Journal of Fluorine Chemistry, 46 (1990) 357–366

Received: March 20 1989; accepted: July 17, 1989

A KINETIC STUDY OF THE EQUILIBRIUM BETWEEN DIOXYGEN MONOFLUORIDE AND DIOXYGEN DIFLUORIDE

G. M. CAMPBELL

Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)

SUMMARY

The equilibrium among dioxygen monofluoride, dioxygen difluoride, and oxygen has been studied in the temperature range 286 to 195 K. Forward and reverse reaction rate constants were determined. An activation energy of 13 kcal/mole was found for both reactions. The equilibrium constant in the middle of the temperature range was found to be 21.5. The estimated heats of formation of O_2F and O_2F_2 were +2.6 and +4.5 kcal/mole.

INTRODUCTION

The infrared vibrational intensity of gaseous dioxygen monofluoride was recently reported [1]. The technique and apparatus used in that work have been used to extend the kinetic measurements over a range of temperatures. The study of these gases is made difficult by their very reactive nature. Because of this, most kinetic studies have been of transient species. There have been a number of studies involving the kinetics of the combination of fluorine atoms with oxygen [2], often in an inert carrier. The studies reported here are the first involving the equilibrium among O_2F, O_2F_2, and O_2 in real time. By using a very large volume photochemical cell and maintaining very low concentrations, the reactivity problems have been abated. The concentrations of O_2F and O_2F_2 are monitored simultaneously, thus avoiding assumptions necessary when only one species can be followed. The long light path ensures adequate signal sensitivity at the low concentrations. The concentrations of all species are uniform throughout the containment vessel. The evidence that an equilibrium exists between these species was presented previously [1].

0022-1139/90/$3.50 © Elsevier Sequoia/Printed in The Netherlands

EXPERIMENTAL

Experiments were conducted in a very long pathlength spectroscopic cell. The sample compartment is 4.5 m long with a 24 cm inside diameter. It is equipped with White cell optics for long distance optical transmission, which allows sensitive *in situ* spectroscopic measurements of reactant and product species. The cell is temperature-programmable between room temperature and about 100 K.

The concentrations of the several gaseous fluoride compounds were monitored by a FTIR spectrometer at a spectral resolution of 2 cm^{-1}. The details of the long pathlength-FTIR spectrometer were described previously [3].

Dioxygen difluoride was prepared by photolysis of equimolar mixtures of O_2 and F_2 in a reaction vessel equipped with a sapphire window on top, through which UV light from a Xe-Hg arc lamp was transmitted. The O_2F_2 produced was stored at 77 K before use.

Before each experiment the 200-liter photochemical cell was brought to temperature equilibrium, as indicated by temperature sensors distributed along the cell walls. A mixture of O_2 and O_2F_2 was then added. FTIR scans were taken periodically with the frequency determined by the rate of O_2F_2 disappearance. This ranged from 25-second intervals, with 20 scans per interval, at the higher temperatures to 5-minute or longer intervals, with 30 scans per interval, at the lower temperatures. The Nicolet Model 20SX spectrometer was used at the higher temperatures but was not available for some of the work done at the lower temperatures. The IBM IR/30S spectrometer was used for much of the low temperature work. The total pressure was monitored continuously. Oxygen concentrations ranged between 50 and 500 micromole/liter, whereas O_2F_2 concentrations were usually about 10 micromole/liter at the start of an experiment. As the amount of O_2F_2 decreased, there was a small increase in the total pressure. This increase in pressure was due to the decomposition and reaction products of the oxygen fluorides. These were mostly O_2 and F_2, but products also included smaller amounts of CF_4, PuF_6, and various freons. The PuF_6 resulted from the fluorination of traces of the decomposition product remaining from previous experiments done in the cell. Since the pressure change was small in comparison with the total pressure, an insignificant error was introduced by assuming that half of the pressure change was due to O_2 from the decomposition of O_2F_2. The total pressure change over the course of an experiment was never greater than the initial partial pressure of O_2F_2. As will be seen later, O_2 was the only decomposition product expected to be involved in the equilibrium reactions under study.

