Problem Set 2

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```
r_jmolk=8.31441
r_barcm3molk=83.1441
r_calmolk=1.987
```

Question 1

Calculate $\bar{V}_{H_2O}$ at $T = 800C$ and $P = 1000bars$ from figure of the compressibility factor as a function of P and T. For reference $P_{crit} = 220.4bar$ and $T_{crit} = 647.3K$ for pure H2O.

Reduced pressure:

```
p=1000
p_crit=220.4
press_reduced=p/p_crit
print(press_reduced)
```

```
## [1] 4.537205
```

Reduced temperature:

```
t=800+273.15
t_crit=647.3
t_reduced=t/t_crit
print(t_reduced)
```

```
## [1] 1.657887
```

From the figure: $Z = 0.88$

$Z \equiv \frac{P\bar{V}}{RT}$ so $\bar{V} = \frac{ZRT}{P}$

```
z=0.88
molar_volume=z*t*r_barcm3molk/p
print(molar_volume)
```

```
## [1] 78.51896
```

We get $78.52cm^3$ as the molar volume of pure water at 800C and 1000 bars.

Question 2

Calculate $\bar{V}_{H_2O}$ and $f_{H_2O}^{P,T}$ at $T = 800C$ and $P = 1000bars$ from the modified Redlich-Kwong equation of state. Use the following formulations for the attraction coefficient (a) and the excluded volume (b) from Bowers and Helgeson (1983) where T is in C.

The modified Redlich-Kwong equation of state is: $P = \frac{RT}{\bar{V}-b} - \frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}$

We are given P and T and thus can rearrange this to be: $0 = P - \frac{RT}{\bar{V}-b} + \frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}$ and now we just need to find a $\bar{V}$ that satisfies this.

```r
t_c=800
a=10^6*(111.3+50.7*exp(-0.983*10^(-2)*t_c))
b=14.6
v_poss<-c(1,10,20,30,40,50,60,70,80,90,100)
outcomes<-p-(r_barcm3molk*t/(v_poss-b))+a/(sqrt(t)*v_poss*(v_poss+b))
print(outcomes) # know we know that the actual molar volume is somewhere in the range of 70 to 80 cm3 (
```

```
##  [1] 225390.08314  34210.54426 -10612.74652  -2254.18772   -956.91436
##  [6]    -468.45602    -206.14167     -36.76336     84.70065    177.59650
## [11]     251.71961
```

```r
v_poss<-c(70,71,72,73,74,75,76,77,78,79,80)
outcomes<-p-(r_barcm3molk*t/(v_poss-b))+a/(sqrt(t)*v_poss*(v_poss+b))
print(outcomes) # getting more specific, it is somewhere between 72 and 73 cm3
```

```
##  [1] -36.763365 -22.897951  -9.468936   3.546752  16.170486  28.422095
##  [7]  40.320006  51.881364  63.122147  74.057266  84.700653
```

```r
v_poss<-c(72,72.1,72.2,72.3,72.4,72.5,72.6,72.7,72.8,72.9,73)
outcomes<-p-(r_barcm3molk*t/(v_poss-b))+a/(sqrt(t)*v_poss*(v_poss+b))
print(outcomes) # let's do one last round between 72.7 and 72.8
```

```
##  [1] -9.4689362 -8.1491332 -6.8334399 -5.5218345 -4.2142951 -2.9108002
##  [7] -1.6113284 -0.3158583  0.9756311  2.2631608  3.5467516
```

```r
v_poss<-c(72.7,72.71,72.72,72.73,72.74,72.75,72.76,72.77,72.78,72.79,72.8)
outcomes<-p-(r_barcm3molk*t/(v_poss-b))+a/(sqrt(t)*v_poss*(v_poss+b))
print(outcomes)
```

