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ACTIVATED COMPLEX THEORY APPLIED TO THE THERMAL DECOMPOSITION OF SOLIDS

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### Author

Shannon, Robert D.

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THERMAL DECOMPOSITION OF SOLIDS

Berkeley, California

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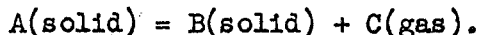
Robert D. Shannon

Lawrence Radiation Laboratory and  
Department of Mineral Technology  
University of California, Berkeley, California

INTRODUCTION

Activated complex theory as developed by Eyring et al.<sup>1</sup> and later extended by others<sup>2,3</sup> has been applied extensively to unimolecular and bimolecular reactions. In recent years Eyring's theory has been used by Penner<sup>3</sup> to predict rates of melting and evaporation, by Wyllie<sup>4</sup> to explain the evaporation coefficient of water, and by Bradley<sup>5</sup> to interpret the condensation coefficient of sulfur. Schultz and Dekker<sup>6</sup> showed that the experimental sublimation rates of rhombic sulfur and benzene agreed with those predicted by absolute reaction rate theory.

The successful application of activated complex theory to evaporation suggests its use in predicting the rates of thermal decomposition of solids. Possibly the least complicated of such reactions are those of the type:



A survey of existing rate data for such reactions reveals rate constants of the same order of magnitude among the hydrates and among those compounds in which  $\text{CO}_2$  is given off. An analysis of these constants by activated complex theory allows a possible interpretation of the mechanism of the reactions and prediction of the experimental rate constants of similar reactions. The decompositions involving  $\text{MgCO}_3$  and  $\text{CaCO}_3$  are most suitable for detailed analysis on the basis of the availability of dependable rate data and infrared crystal spectra.

## THERMAL DECOMPOSITIONS

Thermal decompositions are generally characterized by three stages of reaction.<sup>7</sup> The first is an induction period in which nuclei form. The second stage is an acceleratory period in which the nuclei commence to grow. The final stage is a deceleratory period in which it is possible for the nuclei to grow together to form an interface which advances linearly with time. However, because the effective area over which the reaction occurs decreases, the apparent rate of reaction as determined through weight loss or pressure change decreases. This interface reaction is of greatest interest because of the relatively simple geometry involved.

One can arrive at the following qualitative picture of the interface reaction. After nucleation is completed and only growth of nuclei is occurring, the reaction takes place at the reactant-product interface. The atoms or molecules at the surface of the reactant have vibrational and possibly torsional or rotational degrees of freedom with an assumed Boltzmann distribution of energies. The molecules which have already escaped will have gained translational and rotational degrees of freedom and to arrive at the air-product interface must have diffused through the reacted layer. One assumes that this layer does not exert any noticeable impedance or that the impedance may be corrected for.

One of the earliest attempts to treat quantitatively the rate of surface reactions, e.g., evaporation and decomposition, was made by Polanyi and Wigner.<sup>8</sup> To a first approximation they assumed that molecules which attained a critical energy,  $E$ , would be able to escape from the reactant surface. Then the rate of escape would be proportional to an atomic frequency of vibration and an exponential factor involving the activation energy,  $E$ . This resulted in the often used Polanyi-Wigner equation, in which the critical degree of freedom was that of translation perpendicular to the surface:

$$k_r = \nu \exp\left(-\frac{E}{RT}\right), \quad (1)$$

where:

$k_r$  = first order rate constant

$\nu$  = atomic frequency of vibration

$E$  = activation energy for the process

As a corollary they further assumed that this critical energy could be attained through three degrees of vibrational freedom and introduced a correction factor,  $2E/RT$ , by which the rate would be increased. In Table I, thirty-one reactions are evaluated using the corrected form of the Polanyi-Wigner equation

$$k_r = B \cdot \exp\left(-\frac{E}{RT}\right) = \frac{2E}{RT} \nu \exp\left(-\frac{E}{RT}\right). \quad (2)$$

Comparison of the frequency factor determined experimentally and calculated according to equation (2) shows that only a third of these decompositions provide order of magnitude agreement. This raises some doubt as to the validity of the P-W expression. On the other hand, it may be used to correctly derive the familiar Knudsen equation for the rate of evaporation of solids,<sup>8</sup> giving at least some basis for its use in certain cases. However, the weakness of the expression appears to be that it does not take into account rotational and other vibrational degrees of freedom. Activated complex theory has the advantage that it considers other than vibrational degrees of freedom.

