

1. For the hydrogen peroxide decomposition reaction $\text{H}_2\text{O}_2(l) = \text{H}_2\text{O}(l) + \frac{1}{2} \text{O}_2(g)$:

[10]

- Calculate q , w , ΔU° and ΔH° for the reaction at 25 °C and 1.00 bar.
- Calculate q , w , ΔU and ΔH for the reaction at 25 °C in a bomb calorimeter.
- Does ΔH° increase if the temperature is raised? Justify your answer.
- Does ΔH increase if the pressure is raised? Justify your answer.

Data at 25 °C, 1.00 bar:

$$\begin{aligned}\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}_2, l) &= -187.78 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l) &= -285.830 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) &= -241.818 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{O}_2, g) &= 0\end{aligned}$$

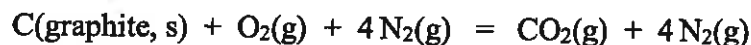
$$\begin{aligned}C_{\text{pm}}^\circ(\text{H}_2\text{O}_2, g) &= 89.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{H}_2\text{O}, l) &= 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{H}_2\text{O}, g) &= 33.577 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{O}_2, g) &= 29.355 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

2. Why is it necessary to include the heat capacity of N_2 in the calculation of adiabatic flame temperatures if air is the source of oxygen for combustion?

[1]

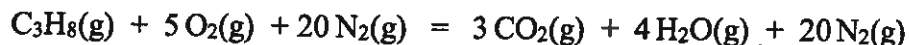
3. Which is hotter, a charcoal barbecue or a propane barbecue?

a) Calculate the adiabatic flame temperature for burning charcoal (assumed to be pure graphite) in air (four moles of N_2 per mole of O_2) at 1.00 bar:



[8]

b) Calculate the adiabatic flame temperature for burning propane in air at 1.00 bar:



Assume the initial temperature is 25 °C the heat capacities are constant.

Data at 25 °C, 1.00 bar:

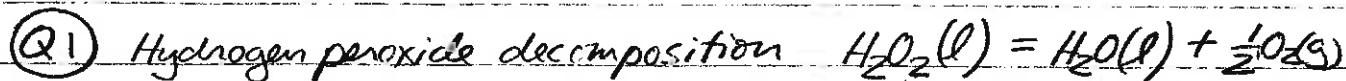
$$\begin{aligned}\Delta H_{\text{fm}}^\circ(\text{CO}_2, g) &= -393.509 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{C}_3\text{H}_8, g) &= -103.89 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) &= -241.818 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{N}_2, g) &= 0 \\ \Delta H_{\text{fm}}^\circ(\text{O}_2, g) &= 0\end{aligned}$$

$$\begin{aligned}C_{\text{pm}}^\circ(\text{CO}_2, g) &= 37.11 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{C}_3\text{H}_8, g) &= 73.51 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{H}_2\text{O}, g) &= 33.577 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{N}_2, g) &= 29.125 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^\circ(\text{O}_2, g) &= 29.355 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

4. Barbecuing using pure oxygen instead of air would *destroy* a barbecue! Why?

[1]

$$\Delta n_{\text{gas}} = +\frac{1}{2} \text{ mol}$$



a) at 25°C and 1.00 bar Reaction at Constant Pressure

Products and reactant are in their standard states
(pure and at $p^\circ = 1 \text{ bar}$ standard pressure), so

$$\begin{aligned} \Delta H &= \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants}) \\ &= (1 \text{ mol}) \Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) + \left(\frac{1}{2} \text{ mol}\right) \Delta H_f^\circ(\text{O}_2, \text{g}) - (1 \text{ mol}) \Delta H_f^\circ(\text{H}_2\text{O}_2, \text{l}) \\ &= (1 \text{ mol}) (-285.830 \text{ kJ mol}^{-1}) + \left(\frac{1}{2} \text{ mol}\right) (0) - (1 \text{ mol}) (-187.78 \text{ kJ mol}^{-1}) \end{aligned}$$

(O₂ is a pure element in its standard state)

$$\Delta H = -98.05 \text{ kJ}$$

$$q = \Delta H = -98.05 \text{ kJ}$$

Why?
(pressure is constant)
 $p_{\text{ext}} = p = p^\circ$

$$w = -\int p_{\text{ext}} dV = -p \int dV = -p \Delta V$$

$$= -p (V(\text{products}) - V(\text{reactants}))$$

(liquid molar volumes negligible)

$$= -p \left[(1 \text{ mol}) V_m(\text{H}_2\text{O}, \text{l}) + \left(\frac{1}{2} \text{ mol}\right) V_m(\text{O}_2, \text{g}) - (1 \text{ mol}) V_m(\text{H}_2\text{O}_2, \text{l}) \right]$$

$$= -p \left(\frac{1}{2} \text{ mol}\right) V_m(\text{O}_2, \text{g}) = -p \left(\frac{1}{2} \text{ mol}\right) \frac{RT}{p} = -\left(\frac{1}{2} \text{ mol}\right) RT$$

$$w = -\left(\frac{1}{2} \text{ mol}\right) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K}) = -1239 \text{ J}$$

