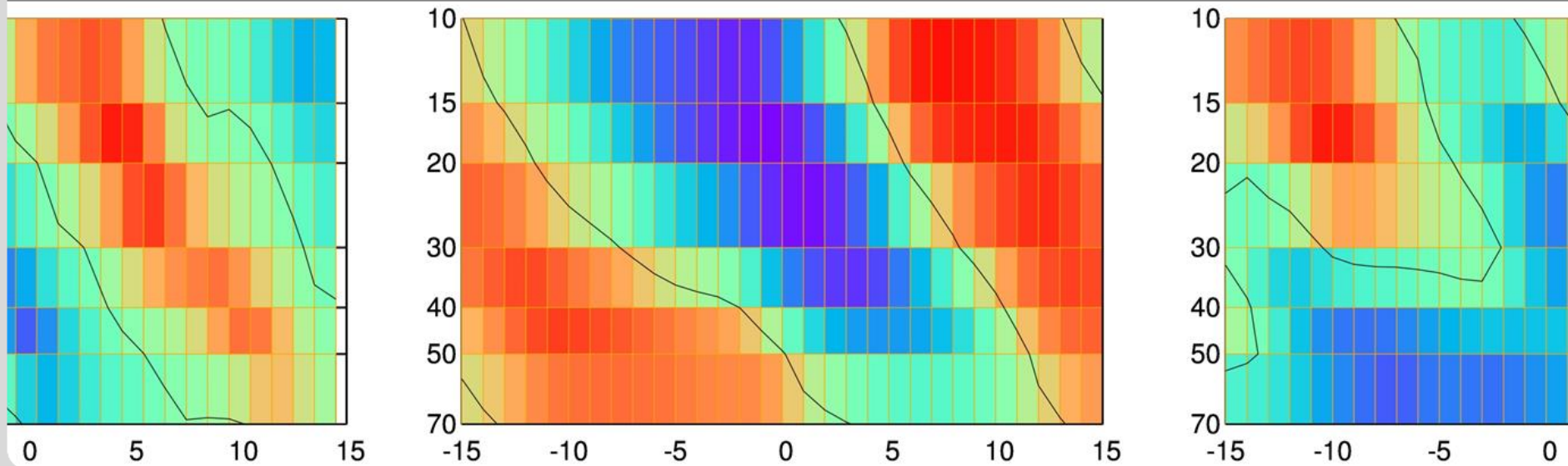


Practical on Modelling (Stratosphere)

Peter Braesicke

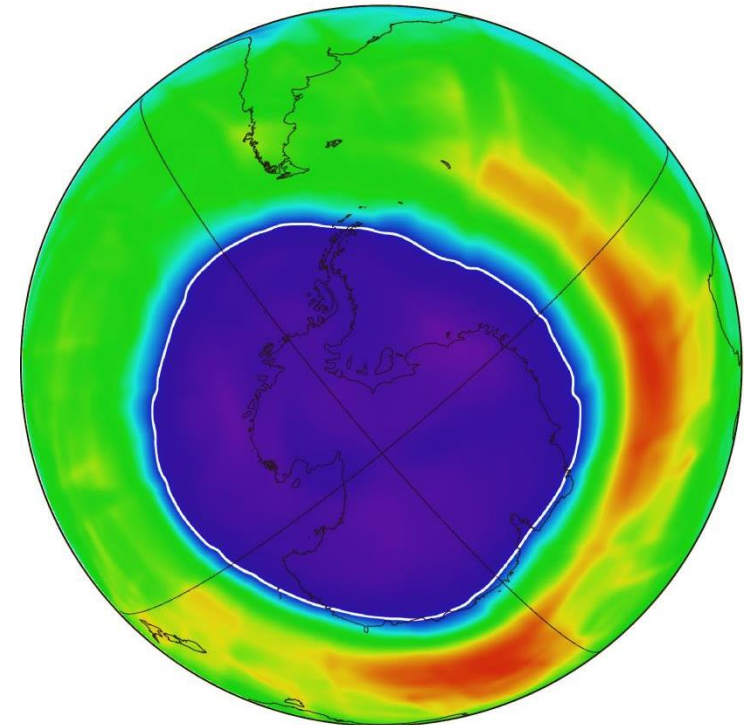
IMK-ASF



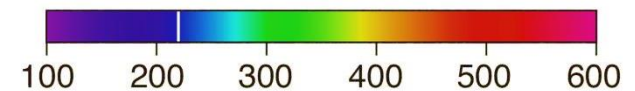
Example: Polar Ozone Depletion

- What is happening?
- Why is it happening?
- What are the important parameters?
- Does Climate change matter?

