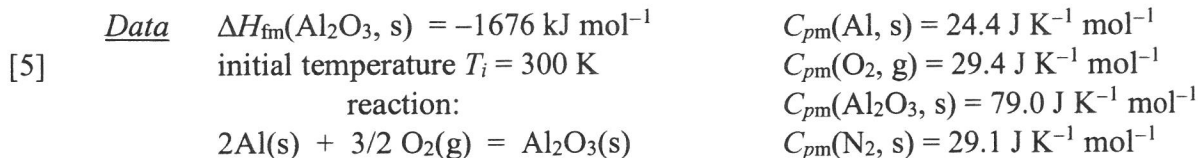


1. Calculate the adiabatic flame temperature for

a) burning aluminum in pure oxygen

b) burning aluminum in air (assumed to be 20 mol % O₂ and 80 mol % N₂)



2. 5.00 moles of liquid water reversibly evaporate at the normal boiling point (100 °C and 1.00 atm).

[5] Calculate q , w , ΔU , ΔH and ΔS . Data $\Delta H_{\text{vap,m}}(\text{H}_2\text{O}, \text{l}) = 43.15 \text{ kJ mol}^{-1}$

3. One mole of NH₃(g) is reversibly heated from 300 K to 1300 K at 1.00 bar pressure.

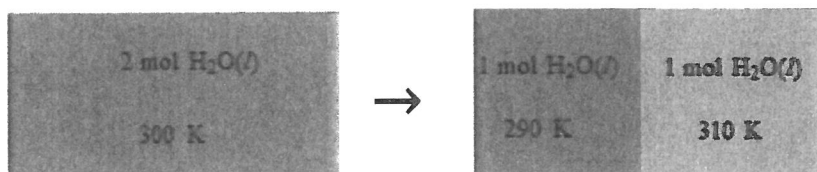
Calculate q , w , ΔU , ΔH and ΔS .

Data The molar heat capacity of NH₃(g) is given by the equation

$$C_{\text{pm}}(T) = a_0 + a_1T + a_2T^2$$

[8] with constants $a_0 = 24.295$, $a_1 = 0.03990$, -7.814×10^{-6} . C_{pm} is in units of J K⁻¹ mol⁻¹ and T is in units of K. *Hints:* $dq = dH = C_p dT$ and $dS = dq/T = (C_p/T)dT$

4. An isolated system ($\Delta U = q = w = 0$) consisting of 2.00 mol H₂O(l) initially at 300 K undergoes the following process, forming 1.00 mole H₂O(l) at 290 K and 1.00 mol H₂O(l) at 310 K.



Data

$$C_{V\text{m}}(\text{H}_2\text{O}, \text{l}) = 74.8 \text{ J K}^{-1}$$

[2] For this process: $w = 0 = -\int p_{\text{ext}} dV$ (so the volume is constant)

$$q = \int_{300\text{K}}^{290\text{K}} C_{V\text{m}} dT + \int_{300\text{K}}^{310\text{K}} C_{V\text{m}} dT = C_{V\text{m}}(290-300)\text{K} + C_{V\text{m}}(310-300)\text{K} = 0$$

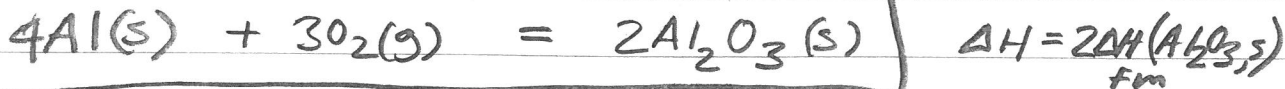
$$\Delta U = q + w = 0$$

a) $\Delta U = q = w = 0$. Not very interesting? *But wait!* Calculate ΔS .

b) Use the result from a to prove the process is *impossible*.

(This question illustrates the law of **thermal equilibrium**: an isolated system with a nonuniform temperature distribution spontaneously converts to a state of uniform temperature, but the reverse process is not observed.)

Q1 a) Aluminium is burned in pure oxygen gas.



