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EFFECT OF TEMPERATURE OSCILLATION ON CHEMICAL REACTION RATES IN THE ATMOSPHERE

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ON CHEMICAL REACTION RATES IN THE ATMOSPHERE

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CONTENTS

	<u>Page</u>
SYMBOLS	v
INTRODUCTION	1
ANALYSIS	1
REFERENCES	8

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Ratio of Mean Rate to Rate at Mean Temperature Versus Temperature Fluctuation Amplitude.....	4
2	Ratio of Mean Rate to Rate at Mean Temperature Versus Activation Energy	5

SYMBOLS

- [A] = Concentration of specie "A"
- [M] = "Third body" concentration
- $\frac{d}{dt}$ = Rate of change with respect to time
- t = Time
- ℓ, m, n, p = Exponents signifying order of reaction
- ΔE = Activation energy of reaction
- R = Universal gas constant
- T = Temperature
- T_0, \bar{T} = Mean temperature
- X_A = Mole fraction of specie "A"
- F' = Pre-exponential factor in Arrhenius reaction rate expression
- F = Same as F' , but associated with rate expression given in terms of mole fractions
- ω = Frequency of sinusoidal oscillation
- β = Amplitude of sinusoidal oscillation
- τ = Period of sinusoidal oscillation
- $\eta(T)$ = Rate of reaction at temperature T
- k_i = Rate of reaction associated with free radical reaction for specie "i"
- f_j = Rate of photolysis associated with specie "j"

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EFFECT OF TEMPERATURE OSCILLATION ON CHEMICAL REACTION RATES IN THE ATMOSPHERE

INTRODUCTION

There has in the recent decade been a very considerable interest in the chemistry of the earth's atmosphere, and many photochemical models have been published. Rather than review the field of photochemical modelling, I refer the interested reader to a recent review article by H. U. Dütsch (1973), which gives a good introduction to the photochemistry of atmospheric ozone and also has a bibliography containing the names of most of the scientists active in the field.

In a very interesting study (1973) Johnston and Whitten examined the production and destruction of atmospheric ozone in terms of the Chapman photochemical theory, ozone transport, and reactions with oxides of nitrogen. They calculate that the globally averaged ozone production rate by the Chapman mechanism is five times larger than the globally averaged destruction rate by the Chapman mechanism. Johnston and Whitten (1973) also calculate ozone transport to the troposphere as being about 1% of the gross rate of ozone formation, using numbers for transport given by Brewer and Wilson (1968).

Johnston and Whitten (1973) show that the excess ozone production rate by the Chapman mechanism can be readily balanced if destruction of ozone by oxides of nitrogen is introduced. A modest background concentration of nitric oxide is assumed to exist in the atmosphere. The explanation is certainly plausible but its validity must await confirmation until sufficiently accurate and extensive measurements of atmospheric nitric oxide become available.

The purpose of the present paper is to consider the possible effect of temperature oscillation on effective reaction rates. The nonlinearity of the Arrhenius expression for the chemical rate is such that the mean rate under a sinusoidal temperature fluctuation will be larger than the rate at the mean temperature. Let us examine how large the difference is likely to be. The author came across the problem some ten years ago when the possible effects of turbulent temperature and density fluctuations on chemical reaction rate measurements needed to be estimated (Glassman and Eberstein, 1963). Now, the effect of temperature fluctuations on atmospheric ozone chemistry will be examined.

ANALYSIS

The chemical reaction for specie "A" is given by an expression of the form

$$\frac{d}{dt} [A] = F [A]^{\ell} [B]^m [C]^n \exp \left[\frac{-\Delta E}{RT} \right] \quad (1)$$

where

$$p = \ell + m + n \quad (2)$$

is the order of reaction. Any of the exponents may be zero. The factor F may be a weak function of temperature, but is generally taken to be constant.