Antarctic Ozone Hole

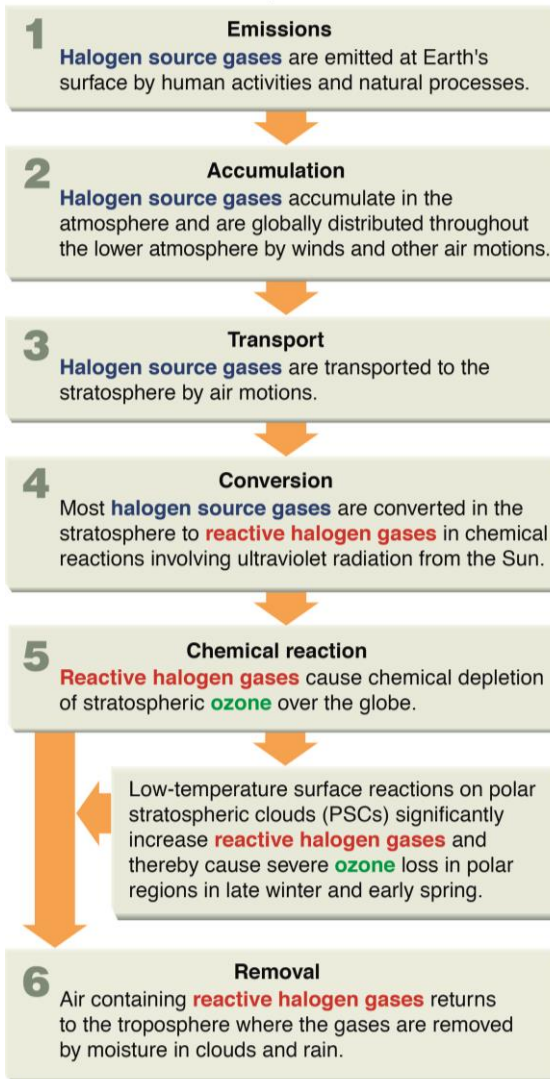


17 September 2009

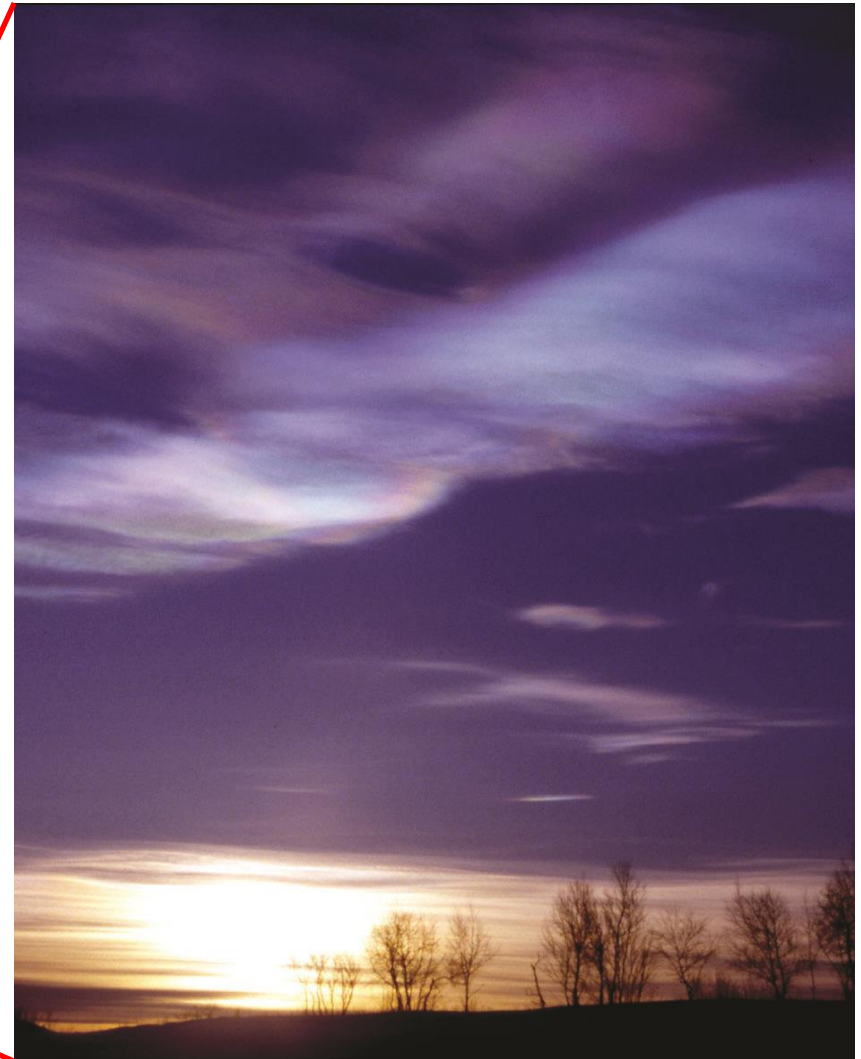


Total ozone (Dobson units)

Principal Steps: Ozone Hole

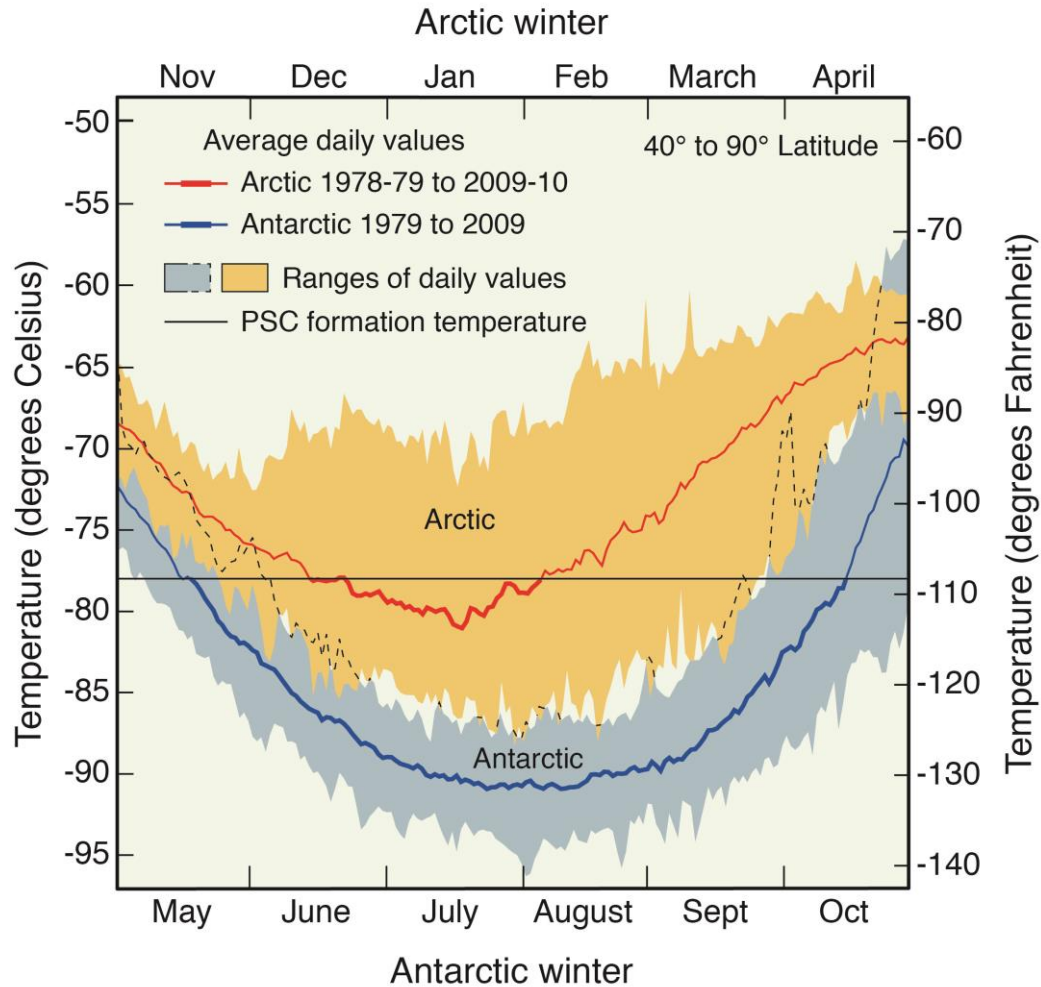


Polar Stratospheric Clouds (PSCs)