To avoid possible interference from carbon-fluorine compounds, the O_2F_2 absorbance was monitored at the 1570 cm^{-1} peak. The peak height absorption cross section for this peak was taken as 3.0×10^{-20} cm^2/molecule [4]. Oxygen monofluoride concentration was monitored at 1490 cm^{-1}. The cross section of this peak was determined to be 3.6×10^{-20} cm^2/molecule [1]. The single peak measurements are believed to be directly related to the total band strength in the low pressure range used in these experiments. A further discussion of this aspect of the study can be found in [4]. The light path length through the cell was usually 64 m, with some data taken at 48 m.

RESULTS AND DISCUSSION

The primary reactions of interest are:

$$2\ O_2F \underset{k_3}{\overset{k_2}{\rightleftharpoons}} O_2F_2 + O_2 \ , \tag{1}$$

$$O_2F + R \xrightarrow{k_4} O_2 + FR \ , \ \text{and} \tag{2}$$

$$O_2F_2 + R \xrightarrow{k_5} O_2F + FR \ , \tag{3}$$

where R refers to other reactants present in the cell. Equation (2) is meant to include all possible reactions that result in a loss of O_2F except for Eq. (1). The time rate of change of the O_2F and O_2F_2 concentrations can be expressed as

$$\begin{aligned} \frac{d(O_2F)}{dt} &= -\,2\ k_2 * (O_2F)^2 + 2\ k_3 * (O_2F_2) * (O_2) \\ &\quad - k_4 * (O_2F) * (R) + k_5 * (O_2F_2) * (R) \ , \end{aligned} \tag{4}$$

and

$$\frac{d(O_2F_2)}{dt} = k_2 * (O_2F)^2 - k_3 * (O_2F_2) * (O_2) - k_5 * (O_2F_2) * (R) \ . \tag{5}$$

The equilibrium constant for Eq. (1) can be expressed as

$$k_{eq} = \frac{(O_2) * (O_2F_2)}{(O_2F)^2} \ . \tag{6}$$

The method of evaluating these equations is described in [1]. Tables 1 and 2 give examples of values calculated for the terms in Eqs. (4) and (5) as functions of time. At 286 K (Table 1), the values of the first two terms that involve the homogenous gas phase equilibrium are larger than the last terms which contain the quantity R. The oxygen fluorides were warmed from liquid N_2 temperature just before introduction to the IR cell. At that temperature they are in the O_2F_2 form and, after being introduced, approach an equilibrium with O_2 and O_2F [Eq. (1)] at the cell temperature. This process is much slower at lower temperatures and, as indicated in Fig. 1, the concentration of O_2F is still increasing during the initial measurements. The concentrations versus time at 286 K are shown in Fig. 2. At lower temperatures (Table 2), the terms containing R are larger than the equilibrium terms. By definition the condition of equilibrium requires that the values of the first two terms be equal. This is very nearly true in the higher temperature example (Table 1) but is not approached in the low temperature example.

TABLE 1

Values of terms in Eqs. (4) and (5) at 286 K

$k_2 = 1.40E\text{-}1$; $k_3 = 6.45E\text{-}3$ (μmole^{-1} s^{-1})

$k_4R = 3.95E\text{-}3$; $k_5R = 4.15E\text{-}2$ (s^{-1})

TIME (s)	$k_2(O_2F)^2$	$k_3(O_2F_2)(O_2)$	$k_4R(O_2F)$	$k_5R(O_2F_2)$
2.50E+01	2.3E-01	2.2E-01	1.6E-03	1.9E-02
5.00E+01	1.5E-01	1.4E-01	1.3E-03	1.2E-02
7.50E+01	9.5E-02	9.1E-02	1.0E-03	7.9E-03
1.00E+02	6.2E-02	5.9E-02	8.3E-04	5.1E-03
1.25E+02	4.1E-02	3.9E-02	6.8E-04	3.4E-03
1.50E+02	2.8E-02	2.6E-02	5.5E-04	2.3E-03

TABLE 2

Values of terms in Eqs. (4) and (5) at 199 K

$k_2 = 6.3E\text{-}6$; $k_3 = 3.0E\text{-}7$ (μmole^{-1} s^{-1})

$k_4R = 4.2E\text{-}4$; $k_5R = 4.5E\text{-}4$ (s^{-1})

