CHAPTER 2   The First Law

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

TOPIC 2A   Internal energy

Discussion questions

2A.1 Describe and distinguish the various uses of the words 'system' and 'state' in physical chemistry.

2A.2 Describe the distinction between heat and work in thermodynamic and molecular terms, the latter in terms of populations and energy levels.

2A.3 Identify varieties of additional work.

Exercises

2A.1(a) Use the equipartition theorem to estimate the molar internal energy relative to $U(0)$ of (i) I_2, (ii) CH_4, (iii) C_6H_6 in the gas phase at 25 °C.
2A.1(b) Use the equipartition theorem to estimate the molar internal energy relative to $U(0)$ of (i) O_3, (ii) C_2H_6, (iii) SO_2 in the gas phase at 25 °C.

2A.2(a) Which of (i) pressure, (ii) temperature, (iii) work, (iv) enthalpy are state functions?
2A.2(b) Which of (i) volume, (ii) heat, (iii) internal energy, (iv) density are state functions?

2A.3(a) A chemical reaction takes place in a container of cross-sectional area 50 cm². As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
2A.3(b) A chemical reaction takes place in a container of cross-sectional area 75.0 cm². As a result of the reaction, a piston is pushed out through 25.0 cm against an external pressure of 150 kPa. Calculate the work done by the system.

2A.4(a) A sample consisting of 1.00 mol Ar is expanded isothermally at 20 °C from 10.0 dm³ to 30.0 dm³ (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas, and (iii) freely (against zero external pressure). For the three processes calculate q, w, and ΔU.

2A.4(b) A sample consisting of 2.00 mol He is expanded isothermally at 0 °C from 5.0 dm³ to 20.0 dm³ (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas, and (iii) freely (against zero external pressure). For the three processes calculate q, w, and ΔU.

2A.5(a) A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,m} = \frac{3}{2}R$, initially at $p_1 = 1.00$ atm and $T_1 = 300$ K, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU, q, and w.
2A.5(b) A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,m} = \frac{5}{2}R$, initially at $p_1 = 111$ kPa and $T_1 = 277$ K, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU, q, and w.

2A.6(a) A sample of 4.50 g of methane occupies 12.7 dm³ at 310 K. (i) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm³. (ii) Calculate the work that would be done if the same expansion occurred reversibly.
2A.6(b) A sample of argon of mass 6.56 g occupies 18.5 dm³ at 305 K. (i) Calculate the work done when the gas expands isothermally against a constant external pressure of 7.7 kPa until its volume has increased by 2.5 dm³. (ii) Calculate the work that would be done if the same expansion occurred reversibly.

Problems

2A.1 Calculate the work done during the isothermal reversible expansion of a van der Waals gas (Topic 1C). Plot on the same graph the indicator diagrams (graphs of pressure against volume) for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which $a=0$ and $b=5.11 \times 10^{-2}$ dm³ mol⁻¹, and (c) $a=4.2$ dm⁶ atm mol⁻² and $b=0$. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take $V_i = 1.0$ dm³, $n = 1.0$ mol, and $T = 298$ K.

2A.2 A sample consisting of 1.0 mol $CaCO_3(s)$ was heated to 800 °C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

2A.3 Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, eqn 1C.3. Evaluate (a) the work

for 1.0 mol Ar at 273 K (for data, see Table 1C.1) and (b) the same amount of a perfect gas. Let the expansion be from 500 cm³ to 1000 cm³ in each case.

2A.4 Express the work of isothermal reversible expansion of a van der Waals gas in reduced variables (Topic 1C) and find a definition of reduced work that makes the overall expression independent of the identity of the gas. Calculate the work of isothermal reversible expansion along the critical isotherm from V_c to xV_c.

2A.5 Suppose that a DNA molecule resists being extended from an equilibrium, more compact conformation with a restoring force $F = -k_f x$, where x is the difference in the end-to-end distance of the chain from an equilibrium value and k_f is the force constant. Use this model to write an expression for the work that must be done to extend a DNA molecule by a distance x. Draw a graph of your conclusion.

