CHAPTER 3 The Second and Third Laws

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

TOPIC 3A Entropy

Discussion questions

3A.1 The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

3A.2 Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

3A.3 Discuss the relationships between the various formulations of the Second Law of thermodynamics.

3A.4 Account for deviations from Trouton's rule for liquids such as water and ethanol. Is their entropy of vaporization larger or smaller than $85\,\mathrm{J\,K^{-1}\,mol^{-1}}$? Why?

Exercises

3A.1(a) During a hypothetical process, the entropy of a system increases by $125\,\mathrm{J\,K^{-1}}$ while the entropy of the surroundings decreases by $125\,\mathrm{J\,K^{-1}}$. Is the process spontaneous?
3A.1(b) During a hypothetical process, the entropy of a system increases by $105\,\mathrm{J\,K^{-1}}$ while the entropy of the surroundings decreases by $95\,\mathrm{J\,K^{-1}}$. Is the process spontaneous?

3A.2(a) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 10.00 kJ of heat from the hot source and generates 3.00 kJ of work. What is the temperature of the organic liquid?
3A.2(b) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 2.71 kJ of heat from the hot source and generates 0.71 kJ of work. What is the temperature of the organic liquid?

3A.3(a) Calculate the change in entropy when 100 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (i) 0 °C, (ii) 50 °C.
3A.3(b) Calculate the change in entropy when 250 kJ of energy is transferred reversibly and isothermally as heat to a large block of lead at (i) 20 °C, (ii) 100 °C.

3A.4(a) Which of $F_2(g)$ and $I_2(g)$ is likely to have the higher standard molar entropy at 298 K?
3A.4(b) Which of $H_2O(g)$ and $CO_2(g)$ is likely to have the higher standard molar entropy at 298 K?

3A.5(a) Calculate the change in entropy when 15 g of carbon dioxide gas is allowed to expand from $1.0\,\mathrm{dm^3}$ to $3.0\,\mathrm{dm^3}$ at 300 K.
3A.5(b) Calculate the change in entropy when 4.00 g of nitrogen is allowed to expand from $500\,\mathrm{cm^3}$ to $750\,\mathrm{cm^3}$ at 300 K.

3A.6(a) Predict the enthalpy of vaporization of benzene from its normal boiling point, 80.1 °C.
3A.6(b) Predict the enthalpy of vaporization of cyclohexane from its normal boiling point, 80.7 °C.

3A.7(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is $146.22\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K.
3A.7(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is $154.84\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K.

3A.8(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = \tfrac{5}{2} R$, is changed from 25 °C and 1.00 atm to 125 °C and 5.00 atm. How do you rationalize the sign of ΔS?

3A.8(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \tfrac{5}{2} R$, is changed from 25 °C and 1.50 atm to 135 °C and 7.00 atm. How do you rationalize the sign of ΔS?

3A.9(a) Calculate ΔS_{tot} when two copper blocks, each of mass 1.00 kg, one at 50 °C and the other at 0 °C are placed in contact in an isolated container. The specific heat capacity of copper is $0.385\,\mathrm{J\,K^{-1}\,g^{-1}}$ and may be assumed constant over the temperature range involved.
3A.9(b) Calculate ΔS_{tot} when two iron blocks, each of mass 10.0 kg , one at 100 °C and the other at 25 °C, are placed in contact in an isolated container. The specific heat capacity of iron is $0.449\,\mathrm{J\,K^{-1}\,g^{-1}}$ and may be assumed constant over the temperature range involved.

3A.10(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against $p_{\mathrm{ex}} = 0$, and (iii) an adiabatic reversible expansion.
3A.10(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from $1.20\,\mathrm{dm^3}$ to $4.60\,\mathrm{dm^3}$ in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against $p_{\mathrm{ex}} = 0$, and (iii) an adiabatic reversible expansion.

3A.11(a) The enthalpy of vaporization of chloroform ($CHCl_3$) is $29.4\,\mathrm{kJ\,mol^{-1}}$ at its normal boiling point of 334.88 K. Calculate (i) the entropy of vaporization of chloroform at this temperature and (ii) the entropy change of the surroundings.
3A.11(b) The enthalpy of vaporization of methanol is $35.27\,\mathrm{kJ\,mol^{-1}}$ at its normal boiling point of 64.1 °C. Calculate (i) the entropy of vaporization of methanol at this temperature and (ii) the entropy change of the surroundings.