#### APPLICATION OF ACTIVATED COMPLEX THEORY

In its simplest form, activated complex theory considers a potential energy surface in which potential energy is plotted vs. a set of normal coordinates for the atoms taking part in the reaction and results in a multidimensional space that is difficult to picture in all but the most elementary cases. One imagines the reactants to go to products via the path of minimum energy. If this path is followed in cross section, the configurational energy of the system usually goes

over a maximum as shown in Fig. 1. The configuration of the atoms at point B is known as the activated complex, while the energy at this point is the activation energy for the process. Then, if the reaction depends on only one normal coordinate and if a Boltzmann distribution of energies is assumed to exist, the familiar equation of absolute reaction rate theory may be derived:<sup>1</sup>

$$k_r = \frac{kT}{h} \frac{Q^*}{Q} \exp\left(-\frac{E}{kT}\right) = B \cdot \exp\left(-\frac{E}{kT}\right) \quad (3)$$

where:

$k_r$  = first order rate constant

$Q^*$  = complete partition function for the activated complex excluding that for the reaction coordinate

$Q$  = complete partition function for the reactant

$E$  = activation energy for the process

$B$  = frequency factor

By knowing the partition function of the reactants and the activated complex and the activation energy for the process, it is theoretically possible to predict the experimental reaction rate. Thus, the problem becomes one of formulation of the partition functions for the reactant atoms and the activated complex. In the case of thermal decompositions, two types will be considered:

(1) the reaction proceeds via loss of the gaseous product directly from the surface of the solid, and (2) the reaction proceeds via the formation of a mobile layer followed by desorption.

#### TYPE 1

In general, it is difficult to find thermal decomposition studies for which one has sufficient crystal spectra data and accurate measurements of rate constants for the reaction. However, the decomposition of calcite has been frequently studied both with powders and single crystals and reliable data exist for the decomposition in vacuum.<sup>9,10</sup> Therefore, this reaction was chosen to best



demonstrate the possibility of using activated complex theory to predict the frequency factor,  $B$ , and consequently the rate of reaction. Calcite has a rhombohedral structure in which the  $\text{CO}_3^-$  groups exist as planar units surrounded by three  $\text{Ca}^{++}$  ions (see Fig. 2). Although the atoms do not exist in the solid as molecules,  $\text{CaCO}_3$  will be considered here as a unit with the appropriate degrees of freedom. The fundamental degrees of freedom of atoms and molecules in the crystal can be listed for  $\text{CaCO}_3$  as:

- (1) Lattice vibrations--low frequency vibrations in which the cationic groups move against the anionic groups, i.e.,  $\text{Ca}^{++}$  vs  $\text{CO}_3^-$ . These vibrations are the analog of the translational degrees of freedom in the vapor and are called external vibrations.
- (2a) Low frequency torsional oscillations of complex units such as  $\text{CO}_3^-$ . These are the analog of rotation in the gaseous state.
- (2b) Free rotation of the carbonate ion.
- (3) Simple vibrations of atomic units within larger units, i.e., the bending and stretching modes of the  $\text{CO}_3^-$  ion. These are called internal vibrations and do not contribute as large a factor to the partition function as the other three degrees of freedom.

By taking into consideration these degrees of freedom for reactant molecules and the activated complex, it becomes possible to formulate the respective partition functions.

#### Reactants

In the decomposition of a carbonate, the partition function can be evaluated on the basis that the cation undergoes only minor changes in position and no changes in energy and that the only atoms actively involved in the reaction are those in the carbonate ion. One can distinguish three different cases:

- (1) No torsional oscillations of the carbonate ion.

- (2) Torsional motion of the planar carbonate group about its three principal axes.
- (3) Free rotation about the three principal axes.

Evidence for the existence of torsional modes in calcite has been postulated by Lander<sup>11</sup> in his study of phase transitions in the carbonates. Calcium carbonate, strontium carbonate, and barium carbonate were found to undergo successive transformations at high temperatures to structures of higher symmetry. The increased symmetry of these phases and an increased coefficient of expansion in a direction perpendicular to the plane of the carbonate ion and an analogy with alkali nitrates led Lander to postulate the onset of torsional oscillation of the carbonate ion. Assuming such torsional activity at the temperatures of the transitions, it is not unreasonable to hypothesize complete rotation of the carbonate ions at decomposition temperatures.

Disregarding the first case on the basis of Lander's work, the probable partition functions for one  $\text{CO}_3^-$  unit in calcite are:

$$Q_1 = f_L^3 f_\lambda^3 f_{\text{vib}}^6$$

$$Q_2 = f_L^3 f_{\text{rot}}^3 f_{\text{vib}}^6$$

where:

$$f_{\text{tr}} = \left[ \frac{2\pi mkT}{h^2} \right]^{\frac{1}{2}}$$

$$f_{\text{rot}} = \left[ \frac{8\pi^2 I kT}{\sigma h^2} \right]^{\frac{1}{2}}$$

$$f_{\text{vib}} = f_L = f_\lambda = [1 - \exp(-\frac{h\nu}{kT})]^{-1}$$

$f_L$  = partition function for a lattice vibration

$f_\lambda$  = partition function for a torsional oscillation

$f_{\text{tr}}$  = translational partition function for a mobile atom at a surface

### Products

After reaction, CaO exists as a solid, CO<sub>2</sub> as a gas. Thus, the partition function for the products of the CO<sub>3</sub><sup>-</sup> ion are written:

$$Q_0 = f_L^3 \quad \left| \quad Q_{CO_2} = f_{tr}^3 \quad f_{rot}^2 \quad f_{vib}^4 \right.$$

$$Q_{prod} = f_L^3 \quad f_{tr}^3 \quad f_{rot}^2 \quad f_{vib}^4$$

Although  $Q_{prod}$  does not appear in the rate expression, it provides a limiting value for the partition function of the activated complex.