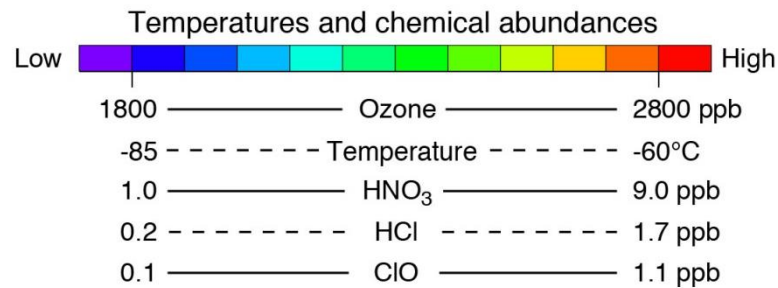
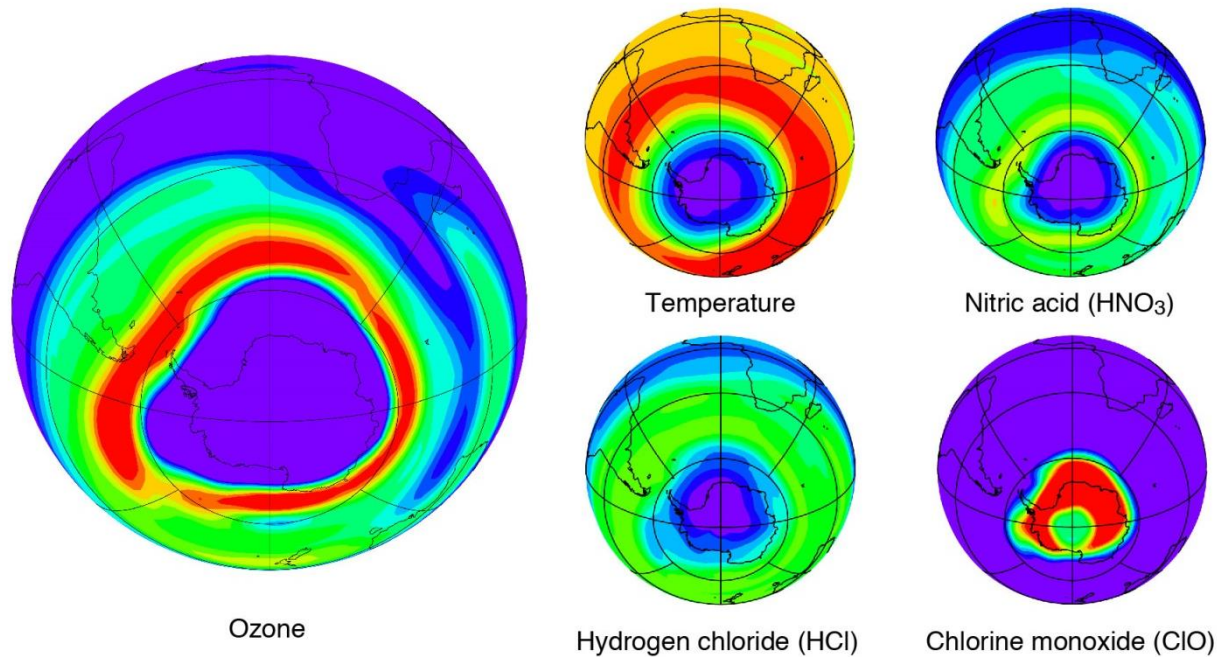
The Trigger: Temperature