3A.12(a) Calculate the change in entropy of the system when 10.0 g of ice at -10.0 °C is converted into water vapour at 115.0 °C and at a constant pressure of 1 bar. The constant-pressure molar heat capacity of $H_2O(s)$ and $H_2O(l)$ is $75.291\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and that of $H_2O(g)$ is $33.58\,\mathrm{J\,K^{-1}\,mol^{-1}}$.
3A.12(b) Calculate the change in entropy of the system when 15.0 g of ice at -12.0 °C is converted to water vapour at 105.0 °C at a constant pressure of 1 bar. For data, see the preceding exercise.

Problems

3A.1 Represent the Carnot cycle on a temperature–entropy diagram and show that the area enclosed by the cycle is equal to the work done.

3A.2 The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) Reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A, $V=4.00\,\mathrm{dm^3}$, $p=1.00\,\mathrm{atm}$, and $T=300\,\mathrm{K}$, that $V_A=10V_B$, $p_C/p_B=5$, and that $C_{p,m}=\frac{7}{2}R$.

3A.3 Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only. (*Hint*: Suppose that two such paths can intersect, and complete a cycle with the two paths plus one isothermal path. Consider the changes accompanying each stage of the cycle and show that they conflict with the Kelvin statement of the Second Law.)

3A.4 To calculate the work required to lower the temperature of an object, we need to consider how the coefficient of performance c (see *Impact* I3.1) changes with the temperature of the object. (a) Find an expression for the work of cooling an object from T_i to T_f when the refrigerator is in a room at a temperature T_h. *Hint*: Write $\mathrm{d}w=\mathrm{d}q/c(T)$, relate $\mathrm{d}q$ to $\mathrm{d}T$ through the heat capacity C_p, and integrate the resulting expression. Assume that the heat capacity is independent of temperature in the range of interest. (b) Use the result in part (a) to calculate the work needed to freeze 250 g of water in a refrigerator at 293 K. How long will it take when the refrigerator operates at 100 W?

3A.5 The expressions that apply to the treatment of refrigerators (Problem 3A.4) also describe the behaviour of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.

3A.6 Calculate the difference in molar entropy (a) between liquid water and ice at –5 °C, (b) between liquid water and its vapour at 95 °C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 J K⁻¹ mol⁻¹ and –41.9 J K⁻¹ mol⁻¹, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

3A.7 The molar heat capacity of chloroform (trichloromethane, $CHCl_3$) in the range 240 K to 330 K is given by $C_{p,m}/(\mathrm{J\,K^{-1}\,mol^{-1}})=91.47+7.5\times10^{-2}\,(T/\mathrm{K})$.

In a particular experiment, 1.00 mol $CHCl_3$ is heated from 273 K to 300 K. Calculate the change in molar entropy of the sample.

3A.8 A block of copper of mass 2.00 kg ($C_{p,m}=24.44\,\mathrm{J\,K^{-1}\,mol^{-1}}$) and temperature 0 °C is introduced into an insulated container in which there is 1.00 mol $H_2O(g)$ at 100 °C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapour is present at equilibrium. From the vapour pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies. (*Hint*: You will need to make plausible approximations.)

3A.9 A sample consisting of 1.00 mol of perfect gas molecules at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of q, w, ΔU, ΔH, ΔS, ΔS_{surr}, and ΔS_{tot} for each path.

3A.10 A block of copper of mass 500 g and initially at 293 K is in thermal contact with an electric heater of resistance 1.00 kΩ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking $C_{p,m}=24.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The experiment is then repeated with the copper immersed in a stream of water that maintains its temperature at 293 K. Calculate the change in entropy of the copper and the water in this case.

3A.11 Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature T_h and the other at T_c, are brought into thermal contact and allowed to reach equilibrium. Evaluate the change for two blocks of copper, each of mass 500 g, with $C_{p,m}=24.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$, taking $T_h=500\,\mathrm{K}$ and $T_c=250\,\mathrm{K}$.