### Activated Complex

It is evident that the value of the partition function for the activated complex must lie somewhere between that of the reactants and the products. The assumption will be made that  $Q^*$  is more similar to  $Q_{react}$  in exothermic reactions and to  $Q_{prod}$  in endothermic reactions, i.e., that  $Q^*$  is more like  $Q_{prod}$  in thermal decompositions.<sup>2</sup> Therefore, one pictures roughly the activated complex as shown in Fig. 3.

One pictures the CO<sub>2</sub> molecule immediately before its escape as: (1) having three lattice vibrational modes--the one perpendicular to the solid surface representing the O...CO<sub>2</sub> bond; (2) rotating freely about an axis perpendicular to the O=C=O axis; and (3) having its normal internal vibrational modes. The second degree of rotational freedom possessed by the gaseous CO<sub>2</sub> is replaced by a torsional mode. The complete partition function for the activated complex is thus given by:

$$Q^\ddagger = Q_0 \times Q_{CO_2}$$

$$Q^\ddagger = f_L^3 \quad f_L^2 \quad f_V \quad f_\lambda \quad f_{rot} \quad f_{vib}^4$$

$$Q^* = f_L^3 \quad f_L^2 \quad f_\lambda \quad f_{rot} \quad f_{vib}^4$$

The reaction coordinate is assumed to be the component of the mode of vibration perpendicular to the surface<sup>6</sup> and represents a bond which exists between

the atom in the solid and the  $\text{CO}_2$  molecule just before it is broken. The partition function of the activated complex does not include the partition function corresponding to this degree of freedom.

It is convenient to divide the experimental frequency factor,  $B$ , into two parts:

$$k_r = B \cdot \exp\left(-\frac{E}{kT}\right) = \frac{kT}{h} \cdot \alpha \cdot \exp\left(-\frac{E}{kT}\right) \quad (4)$$

where:  $\alpha = \frac{Q^*}{Q}$

It is now possible to compare experimental values of the frequency factor or  $\alpha$  with the theoretical values merely by determining the partition functions. In Table II the vibrational frequencies and partition functions for reactant and activated complex are listed for  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . The values of  $\alpha$  have been calculated for both cases of torsional oscillation and free rotation of the carbonate ion. Lattice vibrational frequencies were obtained from infrared reflection and transmission spectra determined by Schaefer,<sup>12</sup> while the internal vibration frequencies were taken from Herzberg.<sup>13</sup> Torsional frequencies were taken from spectra determined by Dows<sup>14</sup> of thick films of solid  $\text{CO}_2$  deposited on AgCl plates. Calculations were made assuming for the torsional frequency: (a) a lower limit of  $60 \text{ cm}^{-1}$ , and (b) an upper limit of  $80 \text{ cm}^{-1}$ . The vibrational frequencies of the  $\text{Ca}\cdots\text{O}$  and  $\text{Mg}\cdots\text{O}$  bonds and the lattice vibrational frequencies of  $\text{MgCO}_3$  were estimated using:

$$\frac{\nu_1}{\nu_2} = \left[\frac{\mu_2}{\mu_1}\right]^{\frac{1}{2}}$$

where:

$\nu_1$  = lattice vibrational frequency of  $\text{CaCO}_3$

$\nu_2$  = lattice vibration frequency of  $\text{CaO}$  or  $\text{MgO}$

$\mu$  = appropriate reduced mass.

The values of  $\alpha$  calculated for  $\text{CaCO}_3$  are:

$$\alpha_1 = \frac{Q^*}{Q} = 3.37 \text{ (torsional oscillation of } \text{CO}_3^- \text{)}$$

$$a_2 = \frac{Q^*}{Q} = \begin{array}{l} \text{(a) } .75 \times 10^{-2} \\ \text{(b) } .58 \times 10^{-2} \end{array} \text{ (free rotation of } \text{CO}_3^- \text{)}$$

$$\alpha_{\text{exp}} \text{ (Ref. 9)} = .6 \times 10^{-2} \quad \alpha_{\text{exp}} \text{ (Ref. 10)} = 1.4 \times 10^{-2}$$

Similar calculations for  $\text{MgCO}_3$  give:

$$\alpha_1 = 2.90$$

$$\alpha_2 = \begin{array}{l} \text{(a) } 1.1 \times 10^{-3} \\ \text{(b) } 0.85 \times 10^{-3} \end{array}$$

$$\alpha_{\text{exp}} \text{ (Ref. 9)} = 1.8 \times 10^{-2}$$

Agreement between the experimental values and those calculated according to the theory is sufficiently good to suggest the possibility of a Type I decomposition involving free rotation of the carbonate ion at the onset of the reaction.