2A.6 A better model of a DNA molecule is the 'one-dimensional freely jointed chain', in which a rigid unit of length l can only make an angle of 0° or 180° with an adjacent unit. In this case, the restoring force of a chain extended by $x=nl$ is given by

$$F = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) \qquad \nu = \frac{n}{N}$$

where k is Boltzmann's constant. (a) What is the magnitude of the force that must be applied to extend a DNA molecule with $N=200$ by 90 nm? (b) Plot the restoring force against ν, noting that ν can be either positive or negative. How is the variation of the restoring force with end-to-end distance different from that predicted by Hooke's law? (c) Keep in mind that the difference in

end-to-end distance from an equilibrium value is $x=nl$ and, consequently, $dx=ldn=Nldv$, and write an expression for the work of extending a DNA molecule. (d) Calculate the work of extending a DNA molecule from $\nu=0$ to $\nu=1.0$. *Hint*: You must integrate the expression for w. The task can be accomplished easily with mathematical software.

2A.7 As a continuation of Problem 2A.6, (a) show that for small extensions of the chain, when $i \ll 1$, the restoring force is given by

$$F \approx \frac{\nu kT}{l} = \frac{nkT}{Nl}$$

(b) Is the variation of the restoring force with extension of the chain given in part (a) different from that predicted by Hooke's law? Explain your answer.

TOPIC 2B   Enthalpy

Discussion questions

2B.1 Explain the difference between the change in internal energy and the change in enthalpy accompanying a process.

2B.2 Why is the heat capacity at constant pressure of a substance normally greater than its heat capacity at constant volume?

Exercises

2B.1(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.
2B.1(b) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2B.2(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\text{J K}^{-1})=$ 20.17+0.3665(T/K). Calculate q, w, and ΔH when the temperature is raised from 25 °C to 100 °C (i) at constant pressure, (ii) at constant volume.

2B.2(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\text{J K}^{-1})=$ 20.17+0.4001(T/K). Calculate q, w, and ΔH when the temperature is raised from 25 °C to 100 °C (i) at constant pressure, (ii) at constant volume.

2B.3(a) When 3.0 mol O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O_2 at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU.
2B.3(b) When 2.0 mol CO_2 is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO_2 at constant pressure is 37.11 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU.

Problems

2B.1 The following data show how the standard molar constant-pressure heat capacity of sulfur dioxide varies with temperature. By how much does the standard molar enthalpy of SO_2(g) increase when the temperature is raised from 298.15 K to 1500 K?

T/K	300	500	700	900	1100	1300	1500
$C_{p,m}^{\ominus}/(\text{J K}^{-1}\text{mol}^{-1})$	39.909	46.490	50.829	53.407	54.993	56.033	56.759

2B.2 The following data show how the standard molar constant-pressure heat capacity of ammonia depends on the temperature. Use mathematical software to fit an expression of the form of eqn 2B.8 to the data and determine the values of a, b, and c. Explore whether it would be better to express the data as $C_{p,m}=\alpha+\beta T+\gamma T^2$, and determine the values of these coefficients.

T/K	300	400	500	600	700	800	900	1000
$C_{p,m}^{\ominus}/(\text{J K}^{-1}\text{mol}^{-1})$	35.678	38.674	41.994	45.229	48.269	51.112	53.769	56.244

2B.3 A sample consisting of 2.0 mol CO_2 occupies a fixed volume of 15.0 dm³ at 300 K. When it is supplied with 2.35 kJ of energy as heat its temperature increases to 341 K. Assume that CO_2 is described by the van der Waals equation of state (Topic 1C) and calculate w, ΔU, and ΔH.

2B.4 (a) Express $(\partial C_V/\partial V)_T$ as a second derivative of U and find its relation to $(\partial U/\partial V)_T$ and $(\partial C_p/\partial p)_T$ as a second derivative of H and find its relation to $(\partial H/\partial p)_T$. (b) From these relations show that $(\partial C_V/\partial V)_T=0$ and $(\partial C_p/\partial p)_T=0$ for a perfect gas.

TOPIC 2C Thermochemistry

Discussion questions

2C.1 Describe two calorimetric methods for the determination of enthalpy changes that accompany chemical processes.

2C.2 Distinguish between 'standard state' and 'reference state', and indicate their applications.

Exercises

2C.1(a) For tetrachloromethane, $\Delta_{vap}H^{\ominus}=30.0\,kJ\,mol^{-1}$. Calculate q, w, ΔH, and ΔU when 0.75 mol $CCl_4(l)$ is vaporized at 250 K and 750 Torr.
2C.1(b) For ethanol, $\Delta_{vap}H^{\ominus}=43.5\,kJ\,mol^{-1}$. Calculate q, w, ΔH, and ΔU when 1.75 mol $C_2H_5OH(l)$ is vaporized at 260 K and 765 Torr.

