

# Problem Set 1

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Due Oct 15, show all work and state any assumptions.

```
system<-data.frame(mineral=c("an","gr","ky","q"),
  thermal_expans=c(14.3,30.0,11.2,8.0),
  compress=c(13.0,7.9,1.9,5.9),
  a=c(0.3914,0.7286,.3039,.0979),
  b=c(1.2556,-4.0986,-1.3390,-.3350)*10^-5,
  c=c(-3036.2,-3128.0,-895.2,-636.2),
  d=c(-2.5832,-6.0774,-2.9040,-.7740),
  S=c(199.3,256.0,82.3,41.5)*10^-3,
  V=c(10.079,12.535,4.414,2.269),
  H=c(-4232.74,-6638.30,-2595.33,-910.80))
```

## Question 1: Thermodynamic Units

Convert thermodynamic units for volume (J/bar) into something more intuitive. Use the attached data table (Table 7 from Holland and Powell 1990) to determine the molar volume of *an*,  $\bar{V}_{an}$  at 1 bar, 25C. Express the volume of one mole of *an* in terms of the volume of a common familiar object.

$$\bar{V} = \frac{J}{bar}$$

$$J = \frac{kg \cdot m^2}{s^2}$$

$$bar = 100,000 Pa$$

$$Pa = \frac{kg}{m \cdot s^2}$$

$$\bar{V} = \frac{\frac{kg \cdot m^2}{s^2}}{100,000 \frac{kg}{m \cdot s^2}} = \frac{1}{100,000} m^3$$

The molar volume of *an* at standard pressure and temperature (1 bar, 25C) is  $10.079 \frac{J}{bar}$  or  $1.0079 \cdot 10^{-4} m^3$ . To put this in perspective, a gallon is  $3.79 \cdot 10^{-3} m^3$  so 37.6 molar volumes of *an* would fit in one gallon.

```
gallon<-3.79e-3
an<-1.007e-4
aningallon<-gallon/an
```

## Question 2: Compressibility and thermal expansion

One expression of the molar volume ( $\bar{V}_j$ ) of a pure substance (*j*) as a function of pressure and temperature is (Holland and Powell 1990):  $\bar{V}_j(P, T) = \bar{V}_j^{P_0, T_0} + \alpha V * (T - T_0) - \beta V * (P - P_0)$

Use this expression to show that  $(\frac{\partial \bar{V}_j}{\partial T})_P$  and  $(\frac{\partial \bar{V}_j}{\partial P})_T$  are constant. [Note that  $\alpha V$  and  $\beta V$  are each single constant parameters in this expression.]

For this expression, all of the terms in blue below are constants under all circumstances, the terms in red are constants for  $(\frac{\partial \bar{V}_j}{\partial T})_P$  and the terms in green are constants for  $(\frac{\partial \bar{V}_j}{\partial P})_T$

$$\bar{V}_j(P, T) = \bar{V}_j^{P_0, T_0} + \alpha V * (T - T_0) - \beta V * (P - P_0)$$

So if we take the derivative of the molar volume with respect to temperature holding pressure constant then all terms in blue or red are constants and thus their derivatives are 0, leaving us with only the derivative of the middle term:

$$\left(\frac{\partial \bar{V}_j}{\partial T}\right)_P = 0 + \frac{d\alpha V T}{dT} - 0 - 0 = \alpha V$$

And for the derivative of the molar volume with respect to pressure holding temperature constant all of the terms in blue or green are constants so:

$$\left(\frac{\partial \bar{V}_j}{\partial P}\right)_T = 0 + 0 - \frac{d\beta V P}{dP} + 0 = -\beta V$$

And as established above, both  $\alpha V$  and  $-\beta V$  are constants.

