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THEORETICAL STUDY OF THE DESIGN OF A CATALYST FOR  
PARA TO ORTHO HYDROGEN CONVERSION.  
FINAL TECHNICAL REPORT  
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The theory of ortho to para hydrogen molecule catalysis on magnetic surfaces was carefully reviewed during the course of this study. The theory was developed from 'first principles' by deriving a master equation, which was then evaluated in a form which includes the effects of the closeness of approach of the H<sub>2</sub> molecule to the surface, the physical state of the molecule on the surface (gas or liquid), and the magnetic state of the catalytic surface: para-magnetic or having collective magnetic excitations due to long range magnetic interactions (ferromagnetic or antiferromagnetic).

The theory was then brought to a numerical stage and evaluated for a variety of models, which were reported in six short reports which were sent to NASA/Lewis. Copies of each of these reports are included as the body of this final report. These reports contain numerical evaluations of the absolute rate of para to ortho hydrogen catalysis for a variety of dimensionless parameters which are useful for describing the rate of catalysis for different materials, and different catalytic conditions. See report VI for the best evaluation and testing of a numerical model (using transition state theory for the migration of hydrogen molecules between catalytic sites) written in VAX FORTRAN 77.

The final conclusions of this study are briefly summarized as follows: regardless of the detailed structure of any catalytic material, the rate of para to ortho hydrogen on a (magnetic) catalytic surface is primarily a function of only two parameters:

(1) **The closeness of approach of the H<sub>2</sub> molecule to the magnetic moments on the catalytic surface:** the catalytic rate is a maximum for a minimum distance of approach of the hydrogen molecule to the surface layer containing the magnetic

moments. A surface layer containing 'bare magnetic moments' would be the best in regards to this criterion.

(2) **The surface lifetime.** The surface lifetime must be as short as possible, or as close as possible to  $10^{-13}$  sec. as can be physically achieved. This lifetime parameter (essentially the surface lifetime) is difficult to control and may be nearly impossible to measure. It appears to be difficult to achieve so short a surface lifetime at the target temperature of 120 K for the hydrogen gaseous phase. Studies of the para  $\rightarrow$  ortho catalytic rate versus lifetime showed considerable degradation of catalytic performance as the surface lifetime rises from its optimum value.

The major differences between different catalytic surfaces were deemed, in the conclusion of this study, to be related to the physical nature of the surface as regards its **molecular surface complexity** and the extent of **physical binding of the H<sub>2</sub> molecules to the surface.**

The molecular surface complexity may be considered to be those features of the surface which prevent **optimum approach** of the hydrogen molecules to the active catalytic sites. The **lifetime of the molecule on the surface** is related to the nature of the peaks and valleys of the adsorption potential that a particular molecule would 'see' as it migrates (by surface diffusion) from one peak of surface potential energy (surface atom or molecule) to another. So the only way a really detailed understanding of this surface catalytic process can be achieved is to model the physical potentials which weakly bind the H<sub>2</sub> molecule to the surface. This requires structural knowledge of the nature of the surface of the catalytic material. Building such information into a model for surface diffusion and binding would then give a more complete picture of the overall process of para to ortho hydrogen catalysis, which could then be used to correlate the relative catalytic activities of different materials. Some experimental knowledge of the **magnetic character of the catalyst** is also considered important for empirical correlation of catalytic activities for different materials.

## Theory of Ortho to Para Catalysis

### I. Practical Equations for the Description of Paramagnetic Catalysis.

July 21, 1989

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#### ABSTRACT

The theory of Petzinger and Scalapino (Physical Review B, 8, 266 (1973) ) has been thoroughly reviewed, and all of the basic equations for paramagnetic para to ortho hydrogen catalysis re-derived. The paper has only a few minor phase errors and errors of omission in description of the theory. Three models (described by Petzinger and Scalapino) for the rate of para to ortho  $H_2$  catalysis were worked out, and uniform agreement obtained to within a constant factor of  $2\pi$ . The analytical methods developed in the course of this study were then extended to two new models, which more adequately describe the process of surface catalysis including transfer of hydrogen molecules onto and off of the surface.

All five equations for the para to ortho catalytic rate of conversion are described here. The two new equations describe the catalytic rate for these models:

H<sub>2</sub> on the surface is a two-dimensional gas with lifetime 'τ'

H<sub>2</sub> on the surface is a two-dimensional liquid undergoing Brownian motion, (diffusion) with surface lifetime 'τ'.

A numerical study of these rate equations will be the subject of the next report.

#### Contents:

- I. General Methodology
- II. Models
- III. Analytical Results for Each Model.
- IV. The Next Step: Numerical Studies.

## I. General Methodology

There are two papers in the literature which appear to have a reasonable physical formulation for the description of both the paramagnetic nature of para to ortho hydrogen catalysis and the characteristics of the solid state surface of the catalyst.

These are:

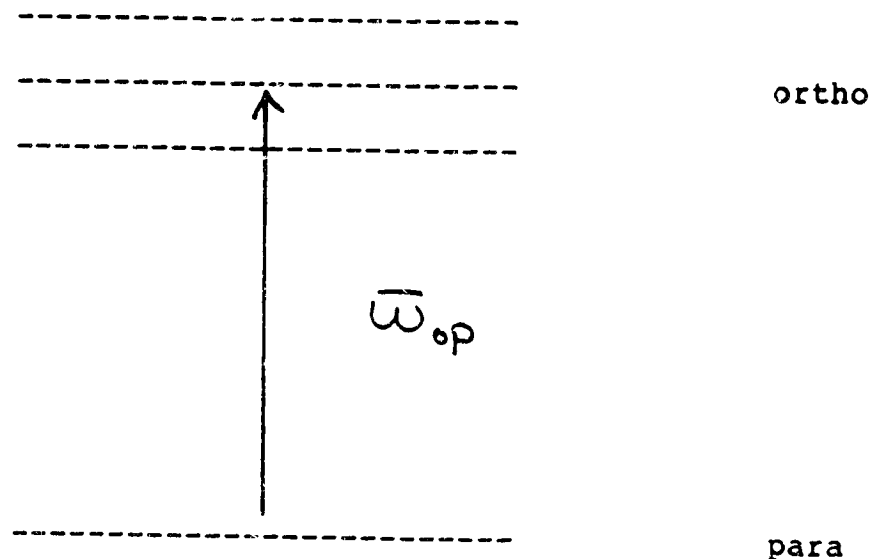
K. G. Petzinger and D. J. Scalapino, 'Para to Ortho Hydrogen Conversion on Magnetic Surfaces', Phys. Rev. 8, 266 (1973).

Y. Ishii, 'Theory of Non-Dissociative Ortho-Para Conversion on Magnetic Surfaces', Progress in Surface Science, 21, 163-203 (1986).

These papers present an overall view of the theory of this catalysis process, and some of their results. However, a great deal of the methodology is omitted (essentially no appendices), so the only way to acquire the technological ability to APPLY their results is to retrace their steps and learn the physical-mathematical methods which led to their conclusions. A good part of this process has now been accomplished, which has led to some new results which may be of use in the practical matter of designing good catalysts for para to ortho hydrogen conversion.

The general description adopted in this study concerns only the lowest para state and lowest ortho states(s). There is only one lowest para state, but the lowest ortho state has nine components (degeneracy = 9), since for this state  $I=1$  and  $L=1$ . ( $3 \times 3 = 9$ ).

The picture is



The average frequency of the transition (in radians/sec) is designated by the symbol  $\bar{\omega}_{op}$ . So the energy of the transition is

$$E(\text{ortho}) - E(\text{para}) = h\bar{\omega}_{op}$$

The practical results are found by integration and summation of terms in a master equation which describes any possible catalytic system of hydrogen molecules of either para or ortho type. Derivation and proof of the correctness of the many terms in this master equation has, up to now, been a major object of this study.

The first step is to derive, for any model, a relaxation function designated by  $\phi(t)$ , which is a function of time:

Each unique model  $\langle \text{----} \rangle$  a unique  $\phi(t)$

The rate of catalysis is then found by integrating the relaxation function over all time:

$$w_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 M_p^2 \frac{1}{h^2} \int_0^{\infty} \Phi(t) dt$$

The general form of  $\Phi(t)$  is as follows:

$$\Phi(t) = e^{-i\bar{\omega}_{opt} t} \sum_{\mu=-2}^{+2} G_{\mu}(\hat{b})$$

$$\textcircled{x} \sum_{\mathbf{q}} \left\langle e^{-i\bar{\mathbf{q}} \cdot [\bar{\mathbf{r}}(t) - \bar{\mathbf{r}}(0)]} \right\rangle_{\text{Ensemble, } H_2}$$

$$\textcircled{x} \sum_{i=x,y,z} \beta_{\mu}^{(i)}(\mathbf{q}) \beta_{\mu}^{(i)}(\mathbf{q}) \left\langle S_{-\mathbf{q}}^{(i)}(t) S_{\mathbf{q}}^{(i)}(0) \right\rangle_{\text{Ensemble, Spins}}$$

The Fourier Transform coefficients,  $\beta_{\mu}^{(i)}(\mathbf{q})$ , have been calculated and agreement obtained (except for some phases) with both earlier authors quoted above. These terms are critical for the purpose of developing a reliable theory.



For each model, then, one must evaluate:

The orientation and selection rule term:

$$G_{\mu}(\hat{b})$$

( $\hat{b}$  = orientation of the molecule).

(integrated over all orientations)

The correlation function for motion of the hydrogen molecules across the surface:

$$\left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{\text{Ensemble, H}_2}$$

The correlation function for the motion of the electronic spins on the surface:

$$\left\langle S_{-q}^{(i)}(t) S_q^{(i)}(0) \right\rangle_{\text{Ensemble, Elec. Spins.}}$$

The electronic spins are the actual catalyzing sites for the conversion of  $H_2$  nuclear spins from para (paired) to ortho (unpaired). In the calculations described here, this term only measures the magnitude of the electron spins and their concentration (paramagnetic case).

In addition, one must evaluate (once and for all) the Fourier Transforms of the dipolar form factors, which give the coupling between the dipolar interaction as a function of spatial coordinates and the extended wave motions of the lattice described as function of the wave vectors  $q$ . Only  $1/2$  of the first Brillouin zone is considered. ( $q = 0$  to  $2\pi/a$  where  $a$  is the lattice constant of the surface).

Once each of the terms above has been evaluated for each model, then the catalytic rate is obtained by an integration over time and a summation over the wave vector  $q$ . A standard method of solid state physics is then used to convert the sum over  $q$  to an integral. Thus, all expressions presented here as analytical equations are essentially integrals over the  $q$  wave vector, which must be determined numerically.

## II. The Models.

Each model described here is for catalysis on a paramagnetic surface, with a certain concentration ( $N_s/N$ ) of paramagnetic sites in the surface.

Model PS-1: The  $H_2$  exists on the surface as a two-dimensional gas with infinite lifetime. ( $H_2$  molecules never exit from the system). In time interval 0 to  $t$ , such a molecule moves a distance over the surface ' $r$ ', where  $r$  is found by knowing the RMS speed of a molecule derived from a 2-dimension Boltzmann distribution of molecular speeds.

Thus:

$$|r(t) - r(0)| = v_{rms} t$$

Model PS-2: The  $H_2$  exists on the surface as a two-dimensional liquid with the  $H_2$  molecules executing a Brownian motion random walk described by a diffusion coefficient ' $D$ '. Thus, by the usual relations for the mean squared displacement of a diffusing particle (in a two dimensional space) the displacement after time  $t$  is:

$$|r(t) - r(0)| = \text{SQRT}(4Dt)$$

Thus there is a different dimensionality in the integrand of the final equations to be integrated, between these different models.

Model PS-3: The  $H_2$  exists, above the catalytic surface, as a dilute gas and simply hops on and off of the surface. The catalysis only occurs on the surface, during the lifetime of a hydrogen molecule on the surface of  $\tau$  seconds.

These new models, worked out new with the methods used to derive the first three above, are more likely to describe the real-world para to ortho hydrogen catalysis situation for paramagnetic catalysis:

Model I: The  $H_2$  molecule exists as a two-dimensional gas on the surface, and hops on and off of the surface into an external extended gaseous phase with temperature  $T$ . The lifetime of an  $H_2$  on the surface is  $\tau$  seconds.

Model II. The  $H_2$  molecule exists on the surface as a two dimensional liquid, and hops on and off of the surface into an external gaseous phase with temperature  $T$ . The lifetime on the surface is again  $\tau$  seconds.

The process of model building then consists of converting the simple picture, given above, into a mathematical description.

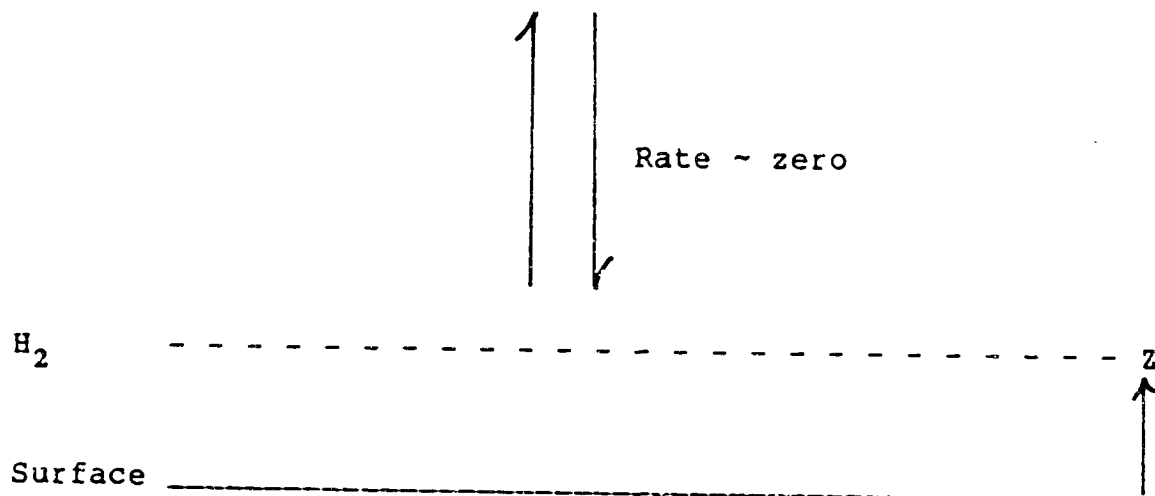
The final step in the process is to express the rates of para to ortho conversion in terms of dimensionless parameters which may then be used to characterize different catalyzing surfaces. The magnetic and structural differences in catalytic rates between different surfaces may then be expressed in terms of the experimental values of these dimensionless parameters.

III. Analytical Results for Each Model.

Model PS-1:  $H_2$  on surface is a Two-dimensional gas.

(Surface lifetime  $\tau = \text{infinite}$ )

( $H_2$  in gaseous phase)



$$W_{p \rightarrow 0} = K \cdot F(\alpha)$$

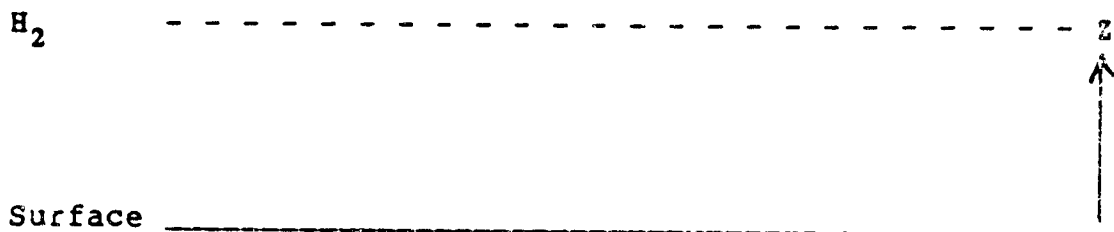
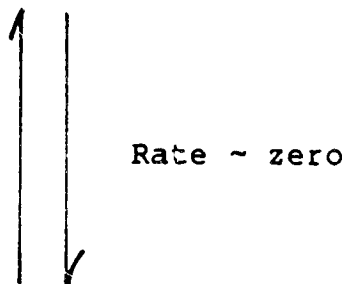
$$F(\alpha) = \frac{\sqrt{\pi} \alpha}{24} \int_0^{2q_c z} x^4 e^{-x} \exp\left\{-\frac{4\alpha^2}{x^2}\right\} dx$$

where

$$\alpha = \frac{\bar{w}_{op} z}{v_{rms}} \quad (\text{dimensionless}).$$

Model PS-2:  $H_2$  on the Surface Exists as a Two-dimensional Liquid.  
 (Surface lifetime  $\tau$  is infinite).

(  $H_2$  in gaseous phase )



$$W_{p \rightarrow 0} = K \cdot G(\gamma)$$

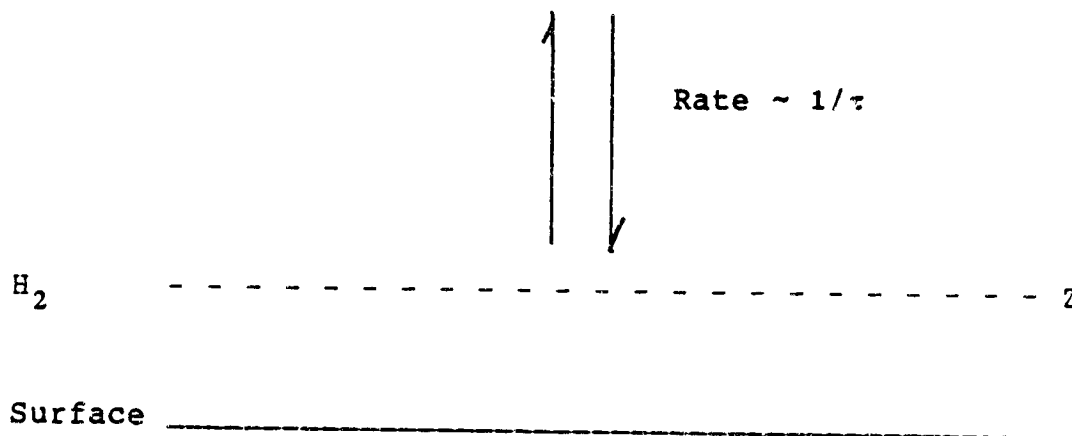
$$G(\gamma) = \frac{4\gamma^4}{3} \int_0^{\infty} \frac{q_c z / \gamma \cdot y^7 e^{-4y} dy}{y^4 + \gamma^2}$$

where

$$\gamma = \frac{\overline{w_{op}} z^2}{4D} \quad (\text{dimensionless})$$

Model PS-3: 'Jump' Model. (Surface Lifetime =  $\tau$  seconds)

(  $H_2$  in gaseous phase )



$$W_{p \rightarrow o} = K \cdot \frac{1}{48} \frac{\Theta}{1 + \Theta^2} \int_0^{2q_c z} x^5 e^{-x} dx$$

where  $\Theta = \bar{\omega}_{op} \tau$ .

where  $W_{p \rightarrow o}$  = rate of para to ortho conversion ( $\text{sec}^{-1}$ )

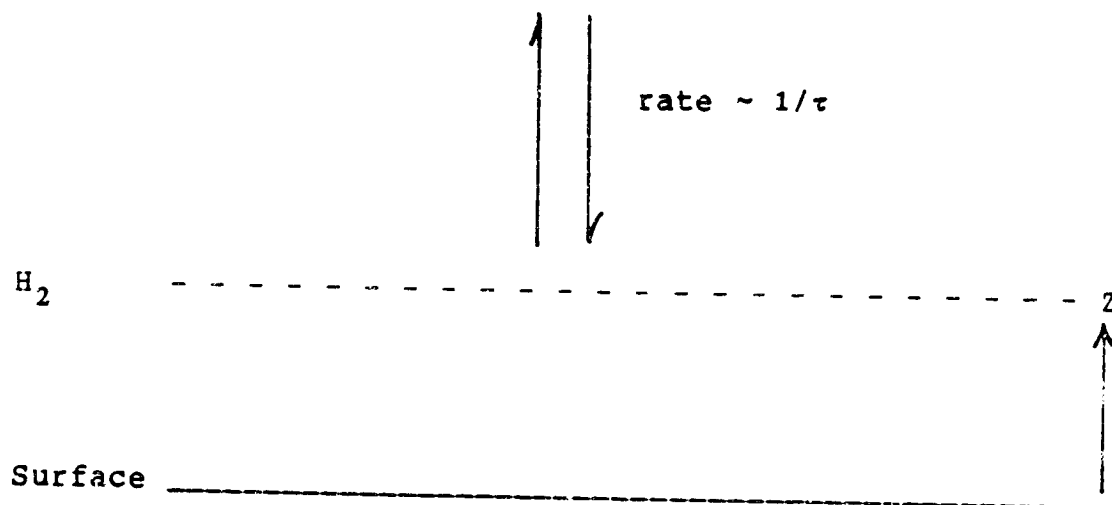
Parameter  $\Theta = \omega_{op} \tau$  is dimensionless.

Rate depends parametrically on  $\Theta$ .

There is also some dependence on the upper limit of the integral:  $2q_c z$ , but the main effect is expressed through the dimensionless parameter  $\Theta$ .

Practical Model I:  $H_2$  on the Surface exists as a two-dimensional gas with finite surface lifetime =  $\tau$  seconds.

(Gaseous Phase)



$$W_{p \rightarrow 0} = K \cdot \left\{ F(\alpha, \sigma) - I(\alpha, \sigma) \right\}$$

where

$$\alpha = \frac{\bar{w}_{op} z}{v_{rms}}$$

$$\sigma = \frac{\left(\frac{1}{\tau}\right) z}{v_{rms}}$$



Practical Model II (Continued)

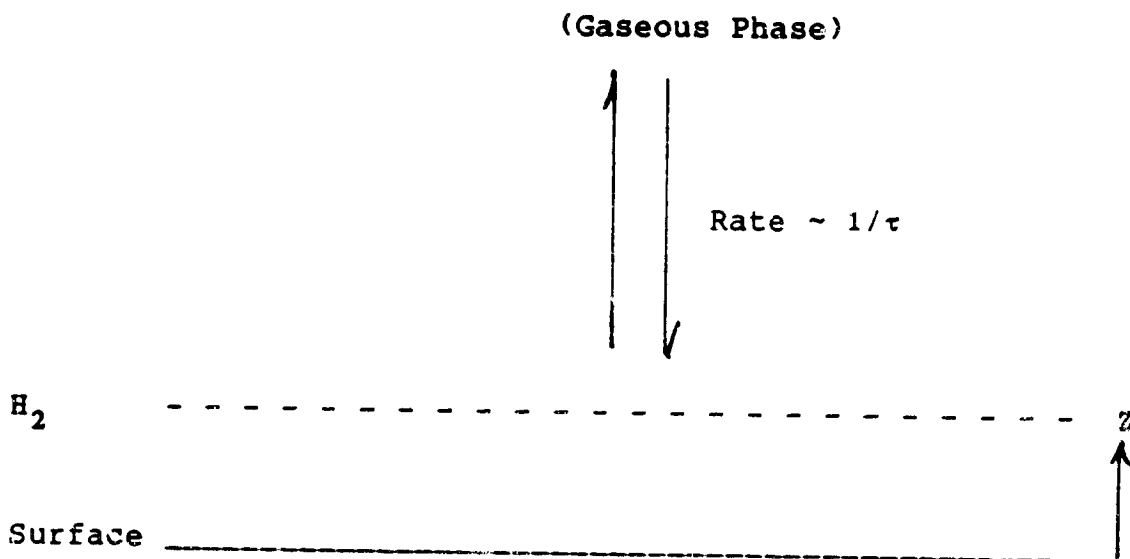
and the Integrals  $F(\alpha, \sigma)$  and  $I(\alpha, \sigma)$  are defined by:

$$F(\alpha, \sigma) = \frac{\sqrt{\pi} \alpha}{24} \int_0^{2q_c z} x^4 e^{-x} \exp\left\{\frac{-4(\alpha^2 - \sigma^2)}{x^2}\right\} dx$$

and

$$I(\alpha, \sigma) = \frac{2\sqrt{\pi}}{3} \cdot \alpha \sigma \cdot \int_0^{2q_c z} x^3 e^{-x} dx$$

Practical Model II :  $H_2$  exists on surface as a two-dimensional liquid,  
with surface lifetime =  $\tau$  seconds.



$$w_{p \rightarrow 0} = K \cdot \left\{ G_1(\gamma, \rho) + G_2(\gamma, \rho) \right\}$$

where  $\gamma = \frac{\bar{\omega}_{op} z^2}{4D}$  (dimensionless)

and  $\rho = \frac{|z|}{\sqrt{4D\tau}}$  (dimensionless)

Practical Model II. (Continued).

$$G_1(\gamma, \rho) = \frac{256\gamma}{3} \int_0^{q_c z/2} \frac{y^7 e^{-4y} dy}{(y^2 + \rho^2)^2 + \gamma^2}$$

and

$$G_2(\gamma, \rho) = \frac{256\gamma}{3} \cdot \rho^2 \cdot \int_0^{q_c z/2} \frac{y^5 e^{-4y} dy}{(y^2 + \rho^2)^2 + \gamma^2}$$

and

$$q_c z = \left( \frac{\pi}{a_0} \right) z$$

where

$a_0$  = lattice constant for the surface lattice.

$z$  = the height of the H<sub>2</sub> molecule above the surface in the adsorbed two-dimensional layer.

Definition of the universal catalytic constant K:

$$K = \frac{4\pi^2}{\hbar} \left( \frac{N_s}{N} \right) \frac{S(S+1)}{3} \left( \frac{b}{a_0} \right)^2 \frac{\mu_P^2 \mu_A^2}{z^6} \left( \frac{1}{2B} \right)$$

where

$$\hbar = h/2\pi$$

$N_s/N$  = the fraction of surface atoms which carry unpaired electronic spins.

$S$  = 'Spin' of the paramagnetic atom on the surface, e.g. 1/2, 1, 3/2, ....

$b$  = bond length of the  $H_2$  molecule.

$a_0$  = lattice constant of the surface layer.

$\mu_P, \mu_A$  = magnetic moments of the proton or the paramagnetic atom.

$z$  = the height of the  $H_2$  molecule above the surface plane containing the paramagnetic catalyzing atoms.

$2B$  = the rotational energy constant of the  $H_2$  molecule when present in the two-dimensional surface layer (may be different from the gaseous phase).

#### IV. The Next Step: Numerical Studies.

The next step is to generate curves, by numerical integration, of the catalytic rate versus values of the dimensionless parameters characteristic of each model. The comparisons will be:

1. Jump model versus  $\theta$ .
2. Model I versus dimensionless parameters  $\alpha$  and  $\sigma$ .
3. Model II versus dimensionless parameters  $\gamma$  and  $\rho$ .

The general expectation is that the families of curves so generated will, in each case, show a peak in catalytic rate for some values of the parameters. Thus, in some cases an increase in a parameter value may lead to an increase in catalytic rate, and in other cases an increase in a parameter value may decrease the catalytic rate. So it will be very to determine which side of the peak is a given catalyst.

The numerical comparison of the models above may yield some more quantitative information as to optimal types of physical systems.

#### The NEXT STEP:

The Ferromagnetic and Antiferromagnetic problems will be the next step. These equations will probably be similar to the ones above, except for resonance terms representing resonant exchange of energy with the many body magnetic excitations, or magnons. This may cause greater catalytic rates than for the paramagnetic case, in certain cases.

# Theory of Ortho to Para Hydrogen Catalysis

## II. Analysis of Three Models Due to Petzinger and Scalapino.

August 10, 1989

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### ABSTRACT

Three simple models for para to ortho hydrogen catalysis on paramagnetic surfaces, originally due to Petzinger and Scalapino, have been numerically simulated. These models are: A two-dimensional liquid on the surface, a two-dimensional gas on the surface (each with infinite surface lifetime), and a dilute gas which hops on and off of the surface with lifetime ' $\tau$ '. The integrals determining the functional dependence on certain macroscopic dimensionless parameters have been evaluated with the IMSL numerical routine QDAGS (Gauss-Konrad rule), and then plotted versus the dimensionless parameter characteristic of the rate of catalysis for each model. The results are presented in a series of graphs for several ranges of the dimensionless parameter for each model, and for different values of the height of the  $H_2$  molecule above the surface. One cannot generally say that one model necessarily leads to higher catalytic rates than another, but the two dimensional gas model clearly peaks at smaller parameter values than the other models and attenuates faster versus its dimensionless parameter. Thus, the two-dimensional gas model leads to larger para to ortho catalytic rates over a smaller parameter range than the other two models considered.

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- I. Analytic Methods
- II. The Models.
- III. Intermediate Equations for the Rate of Para to Ortho Hydrogen Conversion.
- IV. Final Results: Condensed Equations for rate of Catalysis.
- V. Interpretation and Conclusions.
- VI. References.
- VII. Plots.

## I. Analytic Methods.

The rate of para to ortho catalysis of hydrogen molecules in contact with a paramagnetic surface is given as the integral of a relaxation function:

$$w_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \frac{1}{\hbar^2} \int_0^{\infty} \Phi(t) dt$$

The general form of the relaxation function  $\Phi(t)$  is as follows:

$$\Phi(t) = e^{-i \bar{\omega}_o t} \sum_{\mu=-2}^{+2} G_{\mu}(\hat{b})$$

$$\textcircled{x} \quad \sum_{\vec{q}} \left\langle e^{-i \vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2}$$

$$\textcircled{x} \quad \sum_{i=x,y,z} \beta_{\mu}^{(i)*}(q) \beta_{\mu}^{(i)}(q) \left\langle S_{-q}^{(i)}(t) S_q^{(i)}(0) \right\rangle_{E, \text{Spins}}$$

Evaluation of these functions requires evaluation of the orientations terms, the correlation functions and the Fourier Transform coefficients here indicated as  $\beta_{\mu}(q)$ . All of these steps have been independently performed and checked for accuracy.



## II. Models and Assumptions.

It has been established that these assumptions are correct (within a certain degree of approximation) for the problem at hand:

(A) The orientation terms are averaged over all orientations of the  $H_2$  molecules on the surface. The result is:

$$\langle G_\mu(b) \rangle = 4\pi/3$$

(B) The correlation functions for the motion of the  $H_2$  molecule on and off of the surface were evaluated for three models. The results for each model are as follows:

$$\left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2} =$$

$= e^{-\frac{kT}{2m} q^2 t^2}$	2 Dim-gas on surface. $\tau = \text{infinite}$
$= e^{-Dq^2 t}$	2 Dim-liquid on surface. $\tau = \text{infinite}$
$= e^{-t/\tau}$	Dilute gas on surface, Jump Model. $\tau = \text{finite.}$

(C) The correlation function for the motion of the electronic spins on the surface is evaluated for the case of non-interacting spins, with surface concentration  $N_s/N$ . The result is:

$$\left\langle S_{-q}^{(i)}(t) S_q^{(i)}(0) \right\rangle = \frac{N_s}{N^2} \cdot \frac{S(S+1)}{3}$$

(D) The sum over all of the Fourier Transformed 'beta' coefficients is used. This sum is:

$$\sum_{\mu=-2}^{+2} \sum_{i=x,y,z} \beta_{\mu}^{(i)*}(q) \beta_{\mu}^{(i)}(q) =$$

$$2 \left( \frac{4\pi \mu A}{a_0^2} \right)^2 q^4 e^{-2qz}$$

which follows from the detailed evaluation of the Fourier Transforms of the dipolar form factors expanded in the lattice wave vectors  $\vec{q}$ .

### III. Intermediate Equations for the Rate of Para to Ortho Conversion.

A set of equations, which involve double integrations (after transforming the sum over  $\vec{q}$  into an integral over  $\vec{q}$ ), are found for each of the three models considered here. The intermediate equations which must be evaluated in order to find the total rates of para to ortho conversion are as follows:

#### 2 Dim-gas:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \frac{1}{h^2} \frac{4}{3} \left(\frac{N_s}{N}\right) \frac{S(S+1)}{3} \cdot \frac{(6\pi^2 \mu_A)^2}{a_0^2}$$

$$\textcircled{x} \int_0^{q_c} q^s e^{-2q^2} dq \int_0^\infty \cos \bar{\omega}_{op} t e^{-\frac{kT}{2m} q^2 t} dt$$

#### 2 Dim-Liquid:

$W_{p \rightarrow o} = \dots$  the same except for  $\dots$ :

$$\int_0^\infty \cos \bar{\omega}_{op} t e^{-Dq^2 t} dt$$

#### Jump model:

$W_{p \rightarrow o} = \dots$  the same except for  $\dots$ :

$$\int_0^\infty \cos \bar{\omega}_{op} t e^{-t/\tau} dt$$

IV. Final Results: Condensed equations for the rate of para to ortho catalysis.

MODEL PS-1:  $H_2 = 2$  Dimensional gas on the surface,  
residence time  $\tau = \text{infinite}$ .

$$W_{p \rightarrow o} = KF(a)$$

where

$$F(a) = \frac{\sqrt{\pi} \alpha}{24} \int_0^{2q_c z} x^4 e^{-x} \exp\left\{-\frac{4\alpha^2}{x^2}\right\} dx$$

and

$$a = \frac{\bar{\omega}_{op} z}{v_{rms}} \quad (\text{dimensionless})$$

MODEL PS-2:  $H_2 = 2$  Dimensional liquid on the surface,  
residence time  $\tau = \text{infinite}$ .

$$W_{p \rightarrow o} = KG(\gamma)$$

where

$$G(\gamma) = \frac{4^4 \gamma}{3} \int_0^{q_c z/2} \frac{y^7 e^{-4y}}{y^4 + \gamma^2} dy$$

and

$$\gamma = \frac{\bar{\omega}_{op} z^2}{4D} \quad (\text{dimensionless})$$

MODEL PS-3:  $H_2$  = dilute gas: Jump model.

Molecules jump on and off the surface,

with residence time on the surface =  $\tau$  seconds.

$$W_{p \rightarrow 0} = KH(\theta)$$

where

$$H(\theta) = \frac{1}{48} \left( \frac{\theta}{1+\theta^2} \right) \int_0^{2\theta c z} x^5 e^{-x} dx$$

and

$$\theta = \bar{\omega}_{op} \tau \quad (\text{dimensionless})$$

The common coefficient 'K' is, for each case:

$$K = \frac{4\pi^2}{h} \left( \frac{N_s}{N} \right) \frac{S(S+1)}{3} \left( \frac{b}{a_0} \right)^2 \frac{\mu_p^2 \mu_A^2}{z^6} \left( \frac{1}{2B} \right)$$

which has a strong dependence on Z, i.e.  $K \sim 1/z^6$ .

Also:

$N_s/N$  = fraction of surface sites (N) occupied by paramagnetic atoms ( $N_s$ ).

S = the spin of a surface paramagnetic atom.

The integral limit is approximated:

$$q_c Z = \pi(Z/a_0)$$

which follows from:

$q_c = \pi/a_0$  = cut-off value of the wave-vector; limit of first Brillouin zone (i.e. the shortest possible wavelength equals the lattice constant).

and the assumption that the distance of the  $H_2$  from the surface is approximately equal to the surface lattice constant,  $a_0$ . Thus:

Model PS-1: Integral limit =  $2q_c Z = 2\pi(Z/a_0)$

Model PS-2: " " =  $q_c Z/2 = 0.5\pi(Z/a_0)$

Model PS-3: " " =  $2q_c Z = 2\pi(Z/a_0)$

These limits exert considerable influence on the values of the integrals which control the rate of catalysis for each respective model.

## V. Interpretation and Conclusions.

The integrals  $F(\alpha)$ ,  $G(\gamma)$  and  $H(\theta)$  were numerically evaluated using the IMSL program QDAGS, which is appropriate for an integral with finite limits. (The interval  $[A,B]$  is subdivided into subintervals; each subinterval is estimated with a 21-point Gauss-Konrad quadrature rule). The accuracy was set to about six figures (single precision; no difference was noted on switching to double precision).

The FORTRAN code for each integral was written into a single program which then put the data for the three functions versus the dimensionless parameter (for each) into a single file for plotting. The accompanying figures show, on the same plot, a numerical comparison of:

$F(\alpha)$  versus  $\alpha$ .

$G(\gamma)$  versus  $\gamma$ .

$H(\theta)$  versus  $\theta$ .

The first six figures:

G-1 through G-6

are plots versus  $\alpha$  (or  $\gamma$  or  $\theta$ ) over the range 0 to 3, for different heights 'Z' of the  $H_2$  molecule above the paramagnetic surface, measured in units of the surface lattice constant  $a_0$ . The range of values is:

$$Z/a_0 = 0.2, 0.5, 1.0, 2.0, 5.0, 10.0$$

(Figure G-3 is the same as Figure 2 in Petzinger and Scalapino's paper, with, evidently, good numerical agreement!)

