken to be unity. Good agreement was obtained between the thermodynamic method and the experimental shock tube data. In addition, the hydrogen bromide experimental data presented in previous work (ref.1) is recomputed with M's of unity.

Introduction

There are several reasons why it is desirable to relate the reaction kinetic rate constants to thermodynamic data. First, modern kinetic models contain many reactions with many empirical constants to form large mechanisms. These systems are not universal and are complex to assemble from the experimental data base. In contrast, thermodynamic equilibrium calculations have been simplified and systematized and are only species dependent. If the kinetic constants can be related to thermodynamics, it would significantly reduce the work involved in doing kinetic calculations.

Secondly many kinetic constants are still unknown; if these reactions could be computed by using thermodynamic data, the kinetics calculation could be done without performing more experiments.

There already exist several relationships that link thermodynamics to the kinetic rates. In this report an expression is derived which links the individual rate constant to the thermodynamic data. For instance in kinetics textbooks: the ratio equation (1) relates thermodynamic equilibrium constant K_c to the ratio of the forward rate constant k_f to the reverse rate constant k_r:

$$K_c=\frac{k_f}{k_r}\ . \tag{1}$$

Normally, one thinks of kinetics as a path process, however the kinetic rate constants are state variables like K_c. The kinetic constants k are functions only of temperature and are therefore state variables and not path variables. Equation (1) holds not only at equilibrium, but also at every point of the reaction from initial conditions to final state. Furthermore, it is independent of concentration.

It is widely thought that an overall relationship between kinetics and thermodynamics is not possible. All of the kinetic text books principally state that thermodynamics is only for equilibrium calculations whereas kinetics describes the rate of approach to equilibrium; thus, they state that thermodynamics would not be useful for kinetics calculations. However, as stated, relationship (1) holds for all time, not only at equilibrium.

With thermodynamics, the complete energy surface is available for ideal gas mixtures for all compositions (from initial reactants to final products), not only for equilibrium states. This information can be used to compute the kinetic rate constants. The change of system free energy with reaction $\partial G/\partial x$ is known, and is used to compute the kinetic rate of reaction. The current use of system free energy is that when the free energy is minimum, the system is in equilibrium and no further reaction can occur. When the system free energy is above the minimum, reaction can occur. The Gibbs free energy is definitely the driving force for the reaction. We state that the reaction rate is related the the free energy gradient using a proportionality constant D between free energy and the chemical rate. Then using this relationship, the individual kinetic rate constants can be calculated. Only one number for D is used for the complete regime of temperature, pressure, and composition.

The following discussion compares the classical method with the thermodynamic method for the H/O system. In doing this a third body efficiency M needed to be included in the new method to obtain the correct pressure behavior. M is set to unity for all molecules. A comparison of the two methods is made with experimental data for the H/O system. Finally the HBr results from reference 1 are recomputed including M taken as unity and making all stoichiometric coefficients into integers rather than using fractions. In general the agreement with data is very good.

The Classical Method of Kinetic Rate Constants for the H/O System

The classical kinetic method can be described for a particular rate by:

$$\nu_1 S_1+\nu_2 S_2=\nu_3 S_3+\nu_4 S_4\ , \tag{2}$$

where the ν_i are the stoichiometric coefficients for species S_i. The forward rate r_f is given by:

$$r_f = k_f \, C_1^{\nu_1} C_2^{\nu_2} \, . \tag{3}$$

and the kinetic rate constant k_f is defined as:

$$k_f = A_f \, T^{\,n} \exp(-E/RT) \tag{4}$$

The kinetic constants A_f, n, and E are determined by the best fit of the experimental data. A large data base is used to fit the many rate constants.

The data of reference 2 is used for comparing both the clasical and thermodynamic methods. This data is also published in references 3 and 4. This data follows the OH concentration using laser absorption in a shock tube experiment. Weak mixtures of H_2 and O_2 in Argon are used to try to isolate the principle reactions. The range of test conditions was wide from equivalence ratios of 0.05 to 10., pressures of 0.7 to 4.1 atm, and temperatures from 1050 K to 2500 K. Over 200 test points are reported.

Theclassical mechanism given in Reference 2 is shown in table 1:

Table 1. Classical Rate Equations from Ref. 2.

Name	Reaction	A	n	E/R
CL1	H +O2 = OH + O	7.13 E+13	0.0	6957.
CL2	O +H2 = OH + H	1.87 E+14	0.0	6854.
CL3	OH +H2=H2O+H	2.14 E+08	1.52	1736.
CL4	O + H2O=2.0OH	4.51 E+04	2.7	7323.
CL5	O + O = O2+M	1.00 E+17	-1.0	0.
	AR=1., H2=2.9, O2=1.2, H2O=18.5			
CL6	H + H = H2+M	6.4 E+17	-1.0	0.
	AR=1., H2=4.0, H=26., H2O=12.			
CL7	H + O = OH +M	6.2 E+16	-0.6	0.
	AR=1., H2O=5.0			
CL8	H + OH = H2O + M	8.4 E+21	-2.0	0.
	AR=1., H2=2.5, H2O=16.25			
CL9	H + O2 = HO2 + M	7.0 E+17	-0.8	0.
	AR=1., H2=3.33, O2=1.33, H2O=21.3			
CL10	HO2+ H = OH +OH	2.2 E+14	0.0	710.
CL11	HO2+ H = H2 +O2	2.5 E+13	0.0	350.
CL12	HO2+ H = H2O + O	5.0 E+12	0.0	710.
CL13	HO2+ O = O2 +OH	2.0 E+13	0.0	0.
CL14	HO2+ OH =H2O+O2	2.0 E+13	0.0	0.
CL15	HO2+ HO2=H2O2+O2	1.06 E+11	0.0	-855.
CL16	H2O2+M=2.0 OH+M	1.2 E+17	0.0	22900.
	AR=0.67, O2=0.78, H2O=6.0			
CL17	H2O2+H=HO2+H2	1.7 E+12	0.0	1900.
CL18	H2O2+H=H2O+OH	1.0 E+13	0.0	1895.
CL19	H2O2+O=HO2+OH	1.8 E+13	0.0	3225.
CL20	H2O2+OH=H2O+ HO2	7.0 E+12	0.0	720.