Minimum Air Temperatures in the Polar Stratosphere



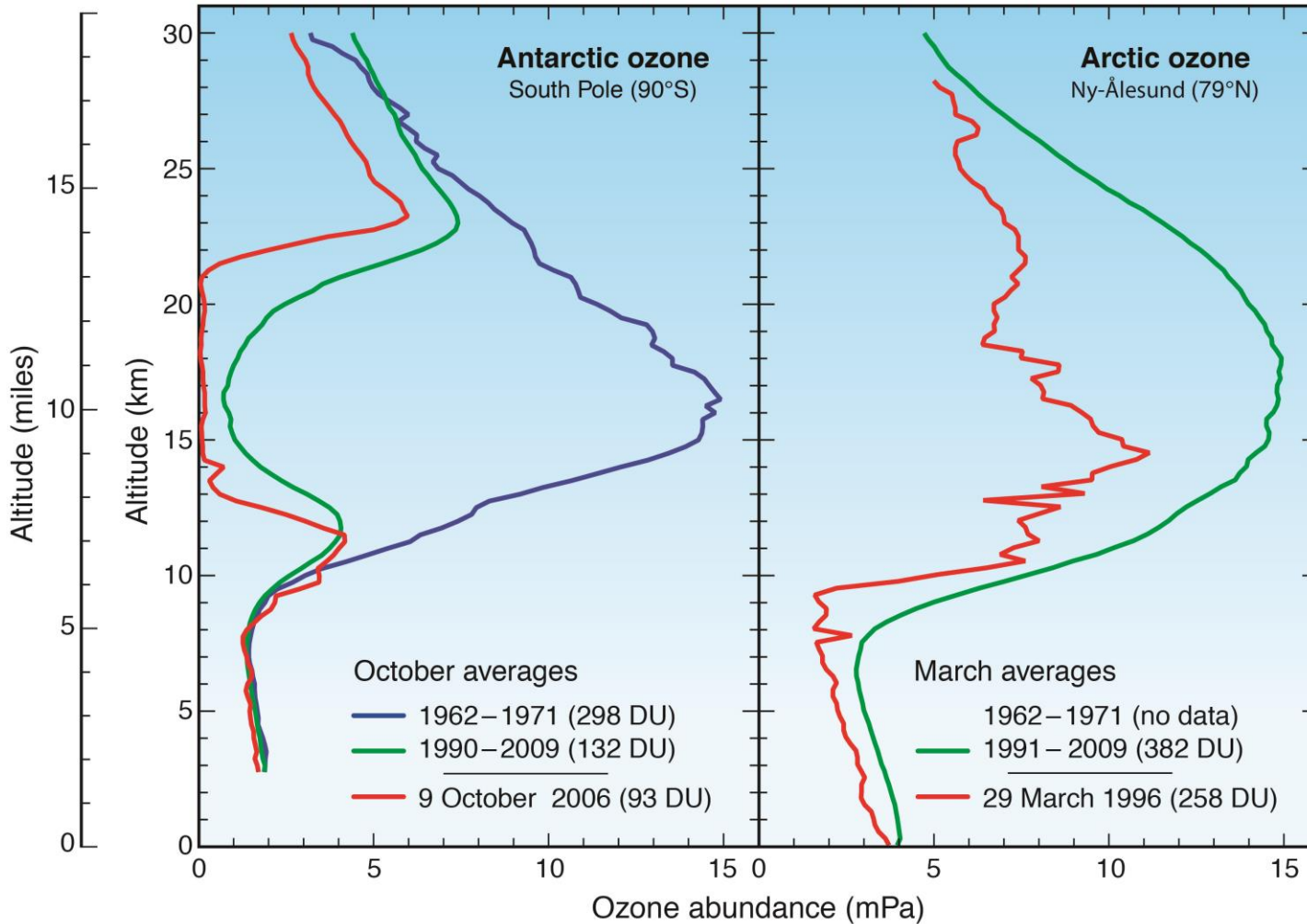
Ozone Depletion

Large ozone depletion in late winter (15 September 2008) at 18-km altitude



Ozone Profiles

Polar Ozone Depletion



Where is the Atmosphere Cold?

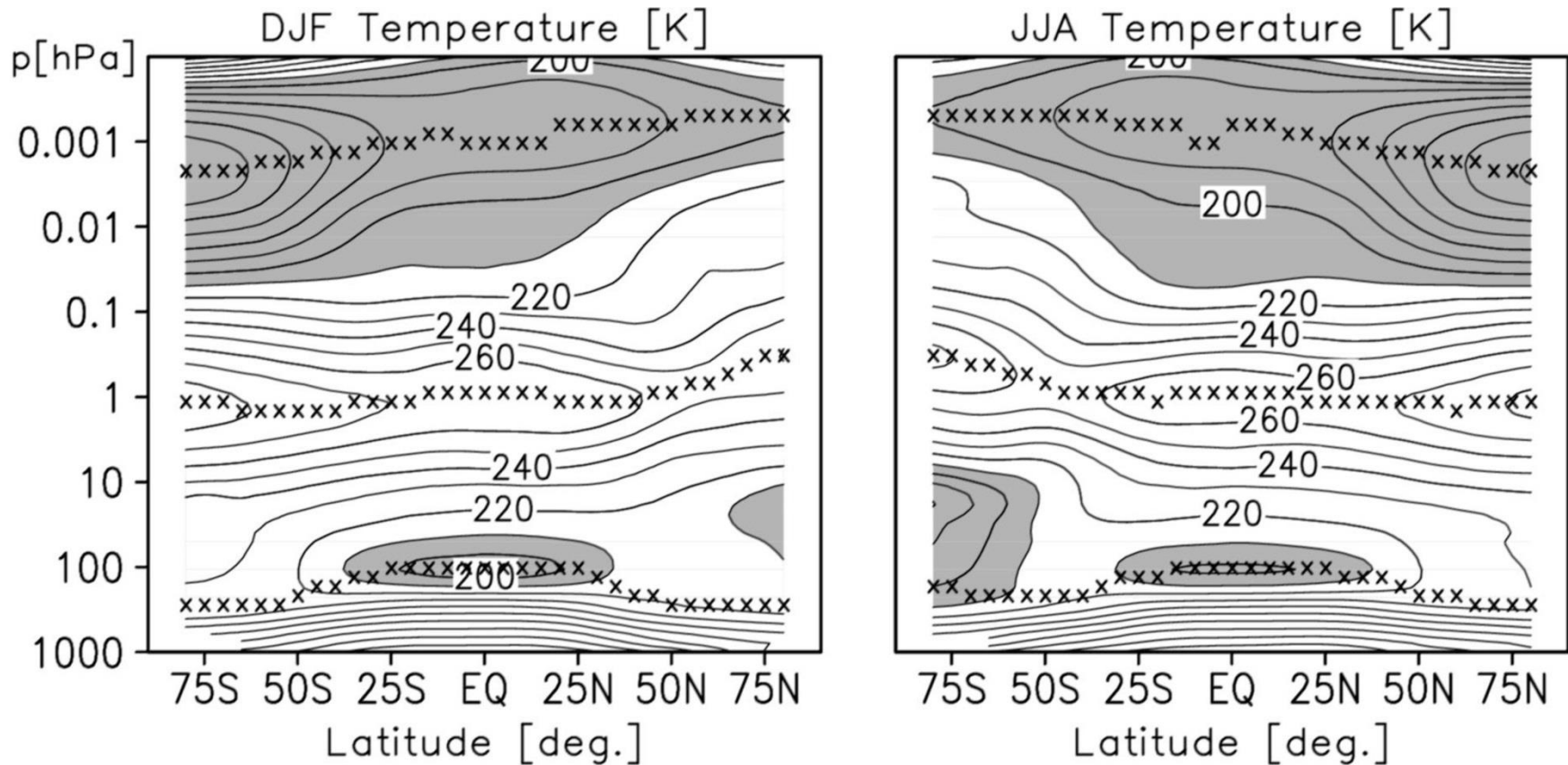


Figure 2: Zonal mean temperature as a function of latitude and pressure for December-January-February (DJF; left) and June-July-August (JJA; right). Crosses indicate the thermal tropopause, stratopause and mesopause (from bottom to top).

