

*This assignment is optional. You lose no marks if you don't hand it in. *Happy Thanksgiving.*

1. For the reaction $2\text{Al (s)} + 3/2 \text{O}_2\text{(g)} = \text{Al}_2\text{O}_3\text{(s)}$:

a) Calculate q , w , ΔU and ΔH at 25 °C and 1.00 bar.

b) Calculate q , w , ΔU and ΔH at 500 °C and 1.00 bar. Use $\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ(T) dT$

c) Calculate q , w , ΔU and ΔH at 25 °C and 500.0 bar. Use $\Delta H(T, p_2) = \Delta H^\circ(T) + \int_{p^\circ}^{p_2} \Delta V(T, p) dp$

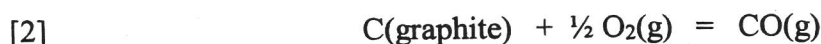
[12] Data at 25 °C, 1.00 bar: $\Delta H_{\text{fm}}^\circ(\text{Al}_2\text{O}_3, \text{s}) = -1675.7 \text{ kJ mol}^{-1}$ $C_{\text{pm}}^\circ(\text{Al}, \text{s}) = 24.35 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{Al}, \text{s}) = 0$ $C_{\text{pm}}^\circ(\text{O}_2, \text{g}) = 29.36 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{O}_2, \text{g}) = 0$ $C_{\text{pm}}^\circ(\text{Al}_2\text{O}_3, \text{s}) = 79.04 \text{ J K}^{-1} \text{ mol}^{-1}$

2. According to the data provided for the previous question, the standard enthalpies of formation of Al(s) and O₂(g) are both zero. Why?
[1]

3. Aluminum metal initially at 25 °C is burned [$2\text{Al(s)} + 3/2 \text{O}_2\text{(g)} = \text{Al}_2\text{O}_3\text{(s)}$] at 1.00 bar pressure using pure oxygen. Calculate the adiabatic flame temperature.
[3]

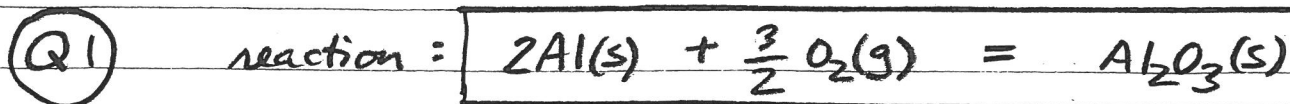
4. Adiabatic flame temperatures for combustion reactions using pure oxygen are significantly higher than adiabatic flame temperatures for combustion in air. Why?
[1]

5. It is difficult to directly measure the enthalpy change for the reaction



due to the very favorable side reaction $\text{C(graphite)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$. Describe an indirect procedure for the accurate measurement of ΔH for the reaction $\text{C(graphite)} + 1/2 \text{O}_2\text{(g)} = \text{CO(g)}$.

6. Enthalpy changes for chemical reactions involving only liquids and solids are almost independent of pressure. Why?
[1]



Data: $\Delta H_{fm}^\circ(\text{Al}_2\text{O}_3) = -1675.7 \text{ kJ mol}^{-1}$

$$C_{pm}^\circ(\text{Al}_2\text{O}_3, s) = 79.04 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{pm}^\circ(\text{Al}, s) = 24.35 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{pm}^\circ(\text{O}_2, g) = 29.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

a) At 25 °C and 1 bar ($p^\circ = 1 \text{ bar} = \text{standard pressure}$)

$$\begin{aligned} \Delta H^\circ &= \Delta H_{fm}^\circ(\text{Al}_2\text{O}_3, s) - 2\Delta H_{fm}^\circ(\text{Al}, s) - \frac{3}{2}\Delta H_{fm}^\circ(\text{O}_2, g) \\ &= -1675.7 \text{ kJ mol}^{-1} - 2(0) - \frac{3}{2}(0) \end{aligned}$$

$$\Delta H^\circ = -1675.7 \text{ kJ mol}^{-1} = q \quad (\text{constant pressure})$$