### Question 3: Equations of state

Use the equation of state for volumes of pure substances from Holland and Powell (1990) and the attached data table (Table 7 from Holland and Powell 1990) to calculate how (i) the molar volume, (ii) thermal expansion, and (iii) compressibility of *an* change along a typical geothermal gradient ( $\approx \frac{25C}{km}$ ) between surface conditions (1 bar and 25C) and those at 35km depth. Plot your results.

```
depth<-seq(0,35,by=0.5)
temp<-depth*25+25+273.15
press<-depth*(10/35)+1*10^-3
```

$$\bar{V}_j^{P,T} = \bar{V}_j^{P_0,T_0} + \alpha V [T - T_0] - \beta V [P - P_0]$$

```
molar_volume<-
  system$V[1]+
  system$thermal_expans[1]*10^-5*(temp-temp[1])-
  system$compress[1]*10^-3*(press-press[1])
```

$$\alpha_j \equiv \frac{1}{\bar{V}_j} \left( \frac{\partial \bar{V}_j}{\partial T} \right)_P$$

Where  $\alpha_j$  is the coefficient given by Holland and Powell (1990). So to get the thermal expansion we need to multiply  $\alpha_j$  by the molar volume of phase  $j$ .

```
thermal_expansion<-system$thermal_expans[1]*10^-5*molar_volume
```

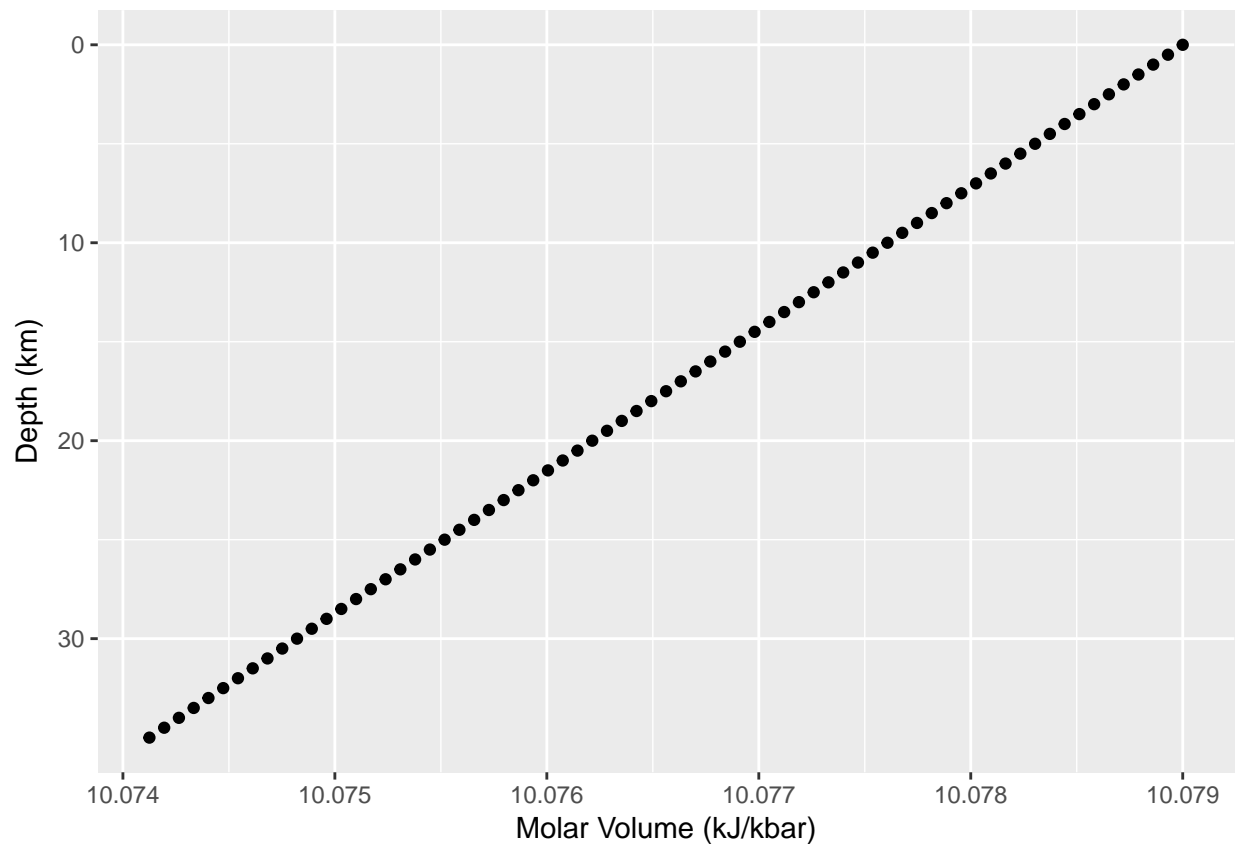
$$\beta_j \equiv \frac{-1}{\bar{V}_j} \left( \frac{\partial \bar{V}_j}{\partial P} \right)_T$$