The following three figures:

H-1 through H-3

are plots versus the independent parameter  $\alpha$  (etc.) over the range 0 to 10, and for heights 'Z' having values:

$$Z/a_0 = 0.5, 1.0, 2.0$$

The last three figures:

I-1 through I-3

are plotted over the range of the independent parameters  $\alpha$  (etc.) over the range 0 to 30, and for the same range of  $Z/a_0$  as for the previous three figures. The purpose of this last set of plots is to emphasize the peaked nature of the catalytic rate for the two-dimensional gas model.

Since all results are derived from the same master equation (accurate to all factors of 2,  $\pi$ , 'e', and the like) it seems reasonable to draw some limited conclusions already from the comparison of these three models for the different parameter ranges and heights of the  $H_2$  layer above the catalytic surface.

#### Some Conclusions:

The two-dimensional gas model peaks over a smaller range of its independent parameter than the other two models. This property is traceable to the presence of an  $\exp(-\alpha^2 \dots)$  terms in the integrand for this model, which does not occur in such a manner (not as an exponential!) attenuating the rate controlling integral for the other two models. (See figures I-1 through I-3).



Another conclusion is that a practical model for para  $\rightarrow$  ortho hydrogen catalysis must incorporate the rate of transfer of the  $H_2$  molecules into the over-all description of the catalytic rate. Such a description of the rate of catalysis would then be expected peak when plotted versus the parameter  $\alpha$  or  $\gamma$ , as well as a peak when plotted versus another dimensionless parameter containing the inverse of the surface lifetime,  $1/\tau$ .

The formal difference between the two dimensionless parameters used for calculating the para to ortho hydrogen conversion rates for the first two models:

$$\alpha = \frac{\bar{w}_{op} z}{v_{rms}}$$

and

$$\gamma = \frac{\bar{w}_{op} z^2}{4D}$$

also accounts for some of the differences between the shapes of the rate curves for the two-dimensional gas case compared to the case of a two dimensional liquid, each with infinite residence time. (This is in addition to the functional differences between the integrands.)

## VI. References

1. R. E. Coffman, Theory of Ortho to Para (Hydrogen) Catalysis. I. Practical Equations for the Description of Paramagnetic Catalysis. July 21, 1989.
2. Petzinger and Scalapino, Physical Review B, 8, 266 (1973).
3. QDAG/DQDAGS: Chapter 4, Integration and Differentiation, p 561. IMSL Math Library, Version 1.0, April 1987. IMSL, 2500 CityWest Boulevard, Houston, Texas. 77042-3020.

VII. Plots.

Each plot presents:

$F(\alpha)$  versus  $\alpha$ .

$G(\gamma)$  versus  $\gamma$ .

$H(\theta)$  versus  $\theta$ .

Plots G-1 thru G-6: the range of the independent parameter is 0 to 3.

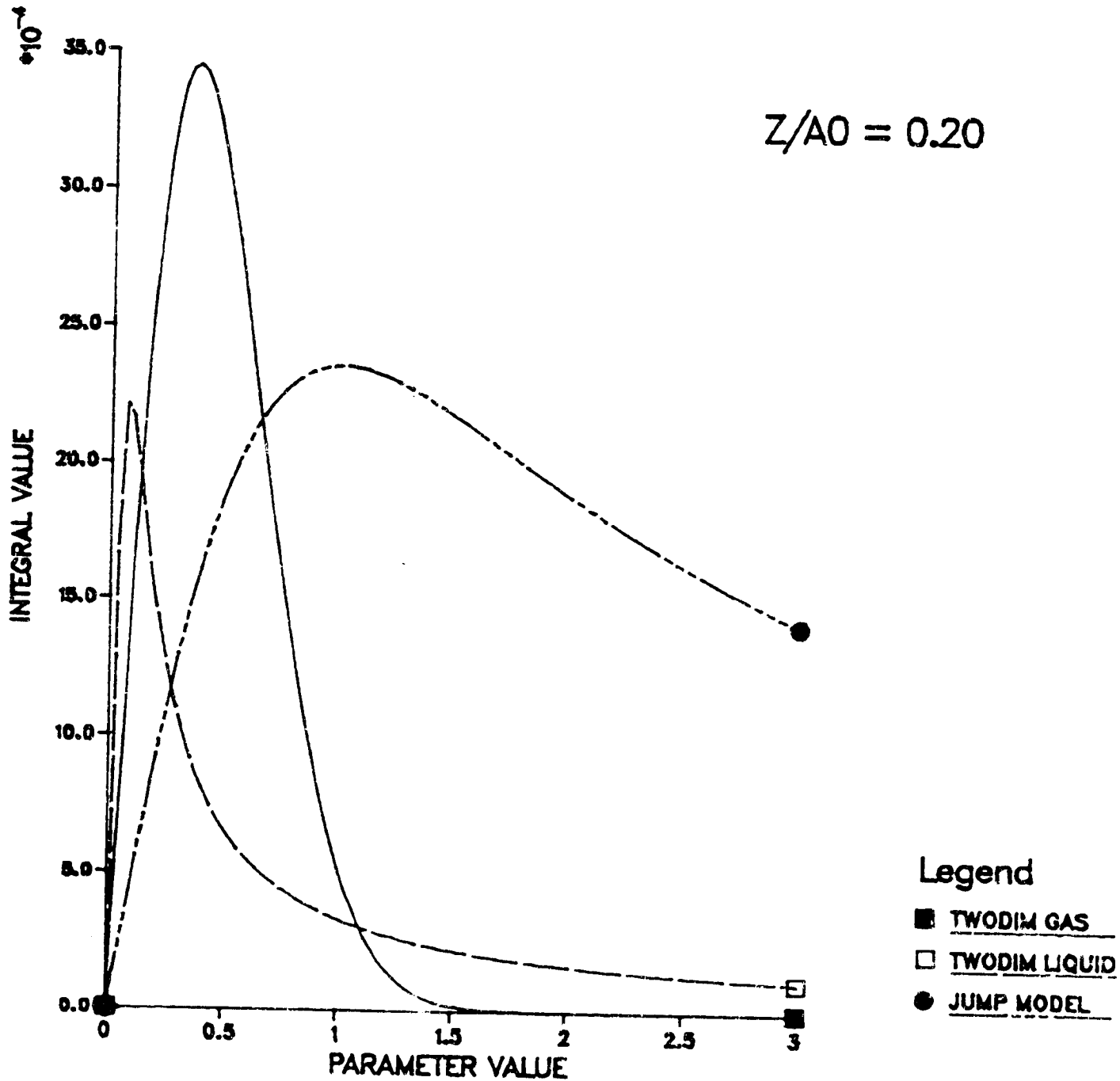
Plots H-1 thru H-3: the range .....is 0 to 10.

Plots I-1 thru I-3: the range .....is 0 to 30.

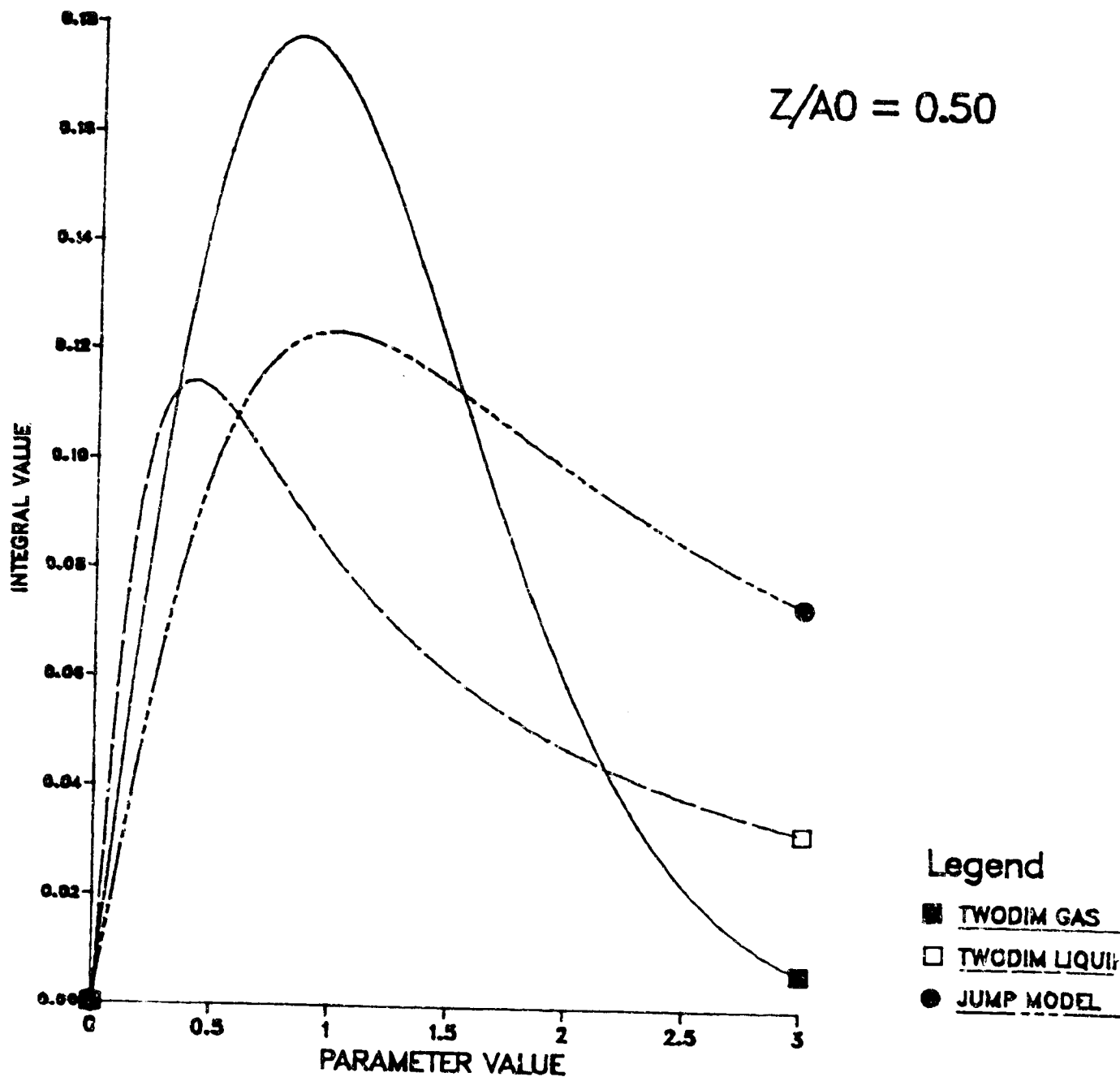
The distance of the Hydrogen molecule above the paramagnetic surface is varied in each series, given as the ratio of  $Z$  to the surface lattice parameter ' $a_0$ '.

Each plot has an 100 subdivisions along the x- or parameter- axis.

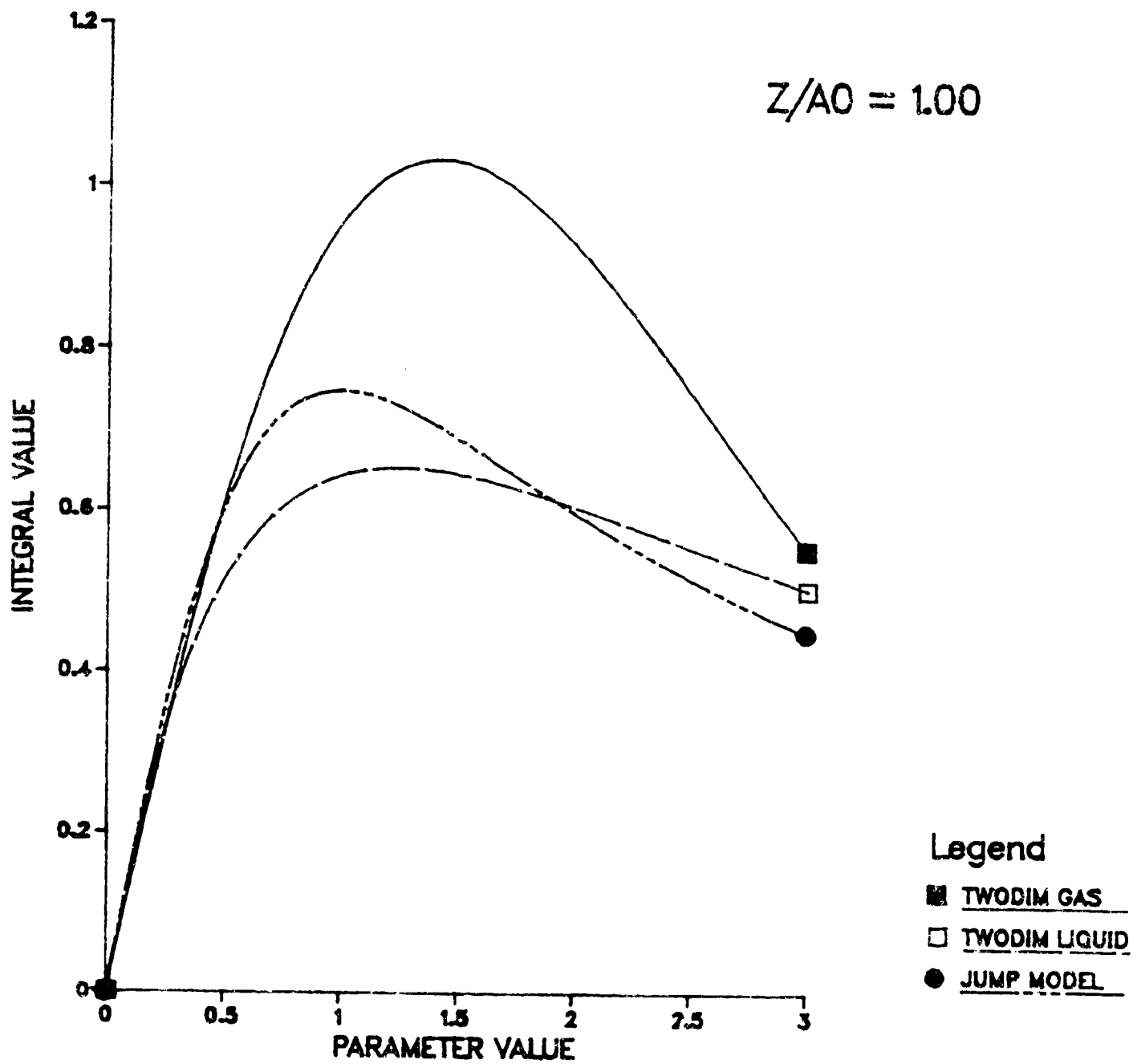
# THREE MODELS FOR PARA $\rightarrow$ ORTHO H<sub>2</sub> CATALYSIS



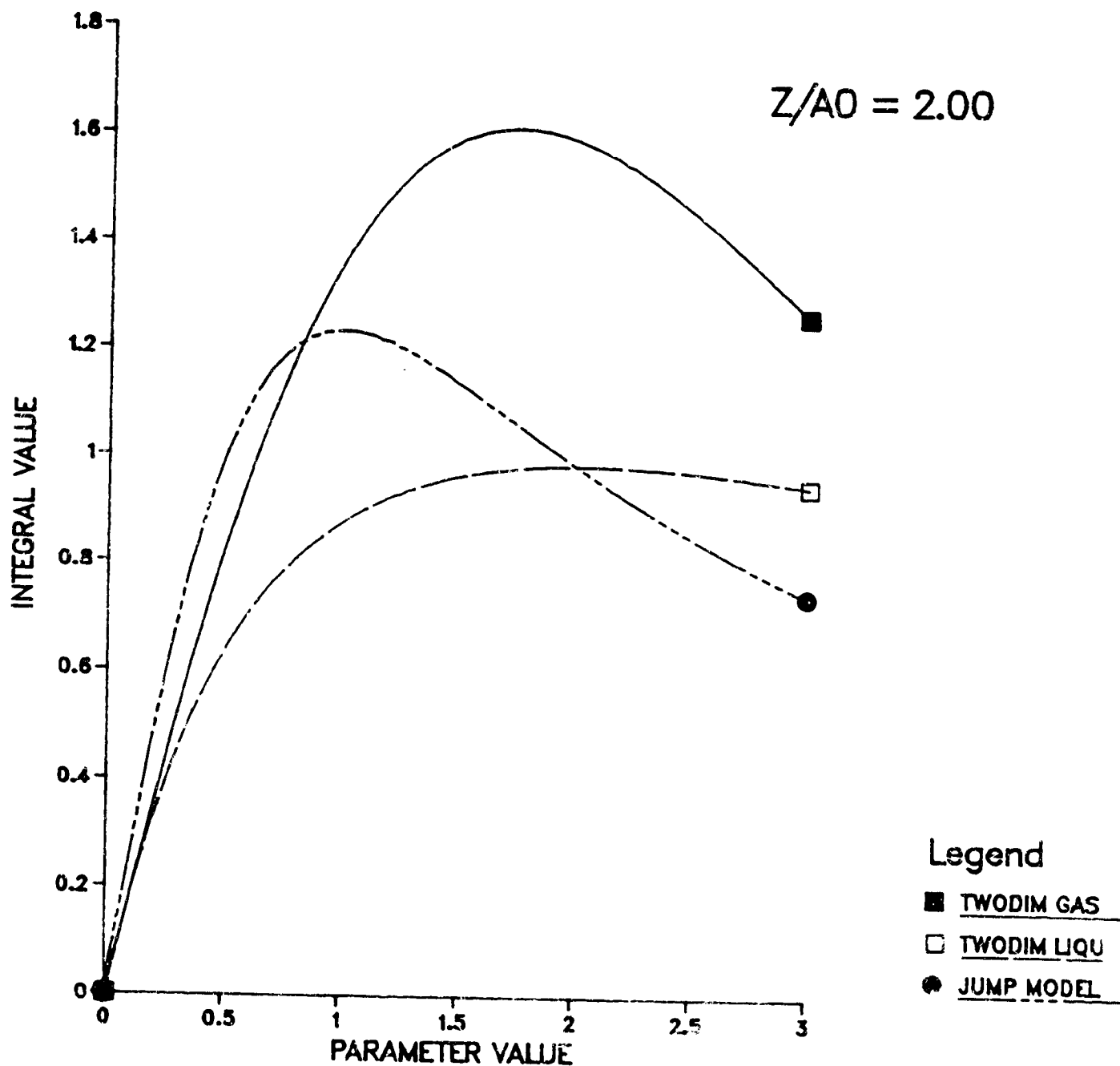
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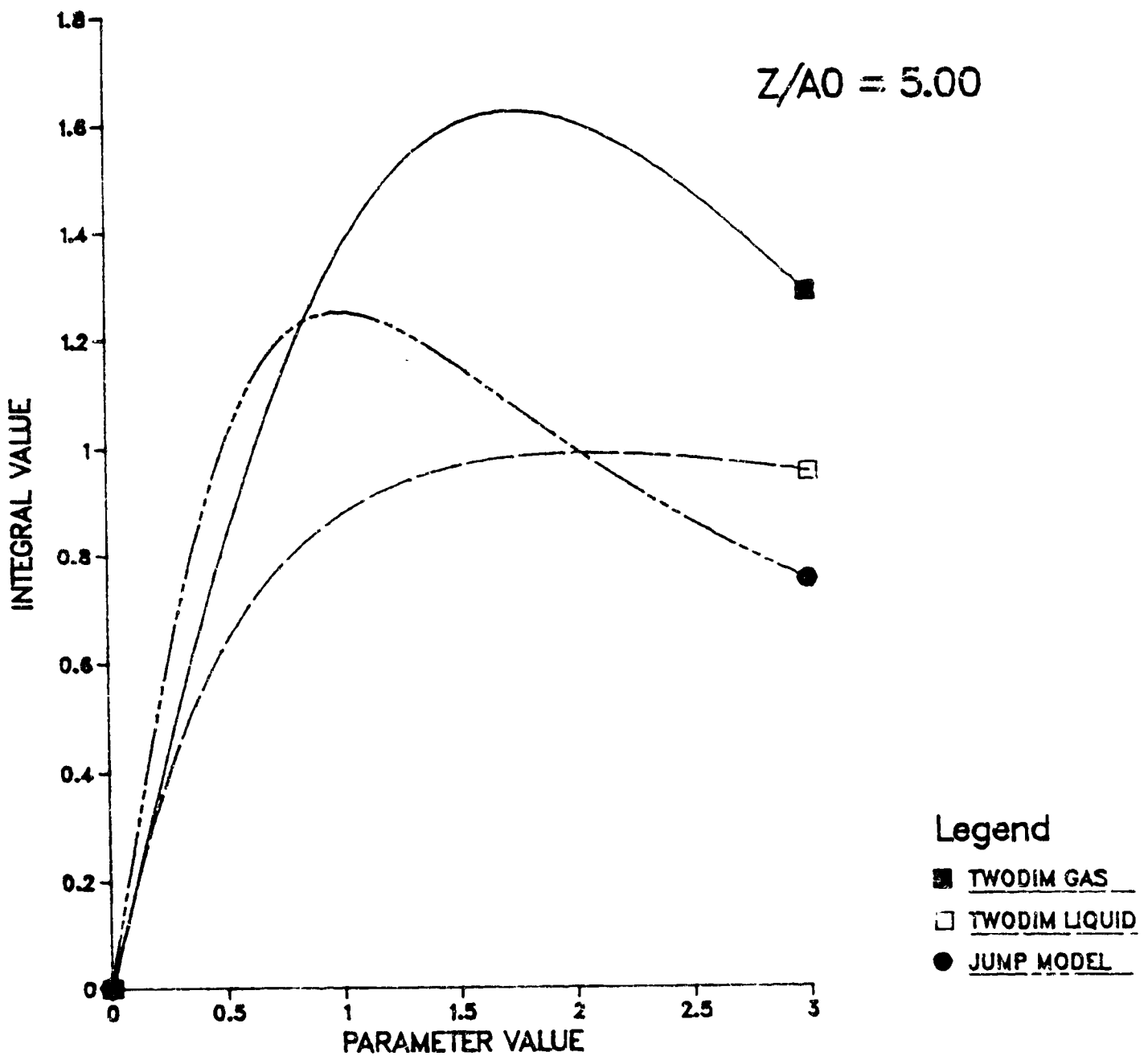
# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS

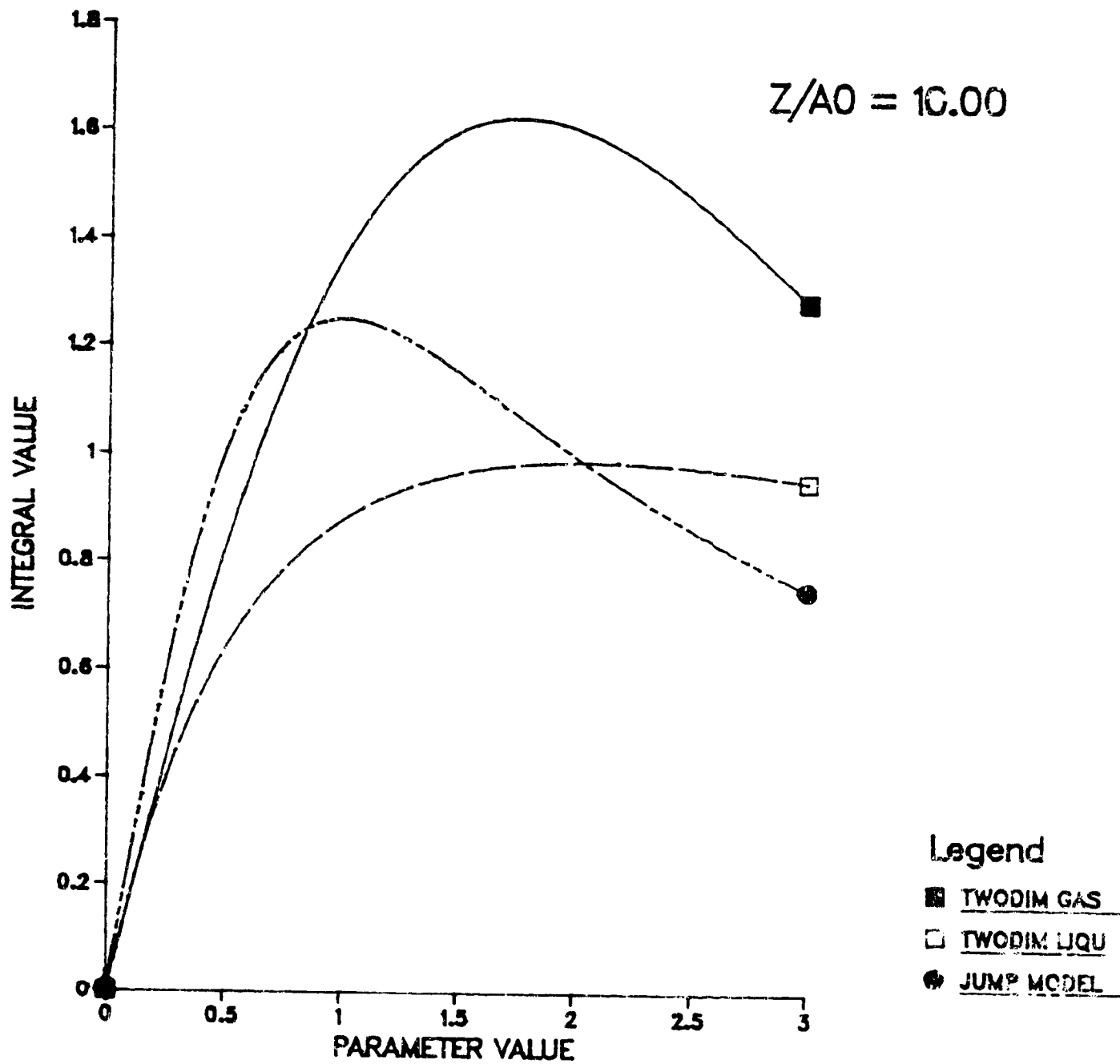


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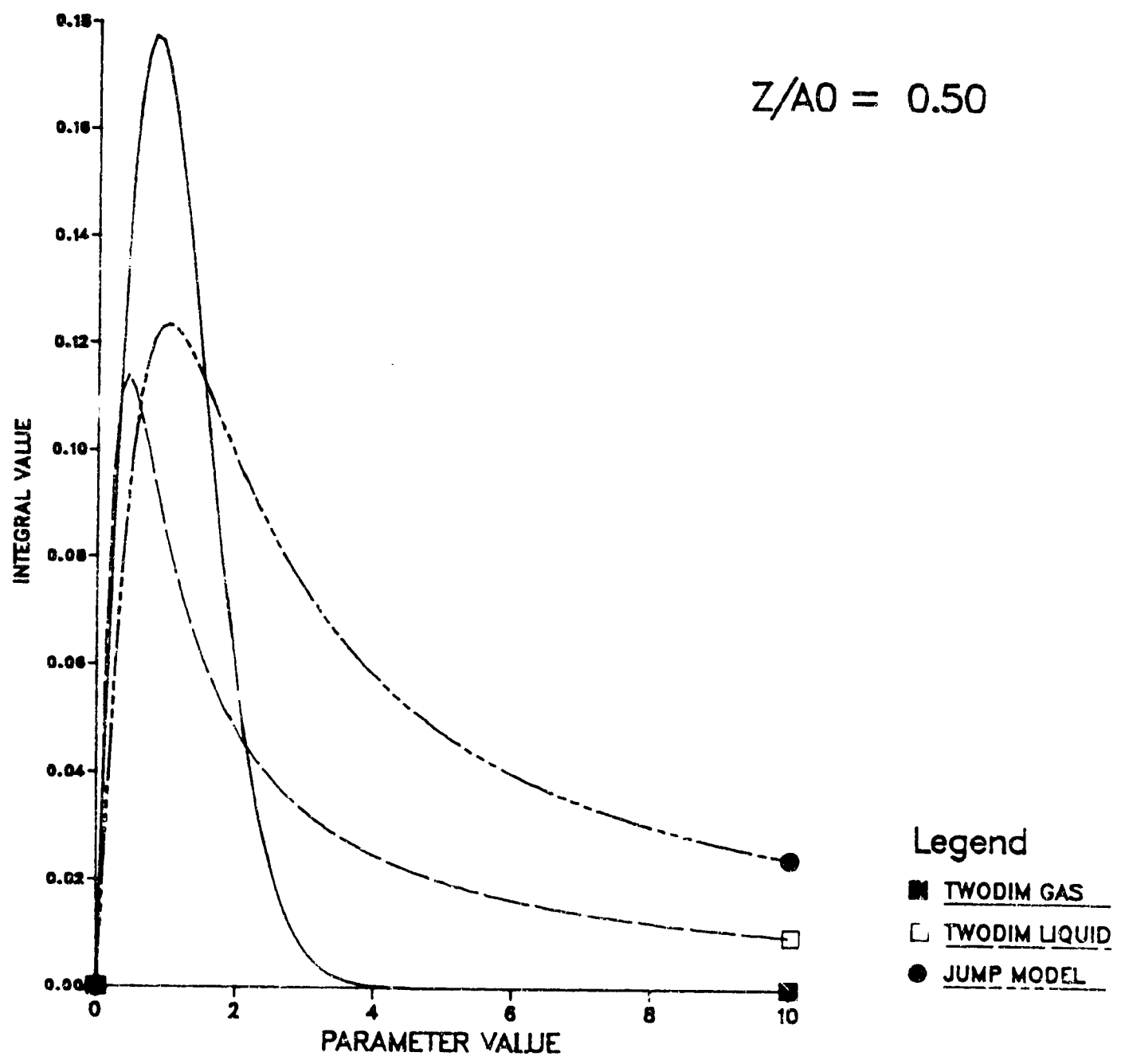




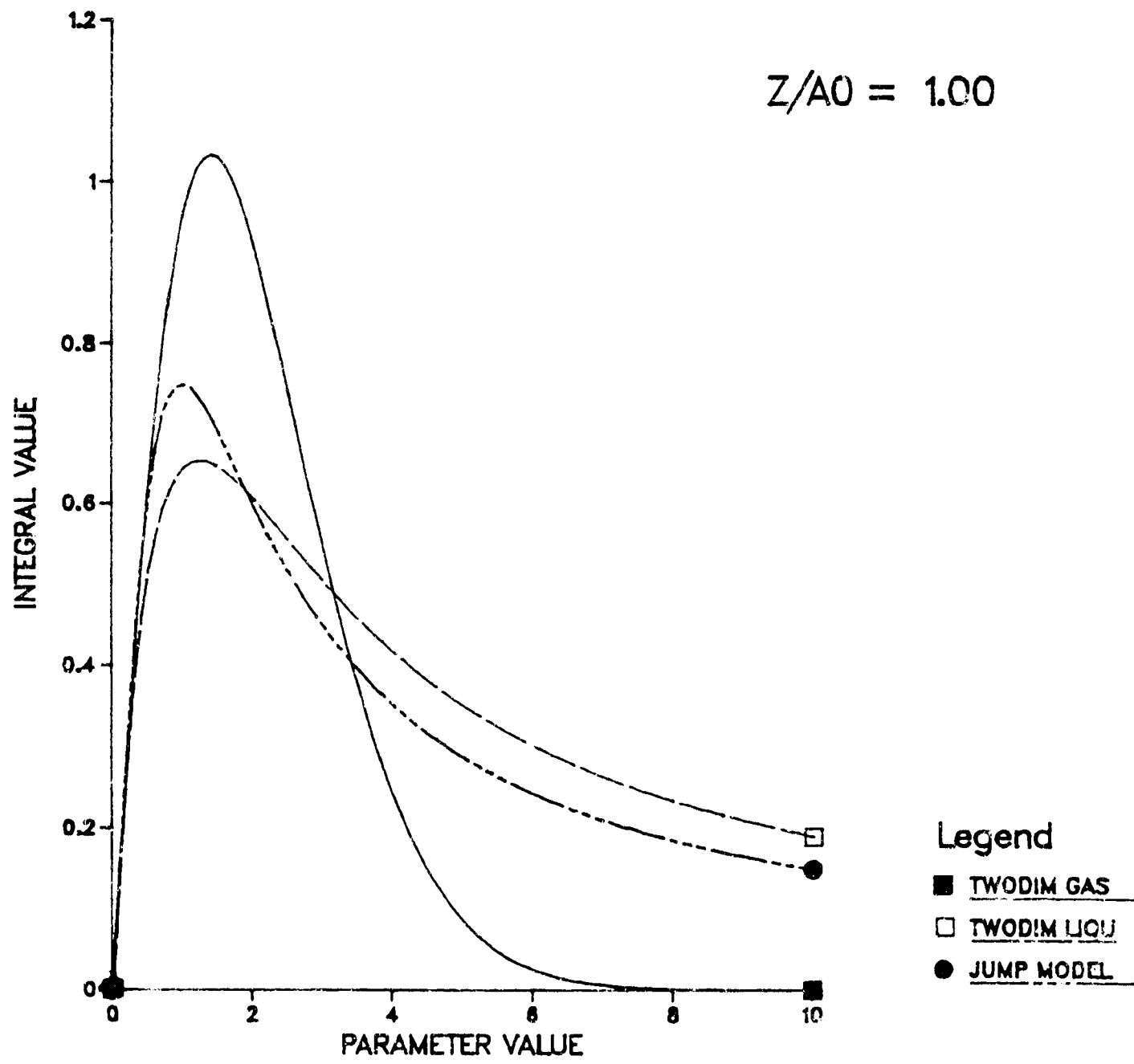
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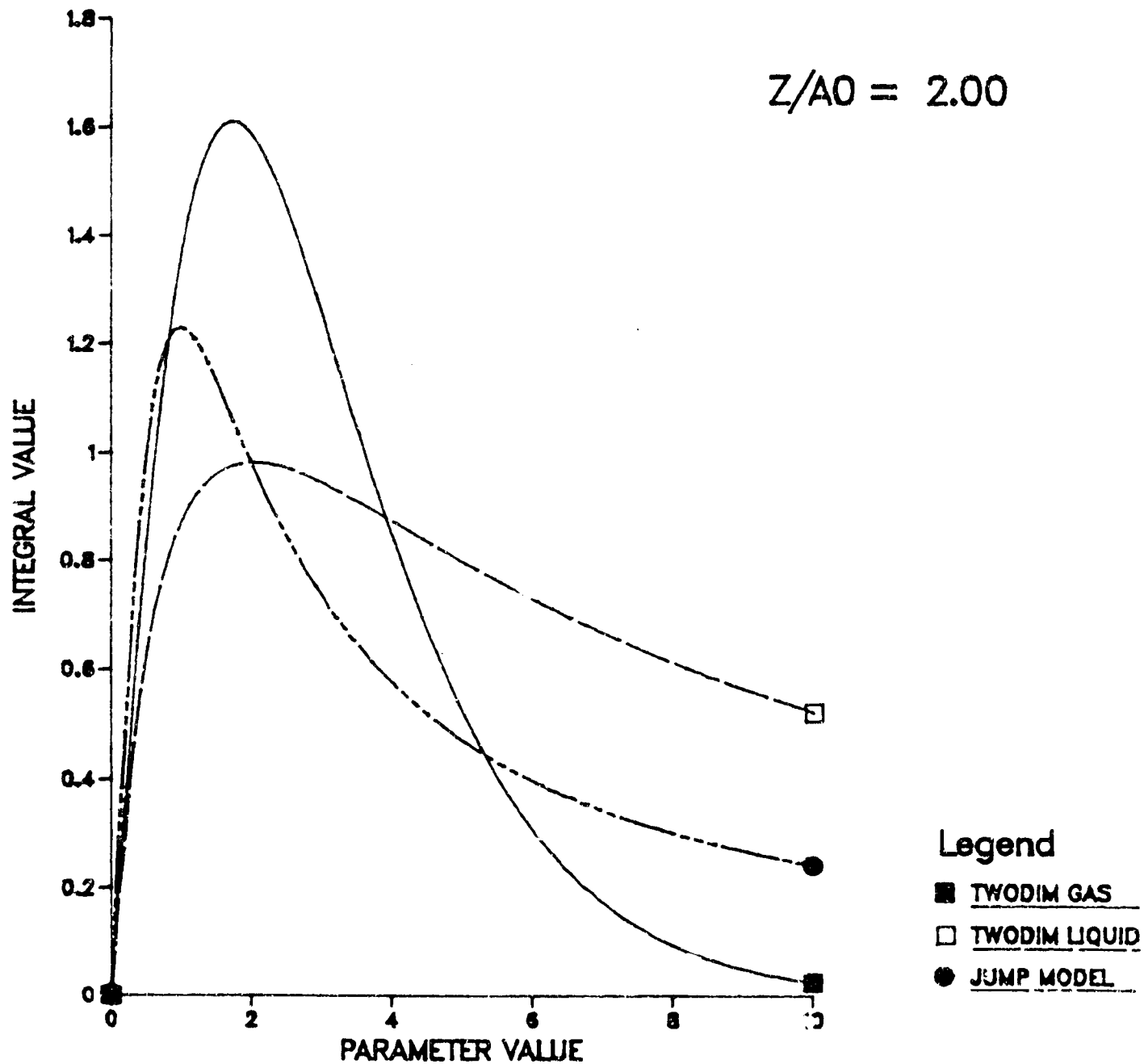
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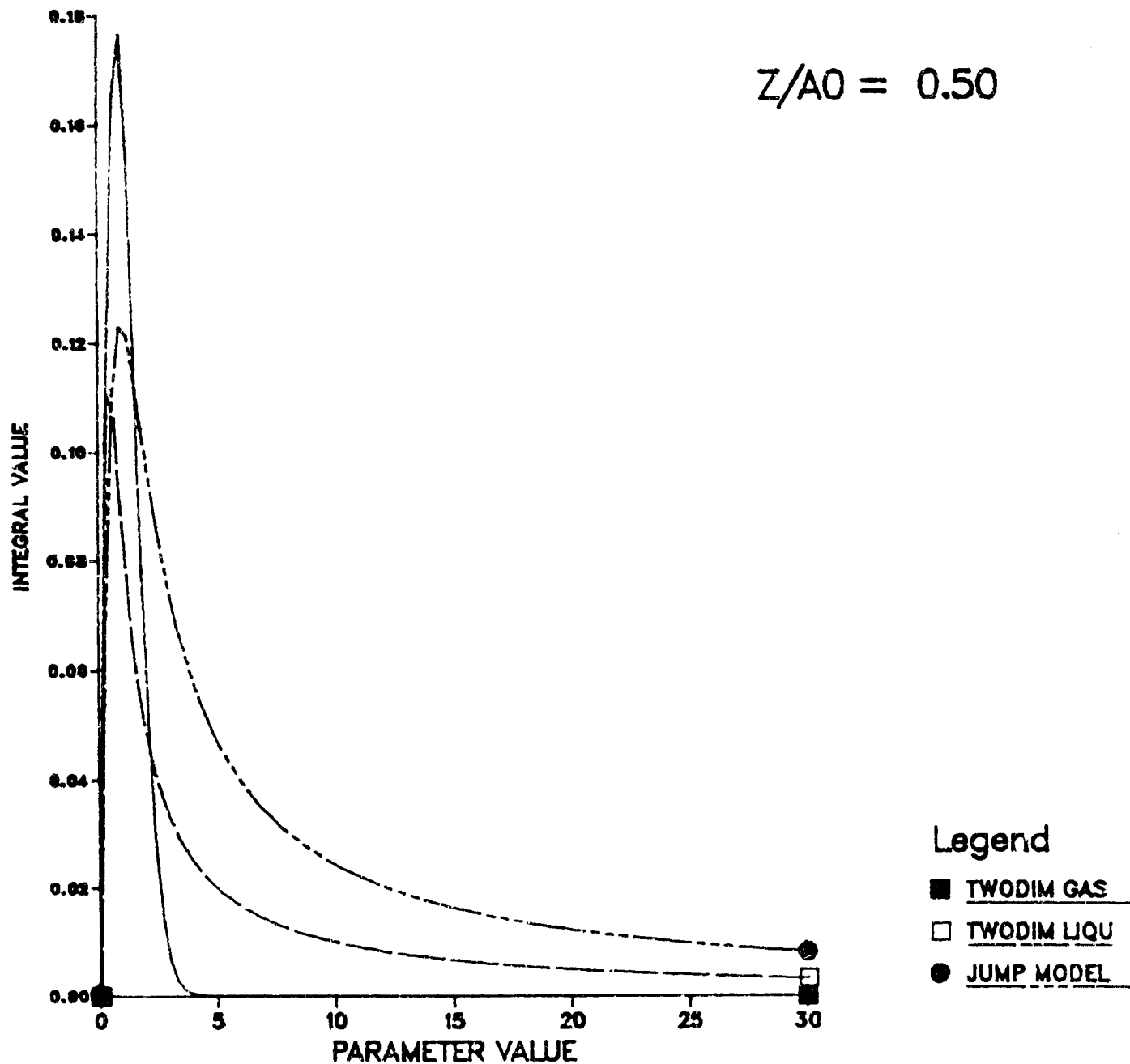
# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