#### TYPE 2

The second type of reaction involves the formation of an activated complex containing greater degrees of freedom, i.e., those corresponding to (a) excitation of rotation in the activated complex, or (b) the translations of a mobile adsorbed layer. Thus, the activated complex will more closely resemble the gaseous phase in degrees of freedom. The partition function for the activated complex is now given by:

$$\text{(a) } Q^* = f_L^3 \cdot f_L^2 \cdot f_{\text{rot}}^3 \cdot f_{\text{vib}}^3 \text{ (free rotation of activated complex)}$$

$$\alpha = \frac{Q^*}{Q} = \frac{f_L^3 \cdot f_L^2 \cdot f_{\text{rot}}^3 \cdot f_{\text{vib}}^3}{f_L^3 \cdot f_\lambda^3 \cdot f_{\text{vib}}^6} \cong \frac{f_L^2 \cdot f_{\text{rot}}^3}{f_\lambda^3 \cdot f_{\text{vib}}^3}$$

$$(b) \quad Q^* = f_L^3 \cdot f_{tr}^2 \cdot f_{rot}^3 \cdot f_{vib}^3$$

$$\alpha \approx \frac{f_{tr}^2 \cdot f_{rot}^3}{f_\lambda^3 \cdot f_{vib}^3}$$

(free rotation and 2D translational freedom of activated complex)

One then evaluates the partition functions for a mobile adsorbed water molecule:

$$f_{tr} = 4.24 \times 10^8 \cdot x_{tr}$$

$$\text{letting } x_{tr} = 100 \text{ \AA at } T = 300^\circ\text{K}$$

$$f_{tr}^2 = 18 \times 10^4$$

$$f_{rot}^3 = 87 \text{ where } ABC = 5.77 \times 10^{-120} \text{ gm-cm}^2$$

$$f_L = 5 \quad f_\lambda = 5$$

The approximate value of  $\alpha$  is:

$$(a) \quad \alpha \approx \frac{100}{5.5} \approx 4$$

$$(b) \quad \alpha \approx \frac{10^2 \cdot 10^4}{10^2 \cdot 5} = 5 \times 10^3$$

providing order of magnitude confirmation of the experimental reaction rates.

#### DISCUSSION

In Table I the frequency factors for most of the thermal decompositions whose rate constants have been measured are listed according to whether the value of  $\alpha$  is less than, approximately equal to, or more than one. It is difficult to generalize in cases where such a large variety of experimental methods has been used. However, certain consistencies are suggested: (1) Most of the reactions involving the loss of  $\text{CO}_2$  have low frequency factors, i.e.,  $\alpha < 1$ , and (2) the majority of the reactions involving the loss of water and those of the decomposition of liquids have frequency factors where  $\alpha > 100$ . Reference to equation 4 shows that one might interpret this in terms of the degrees of freedom possessed by the activated complex and the reactant. It has already been shown that the low values of  $\alpha$  measured for calcite and magnesite

might be understood by postulating rotation of the carbonate ion in the reactant state. Similarly, one easily perceives that a high activity of the escaping molecule, either rotation at the reactant surface or a mobile surface layer, can result in values of  $\alpha$  large enough to explain experimental results. It is perhaps not possible to specify the mechanism further than this general description, but it appears that an analysis of thermal decompositions similar to these described may prove of value. The chief limitations to the method seem to be (1) lack of the complete infrared spectrum for the solid reactant, and (2) reliable rate data taken from reaction of single crystals in which the geometry is well known.

Case 1 involves fewer uncertainties in calculation, these being simply the factors in the partition function involving frequencies attributed to the activated complex. However, even if the vibrational and torsional frequencies of adsorbed  $\text{CO}_2$  molecules were known, the difficulty would still exist as to how close to an adsorbed molecule one wishes to approximate the activated complex.

#### CONCLUSIONS

1. The rates of many thermal decompositions are not satisfactorily explained by the Polanyi-Wigner equations.
2. Using activated complex theory and assuming a mechanism involving rotation of the carbonate ion in the solid, good agreement between experimental and theoretical rate constants was obtained for the thermal decomposition of calcium and magnesium carbonates.
3. Hypothesis of the formation of a mobile surface layer of molecules provides an explanation of the abnormally high rate constants found for the decomposition of hydrates and liquids.

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TABLE Ia

$\alpha < 1$

	Single or Poly xtal	Method	T average	B exptl.	$\frac{2E}{RT}$	B predicted (Eq. 2)	$\frac{KT}{h}$	$\alpha$	Ref.
$Ag_2CO_3 \rightarrow Ag_2O + CO_2$		LAI*	400°K	$2 \times 10^{12}$	58.5	$5.2 \times 10^{14}$	$8.4 \times 10^{12}$	0.24	15
$MgCO_3 \rightarrow MgO + CO_2$	Poly	Weight loss	600°	$2.2 \times 10^{10}$	59	$7 \times 10^{14}$	$1.25 \times 10^{13}$	$1.7 \times 10^{-3}$	9
$CaCO_3 \rightarrow CaO + CO_2$	Poly	Weight loss	1050°	$1.3 \times 10^{11}$	38	$1.4 \times 10^{14}$	$2.2 \times 10^{13}$	$0.6 \times 10^{-2}$	9
	Single	"	"	$3 \times 10^{11}$			$2.2 \times 10^{13}$	$1.4 \times 10^{-2}$	10
$3Pb(OOC)_2 \rightarrow 2PbO + Pb + 4CO_2 + 2CO$	Poly	Pressure change	600°	$1.7 \times 10^{10}$	60	$5 \times 10^{14}$	$\sim 10^{13}$	$1.7 \times 10^{-3}$	17
$Ni(OOC)_2 \rightarrow Ni + 2CO_2$	Poly	Pressure change	550°	$1.7 \times 10^{10}$	55	$5 \times 10^{14}$	$1.15 \times 10^{13}$	$1.5 \times 10^{-3}$	18
$Ni(C_2H_2O_4) \rightarrow 2Ni + H_2 + H_2O + CO + 3CO_2$	Poly	Pressure change	450°	$5.3 \times 10^9$	50	$4.5 \times 10^{14}$	$\sim 10^{13}$	$5.3 \times 10^{-4}$	19
$BaN_6 \rightarrow Ba + 3N_2$	Single	Pressure change	400°	$9.4 \times 10^{11}$	67	$5.4 \times 10^{14}$	$8.4 \times 10^{12}$	0.11	20
$KMnO_4 \rightarrow MnO_2 + K_2MnO_4 + O_2$	Poly, Single	Pressure change	500°	$1.5 \times 10^{11}$	66	$6.6 \times 10^{14}$	$1.04 \times 10^{13}$	$1.5 \times 10^{-2}$	21