Where  $\beta_j$  is the coefficient given by Holland and Powell (1990). So to get the compressibility we need to multiply  $\beta_j$  by the negative molar volume of phase  $j$ .

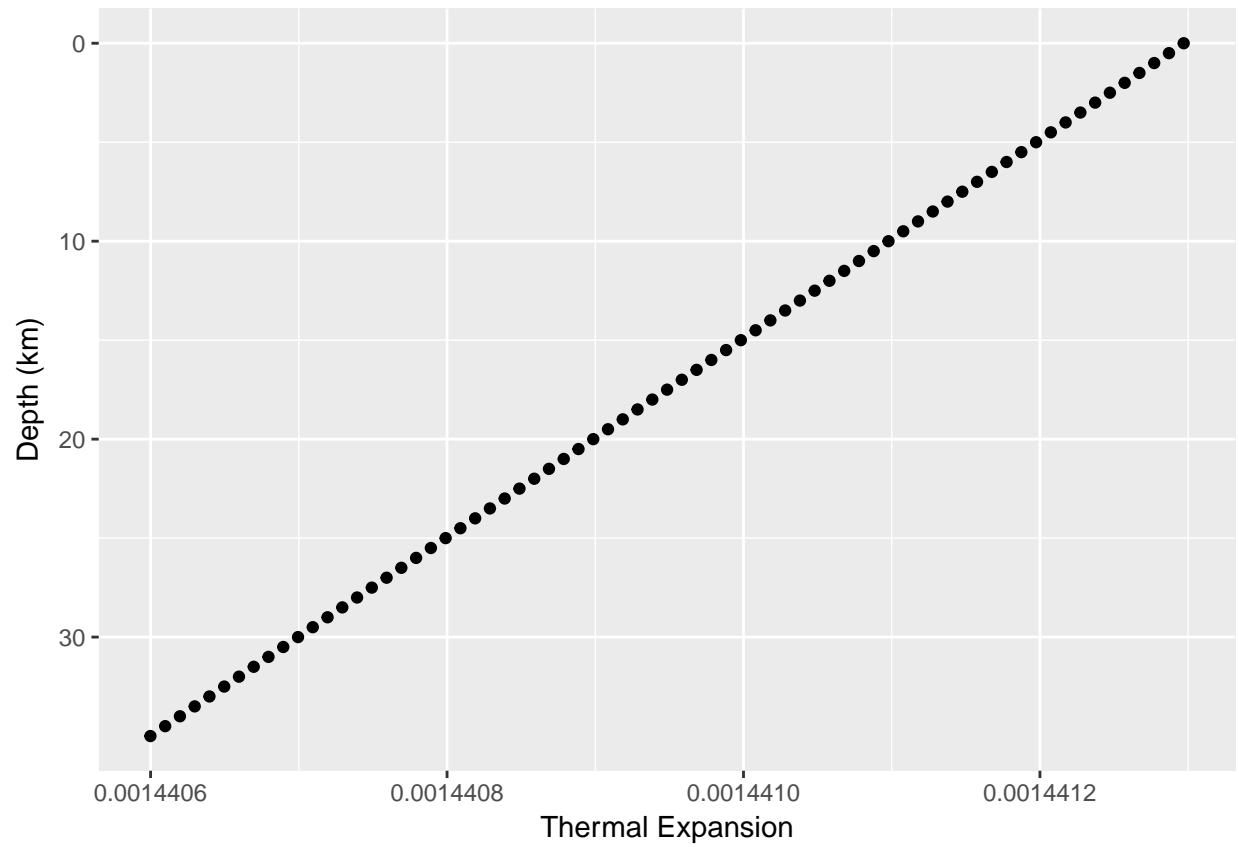
```
compressibility<-system$compress[1]*10-3*-1*molar_volume
```

```
q3_an<-data.frame(depth=depth,  
                  temperature=temp,  
                  pressure=press,  
                  molar_volume=molar_volume,  
                  thermal_expansion=thermal_expansion,  
                  compressibility=compressibility)
```

