NASA-TM-107124

19960011442

NASA Technical Memorandum 107124
AIAA–96–0218

Calculation of Kinetic Rate Constants From Thermodynamic Data

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Prepared for the
34th Aerospace Sciences Meeting & Exhibit
sponsored by the American Institute of Aeronautics and Astronautics
Reno, Nevada, January 15–18, 1996

National Aeronautics and
Space Administration

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Abstract

A new scheme for relating the absolute value for the kinetic rate constant k to the thermodynamic constant K_p is developed for gases. In this report the forward and reverse rate constants are individually related to the thermodynamic data. The kinetic rate constants computed from thermodynamics compare well with the current kinetic rate constants. This method is self consistent and does not have extensive rules. It is first demonstrated and calibrated by computing the HBr reaction from H_2 and Br_2. The method then is used on other reactions.

Symbols

A	proportionality constant in equation (16)
A_f	classical preexponential factor in forward rate constant
C_i	species concentration for species i, moles/cc
D	universal kinetic/thermodynamic link constant - 3 x 10^8 sec^{-1}
E	activation energy, calories/mole
E_c	temperature constant, equation (16)
G	free energy
k	chemical rate constant
kk	chemical rate constant from classical kinetics
kt	chemical rate constant from thermodynamics
K_c	equilibrium constant based on concentrations
K_p	equilibrium constant based on equation (8) or pressure
n_i	number of moles of i per gram of mixture
n_T	total moles of mixture/gram of mixture or 1/molecular weight
N	constant in modified Arrhenius rate expression eq. (4)
p_i	partial pressure of species i, $n_i/n_T \cdot P$ atm
r_f	forward chemical reaction rate, moles/cc-sec
R	universal gas constant 1.987 cal/mole K or 82.05 atm-cc/mole K
S_i	species i chemical symbol
t	time
T	temperature
x	reaction progress variable, moles reacted per gram of mixture
X	Pease's concentration, moles/22.4 liters, ref. 6
Δ	difference operator, products minus reactants

μ^o_i	standard chemical potential for species i
ν_i	stoichiometric molar coefficient for species i

subscripts:

c	value expressed in terms of concentration
f	forward direction
i	for each species i
p	value expressed in terms of pressure
r	reverse direction

Introduction

There are several reasons why it would be desirable to relate the kinetic rate constants to thermodynamic data. First, modern kinetic models contain many reactions with many constants to form large mechanisms.These systems are not universal and are complex to assemble from the experimental data base. Thermodynamic equilibrium calculations, on the other hand, have been simplified and systematized and are only species dependent. Thus,relating the kinetic constants to thermodynamics might reduce the work involved in doing kinetic calculations.

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

The derived relationship that links the chemical rate constants to thermodynamics is the ratio equation (1), where the thermodynamic equilibrium constant K_c has been established as the forward rate constant k_f over the reverse rate constant k_r:

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

Normally one thinks of kinetics as a path process, but 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.

The first hurdle to developing an overall relationship between kinetics and thermodynamics is to overcome the idea that this is impossible. 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. Thus, with thermodynamics, the complete energy surface is available for ideal gas mixtures for all compositions, not only for equilibrium states (from initial reactants to final products). 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 constants.

A second hurdle is the idea that reacting molecules have to go through an activated complex energy barrier to complete the reaction. This state may be estimated from transition state theory to determine the kinetic constants but would be difficult to compute from thermodynamics. But thermodynamics is involved in equation (1). Are the activated complex states the same for both reaction directions? Does the activated complex state would depend on the starting point?

A connection between thermodynamics and the chemical kinetics constants is presented with comparisons to experimental data.

Description of the Method

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:

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

In the thermodynamic derivation, the kinetic rate is assumed to be related to the gradient of the free energy or:

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

The free energy G , ref. 1, is given by:

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

Differentiating G with respect to the reaction progress variable x, and using the facts that $(\partial n_T/\partial x=-\Delta\nu_i)$; for reactants, $(-\nu_i\partial/\partial n_i= \partial/\partial x)$; and for products, $(\nu_i\partial/\partial n_i= \partial/\partial x)$ with equation (2) as the model, this results in:

$$-\frac{1}{RT}\frac{\partial G}{\partial x}=\sum_i \frac{\nu_{fi}\;\mu_{fi}^o}{RT}-\sum_i \frac{\nu_{ri}\;\mu_{ri}^o}{RT}+\sum_i (\nu_{fi} \ln p_{fi})-\sum_i (\nu_{ri} \ln p_{ri}) . \tag{7}$$

