# Compression: Why is this done in multiple steps? 

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## Conclusions:

1. For an ideal gas, we see that the compression work is a factor of the pressure ratio times the initial temperature. Thus starting at a lower temperature, or more likely breaking the compression into a series of discrete steps with intermediate cooling, will require less work.
2. Compressions of permanent gases are ~ideal --if the starting $T$ is well above Tc. (maybe not for CO 2 ). The temperature of the gas increases fast enough so that the gas is roughly ideal throughout the compression!

## Situation of interest: A continuous compression process.

It is often necessary to compress a gas from 1 ATM to ~100 PSIG (~7 ATM) or "pipeline pressure" which could be 1000 PSI or more.
This is done using multiple compression steps, commonly with a compression ratio of 3-4, with intermediate cooling.
We will explore below some of the reasons that multiple steps with cooling is done.

Note that in addition to the thermodynamics discussed here, as a gas is compressed and its volume decreases, the flow area also decreases and so there is some convenience to using separate devices of different cross section. Also if there are separate device, the shaft rotation frequency does not have to be the same for each stage.

## Ideal gas

As will become clear below, we can largely answer the main question just by considering an ideal gas.

The idealization of a process compressor is that compression is essentially adiabatic. This assumption is justified because the residence time in a compressor is short compared to the time scale for heat transfer. Further, while large compressors have a rotating shaft with blades and internal fixed fins, these are designed to create a "smooth" flow path of ever decreasing area. Hence the degree of entropy generation small.

We start with an adiabatic, isentropic ideal gas.

The relation between temperature and pressure is
$\frac{P_{2}}{P_{1}}=\left(\frac{T_{2}}{T_{1}}\right)^{\frac{C_{p}}{R}}$
For a steady state compressor the required power input is the mass flow rate times the enthalpy change.

For an ideal gas $\mathrm{dH}=\mathrm{C}_{\mathrm{P}} \mathrm{dT}$.
Let's get the enthalpy change in terms of the pressure increase. It is easiest to use PR and TR as P2/P1, i.e., the pressure ratio. Re-writing the equation above...

PR == (TR) ^(cp / rr)
$P R=T^{c p / r r}$
ans = Solve[\%, TR]
... Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.
$\left\{\left\{\mathrm{TR} \rightarrow \mathrm{PR}^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right\}\right\}$
Now substitute into the equation for $\Delta \mathrm{H}$

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ln[83]:= \DeltaH = cp ( T2 - T1)
Out[83]= cp (-T1 + T2)
ln[87]:= \DeltaH / . T2 -> T1 TR
Out[87]= cp (-T1 + T1 TR)
ln[88]:=
Ou[88]= cp (-T1 + PR 
```

Now get the enthalpy in terms of just the pressure change;

```
\(\ln [89]:=\) \% / . PR \(\rightarrow\) P2 / P1
Out[89] \(=\mathrm{Cp}\left(-\mathrm{T} 1+\left(\frac{\mathrm{P} 2}{\mathrm{P} 1}\right)^{\frac{\mathrm{rr}}{\mathrm{cp}}} \mathrm{T} 1\right)\)
In[90]:= enthalpychange = FullSimplify[\%]
Out[90]= \(c p\left(-1+\left(\frac{P 2}{P 1}\right)^{\frac{r r}{c p}}\right) \mathrm{T} 1\)
```

We see that the work for any relative pressure increase depends on the initial temperature!
$\ln [\cdot]=$ Plot [(enthalpychange /. $\{\mathrm{cp} \rightarrow 7 / 2 \mathrm{rr}, \mathrm{T} 1 \rightarrow 298$, P1 $\rightarrow$ 1\}) /. rr $\rightarrow$ 8.314, $\{P 2,1 ., 10\}, A x e s L a b e l \rightarrow$ "pressure ratio", "enthalpy change"\}]
enthalpy change


The equation makes the main answer clear. Why do multistage compression? Because the work required for a given compression ratio depends on the initial temperature. We could reduce the amount of work for a compression ratio of 4 , by breaking it into 2 steps of a compression ratio of 2 with intermediate cooling back to the initial temperature.

