

Question 1:

A systematic way to account for deviations from ideal-gas behaviour is the virial expansion:

$$PV = nRT \left(1 + \frac{B(T)}{V/n} + \frac{C(T)}{V^2/n^2} + \dots \right),$$

where the functions $B(T)$, $C(T)$, and so on are called the virial coefficients. When the density of the gas is fairly low, so that the molar volume is large, each term in the series is much smaller than the one before. In many situations, it's sufficient to omit the third term and concentrate on the second, whose coefficient $B(T)$ is called the second virial coefficient (the first coefficient being 1).

Part A: Use the spreadsheet to calculate the second and third virial coefficients

Firstly, equations for the coefficients (in terms of known variables) must be found.

$$PV = nRT$$

$$\frac{V}{n} = \frac{RT}{P}$$

Now, the second coefficient is equal to $\frac{B(T)}{V/n}$. Substituting the denominator of this with the expression found for volume over number of moles gives:

$$\frac{B(T)}{V/n} = \frac{B(T)}{\left(\frac{RT}{P}\right)}$$

$$\frac{B(T)}{V/n} = \frac{B(T)P}{RT}$$

As the source gives values for temperature, the change of the second coefficient may be found across a change in temperature, with pressure remaining a constant (101.3 kPa).

The same formula may be found for the third coefficient, just with the variables being to a power of two. That is,

$$\frac{C(T)}{(V/n)^2} = \frac{C(T)P^2}{(RT)^2}$$

The spreadsheet in which the second and third virial coefficients were calculated across a range of temperatures for Sulfur Hexafluoride (SF_6) is given in Appendix 1.

Part B:

The values for the 2nd and 3rd virial coefficients for Sulfur Hexafluoride calculated in part a show that the ideal gas law generally becomes more accurate as the temperature gets higher. As the temperature gets further away from 0K, the 2nd coefficient approaches zero (up to a point at about 700K), meaning the deviation becomes more and more negligible.