3A.12 According to Newton's law of cooling, the rate of change of temperature is proportional to the temperature difference between the system and its surroundings. Given that $S(T)-S(T_i)=C\ln(T/T_i)$, where T_i is the initial temperature and C the heat capacity, deduce an expression for the rate of change of entropy of the system as it cools.

3A.13 The protein lysozyme unfolds at a transition temperature of 75.5 °C and the standard enthalpy of transition is 509 kJ mol⁻¹. Calculate the entropy of unfolding of lysozyme at 25.0 °C, given that the difference in the constant-pressure heat capacities upon unfolding is 6.28 kJ K⁻¹ mol⁻¹ and can be assumed to be independent of temperature. *Hint*: Imagine that the transition at 25.0 °C occurs in three steps: (i) heating of the folded protein from 25.0 °C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0 °C. Because the entropy is a state function, the entropy change at 25.0 °C is equal to the sum of the entropy changes of the steps.

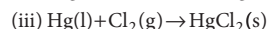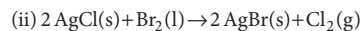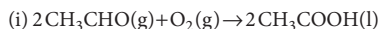# TOPIC 3B The measurement of entropy

Discussion question

3B.1 Discuss why the standard entropies of ions in solution may be positive, negative, or zero.
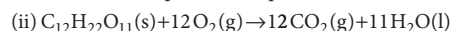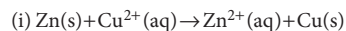
Exercises

3B.1(a) Calculate the residual molar entropy of a solid in which the molecules can adopt (i) three, (ii) five, (iii) six orientations of equal energy at $T=0$.

3B.1(b) Suppose that the hexagonal molecule $C_6H_nF_{6-n}$ has a residual entropy on account of the similarity of the H and F atoms. Calculate the residual for each value of n.

3B.2(a) Calculate the standard reaction entropy at 298 K of

(i) $2\,CH_3CHO(g)+O_2(g)\rightarrow2\,CH_3COOH(l)$

(ii) $2\,AgCl(s)+Br_2(l)\rightarrow2\,AgBr(s)+Cl_2(g)$

(iii) $Hg(l)+Cl_2(g)\rightarrow HgCl_2(s)$

3B.2(b) Calculate the standard reaction entropy at 298 K of

(i) $Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}(aq)+Cu(s)$

(ii) $C_{12}H_{22}O_{11}(s)+12\,O_2(g)\rightarrow12\,CO_2(g)+11\,H_2O(l)$

Problems

3B.1 The standard molar entropy of $NH_3(g)$ is 192.45 J K^{-1} mol^{-1} at 298 K, and its heat capacity is given by eqn 2B.8 with the coefficients given in Table 2B.1. Calculate the standard molar entropy at (a) 100 °C and (b) 500 °C.

3B.2 The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4

T/K	70	100	150	200	250	298
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0 °C and (b) 25 °C.

3B.3 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Resource section*, calculate: (a) the standard enthalpies and entropies at 298 K and 398 K for the reaction $CO_2(g)+H_2(g)\rightarrow CO(g)+H_2O(g)$. Assume that the heat capacities are constant over the temperature range involved.

3B.4 The molar heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

T/K	10	20	30	40	50	60
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	2.09	14.43	36.44	62.55	87.03	111.0

T/K	70	80	90	100	110	150
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	131.4	149.4	165.3	179.6	192.8	237.6

T/K	160	170	180	190	200
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	247.3	256.5	265.1	273.0	280.3

Calculate the molar enthalpy relative to its value at $T=0$ and the Third-Law entropy at each of these temperatures.

3B.5 The compound 1,3,5-trichloro-2,4,6-trifluorobenzene is an intermediate in the conversion of hexachlorobenzene to hexafluorobenzene, and its thermodynamic properties have been examined by measuring its heat capacity over a wide temperature range (R.L. Andon and J.F. Martin, *J. Chem. Soc. Faraday Trans. I*, 871 (1973)). Some of the data are as follows:

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	9.492	12.70	18.18	32.54	46.86	66.36

T/K	100.90	140.86	183.59	225.10	262.99	298.06
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	95.05	121.3	144.4	163.7	180.2	196.4

Calculate the molar enthalpy relative to its value at $T=0$ and the Third-Law molar entropy of the compound at these temperatures.

