



## Exercise-1

☞ Marked questions are recommended for Revision.

### PART - I : SUBJECTIVE QUESTIONS

#### Section (A) : Experimental Observation and critical state

**Commit to memory :**

**Critical point :** At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour.

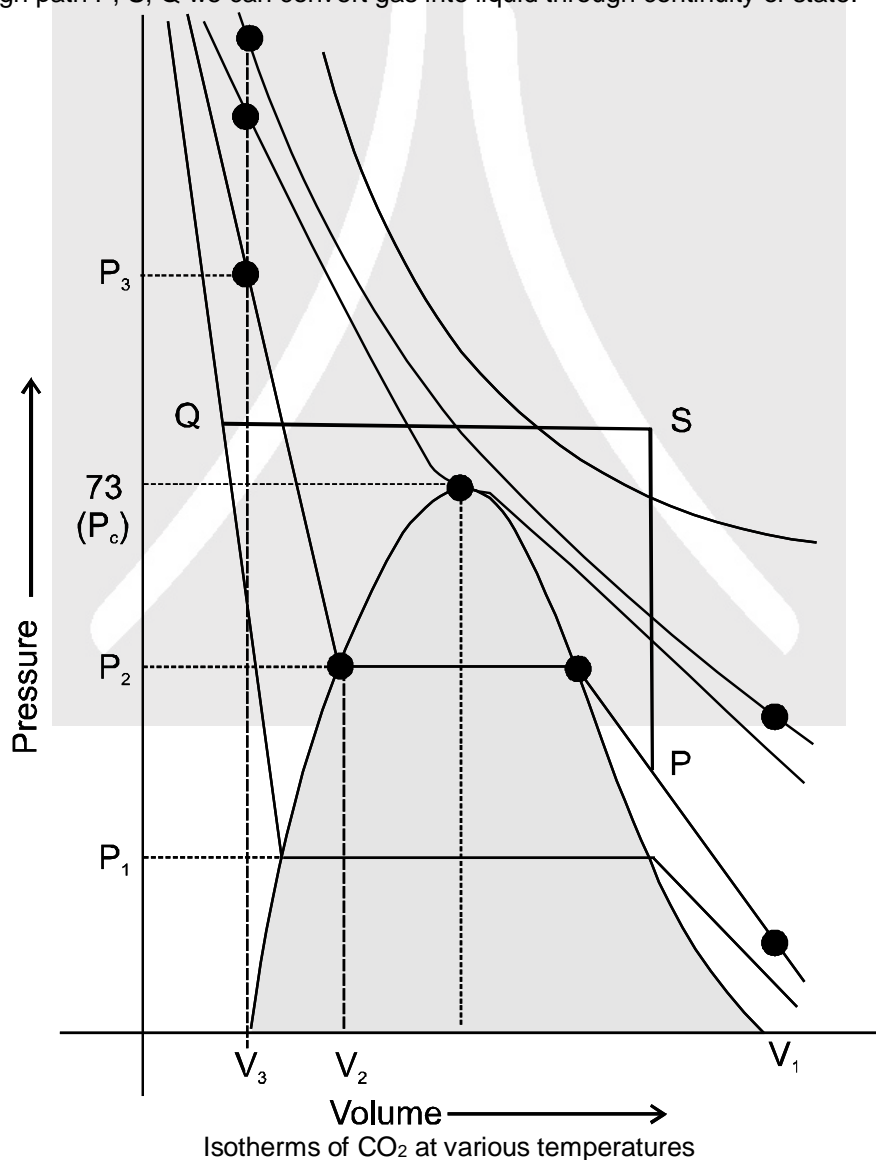
**$T_c$  or critical temperature :** Temperature above which a gas can not be liquified.

**$P_c$  or critical pressure :** Minimum pressure which must be applied at critical temperature to convert the gas into liquid.

**$V_c$  or critical volume :** Volume occupied by one mole of gas at  $T_c$  &  $P_c$ .

A-1. ☞ Identify true and false statements for fixed amount of gas in following isotherm of real gas.

- From point P to point S volume is constant and temperature is increasing.
- From point S to point Q pressure is constant and temperature is decreasing.
- Through path P, S, Q we can convert gas into liquid through continuity of state.





## Section (B) : Vander waal equation and virial equation of state

### Commit to memory :

**Critical point :** At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that

$$P_c = \frac{a}{27b^2} \quad V_c = 3b \quad T_c = \frac{8a}{27Rb}$$

$Z = 1$  for ideal gas; at all pressures for He/H<sub>2</sub> ( $Z = \frac{Pb}{RT} + 1$ );  $Z < 1$  at low pressure (for all other gases)

( $Z = 1 - \frac{a}{V_m RT}$ );  $Z > 1$  at high pressure (for all other gases) ( $Z = \frac{Pb}{RT} + 1$ )

Vander waal's equation is  $\left(P + \frac{an^2}{V^2}\right) (V - nb) = nRT$ ; Boyles' temperature  $T_B = \frac{a}{Rb}$

- B-1.** Explain the physical significance of van der waals parameters.
- B-2.** The critical temperature and critical pressure of a gas are 31°C and 728 atmospheres respectively. Calculate the constants 'a' and 'b'.
- B-3.** Calculate the volume occupied by 2.0 mole of N<sub>2</sub> at 200 K and 8.21 atm pressure, if  $\frac{P_c V_c}{RT_c} = \frac{3}{8}$  and  $\frac{P_r V_r}{T_r} = 2.4$ .
- B-4.** Using the van der Waals equation, calculate the pressure of 10.0 mol NH<sub>3</sub> gas in a 10.0 L vessel at 27°C.  
 $\left(P + n^2 \frac{a}{V^2}\right) (V - nb) = nRT \quad a = 4.2 \text{ L}^2 \cdot \text{atm/mol}^2 \quad b = 0.037 \text{ L/mol}$
- B-5.** If density of vapours of a substance of molar mass 18 g at 1 atm pressure and 500 K is 0.36 kg m<sup>-3</sup>, then calculate the value of Z for the vapours. (Take R = 0.082 L atm mole<sup>-1</sup> K<sup>-1</sup>)
- B-6.** One litre gas at 400 K and 300 atm pressure is compressed to a pressure of 600 atm and 200 K. The compressibility factor is changed from 1.2 to 1.6 respectively. Calculate the final volume of the gas.
- B-7.** Reduced temperature for benzene is 0.7277 and its reduced volume is 0.40. Calculate the reduced pressure of benzene.

