



CHEMISTRY

PHYSICAL, INORGANIC, AND ORGANIC CHEMISTRY

GASEOUS STATE

Solved Examples

1. Arrange following in decreasing 'a' factor (H_2O , CO_2 , Ar)

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Example

1. Arrange following gases according to a' (He , Ar , Ne , Kr).

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2. Arrange the following according to liquification pressure (n-pentane, iso-pentane, neo-pentane)

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3. Two vander walls gases have same value of b but different a values. Which of these would energy greater volume under identical conditions?

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4. The vander waals constant for HCl are $a = 371.843 Kpa. dm^6 mol^{-1}$ and $b = 40.8 cm^3 mol^{-1}$ find the critical constant of this substance.

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5. The vander waals constant for gases A , B and C are as follows:

Gas	$a / dm^6 KPa mol^{-2}$	$b / dm^3 mol^{-1}$
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has

- (i) Highest critical temperature
- (ii) The largest molecular volume
- (iii) Most ideal behaviour around STP ?



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6. Under critical states of a gas for one mole of a gas, compressibility factor is :

- A. $3/8$
- B. $8/3$
- C. 1
- D. $1/4$

Answer: A



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Exercise 1

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

(i) From point P to point S volume is constant and temperature is increasing.

(ii) From point S to point Q pressure is constant and temperature is decreasing.

(iii) Through path P, S, Q we can convert gas into liquid through continuity of state.



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

(i) Keeping pressure constant state x can be converted into state y only by decreasing volume.

(ii) Keeping volume constant state x can be converted into state z only by decreasing pressure.

(iii) State x can never be converted into state z only by increasing pressure at the temperature above C .

(iv) Below temperature C state x can't exist at any pressure.

(v) State x , y and z gas, liquid and liquid vapour respectively.

(vi) State x can be converted into state y at temperature d and pressure F .



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2. Explain the physical significance of vanderWaals parameters.

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3. Calculate van der Waals constants a and b if critical temperature and critical pressure are $30^\circ C$ and 72 atm respectively .

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4. Calculate the volume occupied by 2.0 mole of N_2 at $200K$ and 8.21 atm pressure, if $\frac{P_C V_C}{RT_C} = \frac{3}{8}$ and $\frac{P_r V_r}{T_r} = 2.4$.

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5. Using the van der Waals equation, calculate the pressure of $10.0 \text{ mol } NH_3$ gas in a $10.0L$ vessel at $27^\circ C$.

$$\left(P + n^2 \frac{a}{V^2}\right)(V - nb) = nRT \quad a = 4.2L^2 \cdot \text{atm} / \text{mol}^2 \quad b = 0.037L / \text{mol}$$

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6. If density of vapours of a substance of molar mass 18g mol^{-1} at 1atm pressure and 500K is 0.36kg m^{-3} , then calculate the value of Z for the vapours. (Take $R = 0.082\text{Latm mol}^{-1}\text{K}^{-1}$)

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7. One litre gas at 400K and 300atm pressure is compressed to a pressure of 600atm and 200K . The compressibility factor is changed from $1.2 \rightarrow 1.6$ respectively. Calculate the final volume of the gas.

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8. Reduced temperature for benzene is 0.7277 and its reduced volume is 0.40 . Calculate the reduced pressure of benzene.

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9. The values of a and b for oxygen are $a = 1.360 \text{atmlitre}^2 \text{mol}^{-2}$ and $b = 0.03183 \text{litre/mol}$.

(i) Calculate the value of $\left(b - \frac{a}{RT}\right)$ at 0°C . (ii) Calculate the Boyle's temperature at which $\left(b - \frac{a}{RT}\right) = 0$.

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10. Consider an ideal gas contained in a vessel. If the intermolecular interaction suddenly begins to act, which of the following will happen?

- A. The pressure decreases
- B. The pressure increases
- C. The pressure remains unchanged
- D. The gas collapses

Answer: B

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11. The process 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 molecule
- D. Intermolecular forces of attraction

Answer: D



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12. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

- A. Fewer electrons than O_2
- B. two covalent bonds
- C. V-shape

D. dipole moment

Answer: D

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13. Select incorrect statement:

A. we can condense vapour simply by applying pressure

B. to liquefy a gas must lower the temperature below T_c and also apply pressure

C. at T_c , 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.

Answer: D

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14. However great the pressure , a gas cannot be liquified above its :

- A. Boyle temperature
- B. Inversion temperature
- C. Critical temperature
- D. Room temperature

Answer: C



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15. A real obeying vander Waals equation will resemble ideal gas , if the

- A. constant a & b are small
- B. a is large & b is small
- C. a is small & b is large

D. constant a & b are large

Answer: A



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16. Graph depicting correct behaviour of ideal gas and H_2 gas will be (neglect a):

A. 