3B.6‡ Given that $S_m^\ominus=29.79$ J K^{-1} mol^{-1} for bismuth at 100 K and the following tabulated heat capacity data (D.G. Archer, *J. Chem. Eng. Data* **40**, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

T/K	100	120	140	150	160	180	200
$C_{p,m}/$ $(J\,K^{-1}\,mol^{-1})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11

Compare the value to the value that would be obtained by taking the heat capacity to be constant at 24.44 J K^{-1} mol^{-1} over this range.

3B.7 Derive an expression for the molar entropy of a monatomic solid on the basis of the Einstein and Debye models and plot the molar entropy against the temperature (use T/θ in each case, with θ the Einstein or Debye temperature). Use the following expressions for the temperature-dependence of the heat capacities:

$$\text{Einstein}:\ C_{V,m}(T)=3Rf^E(T)\quad f^E(T)=\left(\frac{\theta^E}{T}\right)^2\left(\frac{e^{\theta^E/2T}}{e^{\theta^E/T}-1}\right)^2$$

$$\text{Debye}:\ C_{V,m}(T)=3Rf^D(T)\quad f^D(T)=3\left(\frac{T}{\theta^D}\right)^2\int_0^{\theta^D/T}\frac{x^4e^x}{(e^x-1)^2}\,dx$$

Use mathematical software to evaluate the appropriate expressions.

3B.8 An average human DNA molecule has 5×10^8 binucleotides (rungs on the DNA ladder) of four different kinds. If each rung were a random choice of one of these four possibilities, what would be the residual entropy associated with this typical DNA molecule?

TOPIC 3C Concentrating on the system

Discussion questions

3C.1 The following expressions have been used to establish criteria for spontaneous change: $dA_{T,V}<0$ and $dG_{T,p}<0$. Discuss the origin, significance, and applicability of each criterion.

3C.2 Under what circumstances, and why, can the spontaneity of a process be discussed in terms of the properties of the system alone?
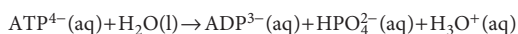
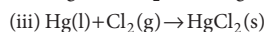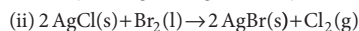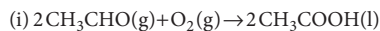‡ These problems were provided by Charles Trapp and Carmen Giunta.

Exercises

3C.1(a) Combine the reaction entropies calculated in Exercise 3B.2(a) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3C.1(b) Combine the reaction entropies calculated in Exercise 3B.2(b) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3C.2(a) Calculate the standard Gibbs energy of the reaction $4\,HI(g)+O_2(g)\rightarrow 2\,I_2(s)+2\,H_2O(l)$ at 298 K, from the standard entropies and enthalpies of formation given in the *Resource section*.

3C.2(b) Calculate the standard Gibbs energy of the reaction $CO(g)+CH_3CH_2OH(l)\rightarrow CH_3CH_2COOH(l)$ at 298 K, from the standard entropies and enthalpies of formation given in the *Resource section*.

3C.3(a) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

3C.3(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

3C.4(a) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions

(i) $2\,CH_3CHO(g)+O_2(g)\rightarrow 2\,CH_3COOH(l)$

(ii) $2\,AgCl(s)+Br_2(l)\rightarrow 2\,AgBr(s)+Cl_2(g)$

(iii) $Hg(l)+Cl_2(g)\rightarrow HgCl_2(s)$

3C.4(b) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions

(i) $Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}(aq)+Cu(s)$

(ii) $C_{12}H_{22}O_{11}(s)+12\,O_2(g)\rightarrow 12\,CO_2(g)+11\,H_2O(l)$

3C.5(a) The standard enthalpy of combustion of ethyl acetate ($CH_3COOC_2H_5$) is $-2231\,kJ\,mol^{-1}$ at 298 K and its standard molar entropy is $259.4\,J\,K^{-1}\,mol^{-1}$. Calculate the standard Gibbs energy of formation of the compound at 298 K.

