

1. For the reaction $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$:

[10] a) Calculate q , w , ΔU and ΔH at 75 °C and 1.00 bar. Use $\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ(T) dT$

b) Calculate q , w , ΔU and ΔH at 25 °C and 50.0 bar. Use $\Delta H(T, p_2) = \Delta H^\circ(T) + \int_{p^\circ}^{p_2} \Delta V(T, p) dp$

Data at 25 °C, 1.00 bar: $\Delta H_{\text{fm}}^\circ(\text{CO, g}) = -110.525 \text{ kJ mol}^{-1}$ $C_{p\text{m}}^\circ(\text{CO, g}) = 29.14 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{O}_2, \text{g}) = 0$ $C_{p\text{m}}^\circ(\text{O}_2, \text{g}) = 29.38 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -393.509 \text{ kJ mol}^{-1}$ $C_{p\text{m}}^\circ(\text{CO}_2, \text{g}) = 37.11 \text{ J K}^{-1} \text{ mol}^{-1}$

2. Why would you expect ΔH for the following reactions to be almost independent of pressure?

[2] a) $\text{CaCl}_2\text{(s)} + 6 \text{H}_2\text{O(l)} = \text{CaCl}_2 \cdot 6\text{H}_2\text{O(s)}$

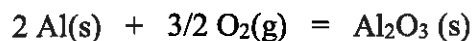
b) $\text{C(graphite)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$

3. 10.0 moles of liquid water are vaporized at 100 °C and 1.00 bar. Calculate q , w , ΔU and ΔH .

[4] Data at 100 °C: $\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O, l}) = -283.516 \text{ kJ mol}^{-1}$ $\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O, g}) = -242.826 \text{ kJ mol}^{-1}$

(this problem shows that enthalpies of formation can also be used to analyze physical processes)

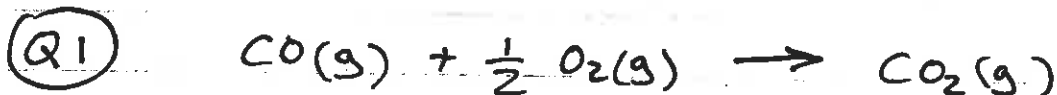
4. Powdered aluminum initially at 25 °C is burned adiabatically at 1.00 bar in pure oxygen.



[4] a) Use $T_f = T_i - \frac{\Delta H^\circ(T_i)}{C_p^\circ(\text{products})}$ to estimate the final temperature of Al_2O_3 .

Data at 25 °C: $\Delta H_{\text{fm}}^\circ(\text{Al}_2\text{O}_3, \text{s}) = -1675.7 \text{ kJ mole}^{-1}$ $C_{p\text{m}}^\circ(\text{Al}_2\text{O}_3, \text{s}) = 24.35 \text{ J K}^{-1} \text{ mol}^{-1}$

b) Burning aluminum in pure oxygen produces a much higher temperature than burning aluminum in air. Why?



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

$$\Delta H_{25^\circ\text{C}}^\circ = (1) \Delta H_{\text{fm}}^\circ(\text{CO}_2, \text{g}) + (-1) \Delta H_{\text{fm}}^\circ(\text{CO}, \text{g}) + \left(-\frac{1}{2}\right) \Delta H_{\text{fm}}^\circ(\text{O}_2, \text{g})$$

$$= -393.509 - (-110.525) - \frac{1}{2}(0)$$

$$\Delta H_{25^\circ\text{C}}^\circ = -282.984 \text{ kJ mol}^{-1}$$

$$\Delta C_{p, 25^\circ\text{C}}^\circ = (1) C_{p,m}^\circ(\text{CO}_2, \text{g}) + (-1) C_{p,m}^\circ(\text{CO}, \text{g}) + \left(-\frac{1}{2}\right) C_{p,m}^\circ(\text{O}_2, \text{g})$$

$$= [37.11 - 29.14 - \frac{1}{2}(29.38)] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_{p, 25^\circ\text{C}}^\circ = -6.72 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$(\Delta n_g = 1 + 1 - \frac{1}{2} = -\frac{1}{2} \text{ mol})$$

$$\Delta V^\circ = V_m^\circ(\text{CO}_2, \text{g}) - V_m^\circ(\text{CO}, \text{g}) - \frac{1}{2} V_m^\circ(\text{O}_2, \text{g})$$

$$= \frac{RT}{p^\circ} - \frac{RT}{p^\circ} - \frac{1}{2} \frac{RT}{p^\circ} = -\frac{1}{2} \frac{RT}{p^\circ}$$

we:
 $\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$

at 75 °C, 1 bar

$$T_1 = 298.15 \text{ K (25 °C)}$$

$$T_2 = 348.15 \text{ K (75 °C)}$$

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

$$= -282984 \text{ J mol}^{-1} + \left(-6.72 \frac{\text{J K}^{-1}}{\text{mol}}\right) (50 \text{ K})$$

$$= -282984 \text{ J mol}^{-1} - 336 \text{ J mol}^{-1}$$

$$\Delta H^\circ(T_2) = -283320 \text{ J} = -283.320 \text{ kJ mol}^{-1} = q \quad \begin{matrix} 75^\circ\text{C} \\ 1 \text{ bar} \end{matrix}$$

$$w = -\int p_{\text{ext}} dV = -\int p dV = -p(V_{\text{mCO}_2} - V_{\text{mCO}} - \frac{1}{2} V_{\text{mO}_2}) = -p\left(\frac{1}{2}\right) \frac{RT}{p}$$