B. 

C. 

D. All of these

Answer: A



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17. If temperature and volume are same, the pressure of a gas obeying van der Waal's 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

Answer: A



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18. At $273K$ temp, and 9 atm pressure, the compressibility fog a gas is 0.9.

The volume of 1 mill-moles of gas at this temperature and pressure is :

- A. 2.24litre
- B. 0.020mL
- C. 2.24mL

D. 22.4mL

Answer: C

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19. Positive deviation from ideal behaviour takes place because of

A. Molecular interaction between atoms and $\frac{PV}{nRT} > 1$

B. Molecular interaction between atoms and $\frac{PV}{nRT} < 1$

C. Finite size of atoms and $\frac{PV}{nRT} > 1$

D. Finite size of atoms and $\frac{PV}{nRT} < 1$

Answer: A

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20. For the non-zero value of the 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. $P = \frac{nRT}{V - b}$

Answer: A



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21. 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. $\frac{RTV}{(1 - a)}$

Answer: C

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22. At low pressures (for 1 mole), the van der 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. $\left(1 + \frac{RTV}{a} \right)$

Answer: A

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23. Calculate the radius of He atoms if its van der Waal's constant 'b' is 24 mL mol^{-1} . (Note: mL=cubic centimeter)

A. 1.355 \AA

B. 1.314 \AA

C. 1.255 \AA

D. 0.355 \AA

Answer: A



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24. In van der Waal's equation of state for a non ideal gas the term that accounts for intermolecular forces is:

A. nb

B. nRT

C. $n^2 a / V^2$

D. $(nRT)^{-1}$

Answer: C

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25. The van der Waals' constant 'a' for the gases O_2 , N_2 , NH_3 and CH_4 are 1.36, 1.39, 4.17 and 2.253 respectively, the gas which can be most easily liquefied is :

A. O_2

B. N_2

C. NH_3

D. CH_4

Answer: C

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26. The correct order of normal boiling of O_2 , N_2 , NH_3 and CH_4 for whom the values of van der Waals constant ' a ' are 1.360, 1.390, 4.170 and $2.253L^2atmmol^{-2}$ 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. $NH_3 < CH_4 < O_2 < N_2$

Answer: B

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27. 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

Answer: C

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28. van der Waals constant b of helium is 24 mL mol^{-1} . Find molecular diameter of helium.

A. $1.335 \times 10^{-10} \text{ cm}$

B. $1.335 \times 10^{-8} \text{ cm}$

C. $2.67 \times 10^{-8} \text{ cm}$

D. $4.34 \times 10^{-8} \text{ cm}$

Answer: C

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29. If v is the volume of one molecule of a gas under given conditions, then van der Waals constant b is

A. $\frac{4V}{N_0}$

B. $4V$

C. $\frac{N_0}{4V}$

D. $4VN_0$

Answer: D



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30. In van der Waals 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. $(RT)^{-1}$

Answer: C



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31. 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. change unpredictably

Answer: B



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32. What is the compressibility factor (Z) for 0.02 mole of a van der Waals's 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. 0.01

Answer: D

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33. The van der Waals parameters for gases W, X, Y and Z are

Gas $a(\text{atmL}^2\text{mol}^{-2})$ $b(\text{Lmol}^{-1})$

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

Answer: D



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34. 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. $B - \frac{b}{a}$

Answer: B

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35. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is called

- A. Critical temperature
- B. Inversion temperature
- C. Boyle temperature
- D. Reduced temperature

Answer: C

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36. The temperature at which the second virial coefficient of a real gas is zero is called .

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37. Consider the following statements : if the van der Waal's parameters of two gases are given as:

$$a \left(\text{atmL}^2 \text{mol}^{-2} \right) b \left(\text{Lmol}^{-1} \right)$$

Gas X: 6.5 0.056

Gas Y: 8.0 0.011

(P): $V_C(X) < V_C(Y)$ (Q): $P_C(X) < P_C(Y)$

(R) : $T_C(X) < T_C(Y)$

Select the correct alternate.