work $w = -\int P_{\text{ext}} dV = -\int p^\circ dV = -p^\circ \int dV$

$$= -p^\circ (V_{\text{products}} - V_{\text{reactants}})$$

$$= -p^\circ [V_m(\text{Al}_2\text{O}_3, s) - 2V_m(\text{Al}, s) - \frac{3}{2}V_m(\text{O}_2, g)]$$

$$= \frac{3}{2} p^\circ V_m(\text{O}_2, g) \quad (\Delta n_g = -\frac{3}{2} \text{ mol})$$

$$= \frac{3}{2} p^\circ \frac{RT}{p^\circ} = \frac{3}{2} RT = -RT \Delta n_g$$

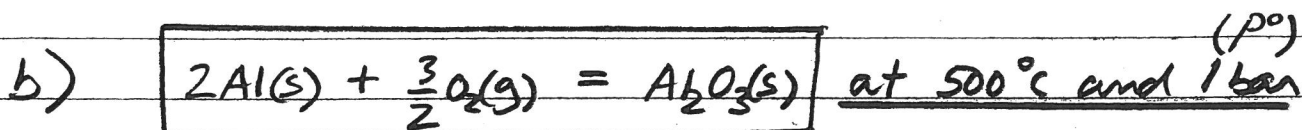
$$= (1.5 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$$

$$w = 3718 \text{ J}$$

(Q1 a) cont.)

$$\Delta U = q + w = -1675.7 \text{ kJ mol}^{-1} + 3.7 \text{ kJ mol}^{-1}$$

$$\Delta U = -1672.0 \text{ kJ mol}^{-1}$$



use $T_1 = 298.15 \text{ K}$ (25°C) and $T_2 = 773.15 \text{ K}$ (500°C)

$$\Delta C_p^\circ = C_p^\circ(\text{products}) - C_p^\circ(\text{reactants})$$

$$= C_{pm}^\circ(\text{Al}_2\text{O}_3, s) - 2C_{pm}^\circ(\text{Al}, s) - \frac{3}{2}C_{pm}^\circ(\text{O}_2, g)$$

$$= 79.04 - 2(24.35) - \frac{3}{2}(29.36)$$

$$\Delta C_p^\circ = -13.7 \text{ J K}^{-1} \text{ mol}^{-1} \quad (\text{assumed to be constant})$$

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ dT = \Delta H^\circ(T_1) + \Delta C_p^\circ(T_2 - T_1)$$

$$= -1675.7 \text{ kJ mol}^{-1} + -13.7 \frac{\text{J}}{\text{K mol}} (500 \text{ K})$$

$$= -1675.7 \text{ kJ mol}^{-1} - 6850 \text{ J mol}^{-1}$$

$$\Delta H^\circ(T_2) = -1682.6 \text{ kJ mol}^{-1}$$

$$= q \quad (\text{the pressure is constant at } p^\circ = 1 \text{ bar})$$

(Q1 b) cont.)

$$\text{work} = -RT \Delta n_g$$

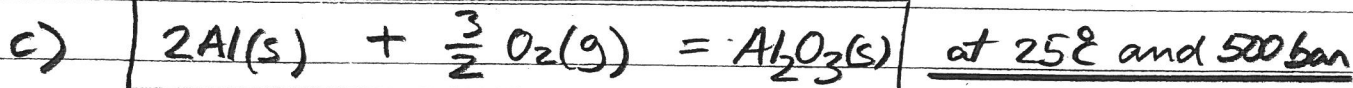
$$= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(773.15 \text{ K})\left(-\frac{3}{2} \text{ mol}\right)$$

$$\boxed{w = 9642 \text{ J}}$$

$$\Delta U = q + w$$

$$= -1682.6 \text{ kJ mol}^{-1} + 9.6 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta U = -1673.0 \text{ kJ mol}^{-1}}$$



use $\underline{p_1 = p^\circ = 1 \text{ bar}}$ and $\underline{p_2 = 500 \text{ bar}}$

$$\begin{aligned}\Delta V &= V(\text{products}) - V(\text{reactants}) \\ &= \cancel{V_m(\text{Al}_2\text{O}_3, s)} - 2\cancel{V_m(\text{Al}, s)} - \frac{3}{2}V_m(\text{O}_2, g) \\ &= -\frac{3}{2}V_m(\text{O}_2, g) \\ &= -\frac{3}{2}\frac{RT}{p}\end{aligned}$$