The classical reaction mechanism consists of 20 reaction steps. Each reaction has three experimental constants with a total of 14 third body efficiencies for a total of 74 constants. In this system there are 9 species, H_2, H, O_2, O, OH, H_2O, HO_2, H_2O_2 and Argon. Reactions CL1, CL2, and CL3 are the principle reactions with CL1 and CL2 producing OH and then OH reacting with H_2 through CL3 to produce H_2O.

The differential kinetics equations were integrated with the NASA Lewis chemical kinetics code LSENS, reference 5. The path was taken to be a constant density case to represent the shock tube data of reference 2. LSENS was used for both the classical and thermodynamics methods. The thermodynamic properties for both the classical and thermodynamic methods were obtained from reference 6. The thermodynamic entropy reference b2 was corrected from one bar pressure to one atmosphere by: **_b2_(1_atm_)=_b2_(1_bar_)-0.01316** for all species.

Thermodynamic Method of Computing the Kinetic Rate Constants

In the thermodynamic derivation, the kinetic rate is assumed to be related to the gradient of the free energy with respect to the reaction progress variable x, or:

$$r_f \;\alpha\; \exp\left(\frac{-1}{RT}\frac{\partial G}{\partial x}\right)\;. \tag{5}$$

The free energy G , ref. 7, is given by:

$$G=\sum_i(\mu_i^o n_i)+\sum_i(n_i\ RT\ \ln(p_i)). \tag{6}$$

Differentiating equation (6) with respect to x, yields:

$$-\frac{1}{RT}\frac{\partial G}{\partial x}=\sum_i\frac{\nu_{f\,i}\ \mu^o_{f\,i}}{RT}-\sum_i\frac{\nu_{r\,i}\ \mu^o_{r\,i}}{RT}+\sum_i(\nu_{f\,i}\ \ln\ p_{f\,i})-\sum_i(\nu_{r\,i}\ \ln\ p_{r\,i})\;. \tag{7}$$

The standard thermodynamic expression for K_p is the first two terms on the right hand side and is expressed as:

$$K_p\ =\ \exp\left(\sum_i\frac{\nu_{f\,i}\ \mu^o_{f\,i}}{RT}-\sum_i\frac{\nu_{r\,i}\ \mu^o_{r\,i}}{RT}\right)\ \text{or}\ =\ \exp\left(\frac{-\Delta G^{\,o}}{RT}\right) \tag{8}$$

K_p is independent of composition or degree of reaction. It represents the difference in chemical potential between the reactants and products. In addition K_c is given by (where R=82.05 atm-cc/mole-K):

$$K_c=K_p(RT)^{-\Delta\nu_i}=K_p(RT)^{(\Sigma\nu_{f\,i}-\Sigma\nu_{r\,i})}\;. \tag{9}$$

At this point, it is important to distinguish chemical kinetic constants, k_p and k_c. When the kinetic rate is given in terms of concentrations, k_c is used; and when the rate is given in terms of pressure p, k_p is utilized.

$$\frac{dc}{dt}=k_c\ C_1^{\nu_1}C_2^{\nu_2}\ ;\ \frac{dp}{dt}=k_p\ p_1^{\nu_1}p_2^{\nu_2}\ ;\ \text{and}\ C_i=\frac{p_i}{RT}\ .$$

Then:

$$k_c=k_p\ (RT)^{(\Sigma\nu_{f\,i}-1)}\ ; \tag{10}$$

similar to K_c and K_p in equation (9).

Returning to equations (5) and (7) and equating the pressure terms (IE. the concentration terms) to the concentration terms in equation (3) for the forward rate, one obtains:

$$k_{c\,f}=DK_p\ (RT)^{\Sigma\nu_{f\,i}-1}\quad \text{for } K_p< 1. \tag{11}$$

where D is a constant to be determined. Equation (11) provides the connection between thermodynamics and the forward chemical kinetic constant that shall be used.

Equation (11) without the K_p inequality cannot hold for both the forward and reverse rates because equation (1) would not be satisfied. Remember that $K_{pr}\equiv 1/K_{pf}$, so when $K_{pf}<1$, then $K_{pr}>1$. To satisfy the kinetic constant ratio equation (1), the reverse rate must be given by:

$$k_{cr}=D(RT)^{\Sigma\nu_{i\,r}-1}\ \text{for } K_{pr}> 1. \tag{12}$$

The proportionality constant D can be a universal constant. But as will be shown in this report, a different value had to be used for the H/O system, $D=7.0\text{x}10^7$, compared to the HBr computation where $D=3.0\text{x}10^8$. For all of the H/O calculations, D was held constant at $7\text{x}10^7$ for all the reactions. The difference in the values for the two systems could be the result of impurities in the HBr measurements which were made in 1906. No sensitivity to surface area, air addition or water vapor was found; but the system was sensitive to iodine which produced pronounced inhibition, ref. 8. Differences could result from the larger concentrations of H_2/Br_2 reactants or the differences in measurement techniques - acid/base titrations for HBr versus laser techniques for the H/O system. Or something may be incomplete in this thermodynamic theory. More comparisons with data are required to completely verify a universal D of $7.0\text{x}10^7$.

One advantage of equations (11) and (12), is that the kinetic constant is continuous through $K_p=1$; and k is defined over the complete range of conditions.