2C.2(a) The standard enthalpy of formation of ethylbenzene is –12.5 kJ mol⁻¹. Calculate its standard enthalpy of combustion.
2C.2(b) The standard enthalpy of formation of phenol is –165.0 kJ mol⁻¹. Calculate its standard enthalpy of combustion.

2C.3(a) The standard enthalpy of combustion of cyclopropane is –2091 kJ mol⁻¹ at 25 °C. From this information and enthalpy of formation data for $CO_2(g)$ and $H_2O(g)$, calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is +20.42 kJ mol⁻¹. Calculate the enthalpy of isomerization of cyclopropane to propene.
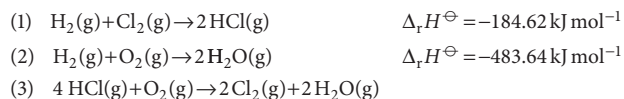**2C.3(b)** From the following data, determine $\Delta_f H^{\ominus}$ for diborane, $B_2H_6(g)$, at 298 K:

(1) $B_2H_6(g)+3\,O_2(g)\rightarrow B_2O_3(s)+3\,H_2O(g)$ $\Delta_r H^{\ominus}=-1941\,kJ\,mol^{-1}$

(2) $2\,B(s)+\frac{3}{2}\,O_2(g)\rightarrow B_2O_3(s)$ $\Delta_r H^{\ominus}=-2368\,kJ\,mol^{-1}$

(3) $H_2(g)+\frac{1}{2}\,O_2(g)\rightarrow H_2O(g)$ $\Delta_r H^{\ominus}=-241.8\,kJ\,mol^{-1}$
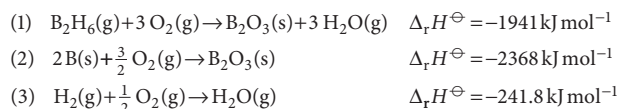
2C.4(a) Given that the standard enthalpy of formation of HCl(aq) is –167 kJ mol⁻¹, what is the value of $\Delta_f H^{\ominus}(Cl^-, aq)$?
2C.4(b) Given that the standard enthalpy of formation of HI(aq) is –55 kJ mol⁻¹, what is the value of $\Delta_f H^{\ominus}(I^-, aq)$?

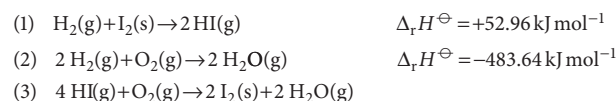**2C.5(a)** When 120 mg of naphthalene, $C_{10}H_8(s)$, was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the calorimeter constant. By how much will the temperature rise when 150 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions?
2C.5(b) When 225 mg of anthracene, $C_{14}H_{10}(s)$, was burned in a bomb calorimeter the temperature rose by 1.75 K. Calculate the calorimeter constant. By how much will the temperature rise when 125 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions? ($\Delta_c H^{\ominus}(C_{14}H_{10},s)=-7061\,kJ\,mol^{-1}$.)

2C.6(a) Given the reactions (1) and (2) below, determine (i) $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ for reaction (3), (ii) $\Delta_f H^{\ominus}$ for both HCl(g) and $H_2O(g)$ all at 298 K.

(1) $H_2(g)+Cl_2(g)\rightarrow 2\,HCl(g)$ $\Delta_r H^{\ominus}=-184.62\,kJ\,mol^{-1}$

(2) $H_2(g)+O_2(g)\rightarrow 2\,H_2O(g)$ $\Delta_r H^{\ominus}=-483.64\,kJ\,mol^{-1}$

(3) $4\,HCl(g)+O_2(g)\rightarrow 2\,Cl_2(g)+2\,H_2O(g)$

2C.6(b) Given the reactions (1) and (2) below, determine (i) $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ for reaction (3), (ii) $\Delta_f H^{\ominus}$ for both HI(g) and $H_2O(g)$ all at 298 K.