```
##  [1] -0.31585833 -0.18653060 -0.05724267  0.07200551  0.20121394
##  [6]  0.33038264  0.45951165  0.58860098  0.71765064  0.84666067
## [11]  0.97563108
```

The modified Redlich-Kwong equation of state predicts a molar volume of water at $T = 800$ and $P = 1000$ of approximately $72.725 cm^3$, slightly lower than the volume prediced by the figure estimate.

Question 3

We are looking for equilibrium conditions in P,T space, so we are going to try to find the conditions where $\Delta \bar{G} = 0$

$$0 = \Delta \bar{G}^\circ (P,T) = \Delta(\bar{H}^\circ)^{1,298} - T_{eq}\Delta(\bar{S}^\circ)^{1,298} + \int_{298}^{T_{eq}} \Delta \bar{C_P}^\circ dT - T_{eq}\int_{298}^{T_{eq}} \frac{\Delta \bar{C_P}^\circ}{T} dT + \int_{1}^{P_{eq}} \Delta \bar{V}^\circ dP$$

But unlike before, we need to break the volume term down into the solid and fluid components as these behave differently:$0 = \Delta \bar{G}^\circ (P,T) = \Delta(\bar{H}^\circ)^{1,298} - T_{eq}\Delta(\bar{S}^\circ)^{1,298} + \int_{298}^{T_{eq}} \Delta \bar{C_P}^\circ dT - T_{eq}\int_{298}^{T_{eq}} \frac{\Delta \bar{C_P}^\circ}{T} dT + \int_{1}^{P_{eq}} \Delta \bar{V_s}^\circ dP + \int_{1}^{P_{eq}} \nu_f \bar{V_f} dP$

From the last problem set we know that the slope doesn't change with P or T so:

$\Delta(\bar{H}^\circ)^{1,298} + \int_{298}^{T_{eq}} \Delta \bar{C_P}^\circ dT \approx \Delta(\bar{H}^\circ)^{1,T}$

$$\Delta(\bar{S}^\circ)^{1,298} + \int_{298}^{T_{eq}} \frac{\Delta\bar{C}_P{}^\circ}{T} dT \approx \Delta(\bar{S}^\circ)^{1,T}$$

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

Once we substitute these in we have:

$$\Delta(\bar{G}^\circ)^{P,T} = \Delta(\bar{H}^\circ)^{1,T} - T\Delta(\bar{S}^\circ)^{1,T} + \Delta\bar{V}_s{}^\circ(P - P_r) + \int_1^{P_{eq}} \nu_f \bar{V}_f{}^\circ dP$$

Now we need to deal with the volume term for our fluids. So our only complication is fugacity. For an ideal gas: $(f_i^\circ)^{P,T} = P$ so $\int_1^P \bar{V}_f{}^\circ dP = \nu_f RT ln(f_f^\circ)^{P,T}$

Using a table of fugacities how can we do this?

$$\Delta(\bar{H}^\circ)^{1,T} - T\Delta(\bar{S}^\circ)^{1,T} + \Delta\bar{V}_s{}^\circ(P - P_r) + \nu_f RT ln(f_f^\circ)^{P,T} = 0$$

$\nu_f = 1$ so we can ignore that.

Now the plan of attack (shown explicitly once in the code):

1. pick a T to start
2. pick a P which sets $(f_i^\circ)^{P,T}$ from the table
3. evaluate $\Delta(\bar{G}^\circ)^{P,T}$
4. Is $\Delta(\bar{G}^\circ)^{P,T} > 0 \rightarrow$ choose a lower pressure, if $\Delta(\bar{G}^\circ)^{P,T} < 0 \rightarrow$ choose a higher pressure
5. iterate

```
h=24184 #cal
s=40.817 #cal K-1
delta_barv_solid=-0.113 #cal bar-1
p_ref<-1
```

First we have to figure out what temperature to start at. We need to find the lowest temperature where the lowest pressure and fugacity give a negative $(\Delta\bar{G}^\circ)^{P,T}$

```
t<-200+273.15
p<-100
f<-15
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this one is really high, but it's already a
```

```
## [1] 7406.22
```

```
t<-300+273.15
f<-68
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #still not an option
```

```
## [1] 5583.932
```

```
t<-400+273.15
f<-87
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #still not an option
```

```
## [1] 2670.221
```

```
t<-500+273.15
f<-92
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) # woo we have a negative! Let's check the te
```

```
## [1] -438.2571
```

```
t<-480+273.15
f<-92
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) # nope, so we'll start at T=500
```

[1] 198.387

Alright so the lowest temperature we care about is 500C, so let's start figuring out the pressure conditions that provide us with equilibrium:

```
t<-500+273.15
p<-100
f<-92
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #we checked this before, now let's check the
```

[1] -438.2571

```
p<-200
f<-170
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

[1] 493.7149

```
#onto the next temperature
t<-520+273.15
p<-200
f<-173
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

[1] -90.95943

```
p<-300
f<-240
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

[1] 413.6364

```
t<-540+273.15
p<-300
f<-245
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

[1] -151.5878

```
p<-400
f<-305
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

[1] 191.0434

```
t<-560+273.15
p<-500
f<-369
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

[1] -93.92964

```
p<-600
f<-417
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

[1] 97.21697

```r
t<-580+273.15
p<-900
f<-562
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest p
```

```
## [1] -7.391314
```

```r
p<-1000
f<-601
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 95.04549
```

```r
t<-600+273.15
p<-1400
f<-794
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest p
```

```
## [1] -29.05094
```

```r
p<-1500
f<-834
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 44.9217
```

```r
t<-620+273.15
p<-2000
f<-1109
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest p
```

```
## [1] -54.86586
```

```r
p<-2100
f<-1152
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 1.344827
```

```r
t<-640+273.15
p<-2800
f<-1603
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest p
```

```
## [1] -14.51159
```

```r
p<-2900
f<-1663
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 40.86201
```

```r
t<-660+273.15
p<-3600
f<-2236
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest p
```

```
## [1] -10.89589
```

```
p<-3700
f<-2312
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 39.77859
```

```
t<-680+273.15
p<-4400
f<-3035
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -32.51085
```

```
p<-4500
f<-3130
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 14.56242
```

```
t<-700+273.15
p<-5300
f<-4162
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -21.30083
```

```
p<-5400
f<-4285
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 23.71636
```

```
t<-720+273.15
p<-6200
f<-5583
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -28.51294
```

```
p<-6300
f<-5739
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 14.57112
```

```
t<-740+273.15
p<-7200
f<-7560
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -4.72697
```

```
p<-7300
f<-7760
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 36.53813
```

```
t<-760+273.15
p<-8100
```

```
f<-9834
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -28.0115
```

```
p<-8200
f<-10082
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 11.81702
```

```
t<-780+273.15
p<-9100
f<-12822
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is negative, so onto the next highest
```

```
## [1] -36.79372
```

```
p<-9200
f<-13130
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) #this is positive, so the actual pressure of
```

```
## [1] 1.579053
```

```
t<-800+273.15
p<-10000
f<-16214
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) # even the highest pressure is negative, so
```

```
## [1] -78.44709
```

```
t<-c(500,520,540,560,580,600,620,640,660,680,700,720,740,760,780)
t<-t+273.15
lower_p<-c(100,200,300,500,900,1400,2000,2800,3600,4400,5300,6200,7200,8100,9100)
upper_p<-c(200,300,400,600,1000,1500,2100,2900,3700,4500,5400,6300,7300,8200,9200)

df<-data.frame(t,lower_p,upper_p)
```
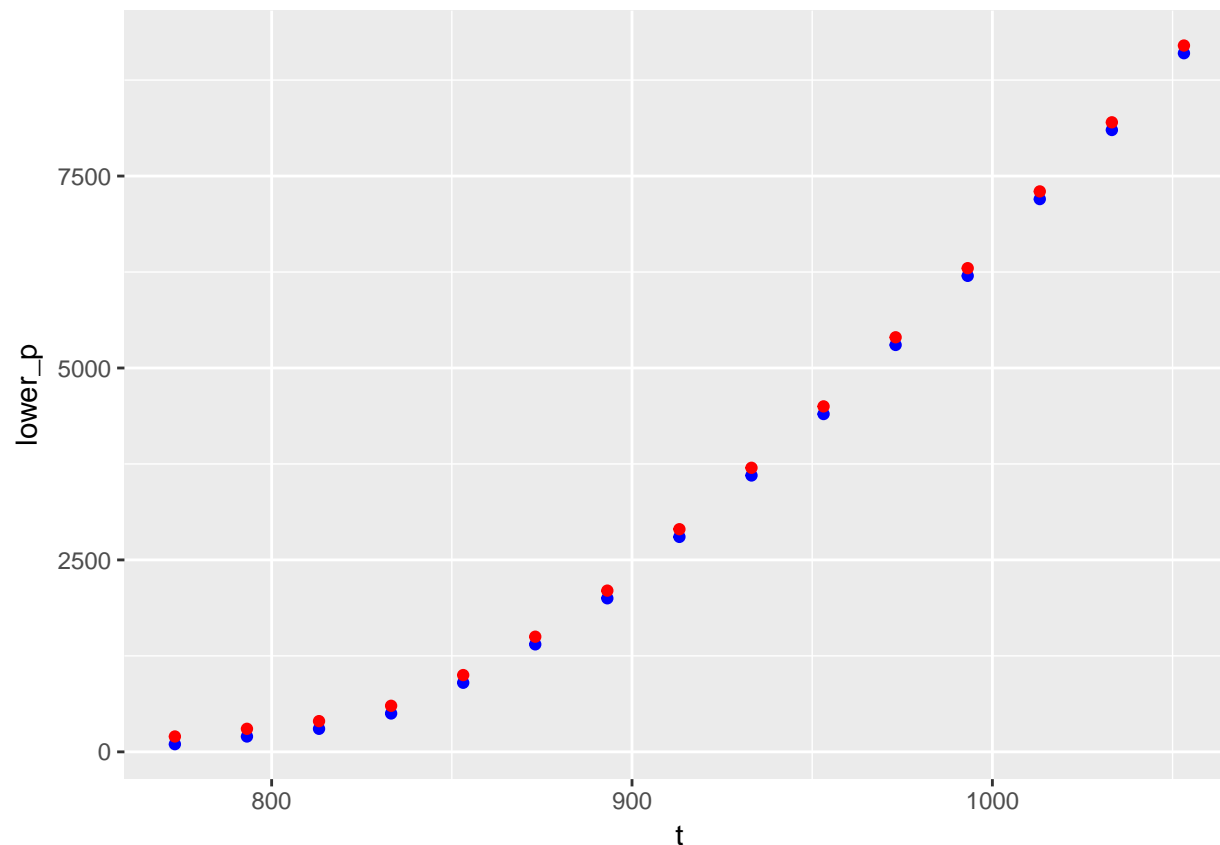
Now that we have our temperatures and pressure ranges, let's plot it:

```
ggplot(df,aes(x=t))+geom_point(mapping=aes(y=lower_p),color='blue')+geom_point(mapping=aes(y=upper_p),co
```

