

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))
```

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* ($\text{CaAl}_2\text{Si}_2\text{O}_8$), \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.

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

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

$$\text{bar} = 100,000 \text{ Pa}$$

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

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

The molar volume of *an* at standard pressure and temperature (1 bar, 25C) is $10.079 \frac{J}{\text{bar}}$ or $1.0079 \times 10^{-4} \text{m}^3$. To put this in perspective, a gallon is $3.79 \times 10^{-3} \text{m}^3$ 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 αV and βV 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:

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

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:

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

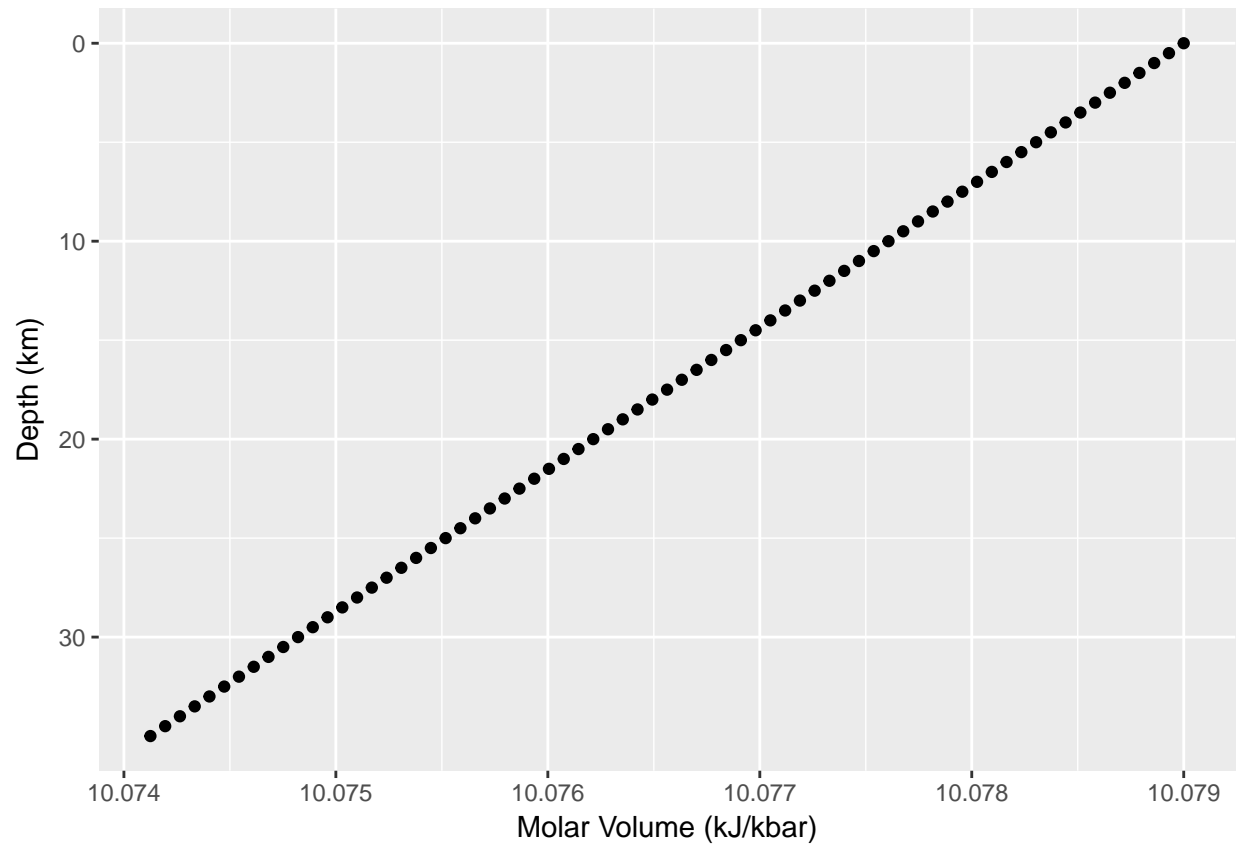
And as established above, both αV and $-\beta V$ are constants.