```
In[91]]= onestep =cp (-1+(4)}\frac{\textrm{rr}}{cp})\textrm{T}
Out[99]=}=(-1+\mp@subsup{4}{}{\frac{\textrm{rr}}{cp}})cp T
In[92]:= twostep = 2 cp (-1+(2)}\mp@subsup{)}{}{\frac{rr}{cp}})\textrm{T}
Out[92]= 2(-1+2 2 cr cp cp T1
    In[96]:= temp = FullSimplify[twostep / onestep]
Out[96]=}\frac{2}{1+\mp@subsup{2}{}{\frac{rr}{c\rho}}
```

    For a diatomic ideal gas, we usually pick \(C p=7 / 2 R\)
    In[97] $:=N[$ temp /. cp $\rightarrow 7 / 2 r r]$
Out[97]= 0.901301

The 10\% reduction in power requirement may seem modest, but for a pipeline, where there is no "value - added" just from the compression, all savings are important. However, it is possible if the total change in pressure is just a factor of 4, the capital costs of the additional compressor and heat exchanger may out-weigh the potential operating cost savings.

## temperature increase??

We should check the final temperature. Starting at 298 K
$\mathrm{T} 2=\mathrm{T} 1(\mathrm{P} 2 / \mathrm{P} 1)^{\frac{\mathrm{r}}{\mathrm{cp}}}$
298. (4) ^(2/7)
442.826

This is probably acceptable, but above 500 K may not be. So for larger compression ratios you would need cooling to prevent the temperature from getting too high. In this case the stainless steel blades are fine, but the seals and bearing components are limiting. (In contrast, for a main turbine for power generation from steam, the steam temperature can't exceed what is safe for the structural integrity of the stainless steel.)

## Larger compression ratio

If you need to do a factor of 16 .