At equilibrium, the free energy is a minimum, $\partial G/\partial x=0$, with the equilibrium constant K_p given by:

$$K_p= \exp\left(\sum_i \frac{\nu_{fi}\mu_{fi}^o}{RT}-\sum_i \frac{\nu_{ri}\mu_{ri}^o}{RT}\right) = \left.\frac{p_3^{\nu 3}p_4^{\nu 4}}{p_1^{\nu 1}p_2^{\nu 2}}\right|_{\text{at equilibrium}} \tag{8}$$

The LHS is the thermodynamic expression for K_p, expressed as:

$$K_p = \exp\left(\frac{-\Delta G^o}{RT}\right), \tag{9}$$

and is independent of composition or degree of reaction. In addition K_c is given by:

$$K_c=K_p(RT)^{-\Delta\nu_i}=K_p(RT)^{(\Sigma\nu_{fi}-\Sigma\nu_{ri})} . \tag{10}$$

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.

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

Then:

$$k_c=k_p \; (RT)^{(\Sigma\nu_{fi}-1)} \; ; \tag{11}$$

similar to K_p and K_c in equation (10).

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

$$k_{cf}=DK_p\ (RT)^{\Sigma v_{fi}-1} \quad \text{for } K_p< 1. \tag{12}$$

where D is a constant to be determined. Note that equation (7) is written for the net rate, whereas equation (3) is for the forward rate. Equation (12) provides the connection between thermodynamics and the forward chemical kinetic constant that shall be used.

Equation (12) without the 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:

$$k_{cr}=D(RT)^{\Sigma v_i-1} \quad \text{for } K_{pr}> 1. \tag{13}$$

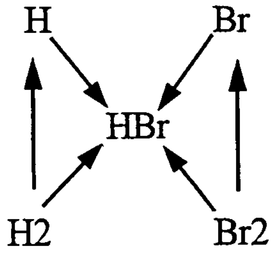
D is an unknown, assumed universal constant. It was determined from the fit of the HBr data presented in the next section. It was found to be 3×10^8 sec^{-1} which is used throughout this report.

The results from the thermodynamic method using equations (12) and (13) to compute the kinetics for all reactions are compared with experimental data. If the chemical potential of the products is greater than the reactants, then $K_p < 1$, and equation (12) is used. If the chemical potential of the products is less than the reactants, then the reaction is a cascade reaction with $K_p > 1$, and equation (13) is used. In this formulation only a single constant D and the thermodynamic base is sufficient to determine the whole kinetic data base.

In the next section the hydrogen bromine reactions are discussed, followed by a subset of the H/O reactions. In the final section, a random selection of rates chosen from reference 4, NSRDS, are presented for comparison.

Calibration and Demonstration of Thermodynamic Kinetics Method using the Hydrogen-Bromine Reactions

The HBr system was chosen for several reasons. It was simple, but yet had interesting complexities. First there are only 5 species involved and they are all in the thermodynamic data set. They are arranged with HBr in the middle as follows:



Secondly, the three classical rates to describe the system are:

$$\begin{array}{rclll} 2\ Br & = & Br2^{*} & C1 & A=1.67\ E+14,\ n=0.,\ \ E=-1844. \\ Br+H_2 & = & HBr+H & C2 & A=3.4\ \ E+12,\ n=0.5,\ E=18300. \\ HBr+Br & = & H+Br_2 & C3 & A=8.13\ E+12,\ n=0.5,\ E=44500. \end{array} \qquad (14)$$

*At low temperatures M is not included, data is from ref. 3.

These are called "elementary reaction rates," because kineticists believe they represent the specie combinations by which the reaction proceeds. The rates for the three reactions are well known and the computed data can be treated like experimental data to match with other prediction methods.

Finally, the overall classical rate for HBr formation is given by:

$$\frac{d(HBr)}{dt} = \frac{k\ [H_2][Br_2]^{1/2}}{5. + \dfrac{[HBr]}{[Br_2]}} . \qquad (15)$$

The rate is inhibited by the HBr product. This is one of the first systems where a mechanism could be written down and solved.

Thermodynamic approach

In order to obtain the constant D, only one point is required. The formation of HBr at 574.3 K , table 2, was used to determine its value at 3 x 10^8. Individual rate comparisons are presented, followed by the predictions of the concentrations.

The classical mechanism rates above (equation (14)) with the thermodynamic predictions could have been used to make concentration predictions. However, a generalized equation set was chosen. All possible reactions are written down to maintain material balances. In computing thermodynamic equilibrium, all species are considered.

