Quiz 9
Chemical Engineering Thermodynamics
March 11, 2021

Consider a gas that follows the equation of state

$$PV/RT = 1 + (b - a/T)\, P/(RT)$$

where b = 20 cm^3/mole; a = 40,000 cm^{3}K/mole; and $C_P = 41.8 + 0.084\, T$(K) J/mol-K.

The gas is under high pressure and is fed through a throttle valve to lower the pressure. The molar density decreases by a factor of 20, $\mathbf{20\, \rho_2 = \rho_1}$.

a) Compare the equation of state to the Van der Waals equation of state. Can this fluid form a liquid state? Does it have excluded volume?
b) What happens to this fluid at very low temperatures? Can this fluid become an ideal gas?
c) If the initial fluid is at 5 MPa and 300K, what is the pressure and temperature of the resulting liquid/vapor mixture after throttling using the inlet stream as the reference state (a real gas with $H = 0$)?
d) What is the change in Gibbs free energy for the throttling process?
e) What is the Gibbs free energy, G, of the exiting stream?

$$\frac{H - H^{ig}}{RT} = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\frac{S - S^{ig}}{R} = -\int_0^P \left[\left((Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right)\right]\frac{dP}{P}$$

Include the attached answer sheet with your answers and a sheet with your work and a description of the solver routine used.

Please use this answer sheet

Include a sheet with your work and a description of solver routine in excel.

a)	**Forms a Liquid?**	**Excluded Volume?**
b)	**At low T?**	**Forms Ideal Gas?**
c)	**P_2 (MPa) =**	**T_2 (K) =**
d)	**ΔG (J/mole) =**	
e)	**G_2 (J/mole) =**	

ANSWERS: Quiz 9
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a)	**Forms a Liquid?** NO	**Excluded Volume?** YES
b)	**At low T?** Excluded Volume goes to ∞	**Forms Ideal Gas?** Can't form i.g. at T => ∞; Can form i.g. At V => ∞; Can form i.g. at P=>0
c)	**P_2 (MPa)** = 0.300 Mpa	**T_2 (K)** = 283K
d)	**ΔG (J/mole)** = 496 J/mole	
e)	**G_2 (J/mole)** = 496 J/mole	

a), b) Van der Waal's

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

a attractive interactions (liquid)

b: excluded volume

$\frac{a}{V^2}$: binary interactions

$$\frac{PV}{RT} = 1 + (b - a/T)\frac{P}{RT}$$

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

$$P\left(1 - \left(b - \frac{a}{T}\right)\frac{1}{V}\right) = \frac{RT}{V}$$

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

Missing $\frac{a}{V^2}$ term

No Liquid State

thermal dependence to "b_{vdW}" $= \left(b + \frac{a}{T}\right)$ excluded volume

~~No Liquid is Possible~~

Can't form an ~~liquid~~ i.g. at $T \to \infty$

Can form i.g. at $V \to \infty$ or at $P \to 0$

Has Excluded Volume

b)

$$Z = 1 + (b - a/T)\frac{P}{RT}$$

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{-bP}{RT^2} + \frac{2aP}{RT^3} = \frac{P}{RT^2}\left(\frac{2a}{T} - b\right)$$

Throttle Valve $\Delta H = 0$

Ref 5 MPa basis $V = \frac{RT}{P} + \left(b - \frac{a}{T}\right)$

$$\Delta H = 0 = (H - H^{ig})_2 - (H - H^{ig})_1 + (H^{ig}_2 - H^{ig}_1)$$

$$\frac{(H - H^{ig})}{RT} = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P dP$$

$$= -\int_0^P \frac{1}{RT}\left(\frac{2a}{T} - b\right) dP$$

$$\left(\frac{H - H^{ig}}{RT}\right) = \frac{P}{RT}\left(b - \frac{2a}{T}\right)$$

$$(H - H^{ig}) = P\left(b - \frac{2a}{T}\right)$$

$$\Delta H = 0 = P_2\left(b - \frac{2a}{T_2}\right) - P_1\left(b - \frac{2a}{T_1}\right) + \int_{T_1}^{T_2} C_p\, dT$$

(1) $0 = P_2\left(b - \frac{2a}{T_2}\right) - P_1\left(b - \frac{2a}{T_1}\right) + 41.8(T_2 - T_1) + \frac{0.084}{2}(T_2^2 - T_1^2)$

(2) EOS $\quad 0 = \frac{P_2 V_2}{RT_2} - 1 - \left(b - \frac{a}{T_2}\right)\frac{P_2}{RT_2}$

(3) $\quad V_2 = 20V_1 = 20\left(\frac{RT_1}{P_1}\left(1 + \left(b - \frac{a}{T_1}\right)\frac{P_1}{RT_1}\right)\right)$

3 equations & 3 unknowns P_2, V_2, T_2

Use Excel Sheet / Solver

$T_2 = 283K \quad P_2 = 0.300 MPa \quad V_2 = 7{,}700 \frac{cm^3}{mol}$

d) $-S \; U \; V$

$H \quad A$

$-P \; G \; T$

$$G = H - ST$$

$$(G - G^{ig}) = \underbrace{(H - H^{ig})}_{\checkmark} - \underbrace{(S - S^{ig})}_{need} T$$

$$\frac{(S - S^{ig})}{R} = -\int_0^P \left[(Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right] \frac{dP}{P}$$

$$= -\int_0^P \left(\frac{P}{RT}\left(b - \frac{a}{T}\right)\right) + \frac{P}{RT}\left(\frac{2a}{T} - b\right)\frac{dP}{P}$$

$$= \int_0^P -\frac{a}{RT^2}\, dP = \frac{-aP}{RT^2}$$

$$(S - S^{ig}) = \left(-\frac{aP}{RT}\right)$$

④

$$(G-G'^{g}) = P\left(\left(b-\frac{2a}{T}\right)+\frac{a}{T}\right)$$

$$(G-G'') = P\left(b-\frac{a}{T}\right)$$

$$\Delta G = (G-G'')_2-(G-G'')_1+(G_2''-G_1'')$$

$$= (G-G'')_2-(G-G'')_1+\int_{T_1}^{T_2} C_p\,dT - T_2\int_{T_1}^{T_2}\frac{C_p}{T}dT$$

Use Excel to Calculate

$$\boxed{\Delta G = 496\ \mathrm{J/mole}}$$

② $\boxed{G_1=0}$ since $H_1=0$ and $S_1=0$ for Referen State