3C.5(b) The standard enthalpy of combustion of the amino acid glycine (NH_2CH_2COOH) is $-969\,kJ\,mol^{-1}$ at 298 K and its standard molar entropy is $103.5\,J\,K^{-1}\,mol^{-1}$. Calculate the standard Gibbs energy of formation of glycine at 298 K.
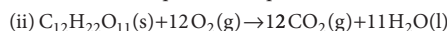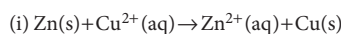
Problems

3C.1 Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B are isothermal; that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas molecules in each section. Initially $T_A=T_B=300\,K$, $V_A=V_B=2.00\,dm^3$. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is $1.00\,dm^3$. Calculate (a) ΔS_A and ΔS_B, (b) ΔA_A and ΔA_B, (c) ΔG_A and ΔG_B, (d) ΔS of the total system and its surroundings. If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given. (Assume $C_{V,m}=20\,J\,K^{-1}\,mol^{-1}$.)

3C.2 Calculate the molar internal energy, molar entropy, and molar Helmholtz energy of a collection of harmonic oscillators and plot your expressions as a function of T/θ^V, where $\theta^V=h\nu/k$.

3C.3 In biological cells, the energy released by the oxidation of foods is stored in adenosine triphosphate (ATP or ATP^{4-}). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP^{3-}):

$$ATP^{4-}(aq)+H_2O(l)\rightarrow ADP^{3-}(aq)+HPO_4^{2-}(aq)+H_3O^+(aq)$$

At pH=7.0 and 37 °C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are $\Delta_rH=-20\,kJ\,mol^{-1}$ and $\Delta_rG=-31\,kJ\,mol^{-1}$, respectively. Under these conditions, the hydrolysis of 1 mol $ATP^{4-}(aq)$ results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at pH=7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 1×10^6 ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre ($1\,W=1\,J\,s^{-1}$)? A computer battery delivers about 15 W and has a volume of $100\,cm^3$. Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires $14.2\,kJ\,mol^{-1}$ of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

TOPIC 3D Combining the First and Second Laws

Discussion questions

3D.1 Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

3D.2 Suggest a physical interpretation of the dependence of the Gibbs energy on the pressure.

Exercises

3D.1(a) Suppose that 2.5 mmol $N_2(g)$ occupies $42\,cm^3$ at 300 K and expands isothermally to $600\,cm^3$. Calculate ΔG for the process.

3D.1(b) Suppose that 6.0 mmol $Ar(g)$ occupies $52\,cm^3$ at 298 K and expands isothermally to $122\,cm^3$. Calculate ΔG for the process.

3D.2(a) The change in the Gibbs energy of a certain constant–pressure process was found to fit the expression $\Delta G/J=-85.40+36.5(T/K)$. Calculate the value of ΔS for the process.

3D.2(b) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/J = -73.1 + 42.8(T/K)$. Calculate the value of ΔS for the process.

3D.3(a) Estimate the change in the Gibbs energy and molar Gibbs energy of $1.0\,dm^3$ of octane when the pressure acting on it is increased from 1.0 atm to 100 atm. The mass density of octane is $0.703\,g\,cm^{-3}$.

3D.3(b) Estimate the change in the Gibbs energy and molar Gibbs energy of $100\,cm^3$ of water when the pressure acting on it is increased from 100 kPa to 500 kPa. The mass density of water is $0.997\,g\,cm^{-3}$.

3D.4(a) Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

3D.4(b) Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

Problems

3D.1 Calculate $\Delta_r G^{\ominus}$ (375 K) for the reaction $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$ from the value of $\Delta_r G^{\ominus}$ (298 K), $\Delta_r H^{\ominus}$ (298 K), and the Gibbs–Helmholtz equation.

3D.2 Estimate the standard reaction Gibbs energy of $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ at (a) 500 K, (b) 1000 K from their values at 298 K.