A. (i) alone

B. (i) and (ii)

C. (i),(ii) and (iii)

D. (ii) and (iii)

Answer: D



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38. Select correct statements(s):

- A. We can condense vapours simply by applying pressure
- B. To liquify a gas one must lower the temperature below T_c and also apply pressure
- C. At T_c , there is no distinction between liquid and vapour state hence density of the liquid is nearly equal to density of the vapour
- D. All the statements are correct statements

Answer: D



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39. For a real gas the $P - V$ curve was experimentally plotted and it had the following appearance. With respect to liquifaction. Choose the correct statement.



- A. at $T = 500K$, $P = 40$ atm, the state will be liquid
- B. at $T = 300K$, $P = 50$ atm, the state will be gas
- C. at $T < 300K$, $P > 20$ atm, the state will be gas
- D. at $300K < T < 500K$, $P > 50$ atm, the state will be liquid.

Answer: D

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40. A real gas most closely approaches the behaviour of an ideal gas at:

- A. 1.5 atm and $200K$
- B. 1 atm and $273K$

C. 0.5 atm and $500K$

D. 15 atm and $500K$

Answer: C

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41. Calculate the compressibility factor for CO_2 if one mole of it occupies 0.4 litre at $300K$ and $40atm$. Comment on the result:

A. 0.40, CO_2 is more compressible than ideal gas

B. 0.65, CO_2 is more compressible than ideal gas

C. 0.55, CO_2 is more compressible than ideal gas

D. 0.62, CO_2 is more compressible than ideal gas

Answer: B

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42. Consider the following statements

$$PV_m = RT \left(1 + \frac{B}{V_m} + \frac{B}{V_m^2} + \dots \right) \text{ Then } V_m .$$

- A. i and ii
- B. i and iii
- C. ii and iii
- D. i,ii and iii

Answer: C

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43. At Boyle's temperature the value of compressibility factor $Z = \left(\frac{PV_m}{RT} = \frac{V_{real}}{V_{ideal}} \right)$ 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

Answer: D



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44. The critical density of the gas CO_2 is $0.44gcm^{-3}$ at a certain temperature. If r is the radius of the molecules, r^3 in cm^3 is approximately. (N is Avogadro number)

A. $\frac{25}{\pi N}$

B. $\frac{100}{\pi N}$

C. $\frac{6}{\pi N}$

D. $\frac{25}{4N\pi}$

Answer: C



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45. 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.

Answer: C



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46. The vander waals constan 'b' of a gas is $4\pi \times 10^{-4} L/mol$. The radius of gas atom can be expressed in secientific notation as $z = 10^{-9} cm$. Calculate the value fo z . (Given $N_A = 6 \times 10^{23}$)

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47. For a fixes amount of real gas when a graph of zv/s was plotted than at very high pressure slope was observed to be $0.01 atm^{-1}$. 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 atm-litre. calculate excluded volume in litres for 20 moles of the real gas.

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48. If C & D are the third & fourth virial coefficients. If $\frac{D}{C} = \frac{V_c}{x}$. Then find the value of x .

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49. Calculate molecular diameter for a gas if its molar excluded volume is $3.2\pi ml$. (in nanometer) (Take $N_A = 6.0 \times 10^{23}$)

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50. 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 $10x$.

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51. 1 mol of CCl_4 vapours at 77°C occupies a volume of 35.0L . If van der Waals constants are $a = 20.39\text{L}^2\text{atmmol}^{-2}$ and $b = 0.1383\text{Lmol}^{-1}$, calculate compressibility factor Z under

(a) Low pressure region

(b) High pressure region

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52. To an evacuated 504.2mL steel container is added 25gCaCO_3 and the temperature is raised to 1500K causing a complete decomposition of the salt. If the density of CaO formed is $3.3\text{g}/$, find the accurate pressure developed in the container using the Van der waals equation of state. The van der waals constants for $\text{CO}_2(\text{g})$ are $a = 4\frac{\text{L}^2 - \text{atm}}{\text{mol}^\circ}$, $b = 0.04\frac{\text{L}}{\text{mol}}$. ($\text{Ca} - 40$, $\text{C} - 12$, $\text{O} - 16$). Report your answer as nearest whole number.



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53. Which of the following statements are correct?

- A. It is not possible to compress a gas at 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. Due to higher kinetic energy of gas molecules above T_c , it is considered as super critical fluid

Answer: B::C::D



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54. Which of the following is correct for critical temperature ?