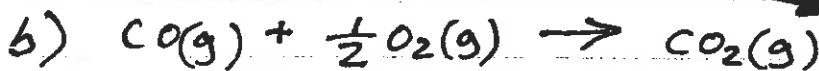
$$w = RT/2 = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (348.15 \text{ K}) / 2 = 1447 \text{ J mol}^{-1} = w$$

$$\Delta U = q + w = \Delta H^\circ + w = -283.320 \frac{\text{kJ}}{\text{mol}} + 1.447 \frac{\text{kJ}}{\text{mol}} = -281.872 \frac{\text{kJ}}{\text{mol}}$$

$p = p^\circ$ constant

(Q1 cont.)

$$\left(\frac{\partial \Delta H}{\partial p}\right)_T = \Delta V$$



at 25°C, 50.0 bar

$$\begin{aligned} \Delta H_{25^\circ\text{C}}^{50\text{bar}} &= \Delta H_{1\text{bar}}^{25^\circ\text{C}} + \int_{1\text{bar}}^{50\text{bar}} \left(\frac{\partial \Delta H}{\partial p}\right)_T dp = \Delta H^\circ(T_1) + \int_{1\text{bar}}^{50\text{bar}} \Delta V dp \\ &= \Delta H^\circ(T_1) + \int_{1\text{bar}}^{50\text{bar}} (V_{\text{mCO}_2} - V_{\text{mCO}} - \frac{1}{2} V_{\text{mO}_2}) dp = \Delta H^\circ(T_1) + \int_{1\text{bar}}^{50\text{bar}} \left(-\frac{1}{2} V_m\right) dp \\ &= \Delta H^\circ(T_1) + \left(-\frac{1}{2}\right) \frac{RT}{p} dp = \Delta H^\circ(T_1) - \frac{RT}{2} \int_{1\text{bar}}^{50\text{bar}} \frac{dp}{p} \\ &= \Delta H^\circ(T_1) - \frac{RT}{2} \ln\left(\frac{50}{1}\right) = -282984 \frac{\text{J}}{\text{mol}} - \frac{8.314(298.15)}{2} \ln\left(\frac{50}{1}\right) \end{aligned}$$

$$\Delta H_{25^\circ\text{C}}^{50\text{bar}} = -282984 \frac{\text{J}}{\text{mol}} - 484.8 \frac{\text{J}}{\text{mol}} = -287,832 \text{ J mol}^{-1}$$

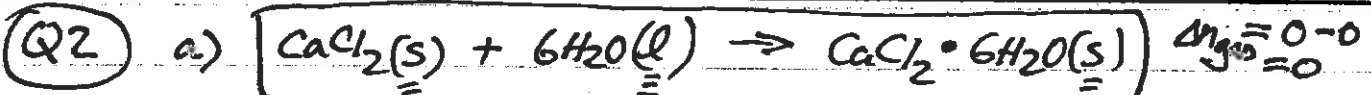
$$\Delta H_{25^\circ\text{C}}^{50\text{bar}} = -287.832 \text{ kJ mol}^{-1} = q$$

$$\Delta n_{\text{gas}} = -\frac{1}{2} \text{ mol} \\ V_m = RT/p$$

$$w = -\int p_{\text{ext}} dV = -p dV = -p \Delta V = -p \left(-\frac{1}{2} \text{ mol}\right) V_m$$

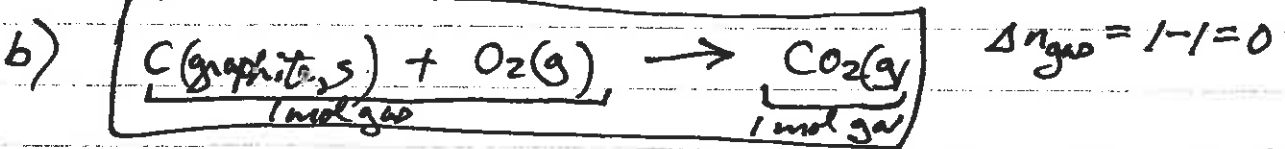
$$w = pV_m/2 = RT/2 = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/2 = 1240 \text{ J}$$

$$\Delta U = q + w = (-287.832 + 1.240) \text{ kJ} = -286.592 \text{ kJ}$$



all solids or liquids \Rightarrow small molar volumes (ΔV even smaller)