```
In \([89]=\) onestep \(=c p\left(-1+(16)^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1\)
Outig] \(=\left(-1+16^{\frac{\mathrm{rr}}{\text { pp }}}\right) \mathrm{Cp} \mathrm{T1}\)
In \([99]=\) twostep \(=2 \mathrm{cp}\left(-1+(4)^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1\)
Outipg = \(2\left(-1+4^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{cp} \mathrm{T1}\)
In[100]:= temp1 = (FullSimplify[twostep / onestep]) / . cp \(\rightarrow 7 / 2\) rr
Out[100] \(=\frac{2}{1+2^{4 / 7}}\)
```

Now going from 1 to 2 steps saves $20 \%$ of the power requirement.
$\ln [101]:=\mathrm{N}[$ temp1]
Out[101]=
0.804507

This energy saving is significant. Also, if we check the temperature -- which was fine for a factor of 4 compression,
$\mathrm{T} 2=\mathrm{T} 1(\mathrm{P} 2 / \mathrm{P} 1)^{\frac{\mathrm{Ir}}{\mathrm{c}}}$
$\ln [-]:=$
Out $[0]=$
658.037
which would be too high for a standard compressor. For large scale process you might even do 3 steps of about 2.5
$16^{\wedge} .333$
2.51751
$\ln [\sigma]:=$ threestep $=3 \mathrm{cp}\left(-1+(2.52)^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1$
Out $[0]=3\left(-1+2.52^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right)$ cp T1
$\ln [\rho]=$ onestep $=\mathrm{cp}\left(-1+(16)^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1$
Out $[0]=\left(-1+16^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{cp} \mathrm{T1}$
This would build in a 25 \% reduction in power requirement:
$\ln [\cdot]:=($ FullSimplify[threestep / onestep]) /. cp $\rightarrow 7 / 2 \mathrm{rr}$
Out $[0]=$
0.750446

A general expression in terms of pressure ratio, pr and number of stages, n can be obtained.
$\ln [\rho]:=$ multistage $=\mathrm{ncp}\left(-1+(\mathrm{pr} \wedge(1 / n))^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1 /\left(\mathrm{cp}\left(-1+(\mathrm{pr})^{\frac{\mathrm{rr}}{\mathrm{cp}}}\right) \mathrm{T} 1\right)$

Out[0]=
$\frac{n\left(-1+\left(p r^{\frac{1}{n}}\right)^{\frac{r r}{c p}}\right)}{-1+p r^{\frac{r r}{c p}}}$
Plot[\{multistage /. \{pr $\rightarrow 4, \mathrm{cp} \rightarrow 7 / 2 \mathrm{rr}\}$, multistage /. \{ pr $\rightarrow$ 9, $\mathrm{cp} \rightarrow 7 / 2 \mathrm{rr}\}$, multistage /. $\{\mathrm{pr} \rightarrow 16, \mathrm{cp} \rightarrow 7 / 2 \mathrm{rr}\}$ \}, $\{n, 1,10\}, A x e s L a b e l \rightarrow\{" n$, number of stages", "power requirement"\}, PlotLegends $\rightarrow$ \{"pressure ratio = 4", "pressure ratio = 9", "pressure ratio = 16"\} ]
power requirement


We see that as we would expect, even "theoretically" as n increases, the benefits of an additional stage diminishes.

## What if the gas is not ideal?

You might like to use your favorite cubic equation of state to answer the question. We might find that the quantitative effect of non ideality is not too large.
We will use van der Waals for this example.
$\ln [16]:=v d w a a l=\left(P+a / v^{\wedge} 2\right)(v-b)==r r T$
Out[16] $=\left(P+\frac{a}{v^{2}}\right)(-b+v)==r r T$