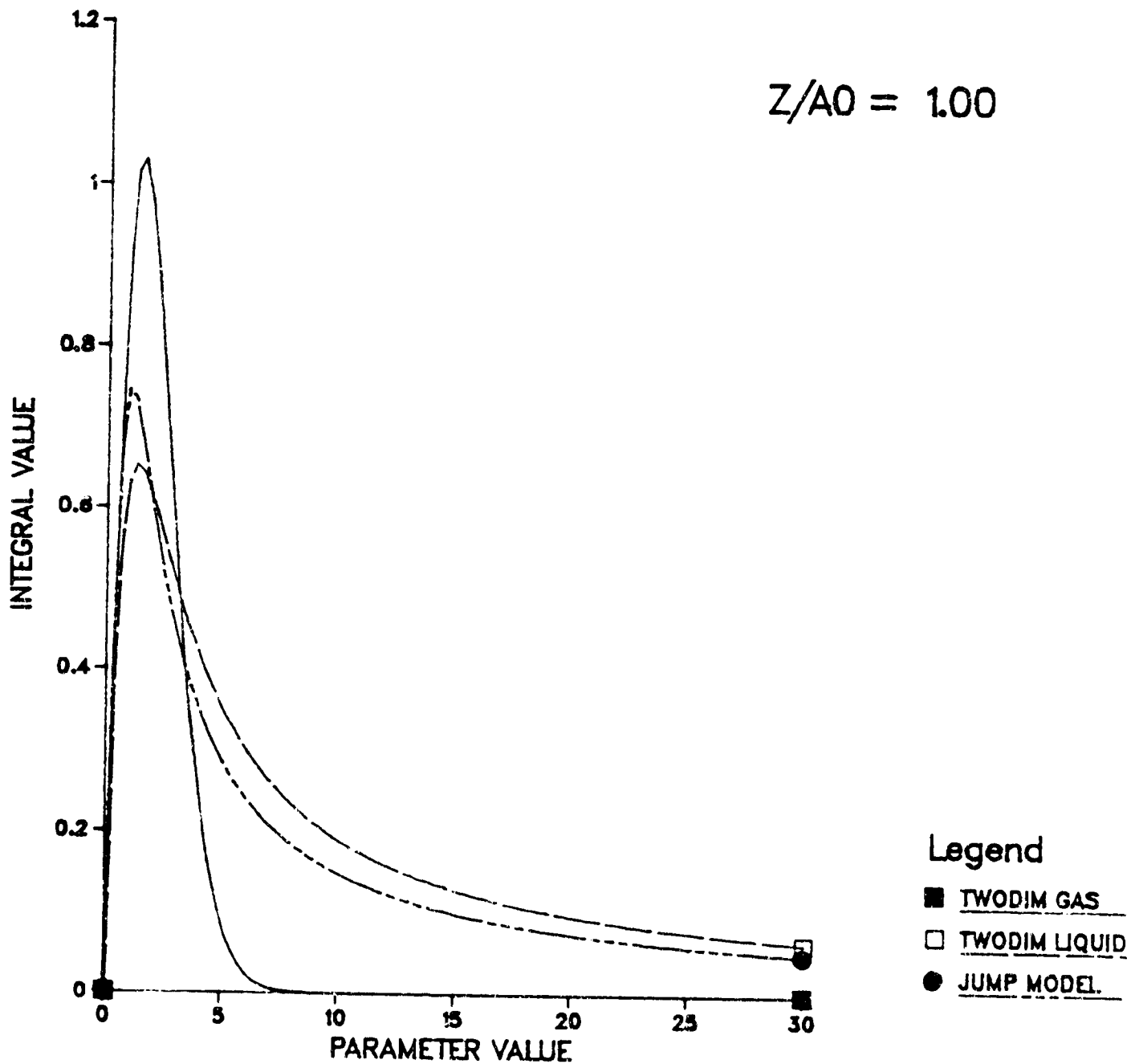
# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



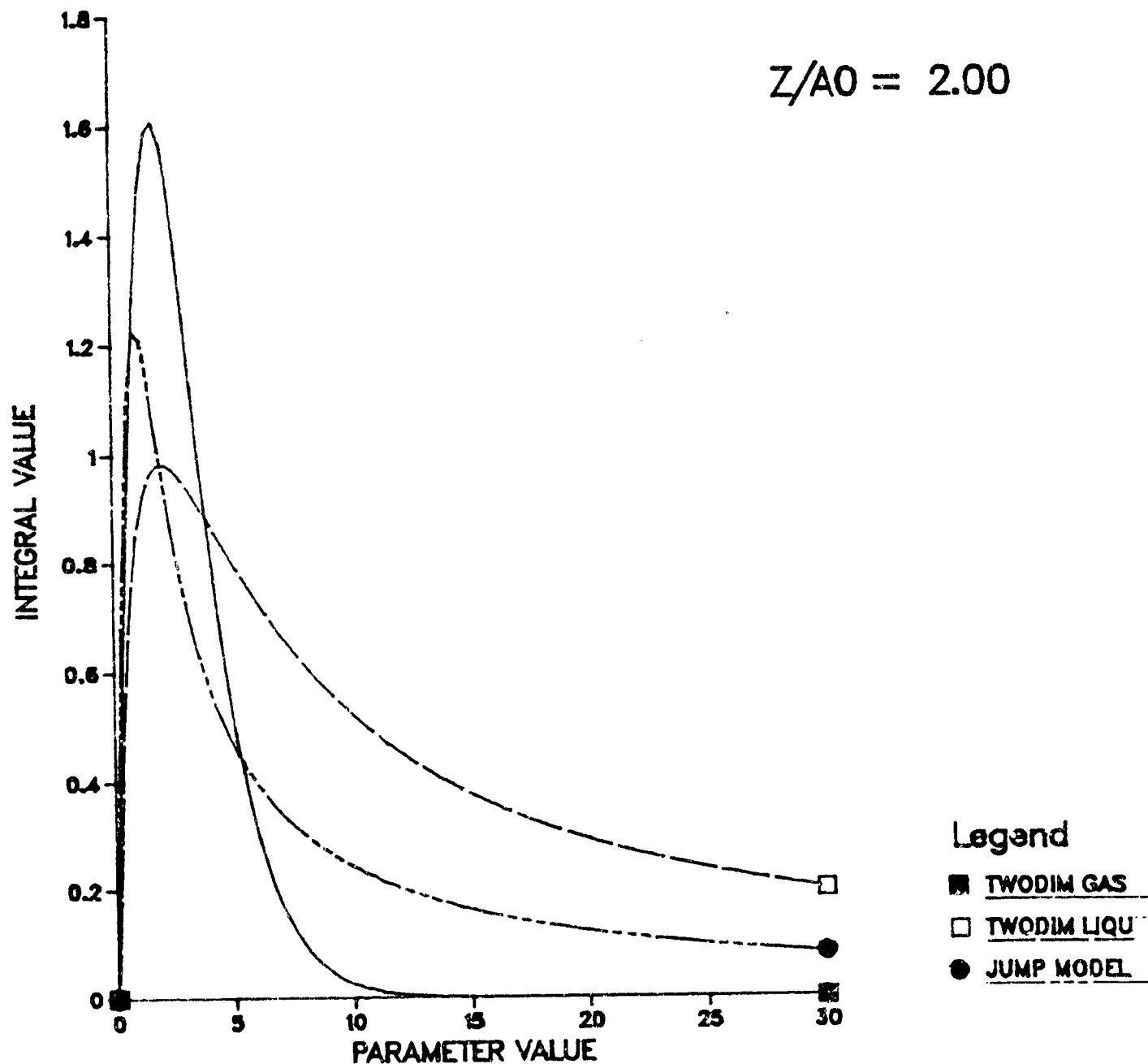
# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



# THREE MODELS FOR PARA → ORTHO H<sub>2</sub> CATALYSIS



## Theory of Ortho to Para Hydrogen Catalysis

### III. Analysis of the Two-dimensional Liquid (Surface Diffusion) Model with Surface Lifetime 'Tau' Seconds.

August 24, 1989

R. E. Coffman  
Chemistry Department  
University of Iowa.

#### Abstract.

The theory for para to ortho hydrogen catalysis on a paramagnetic surface, based on the model of a two-dimensional liquid on the surface (surface diffusion model), has been extended to include the effects of a surface lifetime ' $\tau$ '. The integral which controls the efficiency of para to ortho conversion has been numerically evaluated in terms of two dimensionless parameters. The best set of such dimensionless parameters was found to be the parameter ' $\gamma$ ' used in the analysis of the case of infinite surface lifetime, and a new parameter: the (average) frequency of the para to ortho transition ( $\omega_{op}$ ) times the surface lifetime:  $\omega_{op} \tau$ . Numerical evaluation of the integral which governs the efficiency of the conversion demonstrates some interesting features of this model. One of the most significant findings is that choosing  $\omega_{op} \tau \sim$  an optimal value (about 1.5) leads to a situation



where the catalysis rate is maximum (for given height above the surface of the catalyst) and nearly independent of the parameter ( $\gamma \geq 1.5$ ) which otherwise controls the efficiency of the rate of catalysis. Thus, the residence time 'tau' is of critical importance in achieving optimal paramagnetic catalyst performance.

Table of Contents:

- I. Method of Analysis.
- II. The Two-Dimensional Surface Diffusion Model with lifetime = ' $\tau$ '.
- III. Analysis in Terms of Dimensionless parameters.
- IV. Results.
- V. Conclusions on the Optimal Conditions for Para to Ortho Hydrogen Catalysis.
- VI. References.
- VII. Figures.

## I. Method of Analysis.

The rate of para to ortho catalysis is calculated from the first principles result:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \left(\frac{1}{\hbar^2}\right)^2 \int_0^{\infty} \bar{\Phi}(t) dt$$

where

$$\begin{aligned} b &= H_2 \text{ bond length.} \\ \mu_p &= \text{magnetic dipole moment of the proton} \\ \hbar &= h/2\pi \end{aligned}$$

and

$$\bar{\Phi}(t) = \text{a relaxation function}$$

The general form of  $\bar{\Phi}(t)$  for any magnetic model for the surface catalyst (paramagnetic, ferromagnetic or antiferromagnetic) is as follows:

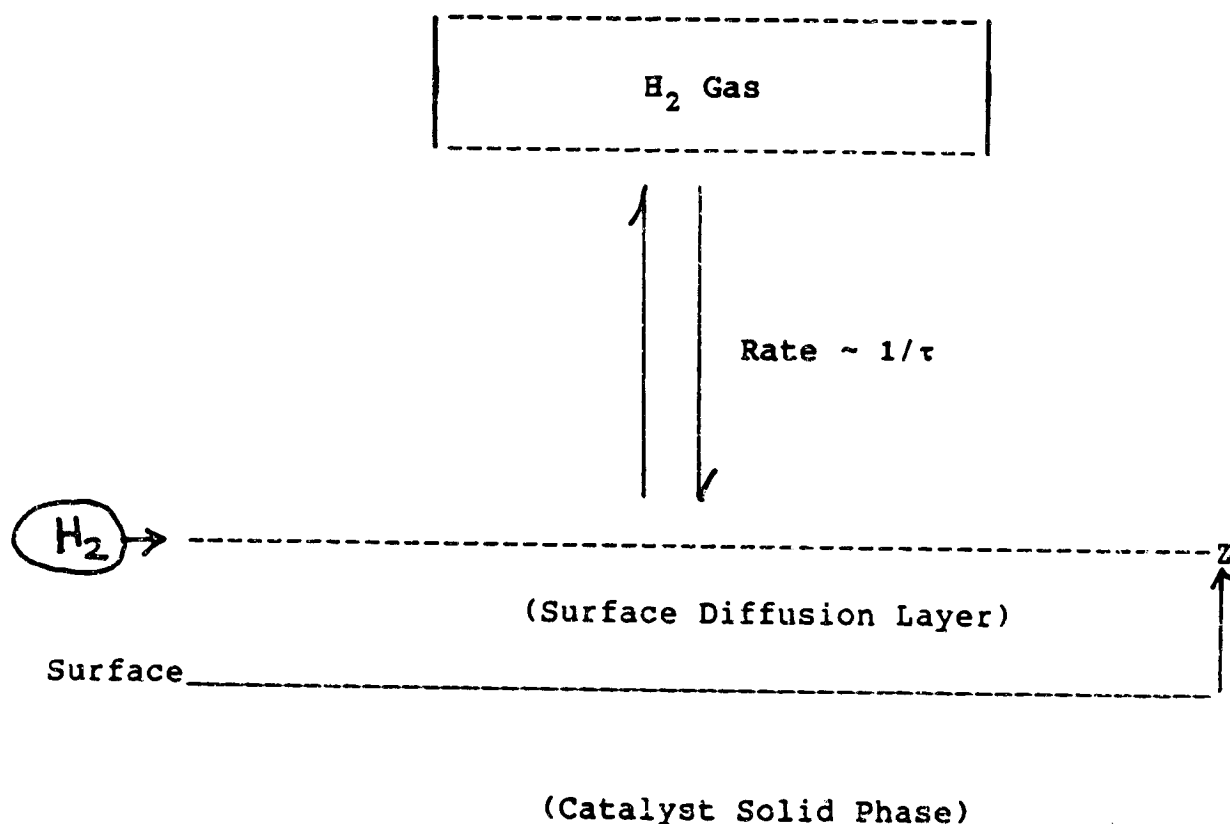
$$\bar{\Phi}(t) = e^{-i\bar{\omega}_{op}t} \sum_{\mu} G_{\mu}(\hat{b}) \quad (\otimes)$$

$$\sum_{\mathbf{q}} \left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2} \sum_{x, y, z} \beta_{\mu}^{(i)}(\mathbf{q}) \beta_{\mu}^{(i)*}(\mathbf{q}) \left\langle S_{-q}^{(i)}(t) S_q^{(i)}(0) \right\rangle$$

The quantity  $\bar{\Phi}(t)$  must then be evaluated according to the physical model under consideration, and then the indicated integrations and summations performed. In practice, the summations are converted to integrals, by standard methods used in solid state physics.

II. The Two-Dimensional Surface Diffusion Model with Surface Lifetime = 'Tau'.

The surface diffusion model with surface lifetime ' $\tau$ ' is developed as indicated in the figure below:



The distance ' $z$ ' is assumed to bisect the surface region of average distance of the  $H_2$  molecules from the surface plane containing the (centers) of regions of space containing the electronic magnetic moments, in turn located in the surface atoms or molecules.

According to this model,  $\Phi(t)$  is determined by evaluating the functional forms of the four different terms which control the form of the relaxation function. Only one term is different for this model, as compared to the model for surface diffusion with infinite lifetime. This is the term for the correlation function for movement of the  $H_2$

molecule in the surface diffusion layer:

$$\left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2} = e^{-Dq^2 t} e^{-t/\tau}$$

Substituting this relation into the expression for  $\Phi(t)$ , and then setting up the expression for the rate of catalysis gives this form of the intermediate result for the rate of para to ortho conversion:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \frac{1}{h^2} \frac{4}{3} \left(\frac{N_s}{N}\right) \frac{S(S+1)}{3} \cdot \frac{16\pi^2 \mu_A^2}{a_0^2}$$

$$\textcircled{x} \int_0^{q_c} \int_0^S e^{-2q^2 t} dq \int_0^\infty \cos \bar{\omega}_{op} t e^{-Dq^2 t} e^{-t/\tau} dt$$

Where:

- D = the diffusion coefficient for H<sub>2</sub> molecular diffusion along the surface of the catalyst.
- $\tau$  = the lifetime of the hydrogen molecules in the surface layer.
- a<sub>0</sub> = the surface lattice constant
- $\mu_A$  = the magnetic moment of the surface atom or molecule 'A'.
- S = the electronic spin of 'A'.

### III. Analysis in Terms of Dimensionless Parameters.

The rate of para to ortho catalysis, for the surface diffusional model with surface lifetime ' $\tau$ ' is given by:

$$W_{p \rightarrow o} = K \left\{ G_1(\gamma, \rho) + G_2(\gamma, \rho) \right\}$$

where

$$\gamma = \frac{\bar{\omega}_{op} z^2}{4D}$$

and

$$\rho^2 = \frac{z^2}{4D\tau}$$

The integrals  $G_1(\gamma, \rho)$  and  $G_2(\gamma, \rho)$  are given by the quantities:

$$G_1(\gamma, \rho) = \frac{256\gamma}{3} \int_0^{q_c z/2} \frac{y^7 e^{-4y} dy}{(y^2 + \rho^2)^2 + \gamma^2}$$

$$G_2(\gamma, \rho) = \frac{256\gamma\rho^2}{3} \int_0^{q_c z/2} \frac{y^5 e^{-4y} dy}{(y^2 + \rho^2)^2 + \gamma^2}$$

where the coefficient  $K$  ( $\sim 1/z^6$ ) is the same as in the two reports prior to this one, and the upper limit of integration is evaluated from:

$$q_c z = \pi(z/a_0)$$

These expressions have the correct limiting form as  $\tau \rightarrow \infty$ . That is, as  $\rho \rightarrow 0$ , the result obtained earlier for surface diffusion with infinite surface lifetime is obtained.

This is not an optimal set of dimensionless parameters for the analysis of the catalytic rate, as numerical calculations of  $W_{p \rightarrow 0}$  versus  $\gamma$  and  $\rho$  quickly show. The problem is that  $\gamma$  and  $\rho$  are a bad mix of both surface properties and the lifetime on the surface. A much better set of dimensionless parameters is this set:

$$\gamma = \frac{\bar{\omega}_{op} z^2}{4D} \quad , \text{ determined by surface properties.}$$

and

$$\omega_{optau} = \omega_{op} \tau \quad , \text{ determined by the para} \rightarrow \text{ortho transition frequency and the lifetime on the surface.}$$

This is a more sensible set of parameters, which gives directly a set of curves which are readily interpretable.

#### IV. Results

In the figures which follow, we have calculated the para to ortho catalysis rate from the expression:

$$w_{p \rightarrow o} = \kappa \left\{ G_1(\gamma, w_{op}\tau) + G_2(\gamma, w_{op}\tau) \right\}$$

where the independent parameters are the dimensionless parameters

$$\gamma = \frac{\bar{w}_{op} z^2}{4D}$$

and

$$w_{op}\tau = w_{op}^* \tau$$

The range of  $w_{op}\tau$  is from zero to any large number greater than 1.0, for example 0 to 100. We would expect, naively, that the para to ortho catalytic rate would peak for a value of  $w_{op}^* \tau \sim$  unity.

The integrals  $G_1(\gamma, w_{op}\tau)$  and  $G_2(\gamma, w_{op}\tau)$  are given by:

$$G_1(\gamma, \bar{w}_{op}\tau) = \frac{256\gamma}{3} \int_0^{q_c z/2} \frac{y^7 e^{-4y} dy}{\left(y^2 + \frac{\gamma}{\bar{w}_{op}\tau}\right)^2 + \gamma^2}$$

and

$$G_2(\gamma, \bar{w}_{op}\tau) = \frac{256\gamma^2}{3\bar{w}_{op}\tau} \int_0^{q_c z/2} \frac{y^5 e^{-4y} dy}{\left(y^2 + \frac{\gamma}{\bar{w}_{op}\tau}\right)^2 + \gamma^2}$$

The range of  $\gamma$  is  $\gamma > 0$ .



The RESULTS are given in the form of two sets of curves.

Set W: W-1 thru W-9.

Plots of  $W_{p \rightarrow 0}$  versus  $w_{optau}$  for various values of 'gamma'. In general, one can see a maximum in the rate for  $w_{optau} \sim 1.5$ , but the results are more informative than this simple rule.

(1) Starting from the high end of the range of 'gamma', the catalytic rate is found to increase as  $\gamma$  decreases, leading towards a maximum catalytic rate at  $\gamma \sim 1.5$ .

(2) For  $\gamma$  becoming still smaller, i.e.  $\gamma < 1.5$ , the entire range of catalytic rate versus  $w_{optau}$  decreases, i.e. for this condition the catalytic efficiency is generally reduced.

Set G: G-1 thru G-2.

In this set, the catalytic rate  $W_{p \rightarrow 0}$  is calculated versus  $\gamma$  for given values of  $w_{optau}$ . Conclusions:

(3) For  $w_{optau} \sim 1.3$  to  $1.5$  (or some such range), the catalytic rate is nearly independent of  $\gamma$  for  $\gamma >$  about  $1.5$

(4) If  $w_{optau} \sim 2, 4, \text{ or } 6$  (or greater) then the catalytic rate shows a marked decrease versus  $\gamma$ .

V. Conclusions on the Optimal Conditions for Para to Ortho Hydrogen Catalysis.

In general this model of surface diffusion which incorporates the surface lifetime constant ' $\tau$ ' shows:

1. Distinct optimal properties.
2. A distinct range of parameters where the catalytic rate is optimal (i.e for given distance  $Z$  above the surface).

3. A strong dependence of the catalytic rate on the surface life time  $\tau$ , expressed through the dimensionless parameter  $\omega_{op} \cdot \tau$ . In particular, the optimum lifetime is given by

$$\tau \sim 1.5/\omega_{op}.$$

A typical value of  $E(\text{ortho}) - E(\text{para})$  is about  $50 \text{ cm}^{-1}$ , from which one finds

$$\omega_{op} = 9.4 \times 10^{12} \text{ radians/sec.}$$

so that

$$\tau = 1.5/(9.4 \times 10^{12}) = 1.6 \times 10^{-13} \text{ sec.}$$

and, generally,:

$$\tau(\text{optimum}) \sim 10^{-13} \text{ sec.}$$

for the optimum surface residence time.

4. Of course, in all of these observations, the rule that the rate  $\sim 1/Z^6$  still holds, so the hydrogen molecule must still come as close as possible to the (plane containing the) paramagnetic centers in order that the rate coefficient (K) be as large as possible.

VI. References.

See the two previous reports:

1. R.E. Coffman, Theory of Ortho to Para (Hydrogen) Catalysis. I. Practical Equations for the Description of Paramagnetic Catalysis. July 21, 1989.

2. R.E. Coffman, Theory of Ortho to Para Hydrogen Catalysis. II. Analysis of Three Models Due to Petzinger and Scalapino. August 10, 1989.

3. Petzinger and Scalapino, Physical Review B, 8, 266 (1973).

---Gives basic methods. Results given in this report are an extension of this work.

VII. Figures.

Set W-1 thru W-9.

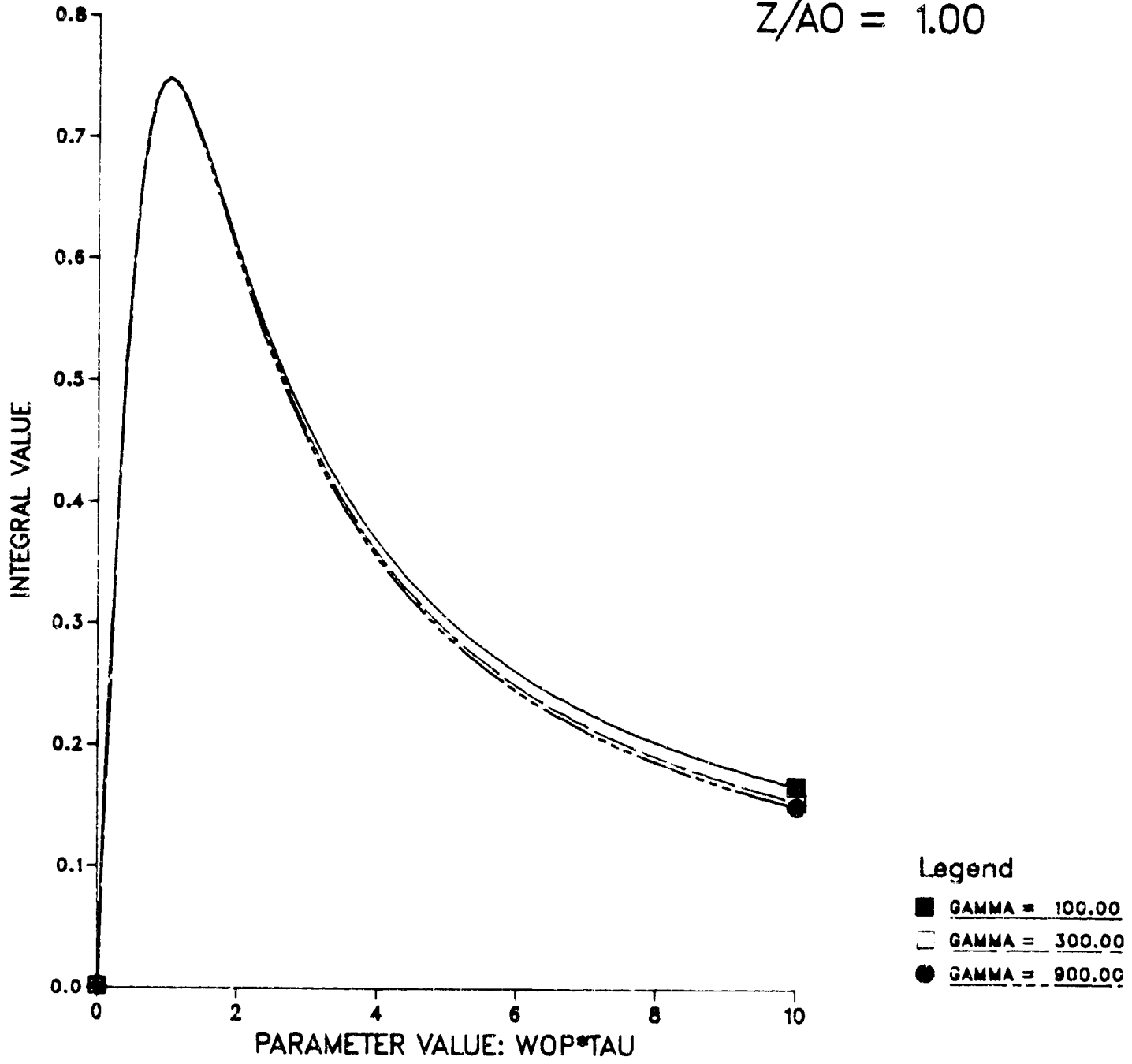
Plots versus  $\omega\tau$  for given values of the parameter  $\gamma$ .

Set G-1 thru G-2.

Plots versus 'gamma' for various values of ' $\omega\tau$ '.

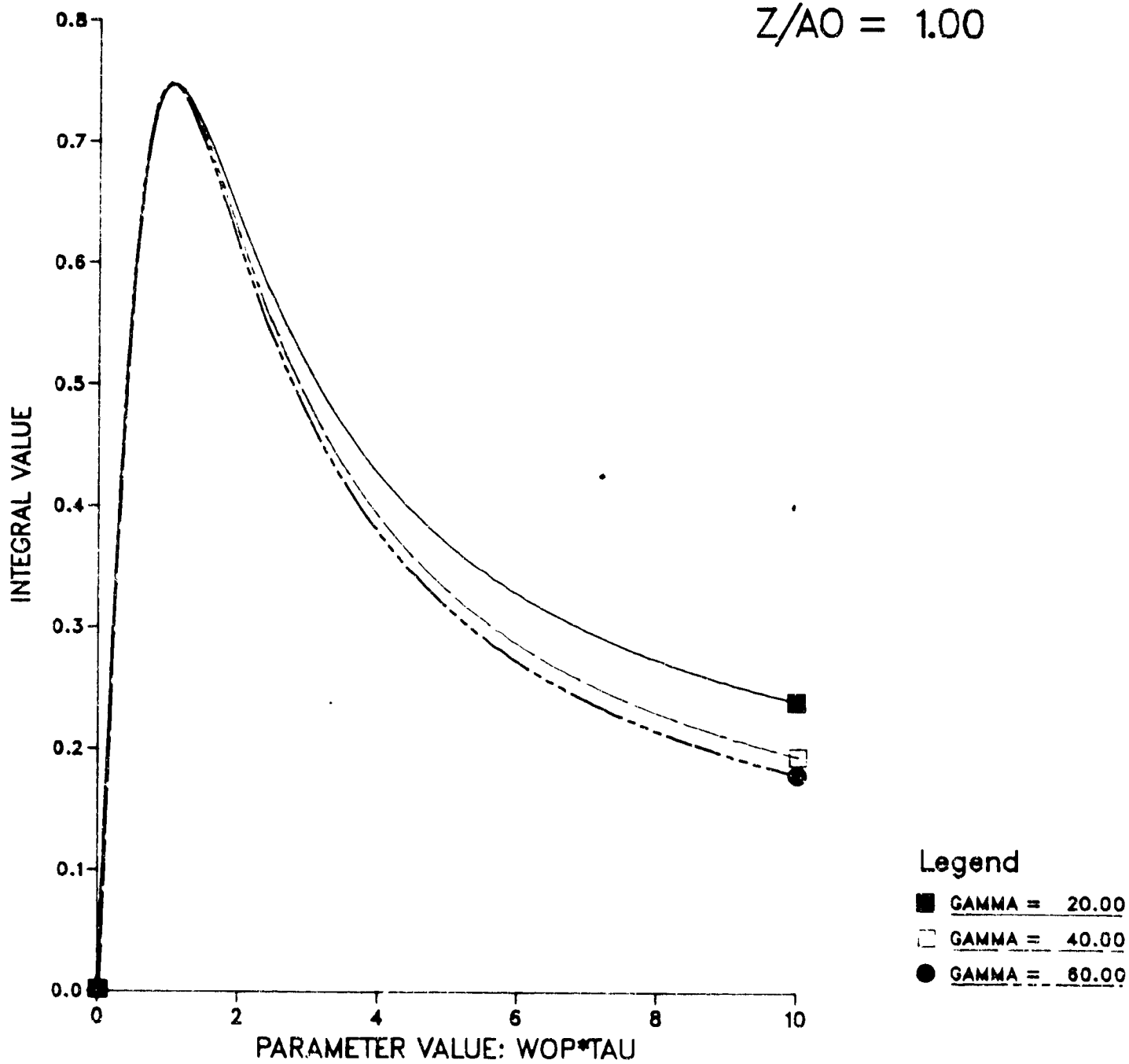
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Z/A0 = 1.00



