Appendix: Theorems on partial differentiation

Classical thermodynamics is concerned with the equilibrium states of systems, and such states are characterised by the values of a small number of macroscopic quantities, the thermodynamic coordinates. One of the principal aims of thermodynamics is to derive relationships between the values of these coordinates for different equilibrium states. For simple systems of the kinds discussed in this book, equilibrium states are characterised by the values of two independent coordinates, and each equilibrium state is represented by a point in a three-dimensional space, using the values of the two independent coordinates and one other. The totality of equilibrium states for such a system is represented by a continuous and single-valued surface in the appropriate three-dimensional space. For example, the equilibrium states achieved by a gaseous system are represented by a continuous surface in a space, using pressure p, volume V and temperature T as coordinates. Any change that is composed of a succession of equilibrium states is represented by a line on this surface and, for an infinitesimal part of any such change, changes in the values of the coordinates are obtained by the use of the partial differential calculus. Two widely used theorems in this calculus will now be considered briefly.

Consider first a continuous and single-valued function

$$y = f(x) \tag{A.1}$$

The differential coefficient at $x = a$ of the function $y = f(x)$ is written as $f'(a)$ and defined by the equation

$$f'(a) = \lim_{x \to a} \left[\frac{f(x) - f(a)}{x - a} \right] \tag{A.2}$$

The function $f'(x)$, whose value at $x=a$ is $f'(a)$, is called the derivative of the function $f(x)$. Putting $x-a = h$, the differential coefficient at $x = a$ becomes

$$f'(a) = \lim_{h\to 0}\left[\frac{f(a+h) - f(a)}{h}\right] \tag{A.3}$$

The tangent to the curve at the point $x = a$, $y = b$ is the limiting position of the chords through that point. Therefore, the tangent at the point (a,b) on the curve has a gradient $f'(a)$.

If the points (a,b) and $(a + h, b + k)$ are both on the curve $y = f(x)$, then

$$\frac{k}{h} = \frac{f(a+h) - f(a)}{h} \tag{A.4}$$

When the two points are close together, h may be treated as a small increment in x and written δx; k may be treated as a small increment in y and written δy. Then

$$f'(x) = \lim_{\delta x\to 0}\left(\frac{\delta y}{\delta x}\right)$$

which is, in the usual notation,

$$f'(x) = \lim_{\delta x\to 0}\left(\frac{\delta y}{\delta x}\right) = \frac{\mathrm{d}y}{\mathrm{d}x} \tag{A.5}$$

For a continuous function, $f(a + h) - f(\mathrm{a})$ may be written

$$f(a+h) - f(\mathrm{a}) = hf'(a) + h\epsilon(h) \tag{A.6}$$

where $\epsilon(h)$ has the property that $\epsilon(h) \to 0$ as $h \to 0$.

Now $f(a + h) - f(a)$ is an increment in f which, when h is small, may be written δf. This increment in f approaches the value $hf'(a)$ in the limit as h tends to zero. Then, if $hf'(a)$ is written $\mathrm{d}f$, Equation (A.6) becomes

$$\delta f = \mathrm{d}f + h\epsilon(h) \tag{A.7}$$

$\mathrm{d}f$ is known as the differential of $f(x)$ at $x = a$ and is a multiple of $f'(a)$, the differential coefficient at $x = a$.

In particular, if $f(x)$ is the function x, $f'(a)$ is unity and h is $\mathrm{d}x$, so that

$$\mathrm{d}f = f'(a)\,\mathrm{d}x \tag{A.8}$$

Equation (A.8) gives, approximately, the change in $f(x)$ arising from a small change in x (see Figure A.1), the error being $h\epsilon(h)$.