Question 3: Equations of state

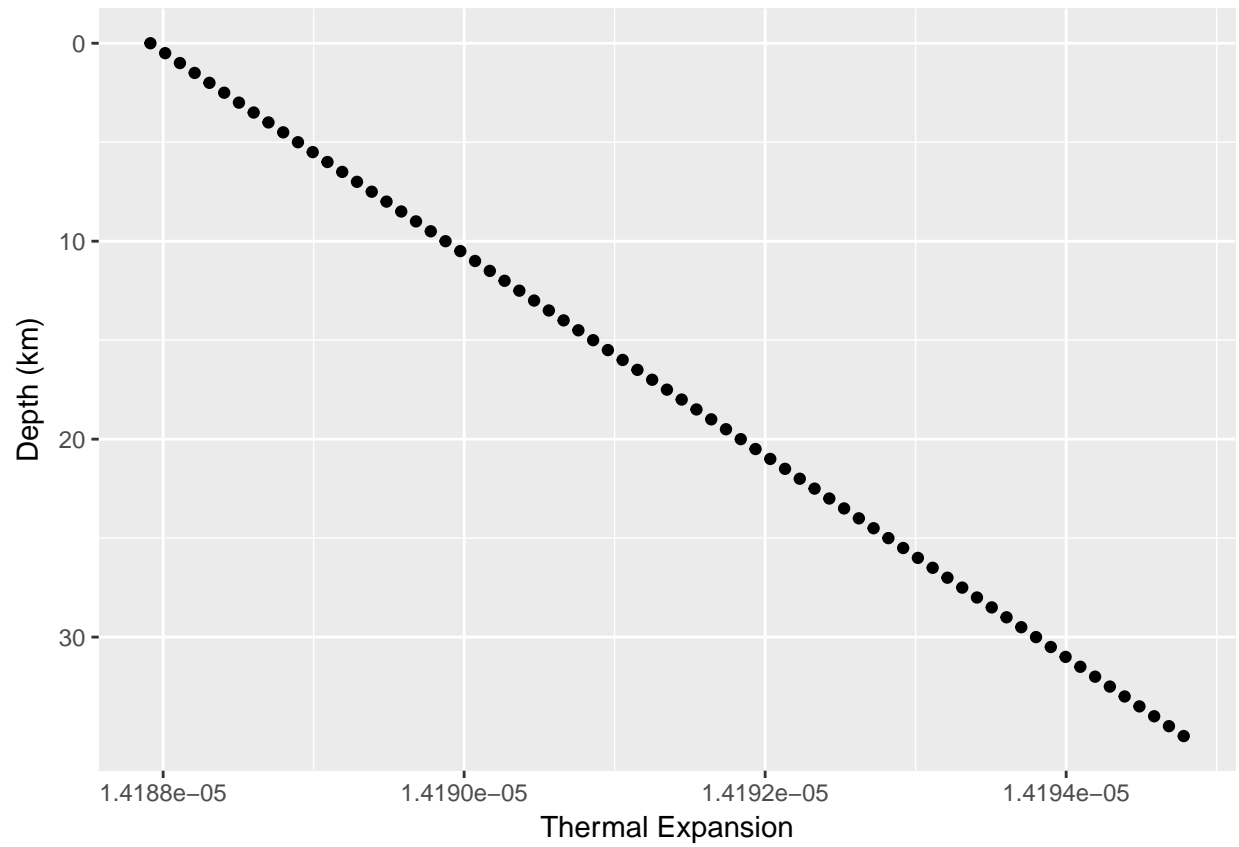
Use the equation of state for volumes of pure substances from Holland and Powell (1990) and the attached data table (Table 7 from Holland and Powell 1990) to calculate how (i) the molar volume, (ii) thermal expansion, and (iii) compressibility of *an* change along a typical geothermal gradient ($\approx \frac{25^\circ\text{C}}{\text{km}}$) 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
molar_volume<-
  system$V[1]+
  system$thermal_expanse[1]*10^-5*(temp-temp[1])-
  system$compress[1]*10^-3*(press-press[1])