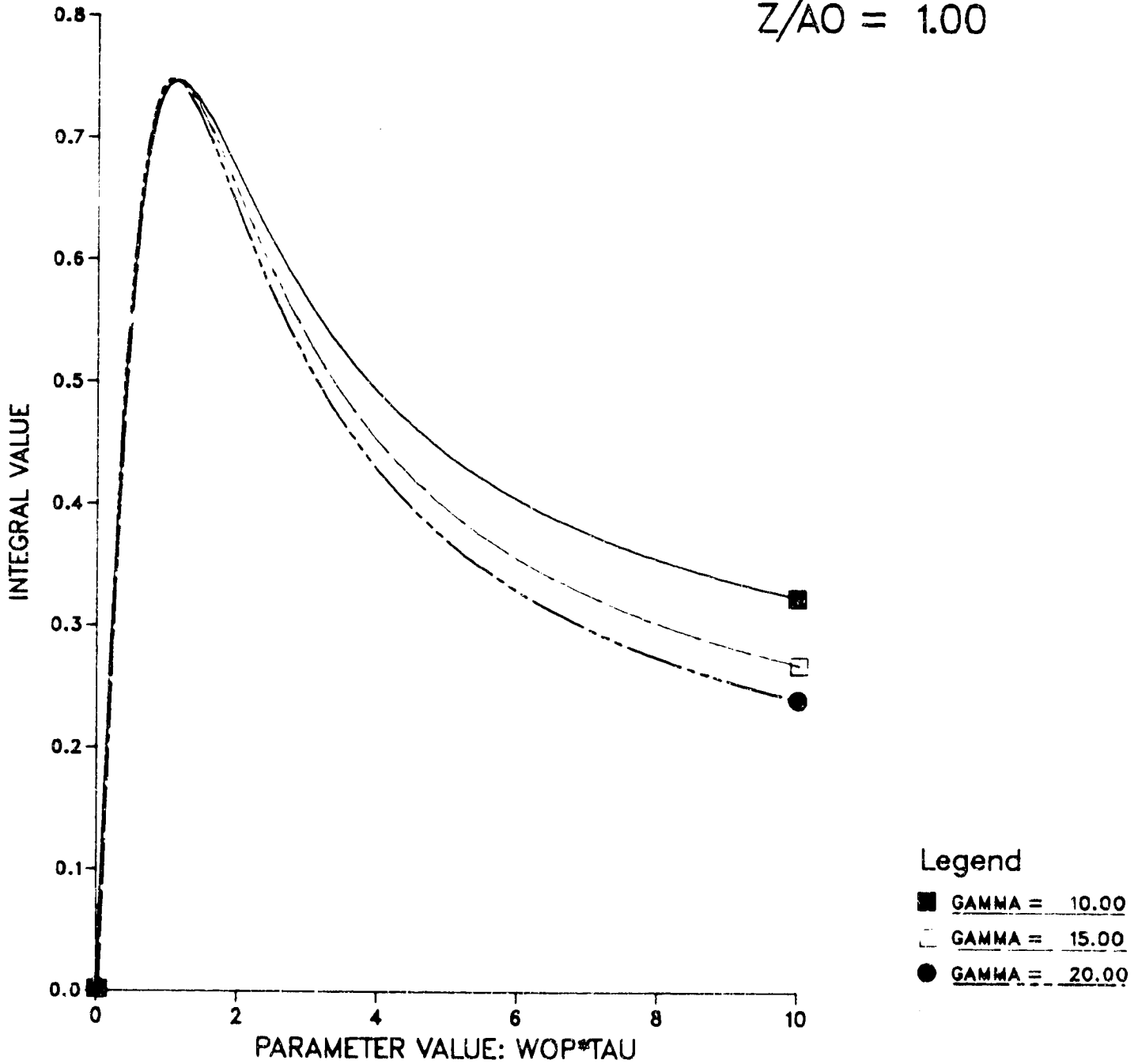
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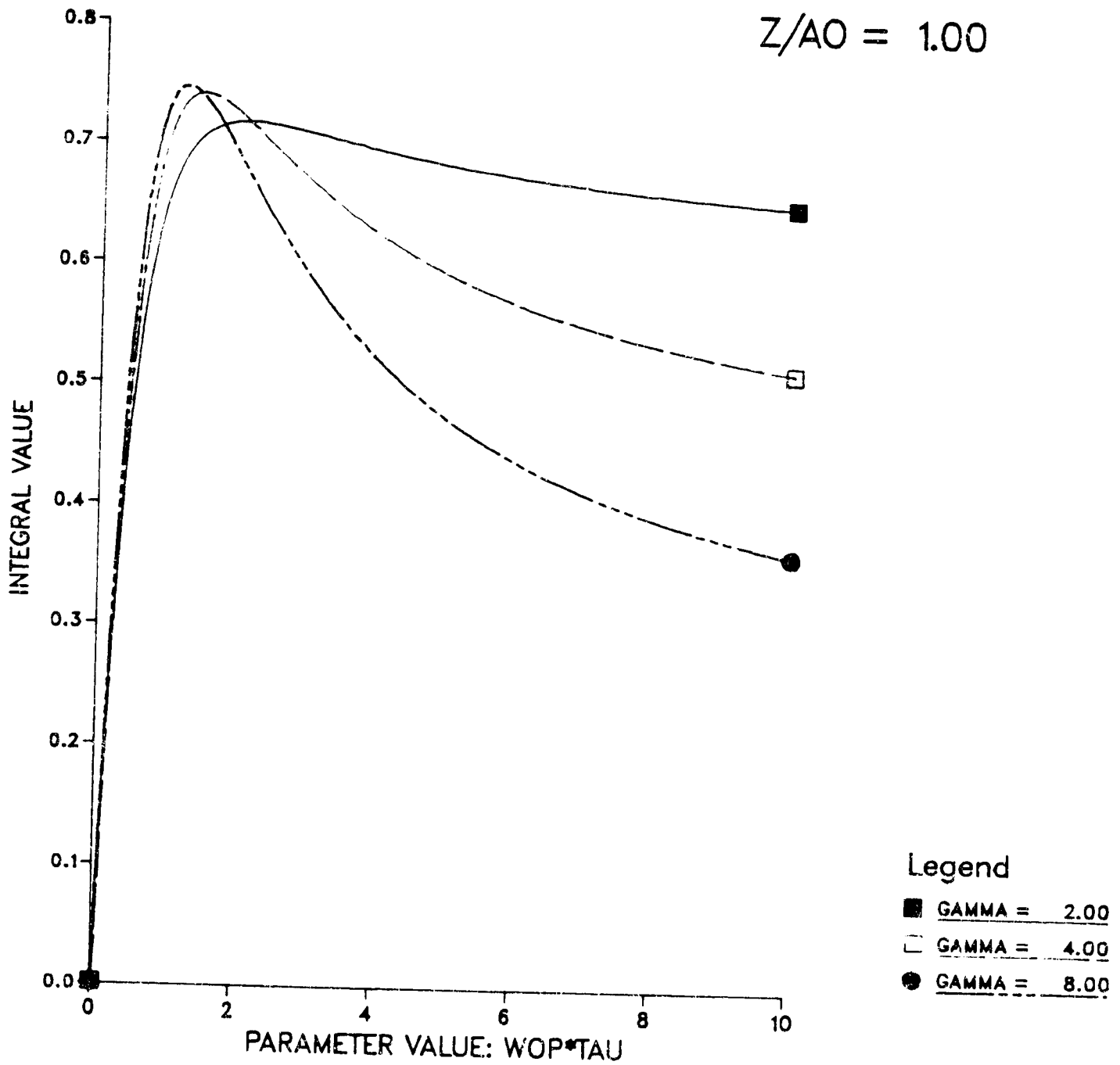
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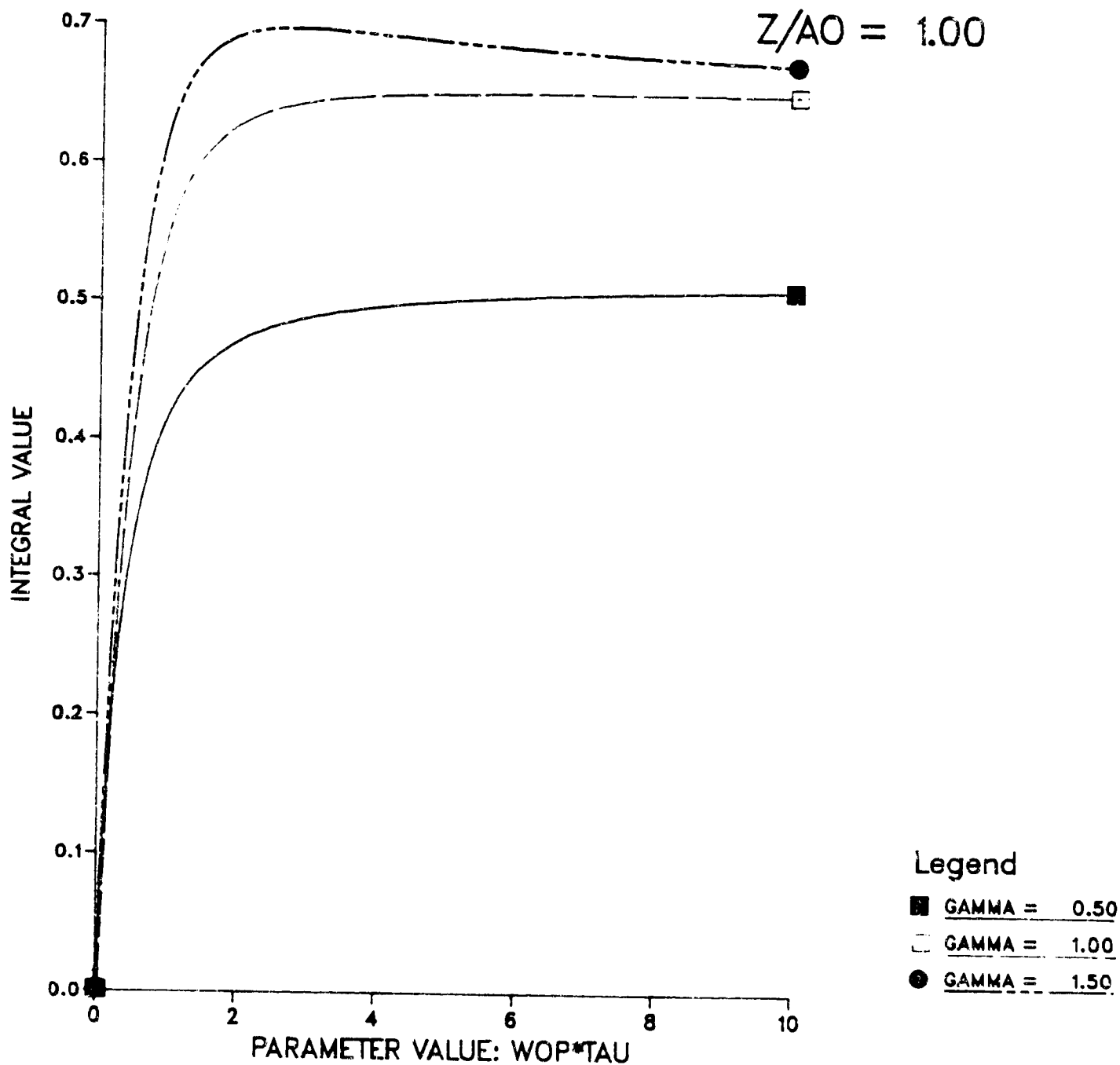




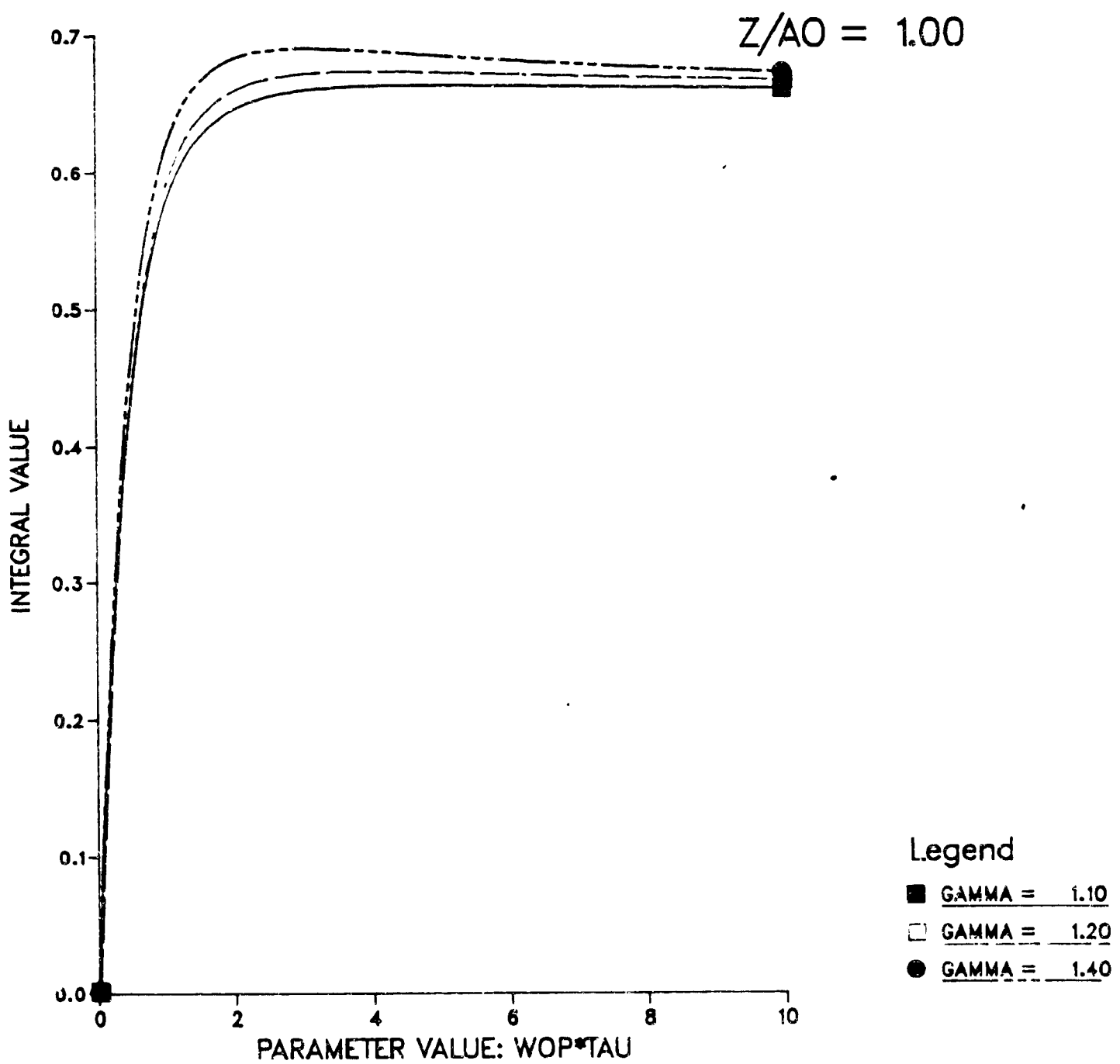
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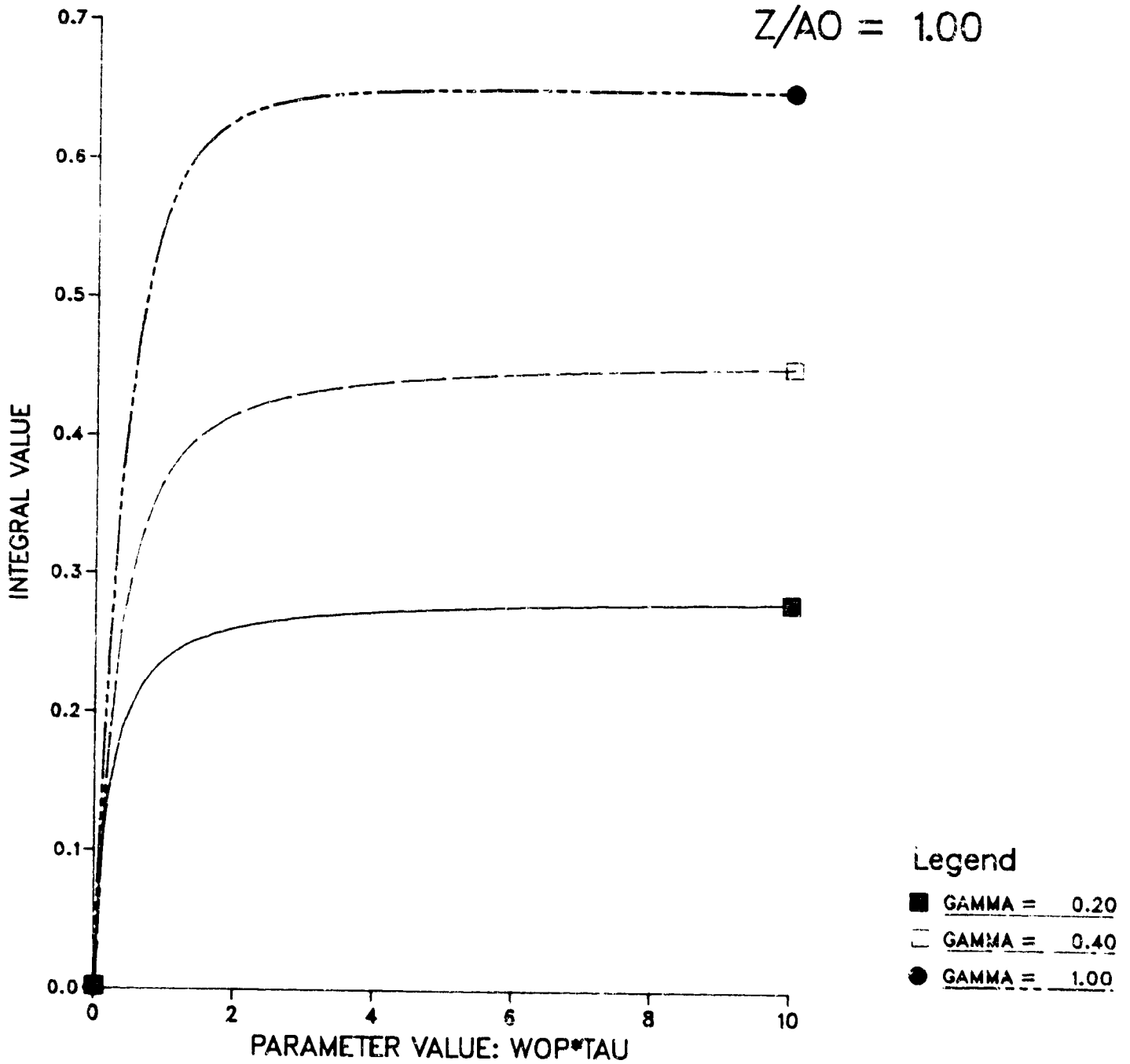
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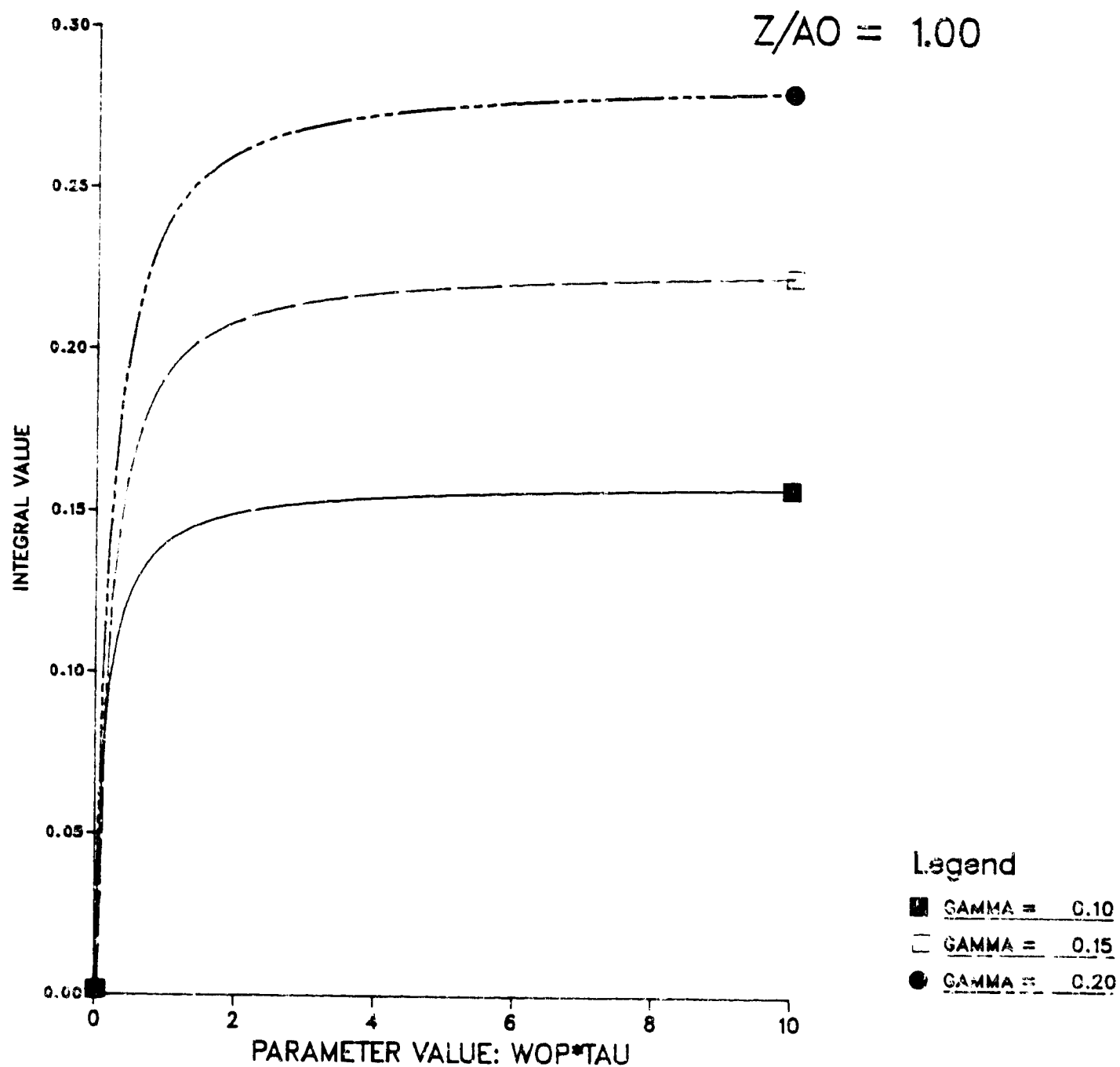
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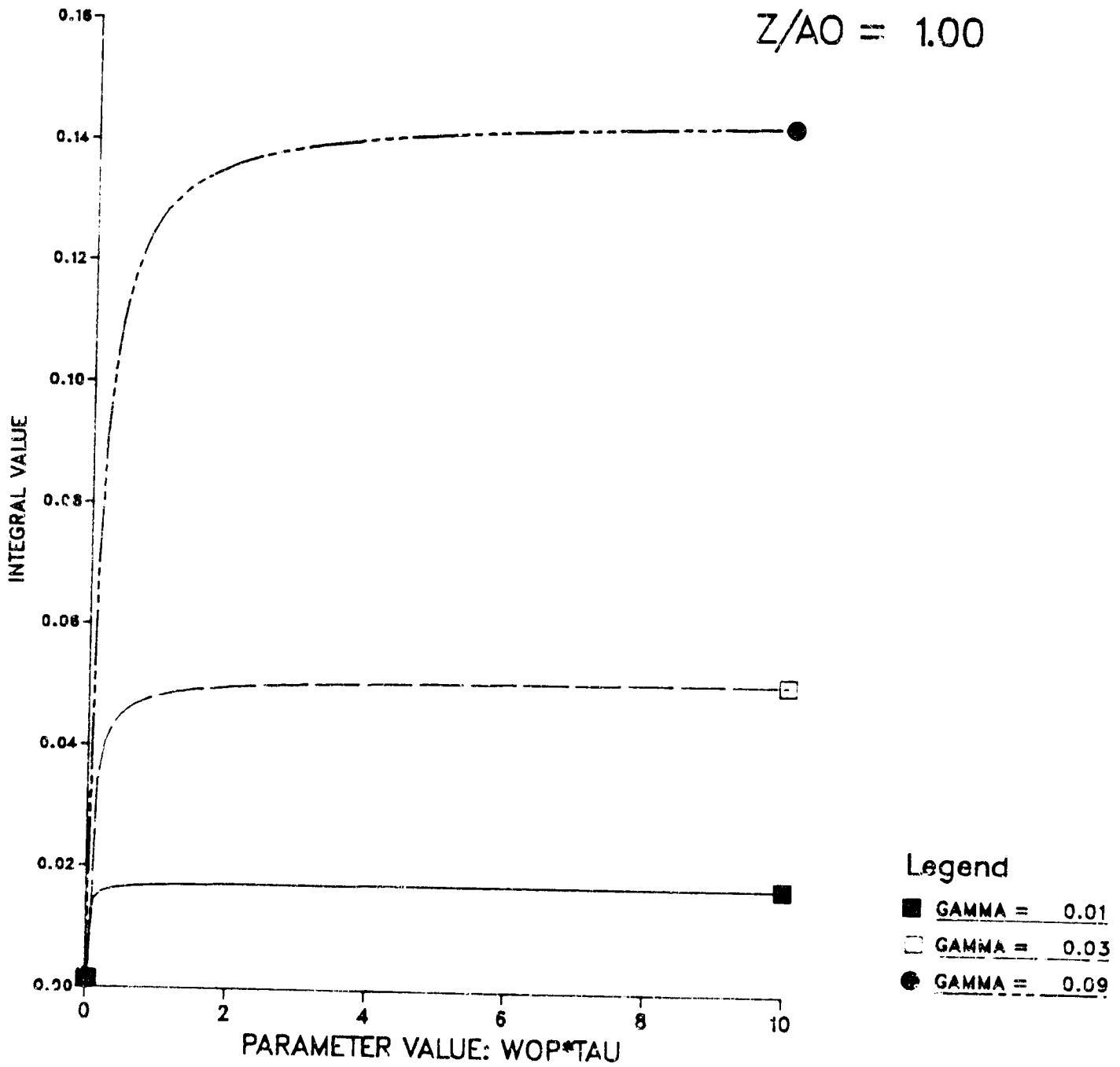


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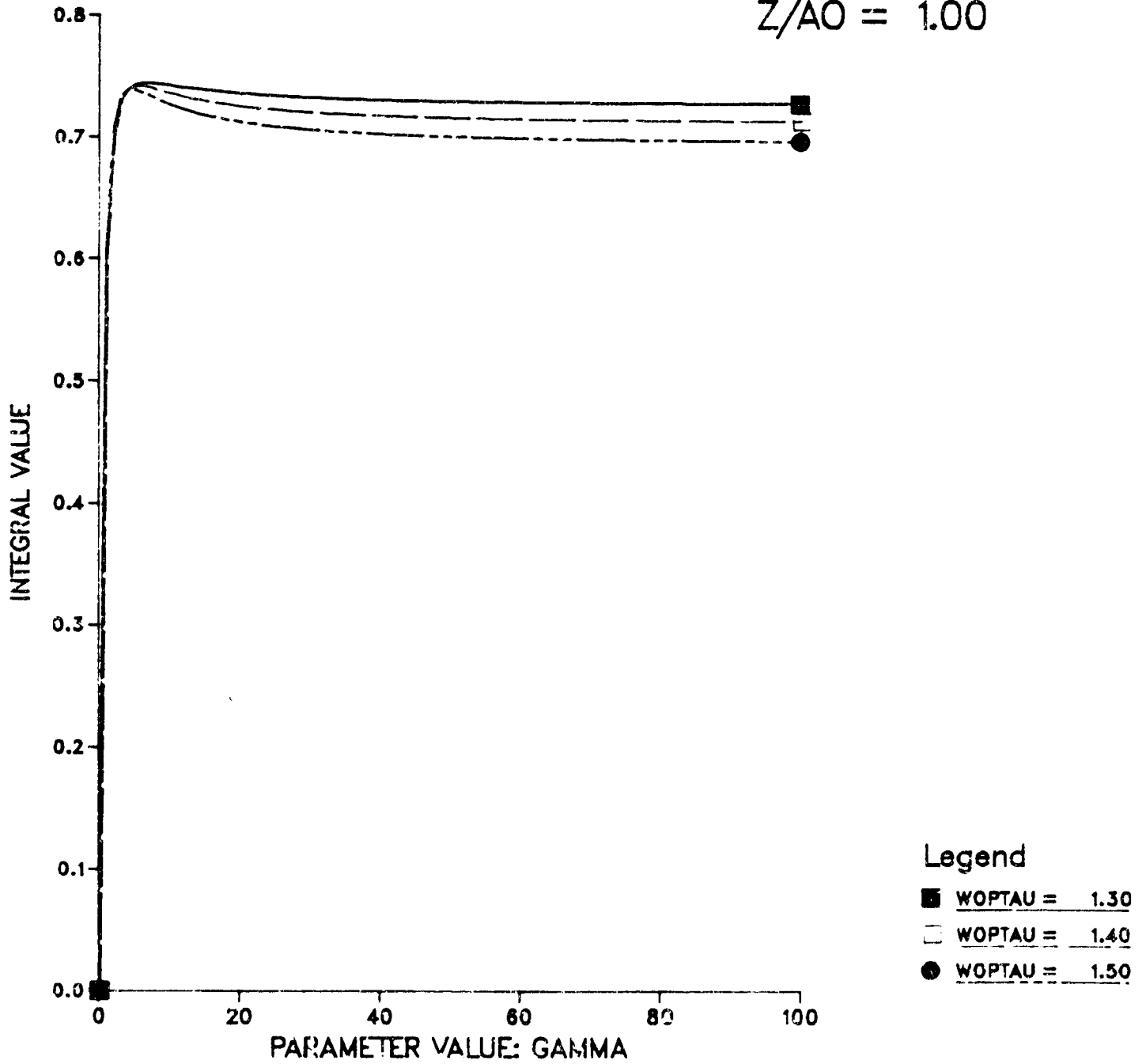
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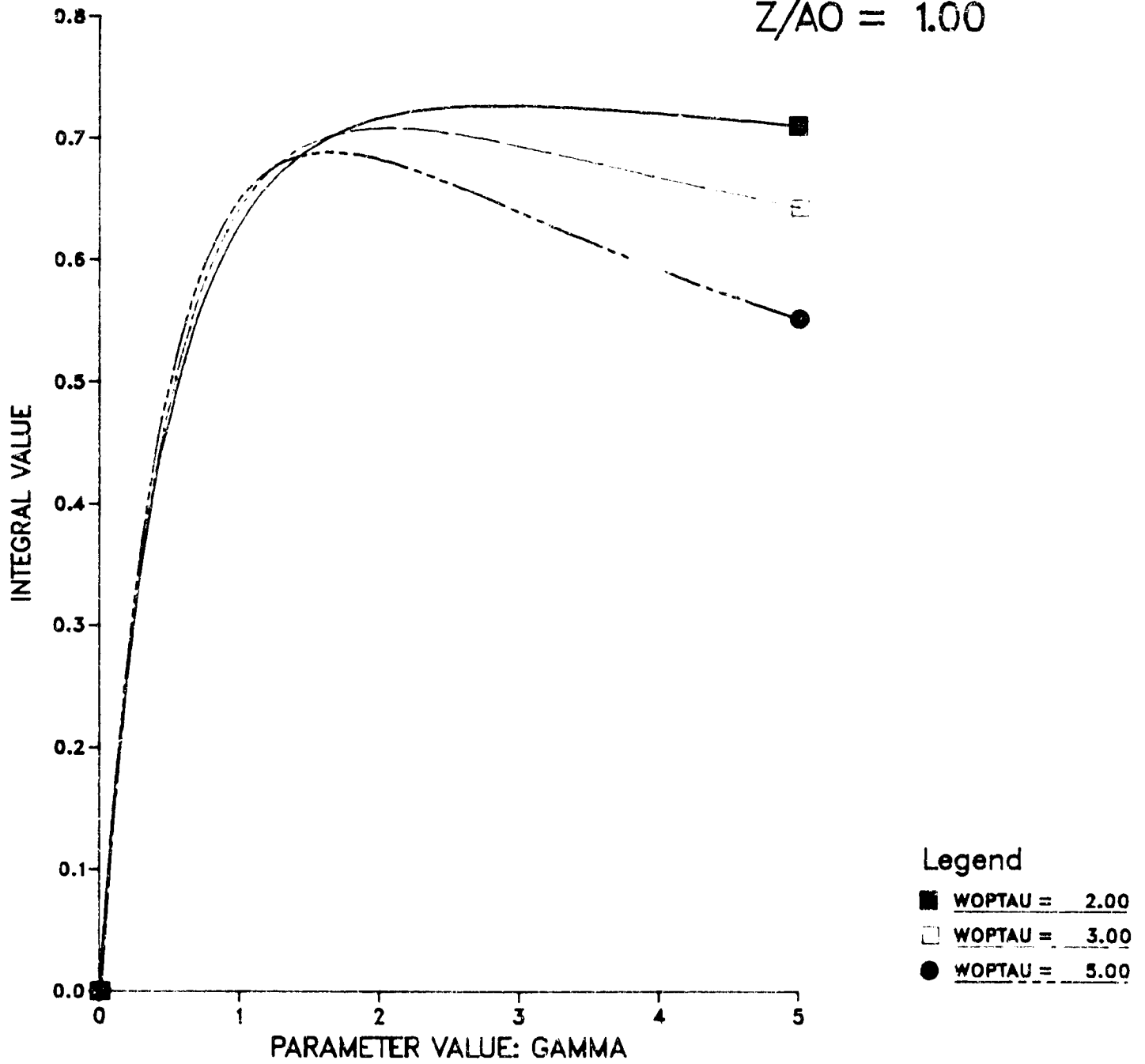
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$Z/AO = 1.00$





## Theory of Para to Ortho Hydrogen Catalysis

### IV. Analysis of the Two-dimensional Gas Model with Surface Lifetime 'Tau' Seconds.

Sept. 15, 1989

R. E. Coffman  
Chemistry Department  
University of Iowa.

#### Abstract.

The theory for para to ortho hydrogen catalysis on a paramagnetic surface, based on the model of a two-dimensional gas on the surface has been extended to include the effects of a surface lifetime ' $\tau$ '. The integral which controls the efficiency of para to ortho conversion has been numerically evaluated in terms of two dimensionless parameters. The best set of such dimensionless parameters was found to be the parameter 'alpha' used in the analysis of the case of infinite surface lifetime, and a new parameter: the (average) frequency of the para to ortho transition ( $\omega_{op}$ ) times the surface lifetime:  $\omega_{op} \cdot \tau$ . Numerical evaluation of the integral which governs the efficiency of the conversion demonstrates much the same features as for the previous model (two dimensional liquid). One of the most significant findings is that choosing  $\omega_{op} \cdot \tau \sim$  an optimal value (about 1.0) leads to a

situation where the catalysis rate is maximum (for given height above the surface of the catalyst) and independent of the parameter alpha as long as alpha is greater than some critical value. We find  $\alpha$ (critical) on the order of 0.5.

Thus, the two fundamental parameters which most control the catalytic rate on a paramagnetic surface are: the height, 'Z', above the paramagnetic surface and the surface residence time ' $\tau$ '. An optimum catalytic efficiency would exist for  $\tau$ (surface)  $\sim 10^{-13}$  sec, a condition which appears to be difficult to achieve.

The main conclusions of this study, for the two-dimensional gaseous surface layer case, are that the optimal gaseous paramagnetic catalyst for the para to ortho hydrogen conversion has:

1. a minimum distance from the catalytic surface to the Hydrogen molecules in the surface layer, and

2. the surface lifetime of the  $H_2$  molecules must be as close to  $10^{-13}$  sec as possible. This is difficult to achieve at a temperature of 120 K, since  $10^{-13}$  sec appears to be a distinct lower bound to the surface residence time of a hydrogen molecule.

Table of Contents:

- I. Method of Analysis.
- II. The Two-Dimensional gas Model with lifetime = 'tau'.
- III. Analysis in Terms of Dimensionless parameters.
- IV. Numerical Evaluation of the rate of Para-->Ortho Conversion.
- V. Results.
- VI. Conclusions on the Optimal Conditions for Para to Ortho Hydrogen Catalysis.
- VII. References.
- VIII. Figures.