3D.3 At 298 K the standard enthalpy of combustion of sucrose is -5797 $kJ\,mol^{-1}$ and the standard Gibbs energy of the reaction is $-6333\,kJ\,mol^{-1}$. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37 °C.

3D.4 Two empirical equations of state of a real gas are as follows:

$$\text{van der Waals}: p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\text{Dieterici}: p = \frac{RTe^{-a/RTV_m}}{V_m - b}$$

Evaluate $(\partial S/\partial V)_T$ for each gas. For an isothermal expansion, for which kind of gas (also consider a perfect gas) will ΔS be greatest? Explain your conclusion.

3D.5 Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

3D.6 (a) Use the Maxwell relations to express the derivatives $(\partial S/\partial V)_T$, $(\partial V/\partial S)_p$, $(\partial p/\partial S)_V$, and $(\partial V/\partial S)_p$ in terms of the heat capacities, the expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_p$, and the isothermal compressibility, $\kappa_T = -(1/V)(\partial V/\partial p)_T$. (b) The Joule coefficient, μ_J, is defined as $\mu_J = (\partial T/\partial V)_U$. Show that $\mu_J C_V = p - \alpha T/\kappa_T$.

3D.7 Suppose that S is regarded as a function of p and T. Show that $TdS = C_p dT - \alpha TVdp$. Hence, show that the energy transferred as heat when the pressure

on an incompressible liquid or solid is increased by Δp is equal to $-\alpha TV\Delta p$, where $\alpha = (1/V)(\partial V/\partial T)_p$. Evaluate q when the pressure acting on $100\,cm^3$ of mercury at 0 °C is increased by 1.0 kbar. ($\alpha = 1.82 \times 10^{-4}\,K^{-1}$.)

3D.8 Equation 3D.6 ($\pi_T = T(\partial p/\partial T)_V - p$) expresses the internal pressure π_T in terms of the pressure and its derivative with respect to temperature. Express π_T in terms of the molecular partition function.

3D.9 Explore the consequences of replacing the equation of state of a perfect gas by the van der Waals equation of state for the pressure-dependence of the molar Gibbs energy. Proceed in three steps. First, consider the case when $a = 0$ and only repulsions are significant. Then consider the case when $b = 0$ and only attractions are significant. For the latter, you should consider making the approximation that the attractions are weak. Finally, explore the full expression by using mathematical software. In each case plot your results graphically and account physically for the deviations from the perfect gas expression.

3D.10‡ Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which bring about the Antarctic ozone hole. Worsnop et al. (*Science* **259**, 71 (1993)) investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere. They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapour, $HNO_3 \cdot nH_2O(s) \rightarrow HNO_3(g) + nH_2O(g)$, for $n = 1$, 2, and 3. Given $\Delta_r G^{\ominus}$ and $\Delta_r H^{\ominus}$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^{\ominus}$ at 190 K.

n	1	2	3
$\Delta_r G^{\ominus}/(kJ\,mol^{-1})$	46.2	69.4	93.2
$\Delta_r H^{\ominus}/(kJ\,mol^{-1})$	127	188	237

Integrated activities

3.1 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1 + Bp)$. Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = \frac{5}{2}R$, $\mu = 0.21\,K\,atm^{-1}$, $B = -0.525(K/T)\,atm^{-1}$ and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

3.2 Discuss the relationship between the thermodynamic and statistical definitions of entropy.

3.3 Use mathematical software, a spreadsheet, or the *Living graphs* on the web site for this book to:

(a) Evaluate the change in entropy of 1.00 mol $CO_2(g)$ on expansion from $0.001\,m^3$ to $0.010\,m^3$ at 298 K, treated as a van der Waals gas.
(b) Allow for the temperature dependence of the heat capacity by writing $C = a + bT + c/T^2$, and plot the change in entropy for different values of the three coefficients (including negative values of c).
(c) Show how the first derivative of G, $(\partial G/\partial p)_T$, varies with pressure, and plot the resulting expression over a pressure range. What is the physical significance of $(\partial G/\partial p)_T$?
(d) Evaluate the fugacity coefficient as a function of the reduced volume of a van der Waals gas and plot the outcome for a selection of reduced temperatures over the range $0.8 \leq V_r \leq 3$.