Alternative Expression of Thermodynamic Method

Another way of stating the thermodynamic method is simply:

$$\text{For } K_p > 1\text{: } k_p = D \text{ or } k_p \text{ is a constant.} \tag{13}$$

Equation (13) is well known for radical/radical recombinations reactions. In this work it has been assumed that D is the same constant for all reactions. How does the activation energy compare between the classical and thermodynamic methods.

Comparison of Activation Energies between Methods

For the classical method, the net activation energy can be computed from equation (4) and is given by:

$$E_{net} = -R\frac{\partial \ln k}{\partial(1/T)} = nRT + E \ . \tag{14}$$

For the thermodynamic method, E_{net} is computed by:

$$\frac{\partial \ln(K_p)}{\partial 1/T} = -\frac{\Delta H^\circ}{R}$$

$$\textit{so}\quad \textit{For}\ K_p<1\text{:}\quad E_{net} = \Sigma(\nu_{f\,i}-1)RT + \Delta H^\circ$$

$$\textit{For}\ K_p>1\text{:}\quad E_{net} = \Sigma(\nu_{f\,i}-1)RT \ .$$

A comparison of the net activation energies at 1500 K is shown in Table 2.

Table 2. Net Activation Energies E_{net} (calories/mole) for Classical and Thermodynamic Methods.

		Evaluated at 1500 K		
Name	**Reaction**	**$\mathrm{Log_{10}K_p}$**	**Classical**	**Thermo**
CL1	H +O2 = OH + O	-1.213	13823.	19039.
CL2	O +H2 = OH + H	0.062	13619.	2980.
CL3	OH +H2=H2O+H	1.544	7980.	2980.
CL4	O + H2O=2.0OH	-1.482	22598.	20043.
CL5	O + O = O2+M AR=1., H2=2.9, O2=1.2, H2O=18.5	10.78	-2980.	2980.
CL6	H + H = H2+M AR=1., H2=4.0, H=26., H2O=12.	9.509	-2980.	2980.
CL7	H + O = OH +M AR=1., H2O=5.0	9.571	-1788.	2980.
CL8	H + OH = H2O + M AR=1., H2=2.5, H2O=16.25	11.05	-5961.	2980.
CL9	H + O2 = HO2 + M AR=1., H2=3.33, O2=1.33, H2O=21.3	1.914	-2384.	2980.

CL10	HO2+ H = OH +OH	6.444	1411.	2980.
CL11	HO2+ H = H2 +O2	7.595	695.	2980.
CL12	HO2+ H = H2O + O	7.926	1411.	2980.
CL13	HO2+ O = O2 +OH	7.657	0.	2980.
CL14	HO2+ OH =H2O+O2	216.6	0.	2980.
CL15	HO2+ HO2=H2O2+O2	4.740	-1699.	2980.
CL16	H2O2+M=2.0 OH+M AR=0.67, O2=0.78, H2O=6.0	-0.215	45502.	52009.
CL17	H2O2+H=HO2+H2	2.855	3775.	2980.
CL18	H2O2+H=H2O+OH	10.84	3765.	2980.
CL19	H2O2+O=HO2+OH	2.917	6408.	2980.
CL20	H2O2+OH=H2O+ HO2	4.400	1431.	2980.

What can be stated is that when K_p is positive, the classical and thermodynamic activation energies are low, except for reaction CL2. For an activation energy of 2980, the kinetic constant increases by a factor of 2.7 when the temperature is increased from 1000 to 3000 K. In kinetics, this is not a large change and is represented by a classical activation energy of zero with an "n" of one.

The third body coefficient for M (unity) is not counted in the k or n expression, because it was not included in either the free energy expression or in the K_c/K_p relation.

Selection of Thermodynamic Reactions

The values of the kinetic constants at 1500 K are given in Table 3 below. Individual rate constants for both the thermodynamic and classical methods are given. The rates included in the thermodynamic set, T1-T26, are shown in Table 3. Essentially all reactions which were possible have been written down. More reactions were included in the thermodynamic model than in the classical set, When $K_p > 1$ or $\log_{10}K_p > 0$, the expression for the rate constant follows equation (12) and does not include K_p

Table 3. Thermodynamic Reactions for the H/O System

ORDER	CLASS	THERMO		Evaluated at T=1500 K		
			<u>ATOM REACTIONS</u>	$\log_{10}K_p$	$\log_{10}k_f^{thermo}$	$\log_{10}k_f^{classical}$
A1	CL6R	T1	M + H2 =2.0H	-9.520	-1.67	0.03
A2	CL5R	T2	M + O2 =2.0O	-10.79	-2.94	-2.05
			<u>OH REACTIONS</u>			
B1	CL7	T3	H + O = OH + M	9.577	12.94	14.89
B2	CL1	T4	H + O2 = OH + O	-1.213	11.72	11.84
B3	CL2	T5	H2 + O = OH + H	0.062	12.94	12.29
B4			H2 + O2 =2.0OH	-1.151	11.79	-------
			<u>H2O REACTIONS</u>			
C1			2.0H + O = H2O + M	20.65	18.03	-------
C2		T6	2.0H + O2 = H2O + O	9.852	18.03	-------
C3		T7	H2 + O = H2O + M	11.12	12.94	-------

