19 Chemical thermodynamics

The gas constant, R, has the value 8.3145 J K^{-1} mol^{-1}; 1 bar is 10^5 N m^{-2}; 1 atmosphere is 1.01325×10^5 N m^{-2}; 1 Torr is 133.3 N m^{-2}.

19.1 4×10^{-3} moles of an ideal gas are held inside a cylinder by a piston such that the volume of the gas is 10 cm^3; the whole assembly is held in a thermostat at 298 K. Calculate the pressure of the gas in N m^{-2}. [Note that the SI unit of volume is m^3.]

(a) Assume that the external pressure is fixed at 1 bar. Explain why the piston moves out when it is released, and why it eventually comes to a stop. What will the pressure of the gas inside the cylinder be when the piston finally stops?

(b) Calculate the volume of the gas inside the cylinder when the piston has come to rest, and hence the work for this irreversible expansion.

(c) State the change in the internal energy, ΔU, of the gas when it undergoes this isothermal expansion. Hence, using the First Law, calculate the heat associated with the expansion, explaining its sign.

(d) Calculate the work associated with reversible isothermal expansion between the same initial and final states as the irreversible expansion described above; hence find the heat. Comment on these values in relation to those for the irreversible expansion.

(e) Determine the enthalpy change of the gas in (i) the reversible and (ii) the irreversible expansion.

19.2 A sample of methane gas of mass 4.50 g has volume 12.7 dm^3 at 310 K. It expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm^3. Assuming methane to be a perfect gas, calculate the work and heat associated with the process, along with the change in the internal energy and enthalpy of the gas. [1 Torr = 133.3 N m^{-2}.]

Calculate these same quantities if the expansion is carried out reversibly.

19.3 For the A $\rightleftharpoons$ B equilibrium, sketch a graph showing how the molar Gibbs energy of a mixture of A and B varies as the composition varies from pure reactant A to pure product B for the following cases: (a) $G^\circ_{m,A} = G^\circ_{m,B}$, (b) $G^\circ_{m,A} < G^\circ_{m,B}$. On your graph indicate the equilibrium composition.

Explain why it is that if the proportions of A and B are not at their equilibrium values, there is always a spontaneous process which will result in the composition moving to its equilibrium value, but that once this point is reached, no further change is possible.

19.4 Consider the equilibrium

$$2A(g) \rightleftharpoons B(g).$$

Using the approach illustrated in section 19.6.3 on page 748, show that for this reaction at equilibrium we have

$$\Delta_r G^\circ = -RT \ln K \quad \text{where} \quad K = \frac{p_{B,eq}/p^\circ}{(p_{A,eq}/p^\circ)^2},$$

and

$$\Delta_r G^\circ = G^\circ_{m,B} - 2G^\circ_{m,A}.$$

19.5 This question and the two which follow concern the equilibrium

$$\mathrm{CO(g)} + 2\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_3OH(g)},$$

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_3OH(g)
$\Delta_f H^\circ$ / kJ mol^{-1}	−110.53		−200.66
S°_m / J K^{-1} mol^{-1}	197.67	130.68	239.81
$C^\circ_{p,m}$ / J K^{-1} mol^{-1}	29.14	28.82	43.89

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.

19.6 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?

19.7 Using the approach described in section 19.8.1 on page 752 and section 19.8.2 on page 753, together with the data given in question 19.5, find the value of $\Delta_r C^\circ_p$ and hence the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 600 K for the equilibrium

$$\mathrm{CO(g)} + 2\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_3OH(g)}.$$

Hence compute $\Delta_r G^\circ$ and K at 600 K. How do your values compare with those found in exercise 17.5?

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

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}.$$

Using the approach illustrated in section 19.7.1 on page 750, show that

$$\Delta_r G^\circ = -RT \ln K$$

where p_{CO_2} is the equilibrium pressure of CO_2 and

$$\Delta_r G^\circ = G^\circ_m(\mathrm{CaO}) + G^\circ_m(\mathrm{CO_2}) - G^\circ_m(\mathrm{CaCO_3}) \quad \text{and} \quad K = \frac{p_{CO_2}}{p^\circ}.$$

The standard enthalpies of formation of $CaCO_3$(s), CO_2(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.

19.9 Thermodynamic data, at 298 K, for the reagents and products of the gas phase reaction

$$2HNO_2(g) \rightleftharpoons H_2O(g) + NO(g) + NO_2(g)$$

are given below.

