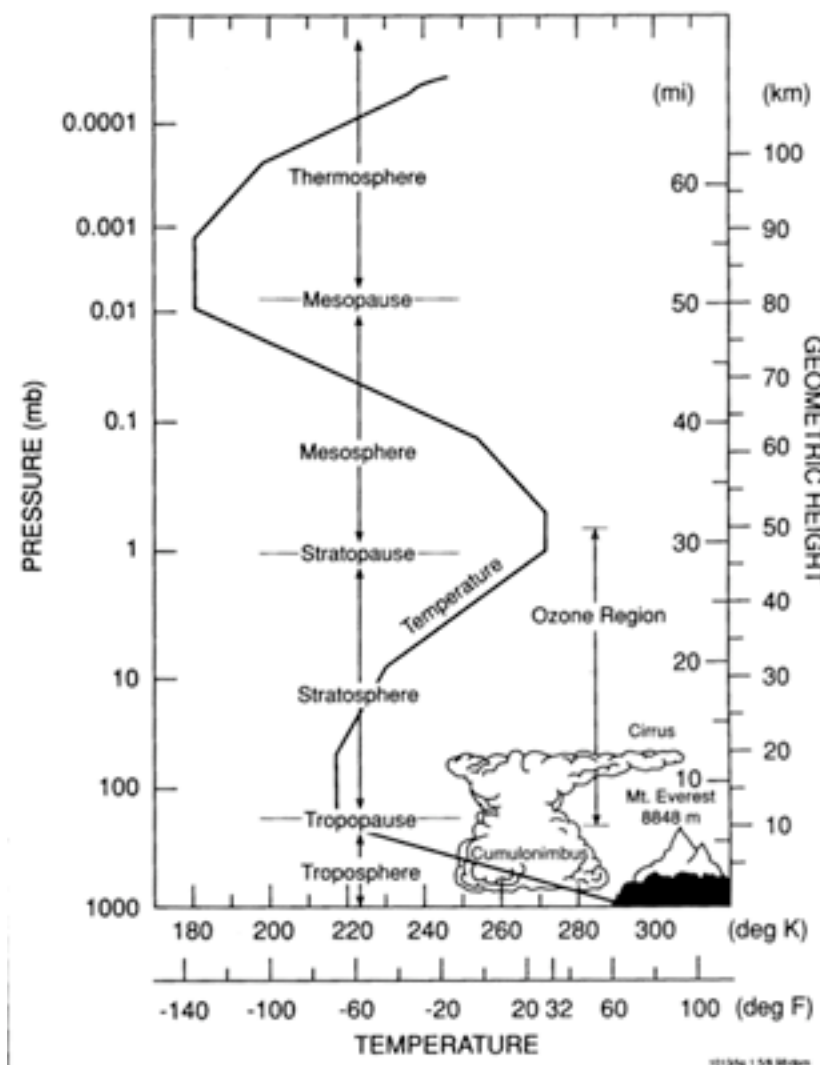


An unstable steady state is a metastable state. Steady state instability exists when the system cannot reach equilibrium (a steady state condition) but oscillates continuously. A system can oscillate, but eventually reach a steady (equilibrium) state.

4. How is the troposphere defined? What altitude range does it occupy? What are typical pressures and temperatures?

The troposphere is the layer of the atmosphere closest to the earth's surface. It ranges from 8-14.5 km in depth (26,000 to 48,000 feet; to give you a sense, the height of Mount Everest is 8850m/29,000ft). The layers of the atmosphere are defined by critical points on the altitude vs. temperature graph. The temperature ranges from about 20°C to -52°C in the troposphere. The pressure ranges from about 1 atm at the surface to 0.1 atm at the tropopause.



Atmospheric Chemistry and Global Change. See Gallery [4] for details.

5. What do the authors consider their most significant finding?

The authors say that the potential for steady state instability is the most significant finding. There may be no equilibrium state for the atmosphere.

- 6. The authors give rate constants for model M1, but don't specify the temperature at which the rate constants were determined. Should they? Can you find the temperature?**

Most rate constants are quite sensitive to temperature, so the temperature should be specified explicitly. A footnote in Table 2 (footnote b, p. 11217) suggests the temperature is 253K (-20°C).

