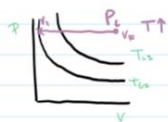


A1: To Perform Reversible, Constant Pressure Expansion



One can manipulate the Surroundings by keeping the System sufficiently small such that the Volume of gas in the Surroundings is so large compared to the System that the System's expansion does not create an appreciable difference in the $P_{\text{surroundings}}$. (Keep $dP_{\text{surroundings}} \approx 0$). Furthermore, the temperature of the system must be increased slowly to create infinitesimal imbalances between System and Surroundings: $T_{\text{sys}} \approx T_{\text{surroundings}} + dT$ over Time the small dT 's sum to create an appreciable increase in the T_{sys} which results in an increase in Volume @ P_{const} by ($PV = nRT$)

A2: It is possible. It could work by closing the system after initiating a slow chemical reaction within that gradually and uniformly increases the temperature of the system. This would utilize chemical work to increase the internal energy of the system rather than through heating. The increase in internal energy is transferred to the ideal gas particles as an increase in kinetic energy which increases its volume at constant pressure by the ideal gas law.

A3:

Fit obtained: $\gamma = 1.671 \pm 0.005$

γ for monoatomic gas = $5/3$ or 1.666
diatomic gas = $7/5$ or 1.4

Thus the gas studied was likely monoatomic

A.4:

$$dU = dq + dw = -pdv = C_v dT$$

$$-\int_{V_1}^{V_2} \frac{nRT}{V} dV = \int_{T_1}^{T_2} C_v dT$$

$$-\int_{V_1}^{V_2} \frac{nR}{V} dV = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

$$-nR \ln\left(\frac{V_2}{V_1}\right) = C_v \ln\left(\frac{T_2}{T_1}\right)$$

$$\ln\left(\frac{V_2}{V_1}\right) = \frac{C_v}{nR} \ln\left(\frac{T_2}{T_1}\right)$$

$$\ln\left(\frac{V_2}{V_1}\right) = \frac{C_v}{C_p - C_v} \ln\left(\frac{T_2}{T_1}\right)$$

$$\ln\left(\frac{V_2}{V_1}\right) = \frac{1}{\gamma - 1} \ln\left(\frac{T_2}{T_1}\right)$$

$$(1 - \gamma) \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{T_2}{T_1}\right)$$

$$\ln\left(\frac{V_2}{V_1}\right)^{1-\gamma} = \ln\left(\frac{T_2}{T_1}\right)$$

$$\left(\frac{V_2}{V_1}\right)^{1-\gamma} = \left(\frac{T_2}{T_1}\right)$$

$$\left(\frac{V_2}{V_1}\right)^{1-\gamma} = \left(\frac{P_2 V_2}{P_1 V_1}\right)$$

$$\left(\frac{V_2}{V_1}\right)^{1-\gamma} \left(\frac{V_1}{V_2}\right) = \frac{P_2}{P_1}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_2}{P_1}$$

$$\frac{V_2^{\gamma}}{V_1^{\gamma}} = \frac{P_2}{P_1}$$

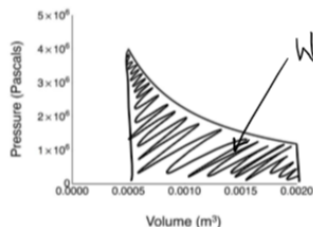
$$\frac{P_2 V_2^{\gamma}}{V_1^{\gamma}} = P_1 \quad \text{let } \lambda = P_1 V_1^{\gamma}$$

$$\boxed{\frac{\lambda}{V^{\gamma}} = P}$$

B3:

$g_{as} = CO_2$
 $T = 300K$
 $n = 1 \text{ mol}$
 $V_1 = 0.0005 \text{ m}^3$
 $V_2 = 0.002 \text{ m}^3$
 $a = 0.3687 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}$
 $b = 4.62 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$

$$\begin{aligned}
 W &= - \int_{V_1}^{V_2} P \cdot dV \\
 &= - \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} + \frac{an^2}{V^2} \right) dV \\
 &= -nRT \int_{V_1}^{V_2} \frac{1}{V-nb} dV + an^2 \int_{V_1}^{V_2} \frac{1}{V^2} dV \\
 &= -nRT \ln(V_2-nb) + nRT \ln(V_1-nb) + \frac{-an^2}{V_2} + \frac{an^2}{V_1} \\
 &= nRT [\ln(V_1-nb) - \ln(V_2-nb)] + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)
 \end{aligned}$$



$$\begin{aligned}
 [W] &= \frac{\text{mol} \cdot \text{m}^3 \cdot \text{Pa}}{\text{K} \cdot \text{mol}} \cdot \text{K} + \frac{\text{Pa} \cdot \text{m}^6}{\text{mol}^2} \cdot \frac{1}{\text{m}^3} \\
 &= \text{Pa} \cdot \text{m}^3 = \text{J}
 \end{aligned}$$

$$\begin{aligned}
 W &= 1 \times 8.3145 \times 300 \times \ln \left(\frac{0.0005 - 1 \times 4.62 \times 10^{-5}}{0.002 - 1 \times 4.62 \times 10^{-5}} \right) + 0.3687 \times 1^2 \left(\frac{1}{0.0005} - \frac{1}{0.002} \right) \\
 W &= -3088.4 \text{ J}
 \end{aligned}$$

