NPTEL ONLINE CERTIFICATION COURSE

Course

On

Chemical Engineering Thermodynamics

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by

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Week - 4

Week outline:

- Property estimation from P-v-T behaviour
- Concept of chemical potential

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For P-v-T curves of pure substances, the quality is zero over

a. saturated solid line
b. saturated liquid line
c. saturated vapour line
d. none of the above

Correct Answer: b. saturated liquid line

Detailed Solution: We know, Quality (x) = $\frac{n_{vap}}{n_{liq}+n_{vap}}$

At saturated liquid line, n_{vap} = 0; i.e., x = 0

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Gibbs-Helmholtz equation provides the effect of

a. change in pressure on Gibbs free energy
b. change in temperature on Gibbs free energy
c. change in pressure on Helmholtz free energy
d. change in temperature on Helmholtz free energy

Correct Answer: b. change in temperature on Gibbs free energy

Detailed Solution:

Gibbs – Helmholtz equation provides the effect of temperature on Gibbs free energy. It can be derived as follows;

$g = h - Ts$ or $(g/T) = (h/T) - s$ or $\left(\frac{\partial(g/T)}{\partial T}\right)_P = \left(\frac{\partial(h/T)}{\partial T}\right)_P - \left(\frac{\partial s}{\partial T}\right)_P$

or $\left(\frac{\partial(g/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P - \frac{h}{T^2} - \left(\frac{\partial s}{\partial T}\right)_P$ or $\left(\frac{\partial(g/T)}{\partial T}\right)_P = \frac{c_p}{T} - \frac{h}{T^2} - \frac{c_p}{T}$

or $\left(\frac{\partial(\Delta g/T)}{\partial T}\right)_P = -\frac{\Delta h}{T^2}$

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Using Ideal gas law, calculate the volume occupied by 2 moles of oxygen at 300 K and 100 bar.

a. 0.125 × 10-3 m^3
b. 0.249 × 10-3 m^3
c. 4.99 × 10-4 m^3
d. 0.998 × 10-3 m^3

Correct Answer: c. 4.99×10^{-4} m^3

Detailed Solution:

According to ideal gas law,

$$V = \frac{nRT}{P} = \frac{2 \times 8.314 \times 300}{100 \times 10^5} = 0.499 \times 10^{-3} m^3$$

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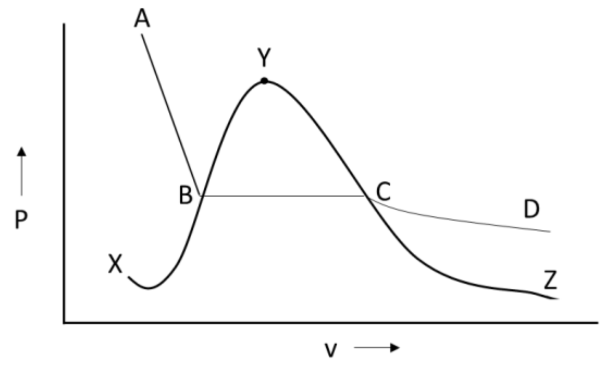
If the P-v diagram for a pure substance is represented by the following figure, then match column I with column II.

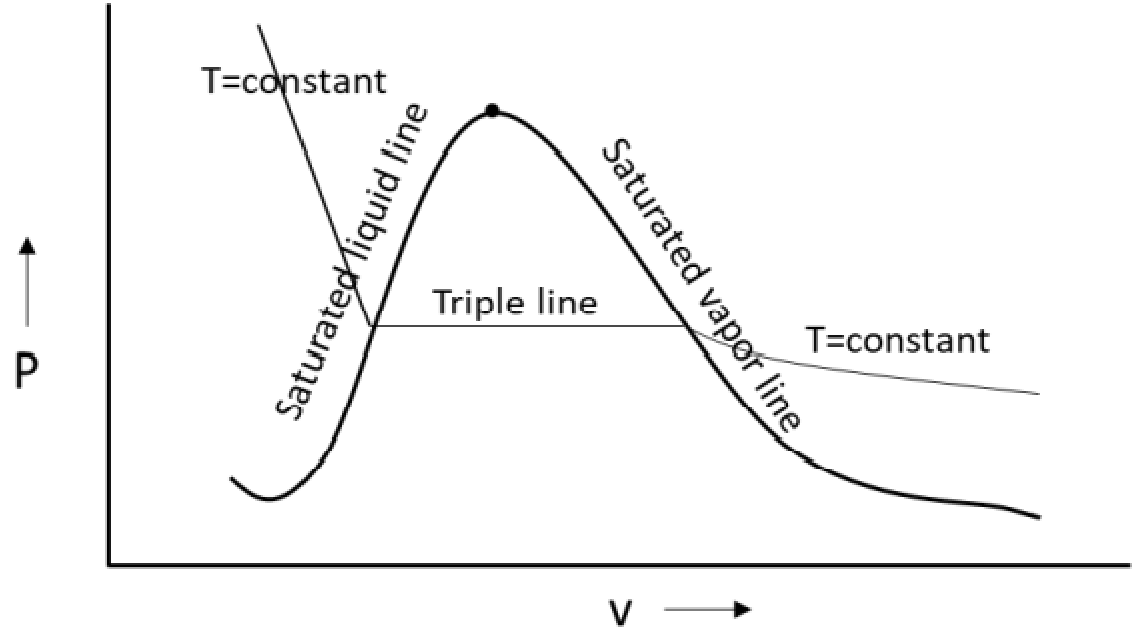


Column I	Column II
A. Line ABCD	1. Triple line
B. Line XBY	2. Saturated vapor line
C. Line YCZ	3. Saturated liquid line
D. Line BC	4. Isotherm

a. A-1, B-4, C-3, D-2
b. A-2, B-1, C-4, D-3
c. A-3, B-2, C-1, D-4
d. A-4, B-3, C-2, D-1