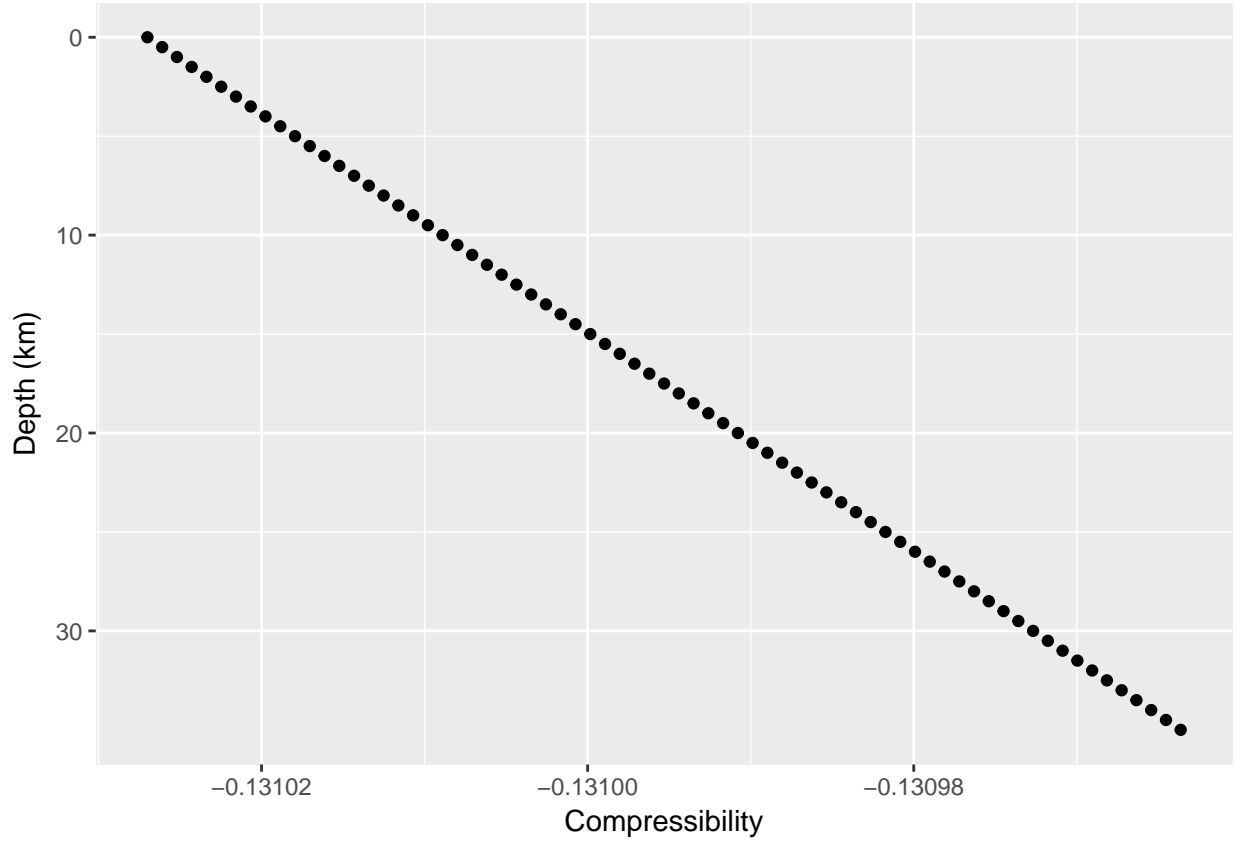
```
ggplot(q3_an,aes(x=molar_volume,y=depth))+  
  geom_point()+  
  scale_y_reverse()+  
  labs(x="Molar Volume (kJ/kbar)",y="Depth (km)")
```



```
ggplot(q3_an,aes(x=thermal_expansion,y=depth))+  
  geom_point()+  
  scale_y_reverse()+  
  labs(x="Thermal Expansion",y="Depth (km)")
```



```
ggplot(q3_an, aes(x=compressibility, y=depth)) +  
  geom_point() +  
  scale_y_reverse() +  
  labs(x="Compressibility", y="Depth (km)")
```