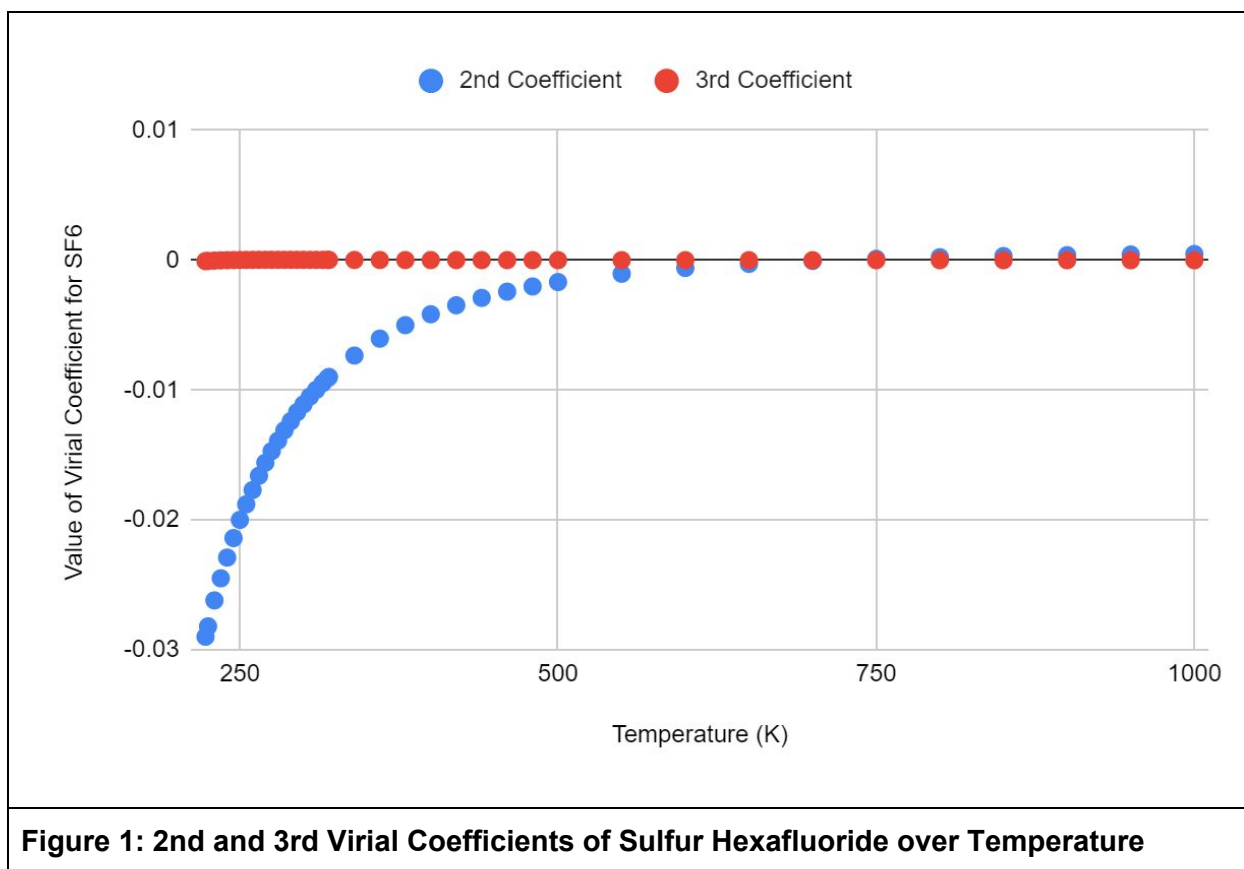


Figure 1 shows that for temperatures of about 250K, the deviation from ideal gas behaviour is about -2%. An important note from the graph is that the 3rd coefficient remains very close to zero through all of the observed temperatures, and thus it is rational to ignore the value altogether for most practical purposes.

Part C:

Figure 1 shows that $B(T)$ has a negative sign for all low-to-medium range temperatures, which may be explained by the relationship that molecules in motion have with each other. As the temperature gets lower, the kinetic energy of each molecule in the gas gets proportionally lower also and you would expect far fewer molecular collisions as a result. The reduction of the kinetic energy (and consequently, the speed) of the molecules results in a fall in pressure of the gas overall, and the negative value of $B(T)$ would, in part, correct this lower than expected pressure. The same reasoning can be applied to the positive sign of $B(T)$ at sufficiently high temperatures. As the kinetic energy (and again, the speed) of the molecules increase, the pressure would increase more than the ideal gas law predicts, largely as a result of the increased number of collisions and greater impact of repulsive forces between molecules. While only Sulfur Hexafluoride was analysed, this behaviour is expected to take place in all gases, albeit at different temperatures.

Part D:

Plotting isotherms for Sulfur Hexafluoride can help to visualise the difference between the ideal gas law and the actual values when corrected with the virial coefficients.