TIME (s)	$k_2(O_2F)^2$	$k_3(O_2F_2)(O_2)$	$k_4R(O_2F)$	$k_5R(O_2F_2)$
4.80E+02	6.4E-04	1.6E-03	1.3E-02	1.4E-02
1.02E+03	6.5E-04	1.3E-03	1.3E-02	1.1E-02
1.44E+03	6.1E-04	1.0E-03	1.3E-02	8.8E-03
2.28E+03	4.7E-04	7.0E-04	1.1E-02	5.9E-03
2.64E+03	4.1E-04	6.0E-04	1.1E-02	5.0E-03
3.24E+03	3.1E-04	4.5E-04	9.4E-03	3.8E-03

The homogenous gas phase reactions are more reproducible as indicated in Figs. 3 and 4. Most of the reactants represented by the term R are believed to be solids under the conditions of these experiments. The reactions involving these reactants would then take place on the walls of the 200-liter cell. This would imply that the rates should depend on the condition of the surface and would not necessarily be reproducible. By using oxygen fluorides to condition the cell before each experiment, the reproducibility was greatly improved as indicated by the uniformity of plots shown in Figs. 5 and 6.

The least square equations of the constants are

$$\ln(k_2) = 20.9 - 6541.3/T \quad , \tag{7}$$

$$\ln(k_3) = 17.74 - 6519.0/T \quad , \tag{8}$$

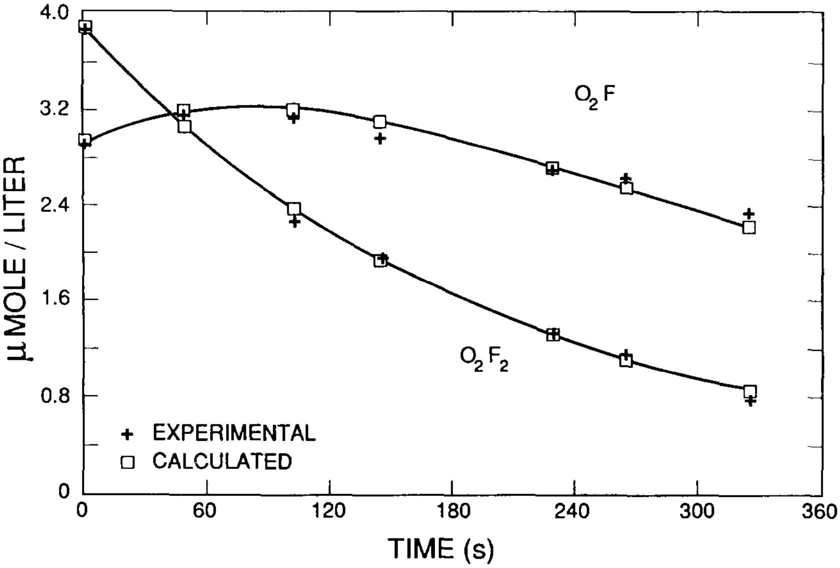

Fig. 1. O_2F and O_2F_2 vs time at 199 K.

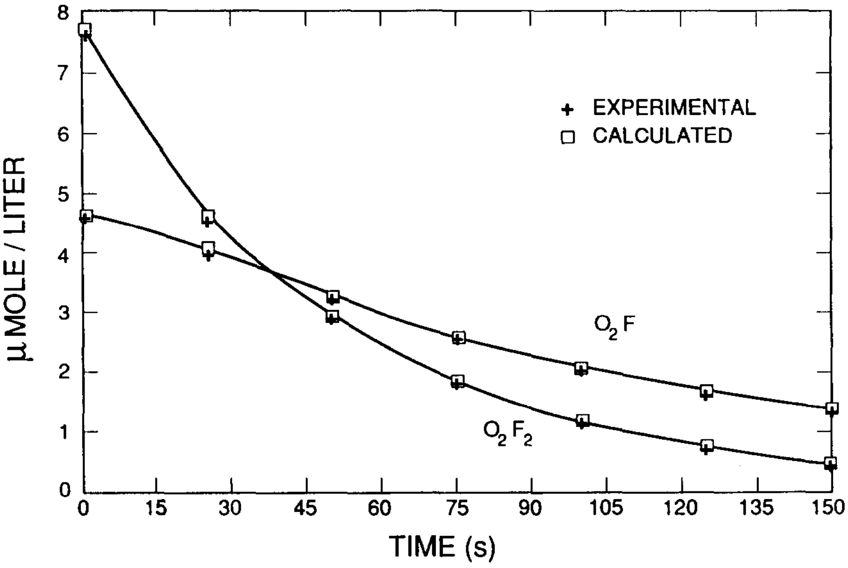

Fig. 2. O_2F and O_2F_2 vs time at 286 K.

