

A Statistical Mechanical Theory of the Lindemann Time Delay in Unimolecular Reactions

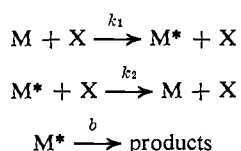
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Abstract: A classical statistical mechanical theory for estimating the time delay in the Lindemann theory of unimolecular reactions as a function of pressure is presented in terms of the parameters in the Kassel integral. The theory is applied to two cases, cyclobutane and methylcyclobutane.

In 1922 Lindemann¹ proposed that "active" molecules were produced in gases by intermolecular collision, necessarily a bimolecular process, but that a time delay between activation and reaction would produce the experimental observation of a first-order gas-phase reaction and, mechanistically, a unimolecular reaction.

This suggestion has since been formulated in the following familiar way. Let M be a decomposable molecule and X be any molecule including M, decomposition products of M, and any added gas molecules. Let M* be, in more modern parlance, a vibrationally excited molecule, sufficiently excited to be termed "activated." Then



Writing the steady-state approximation for the concentration of M*, and letting the symbol represent the concentration in each case

$$\frac{dM^*}{dt} = k_1XM - k_2XM^* - bM^* = 0$$

$$M^* = \frac{k_1XM}{k_2X + b}$$

The rate of reaction to be observed is

$$-\frac{dM}{dt} = bM^* = \frac{bk_1XM}{k_2X + b}$$

At sufficiently high pressure $k_2X \gg b$ and

$$-\frac{dM}{dt} = \frac{bk_1}{k_2} M = k_{\text{obsd}}M$$

or a first-order rate law. At sufficiently low pressure $k_2X \ll b$ and

$$-\frac{dM}{dt} = k_1XM = k_{\text{obsd}}M$$

where k_{obsd} should be proportional to the total pressure.

This behavior was sought for and found in a fair number of cases, for example, the isomerization of cyclopropane,² the decomposition of cyclobutane,³⁻⁵

the isomerization of methyl isocyanide,⁶ and others, except that k_{obsd} was constant for each experimental run and was pressure dependent but did not become strictly proportional to the pressure at any attainable pressures.

All subsequent theories of unimolecular reactions depend on the Lindemann time delay as a starting point including the Hinshelwood theory,⁷ the Kassel theory,⁸ the Slater⁹ theory, and the Marcus-Rice theory.¹⁰ In particular the Kassel theory⁸ leads to the Kassel integral

$$k = \frac{k_{\infty}}{(kT)^s \Gamma(s)} \int_0^{\infty} \frac{z^{s-1} \exp(-z/kT) dz}{1 + \frac{A RT}{a N p} \left(\frac{z}{z + \epsilon_0} \right)^{s-1}} \quad (1)$$

where ϵ_0 = the minimum energy needed for activation, $z = \epsilon - \epsilon_0$ for $\epsilon \geq \epsilon_0$, s = "effective" number of vibrational modes in the molecule, Γ is the gamma function, N is Avogadro's number, $a = 4\sigma^2(8kT/\pi m)^{1/2}$, A is the frequency factor, and p is the pressure.

Now what is the magnitude of the Lindemann time delay? How much time elapses between an activating collision and reaction on the average, *i.e.*, for those active molecules which *do* react? Not one of these theories addresses itself to this question. In certain contexts the lifetimes of active molecules¹¹ have been discussed. The limiting lifetimes of molecules which are activated and then left to their own devices, *i.e.*, at such low pressures that deactivating collisions do not occur, have been calculated, for example, by Trotman-Dickenson¹² and Slater.⁹ But this low pressure limit corresponds in most cases to much lower pressures than those at which measurements are possible. The isomerization of methyl isocyanide⁶ perhaps comes closest to the second-order limit in the experimental range because the number of atoms in the molecule is small.

In principle, the Lindemann time delay must apply to pressures greater than pressures where the calculations have been made in the references cited above

(3) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951).

(4) C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953).

(5) R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

(6) F. W. Schneider and B. S. Rabinovitch, *ibid.*, **84**, 4215 (1962).

(7) C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A113**, 230 (1926).