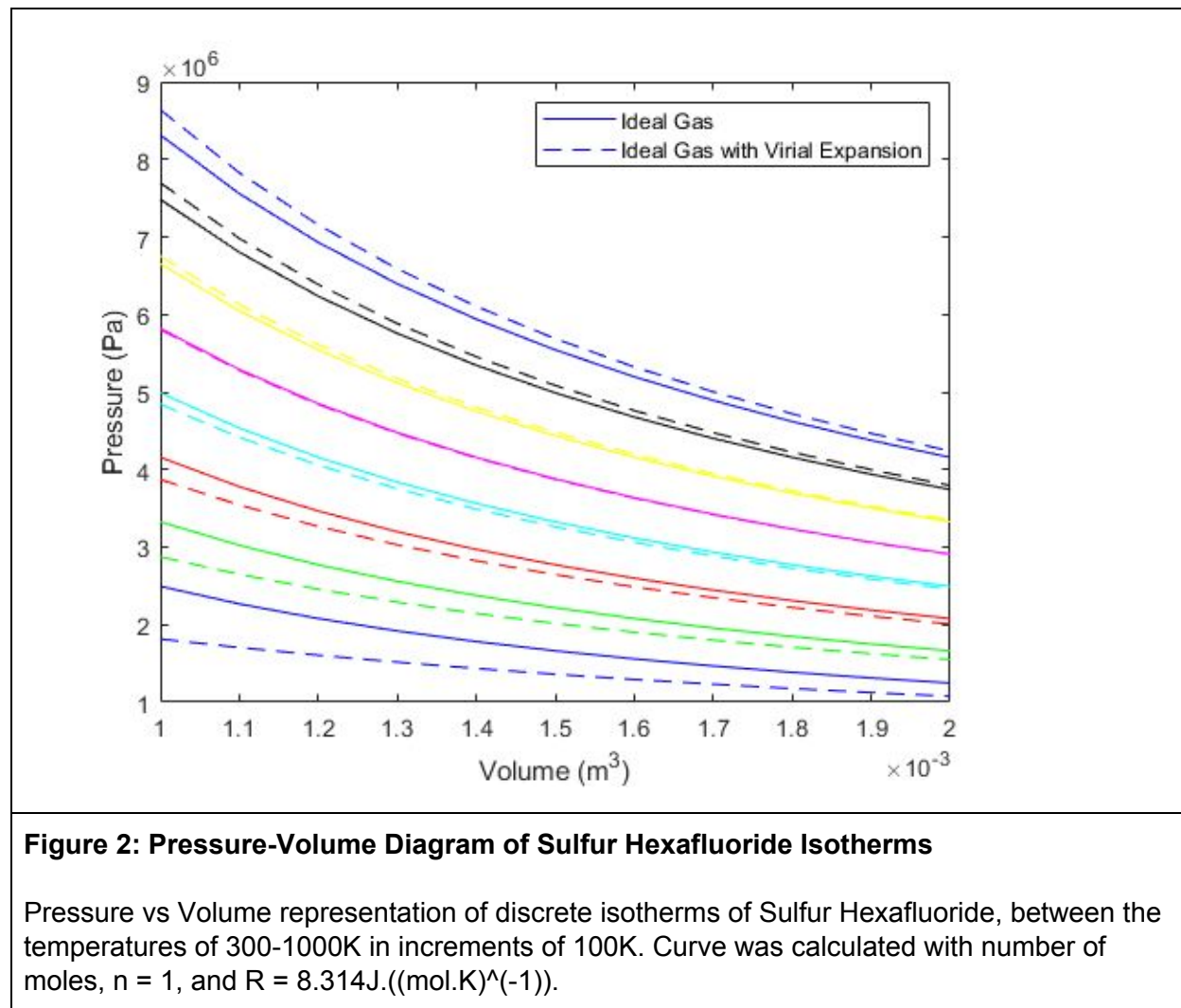
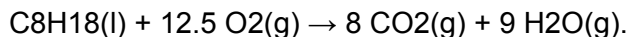


Figure 2 shows the discrepancies between the ideal gas law and the virial expansion. As expected (by the answer in Part C), the virial expansion reduces the calculated pressure value for low temperatures, and increases the value for higher temperatures. At a temperature of about 700K (shown by the magenta isotherm in Figure 2), the second coefficient is much smaller in magnitude than one, so the difference between the two curves appears to be negligible. As the temperature gets further from this rough 700K value, the discrepancies (that is, the absolute magnitude of the difference) become gradually larger.

Question 2:

A jet engine is fuelled by liquid octane (C_8H_{18}) via the combustion reaction



The combustion chamber is maintained at atmospheric pressure throughout the reaction, with air entering at 500 K and exiting as exhaust at 1,000 K. The excess energy from the reaction is used to accelerate the exhaust and thereby propel the aircraft.

Part A:

The enthalpy of formation of octane is $\Delta_f H(C_8H_{18}) = -250 kJ/mol$ at the temperature it enters the combustion chamber and atmospheric pressure, and the mass of exhaust gas generated by the reaction of one mole of octane is 1.8 kg. Using the table of thermodynamic properties given at the back of the exam paper, determine the excess energy per mole of octane burnt and, assuming this energy is fully converted into exhaust kinetic energy, the velocity of the exhaust gas.

