

Molecular interpretation 2.3 *Molecular interactions and the Joule–Thomson effect*

The kinetic model of gases (*Molecular interpretation 1.1*) and the equipartition theorem (*Molecular interpretation 2.2*) imply that the mean kinetic energy of molecules in a gas is proportional to the temperature. It follows that reducing the average speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can be reduced to the point that neighbours can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid.

To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. We saw in Section 1.3 that molecules in a real gas attract each other (the attraction is not gravitational, but the effect is the same). It follows that, if we can cause the molecules to move apart from each other, like a ball rising from a planet, then they should slow. It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any energy to enter from outside as heat. As the gas expands, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbours. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to $\mu > 0$, is observed under conditions when attractive interactions are dominant ($Z < 1$, eqn 1.17), because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant ($Z > 1$), the Joule–Thomson effect results in the gas becoming warmer, or $\mu < 0$.

Checklist of key ideas

- 1. Thermodynamics is the study of the transformations of energy.
- 2. The system is the part of the world in which we have a special interest. The surroundings is the region outside the system where we make our measurements.
- 3. An open system has a boundary through which matter can be transferred. A closed system has a boundary through which matter cannot be transferred. An isolated system has a boundary through which neither matter nor energy can be transferred.
- 4. Energy is the capacity to do work. The internal energy is the total energy of a system.
- 5. Work is the transfer of energy by motion against an opposing force, $dw = -Fdz$. Heat is the transfer of energy as a result of a temperature difference between the system and the surroundings.
- 6. An exothermic process releases energy as heat to the surroundings. An endothermic process absorbs energy as heat from the surroundings.
- 7. A state function is a property that depends only on the current state of the system and is independent of how that state has been prepared.
- 8. The First Law of thermodynamics states that the internal energy of an isolated system is constant, $\Delta U = q + w$.
- 9. Expansion work is the work of expansion (or compression) of a system, $dw = -p_{\text{ex}}dV$. The work of free expansion is $w = 0$. The work of expansion against a constant external pressure is $w = -p_{\text{ex}}\Delta V$. The work of isothermal reversible expansion of a perfect gas is $w = -nRT \ln(V_f/V_i)$.
- 10. A reversible change is a change that can be reversed by an infinitesimal modification of a variable.
- 11. Maximum work is achieved in a reversible change.

- 12. Calorimetry is the study of heat transfers during physical and chemical processes.
- 13. The heat capacity at constant volume is defined as $C_V = (\partial U/\partial T)_V$. The heat capacity at constant pressure is $C_p = (\partial H/\partial T)_p$. For a perfect gas, the heat capacities are related by $C_p - C_V = nR$.
- 14. The enthalpy is defined as $H = U + pV$. The enthalpy change is the energy transferred as heat at constant pressure, $\Delta H = q_p$.
- 15. During a reversible adiabatic change, the temperature of a perfect gas varies according to $T_f = T_i(V_i/V_f)^{1/c}$, $c = C_{V,m}/R$. The pressure and volume are related by $pV^\gamma = \text{constant}$, with $\gamma = C_{p,m}/C_{V,m}$.
- 16. The standard enthalpy change is the change in enthalpy for a process in which the initial and final substances are in their standard states. The standard state is the pure substance at 1 bar.
- 17. Enthalpy changes are additive, as in $\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus$.
- 18. The enthalpy change for a process and its reverse are related by $\Delta_{\text{forward}}H^\ominus = -\Delta_{\text{reverse}}H^\ominus$.
- 19. The standard enthalpy of combustion is the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is also present.
- 20. Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.
- 21. The standard enthalpy of formation ($\Delta_f H^\ominus$) is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The reference state is the most stable state of an element at the specified temperature and 1 bar.
- 22. The standard reaction enthalpy may be estimated by combining enthalpies of formation, $\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus$.
- 23. The temperature dependence of the reaction enthalpy is given by Kirchhoff's law, $\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$.
- 24. An exact differential is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states. An inexact differential is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states.
- 25. The internal pressure is defined as $\pi_T = (\partial U/\partial V)_T$. For a perfect gas, $\pi_T = 0$.
- 26. The Joule–Thomson effect is the cooling of a gas by isenthalpic expansion.
- 27. The Joule–Thomson coefficient is defined as $\mu = (\partial T/\partial p)_H$. The isothermal Joule–Thomson coefficient is defined as $\mu_T = (\partial H/\partial p)_T = -C_p \mu$.
- 28. The inversion temperature is the temperature at which the Joule–Thomson coefficient changes sign.

Further reading

Articles and texts

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Further information

Further information 2.1 Adiabatic processes

Consider a stage in a reversible adiabatic expansion when the pressure inside and out is p . The work done when the gas expands by dV is $dw = -pdV$; however, for a perfect gas, $dU = C_V dT$.