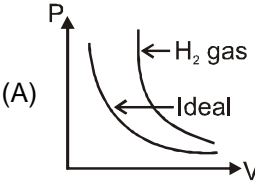
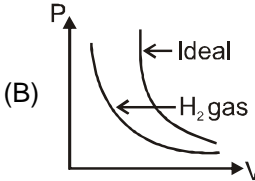
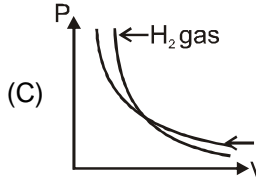
## PART - II : ONLY ONE OPTION CORRECT TYPE

### Section (A) : Experimental Observation and critical state

- A-1.** Consider a real gas placed in a container. If the intermolecular attractions are supposed to disappear suddenly which of the following would happen ?  
 (A) The pressure decreases (B) The pressure increases  
 (C) The pressure remains unchanged (D) The gas collapses
- A-2.** The pressure of real gases is less than the pressure of an ideal gas because of :  
 (A) Increase in number of collisions (B) Finite size of molecule  
 (C) Increases in KE of molecules (D) Intermolecular forces of attraction
- A-3.** The critical temperature of water is higher than that of O<sub>2</sub> because the water molecule has  
 (A) Fewer electrons than O<sub>2</sub> (B) two covalent bonds  
 (C) V-shape (D) dipole moment
- A-4.** Select incorrect statement :  
 (A) we can condense vapour simply by applying pressure  
 (B) to liquefy a gas one must lower the temperature below T<sub>c</sub> and also apply pressure  
 (C) at critical point there is no distinction between liquid and vapour state hence density of the liquid is nearly equal to density of the vapour  
 (D) However great the pressure applied, a gas cannot be liquified below its critical temp.



### Section (B) : Vander waal equation and virial equation of state

- B-1.** A real gas obeying Vander Waal's equation will resemble ideal gas, if the :  
 (A) constants  $a$  &  $b$  are small (B)  $a$  is large &  $b$  is small  
 (C)  $a$  is small &  $b$  is large (D) constant  $a$  &  $b$  are large
- B-2.** The correct graph to  $H_2$  gas is :  
 (A)  (B)  (C)  (D) All of these
- B-3.** If temperature and volume are same, the pressure of a gas obeying Vander Waals equation is :  
 (A) Smaller than that of an ideal gas  
 (B) Larger than that of an ideal gas  
 (C) same as that of an ideal gas  
 (D) none of these
- B-4.** At 273 K temperature and 9 atm pressure, the compressibility for a gas is 0.9. The volume of 1 milli-mole of gas at this temperature and pressure is :  
 (A) 2.24 litre (B) 0.020 mL (C) 2.24 mL (D) 22.4 mL
- B-5.** For the non-zero values of force of attraction between gas molecules, gas equation will be :  
 (A)  $PV = nRT - \frac{n^2a}{V}$  (B)  $PV = nRT + nbP$  (C)  $PV = nRT$  (D)  $P = \frac{nRT}{V-b}$
- B-6.** Compressibility factor for  $H_2$  behaving as real gas is :  
 (A) 1 (B)  $\left(1 - \frac{a}{RTV}\right)$  (C)  $\left(1 + \frac{Pb}{RT}\right)$  (D)  $\frac{RTV}{(1-a)}$
- B-7.** At low pressures (For 1 mole), the Vander Waal's equation is written as  

$$\left[p + \frac{a}{V^2}\right]V = RT$$
 The compressibility factor is then equal to :  
 (A)  $\left(1 - \frac{a}{RTV}\right)$  (B)  $\left(1 - \frac{RTV}{a}\right)$  (C)  $\left(1 + \frac{a}{RTV}\right)$  (D)  $\left(1 + \frac{RTV}{a}\right)$
- B-8.** Calculate the radius of He atoms if its Vander Waal's constant ' $b$ ' is  $24 \text{ ml mol}^{-1}$ .  
 (Note:  $1 \text{ ml} = 1 \text{ cubic centimeter}$ )  
 (A)  $1.355 \text{ \AA}$  (B)  $1.314 \text{ \AA}$  (C)  $1.255 \text{ \AA}$  (D)  $0.355 \text{ \AA}$
- B-9.** In vander Waal's equation of state for a non ideal gas the term that accounts for intermolecular forces is:  
 (A)  $nb$  (B)  $nRT$  (C)  $n^2a/V^2$  (D)  $(nRT)^{-1}$
- B-10.** The values of Vander Waal's constant " $a$ " for the gases  $O_2$ ,  $N_2$ ,  $NH_3$  &  $CH_4$  are 1.36, 1.39, 4.17, 2.253  $L^2 \text{ atm mol}^{-2}$  respectively. The gas which can most easily be liquified is:  
 (A)  $O_2$  (B)  $N_2$  (C)  $NH_3$  (D)  $CH_4$
- B-11.** The correct order of normal boiling points of  $O_2$ ,  $N_2$ ,  $NH_3$  and  $CH_4$ , for whom the values of vander Waal's constant ' $a$ ' are 1.360, 1.390, 4.170 and 2.253  $L^2 \cdot \text{atm} \cdot \text{mol}^{-2}$  respectively, is :  
 (A)  $O_2 < N_2 < NH_3 < CH_4$  (B)  $O_2 < N_2 < CH_4 < NH_3$   
 (C)  $NH_3 < CH_4 < N_2 < O_2$  (D)  $NH_3 < CH_4 < O_2 < N_2$
- B-12.** A gas obeys the equation of state  $P(V - b) = RT$  (The parameter  $b$  is a constant). The slope for an isochore will be :  
 (A) Negative (B) Zero (C)  $R/(V - b)$  (D)  $R/P$



