

CRITICAL PARAMETERS OF A REAL GAS

The equation $(p + \frac{a}{V_m^2})(V_m - b) = RT$ can be expanded to

$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} - RT = 0$. Upon rearranging,

we derive the cubic equation in volume:

$$V_m^3 - (\frac{RT}{P} + b)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0 \quad (i)$$

This cubic equation has three roots. At critical conditions, all three roots are identical, hence

$$V_1 = V_2 = V_3 = V_c = V_m.$$

Alternatively, expressing this as $(V_m - V_c)^3 = 0$ or $V_m^3 + 3V_mV_m^2 - 3V_m^2V_c - V_m^3 = 0$.

By comparing coefficients with equation (i), we derive:

$$V_c^3 = \frac{ab}{P_c}, \quad \frac{RT_c}{P_c} + b = 3V_c$$

Solving these equations, we obtain the critical volume $V_c = 3b$,

$$\text{critical pressure } P_c = \frac{a}{27b^2}, \quad \frac{a}{P_c} = 3V_c^2, \text{ and } T_c = \frac{a}{27Rb}.$$

The critical compression factor, $Z_c = \frac{P_c V_c}{RT_c}$, is equal to $\frac{3}{8}$ for van der Waals' gas.

Andrews Isotherm Curve

This graph illustrates the correlation between pressure (P) and volume during the gas liquefaction process.

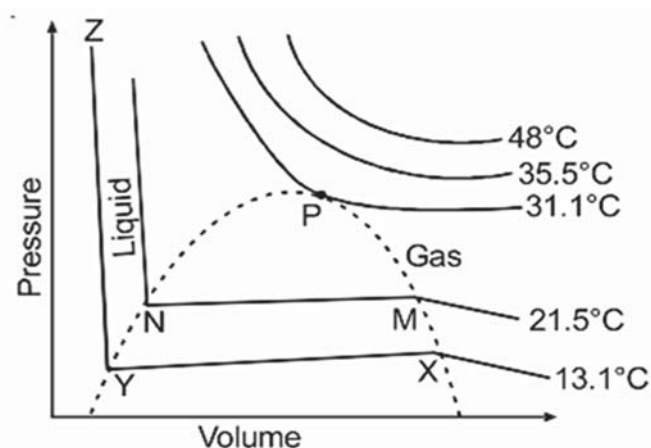


Fig. : Isotherm of CO_2 showing critical region

At the critical point P, the van der Waals equation's three roots are not only real and positive but also identical, equating to the critical volume (V).

Inversion temperature (T_i):

When a compressed gas is released through a fine aperture, the resulting phenomenon can manifest as either cooling, heating, or no discernible change in temperature, contingent upon the initial temperature of the gas. Each gas exhibits a unique temperature known as the inversion temperature (T_i).

- If the actual temperature (T) exceeds the inversion temperature (T_i), the process results in heating.
- Conversely, if the actual temperature (T) is below the inversion temperature (T_i), the outcome is cooling.

- When the actual temperature (T) equals the inversion temperature (T_i), neither heating nor cooling occurs.

The inversion temperature (T_i) is determined by the expression $T_i = \frac{2a}{Rb} = 2T_B$, where "a" and "b" are constants associated with the gas, "R" is the gas constant, and T_B is the Boyle temperature.