Therefore, because for an adiabatic change ($dq = 0$) $dU = dw + dq = dw$, we can equate these two expressions for dU and write

$$C_V dT = -pdV$$

We are dealing with a perfect gas, so we can replace p by nRT/V and obtain

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

To integrate this expression we note that T is equal to T_i when V is equal to V_i , and is equal to T_f when V is equal to V_f at the end of the expansion. Therefore,

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

(We are taking C_V to be independent of temperature.) Then, because $\int dx/x = \ln x + \text{constant}$, we obtain

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Because $\ln(x/y) = -\ln(y/x)$, this expression rearranges to

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

With $c = C_V/nR$ we obtain (because $\ln x^a = a \ln x$)

$$\ln \left(\frac{T_f}{T_i} \right)^c = \ln \left(\frac{V_i}{V_f} \right)$$

which implies that $(T_f/T_i)^c = (V_i/V_f)$ and, upon rearrangement, eqn 2.28.

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so we can use $pV = nRT$ to write

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

However, we have just shown that

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i} \right)^{1/c} = \left(\frac{V_f}{V_i} \right)^{\gamma-1}$$

where we use the definition of the heat capacity ratio where $\gamma = C_{p,m}/C_{V,m}$ and the fact that, for a perfect gas, $C_{p,m} - C_{V,m} = R$ (the molar version of eqn 2.26). Then we combine the two expressions, to obtain

$$\frac{p_i}{p_f} = \frac{V_f}{V_i} \times \left(\frac{V_f}{V_i} \right)^{\gamma-1} = \left(\frac{V_f}{V_i} \right)^{\gamma}$$

which rearranges to $p_i V_i^{\gamma} = p_f V_f^{\gamma}$, which is eqn 2.29.

Further information 2.2 The relation between heat capacities

A useful rule when doing a problem in thermodynamics is to go back to first principles. In the present problem we do this twice, first by expressing C_p and C_V in terms of their definitions and then by inserting the definition $H = U + pV$:

$$\begin{aligned} C_p - C_V &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial U}{\partial T} \right)_p + \left(\frac{\partial(pV)}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V \end{aligned}$$

We have already calculated the difference of the first and third terms on the right, and eqn 2.45 lets us write this difference as $\alpha \pi_T V$. The factor αV gives the change in volume when the temperature is raised, and $\pi_T = (\partial U/\partial V)_T$ converts this change in volume into a change in internal energy. We can simplify the remaining term by noting that, because p is constant,

$$\left(\frac{\partial(pV)}{\partial T} \right)_p = p \left(\frac{\partial V}{\partial T} \right)_p = \alpha p V$$

The middle term of this expression identifies it as the contribution to the work of pushing back the atmosphere: $(\partial V/\partial T)_p$ is the change of volume caused by a change of temperature, and multiplication by p converts this expansion into work.

Collecting the two contributions gives

$$C_p - C_V = \alpha(p + \pi_T)V \quad (2.56)$$

As just remarked, the first term on the right, $\alpha p V$, is a measure of the work needed to push back the atmosphere; the second term on the right, $\alpha \pi_T V$, is the work required to separate the molecules composing the system.

At this point we can go further by using the result we prove in Section 3.8 that

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

When this expression is inserted in the last equation we obtain

$$C_p - C_V = \alpha T V \left(\frac{\partial p}{\partial T} \right)_V \quad (2.57)$$

We now transform the remaining partial derivative. It follows from Euler's chain relation that

$$\left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

Comment 2.8

The Euler chain relation states that, for a differentiable function $z = z(x, y)$,

$$\left(\frac{\partial y}{\partial x} \right)_z \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x = -1$$

For instance, if $z(x, y) = x^2 y$,

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z \frac{d(1/x^2)}{dx} = -\frac{2z}{x^3}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial(z/y)^{1/2}}{\partial z}\right)_y = \frac{1}{y^{1/2}} \frac{dz^{1/2}}{dz} = \frac{1}{2(yz)^{1/2}}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial(x^2y)}{\partial y}\right)_x = x^2 \frac{dy}{dy} = x^2$$

Multiplication of the three terms together gives the result -1 .

and therefore that

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_p (\partial V/\partial p)_T}$$

Unfortunately, $(\partial T/\partial V)_p$ occurs instead of $(\partial V/\partial T)_p$. However, the 'reciprocal identity' allows us to invert partial derivatives and to write

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

Discussion questions

- 2.1** Provide mechanical and molecular definitions of work and heat.
- 2.2** Consider the reversible expansion of a perfect gas. Provide a physical interpretation for the fact that $pV^\gamma = \text{constant}$ for an adiabatic change, whereas $pV = \text{constant}$ for an isothermal change.
- 2.3** Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.
- 2.4** Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.

