2ª lista repetical. 16 Dez 2022

1. a) fusão: $\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$

$\Delta_{fus}V = 60.13 - 56.31 = 3.82\ cm^3\ mol^{-1}$

$T_t = 85.47\ K$

$\frac{dp}{dT} = 0 + 2.3856 \times 1.283 \times T^{0.283} =$

$= 2.3856 \times 1.283 \times 85.47^{0.283} =$

$\uparrow$ T_t

$= 10.778\ MPa\ K^{-1}$

$= 10.778 \times 10^6\ Pa\ K^{-1} =$

$= \frac{\Delta_{fus}H}{85.47 \times \underbrace{3.82 \times 10^{-6}}_{m^3\ mol^{-1}}}$

$\Delta_{fus}H = 3519\ J\ mol^{-1}$

vap: $\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} = \frac{2735.41}{T^2}$

$\Delta_{vap}H = 8.314 \times 2735.41 = 22742\ J\ mol^{-1}$

$\Delta_{subl}H = 3519 + 22742 = 26216\ J\ mol^{-1}$

$$\ln P_2 - \ln P_1 = -\frac{\Delta_{sub}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (2)$$

$$\ln P_t = 11.842 - \frac{2735.41}{85.47} = -20.162$$

$$P_t = e^{-20.162} = 1.752 \times 10^{-9} \text{ bar}$$

$$\ln P_2 - \ln 1.752\times10^{-9} = -\frac{26216}{8.314}\left(\frac{1}{81.0} - \frac{1}{85.47}\right)$$

$$\ln P_2 = -22.202$$

$$P_{subl}(81.0\,K) = e^{-22.202} = 2.28 \times 10^{-10} \text{ bar} < P_t$$

b) 150 K: $P_{vap} = 11.842 - \frac{2735.41}{150.0}$

$P_{vap}(150\,K) = 0.00167$ bar $> 5\times10^{-4}$ bar

início: gás

100 K: $P_{fus} = -717.99 + 2.3856 \times 100.0^{1.283}$

$= 160.2$ MPa $= 1602$ bar > 1000 bar

fim: líquido

O mais simples é levar gás de (150K, 5×10^{-4} bar) a Pvap a 100K, e depois prosseguir a T dt.

100K: $\ln P_{vap} = 11.842 - \frac{2735.41}{100}$

$P_{vap}(100K) = 1.833\times10^{-7}$ bar

$\Delta S_1 = \int_1 \frac{n C_p}{T} dT + nR \ln \frac{P_i}{P_f} =$

$= 1\times63\times\ln\frac{100}{150} + 1\times8.314\times\ln\frac{5\times10^{-4}}{1.833\times10^{-7}}$

$= -25.5 + 65.8 = 40.2\ JK^{-1}$

$\Delta S_2 = -\frac{n\Delta_{vap}H}{T_{vap}} = -\frac{1\times(-22742)}{100} = 227.4\ JK^{-1}$

$\Delta S_3 = \int -\alpha_p V\, dp = -1.93\times10^{-3}\times60.13\times10^{-6}\times(1000 - 1.833\times10^{-7})\times10^{5} = -11.6\ JK^{-1}$

$\Delta S = 40.2 - 227.4 - 11.6 = -198.8\ JK^{-1}$

c) Se fosse ponto (170K, 0.0777 bar) P é baixa. Na curva vap:

$\ln 0.0777 = 11.842 - \frac{2735.41}{T}$

$T = 190.0$ K

A 170 K e 0.0777 bar, estamos no líquido. Caminho pode ser aquecer líquido de 170 K a 190 K a 0.0777 bar, vaporizar, aquecer gás até 200 K, sempre a 0.0777 bar, e depois baixar P até 0.002 bar, a 200 K.

$\Delta H_1 = n C_p \Delta T = 1 \times 99 \times (190 - 170)$
$= 1980 \text{ J}$