In the atmosphere, one generally deals with constant pressure levels for which total density is inversely proportional to temperature. Equation (1) may thus be written:

$$\frac{d[A]}{dt} = \{F X_A^{\ell} X_B^m X_C^n\} T^{-p} \exp \left[\frac{-\Delta E}{RT} \right] \quad (3)$$

Let us now subject the system described by Eq. (3) to a sinusoidal temperature oscillation, and determine the ratio of "mean rate" to "rate at mean temperature." The mole fractions X, and the quantity "F" will be assumed to be unaffected by the temperature fluctuations. We thus have:

$$\frac{T}{T_0} = 1 + \beta \sin \omega t, \quad (4)$$

where β is oscillation amplitude, and:

$$\frac{\overline{\eta(T)}}{\eta(\bar{T})} = \frac{\int_0^{\tau} \left\{ T^{-p} [1 + \beta \sin \omega t]^{-p} \exp \left[\frac{-\Delta E}{RT_0} \frac{1}{1 + \beta \sin \omega t} \right] \right\} dt}{\int_0^{\tau} T_0^{-p} \exp \left[\frac{-\Delta E}{RT_0} \right] dt} \quad (5)$$

The quantity $\eta(T)$ is the temperature sensitive part of $\frac{d[A]}{dt}$, i.e.

$$\eta(T) = T^{-p} \exp \left[\frac{-\Delta E}{RT} \right] \quad (6)$$

$\eta(\bar{T})$ is the rate at the mean temperature \bar{T} , and $\overline{\eta(T)}$ is the mean rate integrated over a cycle for the fluctuating temperature T . T_0 and \bar{T} represent the same quantity. Equation (5) was evaluated numerically for a cycle and some of the results are shown in Figures (1) and (2). In Figure 1 the ratio $\overline{\eta(T)}/\eta(\bar{T})$ is plotted versus the fluctuation amplitude for several values of the overall reaction order p and the quantity $\Delta E/RT$.

Figure 1 shows considerable enhancement of the mean reaction rate for temperature fluctuations exceeding 10%.

Figure 2 shows the reaction rate ratio versus $\Delta E/RT_0$ for $p = 0$ for temperature fluctuations of 10%, 15%, 20% and 25%. It is seen that significant reaction rate enhancement occurs as $\Delta E/RT_0$ goes above 10.

Let us now examine what temperature oscillations and activation energies one may expect in the atmosphere. Most upper atmospheric reactions involve either photochemical dissociation or free radical recombination. These processes have a very weak temperature dependence.

However, reactions like



do have a non-trivial temperature dependence, i.e. (Dütsch, 1973)

$$k = 6 \times 10^{-12} \exp \left(-\frac{2230}{T} \right)$$

giving a value of approximately 10 to the quantity $\Delta E/RT_0$.

In examining the Chapman mechanism, Johnston and Whitten (1973) give the following expression for the steady state concentration which ozone is potentially capable of attaining:

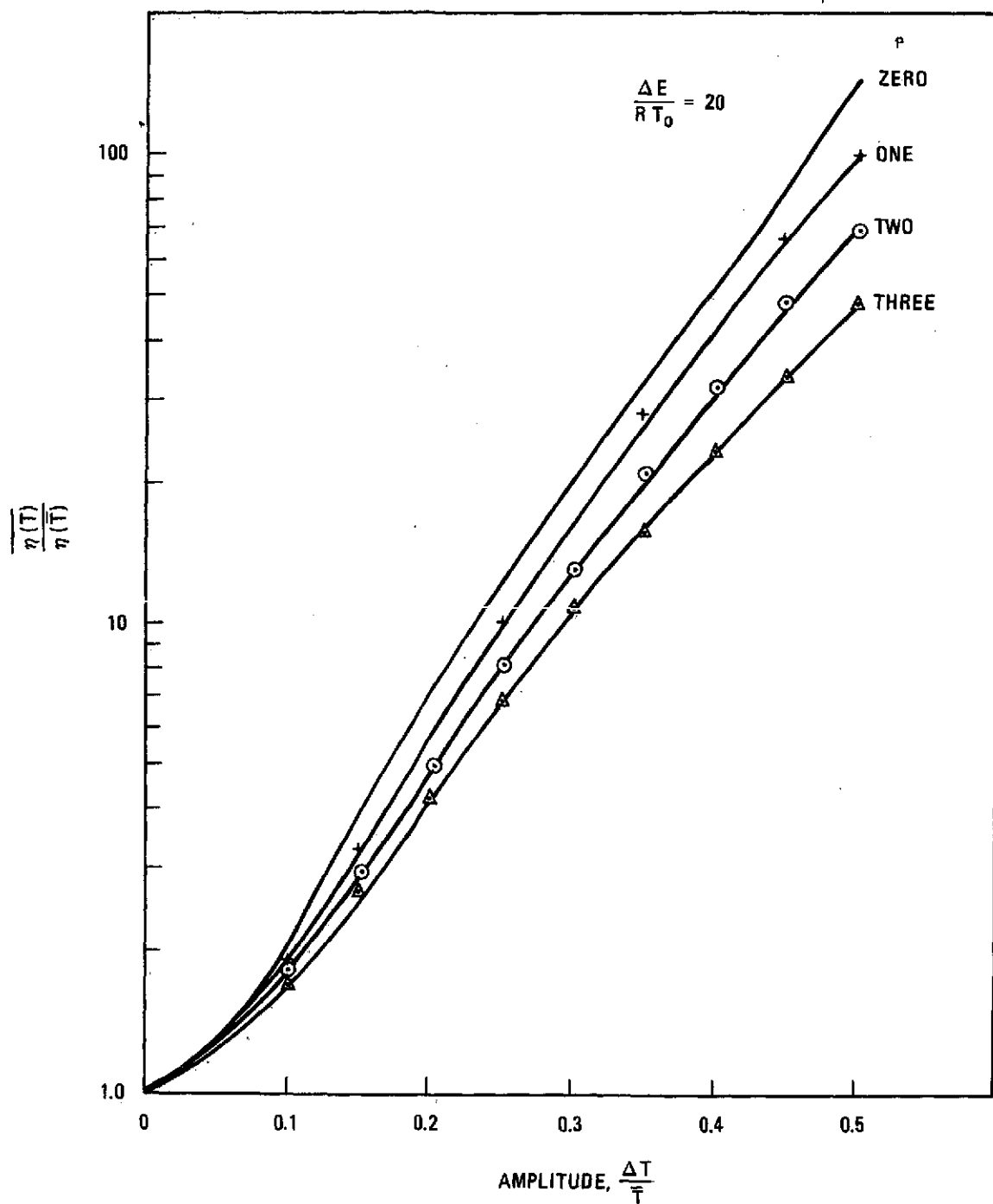


Figure 1. Ratio of Mean Rate to Rate at Mean Temperature
Versus Temperature Fluctuation Amplitude