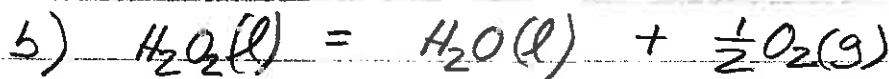
$$\begin{aligned} \Delta U &= q + w \\ &= -98.05 - 1.24 \\ &= -99.29 \text{ kJ} \end{aligned}$$

Reaction at Constant Pressure

$$\Delta H_p = q_p \quad w_p = -RT \Delta n_g$$

$$\Delta U_p = \Delta H_p - RT \Delta n_g = q_p + w_p$$

(Q1 cont.)



thick walls

at 25 °C in a "bomb" calorimeter (constant volume)
($dV=0$)

$$w_v = -\int P_{\text{ext}} dV \rightarrow 0$$

$$w_v = 0$$

To calculate ΔU_v , compress the reaction products at constant pressure (part a) back to the initial volume of the reactant, isothermally (25 °C).

Isothermal compression of $\frac{1}{2}\text{O}_2(g)$ (assumed an ideal gas)

\Rightarrow no change in internal energy

\Rightarrow no change in enthalpy

$$\Delta U_v = \Delta U_p = -99.29 \text{ kJ}$$

$$\Delta H_v = \Delta H_p = -98.05 \text{ kJ}$$

$$q_v = \Delta U_v - w_v = -99.29 \text{ kJ}$$

(notice $q_v \neq \Delta H_v$
(P not constant))

$$c) \Delta C_p^\circ = \sum_i \nu_i C_{p,m}^\circ = (1 \text{ mol}) C_{p,m}^\circ(\text{H}_2\text{O}, l) + \left(\frac{1}{2} \text{ mol}\right) C_{p,m}^\circ(\text{O}_2, g) - (1 \text{ mol}) C_{p,m}^\circ(\text{H}_2\text{O}_2, l)$$

$$= (75.291 + \frac{1}{2} 29.355 - 89.1) \frac{\text{J}}{\text{K}} = \boxed{+0.87 \frac{\text{J}}{\text{K}}}$$

$$\boxed{d\Delta H^\circ/dT = \Delta C_p^\circ > 0}$$

ΔH° increases with T
very small

$$d) \Delta V = \sum_i \nu_i V_{m,i} = (1 \text{ mol}) V_m(\text{H}_2\text{O}, l) + \left(\frac{1}{2} \text{ mol}\right) V_m(\text{O}_2, g) - (1 \text{ mol}) V_m(\text{H}_2\text{O}_2, l)$$

$$= \left(\frac{1}{2} \text{ mol}\right) V_m(\text{O}_2, g) = \left(\frac{1}{2} \text{ mol}\right) \frac{RT}{P} > 0$$

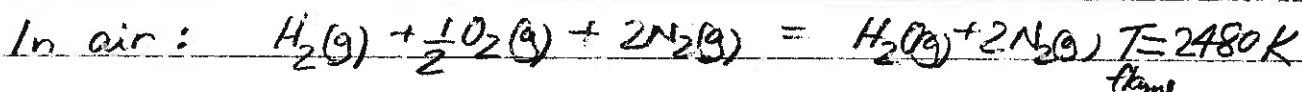
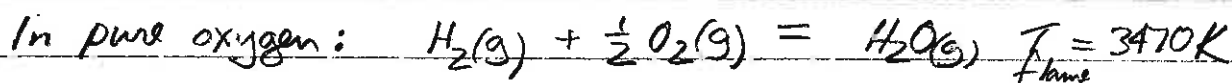
$$\boxed{\left(\frac{\partial \Delta H}{\partial P}\right)_T = \Delta V > 0}$$

ΔH increases with P

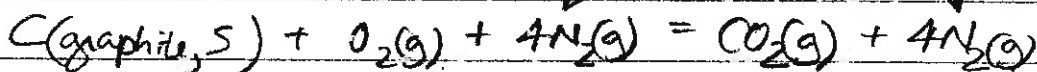
Q2 For every mole of O_2 in (air approximately 20 mol% O_2) there are four moles of inert N_2 .