#### Question 4: Third condition of heterogeneous equilibrium for pure substances

Calculate and plot the pressure-temperature conditions of the *gr-ky-qz-an* equilibrium from the data in the attached table (Table 7 from Holland and Powell 1990). Only consider  $T > 500C$  and  $P < 25kbar$ . [Note that Holland and Powell 1990 use the symbol  $q$  for quartz.]

Derivations:

$$\Delta \bar{G}^{P_{eq}, T_{eq}} = \Delta \bar{H}^{P_0, T_0} - T_{eq} \Delta \bar{S}^{P_0, T_0} + \int_{T_0}^{T_{eq}} \Delta \bar{C}_P dT - T_{eq} \int_{T_0}^{T_{eq}} \frac{\Delta \bar{C}_P}{T} dT + \int_{P_0}^{P_{eq}} \Delta \bar{V} dP = 0$$

Breaking it down by term:

1.

$$\Delta \bar{H}^{P_0, T_0} = 3 * \bar{H}_{an}^{P_0, T_0} - \bar{H}_{gr}^{P_0, T_0} - 2 * \bar{H}_{ky}^{P_0, T_0} - \bar{H}_{qz}^{P_0, T_0}$$

2.

$$T_{eq} \Delta \bar{S}^{P_0, T_0} = T_{eq} \left( 3 * \bar{S}_{an}^{P_0, T_0} - \bar{S}_{gr}^{P_0, T_0} - 2 * \bar{S}_{ky}^{P_0, T_0} - \bar{S}_{qz}^{P_0, T_0} \right)$$

3.

$$\begin{aligned} \int_{T_0}^{T_{eq}} \Delta \bar{C}_P dT &= \int_{T_0}^{T_{eq}} \left[ \Delta a + \Delta bT + \Delta cT^{-2} + \Delta dT^{-1/2} \right] dT = \\ &= \int_{T_0}^{T_{eq}} \Delta a dT + \int_{T_0}^{T_{eq}} \Delta bT dT + \int_{T_0}^{T_{eq}} \Delta cT^{-2} dT + \int_{T_0}^{T_{eq}} \Delta dT^{-1/2} dT \end{aligned}$$

$$\int_{T_0}^{T_{eq}} \Delta \bar{C}_P dT = \Delta a(T_{eq} - T_0) + \frac{1}{2} \Delta b T^2 - \Delta c T^{-1} + 2 \Delta d T^{1/2}$$

Mistake here, need to fix how I put the exponents and the  $(T_{eq} - T_0)$  together here.

