The results obtained for three values of S are given in Table 2 and may be compared with the results found by Lardner[4] using an extension of Biot's method.[3]

It is seen from Eq. (14) that when $S = -1/0.9, \simeq -1.1$, $B = 0$ and the penetration depth also is zero. Actually, the correct value of S for this condition to result is $S = -1$ from Eq. (12), since then the thermal conductivity at the surface is zero and there is no flow of heat.

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Comment on "Dynamic Buckling of Cylinders under Axial Shock-Tube Loading"

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The authors discussed pressure-induced axial buckling of long cylindrical shells,[1] in which strain and pressure measurements were made on cylinders with $R/t = 136$. In examining the reported data with the viewpoint of Ref. 2 (that the stress field could be viewed as static and therefore static buckling theory could be applicable), calculations were made of critical axial strain and the corresponding equivalent static pressure.

Using the relation[3]

$$\sigma = CEt/R \tag{1}$$

in which $C = 0.4$ for $R/t = 136$, the critical strain would be

$$\epsilon = 0.4/136 = 2940\ \mu\ \text{in./in.}$$

which agrees well with the reported values[1] of 2760, 2890, 2700, and 2750 μ in./in. for four test specimens.

The corresponding pressures would be found from the pressure vessel relation

$$p = 2\sigma t/R$$

If E, Young's modulus, is chosen at 10^7 psi for 6061-T6, then $\sigma = 29{,}400$ psi and $p = 430$ psi. However, the authors reported buckling at the cylinder end away from the applied pressure, presumably after a reflection that doubled the critical stress level. Consequently, the initial pressure need only have been 215 psi. The authors[1] reported 218, 251, 214, and 290 psi, respectively, for the four test specimens. It is noteworthy that pressure was applied at successively higher levels. The levels before observation of buckling were 164, 204, 190, and 239 psi for the four specimens.

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Catalyzed Thermal Decomposition of Ammonium Perchlorate

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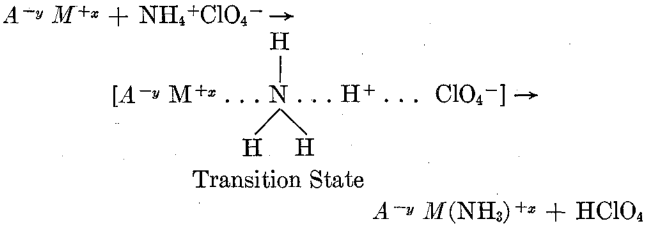
Recent studies[1,2] on the thermal decomposition of ammonium perchlorate strongly indicate that proton transfer, resulting in the formation of ammonia and perchloric acid, is the rate-determining step. In the light of this finding, it is proposed that the effect of catalysts on the thermal decomposition of ammonium perchlorate can now be understood.

The observations in the literature concerning the relative effectiveness of catalysts can be summarized as follows in decreasing order of effectiveness for groups of elements: transition metals, alkaline earths, and alkalis. With respect to specific elements it has been recently shown that the following decreasing order of effectivenss prevails: zinc, cadmium, and magnesium.[3]

It is noteworthy that the ranking for both the groups of elements and the individual elements is the same as the relative stabilities of the ammonia complexes of the respective metal ions.[4] This correlation is of significance because a metal-ammonia complex can facilitate proton transfer by providing a lower activation energy pathway in contrast to the direct transfer of a proton. This process may be depicted in a sketchy manner as follows:



$$A^{-y}M^{+x} + NH_4{}^+ClO_4{}^- \rightarrow$$

$$[A^{-y}M^{+x}\ldots \underset{H\quad H}{\overset{H}{N}}\ldots H^+\ldots ClO_4{}^-] \rightarrow$$

Transition State

$$A^{-y}M(NH_3)^{+x} + HClO_4$$

If the proposed mechanism is correct a number of relationships should hold. Cadmium, which is an effective catalyst for the decomposition of ammonium perchlorate, should be considerably less effective on methyl ammonium perchlorate because the cadmium ammonia complex is several orders of magnitude more stable than the cadmium methylammine complex.[4] Catalysts effective on ammonium perchlorate should not be effective on alkali metal perchlorates. If a catalyst is initially combined with a radical and the resulting complex is more stable than the respective ammonia complex, the catalyst will be deactivated.

Obviously, the proposed mechanism will not explain every observed case of catalysis. However, it is felt that a large group of catalytic effects can be explained by an ammonia-complex mechanism.

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