

7 Thermodynamics and the Second Law

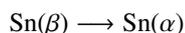
The gas constant, R , has the value $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$. 1 bar is 10^5 N m^{-2} , and 1 atmosphere is $1.01325 \times 10^5 \text{ N m}^{-2}$.

7.1 Following the discussion on page 206, devise some more arrangements of the 14 molecules amongst the given energy levels such that the total energy is 10 units. For each distribution, compute the value of W . Were you able to find a distribution with a value of W greater than distribution (a) from Fig. 7.3 on page 207?

7.2 Imagine that we have two large copper blocks, A and B, which are isolated from the surroundings. Block A is at a temperature of 250 K, and block B is at a temperature of 300 K. As the blocks are large, we can assume that small amounts of heat flowing into or out of them is reversible, and that such a process will not change the temperature of the block. It therefore follows that for an amount of heat q the entropy change of the block is q/T , where T is the temperature of the block.

Compute the entropy change of each block when 10 J of heat flows: (a) from block A to block B; (b) from block B to block A. Using these results, compute the entropy change of the Universe in each case, and hence determine which direction of heat flow is spontaneous.

7.3 Solid elemental tin can exist as two allotropes, called β -tin and α -tin (sometimes these are called white and grey tin, respectively). For the interconversion process



the enthalpy change is -2.1 kJ mol^{-1} , and the entropy change is $-7.1 \text{ J K}^{-1} \text{ mol}^{-1}$, both at 298 K. For the purposes of this question you may assume that these values are independent of temperature.

By computing the entropy change of the Universe for the above process, determine which allotrope is the stable form at: (a) $-10 \text{ }^\circ\text{C}$; (b) $+40 \text{ }^\circ\text{C}$. At what temperature will the two allotropes be in equilibrium with one another?

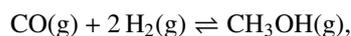
Calculate ΔG for the above process at the two temperatures, and comment on what the resulting values tell you about which allotrope is the stable form.

7.4 Solid elemental sulfur exists in two allotropes, α -sulfur (rhombic) and β -sulfur (monoclinic). The molar entropies of the two allotropes are $31.8 \text{ J K}^{-1} \text{ mol}^{-1}$ for α -sulfur, and $32.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for β -sulfur (at 298 K). The enthalpy change for the conversion of α -sulfur to β -sulfur is 330 J mol^{-1} .

Determine the temperature at which the two allotropes are in equilibrium, and the allotrope which is favoured at temperatures higher than this.

7.5 Explain why it is that an endothermic process can be spontaneous provided (a) it is accompanied by an increase in the entropy of the system, and (b) the temperature exceeds a particular value.

7.6 This question and the one which follows concern the equilibrium



which we are going to investigate as a viable commercial method for the production of methanol. The following data are provided (all at 298 K)

	CO(g)	H ₂ (g)	CH ₃ OH(g)
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-110.53		-200.66
$S_m^\circ / \text{J K}^{-1} \text{mol}^{-1}$	197.67	130.68	239.81

Using these data, determine $\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$ and hence K , all at 298 K. On the basis of your answer, comment on the viability of the reaction as a method for the production of methanol.

7.7 In practice, it is found that the reaction in the previous question only proceeds at a viable rate at 600 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are the same at 600 K as they are at 298 K, find the value of the equilibrium constant at 600 K. Qualitatively, is your answer in accord with Le Chatelier's principle?

7.8 Consider the equilibrium in which solid calcium carbonate decomposes to the oxide plus carbon dioxide



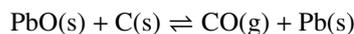
Write down an expression for the equilibrium constant of this reaction in terms of the partial pressure of CO₂.

The standard enthalpies of formation of CaCO₃(s), CO₂(g) and CaO(s) are -1207.6 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -634.9 kJ mol⁻¹ respectively, and the standard entropies are 91.7 J K⁻¹ mol⁻¹, 213.8 J K⁻¹ mol⁻¹ and 38.1 J K⁻¹ mol⁻¹ (all at 298 K). Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 800 K; hence find the equilibrium pressure of carbon dioxide at this temperature.

7.9 The following data are all at 298 K

reaction	$\Delta_r H^\circ / \text{kJ mol}^{-1}$	$\Delta_r S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO(g)}$	-110.53	89.36
$\text{Pb(s)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{PbO(s)}$	-218.99	-100.9

Assuming that these values are independent of temperature, compute $\Delta_r G^\circ$ for the reduction of PbO by carbon



at 298 K and at 700 K. Also, compute the temperature at which $\Delta_r G^\circ$ is zero, and comment on the significance of this value.