- B-13.** If  $v$  is the volume of one molecule of a gas, then van der Waals constant 'b' is: ( $N_0$  = Avogadro's number)
- (A)  $\frac{4V}{N_0}$                       (B)  $4V$                       (C)  $\frac{N_0}{4V}$                       (D)  $4VN_0$
- B-14.** In van der Waal's equation of state for a non-ideal gas, the term that accounts for intermolecular forces is :
- (A)  $(V - b)$                       (B)  $RT$                       (C)  $\left(P + \frac{a}{V^2}\right)$                       (D)  $(RT)^{-1}$
- B-15.** On heating vapours of  $S_8(g)$  decomposes to  $S_2(g)$ . Due to this, the van-der Waal's constant 'b' for the resulting gas.
- (A) increases                      (B) decreases                      (C) remains same                      (D) changes unpredictably
- B-16.** What is the compressibility factor (Z) for 0.02 mole of a van der Waals' gas at pressure of 0.1 atm. Assume the size of gas molecules is negligible.  
Given :  $RT = 20 \text{ L atm mol}^{-1}$  and  $a = 1000 \text{ atm L}^2 \text{ mol}^{-2}$
- (A) 2                      (B) 1                      (C) 0.02                      (D) 0.5
- B-17.** The van der Waals parameters for gases W, X, Y and Z are

Gas	a(atm L <sup>2</sup> mol <sup>-2</sup> )	b(L mol <sup>-1</sup> )
W	4.0	0.027
X	8.0	0.030
Y	6.0	0.032
Z	12.0	0.027

Which one of these gases has the highest critical temperature ?

- (A) W                      (B) X                      (C) Y                      (D) Z
- B-18.** One way of writing the equation of state for real gases is  $PV = RT \left[ 1 + \frac{B}{V} + \dots \right]$ , where B is a constant. An approximate expression for B in terms of the van der Waals constant 'a' and 'b' is :
- (A)  $B = a - \frac{b}{RT}$                       (B)  $B = b - \frac{a}{RT}$                       (C)  $B = RT - \frac{a}{b}$                       (D)  $B = \frac{b}{a}$

### PART - III : MATCH THE COLUMN

1. Match the column :

	Column-I		Column-II
(A)	H <sub>2</sub> gas at NTP	(p)	Molar volume = 22.4 L
(B)	O <sub>2</sub> gas having density more than $\frac{10}{7}$ g/L at NTP	(q)	Molar volume > 22.4 L
(C)	SO <sub>2</sub> gas at NTP having density more than $\frac{20}{7}$ g/L	(r)	More compressible with respect to ideal gas
(D)	He gas at NTP having density less than $\frac{1}{5.6}$ g/L	(s)	Less compressible with respect to ideal gas

2. Match the column :

	Column-I		Column-II
(A)	At low pressure	(p)	$Z = 1 + \frac{pb}{RT}$
(B)	At higher pressure	(q)	$Z = 1 - \frac{a}{V_m RT}$
(C)	At low density of gas	(r)	gas is more compressible
(D)	For H <sub>2</sub> and He at 0°C	(s)	gas is less compressible



## Exercise-2

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### PART - I : ONLY ONE OPTION CORRECT TYPE

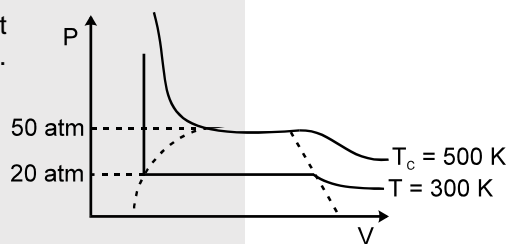
1. ☞ Which of following statement (s) is true  
 I – Slope of isotherm at critical point is maximum.  
 II – Larger is the value of  $T_c$  easier is the liquification of gas.  
 III – Vander waals equation of state is applicable below critical temperature at all pressure.  
 (A) only I (B) I & II (C) II & III (D) only II
2. Consider the following statements: If the van der Waal's parameters of two gases are given as

	a (atm lit <sup>2</sup> mol <sup>-2</sup> )	b (lit mol <sup>-1</sup> )
Gas X	6.5	0.056
Gas Y	8.0	0.011

then (i) :  $V_c(X) < V_c(Y)$  (ii) :  $P_c(X) < P_c(Y)$  (iii) :  $T_c(X) < T_c(Y)$

Select correct alternate:

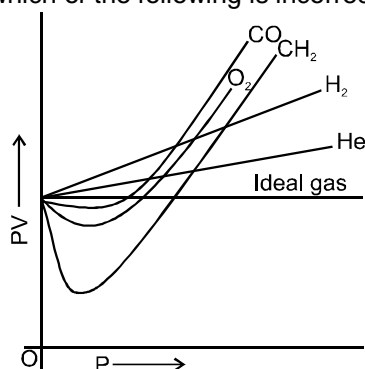
- (A) (i) alone (B) (i) and (ii) (C) (i), (ii) and (iii) (D) (ii) and (iii)
3. ☞ For a real gas the P-V curve was experimentally plotted and it had the following appearance. With respect to liquification. Choose the **correct** statement.
- (A) At  $T = 500$  K,  $P = 40$  atm, the state will be liquid.  
 (B) At  $T = 300$  K,  $P = 50$  atm, the state will be gas  
 (C) At  $T < 300$  K,  $P > 20$  atm, the state will be gas  
 (D) At  $300$  K  $< T < 500$  K,  $P > 50$  atm, the state will be liquid.