## I. Method of Analysis.

The rate of para to ortho catalysis is calculated from the first principles result:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \left(\frac{1}{\hbar}\right)^2 \int_0^{\infty} \Phi(t) dt$$

where

$$\begin{aligned} b &= \text{H}_2 \text{ bond length.} \\ \mu_p &= \text{magnetic dipole moment of the proton} \\ \hbar &= h/2\pi \end{aligned}$$

and

$$\Phi(t) = \text{a relaxation function}$$

The general form of  $\Phi(t)$  for any magnetic model for the surface catalyst (paramagnetic, ferromagnetic or antiferromagnetic) is as follows:

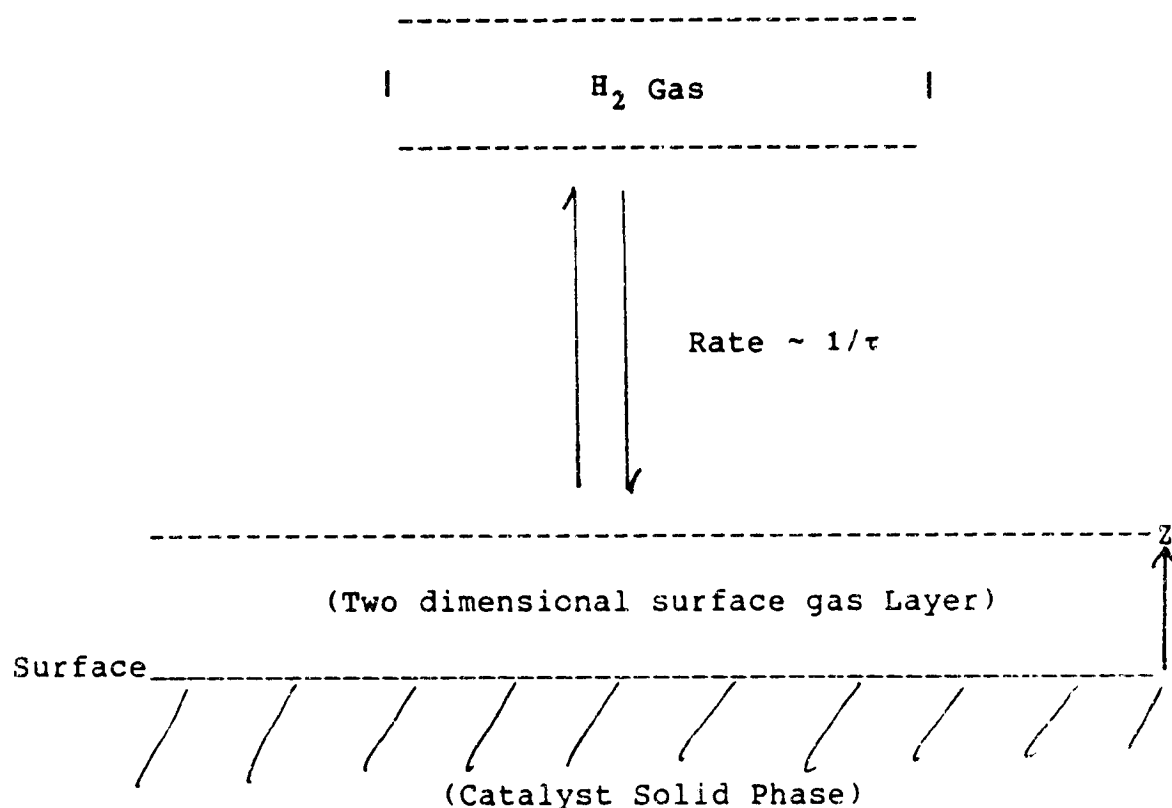
$$\Phi(t) = e^{-i\bar{\omega}_{opt}t} \sum_{\mu} G_{\mu}(\hat{b}) \quad (\otimes)$$

$$\sum_{\mathbf{l}} \left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2} \sum_{x, y, z} \beta_{\mu}^{(i)}(q) \beta_{\mu}^{(i)*}(q) \left\langle S_{-j}^{(i)}(t) S_j^{(i)}(0) \right\rangle$$

The quantity  $\Phi(t)$  must then be evaluated according to the physical model under consideration, and then the indicated integrations and summations performed. In practice, the summations are converted to integrals, by standard methods used in solid state physics.

II. The Two-Dimensional Gas Model with Surface Lifetime = 'Tau'.

The two dimensional surface gas model with surface lifetime ' $\tau$ ' is developed as indicated in the figure below:



The distance ' $z$ ' is assumed to bisect the surface region of average distance of the H<sub>2</sub> molecules from the surface plane containing the (centers) of regions of space containing the electronic magnetic moments, in turn located in the surface atoms or molecules.

According to this model,  $\Phi(t)$  is determined by evaluating the functional forms of the four different terms which control the form of the relaxation function. Only one term is different for this model, as compared to the previous model for a surface two dimensional gas with infinite lifetime. This is the term for the correlation function for movement of the H<sub>2</sub> molecule in the two-dimensional surface gas layer:

$$\left\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \right\rangle_{E, H_2} = e^{-\frac{kT}{2m} q^2 t} e^{-t/\tau}$$

Substituting this relation into the expression for  $\Phi(t)$ , and then setting up the expression for the rate of catalysis gives this form of the intermediate result for the rate of para to ortho conversion:

$$w_{p \rightarrow o} = \frac{16\pi^2}{3\hbar^2} \left( \frac{N_s}{N} \right) \frac{S(S+1)}{3} \left( \frac{b}{a_0} \right)^2 \mu_p^2 \mu_A^2 \quad (\times)$$

$$\int_0^{q_c} q^5 e^{-2q^2} dq \int_0^\infty \cos \bar{\omega}_{op} t e^{-\frac{kT}{2m} q^2 t} e^{-t/\tau} dt$$

Where:

$2kT/m$  = mean squared velocity of the  $H_2$  molecule on the surface.

$\tau$  = lifetime of the hydrogen molecules in the surface layer.

$a_0$  = the surface lattice constant

$\mu_A$  = the magnetic moment of the surface atom or molecule 'A'.

$\mu_p$  = proton magnetic moment.

$S$  = the electronic spin of 'A'.

$q_c$  = cut-off value of the lattice wave vector  $q$ :  $\pi/a_0$ .

### III. Analysis in Terms of Dimensionless Parameters.

This equation for the rate of para to ortho catalysis can only, generally, be evaluated by numerical means. We convert this expression to a form suitable for numerical evaluation by these transformations:

1. Replace  $kT/2m$  by  $v_{rms}^2/4$ .

2. Change the integral over 'q' to an integral over x by means of the transformation:

$$x = 2qZ$$

3. Set the upper limit of the integral over time down from infinity to 'T', where T is chosen to be much larger than the surface residence time ' $\tau$ '.

4. Change the unit of time in the integral over 't' from seconds to the period of the radian frequency:  $y = \omega_{opt}t$ .

5. Introduce the dimensionless constant alpha by the substitution:

$$\alpha = \omega_{op}Z/v_{rms}$$

Thus we obtain, finally, an expression for the rate of para to ortho transition which is:

$$W_{p \rightarrow 0} = \frac{K'}{(2z)^6} \frac{1}{\bar{\omega}_{op}} \int_0^{2q_c z} x^5 e^{-x} dx \int_0^{\bar{\omega}_{op} T} \cos y e^{-\left(\frac{x^2}{16d^2}\right) y^2} e^{-y/\bar{\omega}_{op} T} dy$$

where

$$K' = \frac{16\pi^2}{3\hbar^2} \left(\frac{Ns}{N}\right) \frac{S(S+1)}{3} \left(\frac{b}{a_0}\right)^2 \mu_p^2 \mu_A^2$$

and  $\omega_{op}$  is related to the rotational constant B by

$$\hbar\omega_{op} = 2B$$

The upper limit to the integral over x is determined as before by the relation:

$$q_c z = \pi(z/a_0)$$

which requires that we specify the height above the surface in units of the surface lattice constant.

The last step of the transformation of the form of  $W_{p \rightarrow 0}$  is to substitute  $\hbar/2B$  for  $1/\omega_{op}$  and rearrange the constant terms. The result is:

$$W_{p \rightarrow 0} = \frac{K}{48} \int_0^{2q_c z} x^5 e^{-x} dx \int_0^{\bar{\omega}_{op} T} \cos y e^{-\frac{y}{\bar{\omega}_{op} T}} e^{-\left(\frac{x^2}{16d^2}\right) y^2} dy$$

Where the coefficient K has the same meaning as in previous reports:

$$K = \frac{4\pi^2}{\hbar} \left(\frac{Ns}{N}\right) \frac{S(S+1)}{3} \left(\frac{b}{a_0}\right)^2 \frac{\mu_p^2 \mu_A^2}{z^6} \frac{1}{2B}$$



This expression has the correct limiting form as  $\tau \rightarrow \infty$ . That is, as  $1/\tau \rightarrow 0$ , the result obtained earlier for the two dimensional gas model with infinite surface lifetime is obtained.

This, now, is an optimal set of dimensionless parameters for the analysis of the catalytic rate. This best set of parameters is the set:

$$a = \frac{\bar{\omega}_{op} z}{v_{rms}} \quad , \text{ determined by properties of the 2D gas on the surface,}$$

and

$$w_{optau} = \omega_{op} \tau \quad , \text{ determined by the para-ortho transition frequency and the lifetime on the surface.}$$

This set of dimensionless parameters gives directly a set of curves which are readily interpretable. First, however, we must transform the double integral above to a form suitable for direct numerical integration.

#### IV. Numerical Evaluation of the rate of Para --> Ortho Conversion.

Carrying out a simple rearrangement gives this final form for the rate of para to ortho catalysis of a two-dimensional gas on the surface, each molecule in the surface having lifetime ' $\tau$ ':

$$W_{p \rightarrow o} = \frac{K}{48} \int_0^{2\tau c^2} x^5 e^{-x} \left\{ \int_0^{\bar{\omega}_{op} T} \cos y e^{-\frac{y}{\bar{\omega}_{op} T}} e^{-\left(\frac{x^2}{16\alpha^2}\right) \frac{dy^2}{dy}} \right\} dx$$

The numerical integrations are carried out by a subroutine for direct numerical double integration. For this purpose, we use the IMSL subroutine TWODQ which carries out a two-dimensional iterated integral. This subroutine, in turn, approximates the double integral by iterated calls to subroutine QDAG which uses a Gauss-Konrad quadrature rule for estimation of a single dimensional integral. The over-all numerical procedure is slow, but the accuracy can be controlled at the expense of slower numerical evaluation of each point on the resulting curve of rate versus the parameter value alpha or woptau.

Two FORTRAN programs were written for this calculation:

AMODEL1.FOR plots  $W_{p \rightarrow o}$  (in units of K) versus parameter alpha for three chosen values of woptau.

FMODEL1.FOR plots  $W_{p \rightarrow o}$  (in units of K) versus the frequency parameter woptau for three given values of alpha.

In each case, the resulting file of relative catalytic rate versus alpha (or woptau) was plotted using the TELAGRAF graphics package.

## V. Results

In the figures which follow, we have calculated the para to ortho catalysis rate from the expression:

$$w_{p \rightarrow o} = \frac{1}{48} \int_0^{2\tau cz} x^5 e^{-x} \left\{ \int_0^{\bar{\omega}_{op} T} \cos y e^{-\frac{y}{\bar{\omega}_{op} T}} e^{-\left(\frac{x^2}{16d^2}\right) y^2} dy \right\} dx$$

where the independent parameters are the dimensionless parameters

$$\alpha = \frac{\bar{\omega}_{op} z}{v_{rms}}$$

and

$$w_{optau} = \omega_{op} \tau$$

The range of  $w_{optau}$  is from zero to any large number greater than 1.0, for example 0 to 100. The upper limit to the 'y'-integral is determined by choosing  $T = 20 \tau$ , and the limit to the integral over 'x' is chosen by setting the height  $Z$  equal to one unit of surface spacing, i.e.

$$Z/a_0 = 1.$$

We would expect, naively, that the para to ortho catalytic rate would peak for a value of  $\omega_{op} \tau \sim$  unity. This is about what is observed.

The first set of figures (F-1, F-2, F-3) present the results of calculating the catalytic rate versus  $w_{optau}$  for various values of alpha. The results clearly show that the optimum value of alpha (for any residence time  $\tau$ ) is:

$$\alpha(\text{optimum}) = 0.30$$

Can this optimum be achieved in practice? To answer this question, we calculate the numerical value of  $\alpha$  for:

$$T = 120^{\circ}\text{K}$$

and

$$Z = b = 0.74 \times 10^{-8} \text{ cm}$$

which is the covalent bond length of the hydrogen molecule, and represents the closest possible distance of the  $\text{H}_2$  molecule to a catalytic site. Now, at this temperature (in cgs units):

$$v_{\text{rms}}^2 = 2(8.314 \times 10^7)(120)/2.016$$

so the rms speed of the  $\text{H}_2$  molecule on the surface at 100K would be:

$$v_{\text{rms}} = 99,490 \text{ cm/sec}$$

Now, using the typical value of  $\omega_{\text{op}} = 9.4 \times 10^{12}$  radians/sec, we find:

$$\alpha = (9.4 \times 10^{12})(0.74 \times 10^{-8})/99490 = 0.70$$

Since we expect a larger distance from catalytic site to hydrogen molecule than  $b$ , this means that an optimum of  $\alpha$  (for arbitrary  $\tau$ ) cannot be achieved, except for the unlikely condition that the ortho - para energy difference were reduced by a factor of 2 - 5 from its normal value of about  $50 \text{ cm}^{-1}$ .

The second set of figures (A-1,2,3,4,5,6) presents the relative catalysis rate versus alpha for various values of  $\omega\tau$ . Figure A-4, in particular shows that the maximum catalytic rate is achieved for:

$$\omega_{\text{op}} \cdot \tau = 1.0$$

which is about what we (naively) expect. However, there is an auxiliary condition: That is, if alpha is greater than some critical value, then the catalytic rate stays at its maximum efficiency

independent of the value of alpha.

Figure A-6 pins down this critical value of alpha. This critical value of alpha (for optimum tau) is about:

$$\alpha(\text{critical}) \geq 0.5$$

$$\text{for } \omega_{\text{op}} * \tau = 1.0$$

This condition can be achieved! We note that a typical value of alpha (found above) was  $\alpha = 0.70$  (or larger), so this condition could be met for a considerable range of distances and ortho-para transition frequencies. Therefore, the critical quantity to adjust (besides the distance from the catalytic surface...in the  $1/Z^6$  term) is the residence time ' $\tau$ '.

## VI. Conclusions on the Conditions for Optimal Efficiency for Para to Ortho Hydrogen Catalysis.

In general this model of a two dimensional surface gaseous layer which incorporates the surface lifetime constant ' $\tau$ ' shows:

1. Distinct optimal properties (as for the case of the two-dimensional liquid on the surface).
2. A distinct range of parameters for which the catalytic rate is optimal (for a given distance  $Z$  above the catalytic surface).
3. The optimal conditions can be expressed in terms of the lifetime ' $\tau$ ' and the dimensionless constant ' $\alpha$ ':

$$\tau \sim 1.0/\omega_{op}$$

and the condition on alpha is:

$$\alpha \geq 0.5$$

### 4. Considerations on the lifetime $\tau$ .

Now, since we know that a typical value of  $\omega_{op}$  is  $9.4 \times 10^{12}$  radians/sec, this tells us that the optimum surface residence time is about:

$$\tau(\text{optimum}) \sim 10^{-13} \text{ sec.}$$

While this appears to be a reasonable number, the question is whether it is possible to realize so small a value of the surface lifetime.

To answer this question, we make an estimate of the surface lifetime from some elementary mechanics. We assume that the unit of time for ' $\tau$ ' is the time for an  $H_2$  molecule to travel one lattice constant:  $a_0$ . We take this distance to be two to three Angstroms, or

$$a_0 \sim 2.5 \text{ \AA}$$

Then, at 120 K the rms speed of a hydrogen molecule is

$$v_{\text{rms}} \sim 10^5 \text{ cm/sec}$$

and we estimate the unit of time for  $\tau$  by the simple 'time of flight' relation:

$$a_0 = v_{\text{rms}} \tau$$

from which we find:

$$\tau(\text{unit}) = 2.5 \times 10^8 / 10^5 = 2.5 \times 10^{-13} \text{ sec}$$

We expect, moreover, that the value of  $\tau$  on the surface is some multiple of this unit of time, for example:

$$\tau = n\tau(\text{unit})$$

where we only know for sure that  $n \geq 1$ . For example  $n = 3$  to 4 would raise the lifetime up to about  $10^{-12}$  sec, which would have a considerable effect on reducing the catalytic efficiency. Nevertheless, we see that  $\tau$  is on the order to the desired magnitude, although probably larger.

5. It is clear that a more thorough study of the surface lifetime is in order, since this appears to be one of the most important properties of the catalytic system, the other being the distance  $z$  from the surface layer containing the paramagnetic centers.

VII. References.

See the three previous reports:

1. R.E. Coffman, Theory of Ortho to Para (Hydrogen) Catalysis. I. Practical Equations for the Description of Paramagnetic Catalysis. July 21, 1989.

2. R.E. Coffman, Theory of Ortho to Para Hydrogen Catalysis. II. Analysis of Three Models Due to Petzinger and Scalapino. August 10, 1989.

3. R. E. Coffman, Theory of Para to Ortho Hydrogen Catalysis. III. Analysis of the Two-dimensional Liquid (Surface Diffusion) Model with Surface Lifetime 'Tau' Seconds., August 24, 1989.

4. Petzinger and Scalapino, Physical Review B, 8, 266 (1973).

---Gives basic methods. Results given in this report are an extension of this work.



VIII. Figures.

Figures F-1, F-2, F-3.

The relative catalytic rate (in units of K) versus  $\omega_{op}^* \tau$  for a set of three values of  $\alpha$ , in each figure.

Figure F-3 establishes an optimum value of  $\alpha$  (when considered as a function of  $\omega_{optau}$ ), which is :  $\alpha = 0.30$

Figures A-1, A-2, A-3, A-4, A-5.

The relative catalytic rate (in units of K) are plotted versus the dimensionless parameter  $\alpha$  for three values of  $\omega_{optau}$ , in each plot.

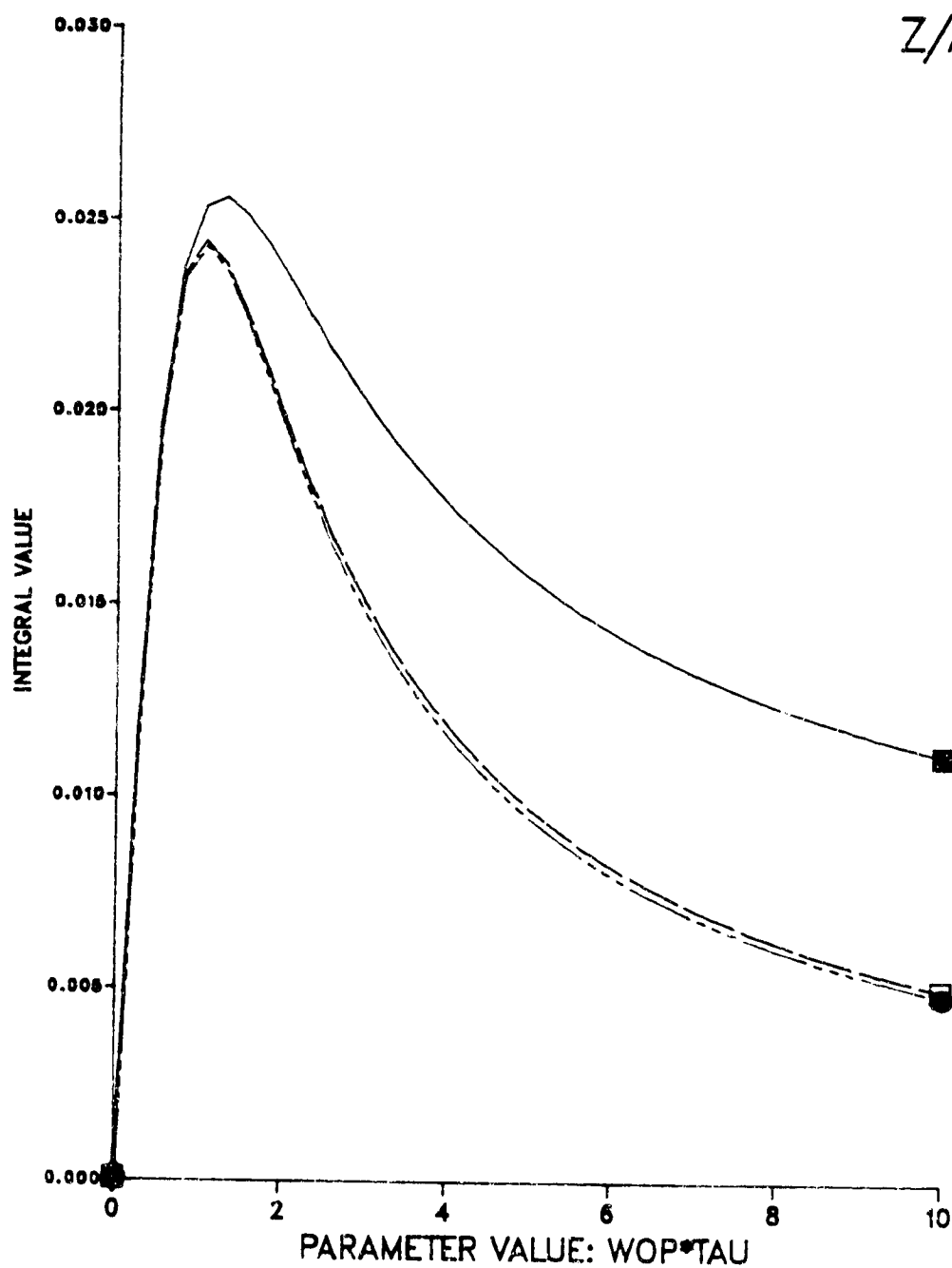
Figure A-4 established that  $\omega_{optau} = 1.0$  gives the maximum relative catalytic rate which is then independent of  $\alpha$  for  $\alpha$  greater than some critical value.

Figures A-5 and A-6.

The critical value of  $\alpha$  (when the catalytic rate is considered as a function of  $\omega_{optau}$ ) is determined by reducing the range of alpha from (0,100) to (0,10) and finally (0,2). The peak in figure A-6 (for  $\omega_{optau} = 1.20$ ) comes at about  $\alpha = 0.45$ . This was rounded off in the report to  $\alpha \sim 0.50$ .

# TWODIM GAS: CAT RATE VERSUS RESIDENCE TIME

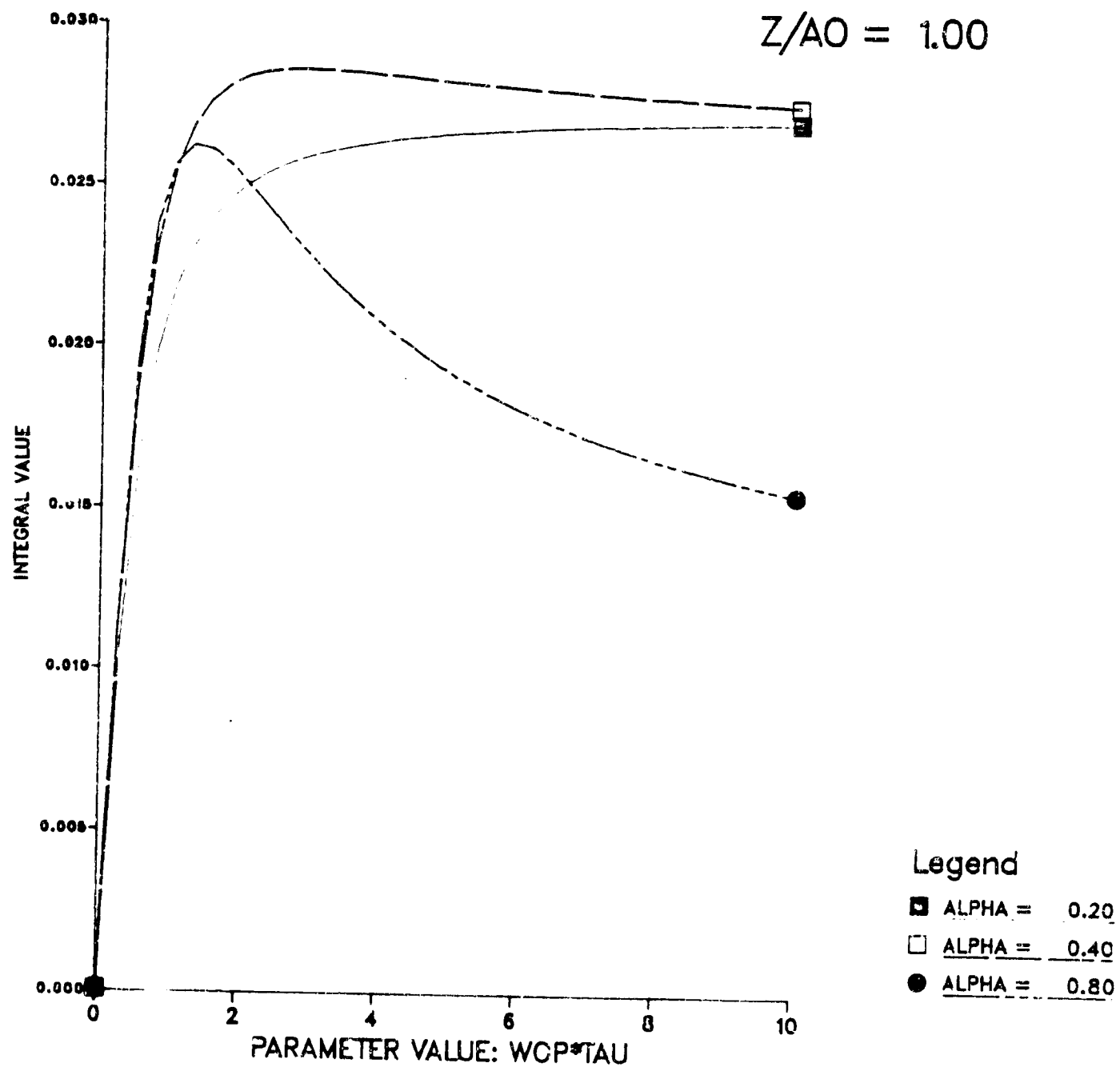
$Z/AO = 1.00$



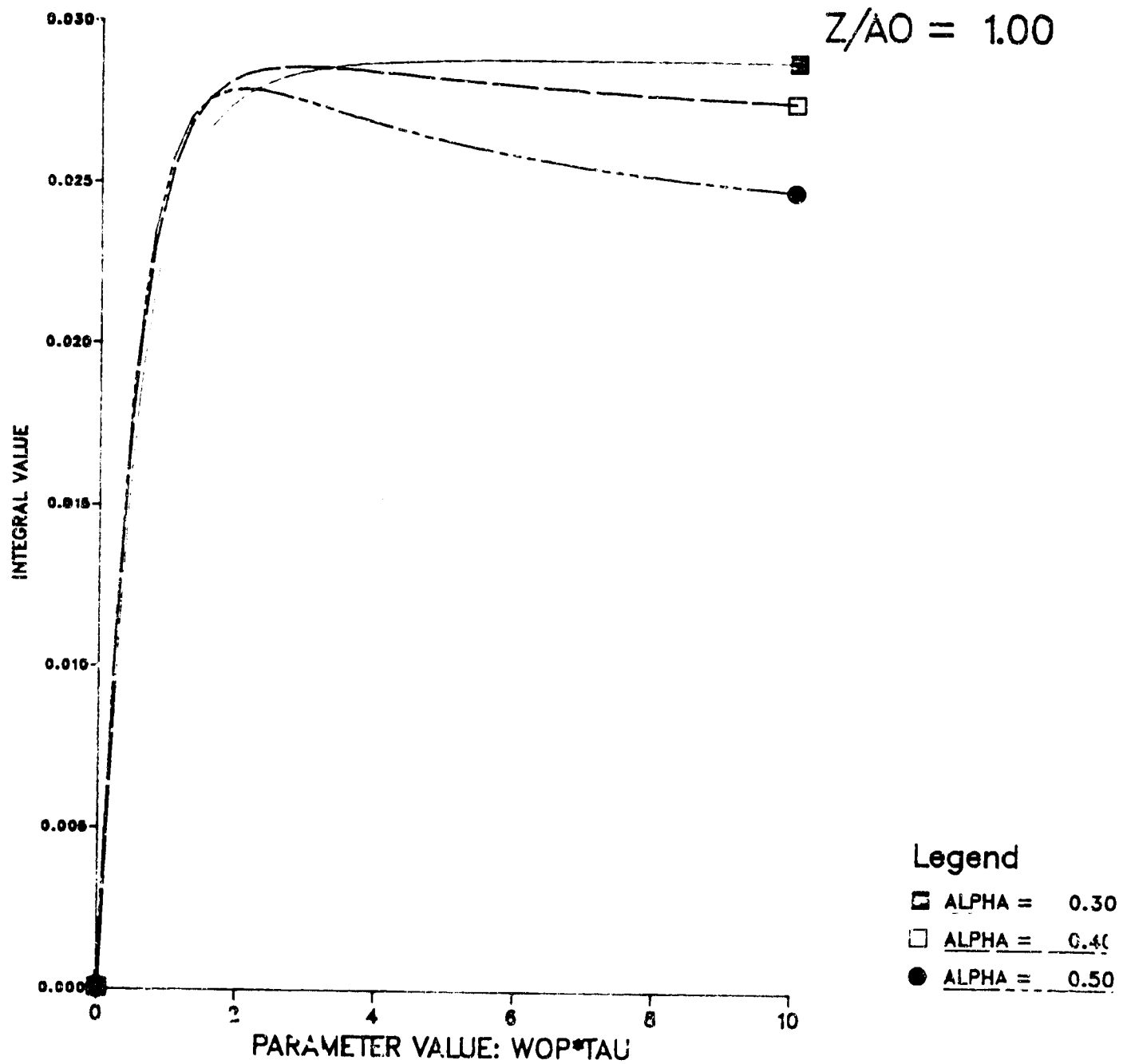
## Legend

- ALPHA = 1.00
- ALPHA = 3.00
- ALPHA = 6.00

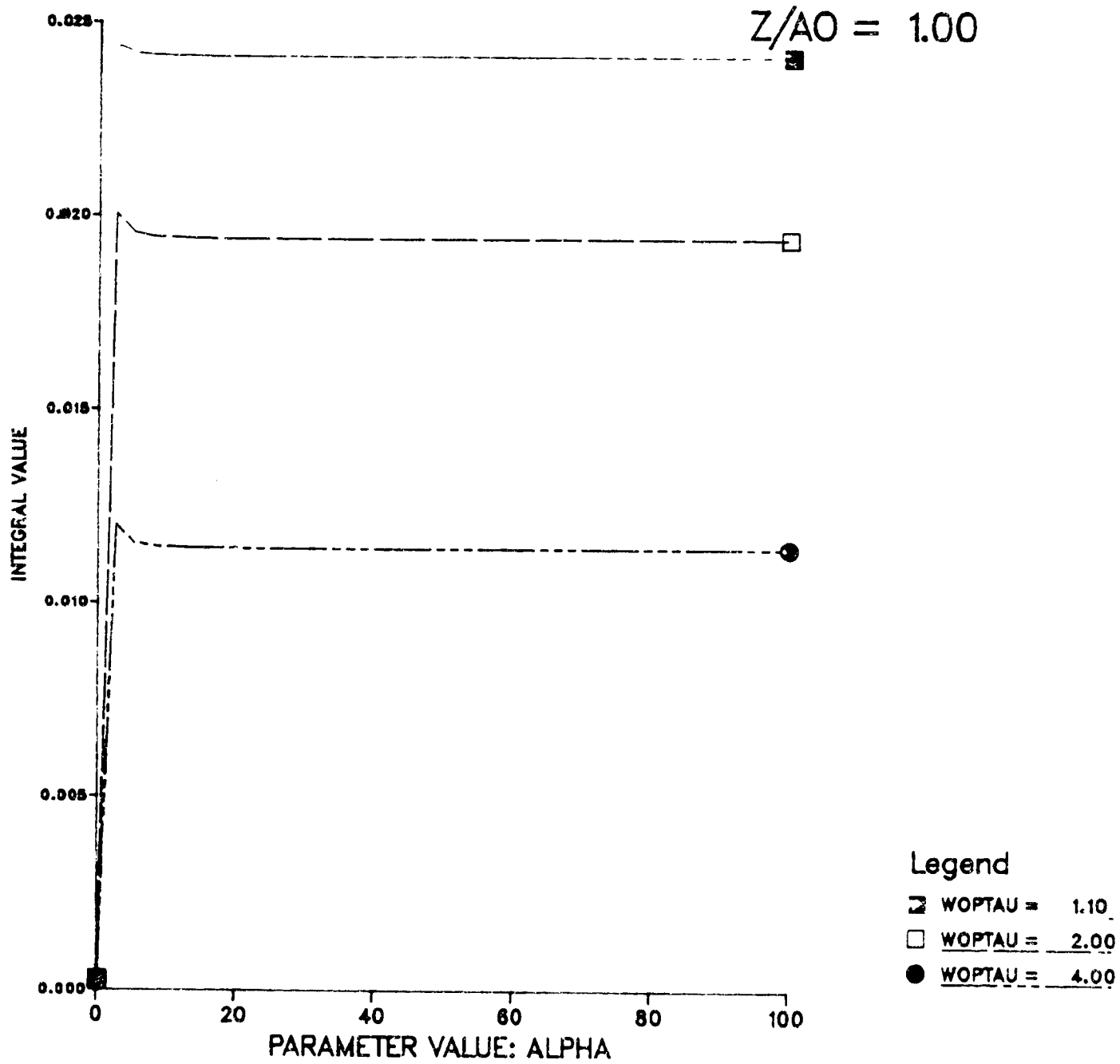
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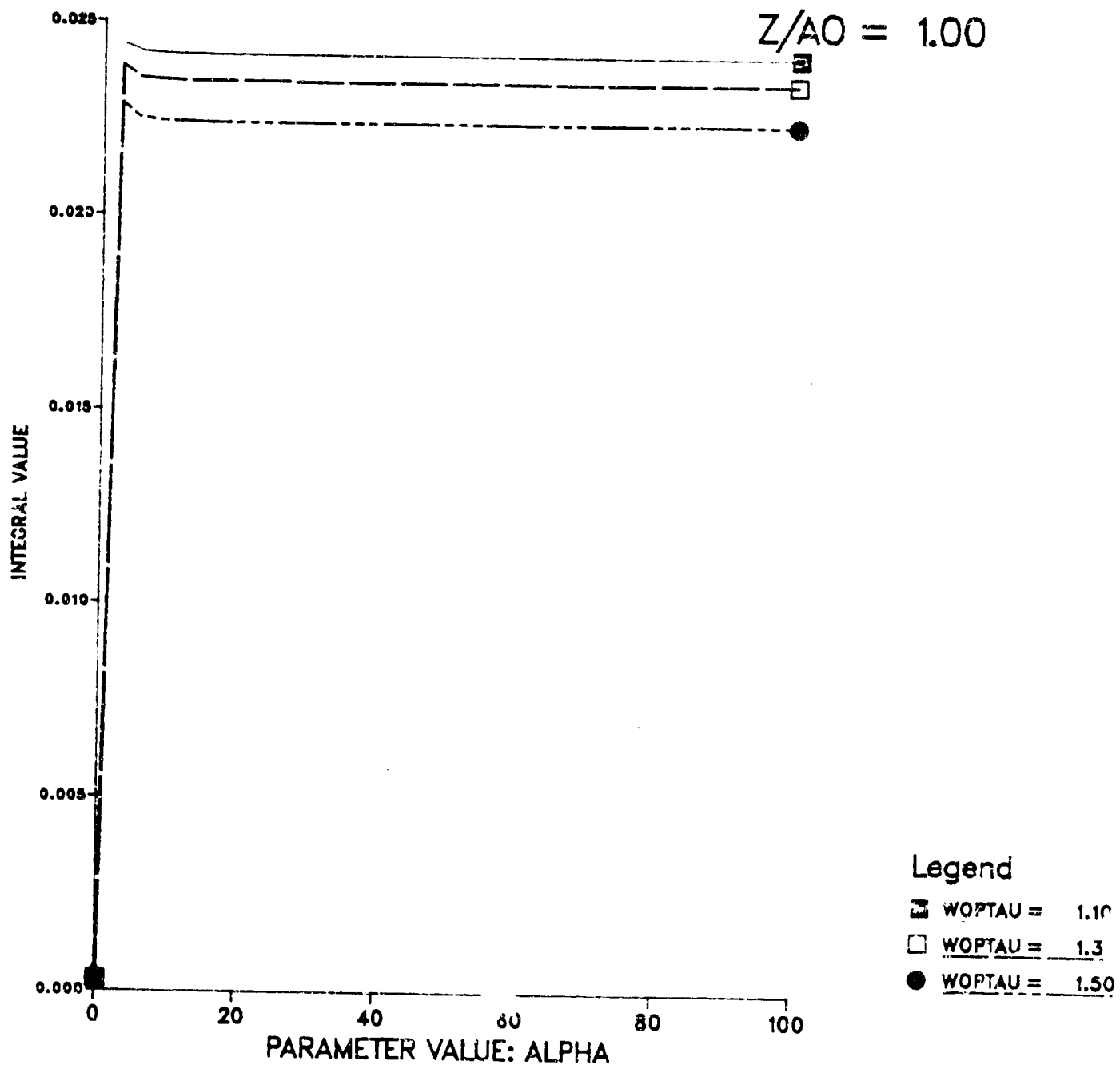
# TWODIM GAS: CAT RATE VERSUS RESIDENCE TIME