(1) $H_2(g)+I_2(s)\rightarrow 2\,HI(g)$ $\Delta_r H^{\ominus}=+52.96\,kJ\,mol^{-1}$

(2) $2\,H_2(g)+O_2(g)\rightarrow 2\,H_2O(g)$ $\Delta_r H^{\ominus}=-483.64\,kJ\,mol^{-1}$

(3) $4\,HI(g)+O_2(g)\rightarrow 2\,I_2(s)+2\,H_2O(g)$

2C.7(a) For the reaction $C_2H_5OH(l)+3\,O_2(g)\rightarrow 2\,CO_2(g)+3\,H_2O(g)$, $\Delta_r U^{\ominus}=-1373\,kJ\,mol^{-1}$ at 298 K. Calculate $\Delta_r H^{\ominus}$.
2C.7(b) For the reaction $2\,C_6H_5COOH(s)+15\,O_2(g)\rightarrow 14\,CO_2(g)+6\,H_2O(g)$, $\Delta_r U^{\ominus}=-772.7\,kJ\,mol^{-1}$ at 298 K. Calculate $\Delta_r H^{\ominus}$.

2C.8(a) From the data in Tables 2C.2 and 2C.3, calculate $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ at (i) 298 K, (ii) 478 K for the reaction $C(graphite)+H_2O(g)\rightarrow CO(g)+H_2(g)$. Assume all heat capacities to be constant over the temperature range of interest.
2C.8(b) Calculate $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ at 298 K and $\Delta_r H^{\ominus}$ at 427 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2C.5 and 2C.6. Assume the heat capacities to be constant over the temperature range involved.

2C.9(a) Estimate $\Delta_r H^{\ominus}$ (500 K) for the combustion of methane, $CH_4(g)+2\,O_2(g)\rightarrow CO_2(g)+2\,H_2O(g)$ by using the data on the temperature dependence of heat capacities in Table 2B.1.
2C.9(b) Estimate $\Delta_r H^{\ominus}$ (478 K) for the combustion of naphthalene, $C_{10}H_8(l)+12\,O_2(g)\rightarrow 10\,CO_2(g)+4\,H_2O(g)$ by using the data on the temperature dependence of heat capacities in Table 2B.1.

2C.10(a) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg^{2+} ions using the following data: enthalpy of sublimation of Mg(s), +167.2 kJ mol⁻¹; first and second ionization enthalpies of Mg(g), 7.646 eV and 15.035 eV; dissociation enthalpy of $Cl_2(g)$, +241.6 kJ mol⁻¹; electron gain enthalpy of Cl(g), –3.78 eV; enthalpy of solution of $MgCl_2(s)$, –150.5 kJ mol⁻¹; enthalpy of hydration of Cl⁻(g), –383.7 kJ mol⁻¹.
2C.10(b) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s), +178.2 kJ mol⁻¹; first and second ionization enthalpies of Ca(g), 589.7 kJ mol⁻¹ and 1145 kJ mol⁻¹; enthalpy of vaporization of bromine, +30.91 kJ mol⁻¹; dissociation enthalpy of $Br_2(g)$, +192.9 kJ mol⁻¹; electron gain enthalpy of Br(g), –331.0 kJ mol⁻¹; enthalpy of solution of $CaBr_2(s)$, –103.1 kJ mol⁻¹; enthalpy of hydration of Br⁻(g), –289 kJ mol⁻¹.

Problems

2C.1 A sample of the sugar D-ribose ($C_5H_{10}O_5$) of mass 0.727 g was placed in a constant-volume bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is –3251 kJ mol⁻¹, gave a temperature rise of 1.940 K. Calculate the enthalpy of formation of D-ribose.

2C.2 The standard enthalpy of formation of bis(benzene)chromium was measured in a calorimeter. It was found for the reaction $Cr(C_6H_6)_2(s)\rightarrow Cr(s)+2\,C_6H_6(g)$ that $\Delta_r U^{\ominus}(583\,K)=+8.0\,kJ\,mol^{-1}$. Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is 136.1 J K⁻¹ mol⁻¹ in its liquid range and 81.67 J K⁻¹ mol⁻¹ as a gas.

2C.3[‡] From the enthalpy of combustion data in Table 2C.1 for the alkanes methane through octane, test the extent to which the relation $\Delta_c H^\ominus = k\{(M/(g\,mol^{-1})\}^n$ holds and find the numerical values for k and n. Predict $\Delta_c H^\ominus$ for decane and compare to the known value.

