2. This question is about atmospheric chemistry

Studying the reactions which take place in the atmosphere is crucial to help understand global climate and thus minimise our impact on the environment. Hydrogen sulfide, H_2S, is a molecule which displays interesting chemistry in the atmosphere. H_2S is present in natural gas and is also particularly common near volcanos.

A sulfur boulder in the crater of a volcano.

The main process by which H_2S is naturally removed from the air is its reaction with the OH radical (the main day-time oxidising agent in the atmosphere). The reaction happens in a single encounter between H_2S and the OH radical.

(a) Give an equation for the reaction of H_2S with the OH radical to form water and another radical.

In order to determine the rate constant of the reaction in **(a)**, dry H_2S was generated in the laboratory by reacting iron(**II**) sulfide with hydrochloric acid.

(b) Give an equation for the generation of H_2S in the laboratory.

The average emission rate of H_2S in the air at a volcanic region can be taken to be 7.65×10^5 molecules cm^{-3} s^{-1}. The concentration of H_2S was measured to be constant over time, which means that the rate with which H_2S is produced is the same as the rate at which H_2S is consumed at this volcanic region.

For a reaction that happens in a single encounter between two species A and B, the rate of reaction is given by:

$$\text{rate} = k \times [A] \times [B]$$

where k is the corresponding rate constant, and [A] and [B] denote the concentrations of A and B, respectively.

(c) Calculate the concentration of H_2S in the atmosphere in units of molecules cm^{-3}.

You should assume that the only removal process of H_2S from the atmosphere is its reaction with the OH radical, and that the average concentration of the OH radical is 1.1×10^6 molecules cm^{-3}. The rate constant for the reaction in part **(a)** was measured to be $k = 4.7 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}.

(d) The average concentration of H_2S is usually expressed in units of μg m^{-3}. Express the concentration of H_2S found in part **(c)** in units of μg m^{-3}.

Natural gas often contains sulfur in the form of H_2S. To minimise the sulfur emission from the desulfurization of natural gas, H_2S is partially combusted to form SO_2 which then reacts with the remaining H_2S to form elemental sulfur.

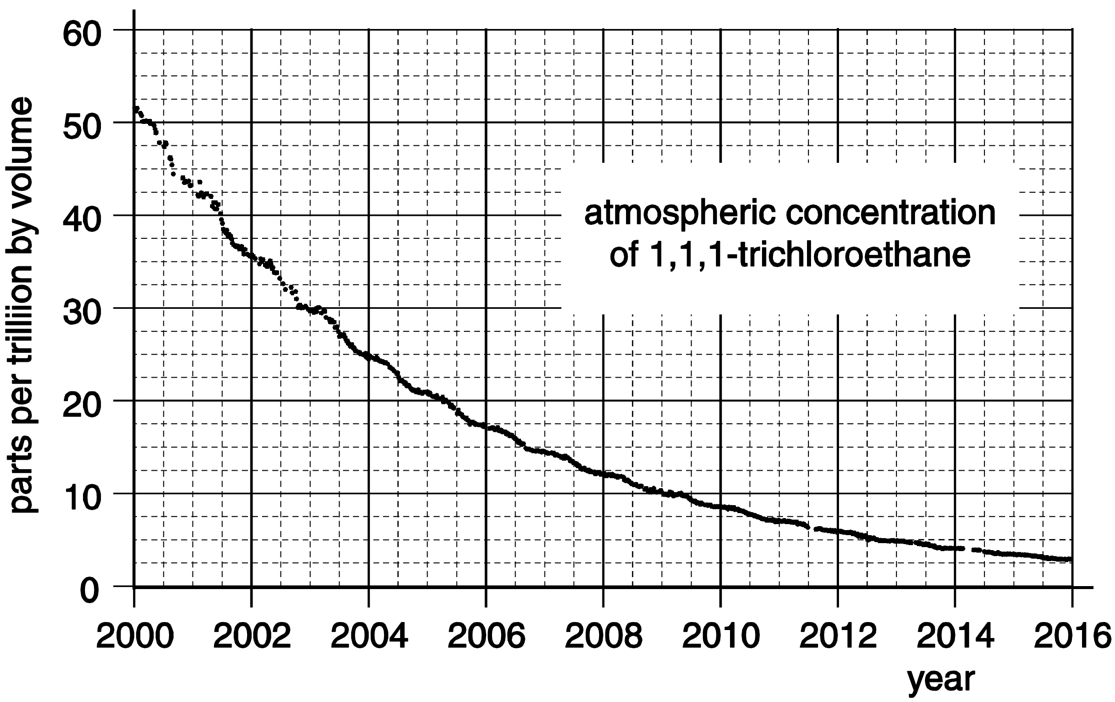
(e) **(i)** Give an equation for the combustion of H_2S.

(ii) Give an equation for the reaction of H_2S with SO_2.

It is very hard to measure the concentration of OH radicals directly, so we often have to resort to indirect methods. In addition to H_2S, the OH radical is able to oxidise other compounds in the atmosphere, such as 1,1,1-trichloroethane. Since the atmospheric emission of 1,1,1-trichloroethane stopped in the 1990s, its change in concentration can be used to indirectly estimate the average global concentration of the OH radical. The concentration profile of 1,1,1-trichloroethane over time shows a simple exponential decay, typical of reactions following first-order kinetics.

(f) **(i)** Using the graph below, estimate the half-life ($t_{1/2}$) of 1,1,1-trichloroethane to the nearest 0.1 years.

(ii) Convert your answer to **f(i)** into seconds. [Take 1 year to be 365.25 days.]



Assuming that the concentration of the OH radicals is constant over time, and that the only removal process of 1,1,1-trichloroethane from the atmosphere is its reaction with OH, we can find the observed rate constant (k_{obs}) of the reaction using the following expression:

$$t_{1/2} = \frac{\ln 2}{k_{obs}}$$

The observed rate constant, k_{obs}, is a product of the second order rate constant ($k_{2nd} = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}) and the concentration of the OH radicals.

(g) Using your value for the half-life of 1,1,1-trichloroethane, calculate the average global atmospheric concentration of OH radicals in molecules cm^{-3}.

(Note: you may not get exactly the same result as the concentration given in the first part of the problem.)