Exercises

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

- 2.1(a)** Calculate the work needed for a 65 kg person to climb through 4.0 m on the surface of (a) the Earth and (b) the Moon ($g = 1.60 \text{ m s}^{-2}$).
- 2.1(b)** Calculate the work needed for a bird of mass 120 g to fly to a height of 50 m from the surface of the Earth.
- 2.2(a)** A chemical reaction takes place in a container of cross-sectional area 100 cm^2 . As a result of the reaction, a piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
- 2.2(b)** A chemical reaction takes place in a container of cross-sectional area 50.0 cm^2 . As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.
- 2.3(a)** A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

Comment 2.9

The reciprocal identity states that

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}$$

For example, for the function $z(x,y) = x^2y$,

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z \frac{d(1/x^2)}{dx} = -\frac{2z}{x^3}$$

We can also write $x = (z/y)^{1/2}$, in which case

$$\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z &= \left(\frac{\partial(z/y)^{1/2}}{\partial y}\right)_z = z^{1/2} \frac{d(1/y^{1/2})}{dy} \\ &= -\frac{z^{1/2}}{2y^{3/2}} = -\frac{z^{1/2}}{2(z/x^2)^{3/2}} = -\frac{x^3}{2z} \end{aligned}$$

which is the reciprocal of the coefficient derived above.

Insertion of this relation into eqn 2.57 produces eqn 2.49.

- 2.5** Explain the significance of the Joule and Joule–Thomson experiments. What would Joule observe in a more sensitive apparatus?
- 2.6** Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.
- 2.7** In many experimental thermograms, such as that shown in Fig. 2.16, the baseline below T_1 is at a different level from that above T_2 . Explain this observation.

- 2.3(b)** A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .
- 2.4(a)** A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,m} = \frac{3}{2}R$, initially at $p_1 = 1.00 \text{ atm}$ and $T_1 = 300 \text{ K}$, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU , q , and w .
- 2.4(b)** A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,m} = \frac{5}{2}R$, initially at $p_1 = 111 \text{ kPa}$ and $T_1 = 277 \text{ K}$, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU , q , and w .
- 2.5(a)** A sample of 4.50 g of methane occupies 12.7 dm^3 at 310 K. (a) 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 dm^3 . (b) Calculate the work that would be done if the same expansion occurred reversibly.
- 2.5(b)** A sample of argon of mass 6.56 g occupies 18.5 dm^3 at 305 K. (a) 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.

(b) Calculate the work that would be done if the same expansion occurred reversibly.

2.6(a) A sample of 1.00 mol H₂O(g) is condensed isothermally and reversibly to liquid water at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ mol⁻¹. Find *w*, *q*, Δ*U*, and Δ*H* for this process.

2.6(b) A sample of 2.00 mol CH₃OH(g) is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ mol⁻¹. Find *w*, *q*, Δ*U*, and Δ*H* for this process.

2.7(a) A strip of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.0 atm and the temperature 25°C.

2.7(b) A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature 23°C.

2.8(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_{p,m}/(\text{J K}^{-1}) = 20.17 + 0.3665(T/\text{K})$. Calculate *q*, *w*, Δ*U*, and Δ*H* when the temperature is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume.

2.8(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_{p,m}/(\text{J K}^{-1}) = 20.17 + 0.4001(T/\text{K})$. Calculate *q*, *w*, Δ*U*, and Δ*H* when the temperature is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

2.9(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.

2.9(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.

2.10(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?

2.10(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?

2.11(a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and 1.0 dm³ to a final volume of 2.0 dm³. Take $\gamma = 1.4$.

2.11(b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm³ to a final volume of 3.0 dm³. Take $\gamma = 1.3$.

2.12(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.

2.12(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.

2.13(a) When 3.0 mol O₂ 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 O₂ at constant pressure is 29.4 J K⁻¹ mol⁻¹, calculate *q*, Δ*H*, and Δ*U*.

2.13(b) When 2.0 mol CO₂ 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 CO₂ at constant pressure is 37.11 J K⁻¹ mol⁻¹, calculate *q*, Δ*H*, and Δ*U*.

2.14(a) A sample of 4.0 mol O₂ is originally confined in 20 dm³ at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate *q*, *w*, Δ*T*, Δ*U*, and Δ*H*. (The final pressure of the gas is not necessarily 600 Torr.)

2.14(b) A sample of 5.0 mol CO₂ is originally confined in 15 dm³ at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate *q*, *w*, Δ*T*, Δ*U*, and Δ*H*. (The final pressure of the gas is not necessarily 78.5 kPa.)