2C.4[‡] Kolesov et al. reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov et al., *J. Chem. Thermodynamics* **28**, 1121 (1996)). In one of their runs, they found the standard specific internal energy of combustion to be $-36.0334\,kJ\,g^{-1}$ at 298.15 K. Compute $\Delta_c H^\ominus$ and $\Delta_f H^\ominus$ of C_{60}.

2C.5[‡] A thermodynamic study of $DyCl_3$ (E.H.P. Cordfunke et al., *J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information

(1) $DyCl_3(s) \rightarrow DyCl_3(aq, in\ 4.0\ M\ HCl)$ $\Delta_r H^\ominus = -180.06\,kJ\,mol^{-1}$

(2) $Dy(s) + 3\,HCl(aq, 4.0\ M) \rightarrow DyCl_3(aq, in\ 4.0\ M\,HCl(aq)) + \frac{3}{2}H_2(g)$

$\Delta_r H^\ominus = -699.43\,kJ\,mol^{-1}$

(3) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(aq, 4.0\ M)$ $\Delta_r H^\ominus = -158.31\,kJ\,mol^{-1}$

Determine $\Delta_f H^\ominus(DyCl_3, s)$ from these data.

2C.6[‡] Silylene (SiH_2) is a key intermediate in the thermal decomposition of silicon hydrides such as silane (SiH_4) and disilane (Si_2H_6). H.K. Moffat et al. (*J. Phys. Chem.* **95**, 145 (1991)) report $\Delta_f H^\ominus(SiH_2) = +274\,kJ\,mol^{-1}$. If $\Delta_f H^\ominus(SiH_4) = +34.3\,kJ\,mol^{-1}$ and $\Delta_f H^\ominus(Si_2H_6) = +80.3\,kJ\,mol^{-1}$, compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) \rightarrow SiH_2(g) + H_2(g)$
(b) $Si_2H_6(g) \rightarrow SiH_2(g) + SiH_4(g)$

2C.7 As remarked in Problem 2B.2, it is sometimes appropriate to express the temperature dependence of the heat capacity by the empirical expression $C_{p,m} = \alpha + \beta T + \gamma T^2$. Use this expression to estimate the standard enthalpy of combustion of methane at 350 K. Use the following data:

	$\alpha/(J\,K^{-1}\,mol^{-1})$	$\beta/(mJ\,K^{-2}\,mol^{-1})$	$\gamma/(\mu J\,K^{-3}\,mol^{-1})$
$CH_4(g)$	14.16	75.5	−17.99
$CO_2(g)$	26.86	6.97	−0.82
$O_2(g)$	25.72	12.98	−3.862
$H_2O(g)$	30.36	9.61	1.184

2C.8 Figure 2.1 shows the experimental DSC scan of hen white lysozyme (G. Privalov et al., *Anal. Biochem.* **79**, 232 (1995)) converted to joules (from calories). Determine the enthalpy of unfolding of this protein by integration of the curve and the change in heat capacity accompanying the transition.
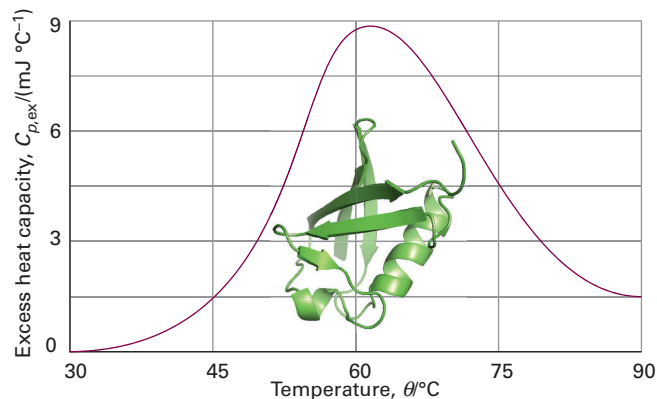

Figure 2.1 The experimental DSC scan of hen white lysozyme.

2C.9 An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

2C.10 In biological cells that have a plentiful supply of oxygen, glucose is oxidized completely to CO_2 and H_2O by a process called *aerobic oxidation*. Muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid ($CH_3CH(OH)COOH$) by a process called *anaerobic glycolysis*. (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K^{-1} the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

TOPIC 2D State functions and exact differentials

Discussion questions

2D.1 Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.

2D.2 Explain why a perfect gas does not have an inversion temperature.