Question 4 Following the same approach as in Question 3, but with different constants and fugacity table.

```
h=23019 #cal
s=38.334 #cal k-1
delta_barv_solid=-0.471 #cal bar-1

t<-350+273.15
p<-1000
f<-1096
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) # this is positive at the lowest pressure, s
```

```
## [1] 7327.317
```

```
t<-700+273.15 # starting here b/c that is the first temperature at which the lowest pressure is negativ
p<-1000
f<-1304
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -885.8257
```

```
p<-2000
f<-3495
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 549.5529
```

```
t<-750+273.15
p<-2000
f<-3483
```

8

```r
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -563.5339
```

```r
p<-3000
f<-7713
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 581.7273
```

```r
t<-800+273.15
p<-3000
f<-7555
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -489.859
```

```r
p<-4000
f<-14509
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 430.6258
```

```r
t<-850+273.15
p<-4000
f<-13999
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -613.9079
```

```r
p<-5000
f<-24268
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 142.912
```

```r
t<-900+273.15
p<-6000
f<-37399
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -233.515
```

```r
p<-7000
f<-58312
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 330.8529
```

```r
t<-950+273.15
p<-8000
f<-83221
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -102.1505
```

```r
p<-9000
f<-125468
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 424.6523
```

```r
t<-1000+273.15
p<-9000
f<-117699
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -487.4001
```

```r
p<-10000
f<-177096
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] 75.15782
```

```r
t<-1050+273.15
p<-9000
f<-111095
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f))
```

```
## [1] -1395.918
```

```r
p<-10000
f<-168130
print(h-t*s+delta_barv_solid*(p-p_ref)+r_calmolk*t*log(f)) # the highest pressure is still negative her
```

```
## [1] -777.5458
```

```r
t<-c(700,750,800,850,900,950,1000)
lower_p<-c(1000,2000,3000,4000,6000,8000,9000)
upper_p<-c(2000,3000,4000,5000,7000,9000,10000)
df<-data.frame(t,lower_p,upper_p)
```

