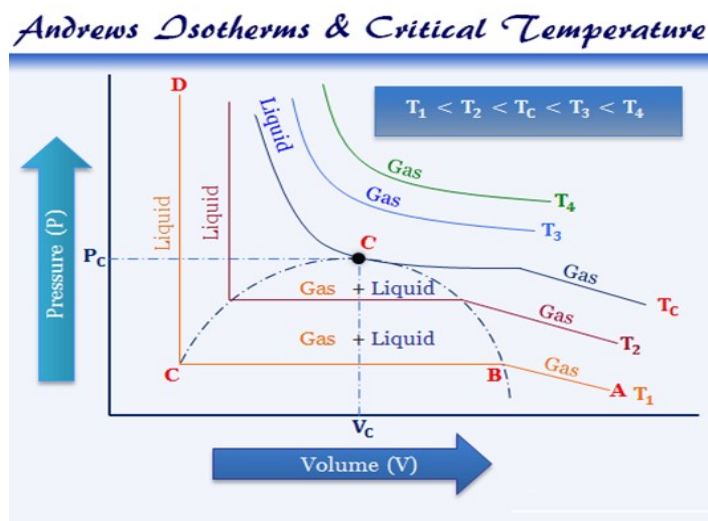


Critical constants of real gas

- Critical constants like critical temperature, critical pressure, and critical volume of gas determine the condition and formula of liquefaction of real and ideal gases.
- Most of the gases in our environment liquefy at ordinary pressure but the suitable lowering of cooling the temperature. But many gases like hydrogen, nitrogen, oxygen, and methane cannot be liquefied at ordinary temperature however high pressure may be used.
- According to the kinetic theory, ideal gas cannot be liquefied at critical temperature because the gas molecules are considered as point masses with no intermolecular attraction.
- Real gases also, cannot be liquefied unless their temperature is below a certain value depending on the properties of gases.
- **The temperature at which the gas can be liquefied is called its critical temperature for learning chemistry or physical chemistry.**

Liquefaction of gases: Andrews's isotherms

In 1869, Thomas Andrews carried out an experiment with a small quantity of carbon dioxide in a glass tube enclosed and sealed by the chemical element mercury. He studied P – V relations for carbon dioxide at different temperatures or the condition of liquefaction at the critical temperature. The condition of liquefaction and critical temperature, pressure, and volume of real gas molecule can be defined by Andrews's isotherms and these terms can be determined in terms of the van der Waals constant.



At high temperatures or above the critical temperature the isotherms for liquefaction of carbon dioxide follow ideal gas law.

At low temperatures or below the critical temperature, the nature of the curves has altogether different appearances.

- As the pressures increase, the volume of the gas decreases in curves A to B. At this point, B liquefaction commences and the volume decreases rapidly as the gas is converted into a liquid with a much higher density.
- Point C, liquefaction of carbon dioxide is complete. The CD of the curve is evidence of this fact.
- AB represents the gaseous state, BC represents liquid or vapor in equilibrium, and CD shows the liquid state only.
- Still higher temperatures at T_2 , we get a similar type of curve to ABCD.
- At temperatures T_C , the horizontal portion is reduced to a mere point, called the critical point or state of the gases.

Every gas can have a limit temperature above which it cannot be liquefied.

Critical Temperature, Pressure, Volume

The critical temperature, pressure, and volume simply represent T_C , P_C , and V_C respectively, and above which the gases cannot be liquefied.

- **What is critical temperature?**

The Critical temperature (T_C) is the maximum temperature at which the gas can be liquefied and the temperature above which the liquid cannot exist.

- **What is critical pressure?**

Critical pressure (P_C) is the maximum pressure required for the liquefaction of gases at the critical temperature.

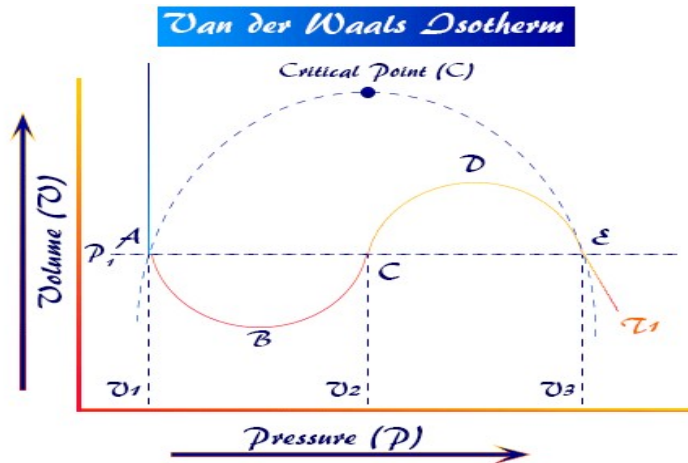
- **What is critical volume?**

Critical volume (V_C) is the volume occupied by one gram mole of gaseous substances at critical temperature and pressure.