Firstly, we need to find the excess energy created as a result of the combustion reaction. Assuming the excess energy is equal to the change in enthalpy of the reaction, we have the excess energy as ΔH , and

$$\Delta H = \Delta H_{product} - \Delta H_{reactant}$$

As there are two products and two reactants in this reaction, we have

$$\Delta H = (8\Delta H_{CO_2} + 9\Delta H_{H_2O}) - (\Delta H_{C_8H_{18}} + 12.5\Delta H_{O_2})$$

As the products are at a higher temperature than their values in the Thermodynamic Properties table (specifically 1000K compared to 298K in the table), we have, for each product (per mole),

$$\Delta H_{product} = \Delta_f H_{product} + C_{p_{product}} \Delta T$$

So, we have for CO_2 ,

$$\begin{aligned}\Delta H_{CO_2} &= \Delta_f H_{CO_2} + C_{p_{CO_2}} \Delta T \\ \Delta H_{CO_2} &= (-393.51 kJ) + (37.11 J/K) \times (1000 - 298 K) \\ \Delta H_{CO_2} &= (-393.51 kJ) + (26051.2 J) \\ \Delta H_{CO_2} &= (-393.51 kJ) + (26.0512 kJ) \\ \Delta H_{CO_2} &\approx -367.5 kJ\end{aligned}$$

And for gaseous H_2O ,

$$\begin{aligned}\Delta H_{H_2O} &= \Delta_f H_{H_2O} + C_{p_{H_2O}} \Delta T \\ \Delta H_{H_2O} &= (-241.82 kJ) + (33.58 J/K) \times (1000 - 298 K) \\ \Delta H_{H_2O} &= (-241.82 kJ) + (23573.16 J) \\ \Delta H_{H_2O} &= (-241.82 kJ) + (23.57316 kJ) \\ \Delta H_{H_2O} &\approx -218.2 kJ\end{aligned}$$

So, for the total change in enthalpy for the combustion reaction, the excess heat is:

$$\Delta H = (8\Delta H_{CO_2} + 9\Delta H_{H_2O}) - (\Delta H_{C_8H_{18}} + 12.5\Delta H_{O_2})$$

$$\Delta H = (8 \times (-367.5) + 9 \times (-218.2)) - ((-250) + 12.5 \times (0)) \text{ kJ}$$

$$\Delta H = (-3012 - 1963.8) - (-250) \text{ kJ}$$

$$\Delta H = 250 - 4975.8 \text{ kJ}$$

$$\Delta H \approx -4726 \text{ kJ}$$

Since ΔH is negative, the combustion reaction is exothermic as expected, meaning that there is a positive yield of energy. Assuming that all of this energy is converted into kinetic energy, $E_k = |\Delta H| = 4726 \text{ kJ}$.

The velocity of the exhaust gas may be found by rearranging the formula for kinetic energy, $E_k = \frac{1}{2}mv^2$

$$\Rightarrow v_{\text{exhaust}} = \sqrt{\frac{2E_k}{m}}$$

Substituting in the values for mass and kinetic energy,

$$v_{\text{exhaust}} = \sqrt{\frac{2 \times 4726000}{1.8}}$$

$$v_{\text{exhaust}} \approx 72 \text{ m/s}$$

Therefore, combusting one mole of octane to a temperature of 1000K in this combustion chamber gives an exhaust velocity of about 72 metres per second in the direction out of the chamber.

Part B: Discuss some of the implicit approximations made in the above calculation.

- It was assumed that the one mole of octane enters the combustion chamber at 298K, and its temperature wasn't impacted by the ambient temperature of the altitude that the jet is at, or any temperature changes to the fuselages as a result of moving at speed in an atmosphere. If the octane was combusted at a higher initial temperature, it would be expected that there would be less kinetic energy in the exhaust gases, resulting in a slower exhaust speed of the gas.
- It was assumed that the enthalpy of formation of Oxygen gas at 500K has a negligible difference to that at 298K, due to the fact that O_2 is likely still the most stable form of Oxygen at temperatures of 500K. If this wasn't the case, and the enthalpy of formation of O_2 at 500K was greater than that at 298K, there would be a far lesser exhaust speed as a result of a smaller change in enthalpy of the combustion reaction.
- The products' enthalpy of formation at 1000K was assumed to be under a constant-pressure process, which in the real world would not likely happen. For such a process to occur, the combustion chamber would need to expand as the products got hotter, and the expansion of the combustion chamber was assumed to be negligible.
- The products and reactants involved were assumed to be ideal gases for ease of calculation, and it was assumed that their behaviour remained ideal at the range of temperatures analysed. In reality, as the temperature of a gas increases, more degrees of freedom become relevant and the products enthalpy of formation would be increased accordingly (as C_p would become larger in direct proportionality to the degrees of freedom).