2.15(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8 \text{ J K}^{-1}$ is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2.15(b) A sample consisting of 1.5 mol of perfect gas molecules with $C_{p,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

2.16(a) A certain liquid has $\Delta_{\text{vap}}H^\circ = 26.0 \text{ kJ mol}^{-1}$. Calculate *q*, *w*, Δ*H*, and Δ*U* when 0.50 mol is vaporized at 250 K and 750 Torr.

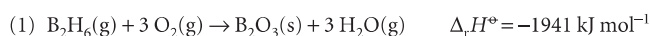
2.16(b) A certain liquid has $\Delta_{\text{vap}}H^\circ = 32.0 \text{ kJ mol}^{-1}$. Calculate *q*, *w*, Δ*H*, and Δ*U* when 0.75 mol is vaporized at 260 K and 765 Torr.

2.17(a) The standard enthalpy of formation of ethylbenzene is -12.5 kJ mol⁻¹. Calculate its standard enthalpy of combustion.

2.17(b) The standard enthalpy of formation of phenol is -165.0 kJ mol⁻¹. Calculate its standard enthalpy of combustion.

2.18(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 CO₂(g) and H₂O(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.

2.18(b) From the following data, determine $\Delta_f H^\circ$ for diborane, B₂H₆(g), at 298 K:



2.19(a) When 120 mg of naphthalene, C₁₀H₈(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 10 mg of phenol, C₆H₅OH(s), is burned in the calorimeter under the same conditions?

2.19(b) When 2.25 mg of anthracene, C₁₄H₁₀(s), was burned in a bomb calorimeter the temperature rose by 1.35 K. Calculate the calorimeter constant. By how much will the temperature rise when 135 mg of phenol, C₆H₅OH(s), is burned in the calorimeter under the same conditions? ($\Delta_c H^\circ(\text{C}_{14}\text{H}_{10}, \text{s}) = -7061 \text{ kJ mol}^{-1}$.)

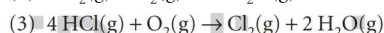
2.20(a) Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

2.20(b) Calculate the standard enthalpy of solution of AgBr(s) in water from the enthalpies of formation of the solid and the aqueous ions.

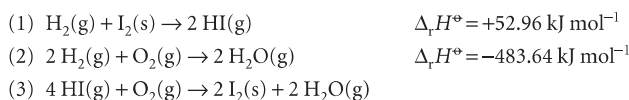
2.21(a) The standard enthalpy of decomposition of the yellow complex H₃NSO₂ into NH₃ and SO₂ is +40 kJ mol⁻¹. Calculate the standard enthalpy of formation of H₃NSO₂.

2.21(b) Given that the standard enthalpy of combustion of graphite is -393.51 kJ mol⁻¹ and that of diamond is -395.41 kJ mol⁻¹, calculate the enthalpy of the graphite-to-diamond transition.

2.22(a) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\circ$ and $\Delta_r U^\circ$ for reaction (3), (b) $\Delta_f H^\circ$ for both HCl(g) and H₂O(g) all at 298 K.



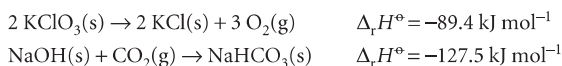
2.22(b) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\circ$ and $\Delta_r U^\circ$ for reaction (3), (b) $\Delta_f H^\circ$ for both HCl(g) and H₂O(g) all at 298 K.



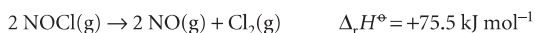
2.23(a) For the reaction $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$, $\Delta_r U^\circ = -1373 \text{ kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\circ$.

2.23(b) For the reaction $2 \text{C}_6\text{H}_5\text{COOH}(\text{s}) + 13 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$, $\Delta_r U^\circ = -772.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\circ$.

2.24(a) Calculate the standard enthalpies of formation of (a) KClO₃(s) from the enthalpy of formation of KCl, (b) NaHCO₃(s) from the enthalpies of formation of CO₂ and NaOH together with the following information:



2.24(b) Calculate the standard enthalpy of formation of NOCl(g) from the enthalpy of formation of NO given in Table 2.5, together with the following information:



2.25(a) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ at 100°C from its value at 25°C.

2.25(b) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$ at 100°C from its value at 25°C.

2.26(a) From the data in Table 2.5, calculate $\Delta_r H^\circ$ and $\Delta_r U^\circ$ at (a) 298 K, (b) 378 K for the reaction $\text{C}(\text{graphite}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$. Assume all heat capacities to be constant over the temperature range of interest.

2.26(b) Calculate $\Delta_r H^\circ$ and $\Delta_r U^\circ$ at 298 K and $\Delta_r H^\circ$ at 348 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2.5 and 2.7. Assume the heat capacities to be constant over the temperature range involved.

2.27(a) Calculate $\Delta_r H^\circ$ for the reaction $\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$ from the information in Table 2.7 in the *Data section*.