If f is a real single-valued function of two independent variables x and y, the partial derivative of $f(x,y)$ with respect to x, written $f_x(x,y)$ or $(\partial f/\partial x)_y$, is defined as

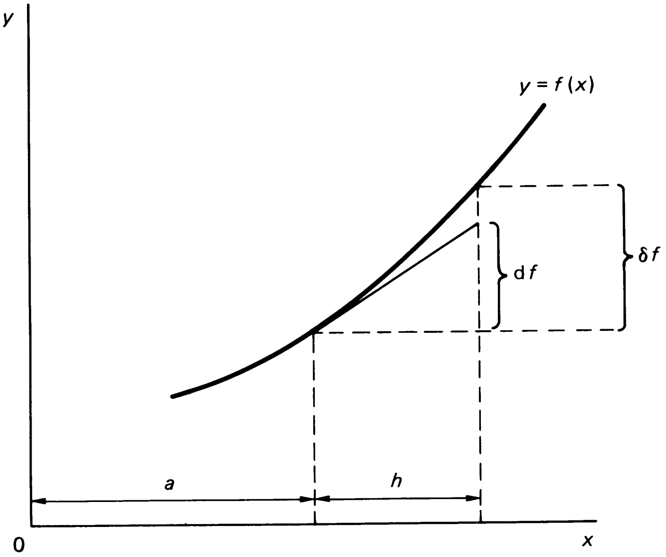

Figure A.1 *Illustrating the differential* df *of the function* y = f(x)

$$f_x(x,y) = \left(\frac{\partial f}{\partial x}\right)_y = \lim_{\delta x \to 0}\left[\frac{f(x + \delta x, y) - f(x,y)}{\delta x}\right] \qquad (A.9)$$

Similarly, the partial derivative with respect to y is

$$f_y(x,y) = \left(\frac{\partial f}{\partial y}\right)_x = \lim_{\delta y \to 0}\left[\frac{f(x, y + \delta y) - f(x,y)}{\delta y}\right] \qquad (A.10)$$

Extending the analysis leading to Equation (A.8) to a function of two variables $f(x,y)$ gives

$$f(a + h, b + k) - f(a,b) = hf_x(a,b) + kf_y(a,b) + \rho\epsilon \qquad (A.11)$$

where ϵ has the property that $\epsilon \to 0$ as $\rho \to 0$. Equation (A.11) may be written

$$\delta f = \mathrm{d}f + \rho\epsilon \qquad (A.12)$$

where

$$\delta f = f(a + h, b + k) - f(a,b)$$

and

$$\mathrm{d}f = hf_x(a,b) + kf_y(a,b)$$

Now, if $f(x,y) = x$, then $f_x(a,b) = 1$ and $f_y(a,b) = 0$, while, if $f(x,y) = y$, $f_y(a,b) = 1$ and $f_x(a,b) = 0$ and, further, $\mathrm{d}x = h$ and $\mathrm{d}y = k$. Therefore,

$$\mathrm{d}f = f_x(a,b)\,\mathrm{d}x + f_y(a,b)\mathrm{d}y$$

or, in the notation favoured in this book,

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \qquad \text{(A.13)}$$

Equation (A.13) may be used to estimate the change in f arising from small changes in x and y, the accuracy increasing as the changes tend to zero.

For a particular thermodynamic system with two independent coordinates, let the coordinates chosen be x, y and z, related by the equation of state

$$F(x,y,z) = 0 \qquad \text{(A.14)}$$

If F is a continuous and single-valued function, x may be expressed explicitly as a function of y and z — that is

$$x = x(y,z)$$

The differential of x may then be written

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z \qquad \text{(A.15)}$$

A similar equation may be written for $\mathrm{d}z$:

$$\mathrm{d}z = \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y + \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x \qquad \text{(A.16)}$$

Substituting for $\mathrm{d}z$ from Equation (A.16) into Equation (A.15) gives

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] \mathrm{d}y \qquad \text{(A.17)}$$

Equation (A.17) must be valid whichever two of the variables x, y, z are taken to be independent. If x and y are chosen to be independent, $\mathrm{d}y$ can be made zero and $\mathrm{d}x$ non-zero. This gives

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1$$

or

$$\left(\frac{\partial x}{\partial z}\right)_y = 1/\left(\frac{\partial z}{\partial x}\right)_y \qquad \text{(A.18)}$$

Equation (A.18) is known as the reciprocal theorem.