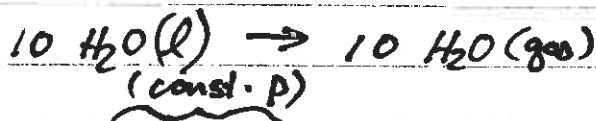
$$\frac{\partial \Delta H}{\partial p} = \Delta V \approx 0 \quad \therefore \Delta H \text{ should be almost independent of } p$$



$$\begin{aligned} \Delta V &= V_{\text{mCO}_2\text{g}} - V_{\text{mO}_2\text{g}} - V_{\text{mCs}} = \frac{RT}{p} - \frac{RT}{p} - (\text{a few mL for Cs}) \\ &= 0 - (\approx 0) = 0 \end{aligned}$$

once again, ΔH is almost independent of p

Q3



per mole: $\Delta H_m = q_m = \Delta H_{fm}^\circ(\text{H}_2\text{O}, g) - \Delta H_{fm}^\circ(\text{H}_2\text{O}, l)$

$$= [-242.826 - (-283.516)] \text{ kJ mol}^{-1}$$

$$\Delta H_m = q_m = 40.69 \text{ kJ mol}^{-1}$$

(RT/p^o) (negligible) ≈ 0.0201

$$w_m = -\int p_{\text{ext}} dV_m = -p^\circ \int dV_m = -p^\circ [V_m(\text{H}_2\text{O}, g) - V_m(\text{H}_2\text{O}, l)]$$

$$w_m = -RT = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) = -3102.4 \text{ J mol}^{-1}$$

$$\Delta U_m^\circ = q_m + w_m = 40.69 \text{ kJ mol}^{-1} - 3.102 \text{ kJ mol}^{-1}$$

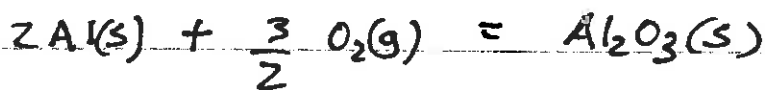
$$= 37.59 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = q = n \Delta H_m^\circ = (10 \text{ mol})(40.69 \text{ kJ mol}^{-1}) = \boxed{406.9 \text{ kJ}}$$

$$w = (10 \text{ mol}) w_m = (10 \text{ mol})(-3102 \text{ J mol}^{-1}) = \boxed{-31.02 \text{ kJ}}$$

$$\Delta U^\circ = n \Delta U_m^\circ = (10 \text{ mol})(37.59 \text{ kJ mol}^{-1}) = \boxed{375.9 \text{ kJ}}$$

Q4



$$T_i = 298.15 \text{ K}$$

$$\Delta H^\circ(T_i) = -1675.7 \text{ kJ}$$

(enthalpy of formation of $\text{Al}_2\text{O}_3(s)$ at 25°C)

$$C_p(\text{product}) = 24.35 \text{ J K}^{-1}$$

(for one mole of $\text{Al}_2\text{O}_3(s)$)

$$T_f = T_i - \frac{\Delta H(T_i)}{C_p(\text{product})} = 298.15 \text{ K} - \left(\frac{-1675700 \text{ J}}{24.35 \text{ J K}^{-1}} \right)$$

$$T_f = (298.15 + 68817) \text{ K} \approx \boxed{69,000 \text{ K}}$$

This T_f is too high
 C_p increases with T ,
and $\text{Al}_2\text{O}_3(s)$ melts

(Q4 cont.)

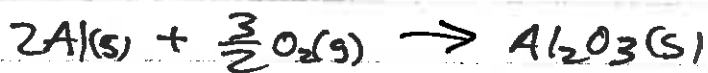
(example, a glowing ember in air bursts into flame in oxygen)

b) burning Al (or anything) in O₂ produces much higher temperatures than burning

Al in air

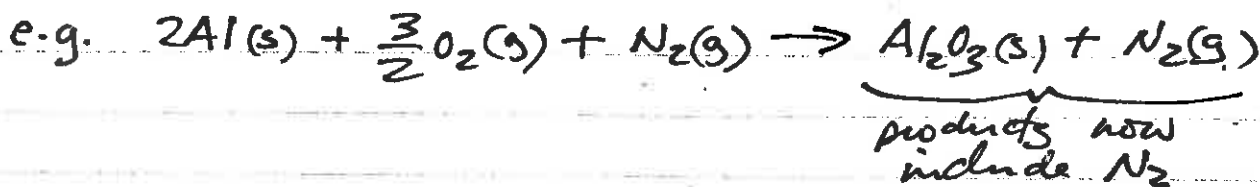
Why?

if pure O₂ is used the only product is Al₂O₃



$$T_f = T_i - \frac{\Delta H(T_i)}{C_p(\text{Al}_2\text{O}_3)}$$

but if air is used the Al₂O₃ and inert N₂ must be heated



$$T_f = T_i - \frac{\Delta H(T_i)}{C_p(\text{Al}_2\text{O}_3) + C_p(\text{N}_2)}$$

same $\Delta H(T_i)$ must now heat Al₂O₃ and N₂

larger heat capacity of the products reduces T_f