	$\Delta_f H^\circ$ / kJ mol^{-1}	S°_m / J K^{-1} mol^{-1}	$C^\circ_{p,m}$ / J K^{-1} mol^{-1}
$HNO_2(g)$	−79.5	254.0	45.6
$H_2O(g)$	−241.8	188.7	33.6
$NO(g)$	90.2	210.7	29.8
$NO_2(g)$	33.2	240.0	37.2

Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 298 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 548 K are the same as those at 298 K, calculate $\Delta_r G^\circ$ at 548 K.

Calculate $\Delta_r C^\circ_p$ and, using this value, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 548 K. Compare the two values of $\Delta_r G^\circ$ you have obtained, and comment on what is the major source of the temperature variation of $\Delta_r G^\circ$ for this reaction. Calculate K for the reaction at 298 K and at 548 K.

19.10 The standard molar entropy of N_2 gas at 298 K is 191.6 J K^{-1} mol^{-1}, and its standard molar constant pressure heat capacity, $C^\circ_{p,m}$, at the same temperature is 29.70 J K^{-1} mol^{-1}.

(a) Using Eq. 19.46 on page 754, find the standard molar entropy of N_2 at 398 K.

(b) A better approximation than assuming that $C^\circ_{p,m}$ is constant is to use a parametrized form which includes a temperature dependence. For example

$$C^\circ_{p,m}(T) = A + BT.$$

Using this expression for $C^\circ_{p,m}$, show that integrating Eq. 19.45 on page 754 between T_1 and T_2 gives the following

$$S^\circ_m(T_2) = S^\circ_m(T_1) + A\ln\left(\frac{T_2}{T_1}\right) + B[T_2 - T_1]$$

(c) For N_2 $A = 28.58$ J K^{-1} mol^{-1} and $B = 3.77 \times 10^{-3}$ J K^{-2} mol^{-1}. Using these values in the expression above, calculate the entropy at 398 K. Comment on the difference between your answer and that obtained in (a).

19.11 The equilibrium constant, K, for the reaction

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

has been measured at a series of temperatures around 700 K as follows

T / K	635.7	670.4	686.0	722.2	760.2
K	0.01950	0.04414	0.07575	0.1971	0.5183

By plotting a graph of $\ln K$ against $1/T$, obtain a value for $\Delta_r H^\circ$ for the above reaction; explain any approximations you have to make. Use your graph to find a value of $\Delta_r G^\circ$ at 700 K, and hence find a value for $\Delta_r S^\circ$ at the same temperature.

19.12 Using the approach illustrated in section 19.9 on page 755 show that the equilibrium constants at T_1 and T_2 are related according to

$$\ln(K(T_2)) - \ln(K(T_1)) = -\frac{\Delta_r H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right].$$

What assumptions are made in deriving this equation?

For the reaction

$$\mathrm{CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)}$$

K is 1.038×10^5 at 298 K and 1.094×10^4 at 350 K. Use the expression above to calculate a value for $\Delta_r H^\circ$. Determine $\Delta_r G^\circ$ at 298 K, and use this value to find $\Delta_r S^\circ$ at this temperature.

19.13 Ketene $O{=}C{=}CH_2$ is a reactive gas which can be prepared by the thermal decomposition of propanone (acetone) vapour

$$\mathrm{CH_3COCH_3(g) \rightleftharpoons O{=}C{=}CH_2(g) + CH_4(g)}$$

Using the approach described in section 7.15 on page 250, complete the following table:

line	propanone	$\rightleftharpoons$	ketene	CH_4
1	n_0		0	0
2	$n_0(1-\alpha)$			
3				

Line 1 gives the initial amount in moles, line 2 gives the amounts in moles at equilibrium, and line 3 gives the mole fractions; α is the fraction of propanone which has decomposed.

Show that the equilibrium constant can be written

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

where p_{eq} is the pressure of the equilibrium mixture. Using this expression, find the value of K which corresponds to 90% decomposition of propanone at a total pressure of 1.2 bar.

At 298 K, $\Delta_r G^\circ$ for this reaction is 42 kJ mol^{-1}, and $\Delta_r H^\circ$ is 81 kJ mol^{-1}. Find the value of the equilibrium constant at 298 K and then, using the relationship below, find the temperature at which there is 90% decomposition of propanone at a total pressure of 1.2 bar.

$$\ln(K(T_2)) - \ln(K(T_1)) = -\frac{\Delta_r H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$