Questions:

- What is a PSC?
 - Many answers! See wikipedia or literature ...
 - Today's answer: Nitric Acid Trihydrate (NAT) (Type Ia)
 - Hydrate: A substance that contains water ...
 - NAT: $(\text{HNO}_3 \cdot 3\text{H}_2\text{O})$

- When do PSCs form (pressure dependent)?
 - Is it cold enough to form PSCs?
 - Do we have enough water (vapour) to form PSCs?
 - Do we have enough HNO_3 (Nitric Acid) to form PSCs?

Lab Measurements ...

GEOPHYSICAL RESEARCH LETTERS, VOL. 15, NO. 8, PAGES 855-858, AUGUST 1988

LABORATORY STUDIES OF THE NITRIC ACID TRIHYDRATE: IMPLICATIONS FOR THE SOUTH POLAR STRATOSPHERE

David Hanson and Konrad Mauersberger

School of Physics and Astronomy, University of Minnesota

Abstract. Vapor pressures of HNO_3 and H_2O have been measured over the trihydrate crystal, formed by vapor deposit on a glass surface. In the temperature range 190 K to 205 K the two phase-equilibrium trihydrate/vapor was studied by adding and removing H_2O . Coexistence equilibria vapor pressures of trihydrate/solid solutions of HNO_3 in ice ('ice') and of mono-/trihydrate were also measured. Results show that for typical mixing ratios of H_2O and HNO_3 found in the lower stratosphere (3 ppm H_2O , 5 ppb HNO_3) the trihydrate would start to form at temperatures about 7 K higher than the ice point. The pressure of atmospheric HNO_3 would rapidly decrease as the atmosphere cools without large changes in partial pressures of H_2O . These laboratory results provide information on the formation of polar stratospheric clouds containing H_2O and HNO_3 .

the stability regions and they concluded that the trihydrate is the crystal that would form.

A nitric acid-water mixture is a complex binary system of which very little has been experimentally investigated at low temperatures. Pickering (1893) as well as Kuester and Kremann (1904) have measured in detail the freezing temperatures of $\text{HNO}_3/\text{H}_2\text{O}$ mixtures for concentrations ranging from pure water to nearly pure HNO_3 . They identified three eutectic points (four-phase equilibria) and isolated two hydrates of nitric acid: a trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) formed from mixtures near an HNO_3 mole fraction of 0.25 and a monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$) formed near 0.50. Clavelin and Mirabel (1979) have calculated vapor pressure curves for various mole fractions of liquid $\text{HNO}_3/\text{H}_2\text{O}$ mixtures based on a collection of room-temperature data. When these vapor pressure curves are extrapolated to lower temperatures, freezing envelopes can be derived as shown by

Providing a Simple Model

The results of this series of measurements is summarized in Table 1. The bounds for the pressures over the trihydrate are as follows: The upper bound for HNO_3 and the lower for H_2O are the pressures over the mono-/trihydrate coexistence. Likewise, the lower bound for HNO_3 and the upper for H_2O are the pressures over the 'ice'/trihydrate coexistence. An equation for the behavior of the vapor over the trihydrate, (equation 1) has been derived and simplified for

the temperature range 180 to 200 K. The exact relation for the straight lines between the coexistence curves can be calculated, however results from equation 1 are within 1% over this temperature range.

$$\text{Log}(P_{\text{HNO}_3}) = m(T) * \text{Log}(P_{\text{H}_2\text{O}}) + b(T), \quad (1)$$

where

$$m(T) = -2.7836 - 0.00088 * T,$$

$$b(T) = 38.9855 - 11,397.0/T + 0.009179 * T$$

for $200 > T > 180$ K, P in Torr.

The composition of the condensed material was measured by rapidly warming the cold glass still and analyzing the resultant vapor. This can be done for only one state of the trihydrate for a set of measurements at a certain temperature and has an accuracy of about 10-20%. The average composition of three measurements was $X = 0.24 \pm 0.02$ when the state of the trihydrate was such as to give a vapor composition $\text{HNO}_3/\text{H}_2\text{O}$ of about 0.02. When the trihydrate gave a vapor composition of about 0.0002, the average HNO_3 mole fraction for six measurements was 0.20 ± 0.04 . From these measurements we conclude that the composition of the trihydrate is significantly less than 0.25 mole fraction, near 0.20, when it is in equilibrium with 'ice'.

Table 1. Expressions for the vapor pressures of H_2O and HNO_3 on the 'ice'/trihydrate (i) and the mono-/trihydrate (m) phase boundaries. $\text{Log}(P) = A - B/T$ with pressure in Torr and temperature in Kelvin.

Constituent	A	B
HNO_3 (m)	13.622	3561.3
H_2O (m)	10.049	2819.2
HNO_3 (i)	12.298	3968.0
H_2O (i)	10.431	2668.7