4. A real gas most closely approaches the behaviour of an ideal gas at -  
 (A) 15 atm and 200 K (B) 1 atm and 273 K (C) 0.5 atm and 500 K (D) 15 atm and 500 K
5. Calculate the compressibility factor for CO<sub>2</sub>, if one mole of it occupies 0.4 litre at 300 K and 40 atm. Comment on the result.  
 (A) 0.40, CO<sub>2</sub> is more compressible than ideal gas (B) 0.65, CO<sub>2</sub> is more compressible than ideal gas  
 (C) 0.55, CO<sub>2</sub> is more compressible than ideal gas (D) 0.62, CO<sub>2</sub> is more compressible than ideal gas
6. ☞ Consider the following statements:  
 The coefficient B in the virial equation of state  
 (i) is independent of temperature  
 (ii) is equal to zero at boyle temperature  
 (iii) has the dimension of molar volume
- $$PV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$
- Which of the above statements are correct.  
 (A) i and ii (B) i and iii (C) ii and iii (D) i, ii and iii
7. At Boyle's temperature, the value of compressibility factor  $Z = (PV_m / RT = V_{real} / V_{ideal})$  has a value of 1, over a wide range of pressure. This is due to the fact that in the van der Waal's equation  
 (A) the constant 'a' is negligible and not 'b'  
 (B) the constant 'b' is negligible and not 'a'  
 (C) both the constant 'a' and 'b' are negligible  
 (D) the effect produced due to the molecular attraction compensates the effect produced due to the molecular volume
8. ☞ The critical density of the gas CO<sub>2</sub> is 0.44 g cm<sup>-3</sup> at a certain temperature. If r is the radius of the molecule, r<sup>3</sup> in cm<sup>3</sup> is: (N is Avogadro number)  
 (A)  $\frac{25}{\pi N}$  (B)  $\frac{100}{\pi N}$  (C)  $\frac{6}{\pi N}$  (D)  $\frac{25}{4N\pi}$



9. The curve of pressure volume (PV) against pressure (P) of the gas at a particular temperature is as shown, according to the graph which of the following is incorrect (in the low pressure region):



- (A)  $H_2$  and He shows +ve deviation from ideal gas equation.  
 (B) CO,  $CH_4$  and  $O_2$  show negative deviation from ideal gas equation.  
 (C)  $H_2$  and He show negative deviation while CO,  $CH_4$  and  $O_2$  show positive deviation.  
 (D)  $H_2$  and He are less compressible than that of an ideal gas while CO,  $CH_4$  and  $O_2$  more compressible than that of ideal gas.

## PART - II : SINGLE OR DOUBLE INTEGER TYPE

- The vander waals constant 'b' of a gas is  $4\pi \times 10^{-4}$  L/mol. The radius of gas atom can be expressed in scientific notation as  $z \times 10^{-9}$  cm. Calculate the value of z. (Given  $N_A = 6 \times 10^{23}$ )
- For a fixed amount of real gas when a graph of  $z$  v/s  $P$  was plotted then at very high pressure slope was observed to be  $0.01 \text{ atm}^{-1}$ . At the same temperature if a graph is plotted b/w  $PV$  v/s  $P$  then for 2 moles of the gas 'Y' intercept is found to be  $40 \text{ atm-liter}$ . Calculate excluded volume in litres for 20 moles of the real gas.
- If C & D are the third & fourth virial coefficients. If  $\frac{D}{C} = \frac{V_C}{x}$  then find the value of x.
- Calculate molecular diameter for a gas if its molar excluded volume is  $3.2 \pi \text{ ml}$ . (in nanometer). Give the answer by multiplying with 10. (Take  $N_A = 6.0 \times 10^{23}$ )
- If the ratio of  $PV_m$  &  $RT$  for a real gas is  $\frac{x}{24}$  at a temp where  $\left(\frac{\partial P}{\partial V_m}\right) = 0$ . The find value of  $10x$ .
- 1 mole of  $CCl_4$  vapours at  $77^\circ\text{C}$  occupies a volume of 35.0 L. If van der Waal's constant are  $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$  and  $b = 0.1383 \text{ L mol}^{-1}$ , calculate compressibility factor Z under, (a) low pressure region (b) high pressure region  
Report your answer as nearest whole number of  $(a + b) \times 10$ .
- To an evacuated 504.2 mL steel container is added 25 g  $CaCO_3$  and the temperature is raised to 1500 K causing a complete decomposition of the salt. If the density of CaO formed is 3.3 g/cc, find the accurate pressure developed in the container using the vander Waals equation of state. The van der waals constants for  $CO_2(g)$  are  $a = 4 \frac{\text{L}^2 - \text{atm}}{\text{mol}^2}$ ,  $b = 0.04 \frac{\text{L}}{\text{mol}}$ . (Ca - 40, C - 12, O - 16). Report your answer as nearest whole number.