C4	CL8	T8	H + OH = H2O + M	11.06	12.94	15.57
C5	CL3	T9	H2 + OH = H2O + H	1.544	12.94	12.66
C6	CL4	T10	O + H2O = 2.0OH	-1.482	11.45	11.11
C7		T11	O2 + H2O = 2.0OH + O	-12.25	0.711	------
C8			2.0H2 + O2 = 2.0H2O	11.46	18.03	------
			HO2 REACTIONS			
D1			H +2.0O = HO2 + M	13.09	18.03	------
D2	CL9	T12	H +O2 = HO2 + M	1.919	12.94	15.31
D3		T13	H2 + 2.0O = HO2 + H	3.195	18.03	------
D4	CL11R	T14	H2 + O2 = HO2 + H	-7.595	5.34	5.70
D5		T15	H2+2.0O2 = 2.0HO2	-5.66	12.35	------
D6	CL10	T16	H +HO2 = 2.0OH	6.444	12.94	14.14
D7		T17	H2 + HO2 =2.0OH + H	-2.690	10.25	------
D8		T18	OH + O = HO2 + M	3.492	12.94	------
D9	CL13R	T19	OH + O2 = HO2 + O	-7.657	5.28	21.29
D10	CL12		H + HO2 = H2O + O	7.926	12.94	12.49
D11		T20	H2 + HO2 = H2O + OH	7.988	12.94	------
D12	CL14	T21	OH + HO2 = H2O + O2	9.139	12.94	13.30
D13			OH + HO2 = H2O + 2.0O	-1.650	11.28	------
			H2O2 REACTIONS			
E1			2.0H + 2.0O = H2O2 + M	19.37	23.11	------
E2		T22	2.0H + O2 = H2O2 + M	8.578	18.03	------
E3			H2 + 2.0O = H2O2 + M	9.854	18.03	------
E4			H2 + O2 = H2O2 + M	-0.936	12.00	------
E5	CL16	T23	M + H2O2 = 2.0OH	-0.215	7.63	10.45
E6	CL17R	T24	H2 + HO2 = H2O2 + H	-2.855	11.08	11.68
E7	CL15		2.0HO2 = H2O2 + O2	4.740	12.94	11.27
E8			2.0HO2 = H2O2 + 2.0O	-6.050	6.89	------
E9		T25	O + H2O = H2O2 + M	-1.267	11.67	------
E10			O2 + H2O = H2O2 +O	-12.05	0.878	------
E11			H + HO2 = H2O2 + M	6.660	12.94	------
E12			2.0H2O = H2O2 + 2.0H	-21.90	-8.97	------
E13	CL18	T26	H2O2 + H = H2O +OH	10.84	12.94	12.48
E14	CL19		H2O2 + O = HO2 + OH	2.917	12.94	12.51
E15	CL20		H2O2 +OH = H2O+ HO2	4.400	12.94	12.64
TOTAL	**42 REACTIONS**					

The important rates were selected to complete the reaction set. The rules for rate selection were:

1. The molecular/molecular reactions (B4, C8, and E4) were eliminated for two reasons; first, they were too fast and required an overall D value of less than 10^4 to obtain agreement with the data. Their reaction rate was fast not only because of a large kinetic constant (large K_p), but also because of the high concentration of the reactants. Secondly, they are not included in the classical mechanism, because their rates are difficult to measure accurately and inclusion in the mechanism represents a parallel path with the free radicals. So inclusion would require a change in free radical rate

constants for agreement with the data. However the HO_2 molecular reactions D4 and D5 were included to obtain the correct ignition delay at lower temperatures. For D4 and D5, the K_p levels are small and the forward rates are consistent with the reaction set.

2. The other rates such as C1, D1, D10, D13, etc., were eliminated because they were very small making their contribution to the overall reaction rate negligible. For example the combination of three radical concentrations combine to a very small overall rate. The subroutine ORDER and RXNTST in the LSENS program were used to organize the process. Subroutine ORDER orders the rates for each species at each output time step. RXNTST verifies that the rates are balanced and that there is no duplication of rates in the system.

There are differences in several of the kinetics constants between the thermodynamic model and the classical model; but these differences balance out for the net system. For example, reaction 1 which is the initial dissociation of H2 is 50 times smaller for the thermodynamic method than the classical.. This appears to be not critical, because after some O is produced by (T2), the OH producing reaction B3 (CL2) generates H.

Thermodynamic Kinetics Constants

Most investigators use kinetics constants in the form of equation (4). Using the thermodynamic method the rate constants for all of the reactions could be computed (see Table 4). The values of K_p were fitted to a logarithmic expression over the temperature range from 1000 to 3000 K. The least squares values were combined with equations (11) and (12) to obtain the values of A_t, n_t, and E_t.

Table 4. Thermodynamic Constants for the H/O System

ORDER	CLASS	THERMO		Evaluated at T=1000 to 3000 K		
			ATOM REACTIONS	A_t	n_t	E_t/R
A1	CL6R	T1	M + H2 =2.0H	2.71E+10	0.982	52575.
A2	CL5R	T2	M + O2 =2.0O	6.88E+12	0.530	60326.
			OH REACTIONS			
B1	CL7	T3	H + O = OH + M	5.74E+09	1.0	0.
B2	CL1	T4	H + O2 = OH + O	2.04E+12	0.606	8673.
B3	CL2	T5	H2 + O = OH + H	5.74E+09	1.0	0.
B4			H2 + O2 =2.0OH	2.84E+12	0.664	9594.
			H2O REACTIONS			
C1			2.0H + O = H2O + M	4.71E+11	2.0	0.0
C2		T6	2.0H + O2 = H2O + O	4.71E+11	2.0	0.0
C3		T7	H2 + O = H2O + M	5.74E+09	1.0	0.
C4	CL8	T8	H + OH = H2O + M	5.74E+09	1.0	0.
C5	CL3	T9	H2 + OH = H2O + H	5.74 E+09	1.0	0.0
C6	CL4	T10	O + H2O = 2.0OH	8.18E+11	0.680	9067.