Now let's plot our data:

```r
ggplot(df,aes(x=t))+geom_point(mapping=aes(y=lower_p),color='blue')+geom_point(mapping=aes(y=upper_p),co
```
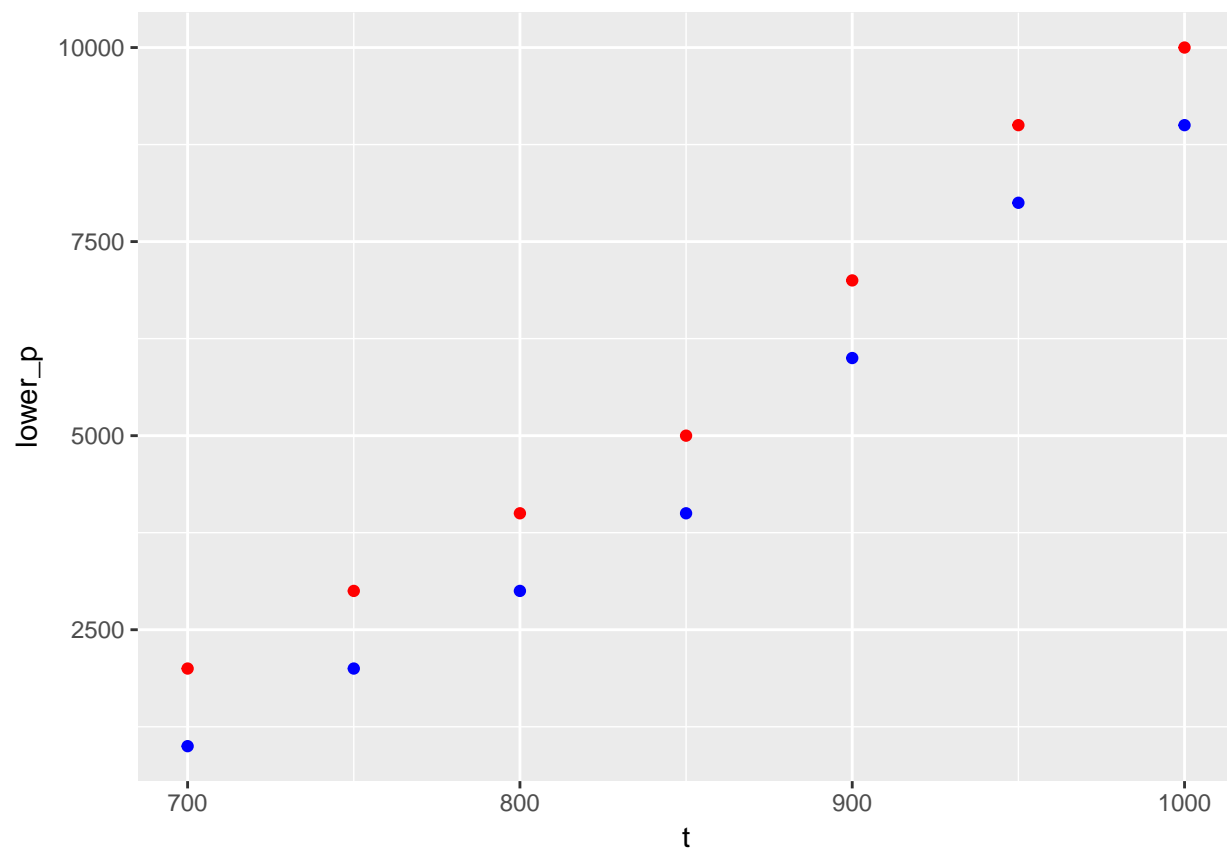
Question 5 Higher pressures than equilibrium pressures yield positive Gibbs free energy while lower pressures than the equilibrium pressures yield negative Gibbs free energy. This means that at higher pressures the reaction will not proceed in the direction written, but rather the reverse reaction is the reaction that will occur spontaneously. At lower pressures the reaction as written is the reaction that will proceed spontaneously.