Principle of continuity of the state:

An examination of the PV curve at the temperature below the critical temperature may be discontinuous or break down during the transformation of gas to liquid. The continuity of the state of matter from the gas to liquid can be explained from the above Andrews isotherm ABCD at temperature, T_1 . Suppose the gas is heated with the specific heat at constant volume along with AB. Then the gas gradually cooling at constant pressure along with BC, and the volume will be reduced considerably. On reaching D the process liquefaction would appear. At point D, the system contains highly compressed gas. But from the Andrews curve, the critical temperature point is the representation of the liquefaction point of the gases. Hence there is hardly a distinction between the liquid and the gaseous state. There is no line of separation between the two phases. **This is known as the principle of continuity of the state.**

Critical temperature pressure and volume formula



With the increase in temperature, the minimum and maximum points come close to each other and at the critical point (C) both maximum and minimum coalesce. The slope and curvature both become zero at this point.

In these conditions, we can calculate the critical temperature, pressure, and volume formula for real gases from the Van der Waals equation.

Critical constants V_c , T_c and P_c

Van der waals equation for 1 mole gas,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{dP}{dV}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{d^2P}{dV^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At critical state, $\left(\frac{dP}{dV}\right)_T = 0$ and $\left(\frac{d^2P}{dV^2}\right)_T = 0$

$$\therefore \frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \text{ and } \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4}$$

From the above two equation,

$$V_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{a}{27b^2}$$

Critical temperature of an ideal gas

For an ideal gas $a = 0$, since there exist no forces of attraction between the molecules. Therefore, the T_c of such gases is equal to zero. Hence the elementary condition for liquefaction of ideal gases is to cool below the critical temperature.

The ideal gas can not be liquefied at the critical temperature or zero Kelvin because practically not possible to attain zero kelvin temperature.

Critical constants from Van der Waals constant

Van der Waals constant for real gas can be determined from the critical constants formula (temperature and pressure). Critical volume in the expression is avoided due to the difficulty of determination. From the critical constants like temperature, pressure, and volume in terms of Van der Waals constants,

- $b = V_c/3$

- $a = 27 R^2 T_c^2/64P_c$

Question: Calculate Van der Waals constant for the gas when critical temperature and pressure = 280.8 K and = 50 atm respectively.

Answer: $a = 0.057 \text{ lit mol}^{-1}$ and $b = 4.47 \text{ lit}^2 \text{ atm mol}^{-2}$

Compressibility factor for real gas

Compressibility factor formula of the gas,

$$\begin{aligned} Z_c &= P_C V_C / RT_C \\ &= 3/8 \\ &= 0.375 \end{aligned}$$

Critical coefficient value = $8/3 = 2.66$

If we compare these values with the experimental values, we found that the agreement is very poor. Because Van der Waals equation at the critical state is not very accurate.

- The experimental value of the compressibility factor for non-polar or slightly polar bonding molecules like helium, neon, argon, oxygen, and methane is close to 0.29.
- For the molecule having polarity or polarization like chlorine, carbon disulfide, chloroform, and ethylene close to 0.26 or 0.27.
- For hydrogen bonding molecules like ammonia, water, and methyl alcohol are close to 0.22 to 0.24.

Problem: The critical constants for water are 647 K, 22.09 MPa, and $0.0566 \text{ dm}^3 \text{ mol}^{-1}$. What is the value of a and b?

Solution: $T_C = 647 \text{ K}$, $P_C = 22.09 \text{ Mpa} = 22.09 \times 10^3 \text{ kPa}$, $V_C = 0.0566 \text{ dm}^3 \text{ mol}^{-1}$.

Therefore, Van der Waals constant,

$$b = V_C/3$$

$$\begin{aligned} &= (0.0566 \text{ dm}^3 \text{ mol}^{-1})/3 \\ &= 0.0189 \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

From the critical constants formula of real gas,

$$\begin{aligned} a &= 3 P_C V_C^2 \\ &= 3 (22.09 \times 10^3) \times (0.0566)^2 \\ &= 213.3 \text{ kPa mol}^{-2} \end{aligned}$$

Question: An atom in the molecule has $T_C = -122 \text{ }^\circ\text{C}$, $P_C = 48 \text{ atm}$. What is the radius of the atom?

Answer: Calculated radius of the atom = $1.47 \times 10^{-8} \text{ cm}$.