Correct Answer: d. A-4, B-3, C-2, D-1

Detailed Solution:



A tank of $5m^3$ volume is filled with 10 kg ammonia at 500K. Determine the pressure exerted by ammonia (i) using the ideal gas law (ii) assuming ammonia obeys van der Waal's equation of state. [Given: a = 422.546 x 10-3 $Pa(m^3 /mol)^2$ and b = 0.037 x 10-3 m^3 /mol, R = 8.314 J/mol.K]

a. (i) 0.283 mPa (ii) 0.305 mPa
b. (i) 0.489 mPa (ii) 0.485 mPa
c. (i) 0.796 mPa (ii) 0.828 mPa
d. (i) 1.264 mPa (ii) 1.399 mPa

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Correct Answer: b. (i) 0.489 mPa (ii) 0.485 mPa

Detailed Solution:

Given:

Temperature, T = 500 K

Volume, V = 5 m^3

Mass = 10 kg

Molar mass of ammonia = 17×10^{-3} kg/mol

No. of moles = $10 / (17 \times 10^{-3}) = 588.235$ moles

Molar volume, $v = 5 / 588.235 = 8.5 \times 10^{-3}$ m^3/mol

Now, <u>case 1: Ideal gas law</u>

We know, Pv = RT

Thus, pressure, $P = RT/v = (8.314 \times 500) / (8.5 \times 10^{-3})$

$= 0.489 \times 10^6$ Pa

= 0.489 MPa

<u>Case 2: van der Waal's equation</u>

We know,

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

$$= \frac{8.314 \times 500}{(8.5 - 0.037) \times 10^{-3}} - \frac{422.546 \times 10^{-3}}{(8.5 \times 10^{-3})^2}$$

$= 0.485 \times 10^6$ Pa

= 0.485 MPa

Determine the pressure exerted by nitrogen using Van der Waals equation of state at 300 K and molar volume of 5 m^3 /mol.

For nitrogen, take R = 8.314 J/mol.K, TC = 126.2 K and PC = 33.9 bar

a. 1496.52 Pa
b. 997.68 Pa
c. 498.84 Pa
d. 249.42 Pa

Correct Answer: c. 498.84 Pa

Detailed solution:

$$a = \frac{27\, R^2\, T_C^2}{64\, P_C} = \frac{27 \times 8.314^2 \times 126.2^2}{64 \times 33.9 \times 10^5} = 0.137\ Pa\ m^6/mol^2$$

$$b = \frac{RT_C}{8\, P_C} = \frac{8.314 \times 126.2}{8 \times 33.9 \times 10^5} = 3.869 \times 10^{-5}\ m^3/mol$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{8.314 \times 300}{5 - 3.869 \times 10^{-5}} - \frac{0.137}{5^2} = 498.84\ Pa$$

If one mole of an ideal gas at 298 K undergoes a reversible isothermal process where the molar volume of the gas changes from 0.023 m^3 /mol to 0.041 m^3 /mol, what is the entropy change associated with the process? Take R = 8.314 J/mol.K

a. 4.806 J/K
b. 8.314 J/K
c. 12.611 J/K
d. 16.319 J/K

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Correct Answer: a. 4.806 J/K

Detailed Solution:

$$ds = \left(\frac{đq}{T}\right)_R = \frac{du + Pdv}{T}$$

For ideal gas, $u = fn(T)$ only

Thus for isothermal conditions, $du = 0$ and $ds = \frac{Pdv}{T}$

For 1 mole of ideal gas, $Pv = RT$

Thus, $ds = \frac{Rdv}{v}$

And Entropy change, $\Delta s = R \ln \frac{v_2}{v_1}$

$$= 8.314 \times \ln\left(\frac{0.041}{0.023}\right)$$

$$= 4.806 \text{ J/K}$$

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Consider the following reaction at 1 bar and 298.15 K:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Given: $$\left.\begin{aligned} \Delta h_R &= -176.2\,\text{kJ/mol} \\ \Delta s_R &= -0.285\,\text{kJ/K.mol} \end{aligned}\right\} \text{at 1 bar \& 298.15K}$$

Comment on the feasibility of the reaction:

a. not feasible
b. feasible
c. Cannot be determined
d. None of the above

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Correct Answer: b. feasible

Detailed Solution:

For constant T& P, criteria of feasibility is $\Delta g \leq 0$.

$\Delta g_R = \Delta h_R - T\Delta s_R = -176.2 + (298.15 \times 0.285) = -176.2 + 84.972 = -91.22\text{kJ/mol} < 0.$
The reaction is feasible.

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- Thank you!

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