Kumar et al., "Van der Waal's equation for an adiabatic process and its Carnot engine efficiency" (2017) (arXiv:1802.01474v1) show that for an adiabatic process the van der Waals equation has a formula similar to ideal for the pressure ratio. The result is,
$\operatorname{In}[v]=$ vdwadiabatic $=(P+a / v \wedge 2)(v-b)^{\wedge} \Gamma$
Out $[=]=\left(P+\frac{a}{v^{2}}\right)(-b+v)^{r}$
where $\Gamma=\mathrm{R} / C_{v}+1$. For the adiabatic process, vdwadiabatic = constant.

If a and $\mathrm{b}=0$, then we would get the ideal gas result, that $\Gamma=C_{P} / C_{v}$ and $\mathrm{p} \mathrm{v}^{\gamma}=$ constant.

It would be good to pick a specific gas and get the numbers correct rather than just showing trends from "made up" constants. Note that any difference in the enthalpy change for the vdWaal gas compared to ideal is both because the volume of the initial state will not match and the difference that the "a" and "b" will have on the compression process.

Choose N2.
We start with:

$$
\begin{aligned}
& \mathrm{a}=\frac{27 R^{2} T_{c}^{2}}{64 P_{c}}, \mathrm{~b}=\frac{R T_{c}}{8 P_{c}} \\
& \mathrm{Tc}=126.6 \mathrm{~K}, \mathrm{Pc}=3.394 \mathrm{MPa}, \mathrm{R}=8.314 \mathrm{MPa} \mathrm{~cm}{ }^{\wedge} 3 / \mathrm{K} / \mathrm{mol} \\
& \ln [f]:=\frac{27 R^{2} T_{C}^{2}}{64 P_{c}} / .\left\{R \rightarrow 8.314 \mathrm{MPa} \mathrm{~cm} \wedge 3 / K / \mathrm{mol}, P_{c} \rightarrow 3.394 \mathrm{MPa}, T_{C} \rightarrow 126.6 \mathrm{~K}\right\} \\
& \frac{137708 \cdot \mathrm{~cm}^{6} \mathrm{MPa}}{\mathrm{~mol}^{2}}
\end{aligned}
$$

$\ln \left[f:=\frac{R T_{c}}{8 P_{c}} / \cdot\left\{R \rightarrow \mathbf{8 . 3 1 4} \mathrm{MPa} \mathrm{cm}^{\wedge} 3 / K / \mathrm{mol}, P_{c} \rightarrow \mathbf{3 . 3 9 4 \mathrm { MPa } , T _ { C } \rightarrow \mathbf { 1 2 6 . 6 } \mathrm { K } \}}\right.\right.$
$\frac{0.306202 \mathrm{~cm}^{3} \mathrm{~T}_{\mathrm{c}}}{\mathrm{K} \mathrm{mol}}$
$\ln [9]=\quad$ V /.
FindRoot [(vdwaal / . \{T $\rightarrow$ 298, rr $\rightarrow$ 8.314, $a \rightarrow 137708, b \rightarrow .306, ~ P \rightarrow .1\}),\{v, 20000\}]$
Out $[=0=24720.3$
As a check ideal:
$\ln [\cdot]:=\mathrm{v} / . \operatorname{FindRoot}[($ vdwaal $/ .\{T \rightarrow 298, r r \rightarrow 8.314, a \rightarrow 0, b \rightarrow 0, P \rightarrow .1\}),\{v, 20000\}]$
Out [0] $=24775.7$
$\ln [\rho]=$
$8.314 \times 298 / .1$
Out $[0=24775.7$
OK. We are off to a good start. Here is the volume as a function of pressure at constant T.
$\ln [25]:=P \operatorname{lot}[$
 $\{P, .1,1\}$, PlotRange $\rightarrow$ All, PlotLegends $\rightarrow$ \{"IsoThermal"\},
PlotStyle $\rightarrow$ Green, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Volume, cm^3/mol"\}]
Volume, $\mathrm{cm}^{\wedge} 3 / \mathrm{mol}$


Out[25]= Pressure, MPa
$\ln [0]:=$ eqeq $=($ vdwaal $/ .\{T \rightarrow 298, r r \rightarrow .08206, a \rightarrow 1.3, b \rightarrow 2\})$
Out $[=]=\left(P+\frac{1.3}{v^{2}}\right)(-2+v)=24.4539$
What is the constant for the adiabatic relation?
$\ln [10]:=\left(P+a / v^{\wedge} 2\right)(v-b)^{\wedge} \Gamma=\left(P 1+a / v 1^{\wedge} 2\right)(v 1-b)^{\wedge} \Gamma$
Out[10]= $\left(P+\frac{a}{v^{2}}\right)(-b+v)^{\Gamma}=\left(P 1+\frac{a}{v 1^{2}}\right)(-b+v 1)^{\Gamma}$