B4:

$$U = \frac{3}{2} nRT - \frac{an^2}{V} \quad \begin{matrix} V_1 = 0.0005 \\ V_F = 0.002 \end{matrix}$$

$$\Delta U = \left(\frac{3}{2} nRT - \frac{an^2}{V_F} \right) - \left(\frac{3}{2} nRT - \frac{an^2}{V_1} \right)$$

$$\Delta U = -\frac{an^2}{V_F} + \frac{an^2}{V_1} = \frac{an^2}{V_1} - \frac{an^2}{V_F} = an^2 \left(\frac{1}{V_1} - \frac{1}{V_F} \right)$$

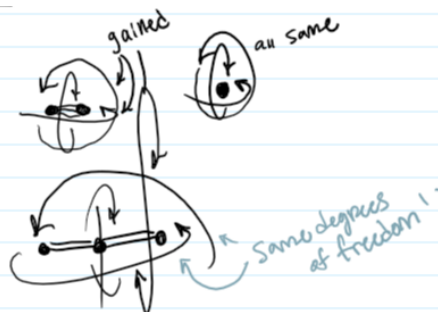
$$\Delta U = 0.3687 \cdot \left(\frac{1}{0.0005} - \frac{1}{0.002} \right) = 553.05 \text{ J}$$

Expansion: $V_F > V_1$
 thus, ΔU always > 0
 and internal energy increases

B5: $\Delta U = 553.05 = q + w = q - 3088.4 \text{ J}$
 $q = 3641.4 \text{ J}$

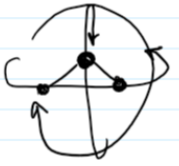
C1:

	C_p	C_v	$C_p - C_v$
Monoatomic:	$\frac{5}{2} nR$	$\frac{3}{2} nR$	nR
Diatomic:	$\frac{7}{2} nR$	$\frac{5}{2} nR$	nR
(Bent) Triatomic:	$\frac{8}{2} nR$	$\frac{6}{2} nR$	nR
Linear Triatomic:	$\frac{7}{2} nR$	$\frac{5}{2} nR$	nR



Because a linear triatomic molecule has the same degrees of freedom as a diatomic molecule kinetic energy is stored in the same modes of rotation and thus the C_p is the same. $\therefore C_p = \frac{7}{2} nR$

C2: C_p for H_2O as the bent triatomic molecule gains an additional mode of freedom. Since moving from monoatomic to diatomic gains two degrees of freedom, and increases by $\frac{7}{2}$ adding one additional degree of freedom must increase the C_p by $\frac{1}{2}$.



$$\therefore C_{p,H_2O} = \frac{8}{2} nR$$

C3: $C_{p,CO_2} = 0.846 \frac{kJ}{kg \cdot K}$

$$C_{p,H_2O} = 1.864 \frac{kJ}{kg \cdot K}$$

The bent molecules fit the predicted heat capacity well

Predicted $C_{p,H_2O} = 1.8456$

$$\text{Predicted } C_{p,CO_2} = \frac{7}{2} \times R \times \frac{1}{MM_{CO_2}} = \frac{7}{2} \times 8.3145 \times \frac{1}{44.01} = 0.6612 \frac{kJ}{kg \cdot K}$$

0.6612 $\frac{kJ}{kg \cdot K}$

The predicted triatomic linear heat capacity is an underestimate of the true value.

$$n = \frac{1000}{MM} \frac{1}{mol} \times \frac{1000}{145}$$

$$\frac{8}{2} nR = [mol \times \frac{Pa \cdot m^3}{mol \cdot K}] \frac{nRT}{V}$$

$$\frac{8}{2} R = \frac{Pa \cdot m^3}{mol \cdot K} \times \frac{1}{8} \times \frac{1000}{kg} \times \frac{1 kJ}{1000 J}$$

$$\frac{8}{2} \times R \times \frac{1}{MM} \times 1000 \times \frac{1}{1000}$$

$$\frac{8}{2} \times 8.3145 \times \frac{1}{18.02} \times 1000 \times \frac{1}{1000}$$

```
In [1]: import pandas as pd
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
import numpy as np
```

A.3

Adiabatic P-V fit using non-linear least squares

Findings:

Found that gas data read from pV_adiabatic.csv is likely monoatomic as fitted value for gamma is 1.671 +/- 0.005 and a monoatomic ideal gas is expected to have a gamma value of 1.666 or 5/3. A diatomic ideal gas would have a gamma of 1.4 or 7/5.

```
In [12]: df = pd.read_csv('pV_adiabatic.csv', header=None)
Xs = df[0]
Ys = df[1]

raw_data, = plt.plot(Xs, Ys, 'ob')
plt.title("Plot of Pressure as Function of Volume for Adiabatic Expansion of Ideal Gas\n")
plt.xlabel("Volume")
plt.ylabel("Pressure")

def adiabatic(v, gamma, _lambda):
    p = _lambda / (v ** gamma)
    return p

g1 = ((5/3) + (7/5)) * 0.5
g2 = Xs[0] * Ys[0] ** g1

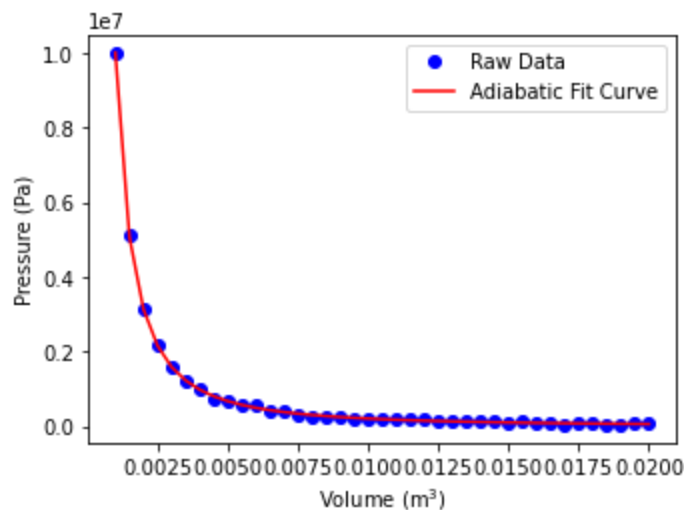
initial_guesses = [g1, g2]

popt, pcov = curve_fit(adiabatic, Xs, Ys, initial_guesses)
fit_curve, = plt.plot(Xs, adiabatic(Xs, *popt), 'r')
plt.legend([raw_data, fit_curve], ["Raw Data", "Adiabatic Fit Curve"])
plt.tight_layout()
plt.ylabel("Pressure (Pa)")
plt.xlabel("Volume (m$^3$)")

perr = np.sqrt(np.diag(pcov))
print("Optimized Coefficient Values: \n\tGamma: {:.3f} +/- {:.3f}\n\tLambda: {:.0f} +/- {:.0f}".format(popt[0], perr[0], popt[1], perr[1]))
```

Optimized Coefficient Values:
 Gamma: 1.671 +/- 0.005
 Lambda: 97 +/- 3

Plot of Pressure as Function of Volume for Adiabatic Expansion of Ideal Gas



B1

VanDerWaals Gas Inspection

Findings:

- A Van Der Waals Gas approaches $+\infty$ when V approaches b^+ while an ideal gas approaches $+\infty$ when V approaches 0
- The attractive component of the Van Der Waals equation influences P significantly at low temperatures causing decreases in pressure at V slightly above the value of b before asymptotically shooting off to $+\infty$
- Higher temperature Van Der Waals gases appear most similar to ideal gases
- As volume decreases overall shapes of the curves at high temperature mirror that of an ideal gas. At intermediate temperatures, the attractive and repulsive interactions start to dominate the behavior of the function and appear to cancel out much of the increase in pressure until sufficiently close to $V = b$ where they approach $+\infty$. Low temperature isotherms are heavily influenced by the attractive component as the value of T is not large enough to overcome the value of $\frac{-a}{V^2}$ at V slightly larger than b .
- At very low temperatures, the pressure appears to go below zero which likely indicates a breakdown of the VDW equation's usefulness as this is a physical impossibility.
- At large V , all isotherms mimic the appearance of ideal gases

```

In [3]: Ts = [200, 230, 270, 300, 400, 800] #in Kelvin
cols = ['k', 'm', 'b', 'g', 'y', 'r']
R = 8.3145
a = 0.3687 # in Pa * m^6 * mol ^-2
b = 4.62e-5 #in m^3 * mol^-1
n = 1

def VDW(V, T, n, a, b, R=R):
    p = ( (n*R*T) / (V - n*b) ) - ( (a * n ** 2) / (V ** 2) )
    return p

def ideal_gas(V, T, n, R=R): #
    p = n*R*T / V #
    return p #

Vs = np.linspace(1e-8, 1e-3, 1000)
Ps = [VDW(Vs, t, n, a, b) for t in Ts]
ideal_Ps = [ideal_gas(Vs, t, n) for t in Ts] #

fig, (ax1, ax2) = plt.subplots(1, 2)

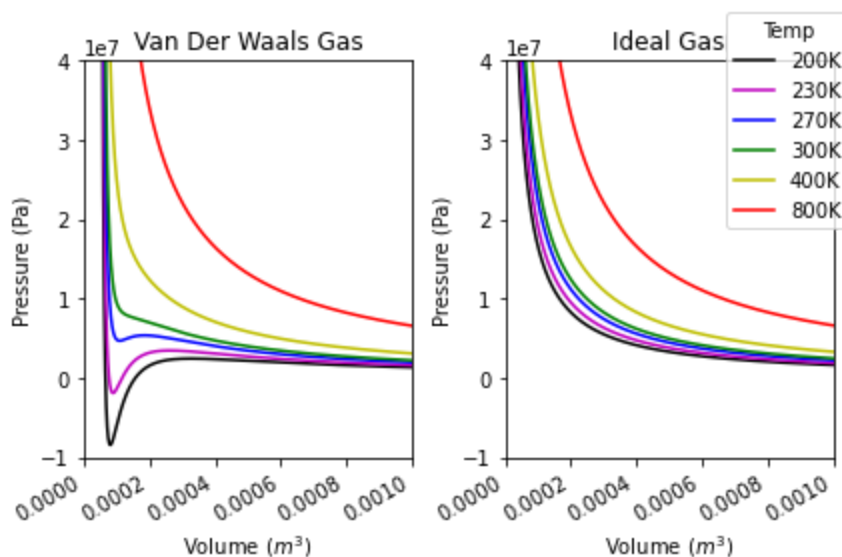
for i, j in enumerate(Ps):
    masked_vdw = np.ma.masked_where(Vs < b, j) #Remove points less than b as pyplot connects points on both sides of discontinuity
    ax1.plot(Vs, masked_vdw, cols[i], label="{}K".format(Ts[i]))
for i, j in enumerate(ideal_Ps):
    ax2.plot(Vs, j, cols[i])

ax1.axis([0, 0.001, -1e7, 4e7])
ax1.set_title("Van Der Waals Gas")
ax1.set_xlabel("Volume (m^3)")
ax1.set_ylabel("Pressure (Pa)")

ax2.axis([0, 0.001, -1e7, 4e7])
ax2.set_title("Ideal Gas")
ax2.set_xlabel("Volume (m^3)")
ax2.set_ylabel("Pressure (Pa)")

fig.autofmt_xdate()
fig.legend(title="Temp")
fig.tight_layout()

```



B2

Compare VDW and Ideal 300 K isotherm

Findings:

- The attractive component is negative and this responsible for decreases in pressure. It is independent of b and decreases towards $-\infty$ as V approaches zero.
- The repulsive component is positive and responsible for an additional increase in pressure for a VDW gas compared to an ideal gas at small V . It is asymptotic reaching a maximum when V approaches b^+ and a minimum when V approaches b^- . Because it generates asymptotes around b , it is the reason that the VDW gas pressure approaches $+\infty$ when V approaches b .
- The repulsive component is scaled by T and increased T leads to a steeper increase in pressure and cancels out more of the attractive component's influence especially around b .
- When summed, the attractive and repulsive components for the 300 K isotherm nearly cancel each other out causing the near-constant pressure behavior until V is sufficiently close to b and the function shoots off to infinity
- The result of all of this is that the van der Waals equation approaches infinity at greater a V than the ideal gas equation. Furthermore, the VDW equation is able to account for the balance between attractive and repulsive interactions and thus when attractive interactions dominate, the P is below that of an ideal gas and when repulsive interactions dominate, the P is above that of an ideal gas.


```

In [11]: p_vdw = VDW(Vs, 300, 1, a, b)
p_ideal = ideal_gas(Vs, 300, 1)
p_second = VDW(Vs, 300, 1, a, b, 0)
p_first = VDW(Vs, 300, 1, 0, b)

ideal, = plt.plot(Vs, p_ideal, 'm')
attractive, = plt.plot(Vs, p_second, '--g')
repulsive, = plt.plot(Vs, p_first, '--r')
vanderwaals, = plt.plot(Vs, p_vdw, 'k')

plt.legend((ideal, attractive, repulsive, vanderwaals), ("Ideal Gas", "Attractive Interaction", "Repulsive Interaction", "Van Der Waals Gas"))
plt.axis([0, 0.001, -7e7, 7e7])
fig.autofmt_xdate()
plt.title("Comparison of Van Der Waals Gas to Components and Ideal Gas\n")
plt.ylabel("Pressure (Pa)")
plt.xlabel("Volume (m3)")

plt.tight_layout()

```

