$\omega = 0.2 \qquad T_c = 425.1\ K \qquad P_c = 37.96$ bar

$T_r = 1.176 \qquad P_r = 1.317$

Example

Calculate the residual enthalpy H^R and the residual entropy S^R of *n*-butane gas at 500 K and 50 bar using the following methods:

Chemica Engineering Dept., KFUPM, CHE303, Handout_9, Residual Properties from EOS

a) The Virial EOS.
b) The RK EOS.
c) Generalized correlations.

(a) $$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right)$$

$$\frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT}$$

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$\frac{dB}{dT} = \frac{RT_c}{P_c}\left(\frac{dB^0}{dT} + \omega\frac{dB^1}{dT}\right)$$

$$\frac{dB^0}{dT} = \frac{1}{T_c}\frac{0.675}{T_r^{2.6}}\ ; \quad \frac{dB^1}{dT} = \frac{1}{T_c}\frac{0.722}{T_r^{5.2}}$$

$$\Rightarrow \frac{dB}{dT} = \frac{R}{P_c}\left(\frac{0.675}{T_r^{2.6}} + \omega\frac{0.722}{T_r^{5.2}}\right)$$

$$= \frac{83.14}{37.96}\left(\frac{0.675}{(1.176)^{2.6}} + 0.2\,\frac{0.722}{(1.176)^{5.2}}\right)$$

$\Rightarrow \beta = 0.09703 \quad ; \quad q = 3.8689$

$$Z = 1 + 0.09703 - (3.8689)(0.09703)\frac{Z - 0.09703}{Z(Z + 0.09703)}$$

by trail and error $Z = 0.6850$

$$\frac{H^R}{RT} = (Z-1) + \left[\frac{d\ln[\alpha(T_r)]}{d\ln(T_r)} - 1\right] q I$$

$$\frac{S^R}{R} = \ln(Z - \beta) + \frac{d\ln[\alpha(T_r)]}{d\ln[T_r]} q I$$

for $\epsilon \neq \sigma \Rightarrow I = \frac{1}{\sigma - \epsilon} \ln\left[\frac{Z + \sigma\beta}{Z + \epsilon\beta}\right]$

$$= 0.13247$$

$\alpha(T_r) = T_r^{-\frac{1}{2}} \Rightarrow \ln[\alpha(T_r)] = \ln(T_r^{-\frac{1}{2}}) = -\frac{1}{2}\ln(T_r)$

$$\Rightarrow \frac{d\ln[\alpha(T_r)]}{d\ln(T_r)} = -\frac{1}{2}$$

$$\Rightarrow \frac{H^R}{RT} = 0.6850 - 1 + (-0.5 - 1)(3.8689)(0.13247)$$
$$= -1.0838$$

$$\frac{S^R}{R} = \ln(0.6850 - 0.09703) - (0.5)(3.8689)(0.13247)$$
$$= -0.78735$$

$$\frac{dB}{dT} = 1.106 \quad \frac{cm^3}{mol \cdot K}$$

$$B = \frac{RT_c}{P_c}\left(B^0 + \omega B^1\right)$$

$$= \frac{(83.14)(425.1)}{37.96}\left(-0.243 + (0.2)\, 0.0519\right)$$

$$= -216.582 \quad \frac{cm^3}{mol}$$

$$\frac{H^R}{RT} = \frac{50}{83.14}\left(\frac{-216.582}{500} - 1.106\right) = -0.926$$

$$\frac{S^R}{R} = -\frac{50}{83.14}\, 1.106 = -0.665$$

$$\Rightarrow H^R = -3849.382 \frac{J}{mol} \quad ; \quad S^R = -5.53 \frac{J}{mol \cdot K}$$

(b) $$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

$$\beta = \Omega \frac{P_r}{T_r} \qquad q = \frac{\Psi\, \alpha(T_r)}{\Omega\, T_r}$$

For R.K. $\alpha(T_r) = T_r^{-\frac{1}{2}}$, $\sigma = 1$, $\epsilon = 0$

$\Omega = 0.08664$, $\Psi = 0.42748$

$$\Rightarrow H^R = -4505 \ \frac{J}{mol}$$

$$S^R = -6.546 \ \frac{J}{mol\text{-}K}$$

(c) $T_r = 1.176$ $P_r = 1.317$ $\omega = 0.2$

For $P_r = 1.2$, $T_r = 1.176$ $\Rightarrow$ $\frac{(H^R)^0}{RT_c} \cong -1.158$ $\frac{(H^R)^1}{RT_c} \cong -0.442$

$(S^R/R)^0 \cong -0.7205$ $(S^R/R)^1 \cong -0.437$

For $P_r = 1.5$, $T_r = 1.176$ $\Rightarrow$ $\frac{(H^R)^0}{RT_c} \cong -1.581$ $\frac{(H^R)^1}{RT_c} \cong -0.434$

$(S^R/R)^0 \cong -1.0080$ $(S^R/R)^1 \cong -0.457$

Therefore, For $P_r = 1.317$ $T_r = 1.176$

by interpolation $\frac{(H^R)^0}{RT_c} = -1.323$ $\frac{(H^R)^1}{RT_c} = -0.439$

$\frac{(S^R)^0}{R} = -0.8326$ $\frac{(S^R)^1}{R} = -0.4448$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} = -1.411$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} = -0.922$$

$$\Rightarrow H^R = -5865.5 \ \frac{J}{mol} \ ; \ S^R = -7.666 \ \frac{J}{mol.K}$$