```
\(\ln [28]:=\) vadiabatric \(=\% 10 / .\{\mathrm{P} 1 \rightarrow .1\), v1 \(->\) 24720.320291594984`,
        \(\Gamma \rightarrow 8.314 /(5 / 2 \times 8.314)+1, \quad r r \rightarrow 8.314, a \rightarrow 137708, b \rightarrow .306\}\)
Out[28]= \(\left(P+\frac{137708}{v^{2}}\right)(-0.306+v)^{1.4}==141660\).
```

$\ln [32]=$ Plot [v/. FindRoot[
(\%28 /. $\{T \rightarrow 298, \Gamma \rightarrow 8.314 /(5 / 2 \times 8.314)+1, r r \rightarrow 8.314, a \rightarrow 137708, b \rightarrow .306\})$,
$\{v, 20000\}],\{P, .1,1\}, P l o t L e g e n d s \rightarrow\{" A d i a b a t i c "\}$, PlotStyle $\rightarrow$ Red]


- Adiabatic
$\ln [26]=$ Show [\%25, \%22]



## Work = Integral [ V dp]

$\ln [38]:=\mathrm{v} / . \operatorname{Table}[F i n d R o o t[\% 28,\{v, 24000\}],\{P, .1,10\}]$
Out [38]= $\{24720.3,4445.97,2797.46,2115.87$, $1731.33,1480.28,1301.69,1167.21,1061.76,976.526\}$

Define some functions. The volumetric equation and the relation for adiabatic compression.