If, instead, dx is made zero and dy non-zero, Equation (A.18) gives

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

or, using the reciprocal theorem,

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{(A.19)}$$

This result is known as the reciprocity theorem, and such equations are known as reciprocity relations.

For a fuller discussion of partial differentiation reference may be made to the following books:

Hilton, P. J. (1958). *Differential Calculus* (London: Routledge and Kegan Paul)

Hilton, P. J. (1960). *Partial Derivatives* (London: Routledge and Kegan Paul)

Sources for numerical values

American Institute of Physics (1963). *Handbook,* 2nd edn (New York: McGraw-Hill)

Hsieh, J. S. (1975). *Principles of Thermodynamics* (Tokyo: McGraw-Hill Kogakusha)

Kaye, G. W. C. and Laby, T. H. (1973). *Tables of Physical and Chemical Constants,* 14th edn (London: Longman)

Nordling, C. and Osterman, J. (1980). *Physics Handbook* (Bromley: Chartwell-Bratt)

Roberts, J. K. and Miller, A. R. (1951). *Heat and Thermodynamics,* 4th edn (London and Glasgow: Blackie)

Answers and hints to exercises

Chapter 2

1 (a) Isolated.
(b) Closed.
(c) Open.
[See Section 2.3.]

2 (a) Non-equilibrium.
(b) Non-equilibrium.
(c) Equilibrium.
(d) Non-equilibrium.
[See Section 2.4.]

3 (a) Quasistatic.
(b) Non-quasistatic.
(c) Quasistatic.
(d) Non-quasistatic.
[See Section 2.2.]

4 (a) False.
(b) False.
(c) False.
(d) False.
(e) False.

Chapter 3

1 The isotherms do not intersect.
[*Hint*: Apply the zeroth law to the hypothetical situation where the isotherms do intersect.]

2 Temperature is a property of a large assembly of atoms; the temperature of a single atom of such an assembly has no meaning.

3 Intensive coordinates: pressure, temperature, load. Extensive coordinates: volume, length.
[See Section 2.1.]

4 (a) False.
(b) False.

5 $\theta_R = 300.4$ units; $\theta_r = 680.7$ units.
[*Hint*: θ_R is defined by the equation

$$\theta_R = aR + b$$

where a and b are constants whose values are determined by the values assigned to the ice point and steam point. θ_r is similarly defined.]

Chapter 4

1 (a) The viscosity of the liquid.
(b) The diffusion of ions through the porous membrane.

2

$$U_f - U_i = W + Q$$

$$U_f - U_i = W + Q + |\Delta m|\, c^2$$

where $|\Delta m|$ is the magnitude of the change in mass resulting from fission and c is the speed of light in a vacuum.

3 (a) Reversible.
(b) Quasistatic.
(c) Non-equilibrium.
(d) Non-equilibrium.
(e) Quasistatic.
[See Sections 2.2 and 4.6.]

4 The heat absorbed by the system during process B is $Q_B = -70$ J. The minus sign indicates that the heat transfer is from the system.
[*Hint*: Because the complete process is cyclic, the total change in internal energy of the system ΔU is zero. Using an obvious notation, $\Delta U = 0 = Q_A + W_A + Q_B + W_B$ and $Q_A = +100$ J, $W_A = -50$ J and $W_B = +20$ J.]

5 Since the interacting systems are otherwise isolated, $\Delta U_A + \Delta U_B = 0$. Therefore, $Q_A + Q_B + W_A + W_B = 0$. But $W_A = W_B = 0$ and, therefore, $Q_A = -Q_B$.

6 $Q = 0$, $W = 0$ and, therefore, $\Delta U = 0$.