C7		T11	O2 + H2O = 2.0OH + O	6.02E+16	1.255	69266.
C8			2.0H2 + O2 = 2.0H2O	4.71E+11	2.0	0.0
			HO2 REACTIONS			
D1			H +2.0O = HO2 + M	4.71E+11	2.0	0.0
D2	CL9	T12	H +O2 = HO2 + M	5.74E+09	1.0	0.0
D3		T13	H2 + 2.0O = HO2 + H	4.71E+11	2.0	0.0
D4	CL11R	T14	H2 + O2 = HO2 + H	2.66E+08	1.515	27281.
D5		T15	H2+2.0O2 = 2.0HO2	2.62E+06	2.05	1986.
D6	CL10	T16	H +HO2 = 2.0OH	5.74 E+09	1.0	0.0
D7		T17	H2 + HO2 =2.0OH + H	3.94E+17	-1.35	10562.
D8		T18	OH + O = HO2 + M	5.74E+09	1.0	0.0
D9	CL13R	T19	OH + O2 = HO2 + O	1.91E+08	1.457	26359.
D10	CL12		H + HO2 = H2O + O	5.74E+09	1.0	0.0
D11		T20	H2 + HO2 = H2O + OH	5.74E+09	1.0	0.0
D12	CL14	T21	OH + HO2 = H2O + O2	5.74 E+09	1.0	0.0
D13			OH + HO2 = H2O + 2.0O	1.19E+14	1.391	24900.
			H2O2 REACTIONS			
E1			2.0H + 2.0O = H2O2 + M	3.87E+13	3.0	0.0
E2		T22	2.0H + O2 = H2O2 + M	4.71E+11	2.0	0.0
E3			H2 + 2.0O = H2O2 + M	4.71E+11	2.0	0.0
E4			H2 + O2 = H2O2 + M	2.51E+03	1.132	-17282.
E5	CL16	T23	M + H2O2 = 2.0OH	7.92E+16	-0.468	26877.
E6	CL17R	T24	H2 + HO2 = H2O2 + H	2.09E+07	1.600	8012.
E7	CL15		2.0HO2 = H2O2 + O2	5.74E+09	1.0	0.0
E8			2.0HO2 = H2O2 + 2.0O	4.44E+13	1.614	41057.
E9		T25	O + H2O = H2O2 + M	7.23E+02	1.15	-17810.
E10			O2 + H2O = H2O2 +O	7.11E+07	1.68	42516.
E11			H + HO2 = H2O2 + M	5.74E+09	1.0	0.0
E12			2.0H2O = H2O2 + 2.0H	7.93E+09	2.68	94564.
E13	CL18	T26	H2O2 + H = H2O +OH	5.74E+09	1.0	0.0
E14	CL19		H2O2 + O = HO2 + OH	5.74E+09	1.0	0.0
E15	CL20		H2O2 +OH = H2O+ HO2	5.74E+09	1.0	0.0

TOTAL 42 REACTIONS

When K_p is greater than one, many rates are computed as the same values. However the net forward rate depends on the concentrations as well as the kinetic constants.

In the next section the results from the classical method and from the thermodynamic method using equations (11) and (12) to compute the kinetics for all reactions are compared with experimental data.

Comparison of Both Methods to Experimental Data

The LSENS code was modified to compute the forward kinetic constant using the Gibbs free energies. One could also use the constants in Table 4. The code already had provisions to calculate the reverse rate from the equilibrium constant, equation (1). Only about five lines had to be added to the code in order to compute the forward rate from the thermodynamic data and equations (11) or (12).

The thermodynamic method was first tested using the classical mechanism equations (CL1-CL20 but with new constants). The experimental data is given in terms of the OH absorption, which is related to concentration by:

$$AB_{OH}=1-\exp(1.5\times10^{7}\ L\ C_{OH}\text{moles/cc}); \quad \textit{where } L=\text{path length in cm.} \tag{15}$$

The agreement between the experimental data and the classical mechanism was excellent for the single test case shown in Figure 1. This single test case was used for the thermodynamic method with the constant D of 3×10^{8} as reported in reference 1. The classical values of M were used. The results show the predicted ignition time was four times too fast.

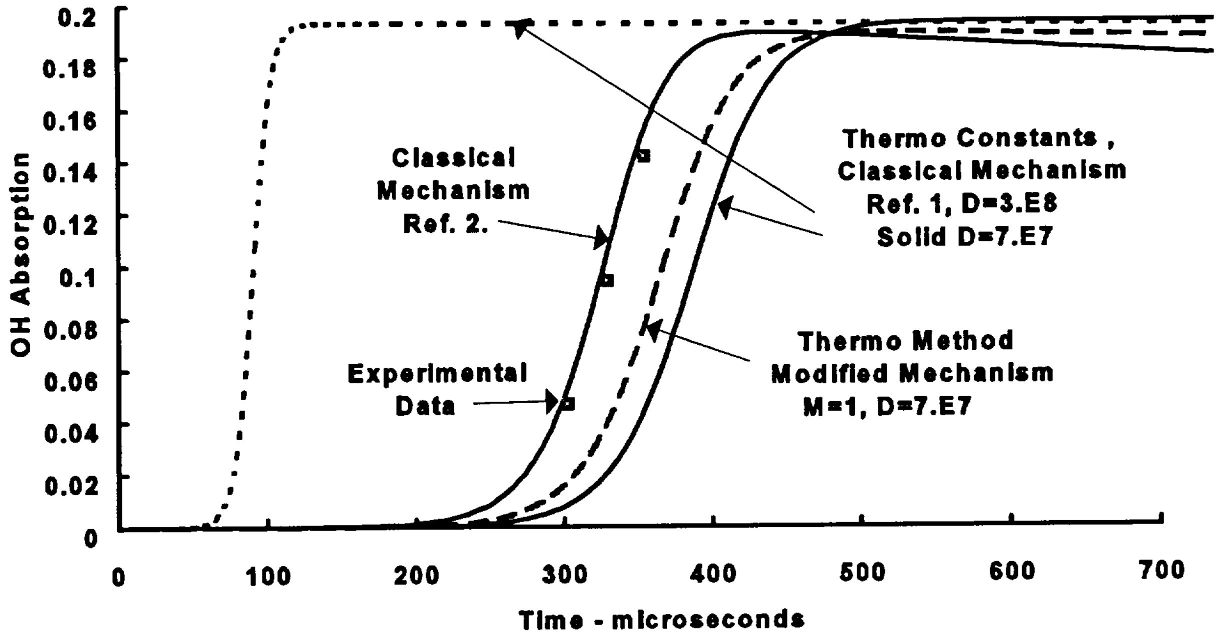

Figure 1: Comparison of Classical and Thermodynamic Predictions to Experimental data, T=1556 K, P=0.751 atm, XH2=0.02, XO2=0.002, or Phi=2.