\* LAI = Linear Advance of Interface

TABLE Ib

$$\alpha \approx 1$$

	Single or Poly xtal	Method	T <sub>average</sub>	B <sub>exptl.</sub>	2E RT	B <sub>predicted</sub> (Eq. 2)	$\frac{KT}{h}$	$\alpha$	Ref.
$2AgO \rightarrow Ag_2O + \frac{1}{2}O_2$	Poly	Pressure increase	400°K	$1.6 \times 10^{13}$	72	$6 \times 10^{14}$	$8.2 \times 10^{12}$	1.9	22
Chrome alum $\rightarrow$ $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow$	Single	LAI*	300°		77	$4.6 \times 10^{14}$	$6.3 \times 10^{12}$	2	23,24
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Single	LAI	300°	$1.6 \times 10^{13}$	55	$3.3 \times 10^{14}$	$6.3 \times 10^{12}$	2.5	25
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Single	LAI	300°	$4.4 \times 10^{12}$	55	$3.3 \times 10^{14}$	$6.3 \times 10^{12}$	0.7	25
$KClO_4(s)$	Poly	Pressure increase	850°	$2.4 \times 10^{13}$	88	$9 \times 10^{14}$	$1.75 \times 10^{13}$	1.4	26
$AgMnO_4$	Poly, Single	Pressure change	400°	$1.6 \times 10^{13}$	74	$5.4 \times 10^{14}$	$8.4 \times 10^{12}$	1.9	27
$BaMnO_4$	Poly, Single	Pressure change	450°	$1.4 \times 10^{14}$	80	$7.2 \times 10^{14}$	$9.4 \times 10^{12}$	$1.5 \times 10$	28
$RbMnO_4$	Poly, Single	Pressure change	500°	$6 \times 10^{13}$	80	$8 \times 10^{14}$	$1.04 \times 10^{13}$	5.7	29

\*LAI = Linear Advance of Interface

TABLE Ic

$\alpha > 1$

	Single or Poly xtal.	Method	T <sub>average</sub>	B <sub>exptl.</sub>	2E RT	B <sub>predicted</sub> (Eq. 2)	$\frac{KT}{h}$	$\alpha$	Ref.
$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$	Poly	Pressure increase	450°	$1.9 \times 10^{17}$	78	$6 \times 10^{14}$	$9.4 \times 10^{12}$	$2.1 \times 10^4$	30
$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O + 4H_2O$	Single	Weight loss	300°	$1 \times 10^{15}$	61	$6 \times 10^{14}$	$6.3 \times 10^{12}$	$1.6 \times 10^2$	31
$CaCO_3 \cdot 6H_2O \rightarrow CaCO_3 + 6H_2O$	Poly		300°	$1 \times 10^{15}$	54	$7 \times 10^{14}$	$6.3 \times 10^{12}$	$1.6 \times 10^2$	32
$Mg(OH)_2 \rightarrow MgO + H_2O$	Poly	Weight loss	600°	$4.5 \times 10^{16}$	46	$5.5 \times 10^{14}$	$1.25 \times 10^{13}$	$3.6 \times 10^3$	33
$NiSO_4 \cdot 7H_2O \rightarrow NiSO_4 \cdot 6H_2O + H_2O$	Single	LAI*	300°	$1.9 \times 10^{16}$	63	$3.8 \times 10^{14}$	$6.3 \times 10^{12}$	$3 \times 10^3$	34
$LiClO_4(1) \rightarrow LiCl + 2O_2$	Melt	Weight loss	550°	$1.6 \times 10^{16}$	113	$5 \times 10^{14}$	$1.15 \times 10^{13}$	$1.4 \times 10^3$	35
$KClO_4(1) \rightarrow KCl + 2O_2$	Melt	Pressure change	850°	$1.3 \times 10^{15}$	83	$.9 \times 10^{15}$	$1.75 \times 10^{13}$	$7.4 \times 10$	26
$KClO_3 \rightarrow KCl + 3/2O_2$	Poly	Volume of gas	800°	$1.2 \times 10^{16}$	82	$.8 \times 10^{14}$	$1.7 \times 10^{13}$	$7 \times 10^2$	36
$Hg(OOC)_2$	Poly	LAI	450°	$6.7 \times 10^{16}$	82	$7 \times 10^{14}$	$9.4 \times 10^{12}$	$7.1 \times 10^3$	37
$NH_4NO_3(1) \rightarrow N_2O + 2H_2O$	Melt		550°	$3 \times 10^{16}$	90	$.1 \times 10^{16}$	$1.15 \times 10^{13}$	$2.6 \times 10^3$	38
$PbO \cdot C_6H(NO_2)_3OH_2 \rightarrow$	Single	Pressure change	500°	$2 \times 10^{15}$	93	$9.3 \times 10^{14}$	$1.04 \times 10^{13}$	$1.9 \times 10^2$	39
$PbN_6 \rightarrow Pb + 3N_2$	Single	Pressure change	500°	$5.6 \times 10^{15}$	74	$7.4 \times 10^{14}$	$1.04 \times 10^{13}$	$5.4 \times 10^2$	40
$2KN_3 \rightarrow 2K + 3N_2$	Single	Pressure change	500°	$2.8 \times 10^{15}$	72	$7.2 \times 10^{14}$	$1.04 \times 10^{13}$	$2.7 \times 10^2$	40

