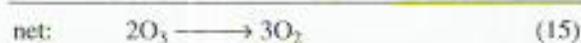
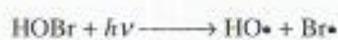


The principal catalytic cycles involving  $\text{ClO}_x$  and  $\text{BrO}_x$  species are believed to be as shown in Cycles 2, 3 and 4.

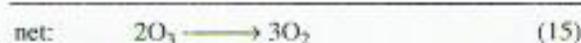
Cycle 2



Cycle 3



Cycle 4



(a) (7 marks) In the mid-latitude lower stratosphere, levels of 'active' chlorine and bromine radicals ( $\text{ClO}_x$  and  $\text{BrO}_x$ ) are influenced by heterogeneous reactions of reservoir molecules taking place on the surface of the sulfate aerosol particles that normally pervade this region.

(i) Explain briefly the significance of the term 'reservoir molecules', and the part such species play in stratospheric ozone chemistry. (About 100–150 words)

(ii) For the physical conditions and background level of aerosol prevalent in the mid-latitude lower stratosphere, recent laboratory studies indicate that the heterogeneous reactions of bromine reservoirs (e.g.  $\text{HBr}$  and  $\text{BrONO}_2$ ) are more rapid than those of the corresponding chlorine compounds. Model calculations which include heterogeneous bromine chemistry predict increases in  $\text{HO} \cdot$  and  $\text{BrO} \cdot$  concentrations above the levels calculated on the basis of gas-phase chemistry alone. Moreover, because of the reaction of  $\text{HO} \cdot$  with  $\text{HCl}$ , the increase in  $[\text{HO} \cdot]$  is expected to lead indirectly to an

increase in the concentration of the  $\text{ClO} \cdot$  radical. Explain very briefly why this should be so. (Two or three short sentences)

(b) (18 marks) The model predictions mentioned in part (a)(ii) have been confirmed by *in situ* measurements aboard the NASA ER-2 aircraft; the abundance of both  $\text{ClO} \cdot$  and  $\text{BrO} \cdot$  in the mid-latitude lower stratosphere is higher than previously thought, by a factor of ten for  $\text{ClO} \cdot$ . Typical volume mixing ratios are currently as follows:

$$\text{ClO} \cdot: 100 \text{ p.p.t.v.} = 100 \times 10^{-12}$$

$$\text{BrO} \cdot: 15 \text{ p.p.t.v.} = 15 \times 10^{-12}$$

Expressions for the rate of ozone loss ( $-\text{d}[\text{O}_3]/\text{d}t$ ) obtained by applying a steady-state treatment to each of Cycles 1–4 in turn are collected in Table 2. Also included in the table are the corresponding values of the rate of loss (expressed in the unit 'parts per billion per day'), calculated from known values of the rate constants and current concentrations of the various species in the mid-latitude lower stratosphere.

Table 2 Information on the rate of ozone loss by Cycles 1, 2, 3 and 4 for current conditions in the mid-latitude lower stratosphere

Cycle	$-\text{d}[\text{O}_3]/\text{d}t$	rate of ozone loss p.p.b.v. per day
1	$2k_{17}[\text{O}_3][\text{HO}_2 \cdot]$	3.8
2	$2k_{18}[\text{ClO} \cdot][\text{HO}_2 \cdot]$	2.5
3	$2k_{19}[\text{BrO} \cdot][\text{HO}_2 \cdot]$	1.3
4	$2k_{20}[\text{BrO} \cdot][\text{ClO} \cdot]$	5.0

Using the information provided in this question (in addition to that in Topic Study 1), produce a concise but well-reasoned discussion of the implications, for past and future ozone levels at mid-latitudes, of the release of chlorine and bromine compounds by human activities. As a basis for your discussion, compare the rate of ozone destruction by Cycles 2, 3 and 4 with the rate due to the 'natural'  $\text{HO}_x$  Cycle 1, and with one another, and consider qualitatively the significance of heterogeneous bromine chemistry for these various processes. Include comment on other factors that may also affect the future state of the ozone layer.

Your answer should be about 400 words in length and suitably structured, not simply a list of points. Make sure that your statements or conclusions are supported by precise references to the information in Table 2 and to other relevant information provided in this question and/or Topic Study 1. Up to 3 marks will be awarded for the overall clarity, structure and coherence of your answer.