7

$$W = \int_{L_i}^{L_f} F\mathrm{d}L = \int_{L_i}^{L_f} \frac{C}{L_0}(L - L_0)\mathrm{d}L$$

$$= \frac{C(L_f - L_i)}{2L_0}(L_f + L_i - 2L_0)$$

Chapter 5

1

$$W = -\int_{V_i}^{V_f} p\mathrm{d}V$$

(a) $pV = 100$

Therefore,

$$W = -\int_1^{25} \frac{100}{V}\mathrm{d}V = -322\ \mathrm{J}$$

The minus sign indicates that the work is done by the system.

(b) $p = 104 - 4V$

Therefore,

$$W = -\int_1^{25} (104 - 4V)\mathrm{d}V = -1248\ \mathrm{J}$$

Again the minus sign indicates that the work is done by the system.

2

$$W = -\int_{V_i}^{V_f} p\mathrm{d}V$$

p is constant and equal to p_0;

$$V_i = V_0 \text{ and } V_f = nV$$

3 *Hint*: Imagine that the initially evacuated cylinder A is connected to another cylinder, B, shown dotted in Figure H.1, fitted with a frictionless, non-leaking piston. Let this cylinder B be of such a size that it contains just the amount of air that will enter cylinder A when the valve is opened. When the first small quantity of air enters cylinder A, the pressure in B falls below atmospheric pressure by a very small amount and the piston of cylinder B is pushed in under a constant pressure p_0.

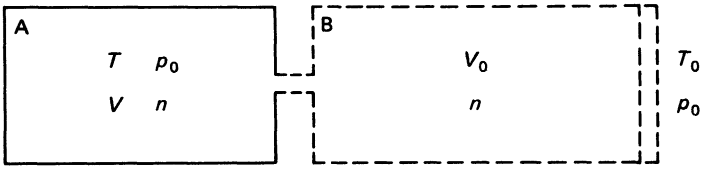

Figure H.1 *Notional model for the flow of air into an evacuated cylinder*

4 From Equation (5.6), if p is held constant,

$$\mathrm{d}V = \left(\frac{\partial V}{\partial \theta}\right)_p \mathrm{d}\theta$$

Now the cubic expansivity β is given by

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_p$$

Therefore, at constant pressure,

$$\frac{\mathrm{d}V}{V} = \beta \mathrm{d}\theta$$

and, if β is constant,

$$V_\mathrm{f} = V_\mathrm{i} \exp\left(\beta(\theta_\mathrm{f} - \theta_\mathrm{i})\right)$$

When β is small, $\exp\left(\beta(\theta_\mathrm{f} - \theta_\mathrm{i})\right) \approx 1 + \beta(\theta_\mathrm{f} - \theta_\mathrm{i})$ and

$$V_\mathrm{f} \approx V_\mathrm{i} + V_\mathrm{i}\beta(\theta_\mathrm{f} - \theta_\mathrm{i})$$

5

$$\text{Linear expansivity} = \frac{1}{L}\left(\frac{\partial L}{\partial \theta}\right)_F = -\frac{(L - L_0)}{2L\theta}$$

$$\text{Young's modulus} = \frac{L}{A}\left(\frac{\partial F}{\partial L}\right)_\theta = \frac{2LF}{A(L - L_0)}$$

6 Use the reciprocity relation

$$\left(\frac{\partial F}{\partial \theta}\right)_L = -\left(\frac{\partial L}{\partial \theta}\right)_F\left(\frac{\partial F}{\partial L}\right)_\theta$$

7 The work done on the surface is given by

$$W = \sigma(A_f - A_i)$$

where A_f and A_i are the final and initial surface areas, respectively. Since the bubble has an 'inside' and an 'outside' surface,

$$W = 2 \times 0.07 \times 4\pi\,(0.1^2 - 0.06^2)$$
$$= 1.13 \times 10^{-2}\ \text{J}$$

8 The work of magnetisation in an infinitesimal reversible process is given by

$$\mathrm{d}W = V\mu_0 H_a \mathrm{d}M \text{ (obtained from Equation 5.33)}$$

Using

$$\chi_m = \frac{M}{H_a} = \frac{C}{\theta}$$

and substituting for H_a gives the result.