For the thermodynamic method, all six interaction equations are listed below in Table 1:

Table 1. Reactions for the Thermodynamic Hydrogen-Bromine Mechanism

Equation	Name	K_p at 574.3 K	k_{cf} cc-mol-sec units at 574.3 K
Br_2=2 Br	T1	9.32E-13	2.90E-4
H_2=2H	T2	4.10E-35	1.24E-26
0.5 H_2+Br=HBr	T3	1.81E11	6.51E10
H+0.5 Br_2=HBr	T4	2.73E22	6.51E10
H+Br=HBr	T5	2.82E28	1.41E13
0.5H_2+0.5Br_2=HBr	T6	1.74E5	3.0 E8

One way to compare the above two methods is to use an empirical least squares fit of K_p as a function of T, as in the last section of reference 4, in the form:

$$K_p = A \exp(Ȩ/RT). \tag{16}$$

For bimolecular reactions where $K_p < 1$, k_f would equal $A(DRT)\exp(Ȩ/RT)$ - a form similar to the Arrhenius expression, equation (4). Comparing Ȩ to E gave a hint of the desired correlation. This comparison has slightly different numbers, but it looked reasonable.

A better method is to plot the two relationships versus temperature. A comparison of the C2 and RC3 kinetics constants by the two methods are shown in figure 1. Equation (12) works well for C2 while equation (13) works for RC3. For RC3 the methods agree at lower temperature, but diverge at higher temperature. The classical relation may be extrapolated out of its range.

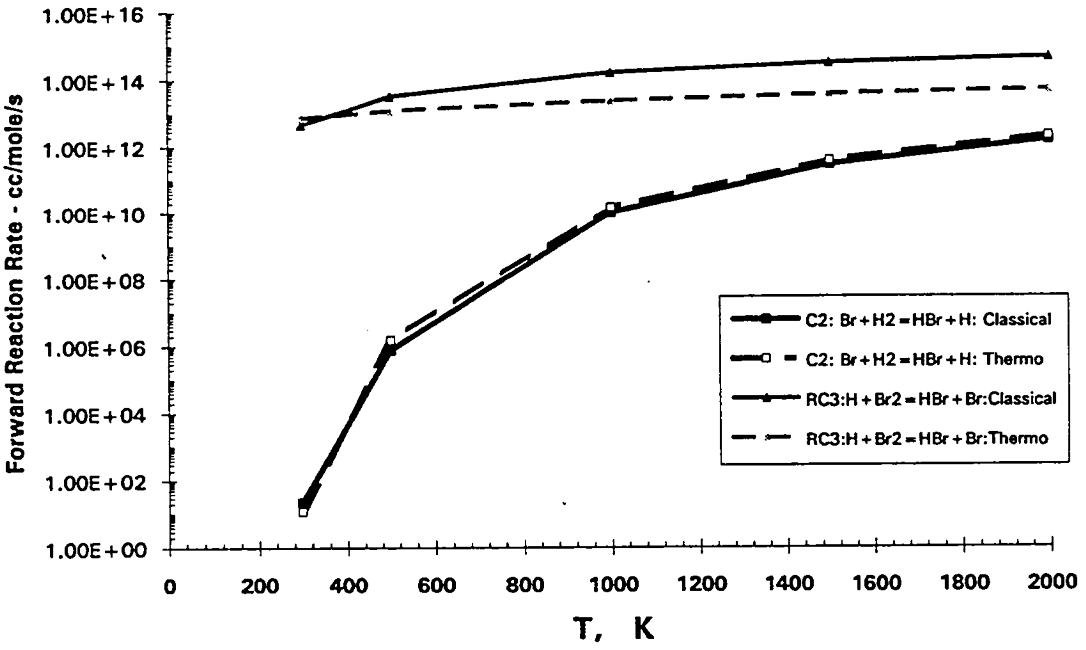


Figure 1. Comparison of classical kinetic equations and thermodynamic predictions for equations C2 and RC3.

The two methods for atom/atom recombinations are shown in figure 2. Differences between the two methods range from 10^{-3} to 10^{6}, but the curves follow the same trend.

