

1. 5.00 moles of liquid water evaporate to form water vapor (assumed to be an ideal gas) at 100 °C and 1.00 atm (the normal boiling point of water).

a) Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$ .

[6] b)  $\Delta S$  for this process is positive. Does this mean the vaporization of water is spontaneous at 100 °C and 1.00 atm? Explain briefly.

Data: At 100 °C and 1.00 atm the density of liquid water is 0.958 g cm<sup>-3</sup> and  $\Delta H_{\text{vap,m}}(\text{H}_2\text{O}, l) = 43.15 \text{ kJ mol}^{-1}$

2. The Second Law shows that the entropy of an isolated system can never decrease. Use this result to prove the conversion of graphite to diamond is impossible at 25 °C and 1.00 bar.

[3] Data at 25 °C and 1.00 bar:

$$\Delta H_{\text{fm}}^\circ(\text{C, graphite}) = 0$$

$$\Delta H_{\text{fm}}^\circ(\text{C, diamond}) = 1.895 \text{ kJ mol}^{-1}$$

$$S_{\text{m}}^\circ(\text{C, graphite}) = 5.74 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_{\text{m}}^\circ(\text{C, diamond}) = 2.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

3. a) At 25 °C, the standard enthalpy of formation of carbon as graphite is zero, but the standard enthalpy of formation of carbon as diamond is 1,895 J mole<sup>-1</sup>. How can carbon have two different enthalpies of formation? Explain briefly.

[4] b) At 25 °C, the standard entropy of carbon as graphite is 5.74 J K<sup>-1</sup> mol<sup>-1</sup>, but the standard entropy of carbon as diamond is 2.38 J K<sup>-1</sup> mol<sup>-1</sup>. How can carbon have two different entropies at 25 °C and 1.00 bar? Explain briefly.

c) How are the entropies of graphite and diamond measured?

d) Question 2 shows that  $\Delta S$  can be determined for impossible reactions! Why is this result important?

4. One of your classmates tidies up their room (*parents will be visiting!*) and claims the resulting decrease in disorder and decrease in the entropy violates the Second Law of thermodynamics.

[2] Is this claim correct? Explain briefly.

5. 1.00 mole of helium (assumed to be an ideal gas with  $C_{V,m} = 3R/2$ ) initially at 300 K and 1.00 bar is reversibly heated to 500 K at 1.00 bar. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$ .

[5]

(Q1) 5.00 moles of liquid water evaporate at 100 °C and 1.00 atm (constant pressure)

$$q_p = \Delta H = n \Delta H_{\text{vap,m}}$$

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

$$q = \Delta H = 215.75 \text{ kJ}$$

$$(P_{\text{ext}} = p = 1 \text{ atm})$$

$$= 101325 \text{ Pa}$$

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

$$= -p(V_f - V_i) = -p[5V_m(\text{g}) - 5V_m(\text{l})]$$

$$V_m(\text{g}) = \frac{RT}{P} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})}{101325 \text{ Pa}}$$

$$= 0.03062 \text{ m}^3 \text{ mol}^{-1} \text{ (30.62 L)}$$

$$V_m(\text{l}) = \frac{\text{molar mass}}{\text{density}} = \frac{18.015 \text{ g mol}^{-1}}{0.958 \text{ g cm}^{-3}}$$

$$V_m(\text{l}) = 18.8 \text{ cm}^3 \text{ mol}^{-1} = 18.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

(very small)

$$w = -pn(V_m(\text{g}) - V_m(\text{l})) = -(101325 \text{ Pa})(5 \text{ mol}) \left(0.0306 - 18.8 \times 10^{-6}\right) \frac{\text{m}^3}{\text{mol}}$$

$$w = -15,500 \text{ J} \quad (\approx -pnV_m(\text{g}) = -RT \Delta n_{\text{gas}})$$

$$\Delta U = w + q = -15.50 \text{ kJ} + 215.75 \text{ kJ} = 200.25 \text{ kJ}$$

(Q1 a) cont.)

at  $100^\circ\text{C}$ , 1 atm (the normal boiling point)  
liquid water and water vapor are in equilibrium



this means evaporation (and condensation)  
are reversible and  $q = q_{\text{rev}}$

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

$$\Delta S = \frac{215750 \text{ J}}{373.15 \text{ K}} = \boxed{578.2 \text{ J K}^{-1}}$$

b)  $\Delta S > 0$ : does this mean the evaporation  
is spontaneous?

**NO!**

The system (5 moles of water) is not isolated.