Chapter 6

1 Atmospheric pressure = 76.3 cm of mercury. Assume that air obeys Boyle's law.

2 Apply Boyle's law. If p_0 is the initial pressure in the vessel of volume V, and v is the volume of the pump barrel, after the first stroke the pressure p_1 is given by

$$p_0 V = p_1(V + v),$$

and after n strokes the pressure p_n is given by

$$p_n = \frac{p_0 V^n}{(V + v)^n}$$

Therefore, after two strokes the pressure is 0.925 atm, a reduction of 0.075 atm, and 100 strokes are needed to reduce the pressure to 0.02 atm.

3 When $pV_m = f(\theta)$, the isothermal compressibility is equal to $1/p$:

$$\kappa_\theta = -\frac{1}{V_m}\left(\frac{\partial V}{\partial p}\right)_\theta \text{ and } \left(\frac{\partial V}{\partial p}\right)_\theta = -\frac{f(\theta)}{p^2}$$

When $pV_m = A + Bp$, the isothermal compressibility is given by

$$\kappa_\theta = \frac{1}{p} - \frac{B}{A + Bp}$$

4 230.3 J.
The work done on the gas is given by

$$W = -\int p\mathrm{d}V$$

In an isothermal reversible process pV = constant, so that $p\mathrm{d}V = -V\mathrm{d}p$ and

$$W = \int V\mathrm{d}p$$

5 Let the volume of gas trapped at the pressure p_u be V. If the gas pressure is measured in mm Hg and h is measured in mm, when the reservoir is raised to give the mercury levels shown in Figure 6.6, the pressure of the trapped gas is $(p_u + h)$ mm Hg and, applying Boyle's law gives

$$p_u V = (p_u + h)\, Ah$$

where A is the area of cross-section of the tube. Then

$$p_u = \frac{Ah^2}{V - Ah}$$

If $Ah \ll V$

$$p_u = \frac{Ah^2}{V}$$

Chapter 7

1 Use the defining equations

$$\frac{Q_1}{Q_2} = -\frac{e^{\tau_1}}{e^{\tau_2}}\,;\ \frac{Q_3}{Q_4} = -\frac{e^{\tau_3}}{e^{\tau_4}}$$

$$\eta_1 = 1 + Q_2/Q_1\ ;\ \eta_2 = 1 + Q_4/Q_3$$

2 The defining equation for τ is

$$\frac{Q_1}{Q_2} = -\frac{e^{\tau_1}}{e^{\tau_2}}$$

When $T = 100$ K,

$$\frac{Q_1}{Q_2} = -\frac{100}{273.16}$$

and, when $T = 273.16$ K, $\tau = 0$.

The temperature in thomsons corresponding to a temperature of 100 K is given by

$$-\frac{e^{\tau}}{e^{0}} = \frac{100}{273.16}$$

i.e. $\tau = -1.00$ Th.

3}
4} Use the equations

$$-W = Q_1 + Q_2 \text{ and}$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

5 (b)

6 No. The engine is more efficient than a Carnot engine operating between the same reservoirs.

7 (c)

8 (d) The device is merely dissipating mechanical energy.

9

$$\text{C.o.P. (heat pump)} = -\frac{Q_1}{W} = \frac{T_1}{T_1 - T_2}$$

$$\text{C.o.P. (refrigerator)} = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}$$

For the dependence of C.o.P on T_2/T_1 see Figure H.2.

10 See Figure H.3.

Chapter 8

1 Assume that the process is reversible.

$$\Delta S = \frac{Q}{T} = \frac{0.64 \text{ kWh}}{373\text{K}} = \frac{0.64 \times 10^3 \times 60 \times 60}{373} = 6180 \text{ J K}^{-1}$$