Exercises

2D.1(a) Estimate the internal pressure, π_T, of water vapour at 1.00 bar and 400 K, treating it as a van der Waals gas. *Hint*: Simplify the approach by estimating the molar volume by treating the gas as perfect.
2D.1(b) Estimate the internal pressure, π_T, of sulfur dioxide at 1.00 bar and 298 K, treating it as a van der Waals gas. *Hint*: Simplify the approach by estimating the molar volume by treating the gas as perfect.

2D.2(a) For a van der Waals gas, $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of nitrogen gas from an initial volume of 1.00 dm³ to 20.00 dm³ at 298 K. What are the values of q and w?
2D.2(b) Repeat Exercise 2D.2(a) for argon, from an initial volume of 1.00 dm³ to 30.00 dm³ at 298 K.

[‡] These problems were provided by Charles Trapp and Carmen Giunta.

2D.3(a) The volume of a certain liquid varies with temperature as

$$V = V^{\ominus}\{0.75 + 3.9 \times 10^{-4}(T/K) + 1.48 \times 10^{-6}(T/K)^2\}$$

where $V^{\ominus}$ is its volume at 300 K. Calculate its expansion coefficient, α, at 320 K.

2D.3(b) The volume of a certain liquid varies with temperature as

$$V = V^{\ominus}\{0.77 + 3.7 \times 10^{-4}(T/K) + 1.52 \times 10^{-6}(T/K)^2\}$$

where $V^{\ominus}$ is its volume at 298 K. Calculate its expansion coefficient, α, at 310 K.

2D.4(a) The isothermal compressibility of water at 293 K is 4.96×10^{-5} atm^{-1}. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.

2D.4(b) The isothermal compressibility of lead at 293 K is 2.21×10^{-6} atm^{-1}. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.

2D.5(a) Given that $\mu = 0.25$ K atm^{-1} for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 85 atm.

2D.5(b) Given that $\mu = 1.11$ K atm^{-1} for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

Problems

2D.1‡ In 2006, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5 °C likely by the year 2100, with 2.0 °C its best estimate. Predict the average rise in sea level due to thermal expansion of sea water based on temperature rises of 1.0 °C, 2.0 °C, and 3.5 °C given that the volume of the Earth's oceans is 1.37×10^9 km^3 and their surface area is 361×10^6 km^2, and state the approximations which go into the estimates.

2D.2 The heat capacity ratio of a gas determines the speed of sound in it through the formula $c_s = (\gamma RT/M)^{1/2}$, where $\gamma = C_p/C_V$ and M is the molar mass of the gas. Deduce an expression for the speed of sound in a perfect gas of (a) diatomic, (b) linear triatomic, (c) nonlinear triatomic molecules at high temperatures (with translation and rotation active). Estimate the speed of sound in air at 25 °C.

2D.3 Starting from the expression $C_p - C_V = T(\partial p/\partial T)_V(\partial V/\partial T)_p$, use the appropriate relations between partial derivatives to show that

$$C_p - C_V = \frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T}$$

Evaluate $C_p - C_V$ for a perfect gas.

2D.4 (a) Write expressions for dV and dp given that V is a function of p and T and p is a function of V and T. (b) Deduce expressions for d ln V and d ln p in terms of the expansion coefficient and the isothermal compressibility.

2D.5 Rearrange the van der Waals equation of state, $p = nRT/(V - nb) - n^2a/V^2$, to give an expression for T as a function of p and V (with n constant). Calculate $(\partial T/\partial p)_V$ and confirm that $(\partial T/\partial p)_V = 1/(\partial p/\partial T)_V$. Go on to confirm Euler's chain relation (*Mathematical background* 2).

2D.6 Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas (see Problem 2D.5). Show, using Euler's chain relation (*Mathematical background* 2), that $\kappa_T R = \alpha(V_m - b)$.

2D.7 The speed of sound, c_s, in a gas of molar mass M is related to the ratio of heat capacities γ by $c_s = (\gamma RT/M)^{1/2}$. Show that $c_s = (\gamma p/\rho)^{1/2}$, where ρ is the mass density of the gas. Calculate the speed of sound in argon at 25 °C.

2D.8‡ A gas obeying the equation of state $p(V - nb) = nRT$ is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

2D.9 Use the fact that $(\partial U/\partial V)_T = a/V_m^2$ for a van der Waals gas (Topic 1C) to show that $\mu C_{p,m} \approx (2a/RT) - b$ by using the definition of μ and appropriate relations between partial derivatives. *Hint*: Use the approximation $pV_m \approx RT$ when it is justifiable to do so.