How hot can the $\text{Al}_2\text{O}_3(s)$ product get?
Under adiabatic conditions (the exothermic heat of the reaction is not lost to the surroundings)

$$T_{\text{final}} = T_i - \frac{\Delta H}{C_p(\text{products})} = T_i - \frac{2\Delta H_{f,m}(\text{Al}_2\text{O}_3,s)}{2C_{p,m}(\text{Al}_2\text{O}_3,s)}$$

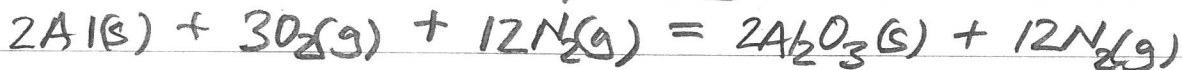
$$T_{\text{final}} = 300\text{K} - \frac{-1,676,000 \text{ J mol}^{-1}}{79.0 \text{ J K}^{-1} \text{ mol}^{-1}} = 300\text{K} + 21,210\text{K}$$

$$= \boxed{21,510\text{K}}$$

b) Aluminium is burned in air.

air \approx 4 moles N_2 for every mole of O_2

inert



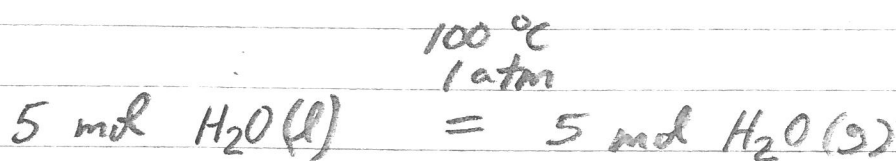
$$C_p(\text{products}) = 2C_{p,m}(\text{Al}_2\text{O}_3,s) + 12C_{p,m}(\text{N}_2,g)$$

$$= 2(79.0) + 12(29.1) = 507.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_{\text{final}} = T_{\text{initial}} - \frac{2\Delta H_{f,m}(\text{Al}_2\text{O}_3,s)}{C_p(\text{products})} = 300\text{K} - \frac{2(-1,676,000) \text{ J mol}^{-1}}{507.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

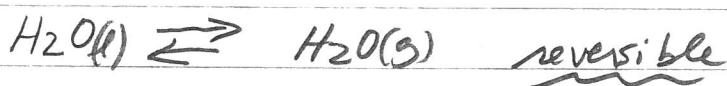
$$= 300\text{K} + 6610\text{K} = \boxed{6910\text{K}} \quad \left(\begin{array}{l} \text{much "cooler"} \\ \text{than burning} \\ \text{in pure O}_2 \end{array} \right)$$

Q2



liquid water and water vapor are in equilibrium at the normal boiling point (100°C , 1 atm):

add heat q , water evaporates; remove heat q an equal amount of water vapor condenses to liquid



And at constant pressure (here 1 atm): $q = \Delta H$

$$q = \Delta H = n \Delta H_{\text{vap,m}}(\text{H}_2\text{O}, \ell)$$

$$= (5.00 \text{ mol}) (43.15 \text{ kJ mol}^{-1})$$

$$= \boxed{215.75 \text{ kJ}}$$

(rev: $p = p_{\text{ext}}$) (const. p)

$$w = -\int p_{\text{ext}} dV = -\int p dV = -p \int dV = -p(V_f - V_i)$$

$$= -p \left[\frac{(5 \text{ mol})RT}{p} - (5 \text{ mol})V_m(\text{H}_2\text{O}, \ell) \right] = -(5 \text{ mol})RT$$

$$= -RT \Delta n_g = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})(5.00 \text{ mol})$$

$$w = \boxed{-15510 \text{ J}}$$

$$\Delta U = q + w = 215.75 \text{ kJ} - 15.51 \text{ kJ}$$

$$\boxed{\Delta U = 200.24 \text{ kJ}}$$

(Q2 cont.)

(T constant)

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T} \int dq_{rev} = \frac{q_{rev}}{T}$$

$$= \frac{215,750 \text{ J}}{373.15 \text{ K}} = \boxed{578.2 \text{ J K}^{-1}}$$

(Q3) 1.00 mol $\text{NH}_3(\text{g})$ is reversibly heated from 300 K to 1300 K at 1.00 bar pressure.