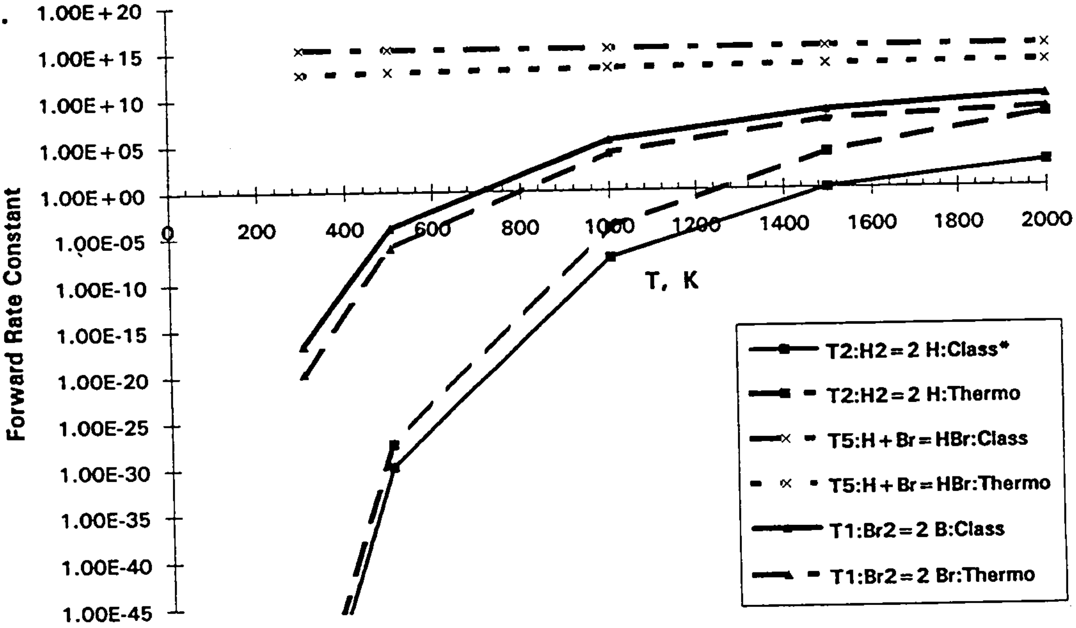


Figure 2. Comparison of classical kinetic equations and thermodynamic predictions for atom reactions using equation (12) and (13).

A better comparison is obtained by plotting the ratio of the thermodynamic HBr rates, kt, to classical kinetic rates, kk, versus temperature in figure 3. A value of one indicates perfect agreement. Using D of 3.0×10^8, the thermodynamic rates are given by equations (12) and (13).

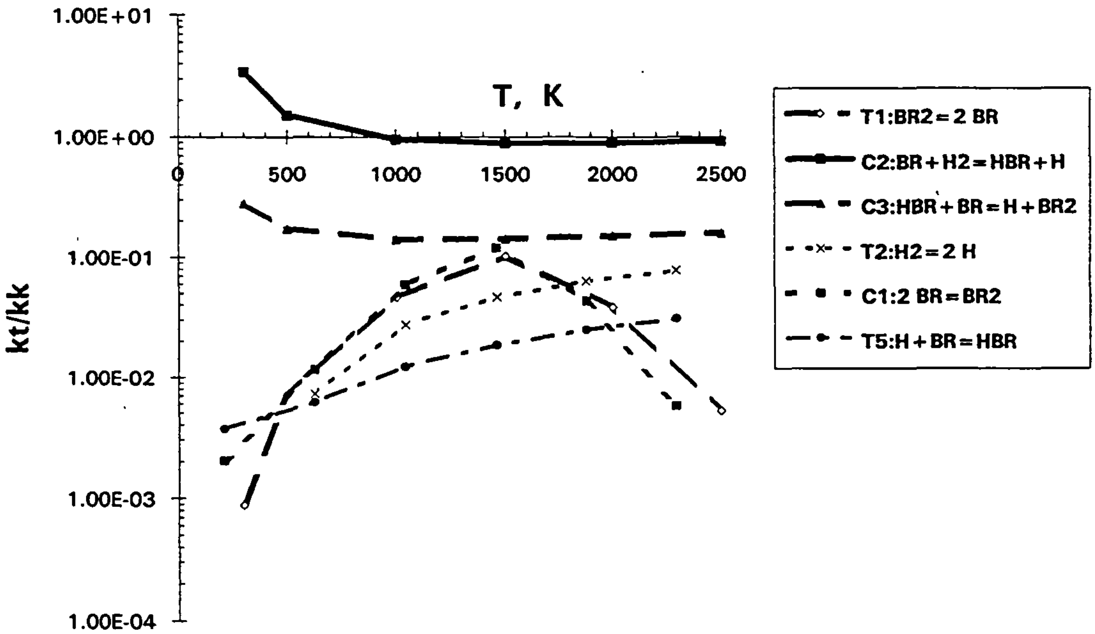


Figure 3: Ratio of thermodynamic rate to kinetic rate versus temperature

Rate C2 agrees very well over a wide temperature range. For rate C3, the ratio is 1/10 the classical; and for the other rates, the ratio at 500 K is 1/100. 500 K is the temperature range where the experimental data is compared. The maximum in the Br curves is caused by K_p going through one at approximately 1500 K.