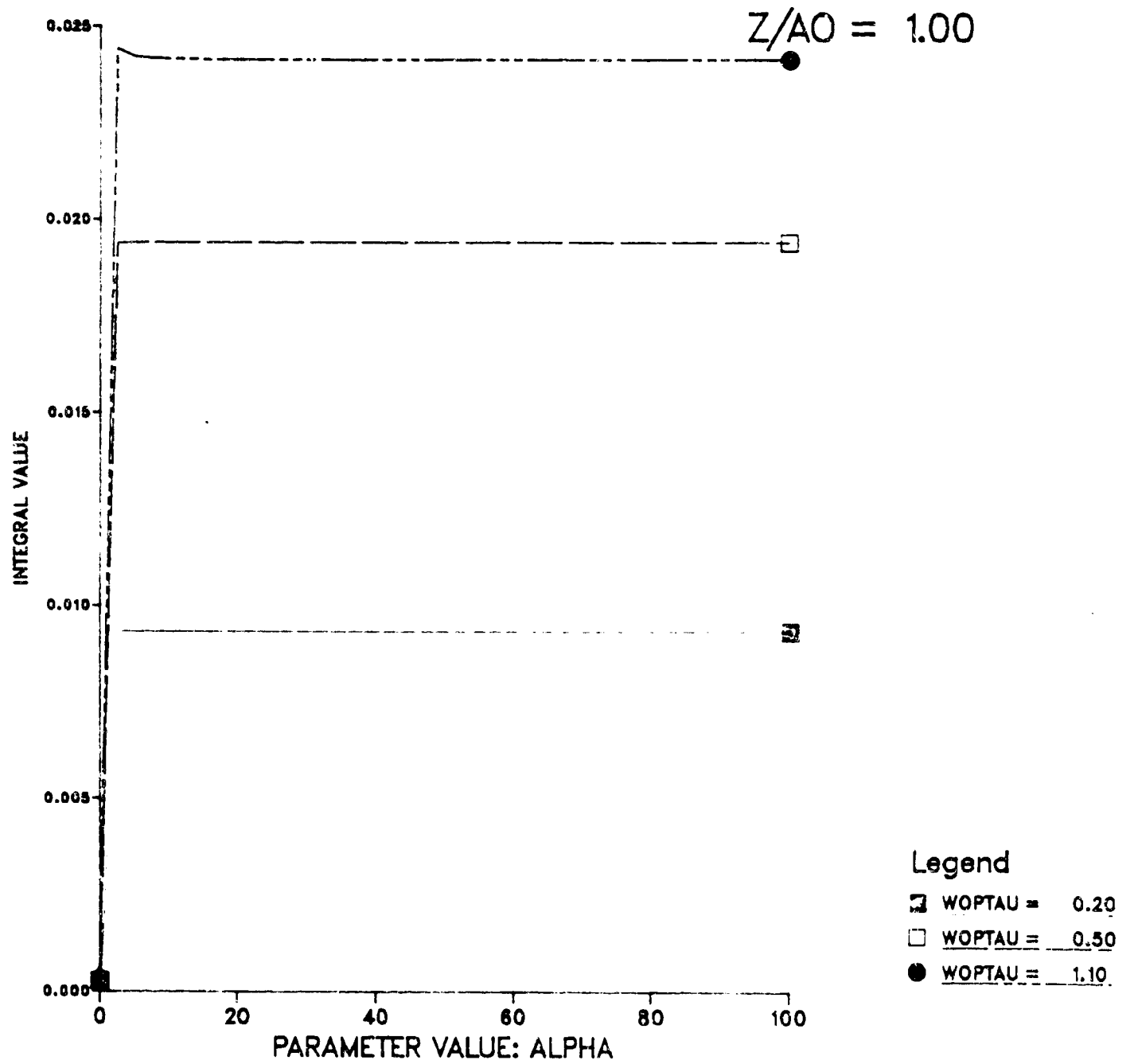
TWODIM GAS: CATALYSIS RATE VERSUS ALPHA FOR GIVEN WOPTAU



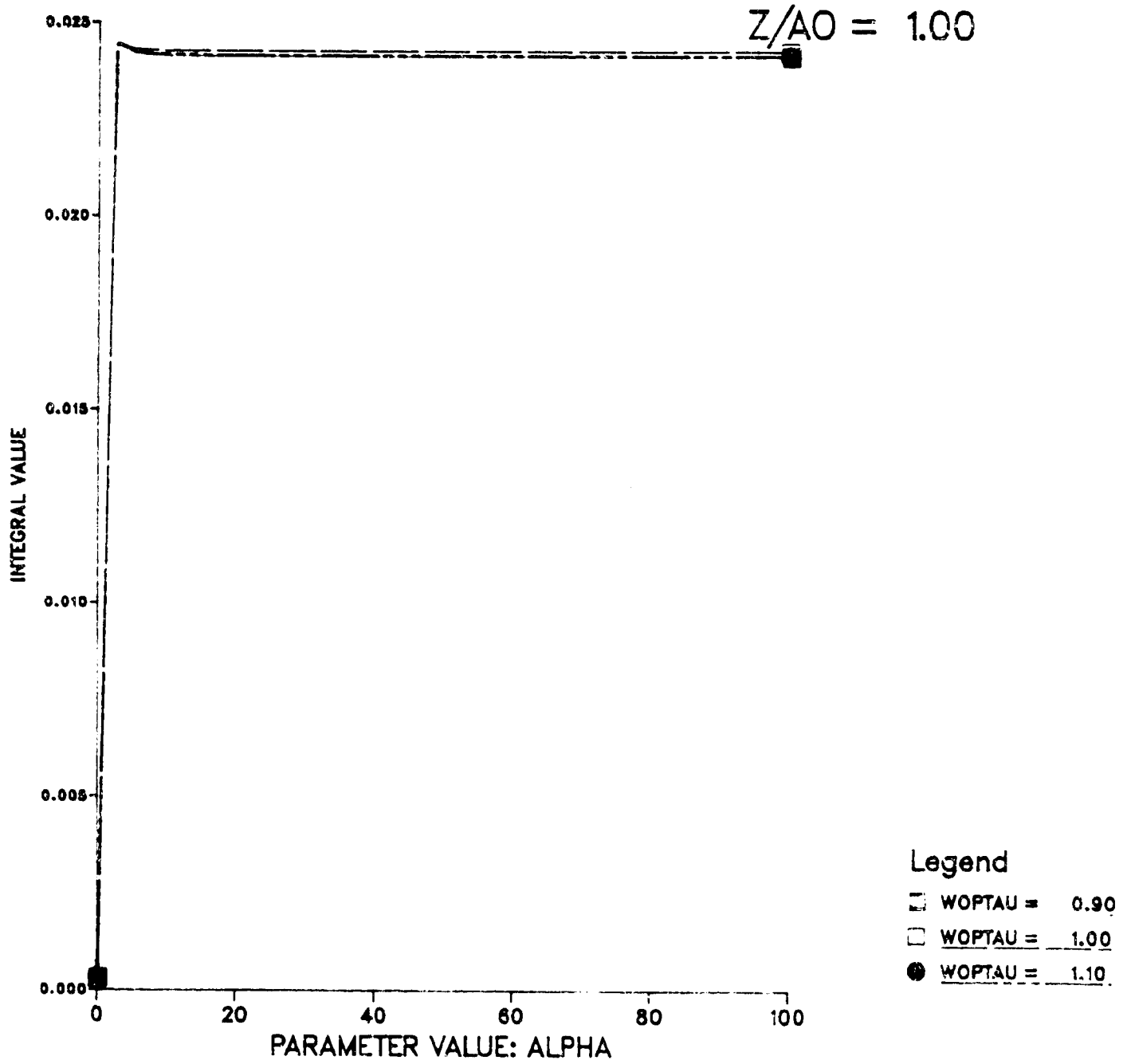
TWODIM GAS: CATALYSIS RATE VERSUS ALPHA FOR GIVEN WOPTAU



TWODIM GAS: CATALYSIS RATE VERSUS ALPHA FOR GIVEN WOPTAU



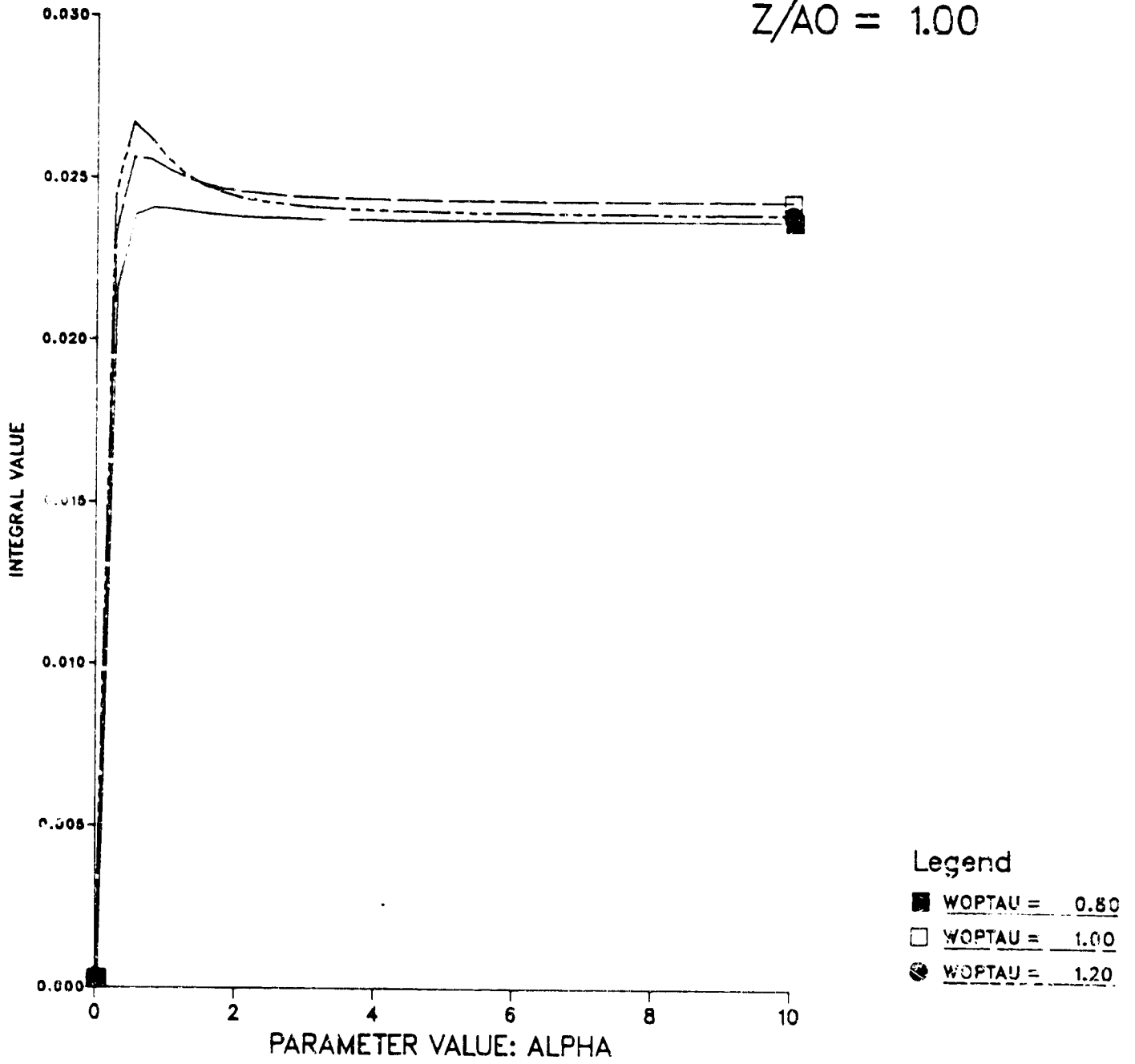
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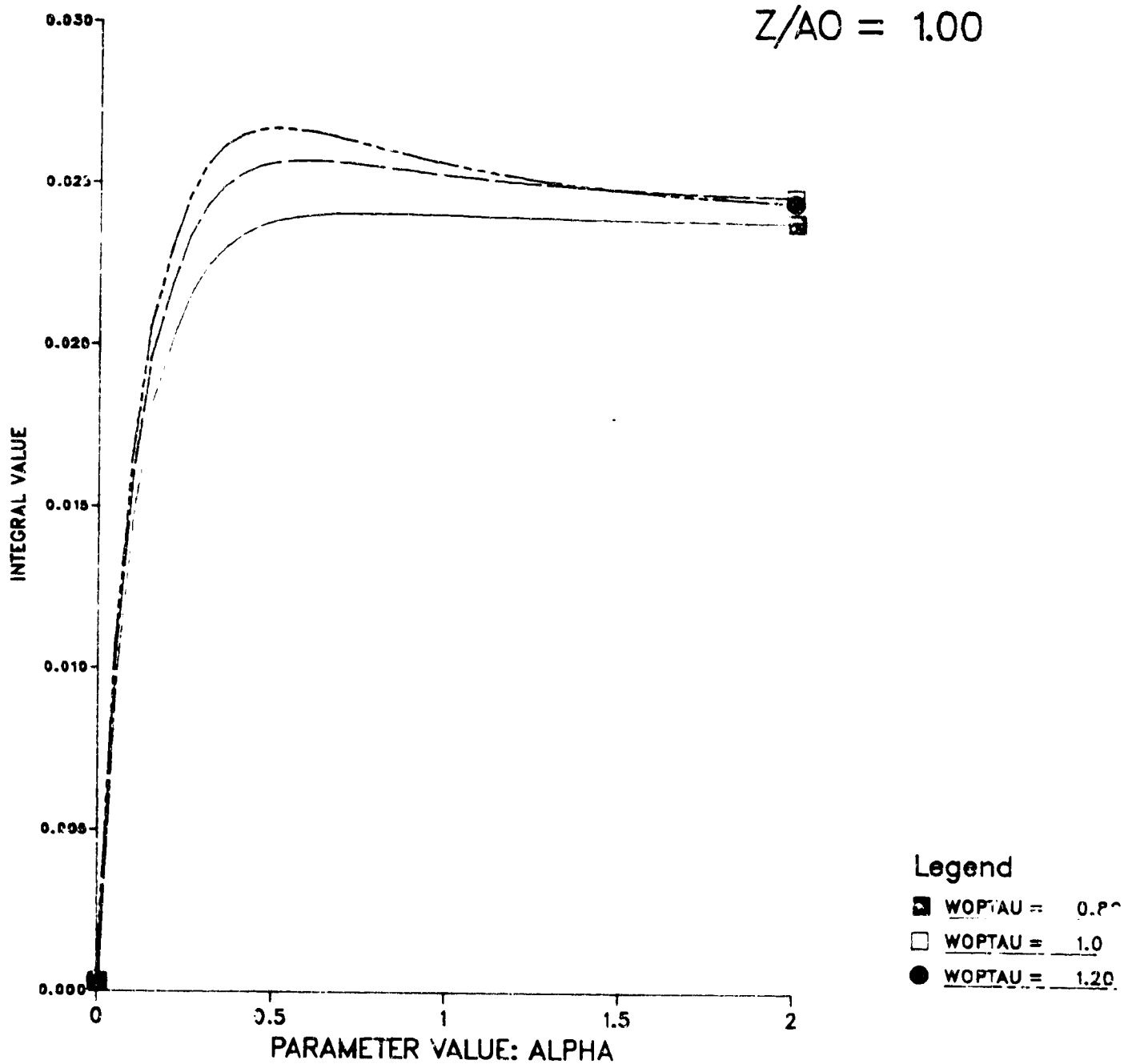


TWODIM GAS: CATALYSIS RATE VERSUS ALPHA FOR GIVEN WOPTAU

Z/AO = 1.00



TWODIM GAS: CATALYSIS RATE VERSUS ALPHA FOR GIVEN WOPTAU



# THEORY OF PARA TO ORTHO HYDROGEN CATALYSIS.

March 14, 1990

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V. General Considerations of the Catalytic Rate for Para to Ortho Hydrogen Conversion in the Vicinity of the Paramagnetic to Ferromagnetic or Antiferromagnetic Phase Transition.

## Abstract.

Most dense magnetic systems become magnetically ordered at a particular critical temperature: The Curie temperature,  $T_C$ , for ferromagnetic systems or the Neel temperature,  $T_N$ , for antiferromagnetic systems. In the magnetically ordered state, the excitation energy for para to ortho hydrogen catalysis may be carried away by the magnetic excitations (magnons) which represent long-range oscillations of the magnetic spins. This gives rise to two important phenomena:

1. An increase in the rate of para to ortho hydrogen catalysis in the magnetically ordered state, compared to the disordered paramagnetic state, and
2. A critical instability in the rate of catalytic conversion near  $T_C$  or  $T_N$  with the result that the rate of change of the catalytic rate constant (for increasing Temperature) near the critical temperature may become negative.

Thus a bad choice of catalytic material for the cooling of an exothermic process (burning of fuel in a jet engine) could lead to decreased catalytic cooling as an increase in temperature demanded increased cooling. A good understanding of this process and experimental measurements of the catalytic process through an appropriate temperature range would be necessary to avoid such a situation.

## RATE OF CATALYSIS INCLUDING MANY-SPIN CORRELATION

The rate of para to ortho hydrogen catalysis was found, in earlier reports, from a simple formula which requires calculation of a relaxation function and performing at least one integration:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \left(\frac{1}{h}\right)^2 \int_0^{\infty} \bar{\Phi}(t) dt$$

where  $\bar{\Phi}(t)$  is, for any magnetic model of the catalytic surface, given by the expression:

$$\bar{\Phi}(t) = e^{-i\bar{\omega}_{op}t} \sum_{\mu} G_{\mu}(\hat{b}) \quad (\otimes)$$

$$\sum_{\mathbf{q}} \left\langle e^{-i\bar{\mathbf{q}} \cdot [\bar{\mathbf{r}}(t) - \bar{\mathbf{r}}(0)]} \right\rangle \sum_{i=x,y,z} \beta_{\mu}^{(i)}(\bar{\mathbf{q}}) \beta_{\mu}^{(i)*}(\bar{\mathbf{q}}) \left\langle S_{-\mathbf{q}}^{(i)}(t) S_{\mathbf{q}}^{(i)}(0) \right\rangle$$

For the paramagnetic case, the correlation function of the magnetic spins on the catalyst surface which is represented by:

$$\langle S_{-\mathbf{q}}(t) S_{\mathbf{q}}(0) \rangle$$

has the simple evaluation:

$$\langle S_{-\mathbf{q}}(t) S_{\mathbf{q}}(0) \rangle = \frac{1}{N} \frac{N_S}{N} \frac{S(S+1)}{3}$$

Where  $N_S$  is the number of spins, and  $N$  is the total number of surface atoms of the same type (but not necessarily all paramagnetic). Therefore,  $N_S/N$  is the fraction of potential catalytic sites on the surface which are paramagnetic. This simple result applies only to the paramagnetic case, i.e. the magnetic spins on the catalyst surface have a

random character and do not interact over a long range.

The correlation function for the magnetic spins on the surface has a more complicated form if interaction with the lattice spin system is to be included in the rate calculation. Assuming that the spin Hamiltonian is pure exchange:

$$\mathcal{H}(S_{\pm} \text{ ins}) = \mathcal{H}(\text{exchange})$$

and then assuming a simplified model (the molecular field or Weiss-field model) for the exchange Hamiltonian, one finds eventually the result (where now  $N_S/N = 1$ ):

$$\langle S_q(t) S_{-q}(0) \rangle = \frac{1}{N} \left\{ \langle S_z^2 \rangle - \langle S_z \rangle^2 + \frac{1}{2} e^{iH_m t} \langle S_+ S_- \rangle + \frac{1}{2} e^{-iH_m t} \langle S_- S_+ \rangle + \langle S_z \rangle^2 \delta_{\vec{q}, \vec{0}} \right\}$$

where  $H_m$  is the energy (per spin) of the effective exchange field which orders the spins in the ferromagnetic or antiferromagnetic state.

The result of this changed form of the correlation function is to modify the terms in the integral over time in the basic expression for the rate constant giving rise to integral terms of more complicated form:

$$\int_0^{\infty} e^{-i(\bar{\omega}_{op} \pm H_m/\hbar)t} (\dots) dt$$

which terms only exist in the ordered magnetic state. (In the disordered state,  $H_m = 0$ ). The real part of the expression for this rate will therefore have a peak in the vicinity of

$$\bar{\omega}_{(0-p)} = H_m/\hbar$$

which will be modified if other motion or relaxation terms are included in the basic expression for the time dependence of  $\bar{Q}(t)$ .

Now, the energy of the internal field  $H_m$  is determined in the molecular field theory by the Brillouin function, represented by the symbol  $B_S$ :

$$H_m = \frac{3kT_c}{S+1} B_S\left(\frac{H_m S}{kT}\right)$$

which is the formula for the effective field energy,  $H_m$ , in a ferromagnetic lattice. Now an antiferromagnetic lattice is made up of two sublattices, each of which is ordered by a similar internal magnetic field, except that each sublattice is ordered in the opposite direction to its neighbor. One notes that  $H_m$  is found as a self-consistent quantity, and that the value of  $H_m$  depends on the ratio  $T/T_c$ . The behavior of  $H_m$  as a function of  $T/T_c$  is well known (both in theory and experiment).  $H_m$  is maximum at  $T=0$  Kelvin, and vanishes at  $T=T_c$ . However, just below the critical temperature ( $T_c$  or  $T_N$ ) the value of the internal field, and the energy associated with it, increases dramatically! This therefore gives rise to an increase in the value of the rate constant  $k$  (para---> ortho) just below the transition temperature as the catalyst goes over from the disordered state to the ordered state. Physically, this increase corresponds to the additional process of para to ortho excitation energy being transferred into long-range magnetic excitations (magnons) which only exist when long-range magnetic order sets in.

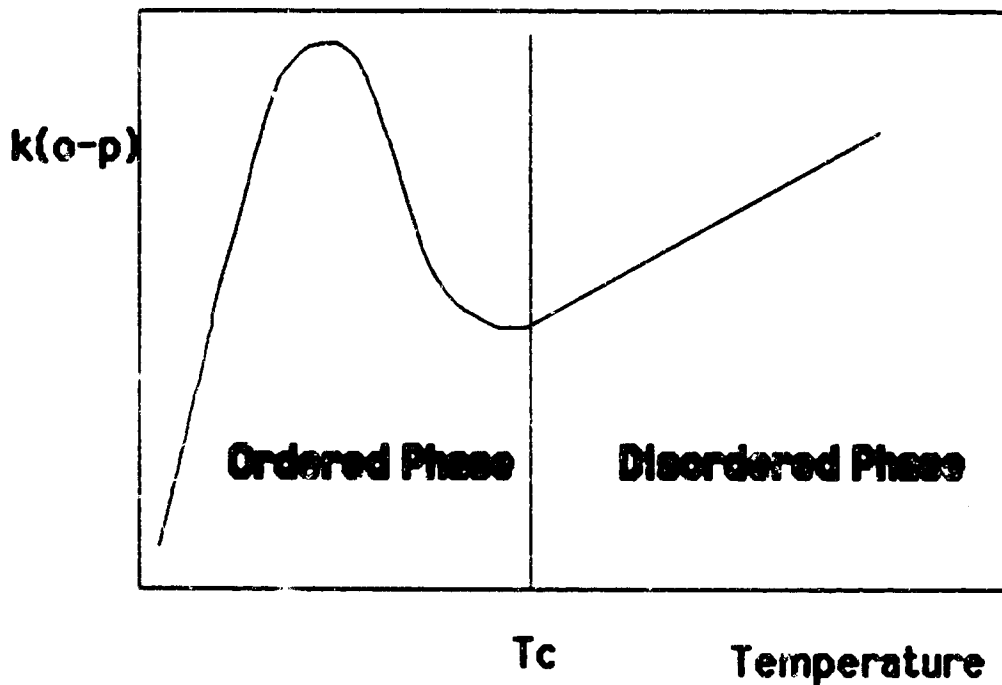


Figure 1 (Conceptual). Rate constant  $k(\text{para} \rightarrow \text{ortho})$  in the vicinity of the magnetic phase transition.

One can readily see from the diagram that just below  $T_C$  or  $T_N$ , the rate of change of the rate constant versus  $T$ :

$$\frac{dk(\text{para} \rightarrow \text{ortho})}{dT} = \text{a negative quantity}$$

which can give rise to the difficulties pointed out earlier.

## NUMERICAL MODELLING OF k(PARA-->ORTHO) IN THE VICINITY OF THE MAGNETIC PHASE TRANSITION.

In the vicinity of the magnetic phase transition, the number and type of magnetic excitations, which cooperate with the para-->ortho transformation, vary rapidly with temperature. The theory developed to this point shows clearly that this process is associated with only one quantity (for any model): the spin correlation function, represented by:

$$\langle S_q(t)S_{-q}(0) \rangle$$

where the brackets indicate ensemble averages. A means must be found to calculate this quantity versus temperature including the effect of the phase transition at the critical temperature  $T_c$  (or  $T_N$ ). If this quantity is then added to the previous expressions for paramagnetic catalysis which include the effects of a surface gas or surface two-dimensional liquid, then one would arrive at a theory for the general behaviour of k(para-->ortho) in the vicinity of the magnetic phase transition (as well as away from it!).

There are two ways to proceed:

(A) Use the molecular field approximation for the magnetic exchange interaction. In this approximation, the exchange interaction is replaced by an effective (large) magnetic field interacting with the Zeeman spin operator of each magnetic spin. The effective field is represented by the Brillouin function which incorporates a temperature dependence and by solving this function by implicit means is found to vary with  $T/T_c$ . This is the minimum requirement for a modelling of the average exchange interaction over the many spin system, which incorporates the phenomenon of a magnetic phase transition. The concept of magnons, and the lattice 'q' or 'k' vector is missing in this model. This is the model worked out by Ishii.

(B) Use the magnon concept and work directly with the spin correlation function using the Fourier transformed spin operators. This model correctly incorporates lattice k-vectors (and magnons!) but does not ordinarily include any average properties of the exchange interaction or have dependence on temperature and display a discontinuity in the vicinity of the magnetic phase transition. Due to these inconsistencies,



this model has not been developed previously since something additional is required in order to make the magnon model work. The extra idea arises from the theory of thermal Green's functions which when applied to the motion of the magnons and the magnon energy leads to a renormalization of the magnon energy in a way which includes a thermal average of the z-component of the spin. The renormalized magnons have the standard energy at T=0 Kelvin, but have monotonically decreasing energy as T → T<sub>C</sub>. That is, they display the correct property of vanishing at the critical temperature, and therefore displaying the phase transition property.

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Reference: D. Wagner, "Introduction to the Theory of Magnetism", Pergamon Press (1972). See Chapter III, Ferromagnetism.

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The idea is this: the conventional magnon energy expression is temperature independent, but the renormalized magnons have energy:

$$\tilde{\epsilon}_k = g\beta H - 2s\sigma(J_0 - J_k)$$

where  $\sigma = \langle S_z \rangle$  (which is proportional to the net magnetization) goes to 0 as T → T<sub>C</sub>. An equation for  $\sigma$  is

$$\sigma(T) = 1 - \frac{4s\sigma(T)}{N} \sum_k \bar{n}_k$$

where  $\bar{n}_k$  = the bose-Einstein population of magnons, i.e.

$$\bar{n}_k = \frac{1}{\exp(\tilde{\epsilon}_k/kT) - 1}$$

We can therefore find an implicit solution for  $\sigma(T)$  at any low temperature, defined by T ≪ T<sub>C</sub>. Now, at high temperature,  $\sigma(T)$  is small by definition, so we can find an explicit solution for  $\sigma(T)$  in the

vicinity of (just below)  $T_c$ . The solution is easily found to be:

$$\sigma(T) = 1 - \frac{2kT}{N} \sum_{\mathbf{k}} (J_0 - J_{\mathbf{k}})$$

where  $J_0$  and  $J_{\mathbf{k}}$  are exchange coefficients ("exchange integrals"). Since the average value of  $S_z$ ,  $\langle S_z \rangle = \sigma$ , = 0 at the critical temperature, we can solve for  $T_c$ :

$$\frac{1}{kT_c} = \frac{2}{N} \sum_{\mathbf{k}} \frac{1}{(J_0 - J_{\mathbf{k}})}$$

Thus, the energy of the renormalized magnons  $\rightarrow$  zero as  $T \rightarrow T_c$ . When incorporated into the theory for the rate constant  $k(\text{para} \rightarrow \text{ortho})$  this will give the result that there will be an increase in the rate constant just below  $T_c$ . How sharp or diffuse this change may be will only be determined by completing the theory for this effect and doing the numerical simulations of the rate constant, versus temperature.

The corollary of this increase in rate constant, will be a negative rate of change of  $k(\text{para} \rightarrow \text{ortho})$  versus increasing temperature for  $T$  just below  $T_c$ . However, we cannot yet say just how far below  $T_c$  this effect will extend.

## Completion of the Project

The earliest phase of this project consisted of working through the classic calculations of the rate of para to ortho hydrogen catalysis. The second stage concerned the working out of a master equation for the rate of paramagnetic catalysis, and then working out numerical results for the specific models of Hydrogen molecules existing on the surface as a two dimensional gas or as a two dimensional liquid. These results, which were summarized in four reports (spring, summer and fall of 1989), were found to be consistent with earlier workers' calculations and gave some insight into the role of residence time on the catalytic surface in determining the rate of catalysis, as well as the complete set of variables which control the net catalytic rate. An important outcome is the idea that there is an optimum rate of catalysis for any paramagnetic model and a given change in one independent parameter may cause an increase in catalytic rate for one catalyst and a decrease for another catalyst. (So it is helpful to infer on which side of optimal a given catalyst is functioning).

The unfinished part of this project is to expand the model(s) to include the effects of a magnetic phase transition from ferromagnetic to paramagnetic, or antiferromagnetic to paramagnetic. This is an important phenomenon to understand since in the vicinity of this transition one may observe negative rates of change of catalyst performance with respect to increasing temperature. As with the other steps in this study, there is a conceptual problem to be solved first, for which I believe I now see the solution. That is, how to include the magnon concept in the modelling in a manner which incorporates the phase change behavior in the vicinity of the critical temperature  $T_C$  (ferromagnetic) or  $T_N$  (antiferromagnetic). One must then proceed to a numerical stage to adequately visualize the significance of these phase change phenomena on the para to ortho hydrogen catalyst rate. These results should be adequate to explain the general behavior of any catalytic system (other than metallic), and give guidance to synthetic and other practical studies.

## Theory of Para to Ortho Hydrogen Catalysis

### VI. The Surface Diffusion Model for Paramagnetic Catalysis Using Transition State Theory for the Migration of Hydrogen Molecules Between Different Catalytic Sites.

April 12, 1991

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#### Abstract

The theory for para to ortho hydrogen catalysis on a paramagnetic surface has been developed based on the model of a two-dimensional liquid on the surface. This model has now been extended to include the effects of a surface lifetime ' $\tau$ ', and a step-size 'd' with an activation energy,  $E_d^*$ , using transition state theory for the surface diffusion coefficient. In this extended model, the dimensionless parameter ' $\gamma$ ' defined by

$$\gamma = \frac{\omega_{op} z^2}{4D}$$

is interpreted with this formula for the diffusion coefficient:

$$D = d^2 \left( \frac{kT}{h} \right) e^{-E_d^*/kT}$$

The important physical parameters which control the catalytic process are now:

z (height above the surface)  
d (diffusion stepsize) and  
 $a_G$  (unit cell length)

all of which are lengths, and

$$E_d^* \text{ (activation energy)}$$

$$(h/2\pi)\omega_{op} \text{ (the first para - ortho splitting)}$$

both of which are energies, and finally the surface lifetime, ' $\tau$ '.

An analysis of the catalytic rate of conversion of para to ortho hydrogen is then developed in terms of four dimensionless parameters constructed from the set of dimensioned parameters above. This new set of parameters is:

$$z/d \quad \text{and} \quad z/a_0$$

which are length ratios,

$$\frac{E_d^*}{(h/2\pi)\omega_{op}}$$

which is a ratio of energies, and finally

$$\omega_{op}\tau$$

which is a dimensionless product of a frequency times the surface lifetime. The integrals for the rate process are then calculated numerically and plotted versus the temperature,  $T$ , in degrees Kelvin.

Careful numerical modelling of this model, for a paramagnetic type catalyst, shows that an optimal choice of parameter values leads to a nearly temperature independent catalytic rate over a wide temperature range (e.g. 50 to 300 K), but a non-optimal choice of parameters may lead to strong temperature dependence over the same range.

The step size of the diffusion process (through  $z/d$ ) and the relative value of the activation energy of surface diffusion seem to have effects primarily related to the shape of the catalytic rate dependence on temperature, while the major determinants of the absolute catalytic rate are the distance from the surface (' $z$ ' through the 'constant' term and the  $z/d$  dimensionless parameter in the integral) and the surface lifetime.

## Table of Contents.

- I. Method of analysis.
- II. The two dimensional surface diffusion model with surface lifetime  $\tau$ .
- III. The para to ortho catalysis rate in terms of dimensionless parameters..
- IV. The transition state model for surface diffusion.
- V. Results of numerical calculations:
  - A. Integral value versus xratio.
  - B. Integral value versus woptau.
  - C. Integral value versus zaratio.
  - D. Integral value versus zdratio.
  - E. Integral value versus woptau for optimal conditions.
- VI. Conclusions.
- VII. References.

### I. Method of Analysis.

The rate of para to ortho hydrogen catalysis is calculated from the first principles results (derived in earlier reports):

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \left(\frac{1}{h/2\pi}\right)^2 \int_0^{\infty} \Phi(t) dt$$

where

- b = the H<sub>2</sub> bond length
- $\mu_p$  = proton magnetic dipole moment.
- h = Planck's constant.
- $\Phi(t)$  = a relaxation function

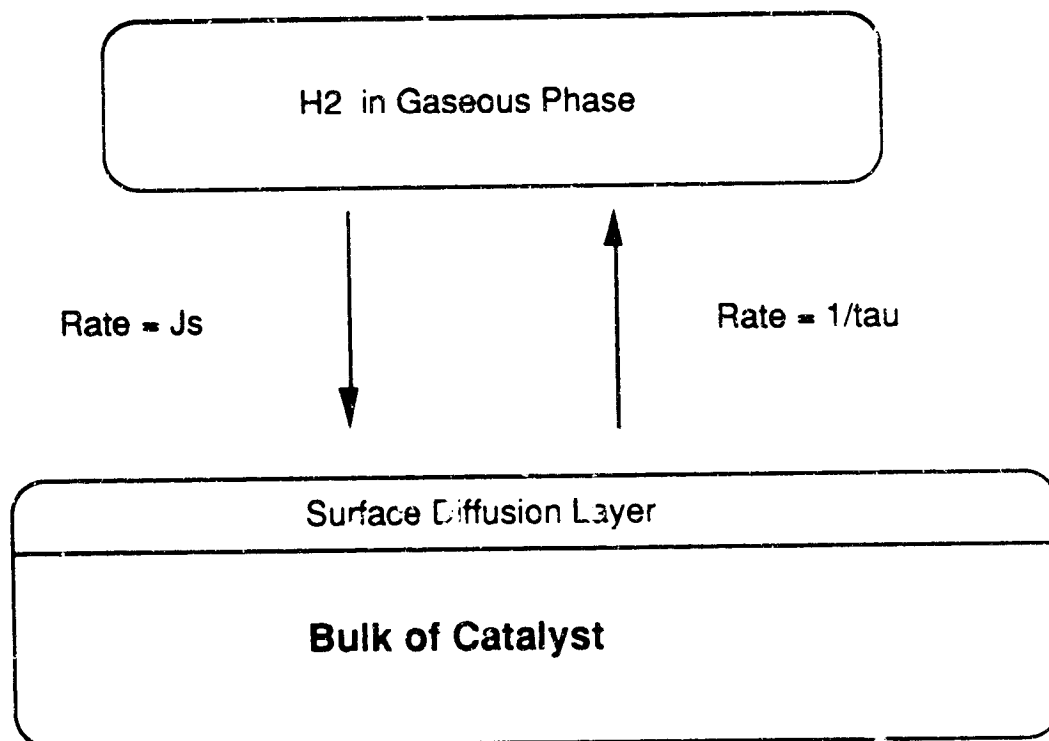
The general form of  $\Phi(t)$  for any magnetic model for the surface catalysis process (whether the surface is paramagnetic, ferromagnetic or antiferromagnetic) is as follows:

$$\Phi(t) = e^{-i\bar{\omega}_{op}t} \sum_{\mu} G_{\mu}(\hat{b}) \quad X$$
$$\sum_{\mathbf{q}} \langle e^{-i\mathbf{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \rangle \sum_{x,y,z} \beta_{\mu}^{(i)}(\mathbf{q}) \beta_{\mu}^{(i)*} \langle S_{\mathbf{q}}^{(i)}(t) S_{\mathbf{q}}^{(i)}(0) \rangle$$

The quantity  $\Phi(t)$  must then be evaluated according to the physical model under consideration, and then the indicated integrations, summations and ensemble averages performed.