$$\Delta H(T_1, p_2) = \Delta H(T_1, p_1) + \int_{p_1}^{p_2} \Delta V dp$$

$$= \Delta H^\circ(T_1) + \int_{p_1}^{p_2} \left(-\frac{3}{2}\frac{RT}{p}\right) dp = \Delta H^\circ(T_1) - \frac{3RT}{2} \int_{p_1}^{p_2} \frac{1}{p} dp$$

$$= \Delta H^\circ(T_1) - \frac{3RT}{2} \ln(p_2/p_1)$$

(Q1 c) cont.)

$$w = \frac{3}{2} RT = 3718 \text{ J}$$

$$\Delta H(T_1, P_2) = -1675.7 \frac{\text{kJ}}{\text{mol}} - \frac{3}{2} \left(\frac{8.314 \text{ J}}{\text{K mol}} \right) (298.15 \text{ K}) \ln \left(\frac{500 \text{ bar}}{1 \text{ bar}} \right)$$

$$= -1675.7 \frac{\text{kJ}}{\text{mol}} - 23110 \frac{\text{J}}{\text{mol}}$$

$$\Delta H(T_1, P_2) = -1698.8 \text{ kJ mol}^{-1}$$

$$= q \quad (\text{pressure constant at 500 bar})$$

$$\Delta U = q + w = -1698.8 + 37$$

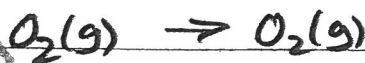
$$\Delta U = -1695.1 \text{ kJ mol}^{-1}$$

notice: changes in temperature and pressure have small effects on ΔH

(Q2)

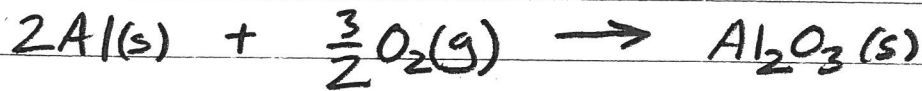
The standard ⁽⁰⁾ enthalpy of formation of a substance is the enthalpy change for the formation of the substance from pure elements in their most stable states at 1 bar.

Al(s) and $\text{O}_2(\text{g})$ are pure elements in their most stable states, so their enthalpies of formation are zero



no reaction, no enthalpy change

(Q3) Calculate the adiabatic ($q=0$) flame temperature for the oxidation of aluminium metal in pure oxygen initially at 25 °C, pressure = 1 bar
 $= p^\circ$



$$T_1 = 298.15 \text{ K (25 °C)}$$

$$T_2 = ? \text{ (flame temperature)}$$

$$\left(\begin{array}{l} C_p(\text{products}) \\ = C_p^\circ(\text{Al}_2\text{O}_3, s) \\ = 79.04 \text{ J K}^{-1} \text{ mol}^{-1} \end{array} \right)$$

$$T_2 = T_1 - \frac{\Delta H^\circ(T_1)}{C_p^\circ(\text{products})}$$

$$= 298.15 \text{ K} - \frac{-1675700 \text{ J mol}^{-1}}{79.04 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$= 298.15 \text{ K} + 21,200 \text{ K}$$

$$T_2 = 21,500 \text{ K}$$

HHHOT!

The actual adiabatic temperature for the oxidation of aluminium is lower than 21,500 K because:

- the heat capacity of Al_2O_3 (assumed constant here) increases with temperature
- $\text{Al}_2\text{O}_3(s)$ melts (absorbing heat, reducing T_2)

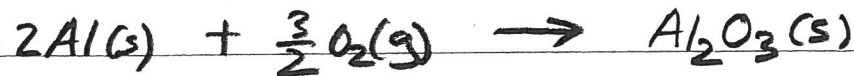
Q4

Adiabatic flame temperatures for combustion reactions in pure oxygen are larger than flame reactions using air because air contains 4 moles of inert N_2 per mole of O_2 .

The N_2 in the reaction products increases the heat capacity of the reaction products, reducing the increase in temperature.