- It was assumed that the combustion reaction would only have two products, which is unlikely in practicality due to things such as incomplete combustion, and impurities in the fuel.
- It was assumed that only the effect of the O_2 in the atmosphere had an effect on the reaction. In reality, there are a multitude of other gases in the atmosphere that may have changed some values in the calculations. This assumption ties directly into the previous assumption (namely impurities in fuel).

Question 3:

Experimental measurements of the heat capacity of graphite at various temperatures and at 1 atmosphere fit reasonably well to the simple formula:

$$C_P = a + bT$$

Where the coefficients are $a = 16.86 J/K$ and $b = 4.77 \times 10^{-3} J/K^2$

Part A:

Use this formula and the attached data tables to determine the entropy of 1 mole of graphite at 398 K.

The total entropy of graphite at some temperature, T_2 in terms of another, T_1 , is given by

$$S = S(T_1) + \Delta S$$

Given that $S(T_1)$ is known, we can find ΔS by

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

Substituting in the initial and final temperatures, as well as the equation for C_P ,

$$\Delta S = \int_{298}^{398} \frac{a + bT}{T} dT$$

$$\Delta S = \int_{298}^{398} \frac{a}{T} + b dT$$

Evaluating and simplifying the integral gives

$$\Delta S = [a \ln(T) + bT]_{298}^{398}$$

$$\Delta S = (a \ln(398) + 398b) - (a \ln(298) + 298b)$$

$$\Delta S = a \ln\left(\frac{398}{298}\right) + 100b$$

Putting this equation into the original equation for the entropy of graphite at 398K, we have

$$S = S(298K) + \left(a \ln\left(\frac{398}{298}\right) + 100b\right)$$

Substituting in known values (including $S(298K) = 5.74 J/K$ from the Thermodynamic Properties table) gives

$$S = 5.74 + 16.86 \ln\left(\frac{398}{298}\right) + 100 \times (4.77 \times 10^{-3}) J/K$$

$$S \approx 11.1 J/K$$

Therefore, given the entropy of graphite at 298K, the entropy at 398K was found to be approximately 11.1 joules per Kelvin.

Part B:

Would a formula of this form be physically reasonable in the limit that $T \rightarrow 0 K$? Explain.

A formula of this form appears to be reasonable as the temperature of graphite approaches 0 Kelvin. You would expect that, at 0K, there would be some amount of energy needed to raise the temperature by 1K. At this time, energy needed would be $C_P = 16.86 J/K$. The function would not be reasonable if it was missing the constant term, given by the coefficient a . If this were the case, at $T = 0K$, the graphite would spontaneously rise in temperature, as no energy would be needed to increase its temperature.

Question 4:

Two identical beakers of water are heated from 20 °C to 100 °C by two different methods:

1. By placing the first beaker on a large hotplate at 100 °C.
2. By placing the second beaker successively in contact with an infinite series of large hot plates. Each hot plate is at a higher temperature than the preceding one by an infinitesimally small amount.

Explaining your answers fully:

Part A:

How would you classify the two different methods?

The first method could be classed as an irreversible and probably quasistatic interaction, as heat flow between two objects is always irreversible. In this instance, the entropy of the universe would most likely be increasing (assuming that the sides and top of the beaker isn't perfectly insulated), as heat would escape out of the beaker as it rises in temperature, meaning that more energy would need to flow into the water to account for the energy lost as heat.

The second method could be classified as a reversible process in practice, due to the fact that for any finite number of hotplates, there would be effectively no temperature change in the water (and thus no heat flow, making the process reversible). This classification is based on the assumption that neither the hotplate nor the beaker radiate heat into their environment, and only transfer energy between each other.