When D was lowered to 7×10^{7} with the classical values of M , the agreement was much better.

However, the thermodynamic method did not provide any method for computing M.

The most confusing thing about third body efficiencies is the variety of values given in the literature. For instance, for the reaction $H_2 + M = 2H + M$, reference 2 give values of M as $H_2=4$, $H=26.$, and $H_20=12$. While reference 9 reports M values of $H_2=0.14T^{-0.4}$, $H_2O=93.8\ T^{-0.25}$, $C\ O=1.6$, $N_2=1.6$, $O_2=1.6$, and $C\ O_2=858/T$. And reference 10 gives values of $H_2=4.1$, $H_2O=15.$, $O_2=2.$, and $N_2=2$. In this report, in order to keep things as simple as possible, all third body efficiencies M were set to unity and all collisions assist in the reaction - even self collisions. So the concentration of the third body M is given by: $C_M=\rho/M_W$.

However to check this approach, computations were made without M; but the fit over the complete temperature and pressure range of the data was poor. It is logical to include M in the set in order to get the correct pressure and temperature dependence for monomolecular reactions. All of the efficiency M values were taken as unity. This is consistent with the free energy formulation from equation (6) and (7), where the concentration of the diluent would affect the mixing term $\sum n_i\ (\ln p_i)$ and would not cancel out when there was a change in the number of moles for the reaction.

There is excellent agreement between the shapes of the OH rise curves for the classical and thermodynamic methods. Good agreement of the OH overshoot was obtained between the classical and thermodynamic methods

With the thermodynamic approach all of the kinetic constants are calculated by the LSENS program using thermodynamic data, so one only needs to write down the chemical reaction to include it in the system.

The final comparisons are shown in Table 5. The times t_{25}, t_{50}, and t_{75}, are the reaction times required to reach 25, 50, and 75 percent of the maximum OH concentration. This table represents the minimum and maximum of the temperatures, and pressures for the 9 different compositions run in ref 2. A total of 200 cases were reported in ref. 2 but only 20 are selected here.

Table 5. Comparison of Classical and Thermodynamic Methods to Experimental Data. *S=Single path length, L = 6.35 cm.
D= Double path length, L=12.7 cm

Case	T K	P atm	XH2	XO2		t25	t50	t75
1S*	1052.	2.289	0.04	0.01	Exper	597.	618.	650.
			$\phi=2$		Class	582.	606.	623.
					Thermo	529.	551.	566.
2S	1074.	0.964	0.04	0.01	Exper	974.	1005.	1050.
					Class	950.	997.	1034.
					Thermo	1222.	1276.	1319.
3S	1115.	2.248	0.04	0.01	Exper	371.	393.	411.
					Class	346.	363.	376.
					Thermo	363.	380.	393.
4S	1155.	0.957	0.02	0.005	Exper	1188.	1274.	1343.
			$\phi=2$		Class	1050.	1216.	1270.
					Thermo	1602.	1709.	1803.
5S	1556.	0.751	0.02	0.005	Exper	302.	329.	354.
					Class	299.	326.	348.
					Thermo	335.	364.	392.
6S	2136.	0.851	0.02	0.005	Exper	81.	92.	101.
					Class	75.	86.	96.
					Thermo	57.	65.	72.
7D	1525.	2.005	0.004	0.001	Exper	628.	703.	770.
			$\phi=2$		Class	605.	657.	702.
					Thermo	711.	773.	832.
8D	2409.	2.095	0.004	0.001	Exper	107.	127.	145.
					Class	94.	111.	128.
					Thermo	71.	82.	93.
9D	1527.	3.770	0.002	0.0005	Exper	573.	647.	704.
			$\phi=2$		Class	635.	690.	737.
					Thermo	751.	816.	880.
10D	2211.	3.715	0.002	0.0005	Exper	137.	158.	178.
					Class	141.	163.	185.
					Thermo	113.	129.	145.
11S	1243.	0.798	0.05	0.005	Exper	804.	863.	907.
			$\phi=5$		Class	738.	785.	821.
					Thermo	1062.	1145.	1216.
12D	2414.	0.725	0.05	0.005	Exper	49.	57.	65.
					Class	44.	52.	60.
					Thermo	29.	34.	39.
13S	1509.	1.629	0.02	0.002	Exper	307.	338.	361.
			$\phi=5$		Class	319.	346.	368.
					Thermo	397.	432.	464.

14D	2501.	2.013	0.02	0.002	Exper	34.	40.	46.
					Class	33.	40.	47.
					Thermo	22.	26.	30.
15S	1521.	3.263	0.01 $\phi=5$	0.001	Exper	298.	328.	352.
					Class	306.	332.	353.
					Thermo	377.	411.	441.
16D	2413.	3.384	0.01	0.001	Exper	41.	49.	57.
					Class	43.	52.	60.
					Thermo	31.	36.	41.
17S	1514.	0.722	0.1 $\phi=10$	0.005	Exper	269.	288.	307.
					Class	252.	274.	292.
					Exper	320.	350.	375.
18D	2492.	0.856	0.1	0.005	Exper	31.	37.	42.
					Class	27.	33.	39.
					Thermo	17.	20.	23.
19S	1424.	1.801	0.0005 $\phi=0.05$	0.005	Exper		797.	
					Class	778.	846.	904.
					Thermo	464.	499.	527.
20D	2427.	2.064	0.0005	0.005	Exper		94.	
					Class	77.	93.	108.
					Thermo	72.	86.	98.

