Example 5.1

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $P(V-b) = RT$

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

$$P(V\text{-}b) = RT \Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$dH = C_p dT + \left(V - \frac{RT}{P} \right) dP = C_p dT + b dP$$

$$\Delta H = \int C_p dT + b(P_2 - P_1)$$

Example 5.2

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $Z = 1 + AP_r / T_r$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(-\frac{AP_r}{T_r^2} \right) \frac{dP_r}{P_r} = AP_r$$

$$\Delta H = \Delta H^{ig} + H_2^R - H_1^R$$

$$= \Delta H^{ig} + A(P_{r2} - P_{r1})RT_c$$

Example 5.3

Derive expressions for H^R, S^R from RK-EOS.

General expressions are:

$$H^R = RT(Z-1) + \int_{V=\infty}^{V} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \qquad ..(1)$$

$$S^R = R \ln Z + \int_{V=\infty}^{V} \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \qquad ..(2)$$

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} = \frac{RT}{V-b} - \frac{a'}{V(V+b)\sqrt{T}} \qquad ..(3)$$

Where, $a' = \dfrac{0.42748R^2 T_C^{2.5}}{P_C}; b = \dfrac{0.08664}{P_C}RT_C$

$$\therefore \ T\left(\dfrac{\partial P}{\partial T}\right)_V - P = T\left[\dfrac{R}{V-b} + \dfrac{a'}{2V(V+b)T^{3/2}}\right]$$

$\therefore$

$$- \left[\dfrac{RT}{V-b} - \dfrac{a'}{V(V+b)T^{1/2}}\right] = \dfrac{3a'}{2V(V+b)T^{1/2}}$$

$$\therefore \ H^R = RT\ (Z-1) + \dfrac{3a'}{2\sqrt{T}}\int\limits_{V=\infty}^{V}\dfrac{dV}{V(V+b)}$$

Putting $Z = PV/RT$ $\qquad \sqrt{\ }$

$$H^R = PV - RT\ -\dfrac{3a}{2b}\ln\left[\dfrac{V+b}{V}\right]$$

Replacing P we get: $H^R = \dfrac{bRT}{(V-b)} - \dfrac{a}{(V+b)} - \dfrac{3a}{2b}\ln\left[\dfrac{V+b}{V}\right]$

Similarly using (2) and (3) one may show:

$$S^R = R\ \ln\dfrac{(PV)}{RT} + R\ln\left(\dfrac{V-b}{V}\right) - \dfrac{a}{2bT}\ln\left(\dfrac{V+b}{V}\right)$$

Example 5.4

Carbon dioxide at upstream conditions $T_1 = 350$ K and $P_1 = 80$ bar is throttled to a downstream pressure of 1.2 bar. Estimate the downstream temperature and ΔS of the gas.

For CO_2: $C_p^{ig}/R = 5.457 + 1.045\times10^{-3}T - \dfrac{1.157}{T^2}\times10^5$

$T_1 = 350K$, $P_1 = 80$ bar, $T_C = 304.2K$, $P_C = 73.8$ bar and $\omega = 0.224$

For the process $H_2 - H_1 = 0$ (Isenthalpic, from energy balance)

Now $H_2 - H_1 = H_2^R - H_1^R + \Delta H^{ig}$ ....(A)

$Tr_1 = T_1/T_c = 1.151$, $Pr_1 = P_1/P_c = 1.084$

If one assume that at 1.2 bar (at exit), the gas is ideal, then:

$H_2^R \simeq 0$; then $\Delta H^{ig} = \int\limits_{T_1}^{T_2}C_p^{ig}dT = H_1^R$ ..... (B)

Use generalized correlations for residual properties, and read from relevant figures for residual properties to find H_1^R at given Tr_1, & Pr_1 and then solve Equation (B) by trial & error to get $T_2 \simeq 280K$

Thus: $\Delta S = S_2^R - S_1^R + \Delta S^{ig} \simeq -S_1^R + \left[C_p \ln \dfrac{T_2}{T_1} - R \ln \dfrac{P_2}{P_1} \right] \simeq 31.5 J / molK$

Example 5.5

Estimate the final temperature and the work required when 1 mol of n-butane is compressed isentropically in a steady-flow process from 1 bar and 50°C to 7.8 bar.