2.27(b) Calculate $\Delta_r H^\circ$ for the reaction $\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ from the information in Table 2.7 in the *Data section*.

2.28(a) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg²⁺ 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 Cl₂(g), +241.6 kJ mol⁻¹; electron gain enthalpy of Cl(g), -3.78 eV; enthalpy of solution of MgCl₂(s), -150.5 kJ mol⁻¹; enthalpy of hydration of Cl⁻(g), -383.7 kJ mol⁻¹.

2.28(b) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca²⁺ 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 Br₂(g), +192.9 kJ mol⁻¹; electron gain enthalpy of Br(g), -331.0 kJ mol⁻¹; enthalpy of solution of CaBr₂(s), -103.1 kJ mol⁻¹; enthalpy of hydration of Br⁻(g), -337 kJ mol⁻¹.

2.29(a) When a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and 0°C to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule–Thomson coefficient, μ , at 0°C, assuming it remains constant over this temperature range.

2.29(b) A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient, μ , at 5°C, assuming it remains constant over this temperature range.

2.30(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 24.8 dm³ at 298 K. What are the values of q and w ?

2.30(b) Repeat Exercise 2.30(a) for argon, from an initial volume of 1.00 dm³ to 22.1 dm³ at 298 K.

2.31(a) The volume of a certain liquid varies with temperature as

$$V = V' \{0.75 + 3.9 \times 10^{-4}(T/\text{K}) + 1.48 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 300 K. Calculate its expansion coefficient, α , at 320 K.

2.31(b) The volume of a certain liquid varies with temperature as

$$V = V' \{0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 298 K. Calculate its expansion coefficient, α , at 310 K.

2.32(a) The isothermal compressibility of copper at 293 K is $7.35 \times 10^{-7} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.32(b) The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.33(a) Given that $\mu = 0.25 \text{ K atm}^{-1}$ 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 15.0 mol N₂ flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

2.33(b) Given that $\mu = 1.11 \text{ K atm}^{-1}$ 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 12.0 mol CO₂ flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

Problems*

Assume all gases are perfect unless stated otherwise. Note that 1 atm = 1.013 25 bar. Unless otherwise stated, thermochemical data are for 298.15 K.

Numerical problems

2.1 A sample consisting of 1 mol of perfect gas atoms (for which $C_{V,m} = \frac{3}{2}R$) is taken through the cycle shown in Fig. 2.34. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate q , w , ΔU , and ΔH for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write in +, -, 0, or ? as appropriate.

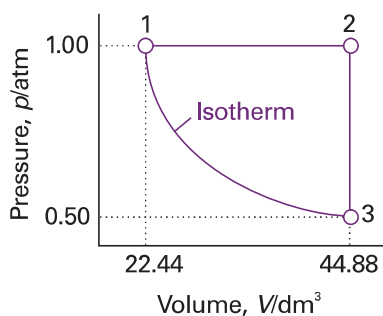


Fig. 2.34

2.2 A sample consisting of 1.0 mol $\text{CaCO}_3(\text{s})$ 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?

2.3 A sample consisting of 2.0 mol CO_2 occupies a fixed volume of 15.0 dm^3 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, and calculate w , ΔU , and ΔH .

2.4 A sample of 70 mmol $\text{Kr}(\text{g})$ expands reversibly and isothermally at 373 K from 5.25 cm^3 to 6.29 cm^3 , and the internal energy of the sample is known to increase by 83.5 J. Use the virial equation of state up to the second coefficient $B = -28.7 \text{ cm}^3 \text{ mol}^{-1}$ to calculate w , q , and ΔH for this change of state.

2.5 A sample of 1.00 mol perfect gas molecules with $C_{p,m} = \frac{7}{2}R$ is put through the following cycle: (a) constant-volume heating to twice its initial volume, (b) reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate q , w , ΔU , and ΔH for each step and overall.

2.6 Calculate the work done during the isothermal reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients a and b appear in the final expression. Plot on the same graph the indicator diagrams for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which $a = 0$ and $b = 5.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, and (c) $a = 4.2 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0$. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take $V_i = 1.0 \text{ dm}^3$, $n = 1.0 \text{ mol}$, and $T = 298 \text{ K}$.

2.7 The molar heat capacity of ethane is represented in the temperature range 298 K to 400 K by the empirical expression $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = 14.73 + 0.1272(T/\text{K})$. The corresponding expressions for $\text{C}(\text{s})$ and $\text{H}_2(\text{g})$ are given in

Table 2.2. Calculate the standard enthalpy of formation of ethane at 350 K from its value at 298 K.