## PART - III : ONE OR MORE THAN ONE OPTION CORRECT TYPE

- Which of the following statements are correct ?  
 (A) It is not possible to compress a gas at a temperature below  $T_C$   
 (B) At a temperature below  $T_C$ , the molecules are close enough for the attractive forces to act and condensation occurs  
 (C) No condensation takes place above  $T_C$   
 (D) Boyle's temperature always greater than  $T_C$ .





2. Which of the following is correct for critical temperature ?  
 (A) It is the highest temperature at which liquid and vapour can coexist  
 (B) At a certain point on isotherm graph, slope is zero.  
 (C) At this temperature, the gas and the liquid phases have different critical densities  
 (D) All are correct
3. The vander waal gas constant 'a' is given by  
 (A)  $\frac{1}{3} V_C$  (B)  $3P_C V_C^2$  (C)  $\frac{1}{8} \frac{RT_C}{P_C}$  (D)  $\frac{27}{64} \frac{R^2 T_C^2}{P_C}$
4. Which of the following are correct statements ?  
 (A) vander Waals constant 'a' is a measure of attractive force  
 (B) van der Waals constant 'b' is also called co-volume or excluded volume  
 (C) 'b' is expressed in  $L \text{ mol}^{-1}$   
 (D) 'a' is expressed in  $\text{atm L}^2 \text{ mol}^{-2}$
5. Select the correct statement(s) :  
 (A) At Boyle's temperature a real gas behaves like an ideal gas at low pressure  
 (B) Above critical conditions, a real gas behave like an ideal gas  
 (C) For hydrogen gas 'b' dominates over 'a' at all temperature  
 (D) At high pressure van der Waals' constant 'b' dominates over 'a'
6. Select incorrect statements for real gas.  
 (A) In low pressure region repulsive forces dominates  
 (B) Volume of gas particles is not negligible in low pressure region  
 (C) Gas behaves ideally at low pressure & low temperature  
 (D) In high pressure region attractive forces dominates
7. Compressibility of real gas will be less than ideal gas when ( $T = \text{temp. of gas } T_b = \text{Boyle's temperature of gas}$ )  
 (A) At very high pressure when  $T > T_b$  (B) At very high pressure when  $T < T_b$   
 (C) At low pressure when  $T > T_b$  (D) At low pressure when  $T < T_b$

## PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

### Comprehension # 1

One of the important approach to the study of real gases involves the analysis of a parameter Z called the compressibility factor  $Z = \frac{PV_m}{RT}$  where P is pressure,  $V_m$  is molar volume, T is absolute temperature

and R is the universal gas constant. Such a relation can also be expressed as  $Z = \left( \frac{V_{m, \text{real}}}{V_{m, \text{ideal}}} \right)$  (where

$V_{m, \text{ideal}}$  and  $V_{m, \text{real}}$  are the molar volume for ideal and real gas respectively). Gas corresponding  $Z > 1$  have repulsive tendencies among constituent particles due to their size factor, whereas those corresponding to  $Z < 1$  have attractive forces among constituent particles. As the pressure is lowered or temperature is increased the value of Z approaches 1. (Reaching the ideal behaviour)

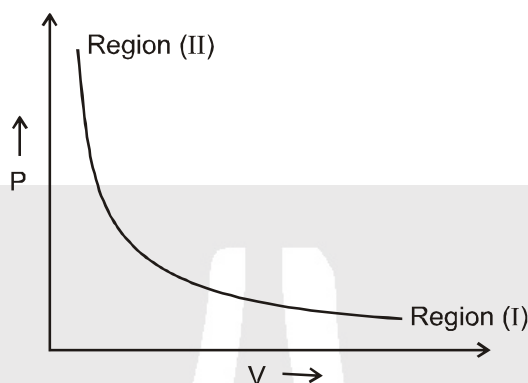
1. Choose the conclusions which are appropriate for the observation stated.

	Observation		Conclusion
I.	$Z = 1$	I.	The gas need not be showing the ideal behaviour
II.	$Z > 1$	II.	On applying pressure the gas will respond by increasing its volume
III.	$Z < 1$	III.	The gas may be liquefied.
IV.	$Z \rightarrow 1$ for low P	IV.	The gas is approaching the ideal behaviour.

- (A) All conclusions are true (B) Conclusions I, II & IV are true  
 (C) Conclusions I, III & IV are true (D) Conclusions III & IV are true



2. For a real gas 'G'  $Z > 1$  at STP, then for 'G' :  
Which of the following is true :  
(A) 1 mole of the gas occupies 22.4 L at NTP  
(B) 1 mole of the gas occupies 22.4 L at pressure higher than that at STP (keeping temperature constant)  
(C) 1 mole of the gas occupies 22.4 L at pressure lower than that at STP (keeping temperature constant)  
(D) None of the above
3. Following graph represents a pressure (P) volume (V) relationship at a fixed temperature (T) for n moles of a real gas. The graph has two regions marked (I) and (II). Which of the following options is true.



- (A)  $Z < 1$  in the region (II)  
(B)  $Z = 1$  in the region (II)  
(C)  $Z = 1$  for the curve  
(D)  $Z$  approaches 1 as we move from region (II) to region (I)

### Comprehension # 2

#### Critical constant of A gas

When pressure is increases at constant temp volume of gas decreases

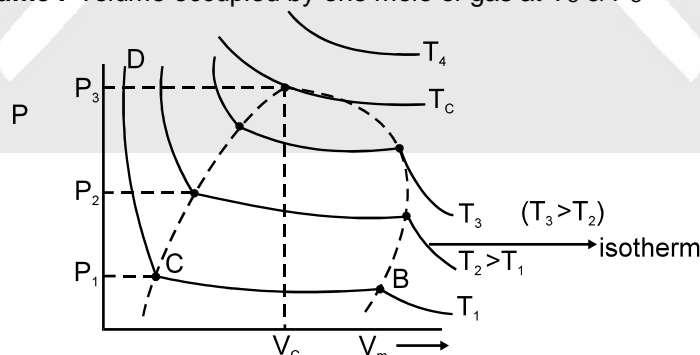
AB → gases, BC → vapour + liquid, CD → liquid

critical point : At this point all the physical properties of liquid phase will be same as the physical properties in vapour such as, density of liquid = density of vapour

**$T_c$  or critical temp** : Temperature above which a gas can not be liquified

**$P_c$  or critical pressure** : minimum pressure which must be applied at critical temp to convert the gas into liquid.