- 7.10 Using the approach described in section 7.15 on page 250, complete the following table for the equilibrium $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$

line	CO(g)	2H ₂ (g)	\rightleftharpoons	CH ₃ OH(g)
1	n_0	$2n_0$		0
2	$n_0(1 - \alpha)$			
3				

Line 1 is the initial amount in moles, line 2 is the amount in moles after a fraction α of the CO has reacted, and line 3 gives the mole fractions.

Hence show that the equilibrium constant is given by

$$K = \frac{\alpha(3 - 2\alpha)^2 (p^\circ)^2}{4(1 - \alpha)^3 p_{\text{eq}}^2},$$

where p_{eq} is the equilibrium pressure.

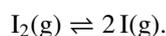
If it can be assumed that the equilibrium constant is such that $\alpha \ll 1$, show that the equilibrium constant can be approximated as

$$K = \frac{9\alpha(p^\circ)^2}{4p_{\text{eq}}^2},$$

hence obtain an expression for α in terms of K and p_{eq} .

Using your value of K from exercise 7.7, find α at 600 K for the case where the total pressure is (a) 1 bar and (b) 50 bar. Comment on your answers in the light of Le Chatelier's principle. Would it be advantageous to run the reaction at high pressure?

- 7.11 At high temperatures molecular iodine dissociates to iodine atoms



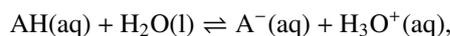
At 298 K, the standard enthalpies of formation of $\text{I}_2\text{(g)}$ and I(g) are $62.44 \text{ kJ mol}^{-1}$ and $106.84 \text{ kJ mol}^{-1}$, respectively, and the standard molar entropies are $260.69 \text{ J K}^{-1} \text{ mol}^{-1}$ and $180.79 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ for the dissociation reaction at 600 K, and hence find the value of the equilibrium constant.

0.008 moles of I_2 are allowed to come to equilibrium in a vessel of volume 1 dm^3 at a temperature of 600 K. Using Eq. 7.34 on page 252 determine the degree of dissociation α at this temperature, and hence the amount in moles of iodine atoms present.

- 7.12 Hydrogen cyanide, HCN, has a $\text{p}K_a$ of 9.21 at 298 K. Compute the pH of a 0.1 mol dm^{-3} solution of HCN. Also, find the ratio of the concentrations of $\text{CN}^-\text{(aq)}$ to HCN(aq) in such a solution.

Methanoic acid has a $\text{p}K_a$ of 3.75 at 298 K. If we prepared an equimolar mixture of hydrogen cyanide and methanoic acid in water, which out of the two conjugate bases CN^- and HCO_2^- would you expect to be present at the higher concentration? Give reasons for your answer.

- 7.13 Imagine preparing a solution of a weak acid AH and its sodium salt NaA. The acid dissociates according to the usual equilibrium



and we can assume that the sodium salt dissociates completely in water. Under these conditions, explain why it is possible to write the acid dissociation constant as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NaA}]_{\text{init}}}{[\text{AH}]_{\text{init}}},$$

where $[\text{NaA}]_{\text{init}}$ is the initial concentration of NaA in the solution, and $[\text{AH}]_{\text{init}}$ is the initial concentration of AH used to make up the solution.

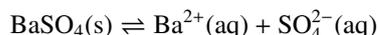
Hence show that the pH of the solution is given by

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NaA}]_{\text{init}}}{[\text{AH}]_{\text{init}}}.$$

Propanoic acid has a $\text{p}K_a$ of 4.87. Compute the pH of a solution with initial concentrations of 0.1 mol dm^{-3} propanoic acid and 0.1 mol dm^{-3} sodium propionate.

Such a solution is called a *buffer* as it has the property that its pH is largely unaltered by the addition of small amounts of H_3O^+ or OH^- ions. Explain, in qualitative terms, why the presence of a reservoir of A^- ions and undissociated AH leads to this buffering action.

- 7.14 Use the following data (all at 298 K) to calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ for the dissolution of $\text{BaSO}_4(\text{s})$ at 298 K:



reaction	$\Delta_r H^\circ / \text{kJ mol}^{-1}$	$\Delta_r S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{BaSO}_4(\text{s}) \rightarrow \text{Ba}^{2+}(\text{g}) + \text{SO}_4^{2-}(\text{g})$	2469	297
$\text{Ba}^{2+}(\text{g}) \rightarrow \text{Ba}^{2+}(\text{aq})$	-1346	-202.5
$\text{SO}_4^{2-}(\text{g}) \rightarrow \text{SO}_4^{2-}(\text{aq})$	-1099	-183

To what do you attribute the insolubility of BaSO_4 ?