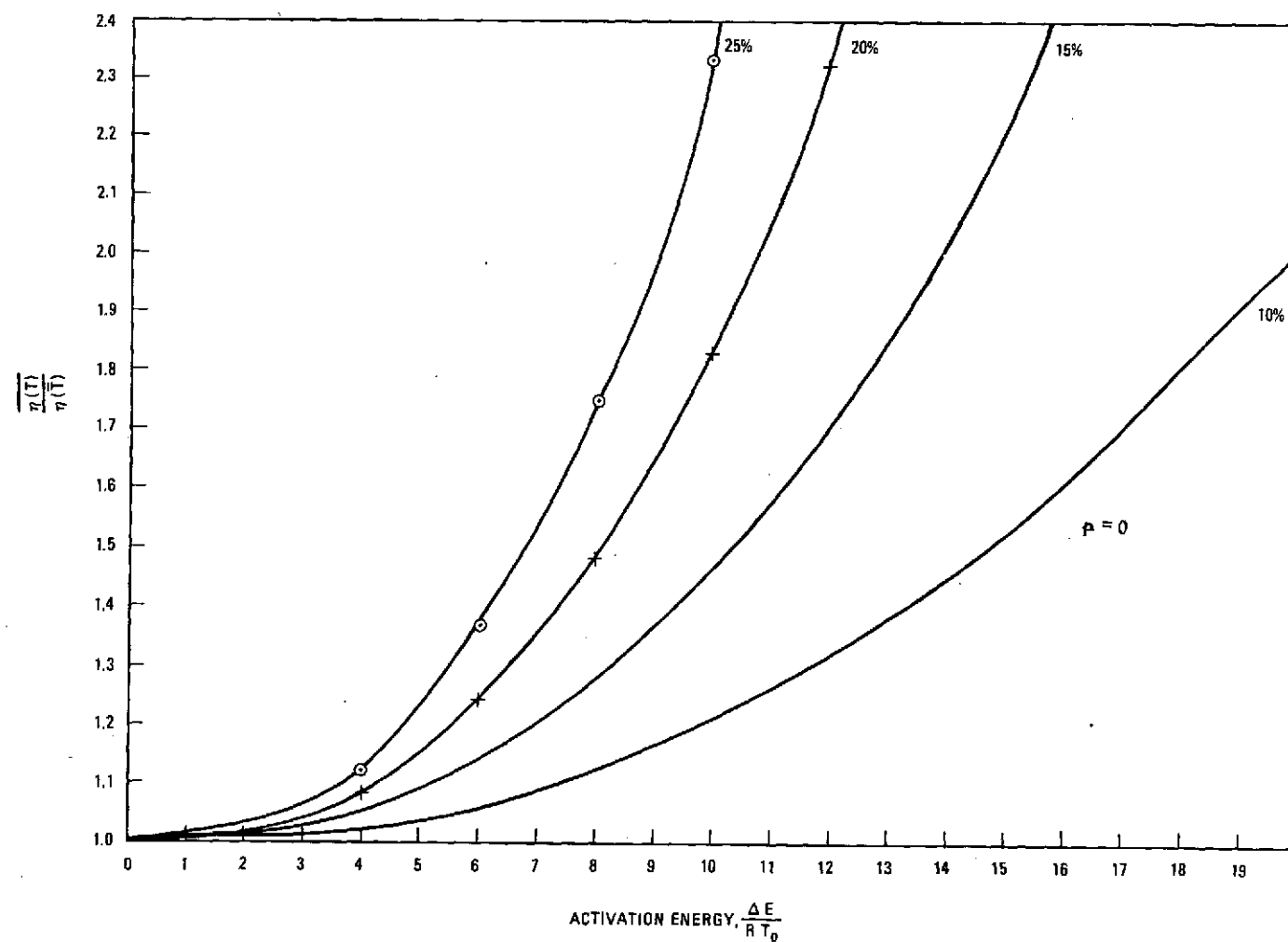


Figure 2. Ratio of Mean Rate to Rate at Mean Temperature Versus Activation Energy

$$\frac{[O_3]_S}{[O_2]} = \left(\frac{f_2 k_2 [M]}{f_3 k_3} \right)^{\frac{1}{2}} \quad (7)$$

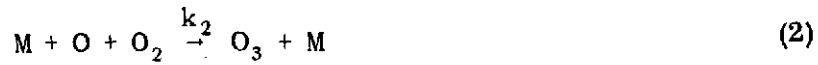
with

$$k_2 = 1.10 \times 10^{-34} \exp \left(\frac{502}{T} \right)$$

and

$$k_3 = 1.33 \times 10^{-11} \exp \left(-\frac{2100}{T} \right)$$

The following reactions have been considered:



At 50 km it is reasonable to take the mean temperature as 260°K, and the fluctuation as $\pm 10\%$ (Theon et al., 1972).

The ratio of photochemical rates associated with the fluxes f_2 and f_3 is assumed to remain unaffected by the oscillation in Eq. (7). The formation rate associated with $k_2 [M]$ is increased by 3% and the destruction rate associated with k_3 is increased by 8.5%. Referring to the quantity in brackets in Eq. (7), one would expect it to decrease by 5.5% resulting in a 3% drop of steady state ozone.

Referring to the table given by Johnston and Whitten (1973), the following values are obtained from the Chapman mechanism:

Global rate of ozone production = 500

Global transport to troposphere = 6

North-South transport ± 4

The above values are in units of 10^{29} molecules/second.

Now, a 3% change in the global production rate is 15 units, or more than the total North-South transport, and more than twice the global transport to the troposphere.

We may conclude that the effect of temperature oscillation on atmospheric photochemistry is comparable to transport effects, but much less than the factor of 5 required by Johnston and Whitten (1973) to balance the ozone produced in the Chapman mechanism.

The above analysis is in many ways preliminary in nature, and a more thorough study is underway. However, the author felt that it is of great importance to make atmospheric modellers aware of the fact that chemical reaction rates in the atmosphere respond in a nonlinear and non-negligible fashion to temperature oscillations in the atmosphere.

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