- 7. Using the mechanism designated M1, apply the steady state approximation to ozone and solve for an expression for the concentration of ozone. Estimate (to an order of magnitude) the steady state concentration of ozone expected for this model when the concentrations of NO and NO₂ are on the order of 10^{9.5} and that of HO₂ is O(10⁷). How does this compare to what model M1 produces?**

From mechanism M1

$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{O}_3] - k_3[\text{HO}_2][\text{O}_3] - k_4[\text{NO}][\text{O}_3] + k_5[\text{NO}_2] - S_{\text{O}_3}$$

when [O₃] is at a steady state

$$\frac{d[\text{O}_3]}{dt} \approx 0 = -k_1[\text{O}_3] - k_3[\text{HO}_2][\text{O}_3] - k_4[\text{NO}][\text{O}_3] + k_5[\text{NO}_2] - S_{\text{O}_3}$$

solving for [O₃]

$$[\text{O}_3]_{ss} = \frac{k_5[\text{NO}_2] - S_{\text{O}_3}}{k_1 + k_3[\text{HO}_2] + k_4[\text{NO}]}$$

rate constants are in /sec and cm³/molecule-sec. Concentrations are in molecules/cm³

$$[\text{O}_3]_{ss} = \frac{(3.9 \times 10^{-3})(10^{9.5}) - (6.0 \times 10^{-4})}{(6.9 \times 10^{-8}) + (1.5 \times 10^{-4})(10^7) + (7.9 \times 10^{-15})(10^{9.5})}$$

$$= 5 \times 10^{11}$$

The graph in Figure 1a shows that the concentration of ozone oscillates around a value of about 3×10^{11} molecules/cm³, which is not far off the steady state estimate.

- 8. The authors suggest that the oscillatory behavior shown in Figure 1 is a switching between two steady state situations, one characterized by high concentrations of NO_x and one by lower concentrations. Roughly what is the concentration of all the NO_x species in the two states predicted by the four different models? How are the phases of the fluctuations in HO_x and NO_x related in each case? What are the key differences in the behaviors of the models?**

Model	Range of NO _x concentrations	Phases NO _x , HO _x
-------	---	--

M1	$10^8 - 4 \times 10^9$	roughly 180° out of phase
M2	$2 \times 10^9 - 10^{11}$	roughly 180° out of phase
M3	$10^{10} - 10^{11}$	roughly 180° out of phase
M4	$10^{14} - 10^{15}$	increases are in phase, but spike in HO _x appears to result in depletion of NO _x (hard to tell from graph)

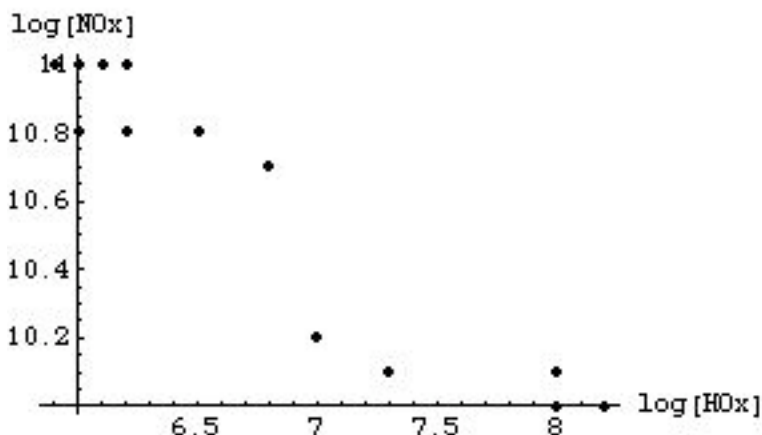
9. The graphs in Figure 1 are too crude for the following to give you truly meaningful results, but this exercise will nonetheless give you a sense of what you might discover by constructing phase portraits from concentration versus time data. Use Figure 1c and sketch the phase behavior of HO_x and NO_x. What do you notice? Do your results support the authors' contentions about the relationship between the two sets of species?

Reading the graph (roughly) I generated the table of data below. I then used Mathematica to create a phase portrait for HO_x and NO_x.

<u>log₁₀(HO_x)</u>	<u>log₁₀(NO_x)</u>
6.0	11.0
6.2	11.0
6.8	10.7
8.0	10.1
8.2	10.0
7.3	10.1
6.2	10.8
6.0	11.0
5.9	11.0
6.0	11.0
6.0	11.0
6.1	11.0
6.5	10.8
8.2	10.0
8.0	10.0
7.0	10.2
6.0	10.8
5.9	11.0
5.9	11.0
6.0	11.0

If the system were switching in a quantized way between two states (let's say one with HO_x concentrations around 10^6 and NO_x around 10^{11} and another with HO_x around 10^8 and NO_x around 10^{10}), you'd expect the phase portrait of the logs of the concentrations to

have just two points on it, at (5,11) and (8,10). In a real experiment, where you had concentrations that varied continuously (not in a quantized, jump like, fashion) you might expect a cluster of points around each of the “attractors” and a line of points joining the two. If you squint at the phase portrait generated by the data in the table above, you might see something like that.



This plot was generated using the commands:

```
data=Transpose[{{6,6.2,6.8,8.0,8.2,7.3,6.2,6.0,5.9,6.0
,6,6.1,6.5,8.2,8.0,7,6.0,5.9,5.9,6.0},{11,11,10.7
,10.1,10.0,10.1,10.8,11,11,11,11,11,10.8,10.0,10,
10.2,10.8, 11,11,11}}]
ListPlot[data, PlotStyle -> PointSize[0.02], AxesLabel-
->{"log[HOx]","log[NOx]"}]
```