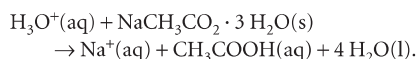
2.8 A sample of the sugar D-ribose ($\text{C}_5\text{H}_{10}\text{O}_5$) of mass 0.727 g was placed in a calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is $-3251 \text{ kJ mol}^{-1}$, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of D-ribose and its enthalpy of formation.

2.9 The standard enthalpy of formation of the metallocene bis(benzene)chromium was measured in a calorimeter. It was found for the reaction $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2 \text{C}_6\text{H}_6(\text{g})$ that $\Delta_r U^\circ(583 \text{ K}) = +8.0 \text{ kJ mol}^{-1}$. 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 $136.1 \text{ J K}^{-1} \text{ mol}^{-1}$ in its liquid range and $81.67 \text{ J K}^{-1} \text{ mol}^{-1}$ as a gas.

2.10† From the enthalpy of combustion data in Table 2.5 for the alkanes methane through octane, test the extent to which the relation $\Delta_c H^\circ = k\{M/(\text{g mol}^{-1})\}^n$ holds and find the numerical values for k and n . Predict $\Delta_c H^\circ$ for decane and compare to the known value.

2.11 It is possible to investigate the thermochemical properties of hydrocarbons with molecular modelling methods. (a) Use electronic structure software to predict $\Delta_c H^\circ$ values for the alkanes methane through pentane. To calculate $\Delta_c H^\circ$ values, estimate the standard enthalpy of formation of $\text{C}_n\text{H}_{2(n+1)}(\text{g})$ by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. (b) Compare your estimated values with the experimental values of $\Delta_c H^\circ$ (Table 2.5) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation $\Delta_c H^\circ = k\{M/(\text{g mol}^{-1})\}^n$ holds and find the numerical values for k and n .

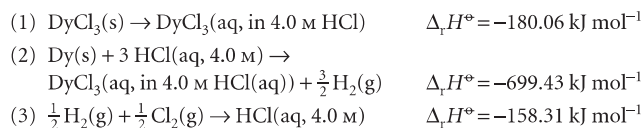
2.12† When 1.3584 g of sodium acetate trihydrate was mixed into 100.0 cm^3 of 0.2000 M $\text{HCl}(\text{aq})$ at 25°C in a solution calorimeter, its temperature fell by 0.397°C on account of the reaction:



The heat capacity of the calorimeter is 91.0 J K^{-1} and the heat capacity density of the acid solution is $4.144 \text{ J K}^{-1} \text{ cm}^{-3}$. Determine the standard enthalpy of formation of the aqueous sodium cation. The standard enthalpy of formation of sodium acetate trihydrate is $-1064 \text{ kJ mol}^{-1}$.

2.13† Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov, S.M. Pimenova, V.K. Pavlovich, N.B. Tamm, and A.A. Kurskaya, *J. Chem. Thermodynamics* **28**, 1121 (1996)). In one of their runs, they found the standard specific internal energy of combustion to be $-36.0334 \text{ kJ g}^{-1}$ at 298.15 K. Compute $\Delta_c H^\circ$ and $\Delta_f H^\circ$ of C_{60} .

2.14† A thermodynamic study of DyCl_3 (E.H.P. Cordfunke, A.S. Booji, and M. Yu. Furkaliouk, *J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information



Determine $\Delta_f H^\circ(\text{DyCl}_3, \text{s})$ from these data.

* Problems denoted with the symbol † were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

2.15‡ Silylene (SiH_2) is a key intermediate in the thermal decomposition of silicon hydrides such as silane (SiH_4) and disilane (Si_2H_6). Moffat *et al.* (H.K. Moffat, K.F. Jensen, and R.W. Carr, *J. Phys. Chem.* **95**, 145 (1991)) report $\Delta_f H^\circ(\text{SiH}_2) = +274 \text{ kJ mol}^{-1}$. If $\Delta_f H^\circ(\text{SiH}_4) = +34.3 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{Si}_2\text{H}_6) = +80.3 \text{ kJ mol}^{-1}$ (CRC Handbook (2004)), compute the standard enthalpies of the following reactions:

- (a) $\text{SiH}_4(\text{g}) \rightarrow \text{SiH}_2(\text{g}) + \text{H}_2(\text{g})$
 (b) $\text{Si}_2\text{H}_6(\text{g}) \rightarrow \text{SiH}_2(\text{g}) + \text{SiH}_4(\text{g})$

2.16‡ Silanone (SiH_2O) and silanol (SiH_3OH) are species believed to be important in the oxidation of silane (SiH_4). These species are much more elusive than their carbon counterparts. C.L. Darling and H.B. Schlegel (*J. Phys. Chem.* **97**, 8207 (1993)) report the following values (converted from calories) from a computational study: $\Delta_f H^\circ(\text{SiH}_2\text{O}) = -98.3 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{SiH}_3\text{OH}) = -282 \text{ kJ mol}^{-1}$. Compute the standard enthalpies of the following reactions:

- (a) $\text{SiH}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SiH}_3\text{OH}(\text{g})$
 (b) $\text{SiH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SiH}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$
 (c) $\text{SiH}_3\text{OH}(\text{g}) \rightarrow \text{SiH}_2\text{O}(\text{g}) + \text{H}_2(\text{g})$

Note that $\Delta_f H^\circ(\text{SiH}_4, \text{g}) = +34.3 \text{ kJ mol}^{-1}$ (CRC Handbook (2004)).

