10.213 PROBLEM 6 SOLUTION

a) - Assume we have an ideal gas at 1 atm. Also assume we have a mechanically reversible, non-flow process. Since pressure is constant,

$$dH = C_p dT + \cancel{\left(\frac{\partial H}{\partial P}\right)_T dP}^{\,0}$$

$$\text{and} \quad \Delta H = \int_{T_0}^{T} C_p dT = Q/n \qquad [J/mol]$$

$$\text{thus} \quad Q = n\Delta H = n\int_{T_0}^{T} C_p dT$$

- We can rewrite this as shown in S+VN to get it into a form that uses an average heat capacity; $\langle C_p \rangle_H$

so,

$$Q = n[\Delta H] = n\left[\langle C_p \rangle_H (T - T_0)\right] \qquad (S+VN,\ 4.9)$$

- S+VN also gives us the formula for $\left[\frac{\langle C_p \rangle_H}{R}\right]$ when C_p^{IG} is of the form $C_p^{IG}/R = A + BT + CT^2 + D/T^2$. Namely:

$$\boxed{\frac{\langle C_p \rangle_H}{R} = A + \frac{B}{2}T_0(\tau + 1) + \frac{C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2}} \qquad (S+VN,\ 4.8) \quad \text{①}$$

$$(\tau = T/T_0)$$

- So,

$$\boxed{Q = n\Delta H = nR\left[\frac{\langle C_p \rangle_H}{R}\right](T - T_0)} \qquad \text{②}$$

- Thus we calculate $\left[\frac{\langle C_p \rangle_H}{R}\right]$ from ① and use it in ② to calculate the heat required.

From APP C., Table C.1 for propane:

$\underline{C_3H_8:}$

$$A = 1.213$$
$$B = 28.785 \times 10^{-3}\ K^{-1}$$
$$C = -8.824 \times 10^{-6}\ K^{-2}$$
$$D = 0$$

and $\tau = T/T_0 = \left(\frac{1200 + 273.15K}{250 + 273.15K}\right) = 2.8159$

so, from ①: $\frac{\langle C_p \rangle_H}{R} = A + \frac{B}{2} T_0 (\tau + 1) + \frac{C}{3} T_0^2 (\tau^2 + \tau + 1) + \cancel{\frac{D}{\tau T_0^2}}^{\,0}$

$$= (1.213) + \frac{(2.879 \times 10^{-2})}{2}(523.15)(2.8159 + 1) + \left(\frac{-8.824 \times 10^{-6}}{3}\right)(523.15)^2(2.8159^2 + 2.8159 + 1)$$

$$= (1.213) + (28.7366) + (-9.4549)$$

$$= \underline{20.4947} \quad \text{[dimensionless]}$$

thus, from ②:

$$Q = n\Delta H = nR\left[\frac{\langle C_p \rangle_H}{R}\right](T - T_0)$$
$$= (12\ \cancel{mol})(20.4947)(8.314\ J/\cancel{mol}\cdot\cancel{K})(1473.15 - 523.15\ \cancel{K})$$
$$= \underline{\underline{1,942.48\ kJ}}$$

(NOTE: Very similar to example 4.2 in S+VN)

b) (NOTE : See example 4.3 in S+VN)

- Now in this case we do not know T. Since $\frac{\langle C_p \rangle_H}{R}$ depends on T (via $\tau = T/T_0$), we must use an iterative scheme to find T. I use the one suggested by S+VN (pg. 122, eqn. (4.10)). Other variations are possible.

- From ② we know that:

$$\underbrace{Q}_{\text{known} = 800\,\text{kJ}} = n\Delta H = \underbrace{nR}_{\text{known}} \underbrace{\left[\frac{\langle C_p \rangle_H}{R}\right]}_{\text{unknown} = f(T)} \underbrace{(T - T_0)}_{\text{unknown} = f(T)}$$

- Rearranging,

$$T = \frac{\{Q/nR\}}{\left[\frac{\langle C_p \rangle_H}{R}\right]} + T_0 \qquad \text{③}$$

- Or in the terminology we will use for iteration,

$$\boxed{T_{i+1} = \frac{\overbrace{\{Q/nR\}}^{\text{known.}}}{\underbrace{\left[\frac{\langle C_p \rangle_H}{R}\right]_{\tau_i}}} + T_0} \qquad \text{③}$$

This is our next guess for T.

This means we evaluate this at $\tau_i = T_i/T_0$.

(Also see S+VN (4.10) for this equation)

- Since $\{Q/nR\}$ is known in this case, we can generate a scheme in which we keep finding better guesses for T until such time as we satisfy some convergence criteria, eg

$$\frac{T_{i+1} - T_i}{T_i} < \epsilon$$

some small number eg 10^{-3}

– So, our scheme is as follows:

(i) Make a first guess, $T_1 = 400°C = 673.15\,K$ say

(ii) Calculate $\tau_i = \frac{T_i}{T_0}$

and $\left[\frac{\langle C_p \rangle_H}{R}\right]_{\tau_i}$ using ①

ITERATE

(iii) Calculate next guess, T_{i+1} from:

$$T_{i+1} = \frac{Q/nR}{\left[\frac{\langle C_p \rangle_H}{R}\right]_{\tau_i}} + T_0 \quad \text{using ③}$$

(iv) Check for convergence

$$\frac{T_{i+1} - T_i}{T_i} < \epsilon$$

YES → go to step (v)