\*LAI = Linear Advance of Interface

TABLE IIa

CaCO<sub>3</sub> T = 1100°K

	Frequency, $\nu$ (cm <sup>-1</sup> )	Partition function, f	
<span style="border: 1px solid black; padding: 2px;">CO<sub>3</sub><sup>=</sup></span>			
Lattice Vibrations	$\nu_1 = 367$	2.64	} $Q_1 = 24.16 \times 10^3$ (torsional oscillation)
	$\nu_2 = 330$	2.84	
	$\nu_3 = 106$	7.8	
Rotation		$6.73 \times 10^4$	
Internal Vibrations	$\nu_1, \nu_2 = 715$	1.64	
	$\nu_3, \nu_4 = 1430$	1.18	
	$\nu_5 = 900$	1.44	} $Q_2 = 27.8 \times 10^6$ (free rotation)
	$\nu_6 = 1100$	1.31	
<span style="border: 1px solid black; padding: 2px;">O<sup>=</sup> ... CO<sub>2</sub></span>			
Lattice Vibrations	$\nu_{Ca \cdot O} = 525$	2.2	
	$\nu_{Ca \cdot O} = 477$	2.17	
	$\nu_{Ca \cdot O} = 157$	5.55	
Torsional Oscillation	(a) ~ 60	13	
	(b) ~ 80	10	
Rotation		31.5	
Internal Vibrations	$\nu_1 = 1345$	1.21	
	$\nu_2, \nu_3 = 667$	1.71	
	$\nu_4 = 2349$	1.04	

TABLE IIb

MgCO<sub>3</sub> T = 600°K

	Frequency, $\nu$ (cm <sup>-1</sup> )	Partition function, f	
<span style="border: 1px solid black; padding: 2px;">CO<sub>3</sub><sup>=</sup></span>			
Lattice Vibrations	$\nu_1 = 433$	1.55	} $Q_1 = 493$ (torsional oscillation) $Q_2 = 1.89 \times 10^6$ (free rotation)
	$\nu_2 = 389$	1.65	
	$\nu_3 = 125$	2.78	
Rotation		$2.72 \times 10^4$	
Internal Vibration	$\nu_1, \nu_2 = 706$	2.86	
	$\nu_3, \nu_4 = 1472$	1.03	
	$\nu_5 = 905$	1.05	
	$\nu_6 = 1124$	1.075	
<span style="border: 1px solid black; padding: 2px;">O<sup>=</sup> ... CO<sub>2</sub></span>			
Lattice Vibrations	$\nu_1 = 581$	1.33	
	$\nu_2 = 522$	1.41	
	$\nu_3 = 168$	3.2	
Torsional Oscillation	(a) 60	7.4	
	(b) 80	5.7	
Rotation		23.4	
Internal Vibrations	$\nu_1 = 1345$	1.04	
	$\nu_2, \nu_3 = 667$	1.28	
	$\nu_4 = 2349$	1.0	



Figure Captions

Figure 1 - Energy vs. distance along the reaction coordinate.

Figure 2 - Structure of calcite. The triangles represent carbonate ions and are situated at the midpoints of the edges. The spheres represent calcium ions and are at the corners and the centers of the faces.

Figure 3 - Activated complex as it may occur in the decomposition of a carbonate.