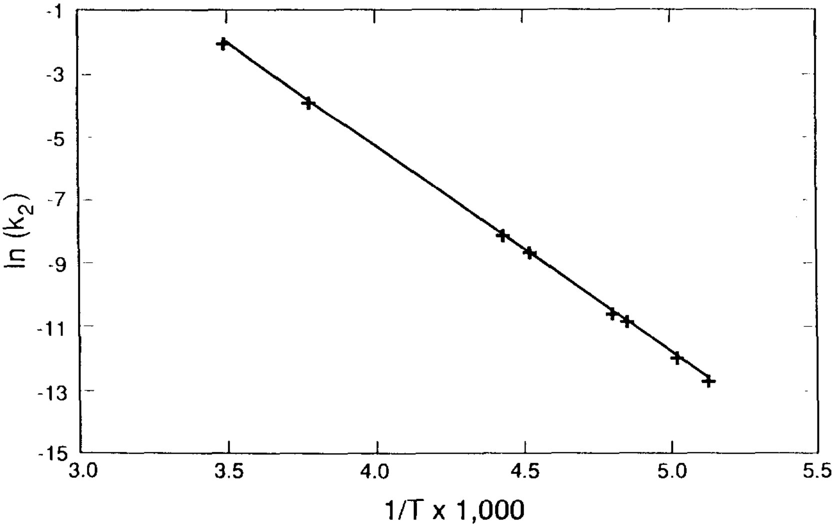

Fig. 3. Natural logarithm of k_2 vs reciprocal temperature.

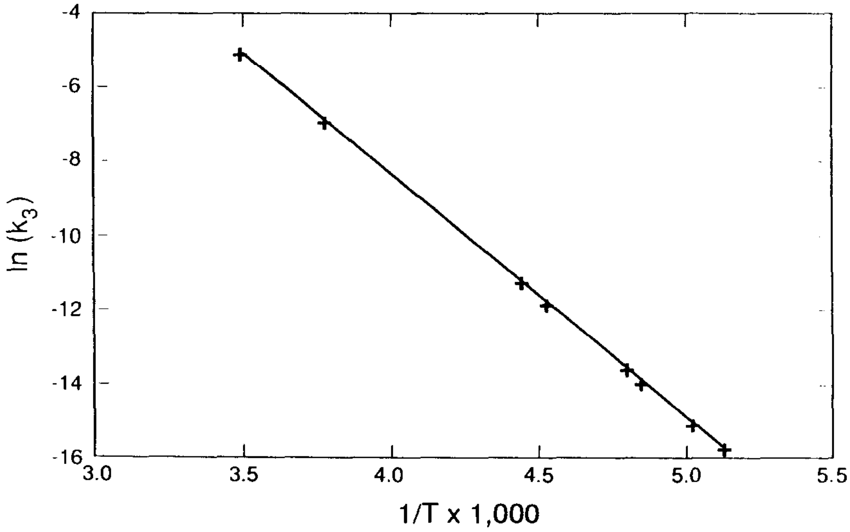

Fig. 4. Natural logarithm of k_3 vs reciprocal temperature.