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

$T_1 = 323$ K, $P_1 = 1$ bar, $P_2 = 7.8$ bar

For the process, $\Delta S = 0$

$T_{r2} = 0.76017$, $P_{r2} = 0.2052$,

$P_{r1} = 0.02639$; hence we assume that at state 1 the residual properties are zero as the gas is at ideal state.

For n-butane : $C_p^{ig} / R = 1.9 + 36.9 \times 10^{-3} T - 11.4 \times 10^{-6} T^2$

Using generalized correlations for state 2 and reading from relevant figures for residual properties one finally obtains the following residual property values at '2':

From generalized correction at point '2' $\dfrac{\left(H^R \right)^o}{RT_C} = -0.5679$, $\dfrac{\left(S^R \right)^o}{RT_C} = -0.05210$

$\Delta S = \displaystyle\int_{T_1}^{T_2} C_p \dfrac{dT}{T} - R \ln \dfrac{P_2}{P_1} + S_2^R - S_1^R$

Assume T_2 and solve iteratively with $\Delta S = 0$ to obtain the final value of T_2 which is $= 381K$.

Next use generalized correlation figures for residual enthalpies; whereby at point '2':

$\dfrac{H^R}{RT_c} = -0.30330$

$W = \Delta H = \Delta H^{ig} + RT_c (H_2^R - H_1^R)$

$= \displaystyle\int_{T_1}^{T_2} C_p^{ig} dT + RT_c (H_2^R - H_1^R)$

Finally, $W = 5678$ J/mol

Example 5.6

Calculate the changes in enthalpy and entropy per mole when a mixture of 70 mole % ethylene (1) and 30 mole% propylene (2) at 323K and 10 bar is taken to 60 bar and 600 K using the generalized compressibility factor approach.

$$C_{p1}^{ig} = 4.196 + 154.565 x 10^{-3} T - 81.076 x 10^{-6} T^2 + 16.813 x 10^{-9} T^3 ;$$

$$C_{p2}^{ig} = 3.305 + 235.821 x 10^{-3} T - 117.58 x 10^{-6} T^2 + 22.673 x 10^{-9} T^3$$

Use pure species data to compute those of mixture.

Thus, $T_{c,mix} = \sum y_i T_{ci} = y_i T_{ci} + y_2 T_{c2} = 307.7 \, K$

(1 = ethylene, 2 = Propylene)

Similarly $P_{c,mix} = \sum y_i P_{ci} = 46.619 \, bar$

$$\omega_{mix} = \sum y_i \omega_i = 0.1055$$

At state 1, $T_{r,mix} = \frac{323}{307.7} = 1.05; P_{r,mix} = \frac{10}{49.619} = 0.2$

Now, $\frac{H^R}{RT_c} = \left(\frac{H^R}{RT_c}\right)^0 + \omega \left(\frac{H^R}{RT_c}\right)^1 ; \frac{S^R}{R} = \left(\frac{S^R}{R}\right)^0 + \omega \left(\frac{S^R}{R}\right)^1$

From Tables at given $T_{r,mix}$ and $P_{r,mix}$

$$\left(\frac{H^R}{RT_c}\right)^0 = -0.205; \left(\frac{H^R}{RT_c}\right)^1 = -0.16$$

$$\left(\frac{S^R}{R}\right)^0 = -0.125, \left(\frac{S^R}{R}\right)^1 = -0.145$$

$$\therefore \frac{H^R}{RT_{c,mix}} = -\{0.205 + 0.1055 \, X \, 0.16\} = -0.222$$

$\therefore$ At state 1 $(H^R)_1 = -0.222 \, X \, 8.314 \, X \, 307.7 = -0.568 \frac{KJ}{mol}$

and $\frac{S^R}{R} = -\{0.125 + 0.145 \, X \, 0.1055\} = -0.14$

Thus, $(S^R)_1 = -0.14 \, X \, 8.314 = -1.164 \frac{J}{mol \, K}$ at state 1

Similarly on repeating the calculation for state 2, T = 600K, P = 60 bar, we obtain

$$(H^R)_2 = -0.874 \frac{kJ}{mol}; (S^R)_2 = -1.3 \frac{J}{mol \, K}$$

Now, $H_2 - H_1 = (H^R)_2 - (H^R)_1 + \Delta H^{ig}$

$\Delta H^{ig} = \int_{T_1}^{T_2} (\sum y_i C_{pi}^{ig}) dT ; where \, C_{pi}^{ig} = a + bT + cT^2 + dT^3 (\frac{kJ}{mol})$