```
\(\ln [49]:=\) vdewaall[ \(\left.v_{-}, P_{-}, a_{-}, b_{-}, r r_{-}\right]:=(P+a / v \wedge 2)(v-b)-r r T\)
\(\ln [50]=\mathrm{vv}\left[\mathrm{P}_{-}, \Gamma_{-}, \mathrm{T} 1_{-}, \mathrm{P} 1_{-}, v_{-}, \mathrm{v} 1_{-}, \mathrm{a}_{-}, \mathrm{b}_{-}\right]:=\)
        \(\left(P+a / v{ }^{\wedge} 2\right)(v-b)^{\wedge} \Gamma-\left(P 1+a / v 1^{\wedge} 2\right)(v 1-b)^{\wedge} \Gamma\)
```

Now make these easily evaluatable. The first is the volume, the second is the temperature
$\ln [144]:=$ g1 [dd_?NumericQ] :=
FindRoot [\{vv[P, 1.4, 298, .1, v, 24720.320291594984`, 137708, .306] , vdewaall[v, P, 137708, .306, T, 8.314]\}, \{v, 15000\}, \{T, 298\}] [ [1, 2] ]
g2 [dd_? NumericQ] : = FindRoot [\{vv[P, 1.4, 298, .1, v, 24720.320291594984, 137708, . 306] , vdewaall[v, P, 137708, . 306, T, 8.314]\}, \{v, 15000\}, \{T, 298\}] [[2, 2]]

In[146]:= Plot[g1[P], \{P,.1, 1\}, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Volume, cm^3/mole"\}]
Volume, $\mathrm{cm}^{\wedge} 3 / \mathrm{mole}$

$\ln [147]:=$
Plot[g2[P], \{P,.1, 1\}, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Temperature, K"\}]
Temperature, K


The work for compression is:
$\ln [148]:=$ NIntegrate [g1[P], \{P,.1, 1\}]
Out[148]= 8042.33


How does this compare to ideal. Note that the initial $T$ and $v$ are not exactly the same.
$\ln [150]:=$ idealvolume $=8.314 \times 298 / .1$
Out[150]=
24775.7
$\ln [61]:=S o l v e\left[p V^{\wedge}(c p / c v)=p 1 V 1^{\wedge}(c p / c v), V\right]$
... Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.
$\operatorname{Out}[61]=\left\{\left\{\mathrm{V} \rightarrow\left(\frac{\mathrm{p} 1 \mathrm{~V} 1^{\mathrm{cp} / \mathrm{cV}}}{\mathrm{p}}\right)^{\frac{\mathrm{cV}}{\mathrm{cp}}}\right\}\right\}$
$\ln [63]:=$ idealwork $=$ Integrate $\left[\left(\frac{p 1 \mathrm{~V} 1^{c p / c v}}{p}\right)^{\frac{c v}{c p}}, p\right]$
Out[63] $=\frac{p\left(\frac{p 1 \mathrm{~V} 1^{c p / c v}}{p}\right)^{\frac{c v}{c p}}}{1-\frac{c v}{c p}}$
$\ln [67]:=$ idealworkfunc =
(idealwork /. \{p1 $\rightarrow$. $1, \mathrm{~V} 1 \rightarrow$ idealvolume, $c p \rightarrow 7 / 2 \times 8.314, c v \rightarrow 5 / 2 \times 8.314\}$ ) -
(idealwork /. \{p1 $\rightarrow$. $1, \mathrm{~V} 1 \rightarrow$ idealvolume, $\mathrm{cp} \rightarrow 7 / 2 \times 8.314, \mathrm{cv} \rightarrow 5 / 2 \times 8.314, \mathrm{p} \rightarrow .1, \mathrm{v} \rightarrow$ idealvolume\})
Out[67] $=-8671.5+\frac{16742 .}{\left(\frac{1}{\mathrm{p}}\right)^{0.285714}}$
$\ln [151]:=$ idealworkfunc / p $\boldsymbol{\rightarrow} \mathbf{1}$
Out[151]= 8070.55
$\ln [152]:=~ P l o t[i d e a l w o r k f u n c,\{p, .1,10\}$,
AxesLabel $\rightarrow$ \{"Pressure, MPa", "Work"\}, PlotLegends $\rightarrow$ \{"Ideal"\}]


In[153]:= Plot[NIntegrate[g1[P], \{P, .1, pz\}],
$\{p z, .1,10\}, A x e s L a b e l \rightarrow\{" P r e s s u r e, ~ M P a ", ~ " W o r k "\}$, PlotLegends $\rightarrow$ \{"van der Waals"\}, PlotStyle $\rightarrow$ Red]

$\ln [154]:=$
Show [\%, \%\%]


We see that up to 10 MPa , very little difference occurs for ideal compared to vdW. The "a" term
$\ln [155]:=$ NIntegrate [g1[P], \{P, .1, 10\}]
Out[155]= 23495.7
$\ln [156]:=$
idealworkfunc / . p $\rightarrow 10$
Out[156]=
23652.3

The temperature gets so high that the gas remains close to ideal through out the compression.
$\ln [157]:=P \operatorname{lot}\left[\left\{g 2[P], 298(P / .1)^{\frac{2}{7}}\right\},\{P, .1,10\}\right.$, AxesLabel $\rightarrow\{$ "Pressure, MPa", "T, K"\},
PlotLegends $\rightarrow$ \{"van der Waals", "ideal"\}, PlotStyle $\rightarrow$ \{Red, Green\} $]$
... FindRoot: The line search decreased the step size to within tolerance specified by Accuracy Goal and PrecisionGoal but was unable to find a sufficient decrease in the merit function. You may need more than MachinePrecision digits of working precision to meet these tolerances.


Compressions of permanent gasses are approximately ideal!

We see that at the end $\mathrm{Tr} \sim 10$ and since $\mathrm{Pc}=3.4 \mathrm{MPa}$, Pr is just getting to 3 .