## II. The Two-dimensional Surface Diffusion Model with Surface Lifetime 'Tau'.

The model for a two dimensional gas on the catalyst surface is developed in accordance with the scheme outlined in this figure:



Here,  $J_s$  represents the rate at which gaseous molecules collide with the surface (calculated from the kinetic theory of gases), and  $1/\tau$  is the rate at which molecules on the surface return to the gaseous phase. The distance 'Z' represents the height of the surface diffusion layer and is defined as the average distance of the hydrogen molecules from the surface plane containing the centers of the electronic spin magnetic moments. It is these magnetic moments, in turn, which create the inhomogeneous surface magnetic field necessary for flipping the nuclear spins of the hydrogen molecules on the surface.

According to this model for para to ortho hydrogen catalysis, the relaxation function  $\Phi(t)$ , is determined by evaluating the functional form of the four different terms which define the function. The most



important term for defining  $\Phi(t)$  in this model is the correlation function for the movement of the  $H_2$  molecules in the surface diffusion layer:

$$\langle e^{-i\vec{q} \cdot [\vec{r}(t) - \vec{r}(0)]} \rangle = e^{-Dq^2t} e^{-t/\tau}$$

Substituting this relation into the expression for the relaxation function,  $\Phi(t)$ , and substitution and evaluation of the other three functions gives, finally, the following expression for the rate of para to ortho conversion:

$$W_{p \rightarrow o} = \left(\frac{b}{2}\right)^2 \mu_p^2 \frac{4}{3} \frac{1}{(h/2\pi)^2} \left(\frac{N_s}{N}\right) \frac{S(S+1)}{3} \frac{16\pi^2 \mu_A^2}{a_0^2} \times$$

$$\int_0^{\infty} q^5 e^{-2qz} dq \int_0^{\infty} \cos \overline{\omega_{op}t}$$

where:

$D$  = the diffusion coefficient for the diffusion of hydrogen molecules over the catalyst surface.

$\tau$  = the lifetime of the hydrogen molecules in the surface layer (i.e. the reciprocal of the rate of escape from the surface).

$a_0$  = the lattice constant of the crystal face comprising the catalyst surface.

$\mu_A$  = the magnetic moment of the surface atom or molecule, of type 'A'.

$S$  = the electronic spin of 'A'.

$\omega_{op}$  = the average splitting in energy between the first para and ortho pair of states, measured in frequency units : radians/sec.

### III. Para to Ortho Hydrogen Catalysis Rate in Terms of Dimensionless Parameters.

The rate of para to ortho hydrogen catalysis, for this model, may be condensed to a simple expression which involves a 'constant' term and two integrals which are functions of dimensionless parameters. The expression for  $W_{p \rightarrow o}$  is :

$$W_{p \rightarrow o} = K \{G_1(\gamma, \overline{\omega_{op}\tau}) + G_2(\gamma, \overline{\omega_{op}\tau})\}$$

where the 'constant' K is defined by:

$$K = \frac{4\pi^2}{(h/2\pi)} \left(\frac{N_s}{N}\right) \frac{S(S+1)}{3} \left(\frac{b}{a_0}\right)^2 \frac{\mu_p^2 \mu_A^2}{Z^6} \left(\frac{1}{2B}\right)$$

and the dimensionless parameters which are arguments of the integrals  $G_1$  and  $G_2$  are defined by:

$$\gamma = \frac{\overline{\omega_{op}Z^2}}{4D}$$

and

$$\overline{\omega_{op}\tau} = \overline{\omega_{op}} * \tau$$

The range of the  $\gamma$  and  $\overline{\omega_{op}\tau}$  parameters is easy to deduce, by studying the physical models for the parameters which, in turn, define them.

The integrals which must be evaluated are defined by:

$$G_1(\gamma, \overline{\omega_{op}\tau}) = \frac{256\gamma}{3} \int_0^{\overline{\omega_{op}\tau}} \frac{y^7 e^{-4y} dy}{\left(y^2 + \frac{\gamma}{\overline{\omega_{op}\tau}}\right)^2 + \gamma^2}$$

for the first integral. The other integral is given by:

$$G_2(\gamma, \overline{\omega_{op}}\tau) = \frac{256\gamma^2}{3\overline{\omega_{op}}\tau} \int_0^{z/d} \frac{y^5 e^{-4y} dy}{\left(y^2 + \frac{\gamma}{\overline{\omega_{op}}\tau}\right)^2 + \gamma^2}$$

These integrals are evaluated numerically on the VAX using the IMSL applied mathematics library.

#### IV. The Transition State Model for Surface Diffusion.

In our previous consideration of the integrals which define the complex behavior of the para to ortho catalysis process, we considered the dimensionless parameter  $\gamma$  strictly as a number with a positive range, e.g.  $\gamma > 0$ . Now, we model  $\gamma$  by introducing the transition state theory expression for diffusion coefficient 'D' expressed in the form:

$$D = d^2 \left( \frac{kT}{h} \right) e^{-E_d^*/kT}$$

where  $d$  = the random-walk steplength,  $kT/h$  = the frequency factor, and  $E_d^*$  = the activation energy for surface diffusion. When this expression for the diffusion coefficient is substituted into the expression for  $\gamma$ , and some rearrangement is done, the result is:

$$\gamma = \frac{\pi}{2} \left( \frac{z}{d} \right)^2 \left[ \frac{(h/2\pi)\overline{\omega_{op}}}{kT} \right] e^{E_d^*/kT}$$

It is helpful to define a set of dimensionless ratios, which are appropriate to the evaluation of the dimensionless parameters  $\gamma$  and  $\overline{\omega_{op}}\tau$ , and the upper limit of the integral. Clearly,  $\gamma$  depends on a ratio of lengths ( $z/d$ ) and two ratios of energies. The natural unit of the activation energy for this problem is clearly the ratio of the activation energy to the fundamental para - ortho energy splitting:

We define this ratio as 'xratio':

$$\text{xratio} = \frac{E_d^*}{(h/2\pi)\overline{\omega_{op}}}$$

Then, the expression for the dimensionless parameter  $\gamma$  becomes:

$$\gamma = \frac{\pi}{2} \left(\frac{z}{d}\right)^2 \left[ \frac{(h/2\pi)\overline{\omega_{op}}}{kT} \right]^{\text{xratio} \cdot (h/2\pi)\overline{\omega_{op}}/kT}$$

Now, instead of the two dimensionless parameters that we had before:

$\gamma$  and  $\omega_{optau}$

we now have a new set of dimensionless parameters:

xratio = (defined above)

zratio =  $z/a_0$

zdratio =  $z/d$

$\omega_{optau} = \overline{\omega_{op}}\tau$

So, the para to ortho catalytic rate will depend on:

$z$  and  $T$

and the four dimensionless parameters above. The sum of the two integrals above was therefore calculated and plotted versus the Temperature  $T$  in degrees Kelvin units. The dependence on ' $z$ ' per se would require a logarithmic plot, and will be studied separately. It is these integrals which define the dependence of the catalytic rate on temperature.

## V. The Results of the Numerical Calculations.

### A. Integral Value versus xratio.

For this calculation, three of the four dimensionless parameters were set to fixed values:

$$\begin{aligned} \text{zaratio} &= 1.00 \\ \text{zdratio} &= 2.00 \\ \text{woptau} &= 1.4 \end{aligned}$$

(It had been determined earlier that an optimal value of frequency times time is woptau on the order of 1.4). Zaratio = 1.00 means a distance of the H<sub>2</sub> molecule from the surface equal to the lattice constant, and zdratio = 2.00 implies a diffusion stepsize of 1/2 of the lattice constant.

The integrals were then calculated with these fixed parameter values, and the ratio of activation energy to para-ortho energy splitting was allowed to vary over these ranges:

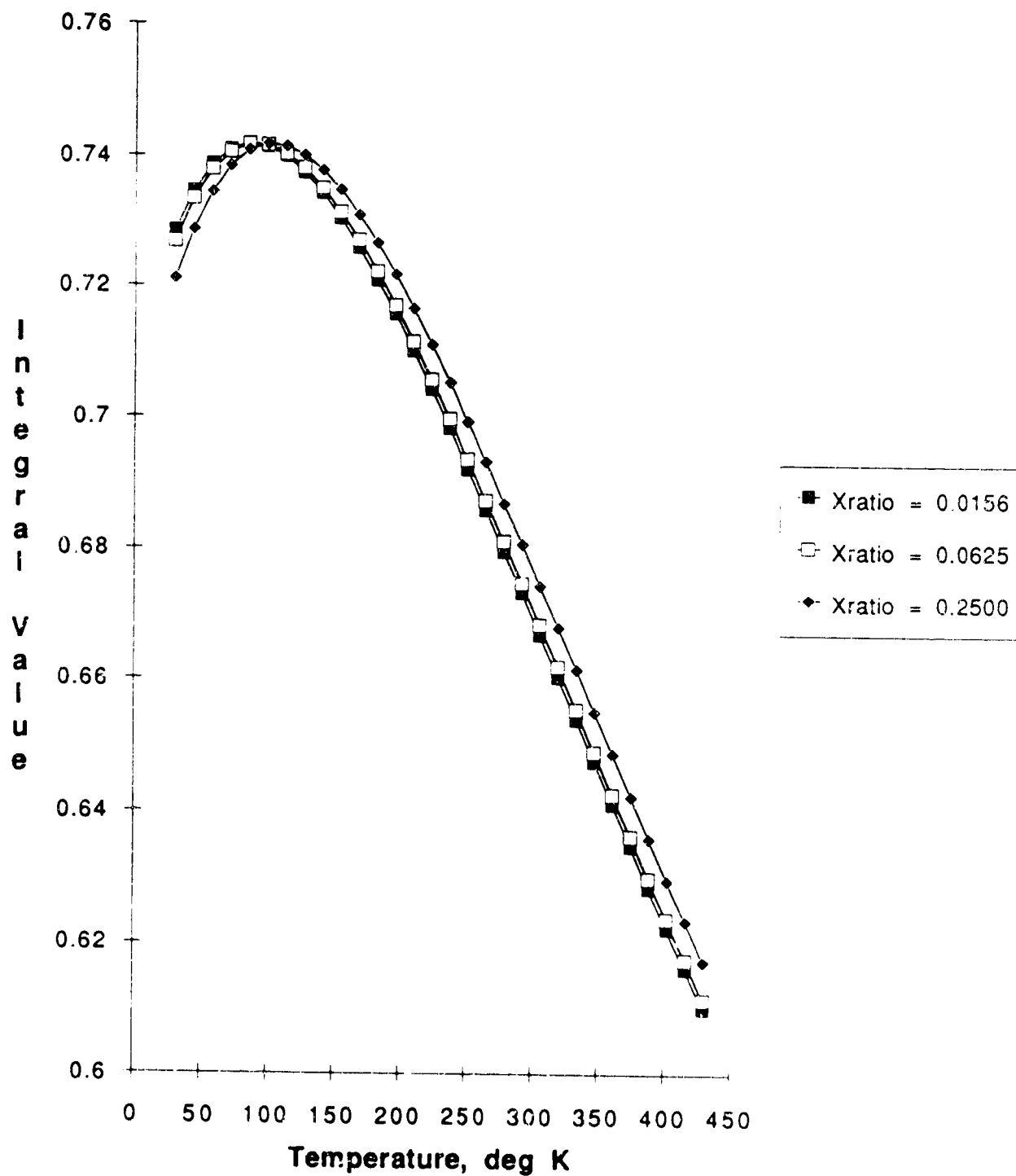
$$\begin{aligned} \text{xratio} &= 0.0156, 0.0625 \text{ and } 0.2500 \\ \text{xratio} &= 0.2500, 1.0000 \text{ and } 4.000 \\ \text{xratio} &= 4.000, 8.000 \text{ and } 16.000 \end{aligned}$$

The quantity plotted is, in each case, the sum of the two integrals defining the catalytic rate, versus the temperature T, in degrees K. Thus:

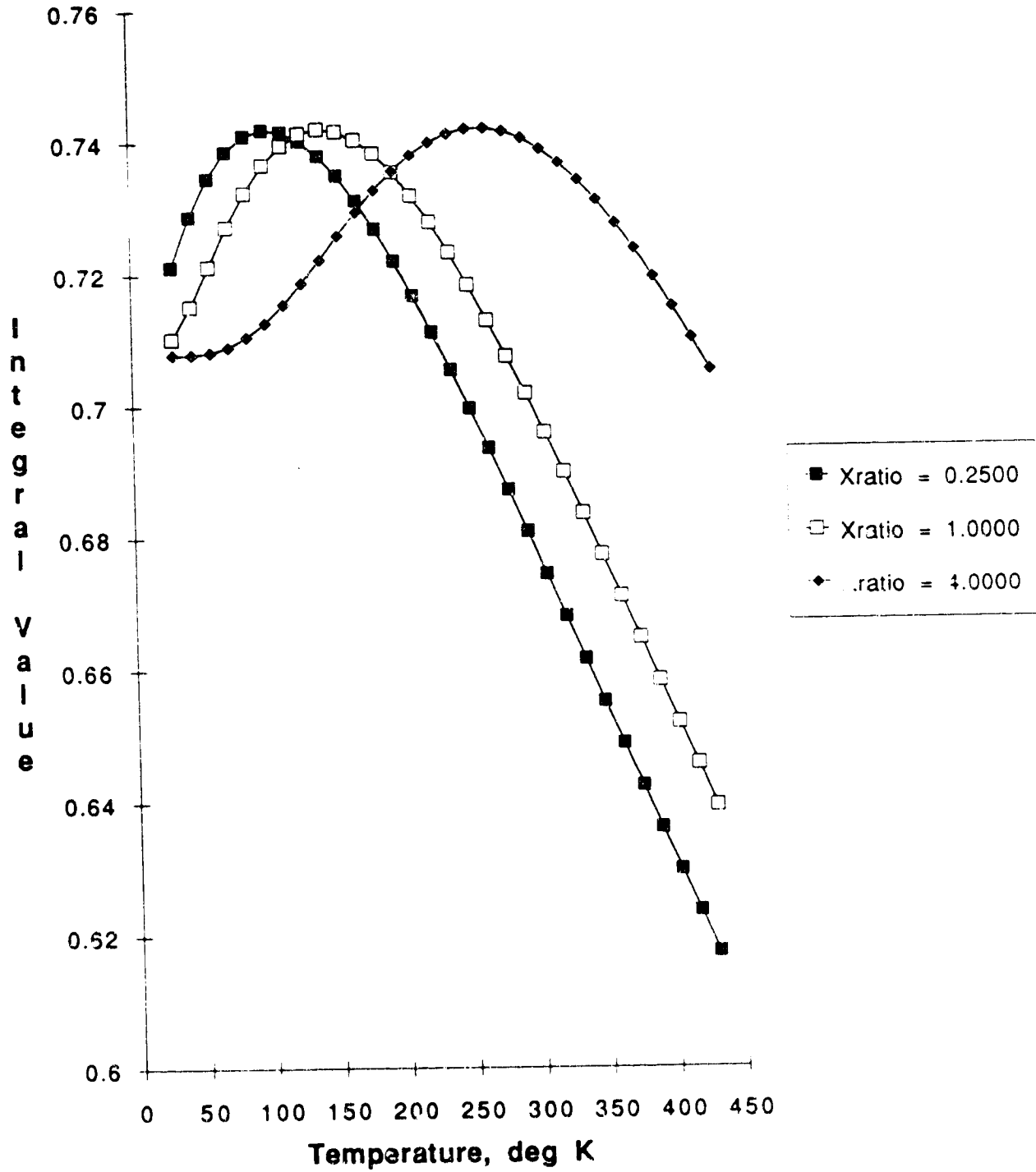
$$\text{'Integral Value'} = G_1(\gamma, \text{woptau}) + G_2(\gamma, \text{woptau})$$

The resulting plots are presented on the next three pages.

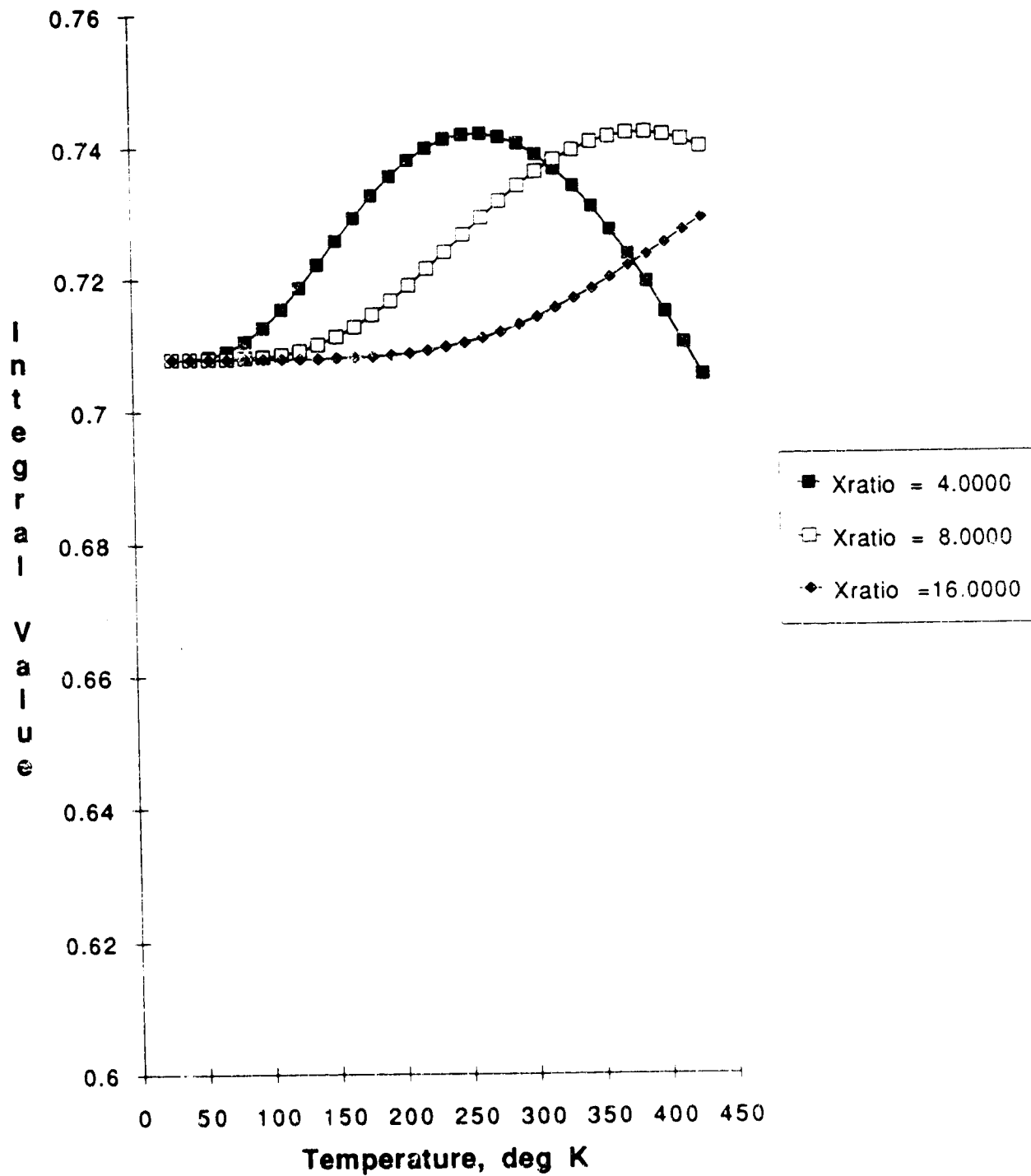
Integral Value: zaratio=1.00, zdratio=2.00, woptau=1.4



Integral Value: zaratio=1.00, zdratio=2.00, woptau=1.4



Integral Value: zaratio=1.00, zdratio=2.00, wo $\tau$ =1.4





## B. Integral Value Versus woptau.

The previous calculation showed a dependence of catalytic rate on the magnitude of the activation energy. In fact, a large activation energy (in relation to the para-ortho energy splitting) may be beneficial. A value of  $xratio = 0.25$  gave a peak in para to ortho catalytic rate at about 150 K, so in the next series  $xratio$  was set to this value.

The three fixed parameters for this series are:

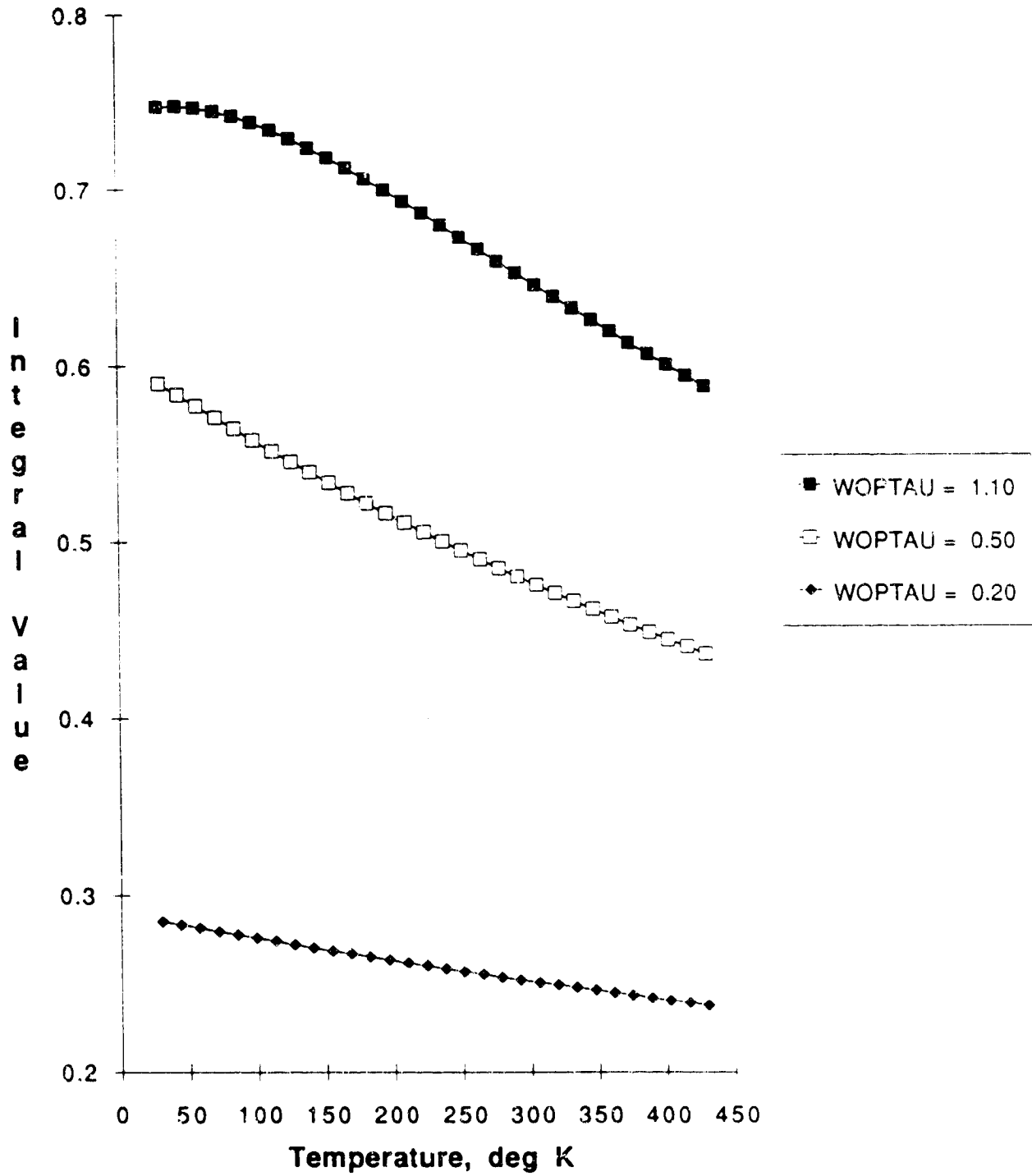
$zratio = 1.00$   
 $zdratio = 2.00$   
 $xratio = 0.25$

and now  $woptau$  is chosen as the variable for each plot. This parameter is chosen to vary over the ranges:

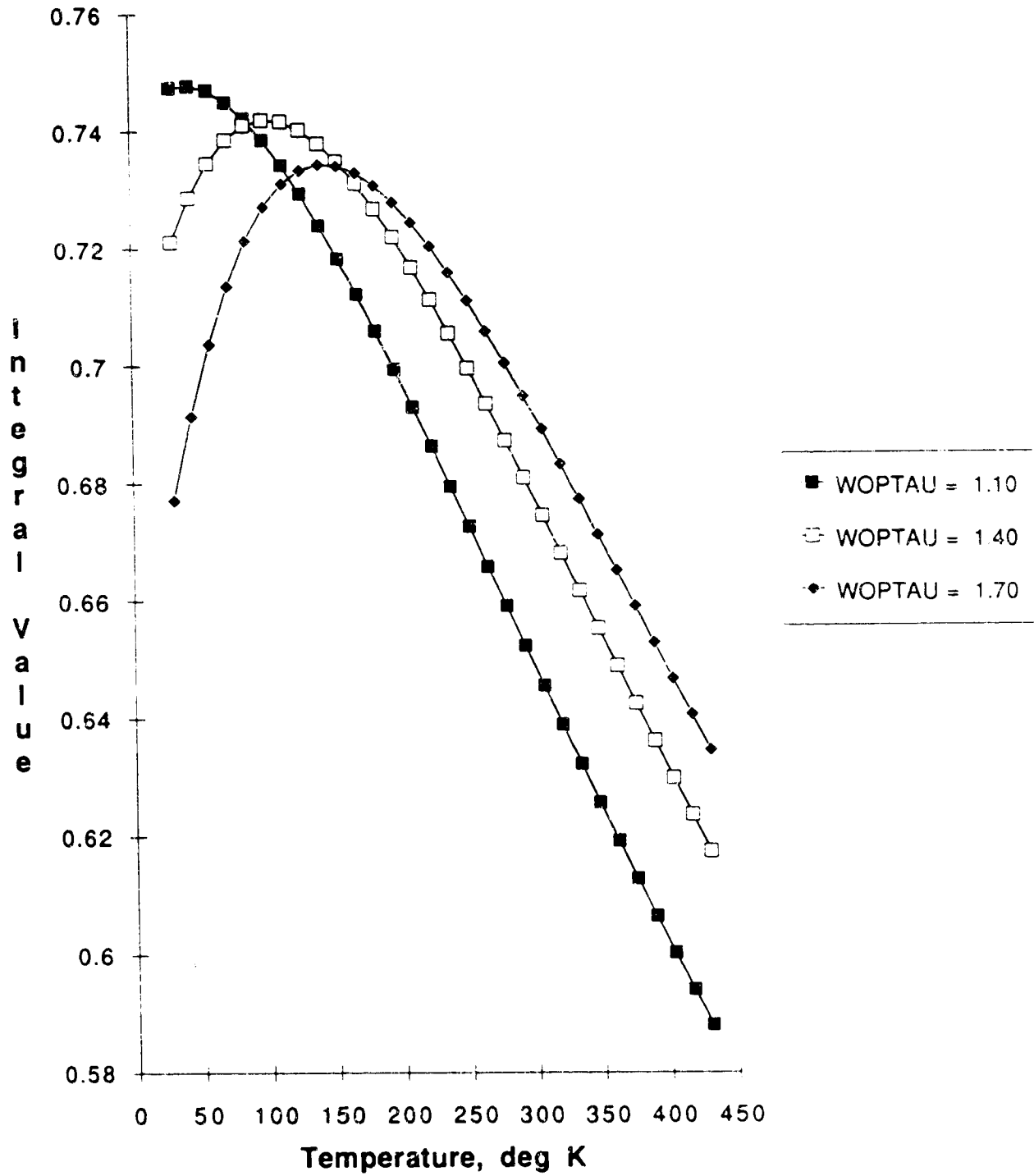
$woptau = 0.20, 0.50, 1.10$   
 $woptau = 1.10, 1.40, 1.70$   
 $woptau = 1.70, 3.00, 5.00$   
 $woptau = 5.00, 10.00, 20.00$

The resulting plots follow on the next four pages:

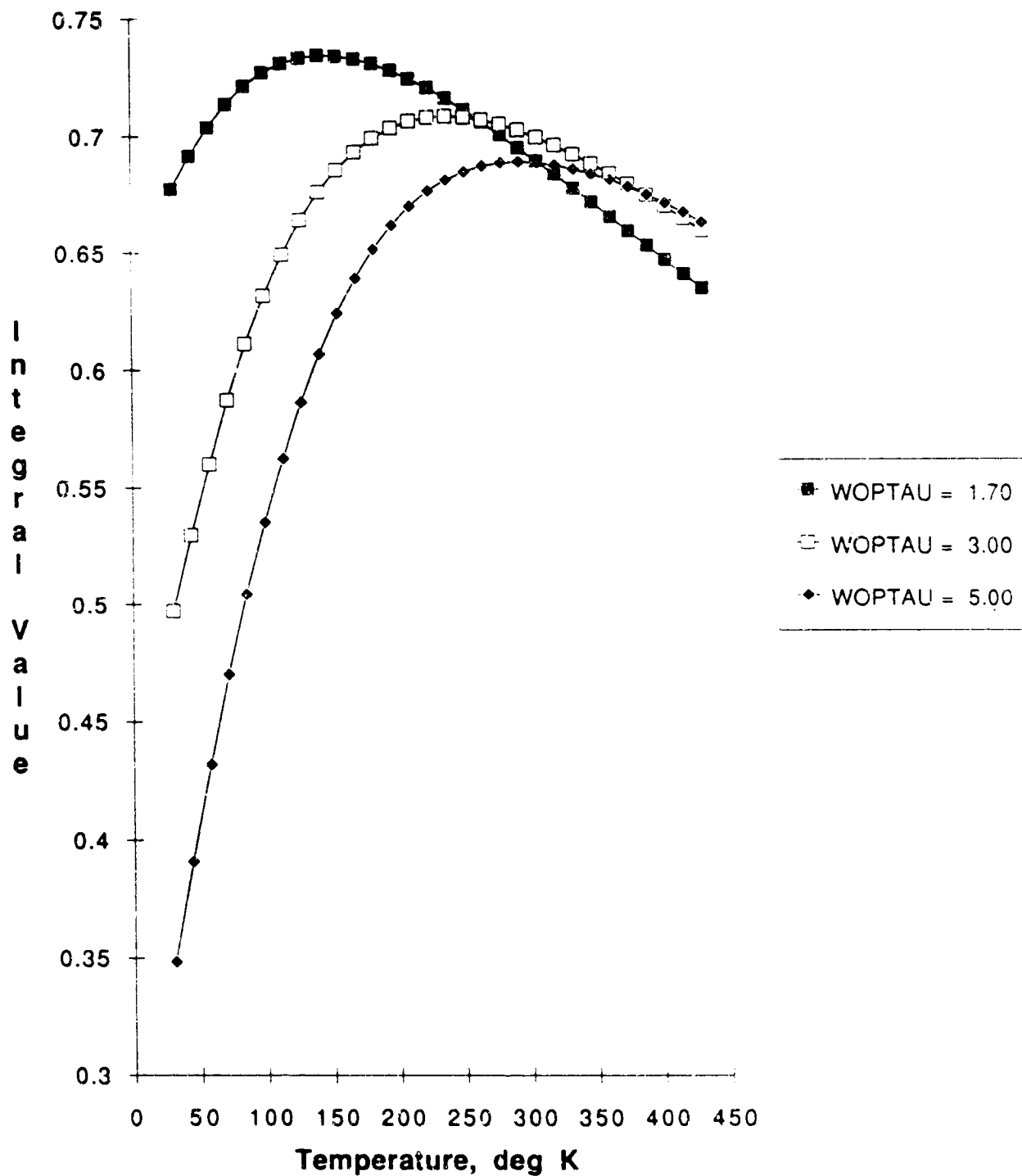
Integral Value: zaratio=1.00, zdratio=2.00, xratio=0.25



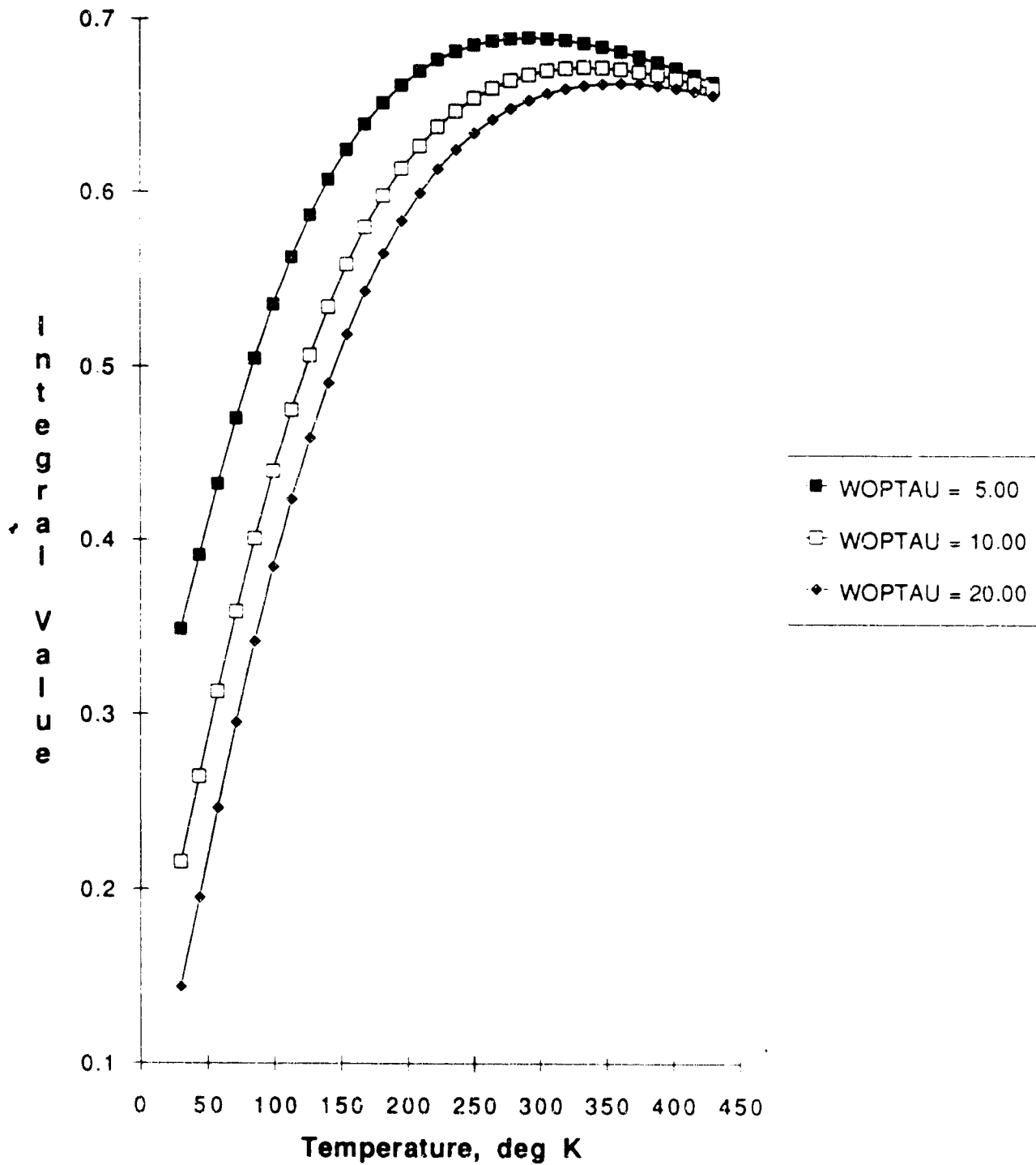
Integral Value: zaratio=1.00, zdratio=2.00, xratio=0.25



Integral Value: zaratio=1.00, zdratio=2.00, xratio=0.25



Integral Value: zaratio=1.00, zdratio=2.00, xratio=0.25



### C. Integral Value Versus zaratio.

The previous calculations and plots show  $w_{optau} = 1.4$  to be an optimal value of the transition frequency times residence time, so these parameters are assigned fixed values:

$$zdratio = 2.00$$

$$w_{optau} = 1.4$$

$$xratio = 0.25$$

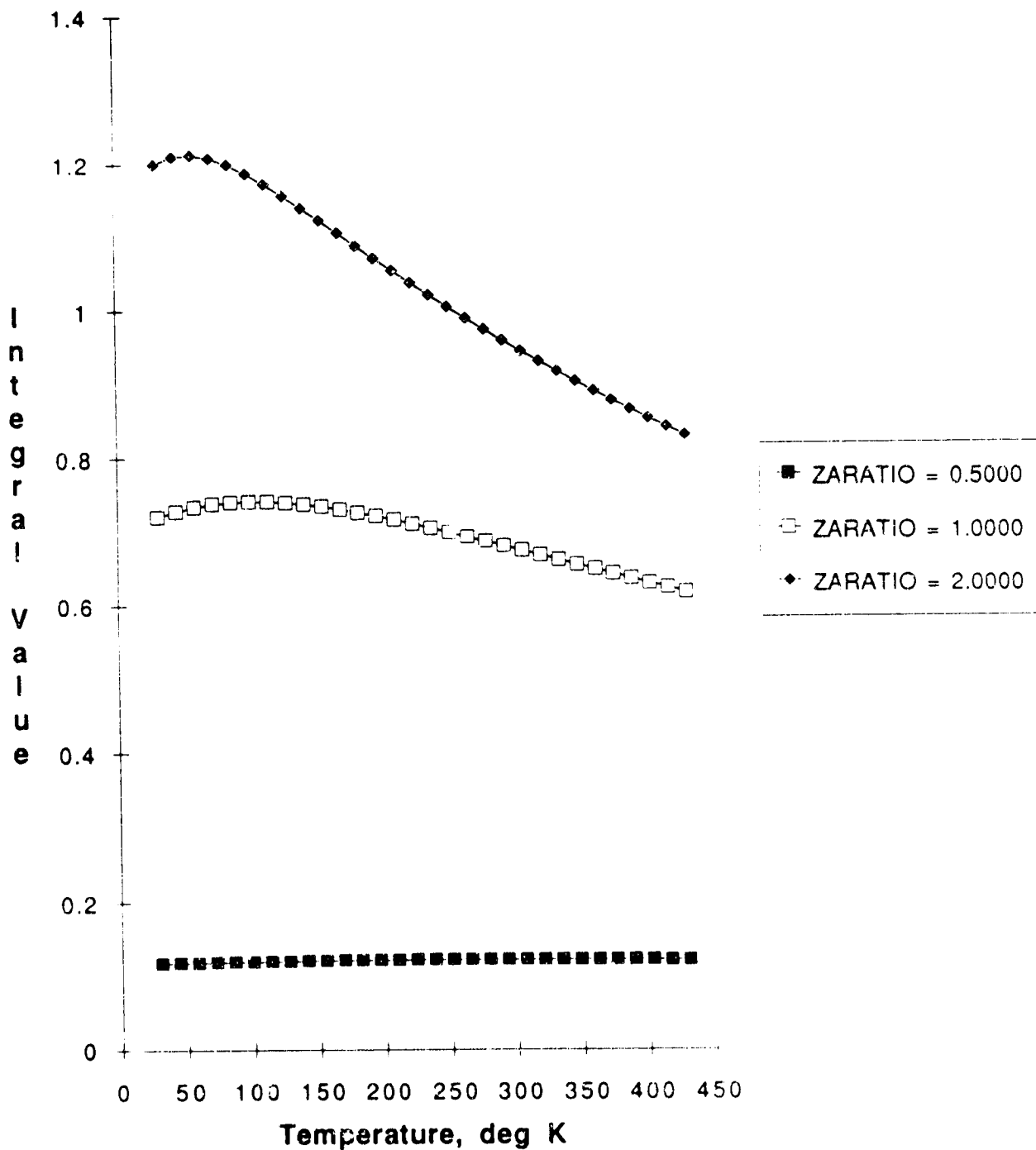
In these calculations the distance from the surface is varied in units of the lattice constant,  $a_0$ . (Remember that the  $1/z^6$  dependence is still present in the 'K' term). The results found here measure the effect of the hydrogen molecule moving through the field gradient of a paramagnetic ion or molecule in the surface layer at various heights from the surface. Thus, for  $z$  much larger than  $a_0$ , the catalytic rate varies purely as  $1/z^6$ . However, as the molecule get significantly within this distance (i.e.  $z < a_0$ , then the rate of catalysis slows down and is slower than indicated by the  $1/z^6$  law).