at constant pressure: $dq = dH$ and $q = \Delta H$

also $C_p = \frac{dq}{dT}$ so $dq = C_p dT$

$$\Delta H = q = \int_{T_i}^{T_f} dq = \int_{T_i}^{T_f} C_p dT$$
$$= \int_{T_i}^{T_f} (a_0 + a_1 T + a_2 T^2) dT$$

important:
 C_p not constant here

$$= a_0 \int dT + a_1 \int T dT + a_2 \int T^2 dT$$

$$= a_0 T \Big|_{T_i}^{T_f} + a_1 \frac{T^2}{2} \Big|_{T_i}^{T_f} + a_2 \frac{T^3}{3} \Big|_{T_i}^{T_f}$$

$$= a_0 (T_f - T_i) + \frac{a_1}{2} (T_f^2 - T_i^2) + \frac{a_2}{3} (T_f^3 - T_i^3)$$

$$= 24.295(1300-300) + \frac{0.03990}{2}(1300^2 - 300^2) - \frac{7.814 \times 10^{-6}}{3}(1300^3 - 300^3)$$

$$= (24295 + 31920 - 5652) \text{ J}$$

$$\boxed{\Delta H = q = 50560 \text{ J}}$$

(Q3 cont.)

$P_{\text{ext}} = P$ (reversible)

heat 1.00 mol NH_3 gas from 300 to 1300 K at 1 bar
(P constant)

$$w = - \int P_{\text{ext}} dV = - \int P dV = -P \int dV$$

$$= -P(V_f - V_i) = -P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right)$$

$$= -nR(T_f - T_i)$$

$$= -(1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1300 - 300) \text{ K}$$

$$w = -8310 \text{ J}$$

$$\Delta U = q + w = 50560 \text{ J} - 8310 \text{ J}$$

$$\Delta U = 42250 \text{ J} = 42.25 \text{ kJ}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_p dT}{T}$$

at constant pressure
 $C_p = \frac{dq}{dT}$

so $C_p dT = dq$

$$\Delta S = \int \frac{a_0 + a_1 T + a_2 T^2}{T} dT = a_0 \int \frac{dT}{T} + a_1 \int dT + a_2 \int T dT$$

$$= a_0 \ln\left(\frac{T_f}{T_i}\right) + a_1(T_f - T_i) + a_2 \left(\frac{T_f^2}{2} - \frac{T_i^2}{2} \right)$$

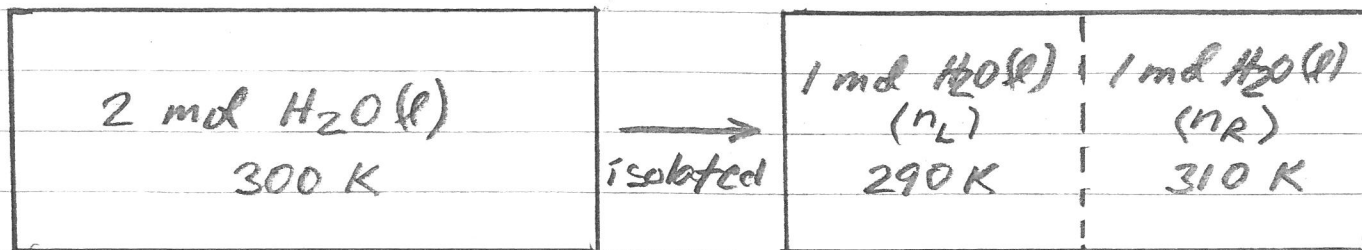
$$= 24.295 \ln\left(\frac{1300}{300}\right) + 0.03990(1300 - 300)$$

$$- (7.814 \times 10^{-6}) \left(\frac{1300^2}{2} - \frac{300^2}{2} \right)$$

$$= 35.625 + 39.90 - 6.251$$

$$\Delta S = 69.27 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q4



a) at constant volume $C_V = \frac{dq}{dT} = nC_{Vm}$

take a reversible path $dS = \frac{dq}{T} = \frac{C_V dT}{T}$

$$\Delta S = \int_{300K}^{290K} \frac{n_L C_{Vm}}{T} dT + \int_{300K}^{310K} \frac{n_R C_{Vm}}{T} dT$$

$$= (1.00 \text{ mol}) C_{Vm} \int_{300K}^{290K} \frac{1}{T} dT + (1.00 \text{ mol}) C_{Vm} \int_{300K}^{310K} \frac{1}{T} dT$$

$$= (1.00 \text{ mol}) C_{Vm} \left[\ln\left(\frac{290}{300}\right) + \ln\left(\frac{310}{300}\right) \right]$$

$$= (1.00 \text{ mol}) (74.8 \text{ J K}^{-1} \text{ mol}^{-1}) [-0.03390 + 0.03279]$$

$$\Delta S = -0.0832 \text{ J K}^{-1}$$

b) $\Delta S < 0$ for an isolated system is impossible
(constant U, V)

($\Delta S \geq 0$) _{U, V} from the Second Law