(8) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

(9) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

(10) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951).

(11) R. A. Marcus, *J. Chem. Phys.*, **20**, 352, 355 (1952).

(12) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth & Co., Ltd., London, 1955.

(1) F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

(2) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953).

and at pressures where measurements may actually be made. In a word, the *effective time delay* must be pressure dependent.

In this paper we address ourselves to the problem of estimating the magnitude of a pressure-dependent time delay. By the nature of things we calculate averages of certain sorts.

Suppose we consider a decomposition reaction which is described by the Kassel integral. Kassel⁸ deduced a formula for the rate constant b as a function of the energy $\epsilon \geq \epsilon_0$.

$$b(\epsilon) = A \left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1} \quad (2)$$

$$A = k_\infty \exp(+\epsilon_0/kT) \quad (3)$$

The average number of collisions per second for one molecule is given according to kinetic theory by

$$an = 4n\sigma^2(\pi kT/m)^{1/2} \quad (4)$$

where n = number molecules per cubic centimeter and σ is the collision diameter. The average time between collisions is

$$\tau = (an)^{-1} \quad (5)$$

Assuming "strong" collisions equivalent to assuming deactivation on every collision of an activated molecule, we will take the maximum life (itself an average) for an activated molecule to be

$$\tau = t_{\max} = (b_{\min})^{-1} = (an)^{-1} \quad (6)$$

In eq 2 we let the value of ϵ for which $b(\epsilon) = b_{\min}$ be ϵ' . Then

$$b_{\min} = an = A \left(\frac{\epsilon' - \epsilon_0}{\epsilon'} \right)^{s-1} \quad (7)$$

$$\epsilon' = \frac{\epsilon_0}{1 - \left(\frac{an}{A} \right)^{1/(s-1)}} = \frac{\epsilon_0}{1 - B} \quad (8)$$

$$\epsilon' - \epsilon_0 = \epsilon_0 B / (1 - B) \quad (9)$$

From classical statistical mechanics the distribution law for a system of s coupled oscillators is

$$f(\epsilon)d\epsilon = (\epsilon/kT)^{s-1} \exp(-\epsilon/kT) d\epsilon / (\Gamma(s)kT) \quad (10)$$

Now we calculate the average value of b , averaged over all energies from ϵ' to infinity, that is, the average of all the lifetimes of molecules which react. These lifetimes are less than τ .

$$\bar{b} = \frac{A \int_{\epsilon'}^{\infty} \left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1} \left(\frac{\epsilon}{kT} \right)^{s-1} \exp(-\epsilon/kT) (d\epsilon/kT)}{\frac{1}{\Gamma(s)} \int_{\epsilon'}^{\infty} \left(\frac{\epsilon}{kT} \right)^{s-1} \exp(-\epsilon/kT) (d\epsilon/kT)} \quad (11)$$

By repeated integration by parts, a straightforward but tedious process, both numerator and denominator may be reduced to a finite sum, giving

$$\bar{b} = A \frac{\left(\frac{\epsilon' - \epsilon_0}{\epsilon'} \right)^{s-1} \sum_{m=1}^{m=s} \frac{1}{(s-m)!} \left(\frac{kT}{\epsilon' - \epsilon_0} \right)^{m-1}}{\sum_{m=1}^{m=s} \frac{1}{(s-m)!} \left(\frac{kT}{\epsilon'} \right)^{m-1}} \quad (12)$$

or

$$\bar{b} = an \frac{\sum_{m=1}^{m=s} \frac{1}{(s-m)!} \left(\frac{kT}{\epsilon_0} \right)^{m-1} \left(\frac{1-B}{B} \right)^{m-1}}{\sum_{m=1}^{m=s} \frac{1}{(s-m)!} \left(\frac{kT}{\epsilon_0} \right)^{m-1} (1-B)^{m-1}} \quad (13)$$

As the pressure is lowered, $\epsilon' \rightarrow \epsilon_0$ and (12) appears indeterminate, but rewriting the numerator yields

$$\text{numerator} = A \sum_{m=1}^{m=s} \frac{(kT)^{m-1} (\epsilon' - \epsilon_0)^{s-m}}{(s-m)! (\epsilon')^{s-1}} \quad (14)$$