Rather than compare individual equations, it is more intuitive to compare the predicted concentrations from the experimental data. The GLSENS program, ref. 5, is used as the kinetic integrator to compute the concentrations. It can handle global reactions and fractional stoichiometric coefficients.

The conditions of Table 2 were used to obtain the constant D. A value of 3×10^8 resulted in a lower prediction 0.1481 at 870 sec, compared to data of 0.1559, but later the predicted results became about 3.5 percent to high. This value produced close agreement with the experimental data. The classical method was 5 percent too low.

Table 2: HBr Mole Fraction Data at 574.3 K ; p=1.8 atm; Table XIII of ref. 6.
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	0.1481
1470	0.2295	0.2165	0.2312
2070	0.2940	0.2797	0.3014
2970	0.3830	0.3559	0.3869
4770	0.4877	0.4613	0.5052
5970	0.5373	0.5086	0.5568
7470	0.5829	0.5512	0.6010
8970	0.6102	0.5814	-
Equilibrium	0.686		

This Table shows a good comparison between both methods and the data.

Reaction T6 (0.5 H_2+0.5 Br_2 = HBr is deliberately left out of the reaction set. If reaction T6 (molecule/molecule) is included in the reaction set, the formation of HBr is very fast with equilibrium being achieved in less than 1 microsecond. Even though k is small, the concentrations of H_2 and Br_2 are high, making the overall rate competitive. Thus, rather than reduce D to include this reaction, T6 is left out of the set in order to integrate the rates more like the classical set. When T6 was not included, the net conversion agreed with the experimental data. The results are shown in Table 2.

In order to determine the temperature sensitivity of the reaction sets, Reference 6 tabulates the experimental k of equation (14) versus temperature. The results are tabulated in Table 3. The comparison is good with additional roll off with T for the thermodynamic set as T decreases.

The decrease in HBr formation rate with increasing HBr initial concentration was investigated next, using Table XII of reference 6 for data. The effect of increased initial HBr concentration is shown in Table 4. The experimental data, given in units of moles/22.4 liters of H2 was converted to moles/cc of HBr by:

$$C_{HBr}(\text{moles/cc})=X(\text{moles } H_2/22.4 \text{ liters})*\frac{2}{22{,}400\text{cc}}$$

Table 3: Predicted Temperature Sensitivity of Reaction Sets
and Comparison with Table XIV of ref. 6.
Initial Conditions : X_{H2}=0.657, X_{Br2}=0.343, time=14.5 min

Temperature K	P_{atm}	$k_{experimental}$ *	$k_{classical}$	$k_{thermodynamic}$
574.3	1.806	25.62	23.06	24.56
550.5	1.731	4.760	4.862	4.186
524.4	1.649	0.7782	0.7386	0.5058
498.7	1.568	0.0970	0.0950	0.0510

* values of k are $(cc/mole)^{0.5}$ min^{-1}

Table 4: Effect of Increased Initial HBr Concentration at 574.3 K and 25 min.
Initial H2 and Br2 = 2.009E-05

Initial HBr^{+}	P atm	**Gain in Conc. HBr**	Classical HBr_T	**Classical ΔHBr**	Thermo HBr_T	**Thermo ΔHBr**
0.	1.89	**1.066E-5**	8.543E-6	**8.543E-6**	9.20E-6	**9.20E-6**
4.11E-5	3.83	**9.540E-6**	4.81E-5	**7.0E-6**	5.49E-5	**1.38E-5**
5.58E-5	4.53	**8.18E-6**	6.25E-5	**6.7E-6**	6.97E-5	**1.39E-5**
7.55E-5	5.46	**7.20E-6**	8.17E-5	**6.2E-6**	8.94E-5	**1.39E-5**
8.62E-5	5.96	**8.25E-6**	9.21E-5	**5.9E-6**	1.00E-4	**1.38E-5**

$^{+}$all concentrations are given in moles/cc

Note that as HBr is added to the mixture, the pressure increases. The classical equations overpredict the suppression of HBr while the thermodynamic method predicts an increase, but is not sensitive to the quantity of HBr added. The dilution of the reactants with HBr is compensated for by the increase in pressure, keeping the concentrations of H_2 and Br_2 fixed. The predicted final concentration of HBr is within 10 percent of the data for both methods.

The final comparison examines the effect of varying the initial H_2 and Br_2 concentrations, using the data from Table XI of ref. 6. The results are shown in Table 5.

