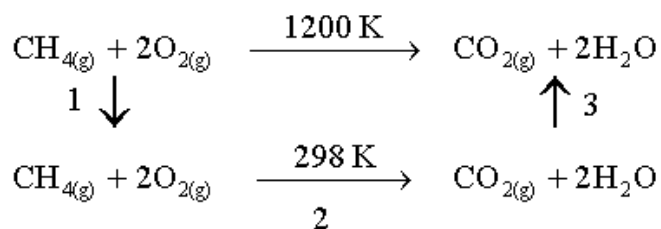


Chemistry 2720 Fall 2001 Test 1 Solutions

1. The best way to do this question is to imagine that the reaction is carried out isothermally at 25°C, the heat generated being drawn out as the reaction proceeds to maintain a constant temperature, and then the heat is added back to warm up the products. The net heat is zero since the system is adiabatic:

$$\begin{aligned}
 q = 0 &= \left\{ \begin{array}{l} \text{heat of} \\ \text{reaction} \end{array} \right\} + \left\{ \begin{array}{l} \text{heating of} \\ \text{products} \end{array} \right\} \\
 &= \Delta \bar{H}_{\text{rxn}}^{\circ} + \bar{C}_{P(\text{BrF}_5)} \Delta T. \\
 \therefore \Delta T &= -\frac{\Delta \bar{H}_{\text{rxn}}^{\circ}}{\bar{C}_{P\text{BrF}_5}}. \\
 \Delta \bar{H}_{\text{rxn}}^{\circ} &= \Delta \bar{H}_{f(\text{BrF}_5)}^{\circ} - \Delta \bar{H}_{f(\text{BrF}_3)}^{\circ} \\
 &= -428.8 - (-255.60) \text{ kJ/mol} = -173.2 \text{ kJ/mol}. \\
 \therefore \Delta T &= \frac{173.2 \times 10^3 \text{ J/mol}}{99.62 \text{ J K}^{-1} \text{ mol}^{-1}} = 1739 \text{ K}. \\
 \therefore T_f &= 1739 + 25^{\circ}\text{C} = 1764^{\circ}\text{C}.
 \end{aligned}$$

2. (a) We can easily calculate the enthalpy of combustion at 298 K. We will need to adjust this enthalpy to 1200 K as follows:



$$\begin{aligned}
 \Delta \bar{H}_1 &= (\bar{C}_{P(\text{CH}_4)} + 2\bar{C}_{P(\text{O}_2)}) \Delta T_1 \\
 &= [35.31 + 2(29.35) \text{ J K}^{-1} \text{ mol}^{-1}] (298 - 1200 \text{ K}) \\
 &= -84.8 \text{ kJ/mol}. \\
 \Delta \bar{H}_2 &= \Delta \bar{H}_{f(\text{CO}_2)}^{\circ} + 2\Delta \bar{H}_{f(\text{H}_2\text{O})}^{\circ} - \Delta \bar{H}_{f(\text{CH}_4)}^{\circ} \\
 &= -393.51 + 2(-241.826) - (-74.81) \text{ kJ/mol} \\
 &= -802.35 \text{ kJ/mol}. \\
 \Delta \bar{H}_3 &= (\bar{C}_{P(\text{CO}_2)} + 2\bar{C}_{P(\text{H}_2\text{O})}) \Delta T_3 \\
 &= [37.1 + 2(33.58) \text{ J K}^{-1} \text{ mol}^{-1}] (1200 - 298 \text{ K})
 \end{aligned}$$

$$\begin{aligned}
&= 94.0 \text{ kJ/mol.} \\
\therefore \Delta \bar{H}_{1200\text{K}} &= \Delta \bar{H}_1 + \Delta \bar{H}_2 + \Delta \bar{H}_3 \\
&= -793.1 \text{ kJ/mol.}
\end{aligned}$$

- (b) The heat capacities of the reactants and products were assumed to be independent of temperature. However, over the large temperature range studied (over 900 K), this is not a particularly good approximation.
- (c) The heat at constant volume is the change in internal energy.

$$\begin{aligned}
E &= H - PV. \\
\therefore \Delta E &= \Delta \bar{H} - \Delta(P\bar{V}) \\
&\approx \Delta \bar{H} - RT\Delta \bar{n}_{\text{gas}}.
\end{aligned}$$

From the balanced reaction, we have $\Delta \bar{n}_{\text{gas}} = 3 - 3 = 0$. Thus $\Delta \bar{E} \approx \Delta \bar{H} = -793.1 \text{ kJ/mol}$.