4.

$$\begin{aligned} -T_{eq} \int_{T_0}^{T_{eq}} \frac{\Delta \bar{C}_P}{T} dT &= -T_{eq} \left[ \int_{T_0}^{T_{eq}} \frac{\Delta a}{T} dT + \int_{T_0}^{T_{eq}} \Delta b dT + \int_{T_0}^{T_{eq}} \Delta c T^{-3} dT + \int_{T_0}^{T_{eq}} \Delta d T^{-3/2} dT \right] \\ -T_{eq} \int_{T_0}^{T_{eq}} \frac{\Delta \bar{C}_P}{T} dT &= -T_{eq} \left[ \Delta a \ln \left( \frac{T_{eq}}{T_0} \right) + \Delta b (T_{eq} - T_0) - \frac{1}{2} \Delta c (T_{eq} - T_0)^{-2} - 2 \Delta d (T_{eq} - T_0)^{-1/2} \right] \end{aligned}$$

5.

$$\begin{aligned} \int_{P_0}^{P_{eq}} \bar{V} dP &= \int_{P_0}^{P_{eq}} \bar{V}^{P_0, T_0} dP + \int_{P_0}^{P_{eq}} \Delta \alpha V [T - T_0] dP - \int_{P_0}^{P_{eq}} \Delta \beta V [P - P_0] dP \\ \int_{P_0}^{P_{eq}} \bar{V} dP &= \bar{V}^{P_0, T_0} [P_{eq} - P_0] + \Delta \alpha V [T - T_0] [P_{eq} - P_0] + \Delta \beta V P_0 [P_{eq} - P_0] - \frac{1}{2} \Delta \beta V [P_{eq} - P_0]^2 \end{aligned}$$

Noticing more mistakes as I go, will fix the incorrect placement of the  $\hat{2}$  later, but I think I continued with it done correctly, not like this.

$$\begin{aligned} \int_{P_0}^{P_{eq}} \bar{V} dP &= \\ P_{eq} \left( \Delta \bar{V}^{P_0, T_0} + \Delta \alpha V [T - T_0] + \Delta \beta V P_0 \right) - P_0 \left( \Delta \bar{V}^{P_0, T_0} + \Delta \alpha V [T - T_0] + \Delta \beta V P_0 - \frac{1}{2} \Delta \beta V P_0 \right) - \frac{1}{2} \Delta \beta V P_{eq}^2 \end{aligned}$$

Now we group terms based on whether they lack any  $P_{eq}$ , have  $P_{eq}$  or have  $P_{eq}^2$  so that we can assign the terms of a polynomial as:  $0 = a P_{eq}^2 + b P_{eq} + c$

$$a = -\frac{1}{2} \Delta \beta V$$

$$b = \Delta \bar{V}^{P_0, T_0} + \Delta \alpha V [T - T_0] + \Delta \beta V P_0$$

$$\begin{aligned} c &= \Delta \bar{H}^{P_0, T_0} - T_{eq} \Delta \bar{S}^{P_0, T_0} + \\ &\quad \Delta a (T_{eq} - T_0) + \frac{1}{2} \Delta b T^2 - \Delta c T^{-1} + 2 \Delta d T^{1/2} \\ &\quad - T_{eq} \left[ \Delta a \ln \left( \frac{T_{eq}}{T_0} \right) + \Delta b (T_{eq} - T_0) - \frac{1}{2} \Delta c (T_{eq} - T_0)^{-2} - 2 \Delta d (T_{eq} - T_0)^{-1/2} \right] \\ &\quad - P_0 \left( \Delta \bar{V}^{P_0, T_0} + \Delta \alpha V [T - T_0] + \Delta \beta V P_0 - \frac{1}{2} \Delta \beta V P_0 \right) \end{aligned}$$

And finally we use the quadratic formula and these terms to solve for the pressure of equilibrium given a temperature of equilibrium.

