## MICROBIAL STERILIZATION IN ULTRA-HIGH VACUUM AND OUTER SPACE: A KINETIC COMPARISON\*

(Research Note)

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There has been a series of papers (Davis *et al.*, 1962; Hotchin *et al.*, 1965; Porter *et al.*, 1961) concerned with the survival of microorganisms in ultra-high vacuum and in space. The correlation between microbial die off in ultra-high vacuum and space is not immediately obvious. It is the purpose of this note to call attention to the fact that from a kinetic viewpoint, D values obtained under ultra-high vacuum,  $10^{-6}$  torr, are not appreciably different from those obtained under  $10^{-17}$  torr, pressure of outer space.

Suppose the microorganisms are being sterilized by a first order chemical reaction, i.e., survival is logarithmic. Then the relationship between the D value and the reaction rate constant, k, is given by

$$D = -\ln(0.1)/k.$$
 (1)

Under the absolute reaction rate theory

$$k = \frac{KT}{h} \exp\left(-\Delta F^{\ddagger}/RT\right),\tag{2}$$

where K is Boltzmann's constant, h is Planck's constant, T is the temperature in degrees Kelvin, R is the gas constant and  $\Delta F^{\ddagger}$  is the free energy of activation.  $\Delta F^{\ddagger}$  may be broken down further as

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T \,\, \Delta S^{\ddagger} + p \,\, \Delta V^{\ddagger},\tag{3}$$

where  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$ , and  $\Delta V^{\ddagger}$  are activation enthalpy, entropy, and volume respectively, and where *p* is pressure (Glasstone *et al.*, 1941).

One normally associates a positive  $\Delta V^{\ddagger}$  with first order reactions. Furthermore, with  $\Delta V^{\ddagger}$  positive, as pressure decreases the reaction rate increases so that from Equation (1) we see that the *D* value decreases. The question we address is how much will *D* decrease for a fixed value of  $\Delta V^{\ddagger}$  as *p* goes from 10<sup>-6</sup> to 10<sup>-17</sup> torr.

Combining Equations (2) and (3) we get the relationship for pressures  $p_1$  and  $p_2$ .

$$\ln(k_{p_1}/k_{p_2}) = \Delta V^{\ddagger}(p_2 - p_1)/RT.$$
(4)

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If we take pressure in atm, the gas constant will be

R = 82.06 cc atm/mole.

From Equations (1) and (4) we find

$$\ln(D_{p_2}/D_{p_1}) = \ln(k_{p_1}/k_{p_2}).$$
(5)

The largest  $\Delta V^{\ddagger}$  value we have seen was recorded for ribonuclease by Kettman *et al.* (1966) as 200 cc/mole. To be safe we will use 10 000 cc/mole. Suppose we assume that  $T=333 \text{ K}=60 \,^{\circ}\text{C}$ . We convert the pressures to atmospheres so that

$$p_1 = 10^{-6} \text{ torr} = (1/7.6) \times 10^{-8} \text{ atm},$$

and

$$p_2 = 10^{-17} \text{ torr} = (1/7.6) \times 10^{-19} \text{ atm}$$

Using these values in Equation (4) we find that

$$\ln(k_{p_1}/k_{p_2}) = \frac{(10^4 \text{ cc/mole})(1/7.6)(10^{-19} - 10^{-8}) \text{ atm}}{(333 \text{ deg})(86.0597 \text{ cc atm/deg mole})}.$$

Using orders of magnitude we see that

$$\ln(k_{p_1}/k_{p_2}) \approx 10^{-10} (10^{-11} - 1). \tag{6}$$

Thus despite the magnitude of the  $\Delta V^{\ddagger}$  chosen the right side of Equation (6) differs from 0 by less than  $10^{-8}$ . This of course implies that the ratio  $k_{p_1}/k_{p_2}$  is so near 1 that in view of Equation (5) an experimenter could not distinguish between D values taken at  $10^{-6}$  and  $10^{-17}$  torr if only first order kinetics is involved in the sterilization.

## References

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