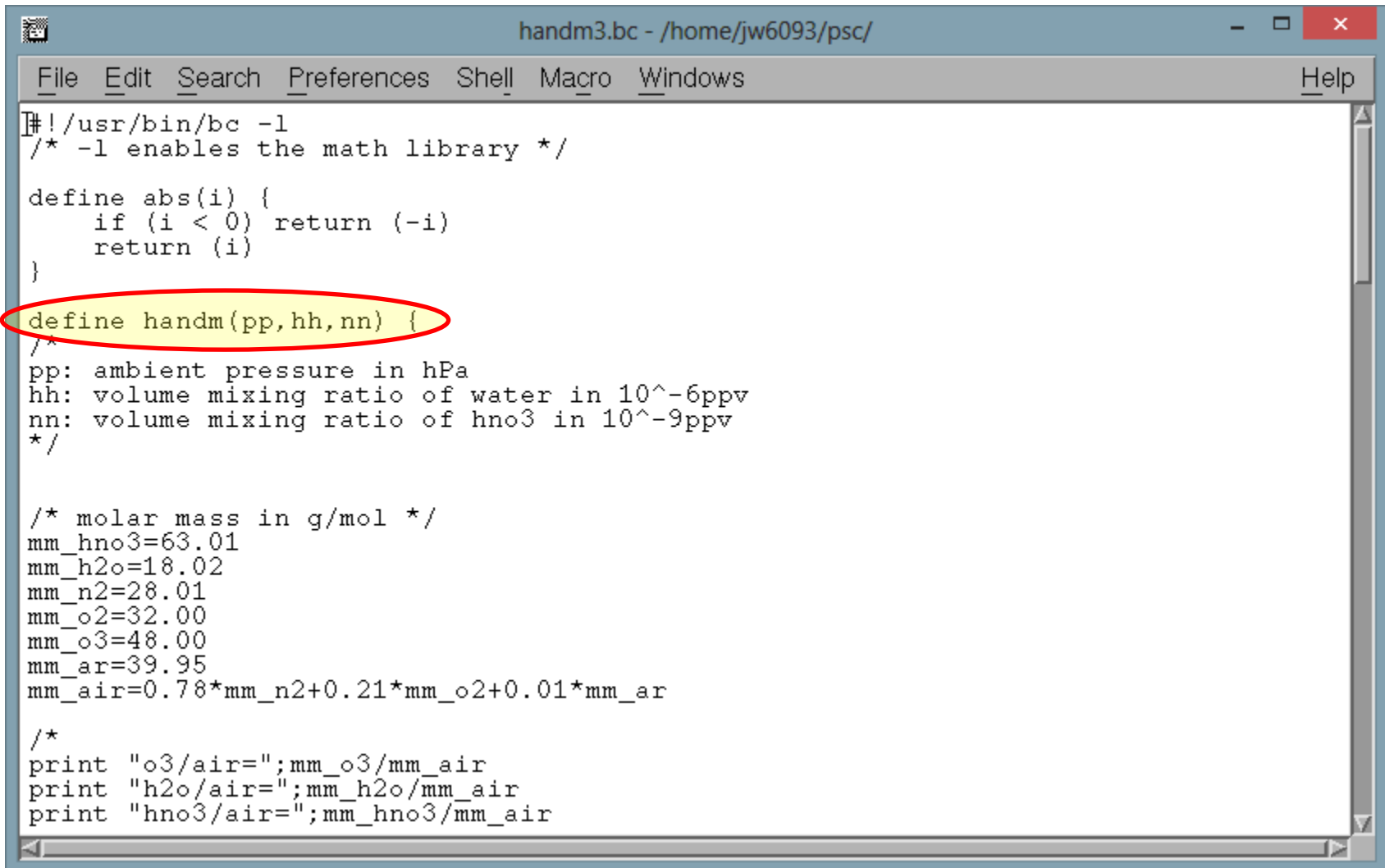
Arbitrary Precision Calculator

```

login
Main Options  VT Options  VT Fonts
bc(1)          General Commands Manual          bc(1)
NAME
bc - An arbitrary precision calculator language
SYNTAX
bc [ -hlwspq ] [long-options] [ file ... ]
VERSION
This man page documents GNU bc version 1.06.
DESCRIPTION
bc is a language that supports arbitrary precision numbers with inter-
active execution of statements. There are some similarities in the
syntax to the C programming language. A standard math library is
available by command line option. If requested, the math library is
defined before processing any files. bc starts by processing code from
all the files listed on the command line in the order listed. After
all files have been processed, bc reads from the standard input. All
code is executed as it is read. (If a file contains a command to halt
the processor, bc will never read from the standard input.)

This version of bc contains several extensions beyond traditional bc
Manual page bc(1) line 1 (press h for help or q to quit)
  
```

Scripting the Problem (1)



```
handm3.bc - /home/jw6093/psc/
File Edit Search Preferences Shell Macro Windows Help
#!/usr/bin/bc -l
/* -l enables the math library */

define abs(i) {
    if (i < 0) return (-i)
    return (i)
}

define handm(pp, hh, nn) {
/*
pp: ambient pressure in hPa
hh: volume mixing ratio of water in 10^-6ppv
nn: volume mixing ratio of hno3 in 10^-9ppv
*/

/* molar mass in g/mol */
mm_hno3=63.01
mm_h2o=18.02
mm_n2=28.01
mm_o2=32.00
mm_o3=48.00
mm_ar=39.95
mm_air=0.78*mm_n2+0.21*mm_o2+0.01*mm_ar

/*
print "o3/air=";mm_o3/mm_air
print "h2o/air=";mm_h2o/mm_air
print "hno3/air=";mm_hno3/mm_air
```

Scripting the Problem (2)

```
handm3.bc - /home/jw6093/psc/
File Edit Search Preferences Shell Macro Windows Help
/* pressure in hPa */
pres=pp
/* temperature in K (initial value; 180 < temp < 200) */
temp=180.0
/* water vapour */
h2o=hh*10^-6
/* reference hno3 (hno3 value in air) */
rhno3=nn*10^-9
hno3=0.0

hno3v1=-10
hno3v2=-10

/* convert pressure to torr */
presintorr=(pres*100.0)*(760.0/101325.0)

incr=0.1

/*
print "Start iteration ... \n";
*/
while ( abs(hno3-rhno3) > 1*10^-18 ) {
prhno3=presintorr*rhno3
logprhno3=l(prhno3)/l(10.0)
/*
print "prhno3=";prhno3
print "logprhno3=";logprhno3
*/
}
```