- A. At is the highest temperature at which liquid and vapour can coexist
- B. Beyond this temperature the gas and the liquid phases have different critical densities
- C. At this temperature, the gas and the liquid phases have different critical densities
- D.

Answer: A::B



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55. The vander waal gas constant 'a' is given by

A. $\frac{1}{3}V_C$

B. $3P_C V_C^2$

C. $(1)(8) \frac{RT_C}{P_C}$

D. $\frac{27}{64} \frac{R^2 T_C^2}{P_C}$

Answer: B::D



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56. 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 $Lmol^{-1}$

D. a' is expressed in $atm L^2 mol^{-2}$

Answer: A::B::C::D



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57. Select the correct statements(s):

- A. At Boyle's temperature a real gas behaves like an ideal gas at low pressure
- B. Above critical conditions, a real behave like an ideal gas
- C. For hydrogen gas 'b' dominates over 'a' all at temperature
- D. At high pressure van der Waals' constatn 'b' dominated over 'a'

Answer: A::B::D



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58. Which is/are correct for real gases?

A. $\lim_{P \rightarrow 0} (PV_m) = \text{constant at constant high temperature}$

B. $\lim_{V_m \rightarrow 0} (PV_m) = \text{constant at constant low temperature}$

C. $\lim_{P \rightarrow 0} \left(\frac{PV_m}{RT} \right) = 1$ at high temperature

D. $\lim_{V \rightarrow 0} \left(\frac{PV_m}{RT} \right) = R$

Answer: A::C

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59. Which of the following statements are incorrect?

A. Molar volume of every gas at *STP* is $22.4L$

B. Under critical states compressibility factor is 1

C. All gases will have equal value of average *KE* at a given temperature

D. At absolute zero, *KE* is $3/2R$.

Answer: A::B::D



60. One of the important approach to the study of real gases involves the analysis of 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 $Z = \left(\frac{V_{mreal}}{V_{mideal}} \right)$ (where V_{mideal} and V_{mreal} are the molar volume for ideal and real gas respectively). Gas corresponding $Z < 1$ 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)

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. Conclusion III & IV are true

Answer: D



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61. One of the important approach to the study of real gases involves the analysis of 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

$Z = \left(\frac{V_{mreal}}{V_{mideal}} \right)$ (where V_{mideal} and V_{mreal} are the molar volume for

ideal and real gas respectively). Gas corresponding $Z < 1$ 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)

For a real gas $Z > 1$ 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

Answer: B

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62. One of the important approach to the study of real gases involves the analysis of 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 $Z = \left(\frac{V_{mreal}}{V_{mideal}} \right)$ (where V_{mideal} and V_{mreal} are the molar volume for ideal and real gas respectively). Gas corresponding $Z < 1$ 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)

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)

Answer: D



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63.

When pressure is increases at constant temp volume of gas decreases

$AB \rightarrow \text{gases}, BC \rightarrow \text{vapour} + \text{liquid}, CD \rightarrow \text{liquid}$

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 VANDERWAAL EQUATIONS:

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

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

since equation is cubic in V_m hence there will be three roots of equation of 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

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

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

$$V_m = V_c$$

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

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

comparing with equation (1)

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

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

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

$$\text{From (i) } \frac{RT_c}{P_c} = 3V_c - b = 9b - b = 8b \Rightarrow T_c = \frac{8a}{27Rb}$$

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.

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

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

using the two T_cP_c and V_c can be calculated by



A scientist proposed the following equation of state

$$P = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}. \text{ If this equation leads to the critical behaviour}$$

then critical temperature is:

A. $\frac{8B}{27RC}$

B. $\frac{B}{8RC}$

C. $\frac{B^2}{3RC}$

D. None of these

Answer: C



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64. 

When pressure is increases at constant temp volume of gas decreases

$AB \rightarrow \text{gases}, BC \rightarrow \text{vapour} + \text{liquid}, CD \rightarrow \text{liquid}$

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 VANDERWAAL EQUATIONS:

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

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

since equation is cubic in V_m hence there will be three roots of equation of 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

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

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

$$V_m = V_c$$

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

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

comparing with equation (1)

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

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

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

$$\text{From (i) } \frac{RT_c}{P_c} = 3V_c - b = 9b - b = 8b \Rightarrow T_c = \frac{8a}{27Rb}$$

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.