If air is used as the source of oxygen for a combustion reaction, the flame includes N_2 , which increases the heat capacity and reduces the adiabatic flame temperature.

Example



Q3 a) Adiabatic flame temperature for the combustion of graphite in air.



$$\Delta H^\circ(25^\circ C) = (1 \text{ mol}) \Delta H_{\text{fm}}^\circ(CO_2, g) - (1 \text{ mol}) \Delta H_{\text{fm}}^\circ(C, \text{graph.}) - (1 \text{ mol}) \Delta H_{\text{fm}}^\circ(O_2, g)$$

inert N_2 makes no contribution to ΔH°

$$= (1 \text{ mol}) (-393.509) \text{ kJ mol}^{-1} = -393.509 \text{ kJ}$$

$$C_p(\text{products}) = (1 \text{ mol}) C_{\text{pm}}^\circ(CO_2, g) + (4 \text{ mol}) C_{\text{pm}}^\circ(N_2, g)$$

N_2 does contribute to $C_p(\text{prod.})$

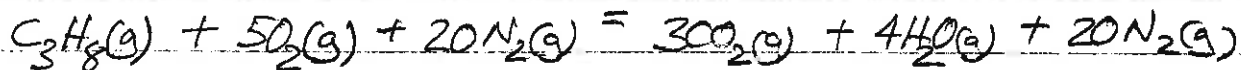
$$= (1 \text{ mol}) (37.11 \frac{\text{J}}{\text{K mol}}) + (4 \text{ mol}) (29.125 \frac{\text{J}}{\text{K mol}}) = 153.61 \frac{\text{J}}{\text{K}}$$

$$T_{\text{flame}} = T_i - \frac{\Delta H^\circ(T_i)}{C_p(\text{prod.})} = 298.15 K - \frac{(-393509 \text{ J})}{153.61 \frac{\text{J}}{\text{K}}} = (298.15 + 2562) K$$

$$T_{\text{flame}} = 2860 K$$

(Q3 cont.)

b) Adiabatic flame temperature for the combustion of propane in air



$$\begin{aligned}\Delta H^\circ(25^\circ\text{C}) &= (3\text{mol})\Delta H_{\text{fm}}^\circ(\text{CO}_2\text{g}) + (4\text{mol})\Delta H_{\text{fm}}^\circ(\text{H}_2\text{Og}) - (1\text{mol})\Delta H_{\text{fm}}^\circ(\text{C}_3\text{H}_8\text{g}) \\ &\quad - (5\text{mol})\Delta H_{\text{fm}}^\circ(\text{O}_2\text{g}) \\ &= (3\text{mol})\left(-393.509 \frac{\text{kJ}}{\text{mol}}\right) + (4\text{mol})\left(-241.818 \frac{\text{kJ}}{\text{mol}}\right) \\ &\quad - (1\text{mol})\left(-103.89 \frac{\text{kJ}}{\text{mol}}\right) - (5\text{mol})(0)\end{aligned}$$

$$\Delta H^\circ(25^\circ\text{C}) = -2043.909 \text{ kJ} \quad (\text{inert N}_2 \text{ ignored, no reaction } \Delta H)$$

$$\begin{aligned}C_p^\circ(\text{products}) &= (3\text{mol})C_{\text{pm}}^\circ(\text{CO}_2\text{g}) + (4\text{mol})C_{\text{pm}}^\circ(\text{H}_2\text{Og}) + (20\text{mol})C_{\text{pm}}^\circ(\text{N}_2\text{g}) \\ &= (3\text{mol})\left(37.11 \frac{\text{J}}{\text{Kmol}}\right) + (4\text{mol})\left(33.571 \frac{\text{J}}{\text{Kmol}}\right) + (20\text{mol})\left(29.125 \frac{\text{J}}{\text{Kmol}}\right)\end{aligned}$$

$$C_p^\circ(\text{products}) = 828.138 \text{ J K}^{-1}$$

$$T_{\text{flame}} = T_i - \frac{\Delta H^\circ(25^\circ\text{C})}{C_p(\text{products})}$$

$$= 298.15 \text{ K} - \frac{-2043909 \text{ J}}{828.138 \text{ J K}^{-1}} = (298.15 + 2468) \text{ K}$$

$$T_{\text{flame}} = 2770 \text{ K}$$

(Q4) Burning charcoal or propane in pure oxygen instead of air generates much higher temperatures.

(Why? No inert N₂, lower heat capacity of the flame.)
Melt the barbecue! (And probably burn down the deck and house)