Example:

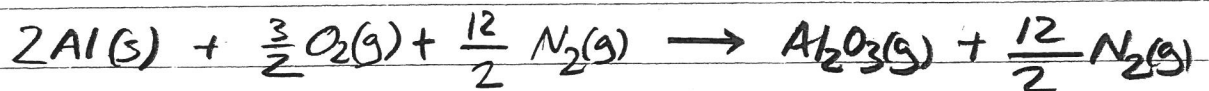
Combustion of Al in pure O_2 :



$$\text{flame temp. } T_2 = T_1 - \frac{\Delta H(T_1)}{C_{pm}(Al_2O_3, s)}$$

no $C_{pm}(N_2, g)$ for combustion in pure O_2

Combustion of Al in air:



$$\text{flame temp. } T_2 = T_1 - \frac{\Delta H(T_1)}{C_{pm}(Al_2O_3, s) + 6C_{pm}(N_2, g)}$$

T_2 for combustion of Al in air is lower than T_2 for combustion of Al in pure O_2 due to

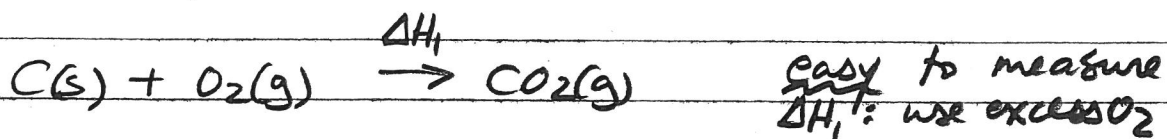
(Q5) The enthalpy change for the reaction



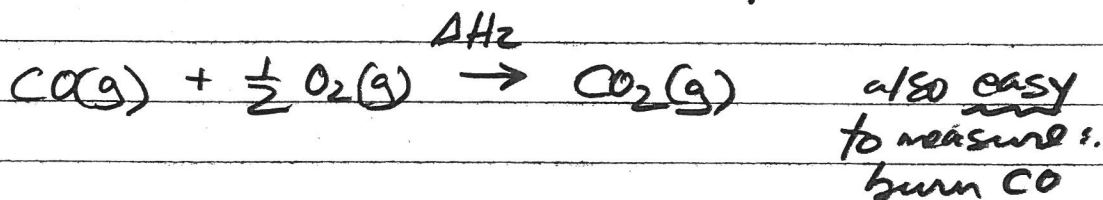
is almost impossible to measure directly because significant amounts of CO_2 [$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$] are formed as a side reaction.

Plan B:

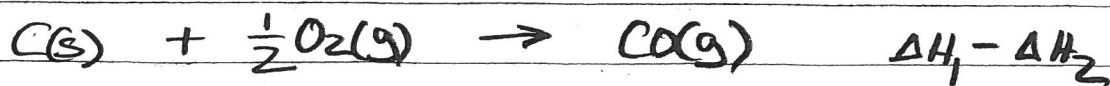
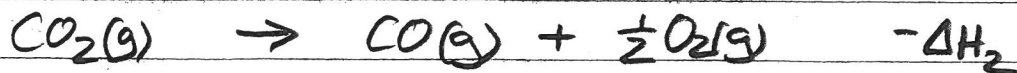
i) measure ΔH_1 for the combustion of C(s) to $\text{CO}_2(\text{g})$



ii) measure ΔH_2 for the combustion of CO(g) to $\text{CO}_2(\text{g})$



thermochemical "algebra":



Q6

Why are enthalpy changes for chemical reactions of liquids and solids almost independent of changes in pressure.

In class, we proved:

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \beta T)$$

thermal expansivity

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

And we saw the thermal expansivities of liquids are very small, almost zero.

As a result, $\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \overset{0}{\beta T})$

$\approx V$ for liquids and solids

And for liquids and solids, volumes are very small ≈ 0 (compared to gas volumes)

$$\left(\frac{\partial H}{\partial p}\right)_T \approx V \approx 0 \text{ for liquids and solids}$$

so $\left(\frac{\partial \Delta H}{\partial p}\right)_T \approx \Delta V \approx 0$

ΔV , the difference in volumes of liquids and solids, is even smaller than the volumes of the liquids and solids.