Scripting the Problem (3)

```

handm3.bc - /home/jw6093/psc/
File Edit Search Preferences Shell Macro Windows Help
ph2o=presintorr*h2o
logph2o=1(ph2o)/1(10.0)
/*
print "ph2o=";ph2o
print "logph2o=";logph2o
*/

m=-2.7836-(0.00088*temp)
b=38.9855-(11397.0/temp)+(0.009179*temp)
/*
print "m=";m
print "b=";b
*/

logphno3=(m*logph2o)+b
/*
print "logphno3=";logphno3
*/
phno3=e(1(10.0)*logphno3)
/*
print "phno3=";phno3
*/
hno3=phno3/presintorr

/*
print "=====\n"
print "hno3=";hno3*10^9
print "rhno3=";rhno3*10^9
print "temp=";temp

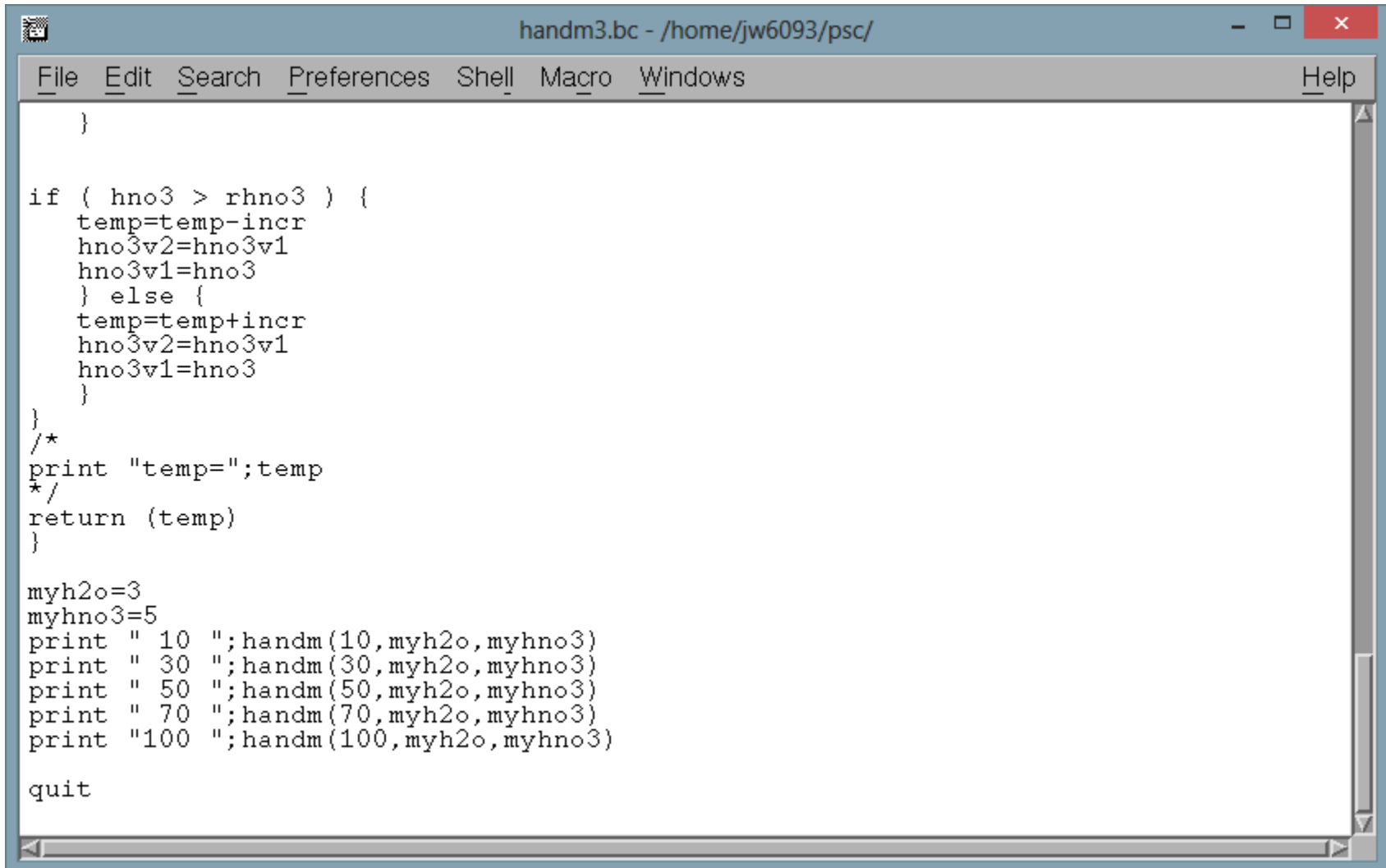
```

Scripting the Problem (4)

```
handm3.bc - /home/jw6093/psc/
File Edit Search Preferences Shell Macro Windows Help
/*
print "=====\n"
print "hno3=";hno3*10^9
print "rhno3=";rhno3*10^9
print "temp=";temp
print "=====\n"
*/
if ( hno3v2 == hno3 ) {
  incr=incr/10.0
}

if ( hno3 > rhno3 ) {
  temp=temp-incr
  hno3v2=hno3v1
  hno3v1=hno3
} else {
  temp=temp+incr
  hno3v2=hno3v1
  hno3v1=hno3
}
}
/*
print "temp=";temp
*/
return (temp)
}
```

Scripting the Problem (5)



```
handm3.bc - /home/jw6093/psc/
File Edit Search Preferences Shell Macro Windows Help
}

if ( hno3 > rhno3 ) {
  temp=temp-incr
  hno3v2=hno3v1
  hno3v1=hno3
} else {
  temp=temp+incr
  hno3v2=hno3v1
  hno3v1=hno3
}
}
/*
print "temp=";temp
*/
return (temp)
}

myh2o=3
myhno3=5
print " 10 ";handm(10,myh2o,myhno3)
print " 30 ";handm(30,myh2o,myhno3)
print " 50 ";handm(50,myh2o,myhno3)
print " 70 ";handm(70,myh2o,myhno3)
print "100 ";handm(100,myh2o,myhno3)

quit
```