2.17 The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. If the decrease in pressure is also measured, we can use it to infer the value of $\gamma = C_p/C_V$ and hence, by combining the two values, deduce the constant-pressure heat capacity. 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 .

2.18 A sample consisting of 1.00 mol of a van der Waals gas is compressed from 20.0 dm³ to 10.0 dm³ at 300 K. In the process, 20.2 kJ of work is done on the gas. Given that $\mu = \{(2a/RT) - b\}/C_{p,m}$, with $C_{p,m} = 38.4 \text{ J K}^{-1} \text{ mol}^{-1}$, $a = 3.60 \text{ dm}^6 \text{ atm mol}^{-2}$, and $b = 0.44 \text{ dm}^3 \text{ mol}^{-1}$, calculate ΔH for the process.

2.19 Take nitrogen to be a van der Waals gas with $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$, and calculate ΔH_m when the pressure on the gas is decreased from 500 atm to 1.00 atm at 300 K. For a van der Waals gas, $\mu = \{(2a/RT) - b\}/C_{p,m}$. Assume $C_{p,m} = \frac{7}{2}R$.

Theoretical problems

2.20 Show that the following functions have exact differentials: (a) $x^2y + 3y^2$, (b) $x \cos xy$, (c) x^3y^2 , (d) $t(t + e^t) + s$.

2.21 (a) What is the total differential of $z = x^2 + 2y^2 - 2xy + 2x - 4y - 8$? (b) Show that $\partial^2 z/\partial y \partial x = \partial^2 z/\partial x \partial y$ for this function. (c) Let $z = xy - y + \ln x + 2$. Find dz and show that it is exact.

2.22 (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.

2.23 (a) Derive the relation $C_V = -(\partial U/\partial V)_T(\partial V/\partial T)_U$ from the expression for the total differential of $U(T, V)$ and (b) starting from the expression for the total differential of $H(T, p)$, express $(\partial H/\partial p)_T$ in terms of C_p and the Joule–Thomson coefficient, μ .

2.24 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

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

Evaluate $C_p - C_V$ for a perfect gas.

2.25 (a) By direct differentiation of $H = U + pV$, obtain a relation between $(\partial H/\partial U)_p$ and $(\partial U/\partial V)_p$. (b) Confirm that $(\partial H/\partial U)_p = 1 + p(\partial V/\partial U)_p$ by

expressing $(\partial H/\partial U)_p$ as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

2.26 (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.

2.27 Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, eqn 1.19. Evaluate (a) the work for 1.0 mol Ar at 273 K (for data, see Table 1.3) and (b) the same amount of a perfect gas. Let the expansion be from 500 cm³ to 1000 cm³ in each case.

2.28 Express the work of isothermal reversible expansion of a van der Waals gas in reduced variables 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 .

2.29‡ 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?

2.30 Use the fact that $(\partial U/\partial V)_T = a/V_m^2$ for a van der Waals gas 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.)

2.31 Rearrange the van der Waals equation of state 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.

2.32 Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas. Show, using Euler's chain relation, that $\kappa_T R = \alpha(V_m - b)$.

2.33 Given that $\mu C_p = T(\partial V/\partial T)_p - V$, derive an expression for μ in terms of the van der Waals parameters a and b , and express it in terms of reduced variables. Evaluate μ at 25°C and 1.0 atm, when the molar volume of the gas is 24.6 dm³ mol⁻¹. Use the expression obtained to derive a formula for the inversion temperature of a van der Waals gas in terms of reduced variables, and evaluate it for the xenon sample.

2.34 The thermodynamic equation of state $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ was quoted in the chapter. Derive its partner

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

from it and the general relations between partial differentials.

2.35 Show that for a van der Waals gas,

$$C_{p,m} - C_{V,m} = \lambda R \quad \frac{1}{\lambda} = 1 - \frac{(3V_r - 1)^2}{4V_r^3 T_r}$$

and evaluate the difference for xenon at 25°C and 10.0 atm.

2.36 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.

2.37‡ A gas obeys the equation of state $V_m = RT/p + aT^2$ and its constant-pressure heat capacity is given by $C_{p,m} = A + BT + Cp$, where a , A , B , and C are constants independent of T and p . Obtain expressions for (a) the Joule–Thomson coefficient and (b) its constant-volume heat capacity.