2 With an obvious notation

$$W + Q_1 + Q_2 + Q_3 = 0 \text{ (first law)}$$

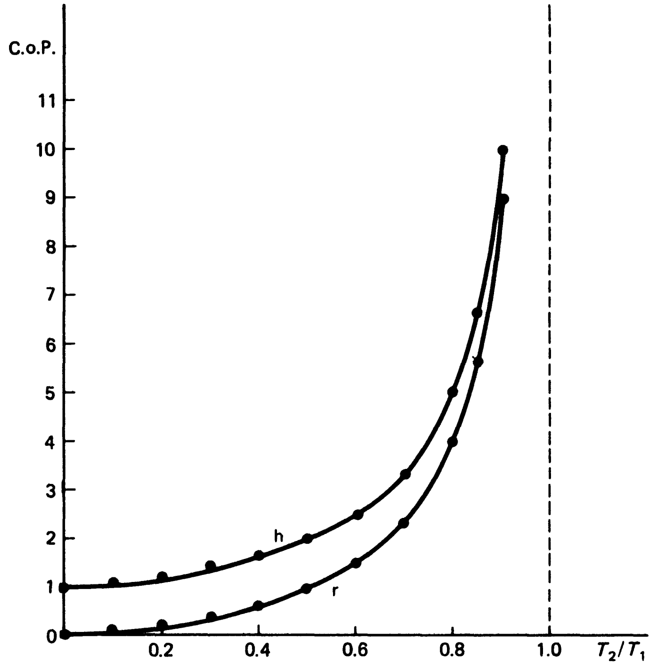

Figure H.2 *The dependence of C.o.P. on* T_2/T_1. *Curve h is for a heat pump and curve r for a refrigerator*

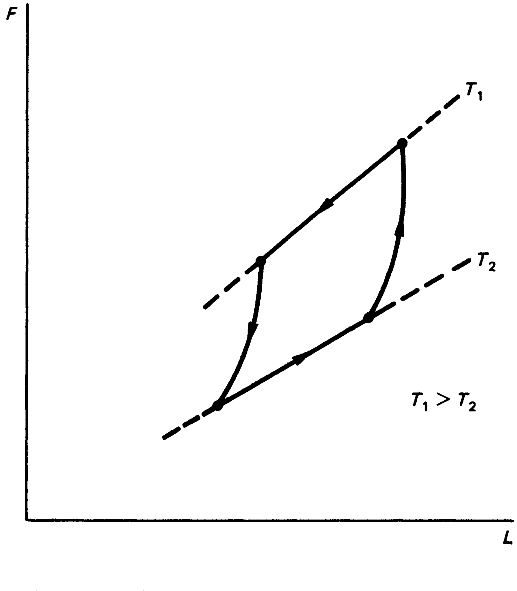

Figure H.3 *The Carnot cycle for a system consisting of a sample of rubber that obeys Hooke's law*

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} = 0 \text{ (second law)}$$

Remembering that the sign convention applies to the working substance,

$$W = -200 \text{ J},\ T_1 = 400 \text{ K},\ T_2 = 300 \text{ K},\ T_3 = 200 \text{ K},\ Q_1 = +1200 \text{ J}$$

Therefore,

$$Q_2 = -1200 \text{ J and } Q_3 = +200 \text{ J}$$

3 See Figure H.4.

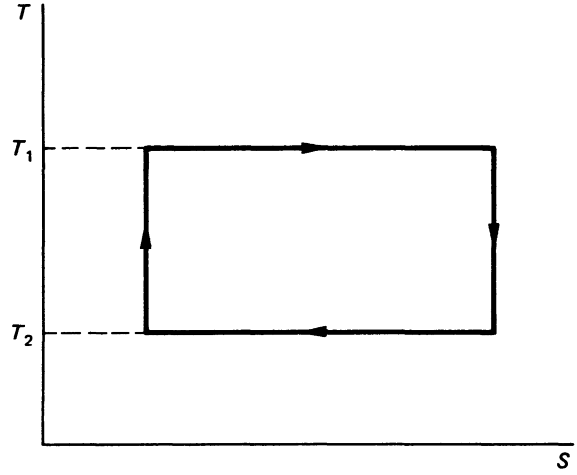

Figure H.4 *A Carnot cycle plotted on a graph of temperature* T *against entropy* S *is a rectangle for all systems*

The area enclosed by the curve is $-W$, where W is the work done on the working substance in one cycle.