Results

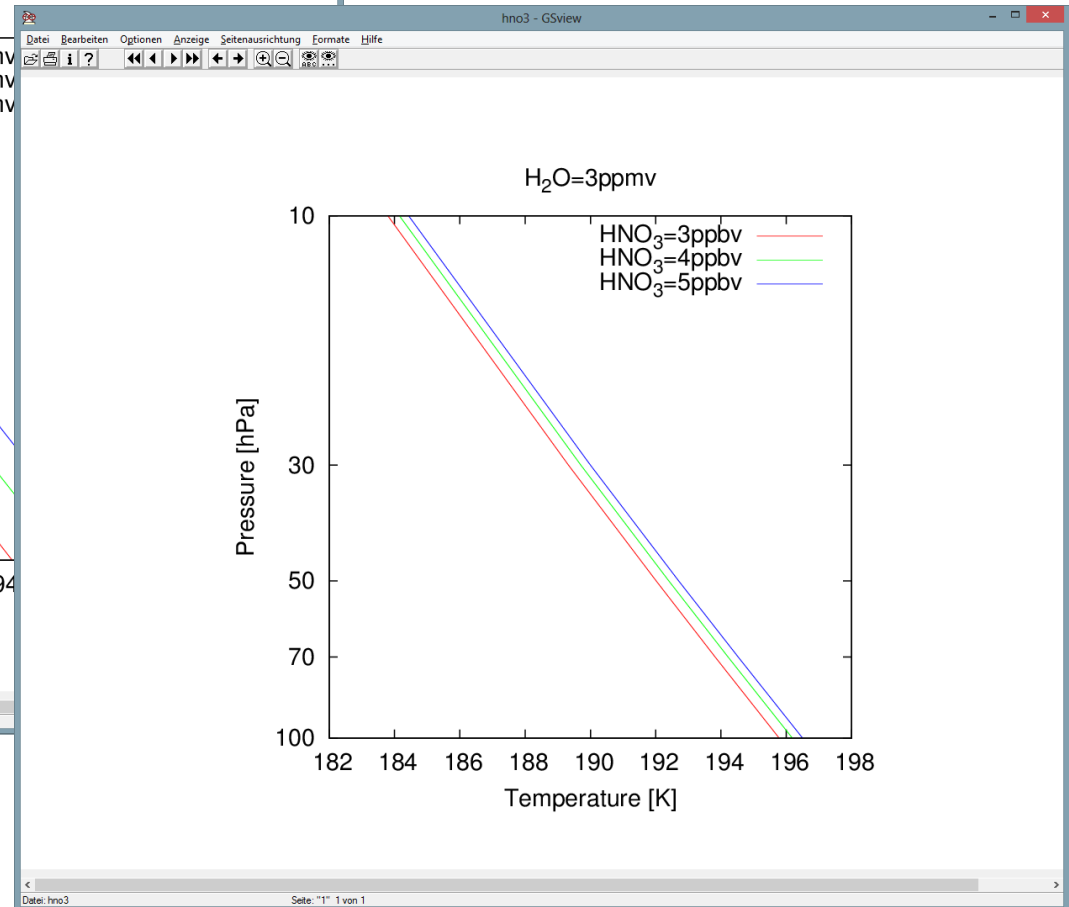
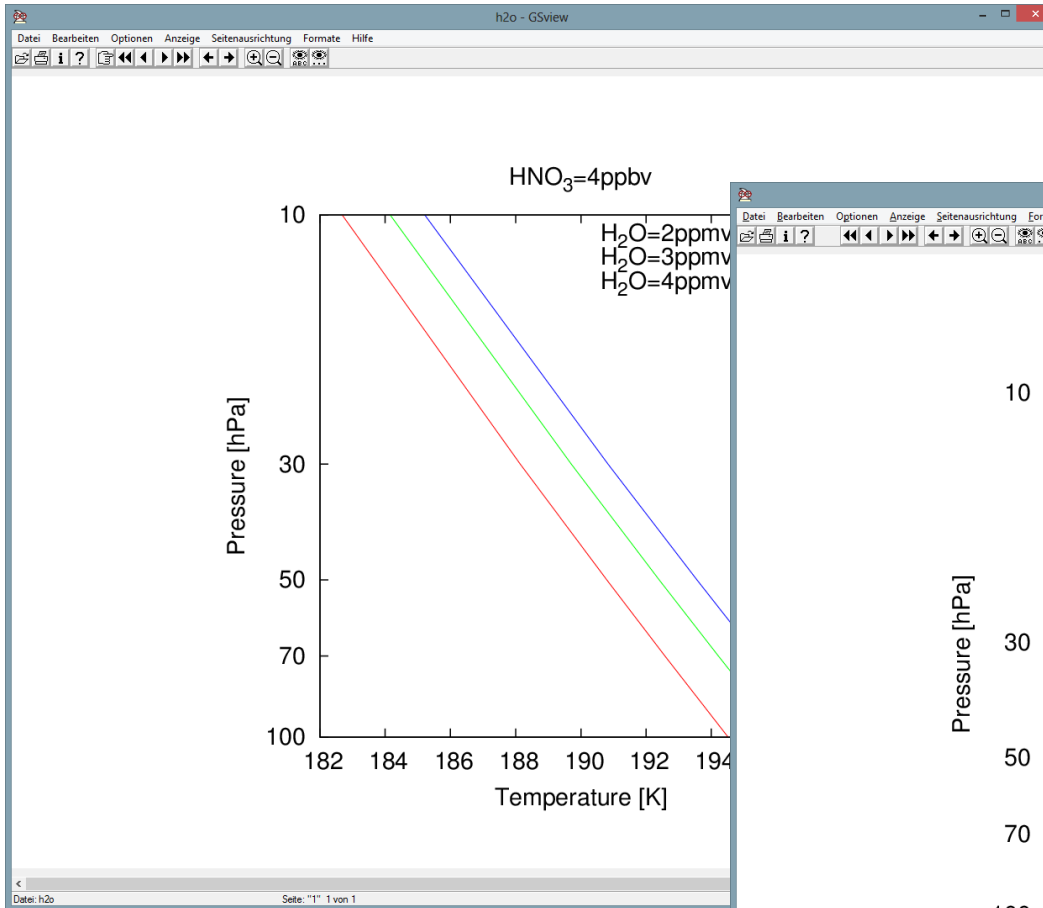
```
xterm
Main Options  VT Options  VT Fonts
sh-4.1$ ls
h2o.gnu  h2o=2.dat  h2o=4.dat  handm2.bc  hno3.gnu  hno3=3.dat  hno3=5.dat
h2o.ps   h2o=3.dat  handm1.bc  handm3.bc  hno3.ps   hno3=4.dat
sh-4.1$ ./handm3.bc
bc 1.06
Copyright 1991-1994, 1997, 1998, 2000 Free Software Foundation, Inc.
This is free software with ABSOLUTELY NO WARRANTY.
For details type `warranty'.
 10 184.428835800000000000000000000000
 30 189.997272128300000000000000000000
 50 192.702986269400000000000000000000
 70 194.527833667200000000000000000000
100 196.500499877200000000000000000000
sh-4.1$ gnuplot

      G N U P L O T
      Version 4.6 patchlevel 3   last modified 2013-04-12
      Build System: CYGWIN_NT-6.2-WOW64 i686

      Copyright (C) 1986-1993, 1998, 2004, 2007-2013
      Thomas Williams, Colin Kelley and many others

      gnuplot home:      http://www.gnuplot.info
      faq, bugs, etc:   type "help FAQ"
```

Graphical Results



Questions?

THANK YOU!