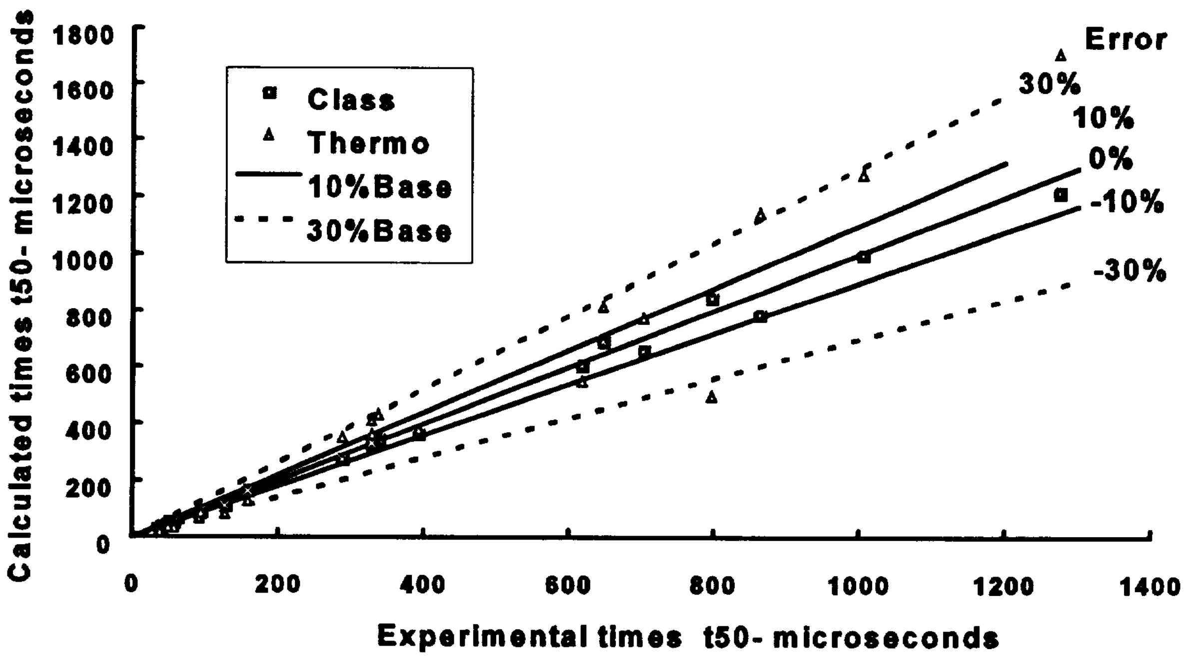

Figure 2: Predictions versus Experimental t_{50}

The classical predictions are the solid square symbols and the thermodynamic predictions are the open triangle symbols in Figure 2 for the t_{50} times from Table 5 above. The classical predictions agree with the experiments to ± 10 % while the thermodynamic predictions agree with the data to ±30%. This is good agreement for the thermodynamic method considering it contains only a single constant D.

Reactions CL1, CL2, and CL3 are the most important reactions of the system. CL1 and CL2 produce OH and CL3 consumes OH to produce H_2O. The ratio of the thermodynamic to classical predictions for these three kinetic constants are shown in Figure 3. Perfect agreement between the two methods would result in a ratio of one.

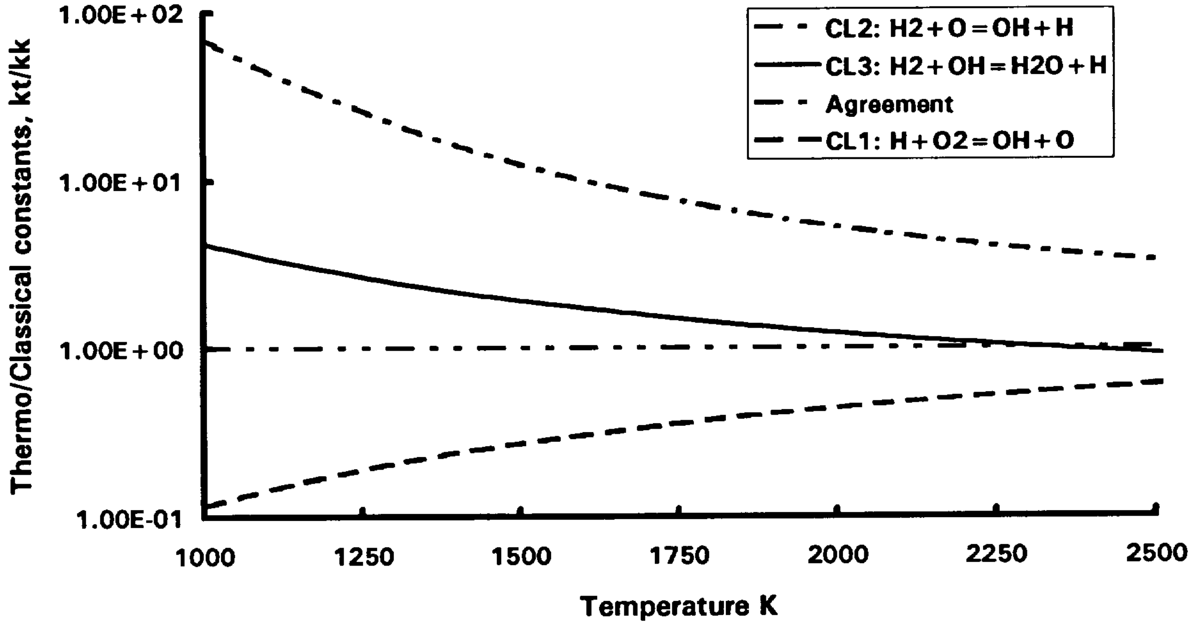

Figure 3: Comparison of Thermodynamic and Classical Rates, D=7.0 E 7.

