1. The compression factor, $Z$, is the ratio of the measured molar volume of a gas, $V_m = \frac{V}{n}$, to the molar volume of a perfect gas, $V_m^\circ$ , at the same pressure $(p)$ and temperature $(T)$; $V =$ volume of $n$ moles of gas. .

   (a) Show that $pV_m = RTZ$
   Ans. $Z = \frac{V_m}{V_m^\circ} \implies pV_m = pV_m^\circ Z = RTZ$

   (b) Most ordinary gases have $Z > 1$ at very high pressures. At intermediate pressures, most gases have $Z < 1$, and at very low pressures, $Z \approx 1$. Explain why.
   Ans. As $p \to 0$, gases tend to behave like perfect gases,
   $\therefore Z|_{p \to 0} \approx \frac{V_m^0}{V_m^\circ} = 1$
   At high pressures, repulsive forces are dominant, since molecules are too close.
   $\therefore$ they have a larger molar volume than a perfect gas, $V_m > V_m^\circ \implies Z > 1$
   At intermediate pressures, attractive forces are reducing the molar volume relative to that of a perfect gas, $V_m < V_m^\circ \implies Z < 1$

   (c) For a real gas, a general equation of state is $pV_m = RT\left(1 + B'p + C'p^2 + \cdots\right)$. Find $\frac{dZ}{dp}$ at very low pressures $(p \to 0)$.
   Ans. $Z = \frac{V_m}{V_m^\circ} = \frac{pV_m}{RT} = 1 + B'p + C'p^2 + \cdots$
   $\therefore \frac{dZ}{dp} = B' + 2pC' + \cdots$. As $p \to 0$, $\frac{dZ}{dp} \to B'$.

   (d) The temperature $(> 0)$ at which $Z \to 1$ is called the Boyle temperature, $T_B$. For helium, $T_B = 22.64$ K; Compare the state of helium gas at temperatures 20K , 22.64 K and 25K.
   Ans. Typically, at the Boyle temperature, $\frac{dZ}{dp}$ or $\frac{dZ}{d\left(\frac{1}{V}\right)} \to 0$ implying that the second virial coefficient (in Virial equation of state) for the gas $\to 0$; and the gas behaves almost as perfect gas for a large range of pressures. So, at $T_B = 22.64$ K, helium behaves as a perfect gas at pressures close to 0and over a large range of pressures. $T = 25K$ is above the Boyle temperature and the range of pressures (close to 0), where helium could behave as nearly a perfect gas must be much lower than at $T_B$. At $T = 22.64$K, it is difficult to say anything without looking at real data, but most likely $Z < 1$ for some pressures close to 0 because only attractive forces may remain at extremely low pressures.

   (e) The second virial coefficient of methane can be approximated by the empirical equation $B(T) = a + be^{-\frac{c}{T^2}}$ , where $a = -0.1993$ bar $^{-1}$, $b = 0.2002$ bar$^{-1}$ , and $c = 1131$K$^2$ with 300 K $< T <$ 600 K. What is the Boyle temperature of methane?
   Ans. At $T = T_B$, $pV_m = RT$
   $\therefore$ all virial coefficients are equal to zero.
   $\therefore a + be^{-\frac{c}{T_B^2}} = 0$
   or, $e^{-\frac{c}{T_B^2}} = -\frac{a}{b}$
   or, $\frac{-c}{T_B^2} = \ln\left(-\frac{a}{b}\right)$
   $\therefore T_B = \sqrt{\frac{-c}{\ln\left(-\frac{a}{b}\right)}} = \sqrt{\frac{-1131}{\ln\left(\frac{0.1993}{0.2002}\right)}} \approx 500$K

   (f) Show that the van der Waals equation leads to values of $Z < 1$ and $Z > 1$, and identify the conditions for which these values are obtained.
   Ans. van der Waals equation : $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

$$\therefore Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

expand for $b < V_m$ : $\frac{1}{1 - \frac{b}{V_m}} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$

or, $Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$

for $Z < 1$, the second term must be large negative (since all later terms are positive)

or, $\frac{a}{RTV_m} > \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots \approx \frac{b}{V_m}$

or, for $Z < 1$, $\frac{a}{RT} > b$

i.e., when attractive forces dominate and when there is sufficient thermal energy to disrupt these forces, and $Z > 1$, when short-range repulsions (size effects) dominate.

2. Derive the critical constants for a van der Waals gas in terms of the $a$ and $b$ coefficients.

   Ans. At the critical point, the $p - V$ isotherm goes through an inflexion, i.e., $\left.\frac{dp}{dV}\right|_{\text{critical}} = \left.\frac{d^2p}{dV^2}\right|_{\text{critical}} = 0$

   $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \implies \frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0 = \frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$

   $\implies V_c = 3b; \; p_c = \frac{a}{27b^2}; \; T_c = \frac{8a}{27Rb}$

3. Obtain the equation for a van der Waals gas in terms of the reduced variables $[\frac{X}{X_C}, X \in \{p, V, T)$ and $X_C$ is the corresponding critical value].

   Ans. $p_r p_C = \frac{RT_r T_C}{V_r V_C - b} - \frac{a}{V_r^2 V_C^2}$

   Using the results from (2) above, $\frac{ap_r}{27b^2} = \frac{\frac{8aT_r}{27b}}{3bpV_r - b} - \frac{a}{9b^2 V_r^2}$ or, $p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$