NPTEL ONLINE CERTIFICATION COURSE

Course

On

Chemical Engineering Thermodynamics

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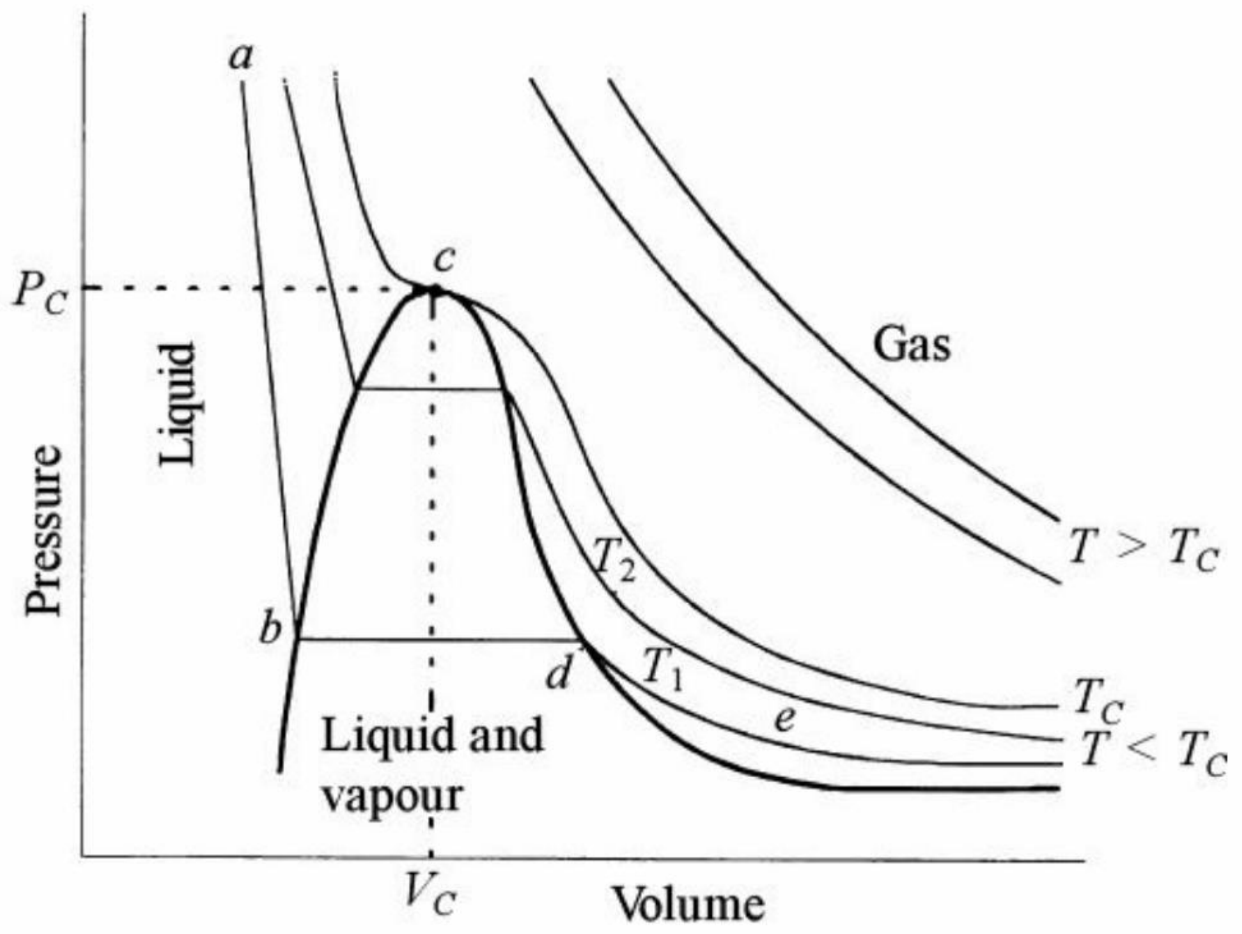
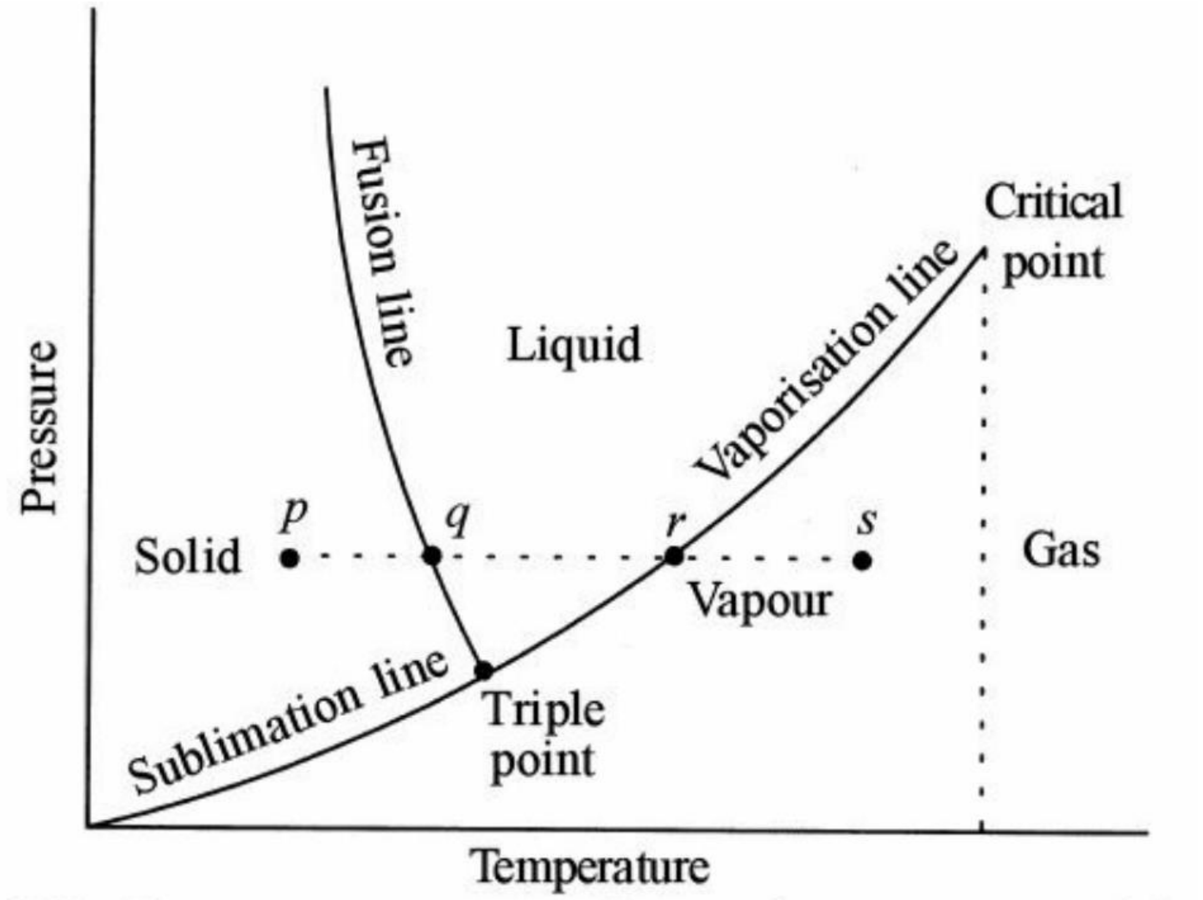
Week - 3