As $n \rightarrow 0$, each term in the series goes to zero except the term where $s = m$. Then we have

$$\text{numerator} = A \left(\frac{kT}{\epsilon_0} \right)^{s-1} \quad (15)$$

and

$$\bar{b}_0 = \frac{A \left(\frac{kT}{\epsilon_0} \right)^{s-1}}{\sum_{m=1}^{m=s} \frac{1}{(s-m)!} \left(\frac{kT}{\epsilon_0} \right)^{m-1}} \quad (16)$$

To get \bar{l} , the average lifetime of these molecules which actually decompose, which we take to be an estimate of the magnitude of the Lindemann time delay, we set

$$\bar{l} = (\bar{b})^{-1} \quad (17)$$

Actually we considered calculating \bar{l} as $(1/\bar{b})$, but one term in the series for this quantity was infinite, making the average infinite, so we contented ourselves with (17).

We have calculated \bar{l} for two cases where Kassel parameters are available, *i.e.*, for cyclobutane⁵ and methylcyclobutane.¹³ The values of the parameters used are shown in Table I.

Table I

	E_0 , cal/mole	A , sec ⁻¹	σ , Å	s
Cyclobutane	63,200	7.02×10^{15}	5.8	18
Methylcyclobutane	63,100	1.06×10^{16}	5.85	26

Values of \bar{l} as a function of pressure were calculated from eq 13, 16, and 17 by IBM 360 computer, and τ values for comparison¹⁴ are shown in Table II.

Table II

p , Torr	—Cyclobutane (723.2°K)—		-Methylcyclobutane (742.5°K)-	
	τ , sec	\bar{l} , sec	τ , sec	\bar{l} , sec
0	∞	5.5×10^{-3}	∞	0.82
10^{-4}	9.6×10^{-4}	1.1×10^{-3}	1.1×10^{-3}	5.1×10^{-3}
10^{-3}	9.6×10^{-5}	3.6×10^{-6}	1.1×10^{-4}	1.1×10^{-5}
10^{-2}	9.6×10^{-6}	8.9×10^{-7}	1.1×10^{-5}	2.1×10^{-6}
10^{-1}	9.6×10^{-7}	1.8×10^{-7}	1.1×10^{-6}	3.4×10^{-7}
10^0	9.6×10^{-8}	3.0×10^{-8}	1.1×10^{-7}	4.7×10^{-8}
10^1	9.6×10^{-9}	4.3×10^{-9}	1.1×10^{-8}	6.0×10^{-9}
10^2	9.6×10^{-10}	5.6×10^{-10}	1.1×10^{-9}	7.1×10^{-10}
10^3	9.6×10^{-11}	6.7×10^{-11}	1.1×10^{-10}	8.2×10^{-11}

(13) T. F. Thomas, P. J. Conn, and D. F. Swinehart, *J. Am. Chem. Soc.*, **91**, 7611 (1969).

(14) Suggested by the referee.

It is apparent that these values of the time delay are averages of a particular sort. Nevertheless, the values seem to be a sensible order of magnitude. It is interesting to note that the effect of increasing the value of s from 18 to 26 increases \bar{t}_0 by a factor of 150. But decreasing s from 18 to 11 (and E_0 to 48.6 kcal, for some molecule with fewer atoms) decreases \bar{t}_0 by a factor of 1040, *i.e.*, to 5.3×10^{-6} sec. \bar{t}_0 is a weak function only of the temperature, decreasing by a factor of less than 5 for a temperature increase of

70° for cyclobutane. \bar{t} is, of course, always smaller than τ , but is approaching τ as the pressure is increased.

We reemphasize that the times calculated by this theory represent an average lifetime for active molecules which actually react. The lifetimes of activated molecules which are deactivated by collision are not counted.