thermal_expansion<-system$thermal_expanse[1]*10^-5/molar_volume
compressibility<-system$compress[1]*10^-3/molar_volume
q3_an<-data.frame(depth=depth,
  temperature=temp,
  pressure=press,
  molar_volume=molar_volume,
  thermal_expansion=thermal_expansion,
  compressibility=compressibility)

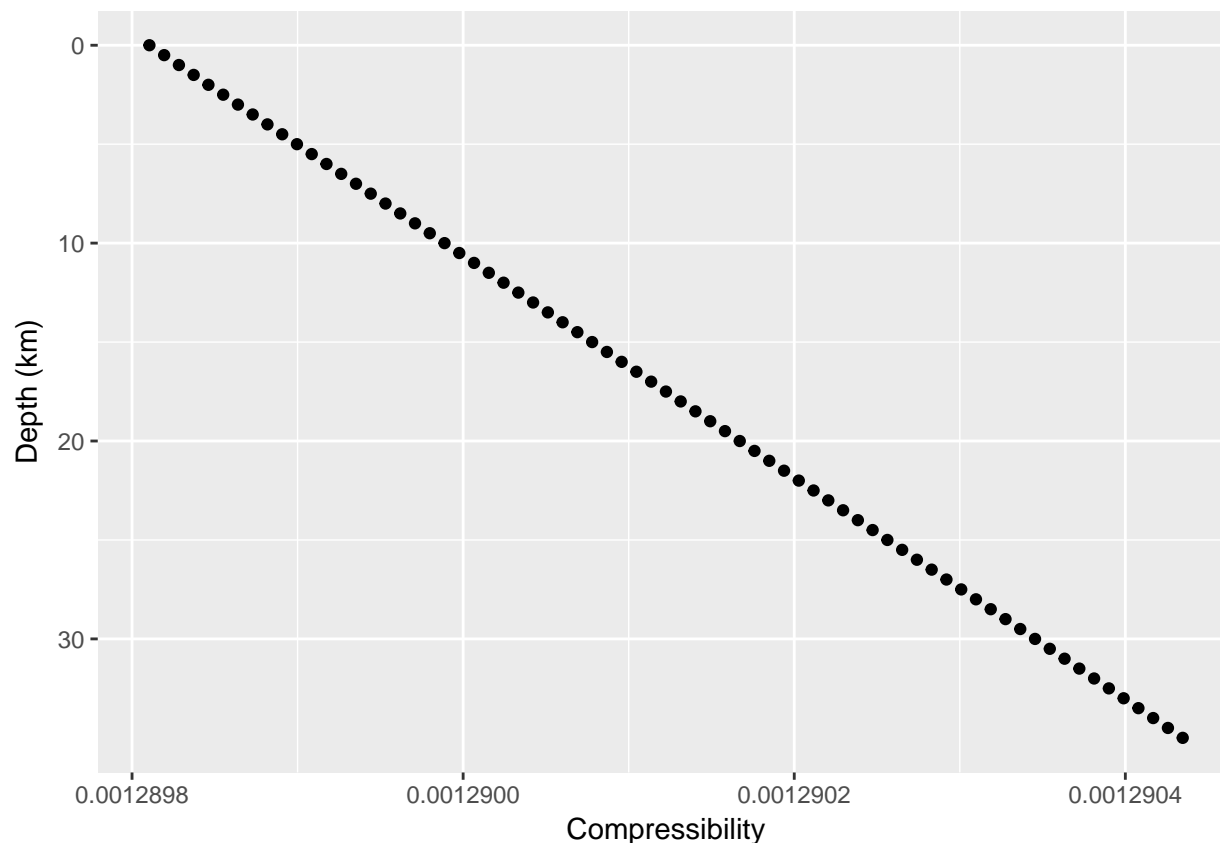
ggplot(q3_an,aes(x=molar_volume,y=depth))+
  geom_point()+
  scale_y_reverse()+
  labs(x="Molar Volume (kJ/kbar)",y="Depth (km)")
```



```
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 SiO_2 .]

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?]