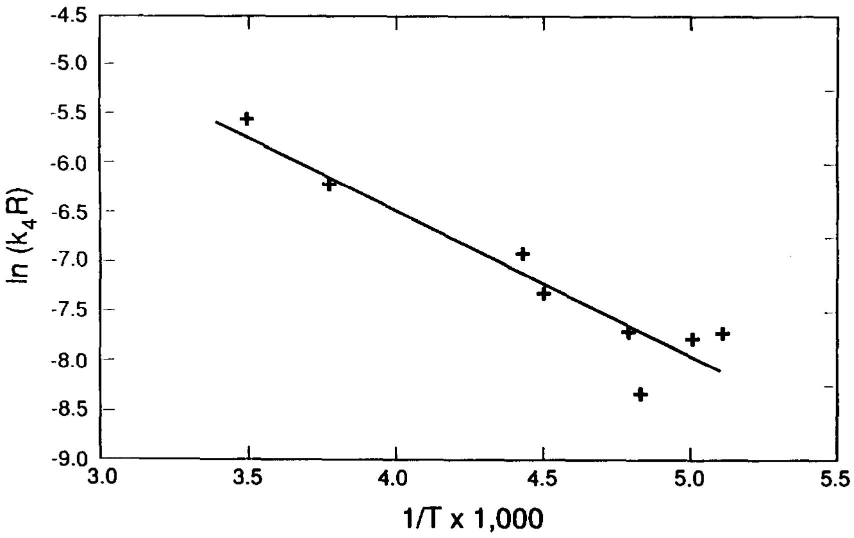

Fig. 5. Natural logarithm of k_4R vs reciprocal temperature.

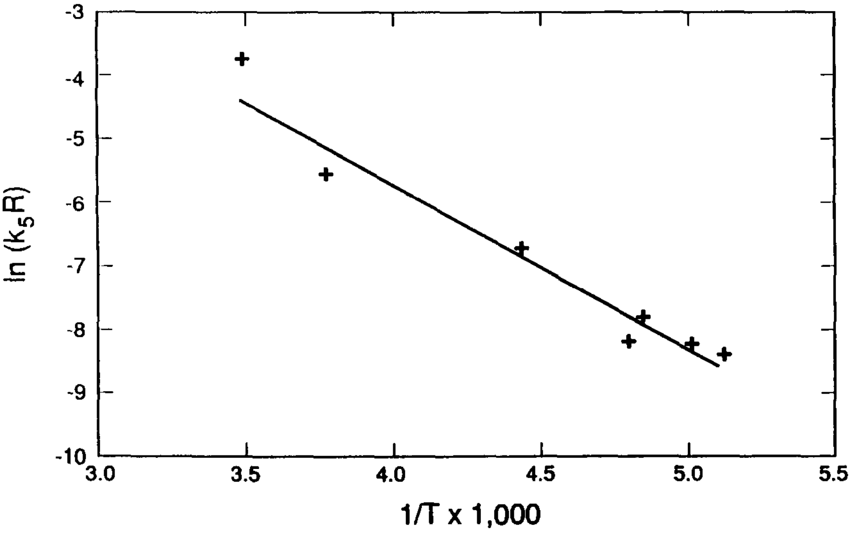

Fig. 6. Natural logarithm of k_5R vs reciprocal temperature.

$$\ln(k_4R) = -.6575 - 1448.0/T \quad , \quad \text{and} \tag{9}$$

$$\ln(k_5R) = 5.275 - 2607.5/T \quad . \tag{10}$$

From Eqs. (7) and (8), it follows that

$$\ln(k_2/k_3) = \ln(k_{eq}) = 3.16 - 22.3/T \quad . \tag{11}$$

Using the relationship for Gibbs free energy,

$$\Delta G = -\ RT\ln(k_{eq}) = +44 - 6.31\ T\ (\text{cal/mole}) \quad , \tag{12}$$

from which the enthalpy change for reaction (1) is 44 calories, making the enthalpy of the formation of $O_2F_{2(g)}$ about twice that of $O_2F_{(g)}$.

From Eq. (1), it can be seen that Eq. (12) is also

$$\Delta G(r) = \Delta G_{(f,g)}(O_2F_2) - 2\Delta G_{(f,g)}(O_2F) \quad , \tag{13}$$

that is, the free energy change of Eq. (1) is equal to the free energy change in the formation of O_2F_2 minus twice the free energy change in the formation of O_2F. The individual changes in free energy can be expressed as

$$\Delta G_{(f,g)}(O_2F_2) = \Delta H_{(f,g)}(O_2F_2) - \Delta S_{(f,g)}(O_2F_2) * T \quad , \tag{14}$$

$$\Delta G_{(f,g)}(O_2F) = \Delta H_{(f,g)}(O_2F) - \Delta S_{(f,g)}(O_2F) * T \quad , \tag{15}$$

where ΔH and ΔS are enthalpy and entropy changes. The free energy change in the reaction expressed in Eq. (1) can be expressed as

$$\Delta G(r) = \Delta H(r) - \Delta S(r) * T \quad . \tag{16}$$

From Eqs. (13) and (16), it is clear that

$$\Delta H(r) = \Delta H_{(f,g)}(O_2F_2) - 2\Delta H_{(f,g)}(O_2F) \quad \text{and} \tag{17}$$

$$\Delta S(r) = \Delta S_{(f,g)}(O_2F_2) - 2\Delta S_{(f,g)}(O_2) \quad . \tag{18}$$