( $q_{\text{system}} = 215750 \text{ J}$      $q_{\text{surroundings}} = -215750 \text{ J}$ )

$\Delta S > 0$  means a process is spontaneous only  
if the system is isolated

$$\begin{aligned} \text{here: } (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}})_{\text{isolated}} &= \frac{q_{\text{sys, rev}}}{T} + \frac{q_{\text{surroundings, rev}}}{T} \\ &= \frac{215750 \text{ J}}{373.15 \text{ K}} + \frac{-215750 \text{ J}}{373.15} = 0 \therefore \text{reversible process} \end{aligned}$$

Q2  $C(\text{graphite}) \stackrel{25^\circ}{=} C(\text{diamond})$   
1 bar

$$q = \Delta H_p \text{ (constant pressure)}$$

$$= \Delta H_{fm}^\circ(\text{diamond}) - \Delta H_{fm}^\circ(\text{graphite})$$

$$= 1.895 \text{ kJ mol}^{-1} - 0$$

$$q = 1.895 \text{ kJ mol}^{-1} \quad \left( q \neq 0 \right)$$

system is not isolated

$$\Delta S = S_m^\circ(\text{diamond}) - S_m^\circ(\text{graphite})$$

$$= (2.38 - 5.74) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = -3.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

can't use  $\Delta S$  to decide if spont. system not isolated

notice  $\int \frac{dq}{T} = \frac{q}{T} = \frac{1895 \text{ J mol}^{-1}}{298.15 \text{ K}}$

$$= 6.35 \text{ J K}^{-1} \text{ mol}^{-1}$$

$\neq \Delta S \therefore$  not a reversible process

$$\Delta S_{\text{total}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}})_{\text{isolated "universe"}}$$

reversibly remove 1895 J heat from surroundings at 298.15 K

$$= \left( -3.36 \frac{\text{J}}{\text{K}} + \frac{-1895 \text{ J}}{298.15 \text{ K}} \right)_{\text{isolated}}$$

$$\Delta S_{\text{tot}} = (-3.36 - 6.35) \frac{\text{J}}{\text{K}} = -9.72 \frac{\text{J}}{\text{K}}$$

impossible!  
 $\Delta S < 0$  for an isolated system (universe)

(Q2 cont.)

another way to show graphite  $\rightarrow$  diamond is impossible at 25  $^{\circ}$ C, 1 bar:

Clausius inequality  $ds \geq \frac{dq}{T}$

$$\Delta S \geq \int \frac{dq}{T} \left( = \frac{1}{T} \int dq = \frac{q}{T} \right)$$

here:  $\Delta S = -3.36 \frac{\text{J}}{\text{K}}$  and  $\frac{q}{T} = \frac{1895 \text{ J}}{298.15 \text{ K}}$

$$\Delta S < \frac{q}{T} \quad \text{impossible}$$

$$= 6.35 \frac{\text{J}}{\text{K}}$$

(violates the Clausius inequality)

another way to show graphite  $\rightarrow$  diamond is impossible at 25  $^{\circ}$ C, 1 bar:

$$\Delta G_{T,P} = \Delta(H - TS) = \Delta H - \Delta(TS)$$

$$= \Delta H - [TS_f - TS_i] = \Delta H - T(S_f - S_i)$$

$$= \Delta H - T\Delta S$$

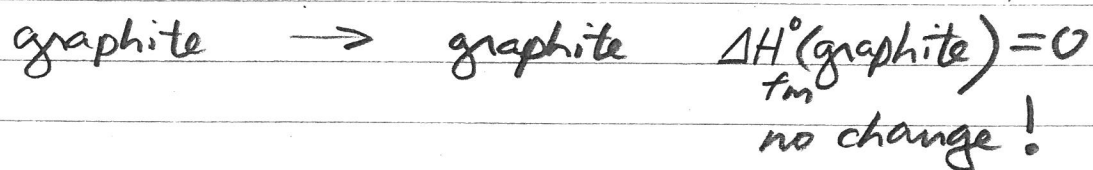
$$= 1895 \text{ J} - (298.15 \text{ K})(-3.36 \text{ J K}^{-1})$$

$$\Delta G_{T,P} = 2897 \text{ J}$$

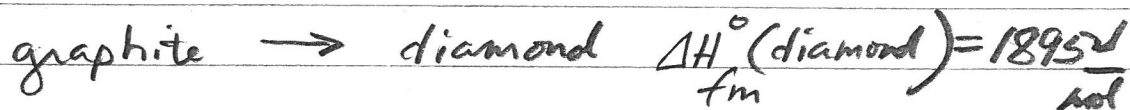
$$\Delta G_{T,P} > 0 \quad \text{impossible!}$$

Q3 a) The standard enthalpy of formation of a substance is the enthalpy change for the formation of the substance from pure elements in their most stable form at 1 bar (standard pressure) at a specified temperature.

From Q2, graphite is the most stable form of carbon at 25 °C and 1 bar, so



But  $\Delta H_{\text{fm}}^{\circ}(\text{diamond})$  is not zero



diamond (tetrahedrally bonded C atoms) has a different structure than graphite (hexagonally bonded C atoms in a plane) and a different enthalpy.

b) ~ Ditto! Graphite and diamond are both carbon, but they have different structures and therefore different physical properties, such as enthalpy and entropy

(Q3 cont.)

c) How are the absolute entropies of graphite and diamond measured?