3. The entropy of the vapor can be calculated by

$$\bar{S}_{\text{g}}(800 \text{ K}) = \bar{S}_1(298.15 \text{ K}) + \Delta \bar{S}_{1(298.15 \rightarrow 337.22 \text{ K})} + \Delta \bar{S}_{\text{vap}} + \Delta \bar{S}_{\text{g}(337.22 \rightarrow 800 \text{ K})}.$$

All we have to do is to calculate the three $\Delta \bar{S}$ terms.

$$\begin{aligned}
\Delta \bar{S}_{1(298.15 \rightarrow 337.22 \text{ K})} &= \int_{298.15}^{337.22} \frac{d\bar{q}_{\text{rev}}}{T} = \int_{298.15}^{337.22} \frac{\bar{C}_p dT}{T} \\
&= (81.6 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{337.22}{298.15} \right) = 10.0 \text{ J K}^{-1} \text{ mol}^{-1}. \\
\Delta \bar{S}_{\text{vap}} &= \int \frac{d\bar{q}_{\text{rev}}}{T} = \frac{1}{T} \int d\bar{q}_{\text{rev}} = \frac{\bar{q}_{\text{rev}}}{T} = \frac{\Delta \bar{H}_{\text{vap}}}{T} = \frac{35270 \text{ J/mol}}{337.22 \text{ K}} \\
&= 104.59 \text{ J K}^{-1} \text{ mol}^{-1}. \\
\Delta \bar{S}_{\text{g}(337.22 \rightarrow 800 \text{ K})} &= (43.9 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{800}{337.22} \right) = 37.9 \text{ J K}^{-1} \text{ mol}^{-1}. \\
\therefore \bar{S}_{\text{g}}(800 \text{ K}) &= 126.8 + 10.0 + 104.59 + 37.9 \text{ J K}^{-1} \text{ mol}^{-1} \\
&= 279.4 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}$$

4. (a) The efficiency is

$$\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} = 1 - \frac{120 + 273.15 \text{ K}}{500 + 273.15 \text{ K}} = 0.491.$$

The heat input requirement is therefore

$$q_{\text{in}} = -\frac{w}{\eta} = \frac{440 \text{ MW}}{0.491} = 895 \text{ MW}.$$

The heat is produced by burning natural gas:

$$V = \frac{895 \times 10^6 \text{ J/s}}{37.0 \times 10^3 \text{ J/m}^3} = 2.42 \times 10^4 \text{ m}^3/\text{s}.$$

There are $3600 \text{ s/h} \times 24 \text{ h} = 8.64 \times 10^4 \text{ s}$ in a day. The natural gas consumption per day is therefore $8.64 \times 10^4 \text{ s} \times 2.42 \times 10^4 \text{ m}^3/\text{s} = 2.09 \times 10^9 \text{ m}^3$ (2.09 billion cubic meters).

(b) The heat input is 895 MW. The work output is 440 MW. Heat is therefore ejected at a rate of $895 - 440 \text{ MW} = 455 \text{ MW}$.

(c)

$$V = \frac{455 \times 10^6 \text{ J/s}}{37.0 \times 10^3 \text{ J/m}^3} = 1.23 \times 10^4 \text{ m}^3/\text{s} \equiv 1.06 \times 10^9 \text{ m}^3/\text{day}.$$

(d) Suppose that we only get 30% efficiency from the electrical generator. We'll have to use more fuel to generate the same amount of electricity. However, the extra heat generated by burning the additional fuel is used. Provided we actually have a use for this extra heat, i.e. provided the heat will be used to replace heating by other means, the efficiency of the generator actually makes very little difference to the economic efficiency of this process. By contrast, if the heat isn't recovered then the extra fuel burned is just wasted.