Part B:

How does the change in entropy (between the initial and final states) compare between the two methods for:

1. The beaker of water?

In both cases, the entropy of the water would have increased after it reaches 100 Celsius. There is a defined change in entropy for a system changing from one temperature to another, given by $\Delta S = \int_{T_i}^{T_f} \frac{C}{T} dT$. This equation describes that there is a positive change in entropy as a system goes to a hotter temperature, and thus the beaker of water will have a higher entropy at 100 Celsius as opposed to 20 Celsius.

2. The hotplate(s)?

In both cases, it can be assumed that the temperature of any of the hotplates is unchanged as the water rises in temperature, or that:

- a. In method 1, the hot plate remains at 100 Celsius throughout the whole process
- b. In method 2, each of the infinite hotplates remains at their respective temperature (infinitesimally hotter than the beaker)

While the beaker's entropy is increased as a result of temperature increase, the hotplates entropy would remain the same throughout the process (as entropy is created by the heating of the hotplates to maintain their temperature, but the entropy of the hotplates themselves is kept constant).

Otherwise, it may be assumed in method 2 that each hotplate actually changes temperature as heat, and therefore entropy, is transferred to the beaker of water. In this case, the entropy of each individual hotplate would be smaller in its final state than in its initial state.

3. The universe?

For method 1, the entropy of the universe is clearly increasing. As the beaker of water heats up, entropy is transferred from the hotplate to the water and it is an irreversible process. But, assuming the beaker is kept at a constant 100 Celsius (a required assumption for the water to eventually reach 100C), entropy is constantly flowing into the hotplate. This entropy flowing into the hotplate is created somehow (from outside the system, and in the universe) and is put into this hotplate-beaker system.

For method 2, the entropy of the universe wouldn't increase, as the process involves a series of reversible entropy transfers.

Question 5:

Part A:

Give a statement of the second law of thermodynamics. Describe in words how this law arises from the microscopic statistics of large systems.

The second law of thermodynamics (according to Schroeder) states that any macroscopic system in equilibrium will be found in the macrostate with the greatest entropy.

For a macroscopic (large compared to microscopic) system composed of many particles moving at velocity in some large volume, we can imagine the distance between each particle as a microstate. Each macrostate of the system would be described by some average distance between the particles. When the system isn't in a static state, meaning that each of the particles are moving in some random direction with respect to one another, the most likely macrostate is the one in which there is a maximum average distance between each of the particles. The multiplicity of the macrostate, in this case, would be the highest possible for all possible macrostates of the system, and thus, the entropy of the system would be the highest possible value. In simpler terms for this example, the entropy of a system is greatest when the average distance between each of the particles is at its maximum possible value.

For a system in equilibrium, there are no outside forces acting on the system. So, for this example, each particle would be free to move in space (and rebound off of the container's boundaries) without an external force altering the distribution and properties of the particles. i.e. the particles would eventually approach a macrostate in which they are at their most random distribution within the container - the macrostate in which there is a maximum average distance between the particles, or the macrostate in which there is greatest entropy. Thus, a system in equilibrium will be found in the macrostate with the greatest possible entropy.

Part B:

Consider a two-state paramagnet which consists of a total of four magnetic dipoles. What is the most likely macrostate of the paramagnet? Calculate the entropy of this state.

The most likely macrostate was determined to be the macrostate with the highest multiplicity, so comparison of each of the macrostates' multiplicities will show the most likely macrostate:

Macrostate	Multiplicity (Ω)
No Dipoles Positive	5
One Dipole Positive	20
Two Dipoles Positive	30
Three Dipoles Positive	20
Four Dipoles Positive	5

Therefore the macrostate with two positive dipoles is the most likely, as it has the highest multiplicity. The entropy of this macrostate is given by

$$S = k \ln(\Omega)$$

Substituting in the values for the multiplicity and Boltzmann's Constant,

$$S = (1.381 \times 10^{-23} J/K) \times \ln(30)$$

$$S \approx 4.7 \times 10^{-23} J/K$$

As expected for a system that consists of a small number of particles, the entropy is very small. Of course, this calculation relies on the assumption that the paramagnet system is in equilibrium and that each of the dipole states is as equally likely as the other. If a magnetic field were to be applied to the paramagnet, you would expect that the macrostate in which all four dipoles are positive to be the most likely, as the constituents of a paramagnet tend to align parallel to an external magnetic field.