4 The resistor does not undergo a change of state and, therefore, its entropy does not change. The entropy change of the water ΔS is given by

$$\Delta S = \frac{I^2Rt}{T}$$

$$= \frac{1 \times 25 \times 10}{280} = 0.9 \text{ JK}^{-1}$$

5 From the first law,

$$\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S$$

Therefore

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \text{ and } \left(\frac{\partial U}{\partial S}\right)_V = T$$

6 The complete system is isolated from its surroundings and has a fixed volume

(a) Using an obvious notation,

$$dU_1 + dU_2 = 0$$

$$dV_1 + dV_2 = 0$$

$$dS_1 + dS_2 = 0$$

Therefore,

$$dU_1 = -dU_2;\ dS_1 = -dS_2$$

Using $dU = TdS - pdV$,

$$0 = T_1\, dS_1 - p_1\, dV_1 + T_2\, dS_2 - p_2\, dV_2$$

or, substituting for dV_2 and dS_2,

$$0 = dS_1(T_1 - T_2) - dV_1(p_1 - p_2)$$

Since, in an infinitesimal reversible process, neither dS_1 nor dV_1 is zero, for this identity to be satisfied,

$$T_1 = T_2 \text{ and } p_1 = p_2$$

That is, both mechanical and thermal equilibrium must obtain.

(b) In this situation

$$dS_1 = dS_2 = 0$$

Therefore, T_1 and T_2 can assume any values consistent with the condition for mechanical equilibrium: $p_1 = p_2$.

Chapter 9

1 Equation (7.18) leads to a defining equation for entropy of

$$dS = \frac{q}{e^T}$$

and an equation of state for 1 mol of molecules of ideal gas of

$$pV_m = Re^T$$

2 Let the number of moles of molecules initially in the vessels of volumes V_0 and V be n_1 and n_2, respectively. Then

$$p_0V_0 = n_1RT_0 \text{ and } p_0V = n_2RT_0$$

When the temperature of the vessel of volume V is changed to T, the numbers of moles of molecules change to, respectively, n_3 and n_4. Then

$$pV_0 = n_3RT_0 \text{ and } pV = n_4RT$$

Since $n_1 + n_2 = n_3 + n_4$, the result follows.

3 The cubic expansivity β is given by

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and for n moles of ideal gas $(\partial V/\partial T)_p = nR/p$.

4 For an ideal gas there is no change in internal energy when it undergoes a reversible isothermal change in volume. For such a process the first law becomes

$$T\mathrm{d}S = q = -p\mathrm{d}V = w$$

Since $pV = nRT$,

$$W = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} p\mathrm{d}V = nRT\ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)$$

and

$$Q = nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) = nRT\ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)$$

5 No. See Dalton's and Leduc's laws.

6 $p' = 1.003\,p$. Use the approach of Exercise 2.

Chapter 10

1 By definition

$$F = U - TS$$

For a closed hydrostatic system

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

so that

$$\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$$

At constant volume

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

and, therefore,

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

A similar proof follows for

$$G = F - V\left(\frac{\partial F}{\partial V}\right)_T$$

2

$$J = S - \frac{U}{T}$$

Therefore

$$dJ = dS - \frac{dU}{T} + \frac{U}{T^2}\,dT$$

Now, from the entropy form of the first law,

$$\frac{dU}{T} = dS - \frac{p dV}{T}$$

and the result follows.