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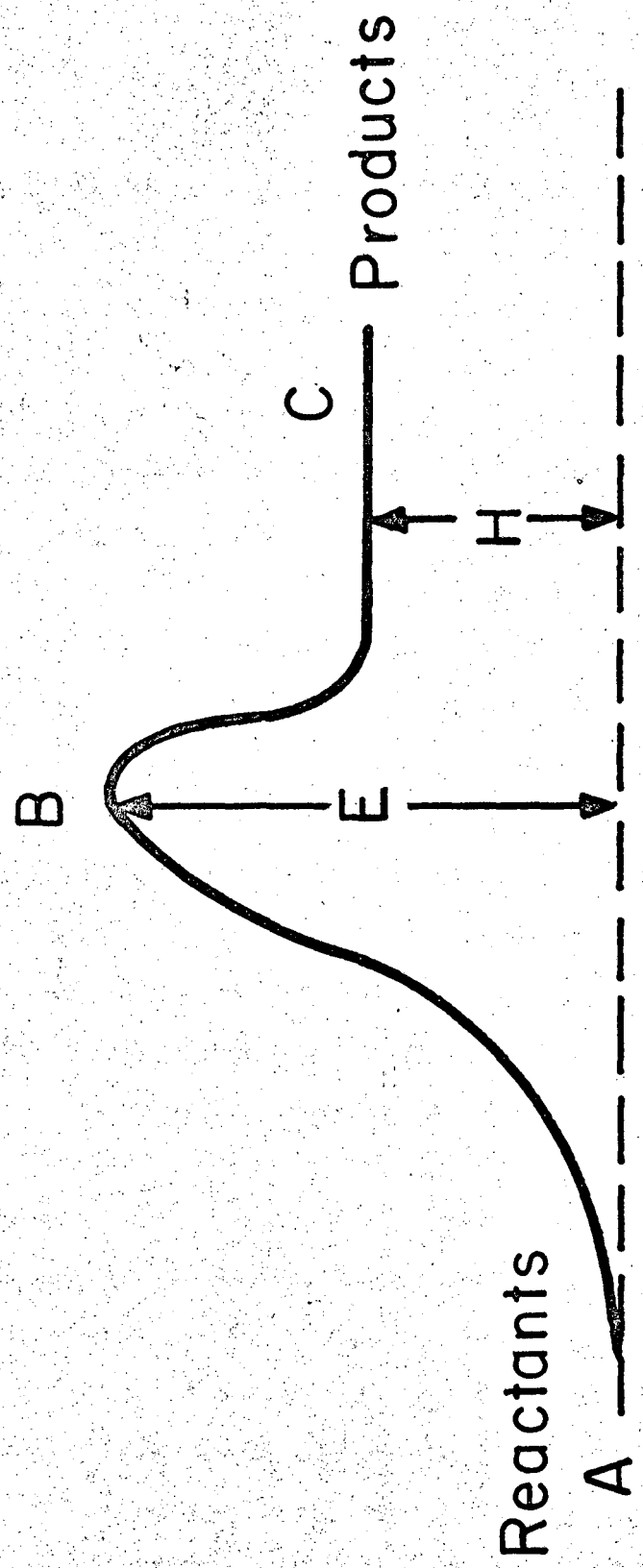


Fig. 1.