**$V_c$  or critical volume** : volume occupied by one mole of gas at  $T_c$  &  $P_c$



#### CRITICAL CONSTANT USING VANDER WAAL EQUATIONS :

$$\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad \Rightarrow \quad (PV_m^2 + a) (V_m - b) = RT V_m^2$$

$$PV_m^3 + aV_m - PbV_m^2 - ab - RTV_m^2 = 0 \quad \Rightarrow \quad V_m^3 + V_m^2 \left( b + \frac{RT}{P} \right) + \frac{a}{P} V_m - \frac{ab}{P} = 0$$





Since equation is cubic in  $V_m$  hence there will be three roots of equation at any temperature and pressure.

At critical point all three roots will coincide and will give single value of  $V_m = V_c$

at critical point, Vander Waal equation will be

$$V_m^3 - V_m^2 \left( b + \frac{RT_C}{P_C} \right) + \frac{a}{P_C} V_m - \frac{ab}{P_C} = 0 \quad \dots(1)$$

But at critical point all three roots of the equation should be equal, hence equation should be :

$$V_m = V_c$$

$$(V_m - V_c)^3 = 0$$

$$V_m^3 - 3V_m^2 V_c + 3V_m V_c^2 - V_c^3 = 0 \quad \dots(2)$$

comparing with equation (1)

$$b + \frac{RT_C}{P_C} = 3V_c \quad \dots(i) \quad \frac{a}{P_C} = 3V_c^2 \quad \dots(ii) \quad \frac{ab}{P_C} = V_c^3 \quad \dots(iii)$$

From (ii) and (iii),  $V_c = 3b$

From (ii)  $P_C = \frac{a}{3V_c^2}$  substituting  $P_C = \frac{a}{3(3b)^2} = \frac{a}{27b^2}$

From (i)  $\frac{RT_C}{P_C} = 3V_c - b = 9b - b = 8b \Rightarrow T_C = \frac{8a}{27Rb}$

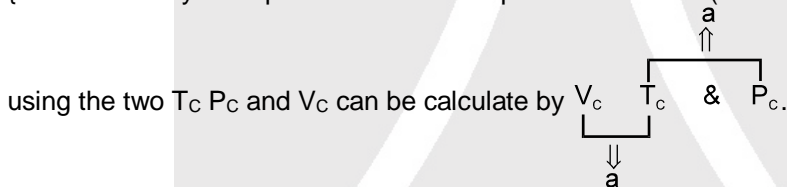
At critical point, the slope of PV curve (slope of isotherm) will be zero at all other point slope will be negative

zero is the maximum value of slope.

$$\left( \frac{\partial P}{\partial V_m} \right)_{T_C} = 0 \quad \dots(i)$$

$$\frac{\partial}{\partial V_m} \left( \frac{\partial P}{\partial V_m} \right)_{T_C} = 0 \quad \dots(ii)$$

{Mathematically such points are known as point of inflection (where first two derivatives become zero)}



4. A scientist proposed the following equation of state  $P = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$ . If this equation leads to the critical behaviour then critical temperature is :

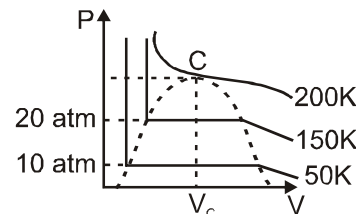
- (A)  $\frac{8B}{27RC}$       (B)  $\frac{B}{8RC}$       (C)  $\frac{B^2}{3RC}$       (D) None of these

5. If the critical constants for a hypothetical gas are  $V_c = 150 \text{ cm}^3 \text{ mol}^{-1}$ ,  $P_c = 50 \text{ atm}$  and  $T_c = 300 \text{ K}$ . Then the radius of the molecule is : [Take  $R = \frac{1}{12} \text{ Ltr atm mol}^{-1} \text{ K}^{-1}$ ]

- (A)  $\left( \frac{75}{2\pi N_A} \right)^{1/3}$       (B)  $\left( \frac{75}{8\pi N_A} \right)^{1/3}$       (C)  $\left( \frac{3}{\pi N_A} \right)^{1/3}$       (D)  $\left( \frac{3}{256\pi N_A} \right)^{1/3}$

6. Identify the wrong statement related to the above graph :

- (A) between 50 K and 150 K temperature and pressure ranging from 10 atm to 20 atm matter may have liquid state.  
 (B) zero is the maximum value of the slope of P-V Curve.  
 (C) If vander waal equation of state is applicable above critical temperature then cubic equation of  $V_m$  will have one real and two imaginary roots.  
 (D) At 100 K and pressure below 20 atm it has liquid state only.

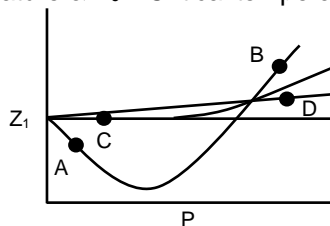




## Comprehension # 3

Answer Q.7, Q.8 and Q.9 by appropriately matching the information given in the three columns of the following table.