NO → go to step (ii) with $T_i = T_{i+1}$

(v) If convergence criteria met, STOP

– I did mine on spreadsheet, as shown below:

Ethylene (Table C.1, S&VN)

A = 1.424
B = 1.439E-02 K^{-1}
C = -4.392E-06 K^{-2}
D = ---

– Final temp,

$T = 1374.5\,K$
$= \underline{1{,}101.3\,°C}$

n = 10 mol
To = 473.15 K
R = 8.314 J/mol*K

$\Delta H = Q/n = 800/10 =$ 80000 J/mol

CALCULATE: $\tau_1 = T_1/T_0$

CALCULATE: $\langle C_p \rangle_H/R$ at τ_1

FIRST GUESS: $T_1 = 400°C$

NEXT GUESS: $T_2 = T_0 + \Delta H/[R^*[\langle C_p \rangle_H/R]]$ with: [<Cp>H/R] at τ_1 from above

T_1 [K]	τ_1 (=T_1/To) [--]	$\langle C_p \rangle_H/R$ (at τ_1) [--]
673.15	1.423	8.217
1644.25	3.475	11.238
1329.37	2.810	10.561
1384.28	2.926	10.700
1372.44	2.901	10.671
1374.90	2.906	10.677
1374.39	2.905	10.676
1374.49	2.905	10.676
1374.47	2.905	10.676
1374.48	2.905	10.676
1374.47	2.905	10.676
1374.47	2.905	10.676

STOP ITERATION

c) – So,
$$\frac{C_p^{IG}}{R} = A + BT + CT^2$$

– Now, from S+VN (4.8) we know that:

$$\frac{\langle C_p \rangle_H}{R} = A + \frac{B}{2} T_1 (1+\tau) + \frac{C}{3} T_1^2 (\tau^2 + \tau + 1) \quad \text{— ①}$$

– where $\tau = T_2/T_1$

– Let's call C_p^{IG} evaluated at the arithmetic mean temp, $\frac{T_1+T_2}{2}$, C_p^*. Thus, with $T_2 = \tau T_1$, we have:

$$\begin{aligned}
\frac{C_p^*}{R} &= A + B\left(\frac{T_1+T_2}{2}\right) + C\left(\frac{T_1+T_2}{2}\right)^2 \\
&= A + \frac{B}{2}\left(T_1 + \tau T_1\right) + \frac{C}{4}\left(T_1 + \tau T_1\right)^2 \\
&= A + \frac{B}{2} T_1 (1+\tau) + \frac{C}{4} T_1^2 (1+\tau)^2 \\
&= A + \frac{B}{2} T_1 (1+\tau) + \frac{C}{4} T_1^2 (\tau^2 + 2\tau + 1) \quad \text{— ④}
\end{aligned}$$

– The difference, Δ, is:

$$\begin{aligned}
\Delta &= \frac{\langle C_p \rangle_H}{R} - \frac{C_p^*}{R} \\
&= \frac{C}{3} T_1^2 (\tau^2 + \tau + 1) - \frac{C}{4} T_1^2 (\tau^2 + 2\tau + 1) \\
&= C T_1^2 \, \frac{4\tau^2 + 4\tau + 4 - 3\tau^2 - 6\tau - 3}{12} \\
&= C T_1^2 \, \frac{\tau^2 - 2\tau + 1}{12} \\
&= \frac{C T_1^2}{12} (\tau - 1)^2 \\
&= \frac{C T_1^2}{12} \left(\frac{T_2}{T_1} - 1\right)^2 \\
&= \frac{C \cancel{T_1^2}}{12} \frac{(T_2 - T_1)^2}{\cancel{T_1^2}} \\
&= \underline{\underline{C (T_2 - T_1)^2 / 12}}
\end{aligned}$$

d) - From c)

$$\Delta = \left| \frac{\langle C_p \rangle_H}{R} - \frac{C_p^*}{R} \right| = C(T_2 - T_1)^2/12 \qquad \text{(5)}$$

- For the conditions in a)

$$\Delta = \left| (-8.824 \times 10^{-6})(1473.15 - 523.15)^2/12 \right|$$

$$= \underline{0.6636}$$

- For the calculation in a),

$$\% \text{ diff} = 100 \left| \frac{\langle Q \rangle_H - Q^*}{\langle Q \rangle_H} \right|$$

where : $\langle Q \rangle_H$ = Q calculated using $\langle C_p \rangle_H$

Q^* = Q calculated using C_p^*

$$= 100 \left| \frac{\cancel{nR} \left[\frac{\langle C_p \rangle_H}{R} \right] \cancel{(T - T_0)} - \cancel{nR} \left[\frac{C_p^*}{R} \right] \cancel{(T - T_0)}}{\cancel{nR} \left[\frac{\langle C_p \rangle_H}{R} \right] \cancel{(T - T_0)}} \right|$$

$$= 100 \left| \frac{\left[\frac{\langle C_p \rangle_H}{R} \right] - \left[\frac{C_p^*}{R} \right]}{\left[\frac{\langle C_p \rangle_H}{R} \right]} \right|$$

$$= 100 \left| \frac{\Delta}{\left[\frac{\langle C_p \rangle_H}{R} \right]} \right|$$ from part (a)

$$= 100 \left(\frac{0.6636}{20.495} \right)$$

$$= \underline{\underline{3.2\ \%}}$$