

April 4, 2008

Problem 1. (6.3)

One mole of a pure species exists in liquid-vapor equilibrium in a rigid container of volume $V = 1\text{L}$, a temperature of 300 K , and a pressure of 1 bar . The enthalpy of vaporization and the second virial coefficient in the pressure expansion are: $\Delta h_{\text{vap}} = 16,628\text{ J/mol}$ and $B' = -1 \times 10^{-7}\text{ m}^3/\text{J}$

Assume the enthalpy of vaporization does not change with temperature. You may neglect the molar volume of the liquid relative to that of the gas.

a. How many moles of vapor are there?

Apply the virial equation of state as a power series expansion of pressure:

$$Z = \frac{Pv}{RT} = 1 + B'P + \text{neglected higher order terms}$$

Substituting $v=V/n$ into the above expression, $n=0.0405\text{ mol}$ vapor

b. $P = 21\text{ bar}$, $T_{\text{final}} = ?$

We will use the Clapeyron equation and neglect the molar liquid volume of the species because $v_L \ll v_{\text{vap}}$. Rewriting the virial equation,

$$v = RT\left(\frac{1}{P} + B'\right)$$

And substituting into the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}}}{(RT(\frac{1}{P} + B'))T}$$

Separating the variables and integrating

$$\int_{P_1}^{P_2} \left(\frac{1}{P} + B'\right) dP = \int_{T_1}^{T_2} \frac{\Delta h_{\text{vap}}}{RT^2} dT$$

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$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) + B'(P_2^{sat} - P_1^{sat}) = \frac{-\Delta h_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting in $P_1 = 1$ bar, $P_2 = 21$ bar, $T_1 = 300$ K, we find that the final temperature $T_2 = 523.3$ K

c. How many moles of vapor are there now?

As before in part a, using the truncated virial equation, we can calculate the number of moles in the vapor phase, neglecting the liquid volume:

$$n = \frac{PV}{RT(1 + B'P)}$$

$n = 0.611 \text{ mol}$

Also acceptable: Using the virial equation as an expansion in volume. Using that form,

$n = 0.69$ mol.

Grading:

1. 1 pt for correct form of Virial Equation
2. 2 pts for $n=0.0405$ mol vapor in part a
3. 1 pt for stating assumption of ideal behavior in part b.
4. 2 pts for Clausius-Clapeyron equation
5. 2 pts for $T=523.3$ K in part b
6. 2 pts for correct answer in part c