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Aqueous Solubilities of Potassium, Rubidium, and Cesium Perchlorates

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Abstract: The solubilities of KClO_4 , RbClO_4 , and CsClO_4 at 25° have been determined in the presence of some uniunivalent strong electrolytes varying the ionic strength from 0.068 to 0.46 M . Contrary to earlier indications, close agreement with simple Debye-Hückel theory was found with RbClO_4 and CsClO_4 generally, and with KClO_4 at lower ionic strengths and with some of the added electrolytes. A water solubility of $0.0683 \pm 0.0003 M$ at 25° for RbClO_4 was found, resolving lack of agreement among previously reported results. The negative logarithms of the thermodynamic solubility product constants derived from the data are: KClO_4 , 1.944; RbClO_4 , 2.542; and CsClO_4 , 2.380.

The low coordinating and associating tendencies of the ions in potassium, rubidium, and cesium perchlorates in water make them ideal for study of interionic effects on their solubility equilibria. The ionic strengths available extend down to 0.068 M for the least soluble, RbClO_4 . This study lies partly in the region about 0.05–0.2 M ionic strength in which deviations from the Debye-Hückel relation in eq 1 often begin to appear as added electrolyte concentration increases. In eq 1

$$\log \gamma_{\pm} = -0.509\sqrt{I}/(1 + A\sqrt{I}) \quad (1)$$

I is ionic strength and γ_{\pm} is the mean molar¹ ionic activity coefficient. Ion pairing could produce solubilities higher than in mixtures following eq 1. Only uniunivalent electrolytes are considered here and the factor A is not significantly different from unity for the ions K^+ , Rb^+ , Cs^+ , Cl^- , and ClO_4^- ,² for I near 0.1 M . If we take the thermodynamic solubility constant³ to be $K_{s_0}\gamma_{\pm}^2 = K_{s_0}^0$ and $K_{s_0} = [\text{M}^+][\text{ClO}_4^-]$, we get from this and eq 1

$$\log K_{s_0} = \log K_{s_0}^0 + 1.018\sqrt{I}/(1 + \sqrt{I}) \quad (2)$$

Molarity at 25° is used throughout this paper.

Several studies of KClO_4 solutions appeared many years ago.^{4–6} It is the most soluble of the three per-

chlorates, 0.148 M , so that rather high ionic strengths were reached in these studies. The last one⁶ implied that specific ion effects are so great that no clear limiting behavior such as given by eq 2 is followed. Of course, the form of eq 2 was not used at that time. For RbClO_4 and CsClO_4 , only pure water solubilities had been reported.^{4,7} The present study was made to find out how the solubilities of the last two vary with ionic strength, to reexamine the behavior of KClO_4 , and to resolve contradictions among published values for the RbClO_4 solubility and thermodynamic data for the Rb^+ ion.

Earlier determinations of solubilities were made by evaporation and weighing of remaining nonvolatile solutes. In the present work, tetraphenylborate precipitation methods were used. Their specificity and reliability make the results reliable to within a few parts per thousand of the solubility molarity.

Experimental Section

Materials. KClO_4 was reagent grade, recrystallized twice from water. CsCl was Fisher reagent certified 99.9%. CsClO_4 was prepared from the CsCl or from 99.9% Cs_2CO_3 (K and K Laboratories, Inc., Plainview, N. Y.) by adding excess HClO_4 and recrystallizing the solid twice from water. RbClO_4 was obtained from G. F. Smith Co. who state that it is normally 0.1–0.3% KClO_4 , but may reach 1% KClO_4 . The various high results previously reported

found in A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 4th ed, W. Linke, Ed., The American Chemical Society, Washington, D. C.: Vol. 1, 1958; Vol. 2, 1965.

(5) A. A. Noyes and C. R. Boggs, *J. Am. Chem. Soc.*, **33**, 1650 (1911).

(6) R. M. Bozorth, *ibid.*, **45**, 2653 (1923).

(7) R. Flatt and A. Jordan, *Bull. Soc. Chim. Fr.*, **47**, 246 (1930); *Helv. Chim. Acta*, **16**, 37 (1933).

(1) J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Reading, Mass., 1964, p 433, gives reasons for the value 0.509 for M units.

(2) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

(3) K_{s_0} is used here for the traditional K_{sp} in accordance with recent international usage. See ref 1 and "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

(4) A summary of solubilities and references to earlier papers are