Figure 6.6-3 (Reprinted with permission from O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles Charts, 2nd ed., John Wiley \& Sons, New York, 1960. This figure appears as an Adobe PDF file on the CD-ROM accompanying this book, and may be enlarged and printed for easier reading and for use in solving problems.)

## Let's check CO2

## What if the gas is not ideal?

You might like to use your favorite cubic equation of state to answer the question. We might find that the quantitative effect of non ideality is not too large.
We will use van der Waals for this example.
$\ln [102]:=\mathrm{vdwaal}=\left(P+a / v^{\wedge} 2\right)(v-b)==r r T$
Out[102] $=\left(P+\frac{a}{v^{2}}\right)(-b+v)==r r T$

Kumar et al., "Van der Waal's equation for an adiabatic process and its Carnot engine efficiency" (2017) (arXiv:1802.01474v1) show that for an adiabatic process the van der Waals equation has a formula similar to ideal for the pressure ratio. The result is,
$\ln [103]:=\operatorname{vdwadiabatic}=\left(P+a / v^{\wedge} 2\right)(v-b)^{\wedge} \Gamma$
Out[103] $=\left(P+\frac{a}{v^{2}}\right)(-b+v)^{\Gamma}$

Out[0]=$\left(P+\frac{a}{v^{2}}\right)(-b+v)^{\Gamma}$
where $\Gamma=\mathrm{R} / C_{v}+1$. For the adiabatic process, vdwadiabatic = constant.

If a and $\mathrm{b}=0$, then we would get the ideal gas result, that $\Gamma=C_{P} / C_{v}$ and $\mathrm{p} \mathrm{v}^{\gamma}=$ constant.

It would be good to pick a specific gas and get the numbers correct rather than just showing trends from "made up" constants. Note that any difference in the enthalpy change for the vdWaal gas compared to ideal is both because the volume of the initial state will not match and the difference that the "a" and "b" will have on the compression process.

## Choose CO2.

We start with:
$\mathrm{a}=\frac{27 R^{2} T_{c}^{2}}{64 P_{c}}, \mathrm{~b}=\frac{R T_{c}}{8 P_{c}}$
$\mathrm{Tc}=304.2 \mathrm{~K}, \mathrm{Pc}=7.376 \mathrm{MPa}, \mathrm{R}=8.314 \mathrm{MPa} \mathrm{cm} \wedge 3 / \mathrm{K} / \mathrm{mol}$
$\ln [104]=\frac{27 R^{2} T_{C}^{2}}{64 P_{c}} / .\left\{R \rightarrow 8.314 \mathrm{MPa} \mathrm{cm} \wedge 3 / K / \mathrm{mol}, P_{c} \rightarrow 7.376 \mathrm{MPa}, T_{C} \rightarrow 304.2 \mathrm{~K}\right\}$
$\frac{365849 . \mathrm{cm}^{6} \mathrm{MPa}}{\mathrm{mol}^{2}}$
$\ln [105]:=\frac{R T_{c}}{8 P_{\boldsymbol{c}}} / .\left\{R \rightarrow \mathbf{8 . 3 1 4 ~ M P a ~ c m}{ }^{\wedge} 3 / K / \mathrm{mol}, P_{c} \rightarrow 7.376 \mathrm{MPa}, T_{C} \rightarrow 304.2 \mathrm{~K}\right\}$
Out[105]= $=\frac{0.140896 \mathrm{~cm}^{3} \mathrm{~T}_{\mathrm{c}}}{\mathrm{K} \mathrm{mol}}$
$\ln [106]:=\mathbf{V} /$.
FindRoot[(vdwaal / . $\{\mathrm{T} \rightarrow 298, \operatorname{rr} \rightarrow 8.314, \mathrm{a} \rightarrow 365849, \mathrm{~b} \rightarrow .141, \mathrm{P} \rightarrow .1\}),\{\mathrm{v}, 20000\}]$
Out[106]=
24627.3

As a check ideal:
$\ln [107]:=\mathrm{v} / . \operatorname{FindRoot[(vdwaal/.\{ T\rightarrow 298,~rr\rightarrow 8.314,a\rightarrow 0,b\rightarrow 0,P\rightarrow .1\} ),\{ v,20000\} ]}$
Out[107]= 24775.7
$\ln [108]:=8.314 \times 298 / .1$
Out[108]= 24775.7
OK. We are off to a good start. Here is the volume as a function of pressure at constant T .
$\ln [109]:=$
Plot[
 $\{\mathrm{P}, .1,1\}, \mathrm{PlotRange} \rightarrow$ All, PlotLegends $\rightarrow$ \{"IsoThermal"\}, PlotStyle $\rightarrow$ Green, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Volume, cm^3/mol"\}]

_ IsoThermal

What is the constant for the adiabatic relation?
In[111]:= adiabatictemp $=\left(P+a / v^{\wedge} 2\right)(v-b)^{\wedge} \Gamma=\left(P 1+a / v 1^{\wedge} 2\right)(v 1-b)^{\wedge} \Gamma$
Out[111]= $\left(P+\frac{a}{v^{2}}\right)(-b+v)^{\Gamma}==\left(P 1+\frac{a}{v 1^{2}}\right)(-b+v 1)^{\Gamma}$
$\ln [113]:=$ vadiabatric $=$ adiabatictemp /. $\{P 1 \rightarrow .1, ~ v 1->24627.307649960392$, $\Gamma \rightarrow 8.314 /(5 / 2 \times 8.314)+1, r r \rightarrow 8.314, a \rightarrow 365849, b \rightarrow .141\}$
Out[113]= $\left(P+\frac{365849}{v^{2}}\right)(-0.141+v)^{1.4}==141446$.
$\ln [114]:=$ Plot [