I have an error here that I can't seem to track down. At this point I've fixed a half dozen mistakes but can't fix the root problem. (Fixed an error where I put a + instead of a - for the  $T_{eq} \Delta \bar{S}^{P_0, T_0}$  term since I handed this in this morning.)

```

# calculating all the deltas
deltaH<-3*system$H[1]-
  system$H[2]-
  2*system$H[3]-
  system$H[4]
deltaS<-10^-3*
  (3*system$S[1]-
  system$S[2]-
  2*system$S[3]-
  system$S[4])
deltaV<-3*system$V[1]-
  system$V[2]-
  2*system$V[3]-
  system$V[4]
deltaa<-3*system$a[1]-
  system$a[2]-
  2*system$a[3]-
  system$a[4]
deltab<-10^-5*
  (3*system$b[1]-
  system$b[2]-
  2*system$b[3]-
  system$b[4])
deltac<-3*system$c[1]-
  system$c[2]-
  2*system$c[3]-
  system$c[4]
deltad<-3*system$d[1]-
  system$d[2]-
  2*system$d[3]-
  system$d[4]
deltathermal<-10^-5*
  (3*system$thermal_expanse[1]-
  system$thermal_expanse[2]-
  2*system$thermal_expanse[3]-
  system$thermal_expanse[4])
deltacompress<-10^-3*
  (3*system$compress[1]-
  system$compress[2]-
  2*system$compress[3]-
  system$compress[4])

# setting up a variable of temperatures to solve for the equilibrium pressure
temp<-seq(500+273.15,1000+273.15,by=10) # in K

#setting the initial temp and pressure
init_temp<-25+273.15
init_press<-1*10^-3

# defining a variable of T-T0
temp_diff<-temp-init_temp

# defining the terms of our polynomial (a and c are switched here from what they are above b/c brain wo

```

```

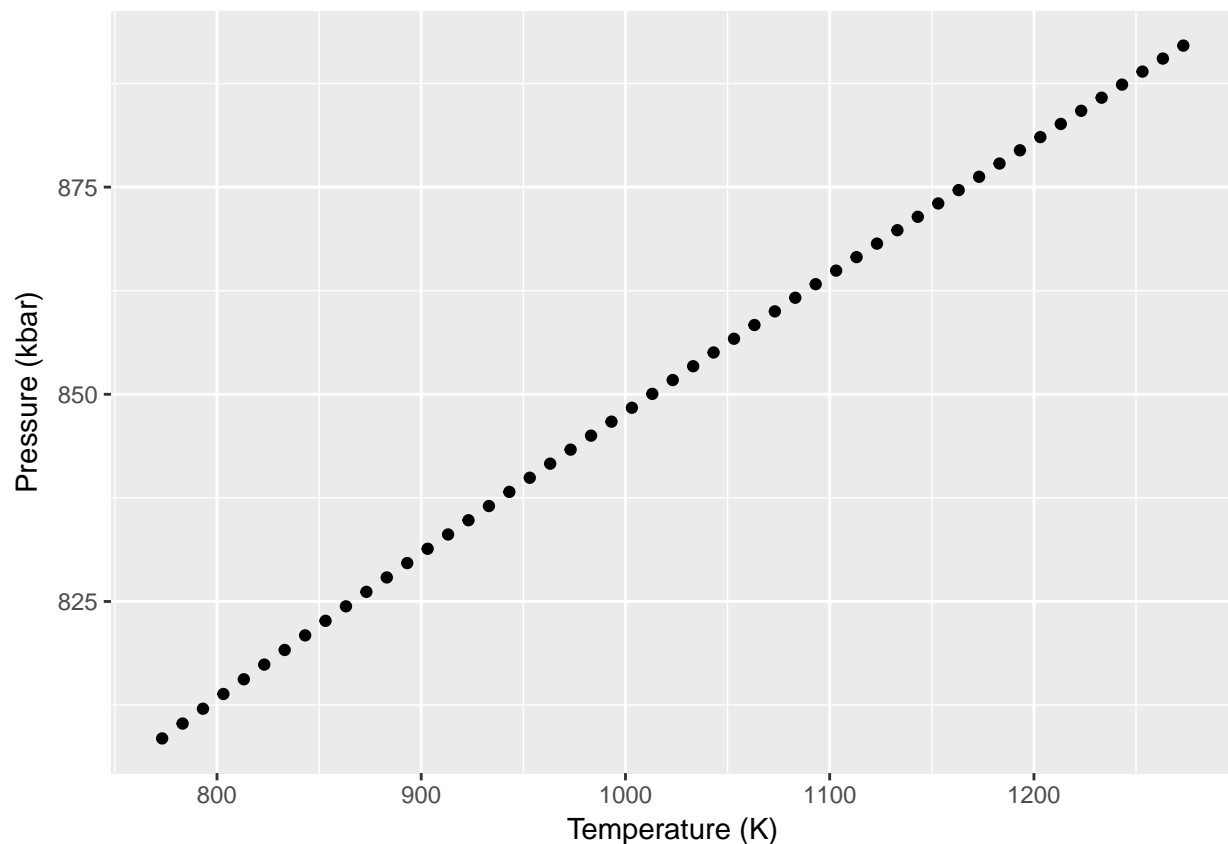
#a<-deltaH+temp*deltaS+
# deltaa*temp_diff+0.5*deltab*temp_diff^(2)-1*deltac*temp_diff^(-1)+2*deltad*temp_diff^(0.5)-
# temp*(deltaa*log(temp_diff)+deltab*temp_diff-0.5*deltac*temp_diff^(-2)-2*deltad*temp_diff^(-0.5))
#b<-deltaV+deltathermal*(temp-init_temp)-deltacompress*init_press
#c<-(-0.5)*deltacompress

a<-deltaH-temp*deltaS+
  deltaa*temp_diff+0.5*deltab*temp_diff^(2)-1*deltac*temp_diff^(-1)+2*deltad*temp_diff^(0.5)-
  temp*(deltaa*log(temp_diff)+deltab*temp_diff-0.5*deltac*temp_diff^(-2)-2*deltad*temp_diff^(-0.5))-
  deltaV*init_press-deltathermal*temp_diff*init_press-0.5*deltacompress*init_press
b<-deltaV+deltathermal*(temp-init_temp)+deltacompress*init_press
c<-(-0.5)*deltacompress
#solving the polynomial
press_plus<-
  (-b+sqrt((b^2)-(4*a*c)))/(2*c) # in kbar
press_minus<-
  (-b-sqrt((b^2)-(4*a*c)))/(2*c) #these are all negatives so don't actually matter here

#making a data frame of the temperatures and pressures of equilibrium
tp<-data.frame(temp,press_plus)

# plotting the temperatures and pressures of equilibrium
ggplot(tp,aes(x=temp,y=press_minus))+geom_point()+labs(x="Temperature (K)",y="Pressure (kbar)")

