Assigned problems for Lecture 4 are listed below. The questions occur in the following editions of “Physical Chemistry” by P.W. Atkins:

10th edition	9th edition	8th edition

Note: The letter “P” in front of a number indicates that the question is in the “Problem” category as opposed to the “Exercise” category in Atkins’ books. Updates are highlighted in yellow.

Question 4.01

1A.1	1.1	1.1

1A.1(a) Could 131 g of xenon gas in a vessel of volume 1.0 dm^3 exert a pressure of 20 atm at 25 °C if it behaved as a perfect gas? If not, what pressure would it exert? (What is meant here, is if it behaved at a van der Waals gas, what pressure would it exert?).
1A.1(b) Could 25 g of argon gas in a vessel of volume 1.5 dm^3 exert a pressure of 2.0 bar at 30 °C if it behaved as a perfect gas? If not, what pressure would it exert? (What is meant here, is if it behaved at a van der Waals gas, what pressure would it exert?).

Question 4.02

1C.1	1.13	1.13

1C.1(a) Calculate the pressure exerted by 1.0 mol C_2H_6 behaving as a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm^3, (ii) at 1000 K in 100 cm^3. Use the data in Table 1C.3 (Table 1.6 in 8th and 9th Eds.).
1C.1(b) Calculate the pressure exerted by 1.0 mol H_2S behaving as a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm^3, (ii) at 500 K in 150 cm^3. Use the data in Table 1C.3 (Table 1.6 in 8th and 9th Eds.).

Question 4.03

1C.3	1.15	1.15

1C.3(a) A gas at 250 K and 15 atm has a molar volume 12 per cent smaller than that calculated from the perfect gas law. Calculate (i) the compression factor under these conditions and (ii) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?
1C.3(b) A gas at 350 K and 12 atm has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate (i) the compression factor under these conditions and (ii) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

Question 4.04

1C.4	1.16	1.16

1C.4(a) In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 m^3. The gas enters the container at 300 K and 100 atm. The mass of the gas is 92.4 kg. Use the van

der Waals equation to determine the approximate pressure of the gas at its working temperature of 500 K. For nitrogen, a = 1.352 dm^6 atm mol^{-2}, b = 0.0387 dm^3 mol^{-1}.
1C.4(b) Cylinders of compressed gas are typically filled to a pressure of 200 bar. For oxygen, what would be the molar volume at this pressure and 25 °C based on (i) the perfect gas equation, (ii) the van der Waals equation? For oxygen, a = 1.364 dm^6 atm mol^{-2}, b = 3.19 × 10^{-2} dm^3 mol^{-1}.

Question 4.05

1C.5	1.17	1.17

1C.5(a) Suppose that 10.0 mol C_2H_6(g) is confined to 4.860 dm^3 at 27 °C. Predict the pressure exerted by the ethane from (i) the perfect gas and (ii) the van der Waals equations of state. Calculate the compression factor based on these calculations.
For ethane, a = 5.507 dm^6 atm mol^{-2}, b = 0.0651 dm^3 mol^{-1}.
1C.5(b) At 300 K and 20 atm, the compression factor of a gas is 0.86. Calculate (i) the volume occupied by 8.2 mmol of the gas under these conditions and (ii) an approximate value of the second virial coefficient B at 300 K.

Question 4.06

1C.6	1.19	1.19

1C.6(a) The critical constants of methane are p_c = 45.6 atm, V_c = 98.7 cm^3 mol^{-1}, and T_c = 190.6 K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules
1C.6(b) The critical constants of ethane are p_c = 48.20 atm, V_c = 148 cm^3 mol^{-1}, and T_c = 305.4 K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

Question 4.07

1C.7	1.20	1.20

1C.7(a) Use the van der Waals parameters for chlorine in Table 1C.3 of the *Resource section* (Table 1.6 in 8th and 9th Eds.) to calculate approximate values of (i) the Boyle temperature of chlorine and (ii) the radius of a Cl_2 molecule regarded as a sphere.
1C.7(b) Use the van der Waals parameters for hydrogen sulfide in Table 1C.3 of the *Resource section* (Table 1.6 in 8th and 9th Eds.) to calculate approximate values of (i) the Boyle temperature of the gas and (ii) the radius of a H_2S molecule regarded as a sphere.

Question 4.08

1C.8	1.21	1.21

1C.8(a) Suggest the pressure and temperature at which 1.0 mol of (i) NH_3, (ii) Xe, (iii) He will be in states that correspond to 1.0 mol H_2 at 1.0 atm and 25 °C.
1C.8(b) Suggest the pressure and temperature at which 1.0 mol of (i) H_2S, (ii) CO_2, (iii) Ar will be in states that correspond to 1.0 mol N_2 at 1.0 atm and 25 °C.

Question 4.09

1C.11	P1.17	P1.17

1C.11 A scientist proposed the following equation of state:

$$p = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$$

Show that the equation leads to critical behaviour. Find the critical constants of the gas in terms of B and C and an expression for the critical compression factor.

Question 4.10

1C.14	P1.20	P1.20

1C.14 The equation of state of a certain gas is given by $p = RT/V_m + (a + bT)/V_m^2$, where a and b are constants. Find $(\partial V/\partial T)_p$.

Clarifications:

Question 4.04

1C.4	1.16	1.16

Ex. 1.16b, 8th Ed. You will not be required to solve a polynomial on your calculator - do not agonize over this.

Question 4.06

1C.6	1.19	1.19

Ex. 1.19b, 8th Ed. You might wonder why Atkins chooses to use $2r$ instead of just r in this calculation. The reason is that the $V - nb$ term in the van der Waals equation, which accounts for the *excluded volume* of the gas particles, is normally taken to be ca. 4 times the volume of the gas molecules. I believe that he takes the cube of $2r$ as opposed to r to account for this factor. Remember, the excluded volume is not precisely the exact volume of the molecules, but quite a bit larger, to take their collision pathways into account.