For a hypothetical real gas Z (Compressibility factor) v/s pressure curves are given at different temperatures, ( $T_b$  = Boyle's temperature &  $T_c$  = Critical temperature)



Column-1		Column-2		Column-3	
(I)	Point A	(i)	$T < T_b$	(P)	$Z = 1$
(II)	Point B	(ii)	$T > T_b$	(Q)	$Z > 1$
(III)	Point C	(iii)	$T = T_b$	(R)	$Z < 1$
(IV)	Point D	(iv)	$T = T_c$	(S)	Z is negative

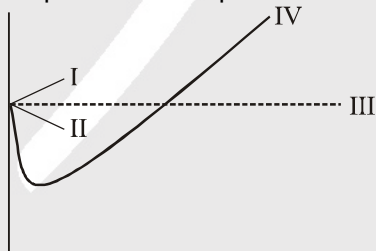
7. Select correct combination when gas is more compressible than ideal gas  
 (A) I (i) R                      (B) I (ii) R                      (C) I (iii) P                      (D) I (iv) P
8. Select correct combination when gas is less compressible than ideal gas  
 (A) II (iii) R                      (B) II (i) Q                      (C) IV (iii) Q                      (D) IV (ii) S
9. Select correct combination when gas behaves ideally  
 (A) I (i) R                      (B) III (iii) P                      (C) II (i) Q                      (D) iv (ii) Q

## Exercise-3

\* Marked Questions may have more than one correct option.

### PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

- 1.\* Figure displays the plot of the compression factor Z verses p for a few gases [JEE-2006, 5/184]



Which of the following statements is/are correct for a van-der waals gas :

- (A) The plot I is applicable provided the vander waals constant a is negligible.  
 (B) The plot II is applicable provided the vander waals constant b is negligible.  
 (C) The plot III is applicable provided the vander waals constants a and b are negligible.  
 (D) The plot IV is applicable provided the temperature of the gas is much higher than its critical temperature.
2. Match gases under specified conditions listed in Column-I with their properties / laws in Column-II. [JEE-2007, 6/162]

	Column-I		Column-II
(A)	Hydrogen gas ( $P = 200 \text{ atm}$ , $T = 273 \text{ K}$ )	(p)	compressibility factor $\neq 1$
(B)	Hydrogen gas ( $P \sim 0$ , $T = 273 \text{ K}$ )	(q)	attractive forces are dominant
(C)	$\text{CO}_2$ ( $P = 1 \text{ atm}$ , $T = 273 \text{ K}$ )	(r)	$PV = nRT$
(D)	Real gas with very large molar volume	(s)	$P(V - nb) = nRT$



- 3.\* A gas described by van der Waals equation [JEE-2008, 4/82]  
 (A) behaves similar to an ideal gas in the limit of large molar volumes  
 (B) behaves similar to an ideal gas is in limit of large pressures  
 (C) is characterised by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.  
 (D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

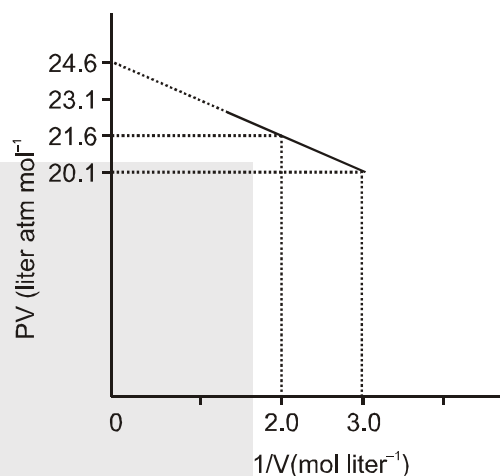
4. The term that corrects for the attractive forces present in a real gas in the vander Waals equation is : [JEE-2009, 3/80]

- (A)  $nb$  (B)  $\frac{an^2}{V^2}$  (C)  $-\frac{an^2}{V^2}$  (D)  $-nb$

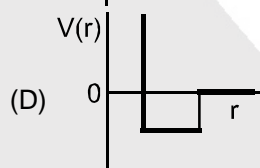
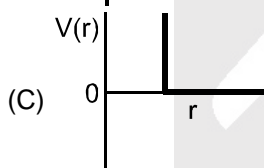
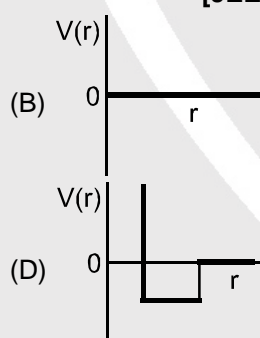
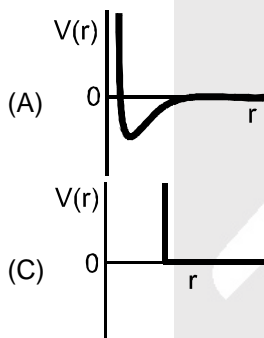
5. For one mole of a van der Waals gas when  $b = 0$  and  $T = 300$  K, the  $PV$  vs.  $1/V$  plot is shown below. The value of the vanderWaals constant  $a$  ( $\text{atm.liter}^2 \text{ mol}^{-2}$ ) :

[JEE-2012, 3/136]

- (A) 1.0  
 (B) 4.5  
 (C) 1.5  
 (D) 3.0



6. One mole of a monoatomic real gas satisfies the equation  $p(V - b) = RT$  where  $b$  is a constant. The relationship of interatomic potential  $V(r)$  and interatomic distance  $r$  for the gas is given by [JEE(Advanced)-2015, 4/168]



## PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

### JEE(MAIN) OFFLINE PROBLEMS

1. In vander Waal's equation of state of the gas law, the constant 'b' is a measure of: [AIEEE-2004, 3/225]  
 (1) Intermolecular collisions per unit volume (2) Intermolecular attractions  
 (3) Volume occupied by the molecules (4) Intermolecular repulsions
2. 'a' and 'b' are vander Waals' constants for gases. Chlorine is more easily liquefied than ethane because: [AIEEE-2011, 4/120]  
 (1)  $a$  and  $b$  for  $\text{Cl}_2 > a$  and  $b$  for  $\text{C}_2\text{H}_6$   
 (2)  $a$  and  $b$  for  $\text{Cl}_2 < a$  and  $b$  for  $\text{C}_2\text{H}_6$   
 (3)  $a$  and  $\text{Cl}_2 < a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 > b$  for  $\text{C}_2\text{H}_6$   
 (4)  $a$  for  $\text{Cl}_2 > a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 < b$  for  $\text{C}_2\text{H}_6$



3. The compressibility factor for a real gas at high pressure is : [AIEEE-2012, 4/120]  
 (1)  $1 + RT/pb$  (2) 1 (3)  $1 + pb/RT$  (4)  $1 - pb/RT$
4. If Z is a compressibility factor, vander Waals equation at low pressure can be written as : [JEE(Main) 2014, 4/120]  
 (1)  $Z = 1 + \frac{RT}{Pb}$  (2)  $Z = 1 - \frac{a}{VRT}$  (3)  $Z = 1 - \frac{Pb}{RT}$  (4)  $Z = 1 + \frac{Pb}{RT}$

### JEE(MAIN) ONLINE PROBLEMS

1. Vander Waal's equation for a gas is stated as,  $P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$ .  
 This equation reduces to the perfect gas equation,  $P = \frac{nRT}{V}$  when,  
[JEE(Main) 2014 Online (09-04-14), 4/120]  
 (1) temperature is sufficiently high and pressure is low.  
 (2) temperature is sufficiently low and pressure is high.  
 (3) both temperature and pressure are very high.  
 (4) both temperature and pressure are very low.
2. When does a gas deviate the most from its ideal behaviour ?  
[JEE(Main) 2015 Online (11-04-15), 4/120]  
 (1) At low pressure and low temperature (2) At low pressure and high temperature  
 (3) At high pressure and low temperature (4) At high pressure and high temperature
3. At very high pressures, the compressibility factor of one mole of a gas is given by :  
[JEE(Main) 2016 Online (09-04-16), 4/120]  
 (1)  $1 + \frac{pb}{RT}$  (2)  $\frac{pb}{RT}$  (3)  $1 - \frac{b}{VRT}$  (4)  $1 - \frac{pb}{RT}$
4. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are :  
[JEE(Main) 2018 Online (12-01-19), 4/120]  
 (1)  $2P_A = 3P_B$  (2)  $P_A = 2P_B$  (3)  $3P_A = 2P_B$  (4)  $P_A = 3P_B$



# Answers

## EXERCISE - 1

### PART - I

- A-1. (i) T (ii) T (iii) T
- B-1. **Significance of constant 'b'.** The constant 'b' is called co-volume or excluded volume per mole of a gas. Its units are litre mol<sup>-1</sup>. The volume of 'b' is four times the actual volume of the molecules.  
**Significance of constant 'a'.** The value of constant 'a' gives the idea of magnitude of attractive forces between the molecules of the gas. Its units are atm L<sup>2</sup> mol<sup>-2</sup>. Larger the value of a, larger will be the intermolecular attraction among the gas molecules.
- B-2.  $a = 0.36 \text{ atm litre}^2 \text{ mole}^{-2}$ ,  $b = 4.28 \times 10^{-3} \text{ litre/mole}$
- B-3. 3.6 L
- B-4. 21.37 atm.      B-5.  $\frac{50}{41}$
- B-6.  $\frac{1}{3}$  litre      B-7. 10.358 atm

### PART - II

- A-1. (B)    A-2. (D)    A-3. (D)
- A-4. (D)    B-1. (A)    B-2. (A)
- B-3. (A)    B-4. (C)    B-5. (A)
- B-6. (C)    B-7. (A)    B-8. (A)
- B-9. (C)    B-10. (C)    B-11. (B)
- B-12. (C)    B-13. (D)    B-14. (C)
- B-15. (B)    B-16. (D)    B-17. (D)
- B-18. (B)

### PART - III

1. (A) - q,s ; (B) - r ; (C) - r ; (D) - q,s
2. (A) - q,r ; (B) - p,s ; (C) - q,r ; (D) - p,s

## EXERCISE - 2

### PART - I

1. (B)    2. (D)    3. (D)
4. (C)    5. (B)    6. (C)
7. (D)    8. (D)    9. (C)

### PART - II

1. 5    2. 4    3. 3
4. 2    5. 90    6. 20
7. 62 atm.

### PART - III

1. (BCD)    2. (AB)    3. (BD)
4. (ABCD)    5. (AD)    6. (ABCD)
7. (ABC)

### PART - IV

1. (D)    2. (B)    3. (D)
4. (C)    5. (D)    6. (D)
7. (A)    8. (B)    9. (B)

## EXERCISE - 3

### PART - I

- 1.\* (ABC)
2. A - p, s ; B - r ; C - p, q ; D - r
- 3.\* (AC) or (ACD)
4. (B)    5. (C)    6. (C)

### PART - II

#### JEE-MAIN OFFLINE PROBLEMS

1. (3)    2. (4)    3. (3)
4. (2)

#### JEE-MAIN ONLINE PROBLEMS

1. (1)    2. (3)    3. (1)
4. (1)