$\Delta H_2 = 1 \times 22742 = 22742 \text{ J}$

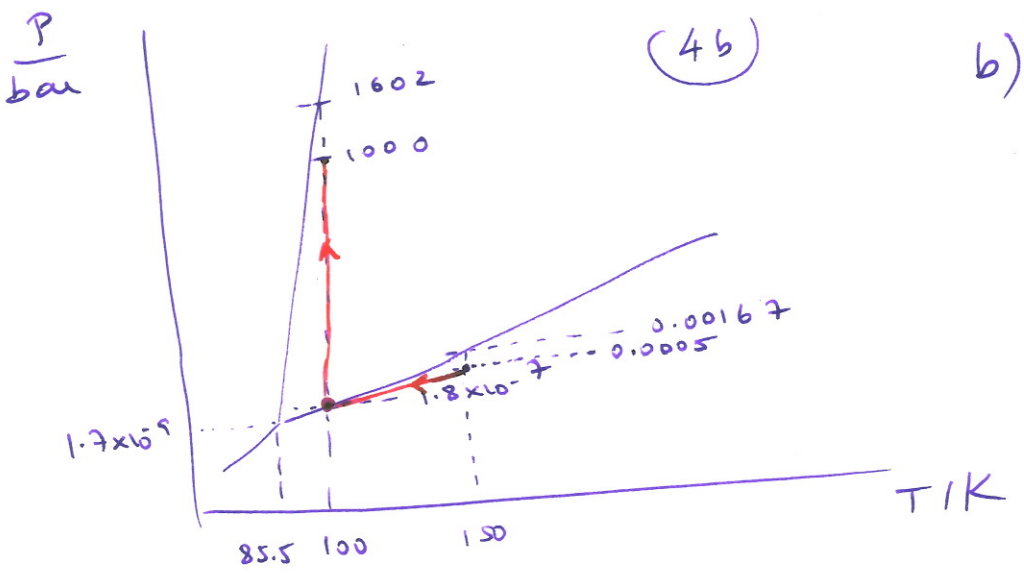
$\Delta H_3 = 1 \times 63 \times (200 - 190) = 630 \text{ J}$

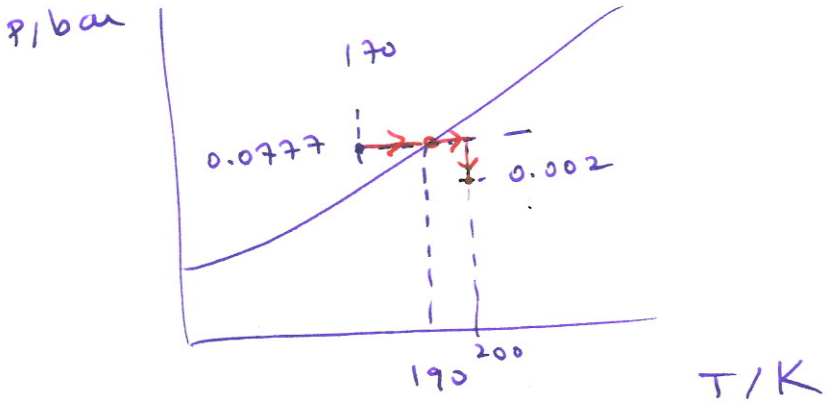
$\Delta H_4 = 0$ T cte, gperfeito

$\Delta H = 1980 + 22742 + 630 + 0 =$
$= 25352 \text{ J}$

(4b)

b)


p
bar
1602
1000
0.00167
0.0005
1.8x10⁻⁷
1.7x10⁹
T/K
85.5
100
150


p/bar
170
0.0777
0.002
190
200
T/K

c)

2. (5)

a) $V^*_{MeOH,m} = 40.75\ cm^3\ mol^{-1}$

$V^*_{ACN,m} = 52.90\ cm^3\ mol^{-1}$

$n_{MeOH} = \frac{1000}{40.75} = 24.540\ mol$

$n_{ACN} = \frac{1000}{52.90} = 18.904\ mol$

$n_t = 43.443\ mol$

$x_{ACN} = \frac{18.904}{43.443} = 0.435$

$x_{MeOH} = \frac{24.540}{43.443} = 0.565$

$x_{MeOH} = 0.565$ → $V_{MeOH,m} = 40.53\ cm^3\ mol^{-1}$

$V_{ACN,m} = 52.73\ cm^3\ mol^{-1}$

$V_m = 0.565 \times 40.53 + 0.435 \times 52.73 =$

$= 45.839\ cm^3\ mol^{-1}$

$V = V_m n_t = 45.839 \times 43.443 = 1991.4\ cm^3$

$\Delta V_m = V - V$ (constituents separated)

$= 1991.4 - 2000 = -8.6\ cm^3$

b) $x_{MeOH} = 0.90$ $x_{ACN} = 0.10$ (6)

$x_{MeOH} = 0.90$ } $V_{MeOH,m} = 40.70\ cm^3\ mol^{-1}$

$V_{ACN,m} = 52.20\ cm^3\ mol^{-1}$

18.904 mol ACN — 10% of mix sol~

189.04 mol — 100%

mix sol~ :

189.04 mol

/ —

18.904 mol ACN 170.132 mol MeOH

$V(mix\ sol^{\sim}) = 18.904 \times 52.20 +$

$+ 170.132 \times 40.70 = 7911\ cm^3$