Combining the entropy values of the reactants [5] with those of the products calculated by Lyman [6], $\Delta S_{(f,g,250)}$ (O_2F_2) = −30.93 eu and $\Delta S_{(f,g,250)}$ (O_2F) = −10.97 eu. When these entropy changes and the mid-temperature free energy from Eq. (12) are combined with Eqs. (13)–(18) we find

$$\Delta G_{(f,g,250)}(O_2F) = +2.60 + 0.01097\ T \ , \quad (\text{kcal/mole}) \tag{14}$$

$$\Delta G_{(f,g,250)}(O_2F_2) = +4.49 + 0.03093\ T \ , \quad (\text{kcal/mole}) \tag{15}$$

Kirshenbaum [7] reports +4.73 ±0.30 kcal/mole for $\Delta H_{(f,g,298.15)}(O_2F_2)$. Chase et al. [8] estimated a value of +2.4 kcal/mole for $\Delta H_{(f,g,298.15)}$ (O_2F). They assumed that the enthalpy resulting from the extraction of one F atom from O_2F_2 (to produce O_2F + F) would equal half the enthalpy change from the dissociation of O_2F_2 to O_2 plus two F atoms. In a recent publication, Lyman and Holland [9] report +5.49 ±0.40 kcal/mole for $\Delta H_{(f,g,298.15)}$ (O_2F). The equilibrium data would indicate that the values from [7] and [9] are not consistent in that these data require O_2F to be more stable than O_2F_2 at room temperature, and $\Delta H_{(f,g,298.15)}$ (O_2F) to be approximately half that of $\Delta H_{(f,g,298.15)}$ (O_2F_2). The equilibrium data are in good agreement with the data from [7] and [8].

From Eqs. (7) and (8), it can be deduced that the enthalpy of activation of the homogeneous gas phase reactions, Eq. (1), is 13 kcal/mole. Equations (9) and (10) include heterogeneous reactions and are likely to involve significant entropy of activation [10] and thus be more difficult to reduce. Schumacher and Frisch [11] have measured the rate of decomposition of O_2F_2 without specifying the reaction mechanism. They report an enthalpy of activation of 17.3 kcal/mole. Similar measurements by Abney [12] over the temperature range 235 to 271 K resulted in 10.4 kcal/mole for the enthalpy of activation. This would be in agreement with a reasonable combination of the rates given in Eqs. (8) and (9).

ACKNOWLEDGMENTS

Jerry Dunn prepared nearly all of the O_2F_2 used in these experiments.

REFERENCES

1 G. M. Campbell, J. Mol. Struct., 189 (1988) 301.

2 D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data, 11 (1982) 327.

3 K. C. Kim and G. M. Campbell, J. Appl. Spectrosc., 39 (1985) 625.

4 K. C. Kim and G. M. Campbell, J. Mol. Struct., 129 (1985) 263.

5 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, 'Selected Values of the Thermodynamic Properties of the Elements,' American Society for Metals, Metals Park, Ohio, 1973.

6 J. Lyman, Los Alamos National Laboratory, personal communication (October 1988).

7 A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, J. Am. Chem. Soc. 81 (1959) 6398.

8 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, 'JANAF Thermochemical Tables, Third Edition,' J. Chem. Ref. Data, Suppl. 1, 14 (1985).

9 John L. Lyman and Redus Holland, J. Phys. Chem., 92 (1988) 7232.

10 S. Glasstone, K. J. Laidler, H. Eyring, 'The Theory of Rate Processes.' (McGraw-Hill, New York, 1941), 196.

11 H. J. Schumacher and P. Frisch, Z. Physik, Chem. B37 (1937) 1.

12 K. D. Abney, Los Alamos National Laboratory, personal communication (May 1988).