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

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

using the two $T_c P_c$ and V_c can be calculated by



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 $R = \frac{1}{12} \text{ L atm mol}^{-1} \text{ K}^{-1}$]

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. $\left(\frac{3}{256\pi N_A}\right)^{1/3}$

Answer: D



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of any temperature and pressure. At critical point all three roots will

coincide and will given single value of $V_m = V_c$ at critical point. Vander

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

equation should be:

$$V_m = V_c$$

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

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

using the two $T_c P_c$ and V_c can be calculated by



Identify the wrong statement related to the above graph:



- A. between $50K$ and $150K$ 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 $100K$ and pressure below 20 atm it has liquid state only

Answer: A:D

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66. A gas described by van der Waals equation .

- A. behaves similar to an ideal gas in the limit of larger molar volumes
- B. behaves similar to an ideal gas is in limit of larger pressure

- C. is characterised by van der Waals coefficients that are dependent on the identify of the gas but an independent of the temperature.
- D. has the pressure that is lower than the pressure exerted by same gas behaving ideally

Answer: A::C::D

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67. The term that corrects for the attractive forces present in a real gas in the van der Waal's equation is

A. nb

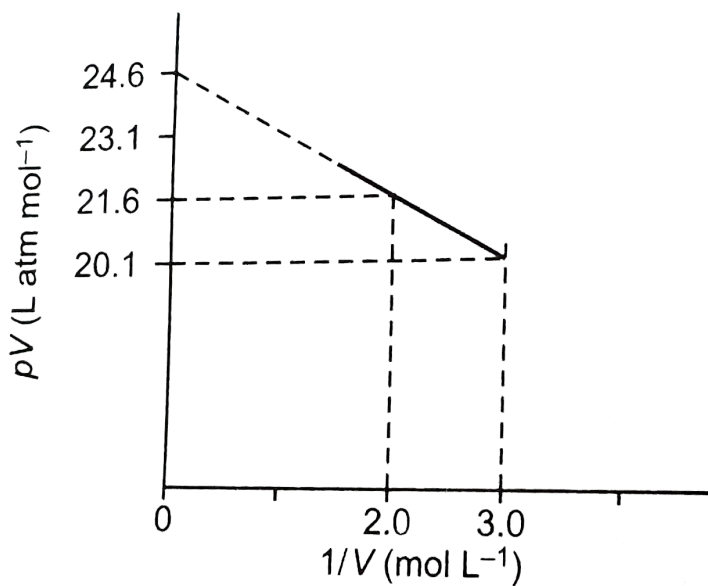
B. $\frac{an^2}{V^2}$

C. $-\frac{an^2}{V^2}$

D. $-nb$

Answer: B

68. For one mole of a van der Waals' gas when $b = 0$ and $T = 300K$, the pV vs $1/V$ plot is shown below. The value of the vander Waals' constant a (atm L mol^{-2})



- A. 1.0
- B. 4.5
- C. 1.5
- D. 3.0

Answer: C



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69. 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

A. 

B. 

C. 

D. 

Answer: C



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70. In van der Waals' equation of state of the gas law the constant 'b' is a measure of .

- A. Intermolecular collisions per unit volume
- B. Intermolecular attractions
- C. Volume occupied by the molecules.
- D. Intermolecular repulsions

Answer: C



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71. 'a' and 'b' are van der Waals' constants for gases Chlorine is more easily liquefied than ethane because .

- A. a and b for $Cl_2 > a$ and b for C_2H_6
- B. a and b for $Cl_2 < a$ and b for C_2H_6
- C. a and $Cl_2 < a$ for C_2H_6 but b for $Cl_2 > b$ for C_2H_6

D. a for $CI_2 > a$ for C_2H_6 but b for $CI_2 < b$ for C_2H_6

Answer: D



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72. The compressibility factor for a real gas at high pressure is .

A. $1 + RT/pb$

B. 1

C. $1 + pb/RT$

D. $1 - pb/RT$

Answer: C



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73. If Z is a compressibility factor, van der Waals' equation at low pressure can be written as

A. $Z = 1 + \frac{RT}{Pb}$

B. $Z = 1 - \frac{a}{VRT}$

C. $Z = 1 - \frac{Pb}{RT}$

D. $Z = 1 + \frac{Pb}{RT}$

Answer: B



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Exercise 2

1. Which of following statements (s) is true

I -Slope of isotherm at critical point is maximum.

II-Larger is the value of T_c easler 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

Answer: B



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Exercise 3

1. Figure displays the plot of the compression factor Z versus p for a few gases



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 a 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

Answer: A::B::C



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