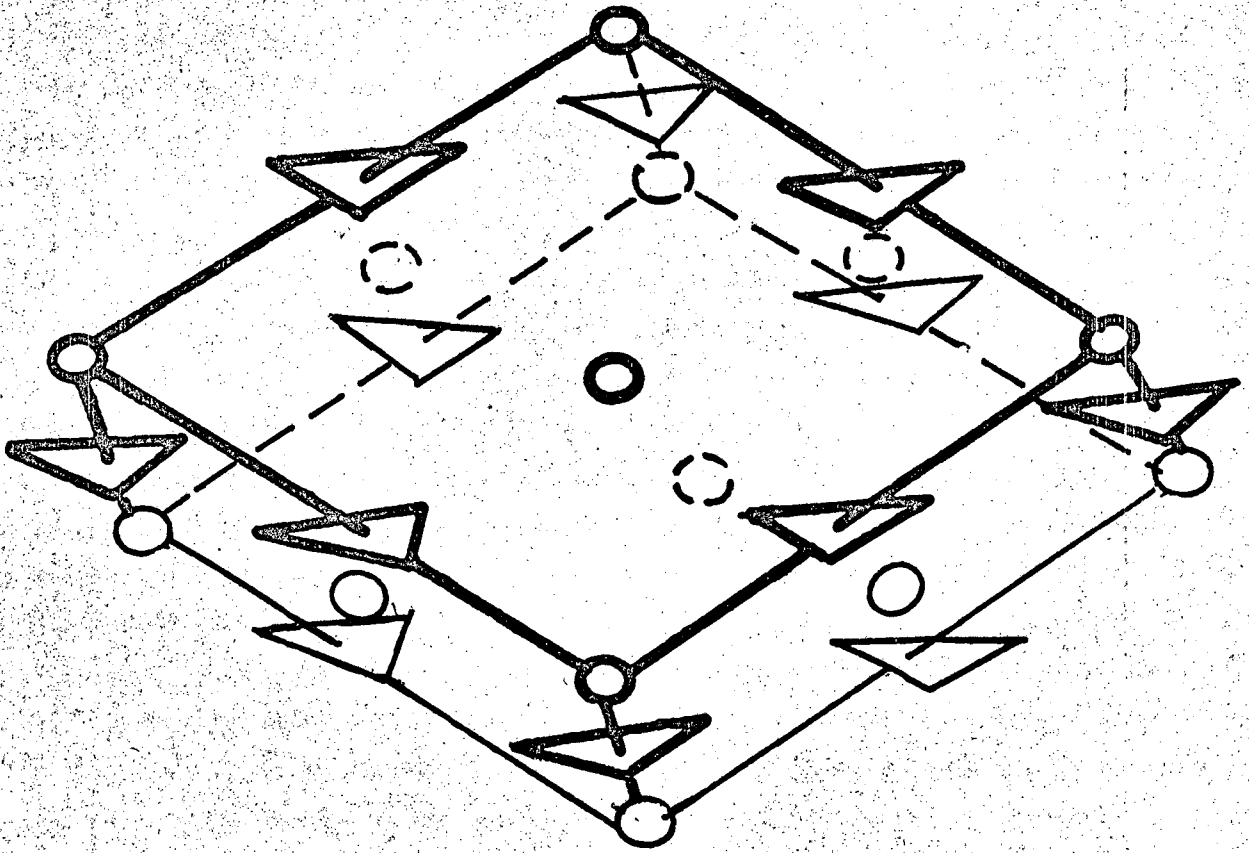
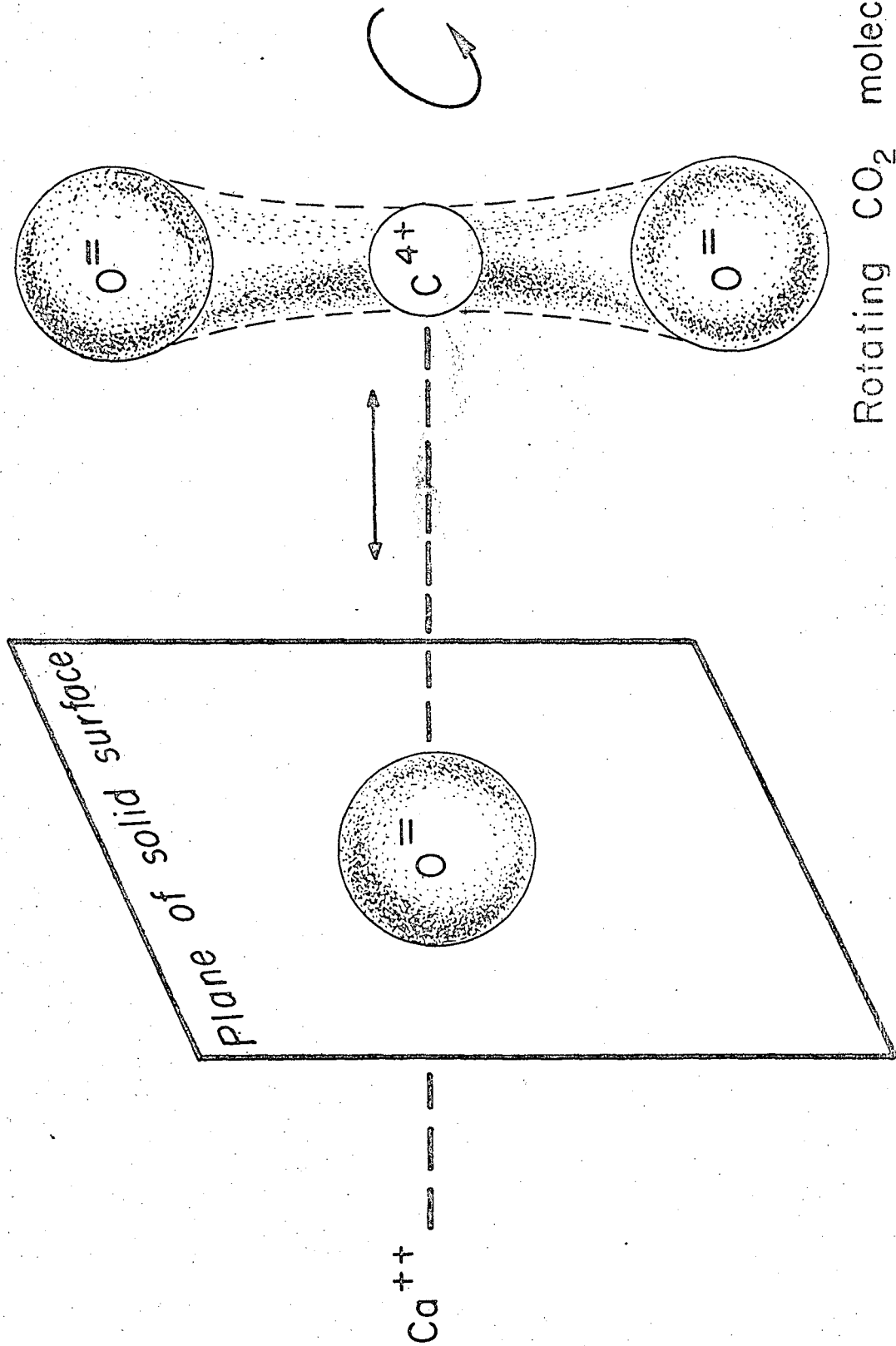


Fig. 2.

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Rotating  $CO_2$  molecule

Fig. 3.

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