Appendices:

Appendix 1: Index of Sulfur Hexafluoride, with 2nd, 3rd Virial Coefficients

T (K)	B(T) ($\text{cm}^3 \cdot \text{mol}^{-1}$)	C(T) ($\text{cm}^6 \cdot \text{mol}^{-2}$)	2nd Coefficient	3rd Coefficient
223	-528.8	-22326	-0.029	-0.0000671
225	-518.2	-18470	-0.0282	-0.0000545
230	-493.3	-10258	-0.0262	-0.000029
235	-470.2	-3741	-0.0245	-0.0000101
240	-448.6	1426	-0.0229	0.0000037
245	-428.5	5517	-0.0214	0.0000137
250	-409.7	8747	-0.02	0.0000209
255	-392	11283	-0.0188	0.0000259
260	-375.5	13261	-0.0177	0.0000293
265	-359.9	14789	-0.0166	0.0000315
270	-345.3	15952	-0.0156	0.0000327
275	-331.4	16820	-0.0147	0.0000332
280	-318.4	17449	-0.0139	0.0000333
285	-306	17885	-0.0131	0.0000329
290	-294.3	18164	-0.0124	0.0000323
295	-283.2	18317	-0.0117	0.0000315
300	-272.6	18368	-0.0111	0.0000305
305	-262.6	18337	-0.0105	0.0000295
310	-253	18240	-0.00998	0.0000284
315	-243.9	18091	-0.00947	0.0000273
318.7	-237.5	17955	-0.00911	0.0000264
320	-235.2	17902	-0.00899	0.0000261
340	-204.1	16896	-0.00734	0.0000218
360	-177.9	15733	-0.00604	0.0000181
380	-155.4	14585	-0.005	0.0000151
400	-136.1	13526	-0.00416	0.0000126
420	-119.1	12580	-0.00347	0.0000107
440	-104.3	11750	-0.0029	0.00000907
460	-91.1	11030	-0.00242	0.00000779
480	-79.4	10408	-0.00202	0.00000675
500	-68.8	9873	-0.00168	0.0000059

550	-46.7	8843	-0.00104	0.00000437
600	-29.1	8141	-0.000593	0.00000338
650	-14.9	7661	-0.00028	0.00000271
700	-3.1	7334	-0.0000541	0.00000224
750	6.8	7112	0.000111	0.00000189
800	15.2	6964	0.000232	0.00000163
850	22.4	6867	0.000322	0.00000142
900	28.7	6807	0.00039	0.00000126
950	34.2	6773	0.00044	0.00000112
1000	39.1	6758	0.000478	0.00000101

Appendix 2: MATLAB Code for Sulfur Hexafluoride Isotherms

```

T = load('Temperature.txt'); %loads temperature data for SF6
BT = load('Second_Order.txt'); %loads coefficient data for SF6
c = 1;
%define temperatures to be plotted
Temps = [300, 400, 500, 600, 700, 800, 900, 1000];
for i = 1:length(BT)
    for a = 1:length(Temps)
        if T(i) == Temps(a)
            Coef(c) = BT(i);
            c = c + 1;
        end
    end
end
End
%number of moles of gas, can be changed to any positive number
n = 1;
%define range of volumes to be displayed, in m^3
V = [0.001:0.0001:0.002];
%define colours of each of the isotherms, same number of colours as there are isotherms
colour = ["b", "g", "r", "c", "m", "y", "k", "b"];
for i = 1:length(Temps)
    P = ((n * 8.314 * Temps(i)) ./ V); %standard ideal gas law
    PVir = ((n * 8.314 * Temps(i)) ./ V) .* (1 + (Coef(i) ./ (1000000 .* V))); %ideal gas with virial
    expansion
    lineOne = strcat("-", colour(i));
    lineTwo = strcat("--", colour(i));
    plot(V, P, lineOne);
    hold on;
    plot(V, PVir, lineTwo);
    legend('Ideal Gas', 'Ideal Gas with Virial Expansion');
    axis([(1 * 10^(-3)), (2 * 10^(-3)), (1 * 10^6), (9 * 10^6)]);
    xlabel('Volume (m^3)');
    ylabel('Pressure (Pa)');
end

```