Thus, $\Delta H^{ig} = \int_{T_1}^{T_2} (\Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3) dT$

Where, $\Delta a = \sum y_i a_i$; $\Delta b = \sum y_i b_i$; $\Delta c = \sum y_i c_i$; $\Delta d = \sum y_i d_i$

For component 1,

$$C_{P_1}^{ig} = 4.196 + 154.565 \ X \ 10^{-3} \ T - 81.076 \ X \ 10^{-6}T^2 + 16.183 \ X \ 10^{-9} \ T^3$$

Similarly,

$$C_{P_2}^{ig} = 3.305 + 235.821 \ X \ 10^{-3} \ T - 117.58 \ X \ 10^{-6}T^2 + 22.673 \ X \ 10^{-9} \ T^3$$

$\therefore \Delta a = 0.7 \ X \ 4.196 + 0.3 \ X \ 3.305 = 3.9287$

Similarly, $\Delta b = 70.7463 \ X \ 10^{-3}$; $\Delta c = -92.0272 \ X \ 10^{-6}$ and $\Delta d = 18.571 \ X \ 10^{-9}$

Hence, $\Delta H^{ig} = \int_{T_1}^{T_2}(\Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3)dT = 5.091 \ kJ/mol$

$$\therefore H_2 - H_1 = (H^R)_2 - (H^R)_1 + \Delta H^{ig} = -0.874 - (-0.568) + 5.091 = 4.785 \ kJ/mol$$

$$S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig}$$

Now, $\Delta S^{ig} = \int_{T_1}^{T_2} C_{p,mix}dT/T - Rln \ P_2/P_1$

$$= \int_{T_1}^{T_2}(\Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3)\frac{dT}{T} - Rln(\frac{60}{10})$$

Final answer on substitution of all parameters

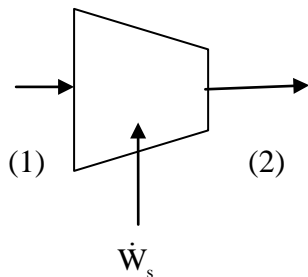$$\Delta S^{ig} = -3.502 \frac{J}{mol \ K}$$

$$S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig} = -1.3 - (-1.164) - 3.502 = -3.638 \frac{J}{mol \ K}$$

Example 5.7

A certain gas is compressed adiabatically from 293 K and 135 KPa to 550 KPa. What is the work needed? What is the final T_2? Assume ideal gas behavior. Compressor $\eta = 0.8$.

For the gas: $C_p{}^{ig} = 1.65 + 8.9 \ x \ 10^{-3}T - 2.2 \ x \ 10^{-6} \ T^2$

For rev. process $\Delta S = S_2 - S_1 = 0$

Flow process thus lead to:

$$\Delta S = \int_{T_1}^{T_2} C_p^{ig} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dP}{P} \quad \therefore \Delta$$

(1)   (2)

$\dot{W}_s$

$$\therefore \int_{293}^{T_2} (1.65 + 8.9 \ x \ 10^{-3} \ T - 2.2 \ x \ 10^{-6} \ T^2) \frac{dT}{T} = 8.314 \ ln \left(\frac{550}{135}\right)$$

$\Rightarrow T_2{}^{reversible}$ (by iteration) $\simeq$ 395 K

By first Law $Q (=0) + W_s = \Delta H$

$\therefore W_s$ (isentropic, reversible) $= H_2 - H_1 = \int\limits_{T_1}^{T_2} C_p^{ig} \, dT$

$\therefore W_S^{reversible} = \int\limits_{293}^{395} [1.65 + 8.9 \text{ x } 10^{-3}T - 2.2 \text{ x } 10^{-6}T^2) \, dT \simeq 3960$ J/mol.

$\therefore$ Thus actual work needed $= W_S^{rev}/\eta$

$\qquad\qquad\quad = 3960/0.8 = 4950$ J/mol

$\therefore W_S^{rev} = \Delta H = \int\limits_{T_1}^{T_2} C_p^{ig} \, dT$

$\therefore 4950 = \int\limits_{293}^{T_2^{irrev}} [1.65 + 8.9 \text{ x } 10^{-3}T - 2.2 \text{ x} 10^{-6}T^2] \, dT$

$\qquad\qquad \Rightarrow T_2$ (actual) $\simeq 420^{o}K \Rightarrow 147^{o}C$