2D.10‡ Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative is 2,2-dichloro-1,1,1-trifluoroethane (refrigerant 123). Younglove and McLinden published a compendium of thermophysical properties of this substance (B.A. Younglove and M. McLinden, *J. Phys. Chem. Ref. Data* **23**, 7 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 1.00 bar and 50 °C given that $(\partial H/\partial p)_T = -3.29 \times 10^3$ J MPa^{-1} mol^{-1} and $C_{p,m} = 110.0$ J K^{-1} mol^{-1}. (b) Compute the temperature change which would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50 °C.

2D.11‡ Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). A compendium of thermophysical properties of this substance has been published (R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* **23**, 657 (1994)) from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K):

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg^{-1})	426.48	426.12	425.76

(The specific constant-pressure heat capacity is 0.7649 kJ K^{-1} kg^{-1}.) (b) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg^{-1})	461.93	459.12	42B.15

(The specific constant-pressure heat capacity is 1.0392 kJ K^{-1} kg^{-1}.)

TOPIC 2E Adiabatic changes

Discussion questions

2E.1 Why are adiabats steeper than isotherms?

2E.2 Why do heat capacities play a role in the expressions for adiabatic expansion?

Exercises

2E.1(a) Use the equipartition principle to estimate the values of $\gamma=C_p/C_V$ for gaseous ammonia and methane. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at 25 °C?

2E.1(b) Use the equipartition principle to estimate the value of $\gamma=C_p/C_V$ for carbon dioxide. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at 25 °C?

2E.2(a) Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 dm³ at 273.15 K to 3.0 dm³.

2E.2(b) Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm³ at 298.15 K to 2.00 dm³.

2E.3(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V=20.8$ J K^{-1} is initially at 4.25 atm and 300 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2E.3(b) A sample consisting of 2.5 mol of perfect gas molecules with $C_{p,m}=20.8$ J K^{-1} mol^{-1} is initially at 240 kPa and 325 K. It undergoes reversible adiabatic expansion until its pressure reaches 150 kPa. Calculate the final volume and temperature and the work done.

2E.4(a) A sample of carbon dioxide of mass 2.45 g at 27.0 °C is allowed to expand reversibly and adiabatically from 500 cm³ to 3.00 dm³. What is the work done by the gas?

2E.4(b) A sample of nitrogen of mass 3.12 g at 23.0 °C is allowed to expand reversibly and adiabatically from 400 cm³ to 2.00 dm³. What is the work done by the gas?

2E.5(a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 67.4 kPa and 0.50 dm³ to a final volume of 2.00 dm³. Take $\gamma=1.4$.

2E.5(b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 97.3 Torr and 400 cm³ to a final volume of 5.0 dm³. Take $\gamma=1.3$.

Problem

2E.1 The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. The value of $\gamma=C_p/C_V$ can be inferred if the decrease in pressure is also measured and the constant-pressure heat capacity deduced by combining the two values. A fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its volume; as a result, the temperature fell from 298.15 K to 248.44 K and its pressure fell from 202.94 kPa to 81.840 kPa. Evaluate C_p.

Integrated activities

2.1 Give examples of state functions and discuss why they play a critical role in thermodynamics.

2.2 The thermochemical properties of hydrocarbons are commonly investigated by using molecular modelling methods. (a) Use software to predict $\Delta_f H^\ominus$ values for the alkanes methane through pentane. To calculate $\Delta_c H^\ominus$ values, estimate the standard enthalpy of formation of C$_n$H$_{2n+2}$(g) by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for CO$_2$(g) and H$_2$O(l). (b) Compare your estimated values with the experimental values of $\Delta_c H^\ominus$ (Table 2C.4) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation $\Delta_c H^\ominus=\text{constant}\times\{(M/(\text{g mol}^{-1})\}^n$ holds and determine the numerical values of the constant and n.

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

(a) Calculate the work of isothermal reversible expansion of 1.0 mol CO$_2$(g) at 298 K from 1.0 m³ to 3.0 m³ on the basis that it obeys the van der Waals equation of state.

(b) Explore how the parameter γ affects the dependence of the pressure on the volume. Does the pressure–volume dependence become stronger or weaker with increasing volume?