```
        {P,.1,1}, PlotLegends }->\mathrm{ {"Adiabatic"}, PlotStyle }->\mathrm{ Red]
```


$\ln [115]:=$
Show [\%109, \%114]
Volume, $\mathrm{cm}^{\wedge} 3 / \mathrm{mol}$


## Work = Integral [ V dp]

Define some functions. The volumetric equation and the relation for adiabatic compression.
$\ln [116]:=$ vdewaall[ $\left.v_{-}, P_{-}, a_{-}, b_{-}, r r_{-}\right]:=(P+a / v \wedge 2)(v-b)-r r T$
$\ln [117]:=\mathrm{vv}\left[\mathrm{P}_{-}, \Gamma_{-}, \mathrm{T} 1_{-}, \mathrm{P} 1_{-}, \mathrm{v}_{-}, \mathrm{v} \mathbf{1}_{-}, \mathrm{a}_{-}, \mathrm{b}_{-}\right]:=$ $(P+a / v \wedge 2)(v-b)^{\wedge} \Gamma-\left(P 1+a / v 1^{\wedge} 2\right)(v 1-b)^{\wedge} \Gamma$

Now make these easily evaluatable. The first is the volume, the second is the temperature
$\ln [132]:=$ g1 [dd_?NumericQ] := FindRoot [ $\{\mathrm{vv}[\mathrm{P}, 1.4,298, .1, \mathrm{v}, 24627.307649960392$, 365849 , 141 ] , vdewaall[v, P, 365 849, . 141, T, 8.314]\}, \{v, 15000$\},\{T, 298\}][$ [1, 2] ]
g2 [dd_? NumericQ] := FindRoot[\{vv[P, 1.4, 298, .1, v, 24627.307649960392`, 365 849, .141], vdewaall[v, P, 365 849, .141, T, 8.314]\}, \{v, 15000\}, \{T, 298\}] [ [2, 2]]
$\ln [134]:=$

Out[134]=
$\ln [135]:=$
Plot[g2[P], \{P,.1, 1\}, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Temperature, K"\}] Temperature, K


The work for compression is:
$\ln [136]:=$ NIntegrate[g1[P], \{P,.1,1\}]
Out[136]=
$\ln [137]:=\mathrm{Plot}[$ NIntegrate[g1[P], $\{P, .1, \mathrm{pz}\}],\{\mathrm{Pz}, .1,1\}]$


How does this compare to ideal. Note that the initial $T$ and $v$ are not exactly the same.
$\ln [124]:=$
idealvolume $=8.314 \times 298 / .1$
Out[124]= 24775.7
$\ln [125]:=S o l v e\left[p V^{\wedge}(c p / C v)==p 1 V 1^{\wedge}(c p / C v), V\right]$
$\ldots$ Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[125] $=\left\{\left\{\mathrm{V} \rightarrow\left(\frac{\mathrm{p} 1 \mathrm{~V} 1^{\mathrm{cp} / \mathrm{cV}}}{\mathrm{p}}\right)^{\frac{\mathrm{cV}}{\mathrm{cp}}}\right\}\right\}$
$\ln [126]:=$ idealwork $=$ Integrate $\left[\left(\frac{\mathrm{p} 1 \mathrm{~V} 1^{\mathrm{cp} / \mathrm{cv}}}{\mathrm{p}}\right)^{\frac{\mathrm{cv}}{c p}}, \mathrm{p}\right]$
Out $[126]=\frac{p\left(\frac{p 1 v 1^{c p / c v}}{p}\right)^{\frac{c v}{c p}}}{1-\frac{c v}{c p}}$
$\ln [127]:=$ idealworkfunc =
(idealwork / . \{p1 $\rightarrow$. $1, \mathrm{~V} 1 \rightarrow$ idealvolume, $c p \rightarrow 7 / 2 \times 8.314, c v \rightarrow 5 / 2 \times 8.314\}$ ) -
(idealwork /. \{p1 $\rightarrow$. $1, \mathrm{~V} 1 \rightarrow$ idealvolume, $c p \rightarrow 7 / 2 \times 8.314, c v \rightarrow 5 / 2 \times 8.314, p \rightarrow .1, v \rightarrow$ idealvolume\})

Out[127]= $-8671.5+\frac{16742 .}{\left(\frac{1}{p}\right)^{0.285714}}$
$\ln [128]:=$
idealworkfunc / . p $\rightarrow 1$
Out[128]=
8070.55
$\ln [138]:=$
Plot[idealworkfunc, \{p,.1, 10\}, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Work"\}, PlotLegends $\rightarrow$ \{"Ideal"\}]

$\ln [139]:=\mathrm{Plot}[N I n t e g r a t e[g 1[P],\{P, .1, \mathrm{Pz}\}]$, \{pz, .1, 10\}, AxesLabel $\rightarrow$ \{"Pressure, MPa", "Work"\}, PlotLegends $\rightarrow$ \{"van der Waals"\}, PlotStyle $\rightarrow$ Red]

$\ln [140]=$
Show [\%, \%\%]


We see that up to 10 MPa , very little difference occurs for ideal compared to vdW. The "a" term
$\ln [141]:=$ NIntegrate [g1[P], \{P, .1, 10\}]
Out[141]= 23224.9
$\ln [142]:=$ idealworkfunc /.p $\boldsymbol{\rightarrow} \mathbf{1 0}$
Out[142]=
23652.3

The temperature gets so high that the gas remains close to ideal through out the compression.

$$
\begin{aligned}
\operatorname{In}[143]:= & P \operatorname{lot}\left[\left\{\mathrm{~g} 2[\mathrm{P}], 298(\mathrm{P} / .1)^{\frac{2}{7}}\right\},\{\mathrm{P}, .1,10\}, \text { AxesLabel } \rightarrow\{\text { "Pressure, MPa", "T, K" }\},\right. \\
& \text { PlotLegends } \rightarrow\{\text { "van der Waals", "ideal" }\}, \text { PlotStyle } \rightarrow\{\text { Red, Green }\}]
\end{aligned}
$$