Use calorimetry to measure the heat capacities of graphite and diamond, at constant pressure.

definitions:  $C_p = \frac{dq_{P(\text{rev})}}{dT}$   $dS = \frac{dq_{\text{rev}}}{T}$  (1 bar)

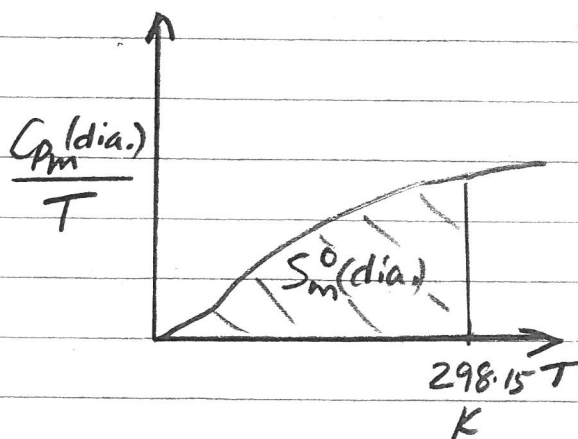
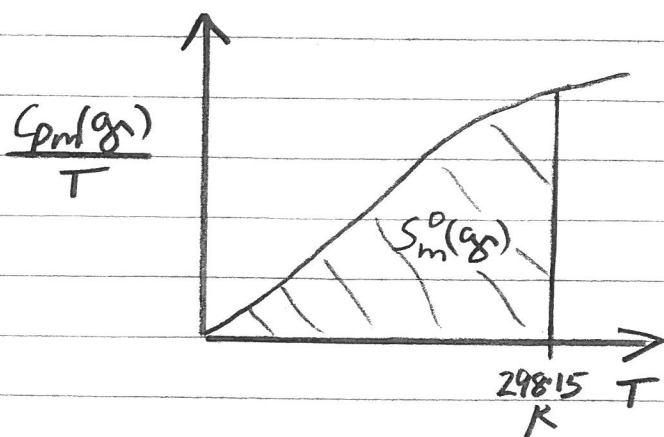
so  $dS = \frac{C_p}{T} dT$  and  $\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$

O (perfect crystal)

$$S_m^{\circ}(\text{graphite}, T) = S_m^{\circ}(\text{graphite}, 0\text{K}) + \int_0^T \frac{C_{pm}(\text{gr.})}{T} dT$$
$$= \int_0^T \frac{C_{pm}(\text{gr.})}{T} dT$$

similarly:

$$S_m^{\circ}(\text{diamond}, T) = \int_0^T \frac{C_{pm}(\text{dia.})}{T} dT$$



Q4 Tidying up a room and the resulting decrease in the entropy of the room is not a violation of the Second Law.

Why? Because the room is not an isolated system, it is being acted upon by the student (the "surroundings"), who expends metabolic energy with an increase in entropy due to the spontaneous biochemical reactions.

The overall entropy of the universe (an isolated system) increases.

Also, moving macroscopic objects (e.g., hiding empty booze bottles under the bed) has very little effect on the entropy because virtually all of the entropy is due to the microscopic arrangement of atoms and molecules over energy levels — internal entropy independent of an object's location.



Q5

1.00 mole of helium (assumed to be an ideal gas with  $C_{vm} = 3R/2$ ) at 300 K, 1.00 bar is heated reversibly to 500 K at const. pressure.

$$\left( \begin{aligned} \text{note: } C_{pm} &= C_{vm} + R \text{ (ideal gas)} \\ &= 3R/2 + R \\ &= 5R/2 \end{aligned} \right)$$

$$W = - \int P_{\text{ext}} dV \quad (\text{but } P = P_{\text{ext}} = 1.00 \text{ bar (const.)})$$

$$= - \int P dV = -P \int dV$$

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

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

$$= - (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (500 - 300) \text{ K}$$

$$W = -1663 \text{ J}$$

( $W < 0$  because the expanding gas does work on the surroundings)

$$C_p = \frac{dq_p}{dT} \text{ so } dq_p = C_{pm} dT \text{ and}$$

$$q_p = \int dq_p = \int C_p dT = \int n C_{pm} dT = \int n \frac{5}{2} R dT$$

$$= n \frac{5}{2} R \int dT = n \frac{5}{2} R (T_f - T_i) = (1.00 \text{ mol}) \frac{5}{2} (8.314 \frac{\text{J}}{\text{K mol}}) 200 \text{ K}$$

$$q = 4157 \text{ J} = \Delta H \text{ (p constant)}$$

(Q5 cont.)

$$\Delta U = q + w = 4157 \text{ J} - 1663 \text{ J}$$

$$\boxed{\Delta U = 2494 \text{ J}} \quad (= nC_{vm} \Delta T)$$

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int \frac{dq_{rev}}{T} \quad \text{for reversibly heating} \\ \text{1.00 mole of He}$$

$$= \int \frac{C_p dT}{T}$$

$$= \int \frac{n C_{pm} dT}{T} \quad \left( \begin{array}{l} n = 1.00 \text{ mol} \\ C_{pm} = \frac{5}{2} R \end{array} \right)$$

$$= n C_{pm} \int \frac{1}{T} dT$$

$$= n C_{pm} \ln(T_f/T_i)$$

$$= (1.00 \text{ mol}) \frac{5}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{500 \text{ K}}{300 \text{ K}}\right)$$

$$\boxed{\Delta S = 10.62 \text{ J K}^{-1}}$$