The plots shown on the next two pages are for:

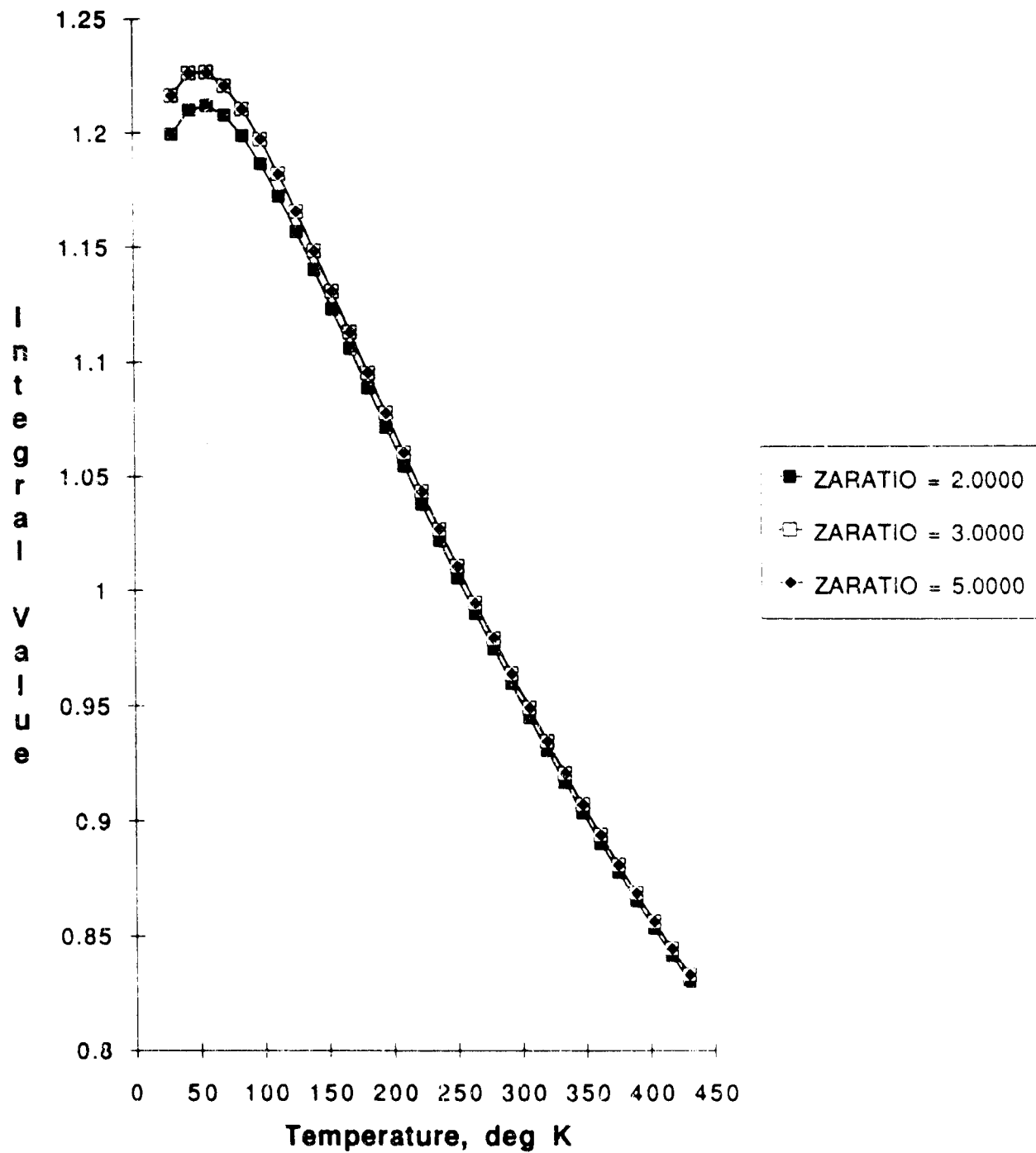
$$zaratio = 0.500, 1.00, 2.00$$

$$zaratio = 2.000, 3.00, 5.00$$

Catalytic Integral: zdratio=2.0, woptau=1.4,  
xratio=0.25



**CATALYTIC INTEGRAL: zratio=2.0, woptau=1.4,  
xratio=0.25**





#### D. Integral Value Versus zratio.

The previous set of integral calculations for various values of the ratio of height  $z$  to the lattice constant  $a_0$ , showed only a small dependence on this parameter. (The dependence is accentuated only for close distance of approach of the  $H_2$  molecule to the surface). Therefore, zratio is now set to a neutral value: zratio = 1.00. So, we now fix these dimensionless parameters to these values:

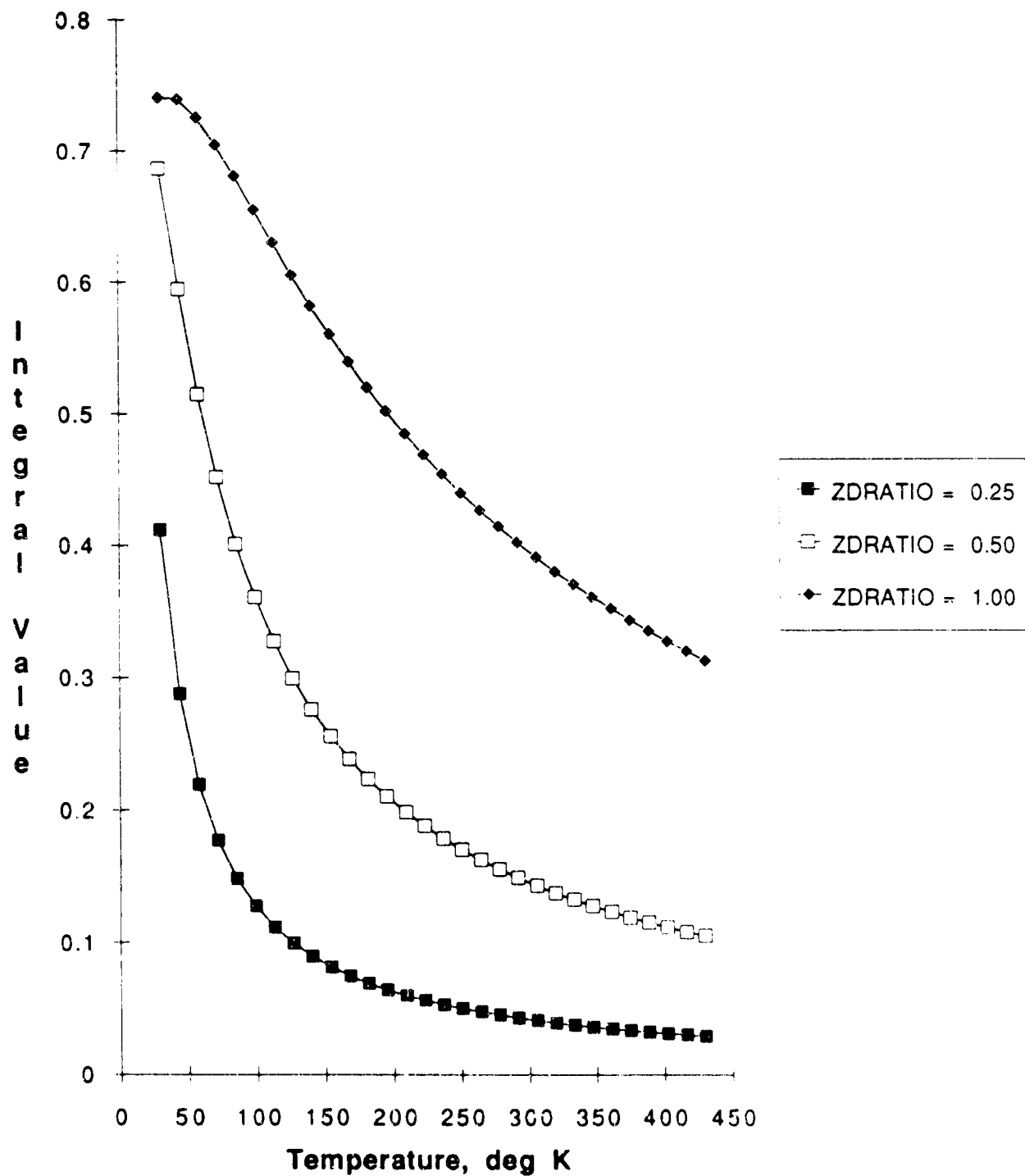
$$\begin{aligned} \text{zratio} &= 1.00 \\ \text{woptau} &= 1.4 \\ \text{xratio} &= 0.25 \end{aligned}$$

The integrals were then calculated for the fixed set of parameters above and a range of the dimensionless parameter zratio (the ratio of  $z/d$  or height of the  $H_2$  above the surface compared to the stepsize of the diffusion process). The ranges selected were:

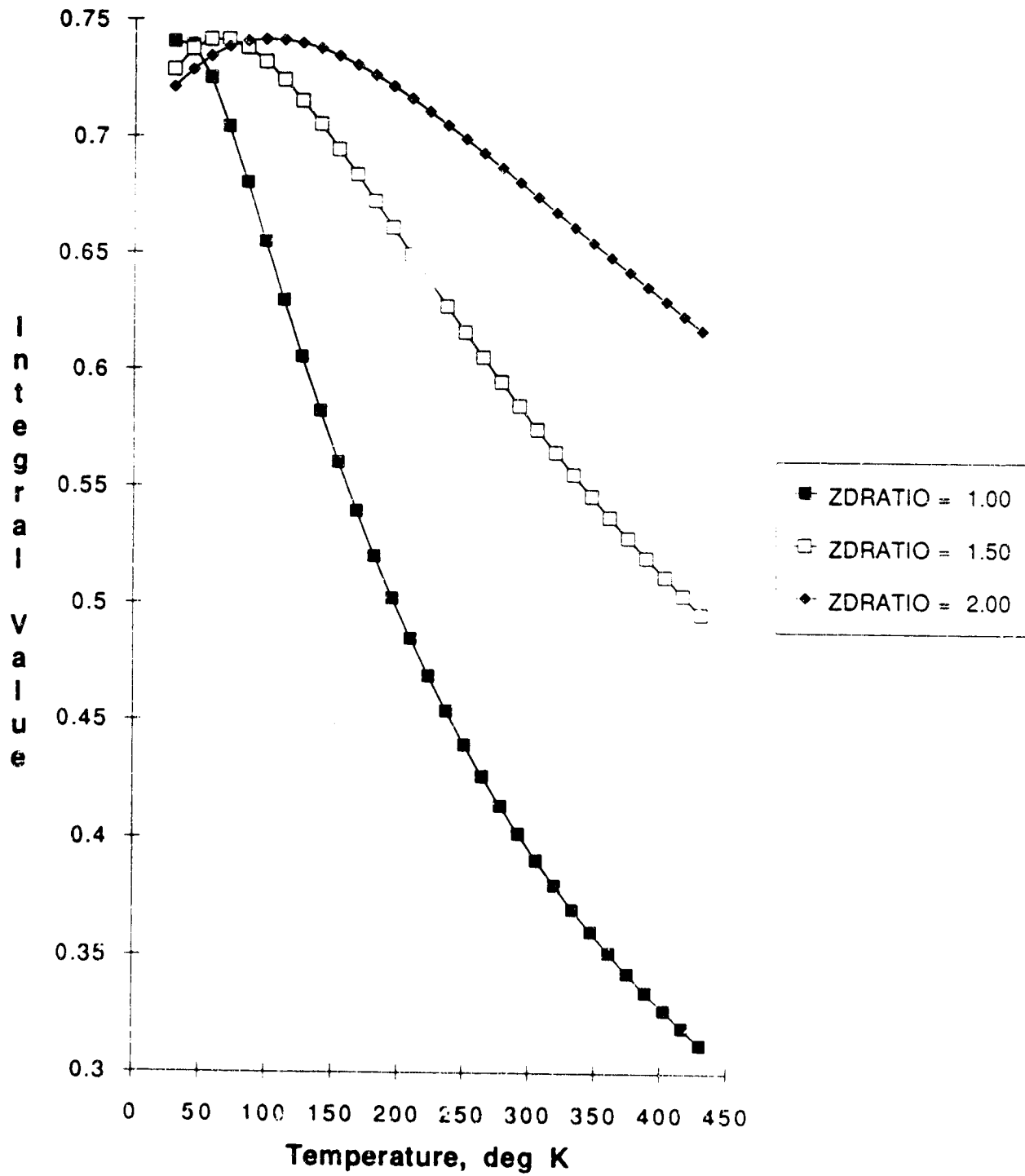
$$\begin{aligned} \text{zratio} &= 0.25, 0.50, 1.00 \\ \text{zratio} &= 1.00, 1.50, 2.00 \\ \text{zratio} &= 2.00, 3.00, 4.00 \end{aligned}$$

The results are shown on the next three pages:

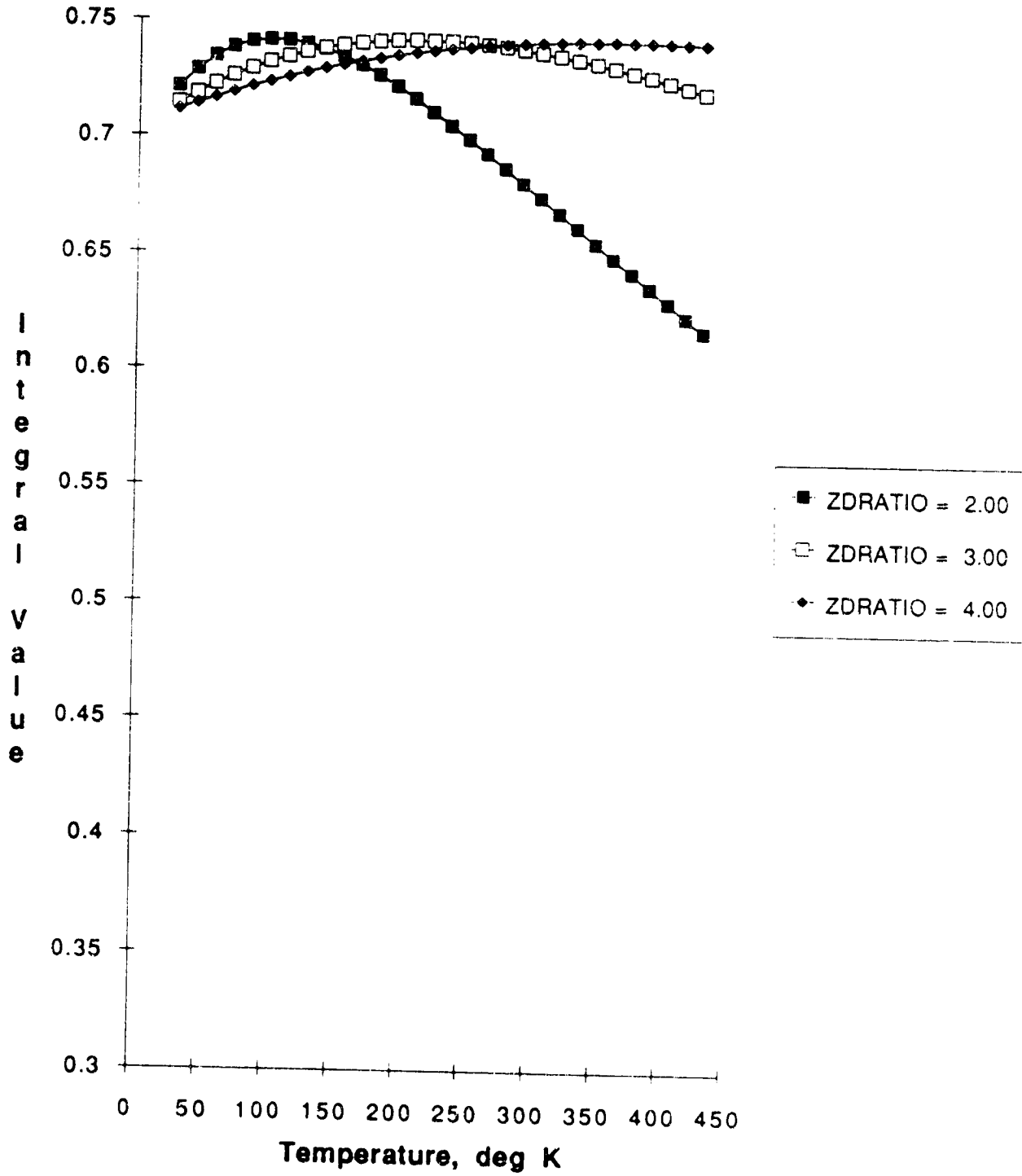
Integral Value: zaratio=1.0, wopectau=1.4, xratio=0.25



INTEGRAL VALUE: zaratio=1.0, wo $\tau$ =1.4, xratio=0.25



INTEGRAL VALUE: zaratio=1.0, woptyau=1.4, xratio=0.25



### E. Integral Value Versus $w_{optau}$ for Optimal Conditions.

This last set of calculations is for the variation of the integral value controlling the shape and temperature dependence of the para to ortho catalysis rate assuming that optimal conditions have been chosen for:

zaratio: height  $z$  above the surface in units of  $a_0$ .

zdratio: the distance  $z$  compared to the diffusion step size.

xratio: the relative size of the activation energy for diffusion, compared with the para to ortho unit of energy splitting.

Now, the previous calculation showed that a large stepsize for the diffusion mechanism gives a catalytic rate nearly independent of temperature. So we optimize the value of zdratio at a value of about 4. We also found in the first part of this integral study (part A), that a 'large' activation energy (compared to the para-ortho energy unit) leads to a catalytic rate showing small dependence on the temperature. Thus we fix the value of xratio at about 12.0. Therefore, we have selected these fixed values of the dimensionless parameters:

$$\begin{aligned} \text{zaratio} &= 1.00 \\ \text{zdratio} &= 4.00 \\ \text{xratio} &= 12.0 \end{aligned}$$

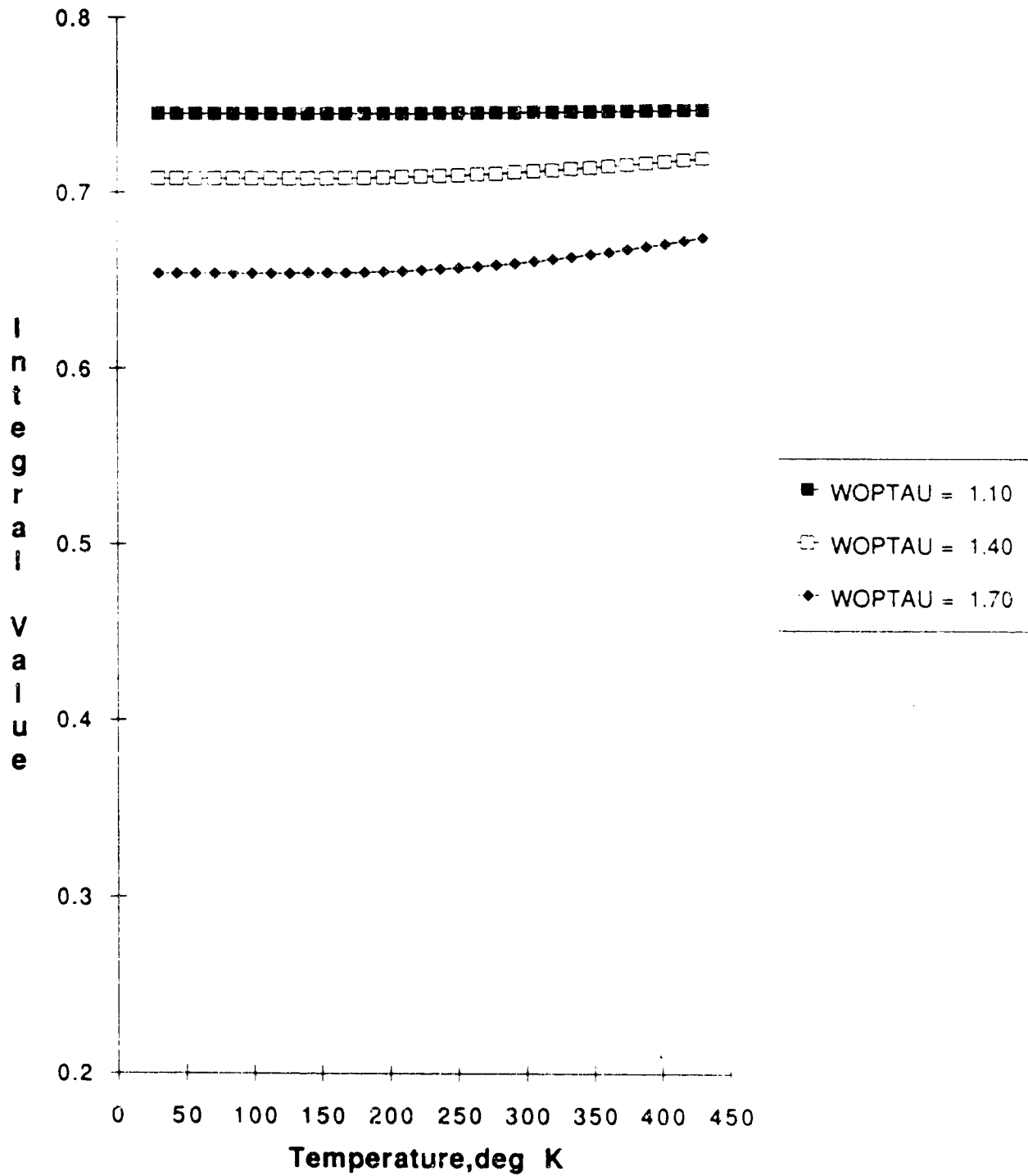
That is, we have chosen a large value of the activation energy for diffusion, since for large values of the activation energy for diffusion there is nearly a constant rate of catalysis versus temperature.

We have then calculated the integral value for these values of  $w_{optau}$ :

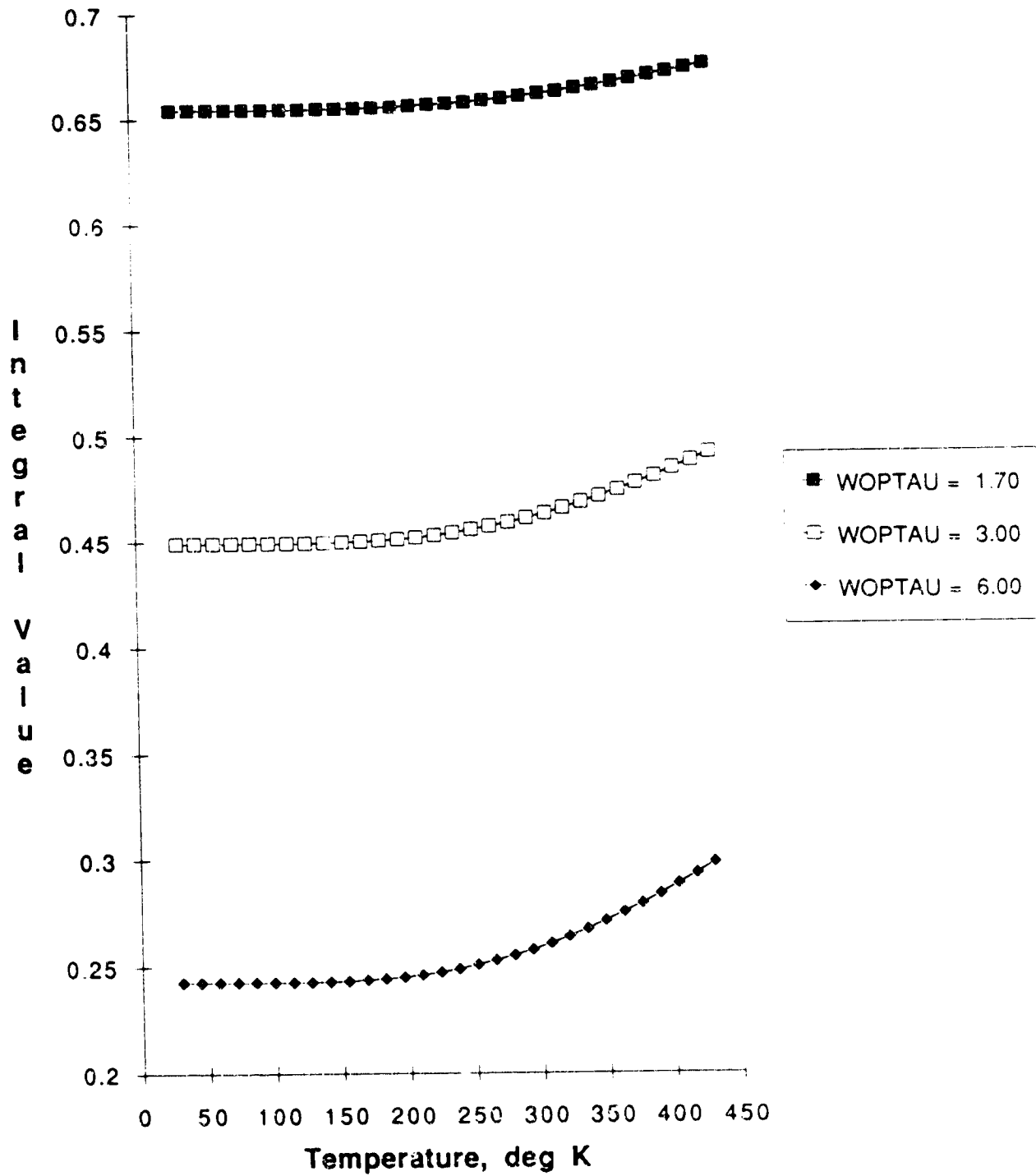
$$\begin{aligned} w_{optau} &= 1.10, \quad 1.40, \quad 1.70 \\ w_{optau} &= 1.70, \quad 3.00, \quad 6.00 \end{aligned}$$

The results are shown on the next two pages.

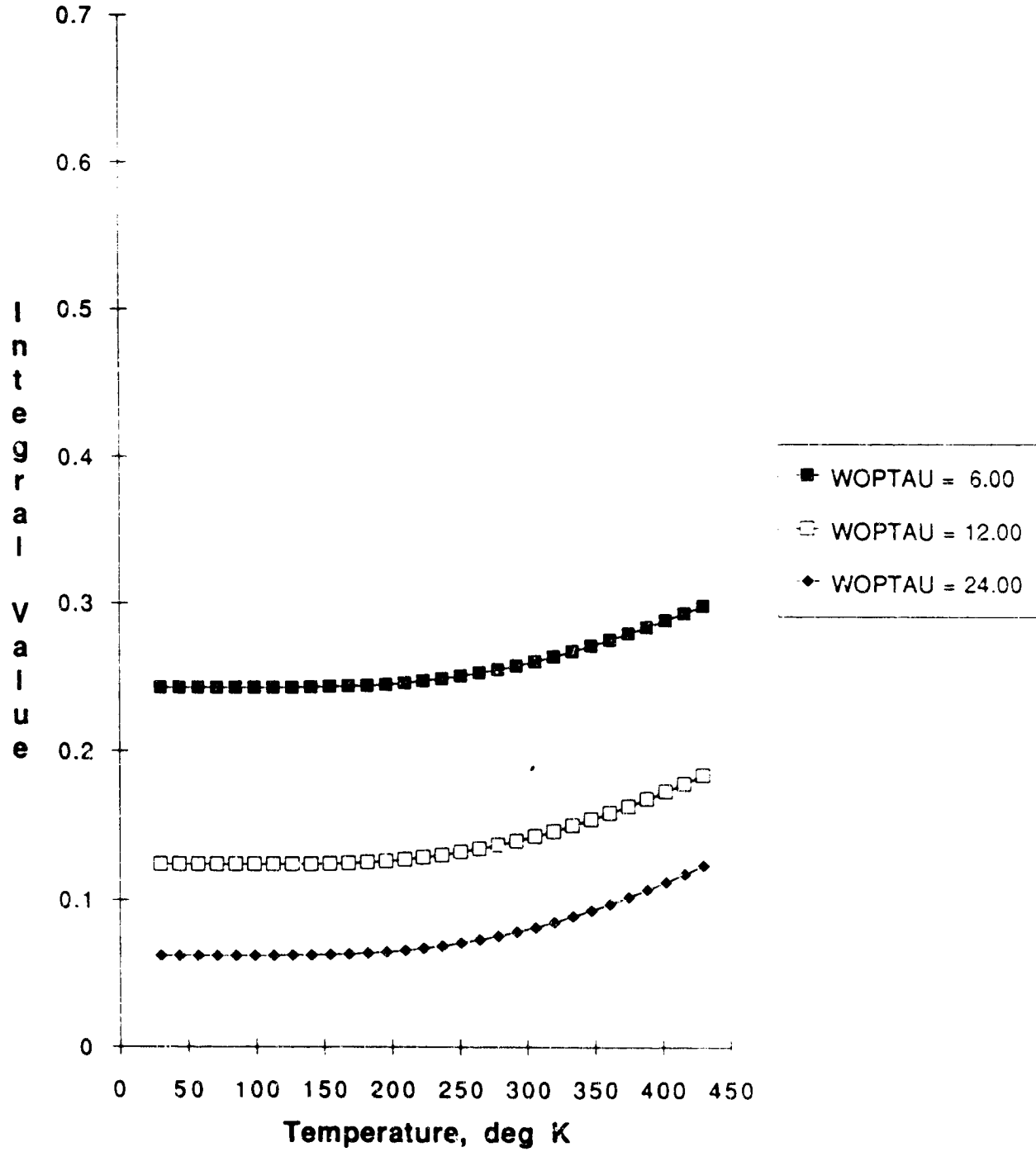
Integral Value: zaratio=1.00, zdratio=4.00, xratio=12.0



Integral Value: zaratio=1.00, zdratio=4.0, xratio=12.0



Integral Value: zaratio=1.00, zdratio=4.00,  
xratio=12.00





## VI.. Conclusions.

Magnetic catalysts for the para to ortho conversion may be classified in terms of three types of magnetic phases:

paramagnetic  
ferromagnetic  
antiferromagnetic

For catalysts in the paramagnetic phase, we have derived some quantitative results on the behavior of the para to ortho hydrogen conversion on the assumption that the hydrogen on the surface behaves as a two-dimensional liquid, so that the molecules of  $H_2$  migrate from one site to another by a Brownian motion mechanism, i.e. by surface diffusion.

The diffusion coefficient 'D' was then modelled using transition state theory thus incorporating the stepsize 'd', and an activation energy for surface diffusion. The numerical expression for the rate of catalysis was then analyzed in terms of four dimensionless parameters:

xratio  
zaratio  
zdratio  
woptau

and the height from the surface, z, and the absolute temperature, T. The first three parameters seem only to affect the shape of the catalytic rate versus T, while the most important overall parameters are:

woptau and z

Thus, the height above the surface, z, and the residence time,  $\tau$ , seem to be the most important determinants of catalytic activity. This is particularly evident in the last set of plots given above (E), for which the catalytic rate was found to be nearly constant versus the temperature for any given value of the surface lifetime. But, increasing the surface lifetime was found to measurably degrade the catalyst performance.

The next step, from here, is to study a physical model for the residence time,  $\tau$ , and the processes that control it. The result will be a more or less complete phenomenological theory for this catalytic process. One early conclusion: it appears likely that the major differences between different paramagnetic catalysts in terms of their catalytic activity are the differences in how close the  $H_2$  molecules (in the surface layer) approach the catalytic site(s), and the length of time that the molecules are resident on the surface after once being adsorbed from the gaseous phase. Since this (process of adsorption) is a purely physical process, with a weak binding energy, such residence times are inherently very short. The trick (to obtain optimal catalytic activity) is to shorten the residence time to a value such that the parameter designated as 'woptau' becomes as close as possible to unity!

## VII. Literature and References.

### Five (Unpublished) Previous Reports:

1. R. E. Coffman, 'Theory of Ortho to Para (Hydrogen) Catalysis. I. Practical Equations for the Description of Paramagnetic Catalysis'. July 21, 1989.
2. R. E. Coffman, 'Theory of Ortho to Para Hydrogen Catalysis. II. Analysis of Three Models Due to Petzinger and Scalapino'. August 10, 1989.
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