Applications: to biology, materials science, and the environment

2.38 It is possible to see with the aid of a powerful microscope that a long piece of double-stranded DNA is flexible, with the distance between the ends of the chain adopting a wide range of values. This flexibility is important because it allows DNA to adopt very compact conformations as it is packaged in a chromosome (see Chapter 18). It is convenient to visualize a long piece

of DNA as a *freely jointed chain*, a chain of N small, rigid units of length l that are free to make any angle with respect to each other. The length l , the *persistence length*, is approximately 45 nm, corresponding to approximately 130 base pairs. You will now explore the work associated with extending a DNA molecule. (a) 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*. Systems showing this behaviour are said to obey *Hooke's law*. (i) What are the limitations of this model of the DNA molecule? (ii) Using this model, write an expression for the work that must be done to extend a DNA molecule by x . Draw a graph of your conclusion. (b) 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

$$F = \frac{kT}{2l} \ln \left(\frac{1+v}{1-v} \right) \quad v = x/Nl$$

where $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ is *Boltzmann's constant* (not a force constant). (i) What are the limitations of this model? (ii) What is the magnitude of the force that must be applied to extend a DNA molecule with $N = 200$ by 90 nm? (iii) Plot the restoring force against v , noting that v 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? (iv) Keeping in mind that the difference in end-to-end distance from an equilibrium value is $x = nl$ and, consequently, $dx = ldn = Nldv$, write an expression for the work of extending a DNA molecule. (v) Calculate the work of extending a DNA molecule from $v = 0$ to $v = 1.0$. *Hint*. You must integrate the expression for w . The task can be accomplished easily with mathematical software. (c) Show that for small extensions of the chain, when $v \ll 1$, the restoring force is given by

$$F \approx \frac{vkT}{l} = \frac{nkT}{Nl}$$

Hint. See Appendix 2 for a review of series expansions of functions. (d) Is the variation of the restoring force with extension of the chain given in part (c) different from that predicted by Hooke's law? Explain your answer.

2.39 There are no dietary recommendations for consumption of carbohydrates. Some nutritionists recommend diets that are largely devoid of carbohydrates, with most of the energy needs being met by fats. However, the most common recommendation is that at least 65 per cent of our food calories should come from carbohydrates. A $\frac{3}{4}$ -cup serving of pasta contains 40 g of carbohydrates. What percentage of the daily calorie requirement for a person on a 2200 Calorie diet (1 Cal = 1 kcal) does this serving represent?

2.40 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?

2.41 Glucose and fructose are simple sugars with the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$. Sucrose, or table sugar, is a complex sugar with molecular formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is given off as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

2.42 In biological cells that have a plentiful supply of O_2 , 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 ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$) by a process called *anaerobic glycolysis* (see *Impact 17.2*). (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?

2.43 You have at your disposal a sample of pure polymer P and a sample of P that has just been synthesized in a large chemical reactor and that may contain impurities. Describe how you would use differential scanning calorimetry to determine the mole percentage composition of P in the allegedly impure sample.

2.44† Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. Seakins *et al.* (P.W. Seakins, M.J. Pilling, J.T. Niiranen, D. Gutman, and L.N. Krasnoperov, *J. Phys. Chem.* **96**, 9847 (1992)) report $\Delta_f H^\circ$ for a variety of alkyl radicals in the gas phase, information that is applicable to studies of pyrolysis and oxidation reactions of hydrocarbons. This information can be combined with thermodynamic data on alkenes to determine the reaction enthalpy for possible fragmentation of a large alkyl radical into smaller radicals and alkenes. Use the following set of data to compute the standard reaction enthalpies for three possible fates of the *tert*-butyl radical, namely, (a) $\text{tert-C}_4\text{H}_9 \rightarrow \text{sec-C}_4\text{H}_9$, (b) $\text{tert-C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$, (c) $\text{tert-C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$.

Species:	C_2H_5	$\text{sec-C}_4\text{H}_9$	$\text{tert-C}_4\text{H}_9$
$\Delta_f H^\circ / (\text{kJ mol}^{-1})$	+121.0	+67.5	+51.3

2.45† In 1995, 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 $1.37 \times 10^9 \text{ km}^3$ and their surface area is $361 \times 10^6 \text{ km}^2$, and state the approximations that go into the estimates.

2.46† 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 $(\partial H / \partial p)_T = -3.29 \times 10^3 \text{ J MPa}^{-1} \text{ mol}^{-1}$ and $C_{p,m} = 110.0 \text{ J K}^{-1} \text{ mol}^{-1}$. (b) Compute the temperature change that would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50°C.

2.47† Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (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 $0.7649 \text{ kJ K}^{-1} \text{ kg}^{-1}$.)

(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	456.15

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