The discrepancy is greater at the lower temperature than at a higher temperature. This is because the free radical concentrations are low at low temperatures, making measurement accuracy low. Also at low temperature the rates are slow so that systematic errors are magnified on a ratio scale. In addition if an error is present in one rate, it can propagate to other reactions because of the coupling effect. So the higher consumption rate of CL2 is compensated by the low rate of CL1 and the high consumption rate of CL3.

Reevaluation of the Hydrogen-Bromine System

From the above study and the inclusion of the third body efficiencies in the rate equations, the hydrogen-bromine system from ref.1 was recomputed to determine if there was still a difference in the value of D between the two systems. The rate equations used for this study were:

1. $M + Br_2 = 2\ Br + M$	The equations in ref. 1 were:	T1	$Br_2=2\ Br$
2. $M + H_2 = 2\ H + M$		T2	$H_2 = 2\ H$
3. $Br + H_2 = HBr + H$		T3	$0.5H_2+Br=HBr$
4. $H + Br_2 = HBr + Br_2$		T4	$H+0.5Br_2=HBr$
5. $M + H + Br = HBr + M$		T5	$H+Br= HBr$

Reference 1 treated the "mechanism" equations as simply mass balance equations between species. This report is treating the "mechanism" as all possible interactions between species with the path determined by the Gibbs free energy gradient. The new equations are essentially the classical mechanism or the thermodynamic equations without the previously used fractional stoichiometric coefficients. The molecule/molecule reaction between H_2 and Br_2 ($H_2+Br_2=2\ HBr$) was not included. The best value of D for comparison to the HBr data was still $3x10^8$, which is the same as determined in ref.1. The values of the new predicted results are shown in Table 6.

Table 6. HBr Mole Fraction Data at 574.3 K ; p=1.8 atm.
Initial Conditions: $X_{H2}=0.657$ $X_{Br2}=0.343$

Time seconds	Data X_{HBr}	Classical X_{HBr}	Thermodynamic X_{HBr}
870	0.1559	0.1404	0.1855
1470	0.2295	0.2165	0.2580
2070	0.2940	0.2797	0.3106
2970	0.3830	0.3559	0.3668
4770	0.4877	0.4613	0.4389
5970	0.5373	0.5086	0.4710
7470	0.5829	0.5512	0.5015
8970	0.6102	0.5814	0.5240
Equilibrium	0.686		

The thermodynamic method is initially 19% too high, crosses the experimental data at a time of 2440 seconds and finishes 14% too low. Decreasing the value of D would decrease the concentration for all times and shift the crossover point to an earlier time. A value of D of 3×10^8 was considered to give good agreement with the data. The classical values are within 10% for the whole time series.

Comparison of Other Hydrogen-Bromine Data with Model

Now that D is fixed, the computed results can be compared with other data. In general the prediction of the effects of temperature was much better than the results of ref.1. These calculations included the effect of third bodies M, and did not use fractional coefficients in the reaction set. The calculations of the effect of increased HBr concentration, reduced temperatures, and changing initial conditions compared well. It is possible that the difference in the value of D for the two systems could be a result of the measurement techniques, impurities, or the large concentrations of the reactants. The HBr data was obtained using acid/base titration techniques with reaction times of minutes compared to the H/O system which used laser absorption with reaction times of microseconds. As yet unpublished work on the C_xH_y/CO/NO system suggests that in general 7×10^7 works well for D.

Conclusions

The thermodynamic method adequately predicted the reaction rate constants for the Hydrogen/Oxygen system. The thermodynamic method is based on the gradient of the Gibbs free energy and a single proportionality constant D to determine the kinetic rate constants. Using this method the rate constants for any gas phase reaction can be computed from thermodynamic properties. Any gas phase kinetic constant can be computed given the thermodynamic data from the equations:

$$k_{c\,f}=DK_p\,(RT)^{\Sigma\nu_{fi}-1} \quad \text{for } K_p< 1. \tag{11}$$

$$\text{or } k_c=D(RT)^{\Sigma\nu_{fi}-1} \text{ for } K_p> 1. \tag{12}$$

The deviation between predictions and experimental data for the thermodynamic method was greater than for the classical method, but there is only one constant D (7×10^7)in the thermodynamic method to determine the whole H/O system. All of the third body efficiencies M are taken to be unity. This new thermodynamic based kinetics model appears very simple; but it appears to work. There was a larger deviation with experimental data, however there is probably error in the experimental data which cannot be compensated for with only one constant. One reason that this method has been shown to work is that the experimental data is very good, so that this thermodynamic method is able to match with it.

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13. ABSTRACT ***(Maximum 200 words)***

A new method for predicting chemical rate constants using thermodynamics has been applied to the hydrogen/oxygen system. This method is based on using the gradient of the Gibbs free energy and a single proportionality constant D to determine the kinetic rate constants. Using this method the rate constants for any gas phase reaction can be computed from thermodynamic properties. A modified reaction set for the H/O system is determined. All of the third body efficiencies M are taken to be unity. Good agreement was obtained between the thermodynamic method and the experimental shock tube data. In addition, the hydrogen bromide experimental data presented in previous work is recomputed with M's of unity.

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