Table 5: Effect of Changing Initial Concentrations of H_2 and Br_2, Temperature 574.3 K

Initial H_2 Mole Fraction	Initial Br_2 Mole Fraction	Pressure atm	Time minutes	Exper HBr moles/cc	Classic HBr moles/cc	Thermo HBr moles/cc
0.657	0.343	1.805	14.5	5.97E-6	5.38E-6	5.65E-6
0.655	0.345	0.9252	19.5	2.87E-6	2.67E-6	3.78E-6
0.380	0.620	1.718	15.0	4.39E-6	4.13E-6	1.01E-5★
0.378	0.622	0.8638	15.0	1.70E-6	1.52E-6	5.12E-6★
0.5	0.5	1.010	20.0	3.14E-6	2.9E-6	6.11E-6★
0.5	0.5	3.787	25.0	2.44E-5	2.24E-5	2.75E-5
0.5	0.5	2.840	15.0	1.10E-5	9.95E-6	1.34E-5
0.5	0.5	1.893	15.0	5.98E-6	5.56E-6	8.94E-6

★ Indicates large deviation from experimental data

Both the classical and thermodynamic predictions agree well with the experimental data, except for the three starred cases where the H_2 was low. For the thermodynamic kinetic set T3 (0.5 H_2 + Br=HBr) is in equilibrium and is waiting for T1 (Br_2=2 Br) for bromine. The time constant for T1 at the low temperature of 574.3 K is 60 minutes ($1./k_f$). So HBr can be expressed as:

$$\mathrm{HBr} = K_{T3}\, H_2^{1/2}\mathrm{Br}\ ;\quad \frac{d\mathrm{Br}}{dt} = -2\frac{d\mathrm{Br}_2}{dt} - \frac{d\mathrm{HBr}}{dt}$$

The major difference in deriving mechanisms is that the classical method assumes that C1 ($2Br=Br_2$) is equilibrated, whereas in actuality it is the rate controlling step and the rate of formation of HBr (T3) is equilibrated.

This comparison shows that the thermodynamic method is promising for predicting reacting performance. However more examples are required to show that the results are not a peculiarity of the HBr system.

Demonstration of Thermodynamic Kinetics Method on the Hydrogen/Oxygen System.

To determine how the thermodynamic method worked on another system, the first six rates of the H/O system from a recent publication, reference 7 are compared. The ratio of thermodynamic to classical rates are shown in figure 4.

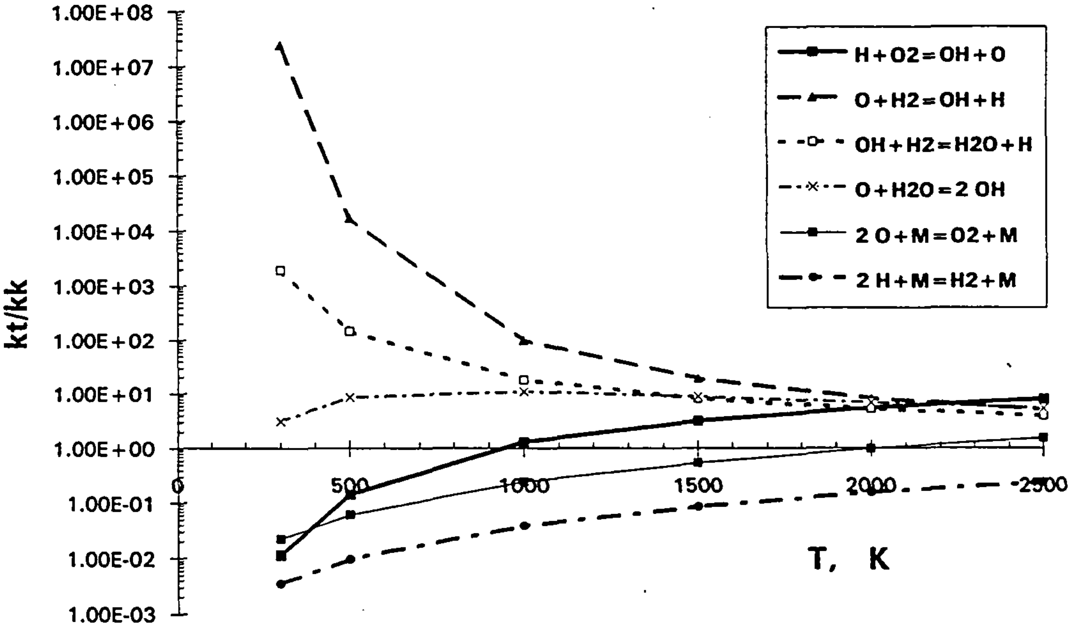


Figure 4. Ratio of thermodynamic kinetics constant to classical kinetics data for some reaction of the Hydrogen/Oxygen system.