```





## Question 5: Thermodynamic simplifications

Your plot in Question 4 should be very nearly a straight line in  $P - T$  space. Discuss how this result might enable you to simplify the expression you used to make your calculations in Question 4. [Hint: are there any terms that you can ignore? Why?]

Most of the pressure integral can be avoided as the compressibility, thermal expansion and initial pressure are quite small and their effect is minimal on the terms in which they play a part.

Obviously this suffers from the same error as Q4, but as can be seen, the error can't be in these areas as they make almost no difference.

```
a<-deltaH-temp*deltaS+
  deltaa*temp_diff+0.5*deltab*temp_diff^(2)-1*deltac*temp_diff^(-1)+2*deltad*temp_diff^(0.5)-
  temp*(deltaa*log(temp_diff)+deltab*temp_diff-0.5*deltac*temp_diff^(-2)-2*deltad*temp_diff^(-0.5))#-
  # deltaV*init_press-deltathermal*temp_diff*init_press-0.5*deltacompress*init_press
b<-deltaV#+deltathermal*(temp-init_temp)+deltacompress*init_press
c<-(-0.5)*deltacompress
#solving the polynomial
press_plus<-
  (-b+sqrt((b^2)-(4*a*c)))/(2*c) # in kbar
press_minus<-
  (-b-sqrt((b^2)-(4*a*c)))/(2*c) #these are all negatives so don't actually matter here

#making a data frame of the temperatures and pressures of equilibrium
tp<-data.frame(temp,press_plus)

# plotting the temperatures and pressures of equilibrium
ggplot(tp,aes(x=temp,y=press_minus))+geom_point()+labs(x="Temperature (K)",y="Pressure (kbar)")
```