Week outline:

- Gibbs free energy as a function of temperature and pressure
- P-v-T behaviour of gases
- EoS (Equation of States)



P-V-T behavior of pure fluids (e.g. Water).



P-T diagram of pure material.

Van der Waals EoS

van der Waals proposed the following equation to explain the *P-V-T* behaviour of real gases.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$V_C = 3\,b; \qquad T_C = \frac{8\,a}{27\,Rb}; \qquad P_C = \frac{RT_C}{2b} - \frac{a}{9b^2}$$

The last two identities can be solved to get the van der Waals constants as

$$a = \frac{27\,R^2\,T_C^2}{64\,P_C}; \qquad b = \frac{RT_C}{8\,P_C}$$

Redlich-Kwong EoS

The Redlich–Kwong equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

$$a = \frac{0.4278\, R^2 T_C^{2.5}}{P_C}; \qquad b = \frac{0.0867\, RT_C}{P_C}$$

Soave Redlich-Kwong EoS

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

where $a = \dfrac{0.42748 R^2 T_c^2 \alpha}{P_c}$

$$b = \frac{0.08664 R T_c}{P_c}$$

$$\sqrt{\alpha} = 1 + S(1 - \sqrt{T_r})$$

$$S = 0.48 + 1.574\omega - 0.176\omega^2$$

Peng Robinson EoS

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$

where $a = 0.45724\frac{R^2T_c^2\alpha}{P_c}$

$$b = 0.07780\frac{RT_c}{P_c}$$

$$\sqrt{\alpha} = 1 + S(1-\sqrt{T_r})$$

$$S = 0.374\ 64 + 1.542\ 26\omega - 0.269\ 92\omega^2$$

The relation ds = $\frac{dQ}{T}$ is valid for

a. Any reversible process
b. Any irreversible process
c. Adiabatic reversible process
d. Adiabatic irreversible process

Correct Answer: a. Any reversible process

Detailed Solution: The relation ds = $\frac{dQ}{T}$ is valid only when a process is reversible irrespective of the type of process.

For an ideal gas undergoing isothermal process, the change in internal energy (ΔU) is _____

a. 0
b. 1
c. ∞
d. ΔQ

Correct Answer: a. 0

Detailed Solution: For an ideal gas, U= fn(T) only. As T = constant for isothermal process, hence $\Delta U = 0$.

One kilo mol CO_2 occupies a volume of 0.381 m^3 at 313 K. Compare the pressures given by

(a)Ideal gas equation

(b) van der Waals equation, Take the van der Waals constants to be a = 0.365 Nm^4/mol^2 and b = 4.28

Solution The molar volume of CO_2 is

$$V = 0.381 \square 10^{-3} \text{ m}^3 \text{/mol}$$

(a) Ideal gas equation: $P = RT/V = 8.314\,(313)/(0.381 \square 10^{-3}) = 68.30 \square 10^5 \text{ N/m}^2 =$ 68.30 bar

(b) van der Waals equation: Equation (3.29) may be rearranged as

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

$$= \frac{8.314\,(313)}{(0.381 \times 10^{-3}) - (0.428 \times 10^{-4})} - \frac{0.365}{(0.381 \times 10^{-3})^2}$$

$$= 51.8 \times 10^5 \text{ N/m}^2 = 51.8 \text{ bar}$$

What is the critical pressure of CO_2 gas if the reduced pressure at 14.28 atm is 0.196?

a. 2.79 atm
b. 25.18 atm
c. 50.82 atm
d. 72.86 atm

Correct Answer: d. 72.86 atm

Detailed solution: Critical pressure, $P_C = P / P_r = 14.28 / 0.196 = 72.86$ atm

If the specific internal energy of a substance is given by the equation: u (kJ/kg) = 201 + 0.482T, where T is in K, then what is the value of c_v?

a. 0.881 kJ/kg K
b. 0.718 kJ/kg K
c. 0.656 kJ/kg K
d. 0.482 kJ/kg K

Correct Answer: d. 0.482 kJ/kg K

Detailed Solution: u = 201 + 0.482T (kJ/kg) c_v = ($\partial u/\partial T$) v = 0.482 kJ/k

- Thank you!