At higher temperatures, disagreements were on the order of one order of magnitude; however, at the low temperature of 500 K, the discrepancy is large - 10^4 for the $O+H_2$ reaction. This is because the free radical concentration is low at low temperatures, making measurement accuracy low. Also at low temperature the rates are low so that systematic errors are magnified on a ratio scale. The recommended temperature range for this data is 1400 to 1900 K. The accuracy of the data is estimated to be 13 percent, whereas the deviation of the thermodynamic prediction is an order of magnitude, at high temperature.

The error decreases as the temperature increases, approaching a factor of 10 at 2500 K. Again below 1000 K, the classical kinetic data is an extrapolation of high temperature which may account for the large deviation and errors look bigger. These thermodynamic predictions were made with no change in D ($3x10^8$).

Demonstration of the Thermodynamic Kinetic Method on a Random Selection of Rates

As a final comparison, the thermodynamic kinetic method is compared to the classical method for a random selection of kinetic rates. Rates from reference 4, five with a thermodynamic constant greater than one, $K_p > 1$, and then five reactions where $K_p < 1$ were selected. The first rates listed were with $K_p > 1$, which turned out to involve the hydrogen atom H. These are shown in figure 5.

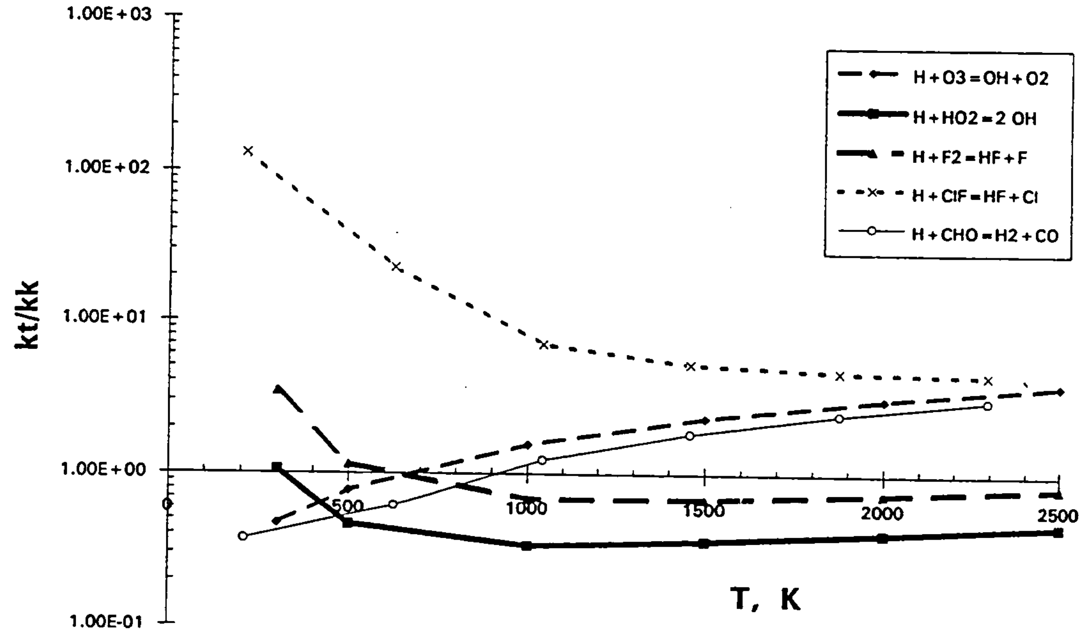


Figure 5. Ratio of thermodynamic rate to kinetic rate for $K_p > 1$, ref. 4.

When $K_p > 1$, the rates are given by equation (13) or for a bimolecular reaction the rate is k_{cf} = DRT. When $K_p > 1$, the rate constant is independent of the initial chemical potential, as long as the final chemical potential is below the initial value. The agreement is very good, especially for the ozone O_3 and the peroxide HO_2 reactions.

The comparison with $K_p < 1$ is shown in figure 6.

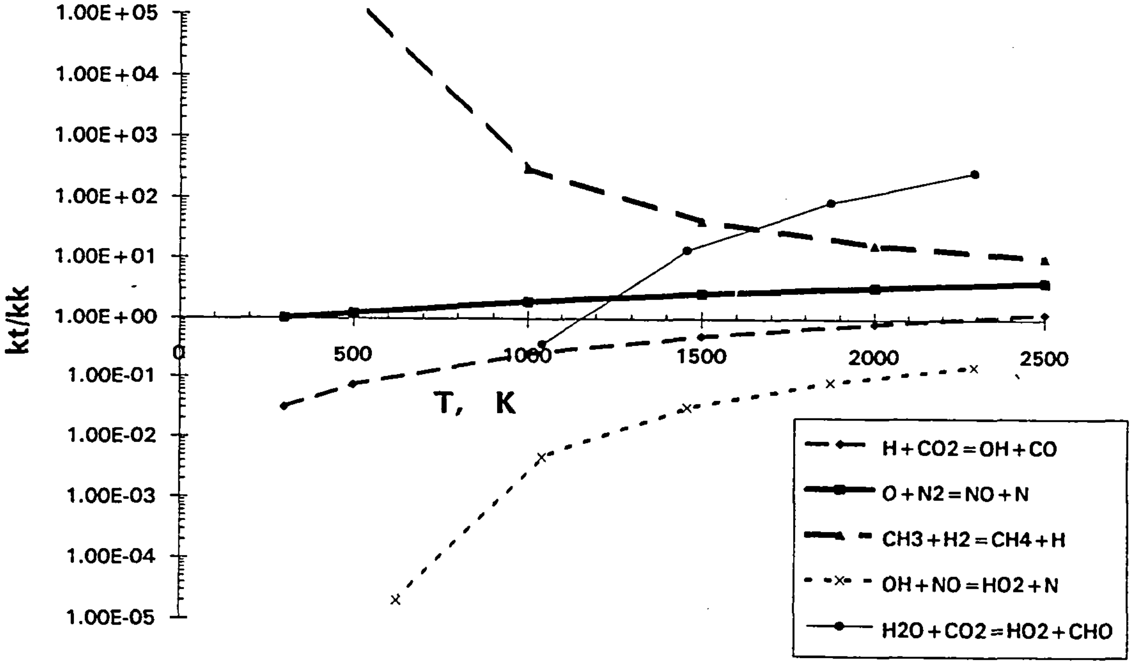


Figure 6: Ratio of thermodynamic rate to kinetic rate for $K_p < 1$.

Comparing the deviations in figures 5 and figure 6 shows that about the same trends occur with large errors at low temperatures and decreasing as the temperature increased. The value of D is still 3×10^8.

In general the thermodynamic predictions show the same trend as the classical kinetic rates. More comparisons need to be carried out to extensively validate the thermodynamic method for kinetic rate prediction.

Conclusions

Using thermodynamic data to compute chemical kinetics constants may be a viable alternative for gas phase reactions. The value of the proportionality constant D appears to be universal and equal to 3×10^8 for the cases studied. Changing the value of D would only shift the predicted kinetic rate constant higher or lower for both the forward and reverse rate for the whole temperature range.

The thermodynamic method is given by:

$$k_c = DK_p\,(RT)^{\Sigma\nu_{fi}-1} \text{ for } K_p < 1 \quad \text{or}$$
$$k_c = D(RT)^{\Sigma\nu_{fi}-1} \text{ for } K_p > 1 \qquad (12)\&(13)$$
$$\text{where } D = 3\text{x}10^{8} \text{ sec}^{-1}.$$

No specific mechanism is used. All of the species have to interact according to their standard free energy level, μ_i^o. All species have a chance to interact like in the equilibrium code.

There is a strong corellation between the two methods. It is remarkable that for the reactions studied, this simple thermodynamics kinetics model works so well and is consistant for a variety of systems.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE December 1995	3. REPORT TYPE AND DATES COVERED Technical Memorandum

4. TITLE AND SUBTITLE

Calculation of Kinetic Rate Constants From Thermodynamic Data

5. FUNDING NUMBERS

WU–505–62–52

6. AUTHOR(S)

C. John Marek

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–10043

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM–107124
AIAA–96–0218

11. SUPPLEMENTARY NOTES

Prepared for the 34th Aerospace Sciences Meeting & Exhibit sponsored by the American Institute of Aeronautics and Astronautics, Reno, Nevada, January 15–18, 1996. Responsible person, C. John Marek, organization code 2560, (216) 433–3584.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 07

This publication is available from the NASA Center for Aerospace Information, (301) 621–0390.

12b. DISTRIBUTION CODE

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

A new scheme for relating the absolute value for the kinetic rate constant k to the thermodynamic constant K_p is developed for gases. In this report the forward and reverse rate constants are individually related to the thermodynamic data. The kinetic rate constants computed from thermodynamics compare well with the current kinetic rate constants. This method is self consistent and does not have extensive rules. It is first demonstrated and calibrated by computing the HBr reaction from H_2 and Br_2. The method then is used on other reactions.

14. SUBJECT TERMS

Combustion; Kinetics; Hydrogen bromine; Thermodynamic data

15. NUMBER OF PAGES	18
16. PRICE CODE	A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

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