3 Use the appropriate analogue of the Gibbs–Helmholtz equations, i.e.

$$U = F + T\left(\frac{\partial F}{\partial T}\right)_L \text{ and } G = F - L\left(\frac{\partial F}{\partial L}\right)_T$$

together with the result that, in a reversible isothermal process, the work done on a system is equal to the increase in F. Then

$$\Delta U = \frac{L_0^2}{2}\,(2aT - 3bT^2)$$

$$\Delta G = \frac{5L_0^2}{2}\,(aT - bT^2)$$

Chapter 11

1 Writing $V = V(T, p)$, the change in volume in an infinitesimal process may be written

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = V\beta dT - \kappa_T V dp$$

where β is the cubic expansivity and κ_T is the isothermal compressibility. At constant volume dV is zero and, assuming that κ_T and β are constant,

$$\beta\Delta T = \kappa_T \Delta p$$

When $\Delta T = 1$ K,

$$\Delta p = \frac{50 \times 10^{-6}}{14 \times 10^{-12}} = 3.6 \times 10^{6}\text{Pa}$$

2 (a) Apply conservation of internal energy. The final equilibrium temperature T_f is given by

$$T_\mathrm{f} = \frac{c_1 T_1 + c_2 T_2}{c_1 + c_2}$$

(b) Apply conservation of entropy. Then

$$T_\mathrm{f} = T_1^{(c_1/c_1+c_2)} T_2^{(c_2/c_1+c_2)}$$

3

$$C_{p,\mathrm{m}} = aT^3 + bT$$

$$\mathrm{d}Q_\mathrm{R} = C_p \mathrm{d}T \; ; \; \mathrm{d}S = \frac{\mathrm{d}Q_\mathrm{R}}{T} = \frac{C_p \mathrm{d}T}{T}$$

Therefore,

$$\Delta S_\mathrm{m} = \int_1^9 \left(\frac{aT^3}{T} + \frac{bT}{T}\right)\mathrm{d}T$$

$$= 8.5 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}$$

4 Write Newton's law of cooling in the form

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = C_\mathrm{p}\frac{\mathrm{d}T}{\mathrm{d}t} = -\text{ constant } (T - T_\mathrm{s})$$

Integration gives

$$C_\mathrm{p}\ln(T - T_\mathrm{s}) = -K't + K''$$

where K' and K'' are constants.

The time for the temperature to fall from 333 K to 293 K is 8.2 min.

5 Use the method of cooling (Section 11.5.2). At 460 K the value of W is 25W and dT/dt is $-$ 0.154 K s^{-1}, giving a specific heat capacity of 1080 J kg^{-1} K^{-1}.

6 Writing U_m as a function of T and p show that, at constant T,

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

which, for the gas in question, is equal to

$$T\frac{dB}{dT}$$

7 Imagine that the air that enters the cylinder is contained in an imaginary piston, as in Figure H.1.

The work done by the atmosphere on the gas that enters the cylinder is $W = p_0V_0$, while the heat transfer is zero. The change in internal energy of the gas in an infinitesimal part of the process is given by

$$dU = C_V\, dT = -\, p dV$$

Therefore, in the complete process,

$$\Delta U = nC_{V,m}(T - T_0) = p_0V_0$$

But, $p_0V_0 = nRT_0$ (ideal gas equation) and $C_{p,m} - C_{V,m} = R$ (Equation 11.22). Therefore,

$$nC_{V,m}(T - T_0) = nRT_0 = n(C_{p,m} - C_{V,m})T_0$$

and

$$\frac{T}{T_0} - 1 = \frac{C_{p,m}}{C_{V,m}} - 1$$

or $T = \gamma\, T_0$.

8 Write $H = H(T,p)$ to give

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

and use

$$dH = TdS + Vdp$$

to obtain expressions for the partial derivatives, modified, if necessary, with a Maxwell relation.

9 The approach outlined in Exercise 8 will enable all the equations to be derived.

10 Start with Equation (10.4):

$$dU - T_0\, dS < w$$

In this situation w may be written $w = -\, p_0dV$. Then

$$dU - T_0dS + p_0dV < 0$$

When the process is adiabatic, dS is zero and the equation becomes

$d(U + p_0V) < 0$ or $dH < 0$. The process will occur when $dH < 0$.

Chapter 12

1 The result is Figure H.5. In a reversible isothermal process T is a constant and so is U for an ideal gas. When an ideal gas changes its temperature reversibly, as in an isentropic process,

$$dU = C_V dT$$

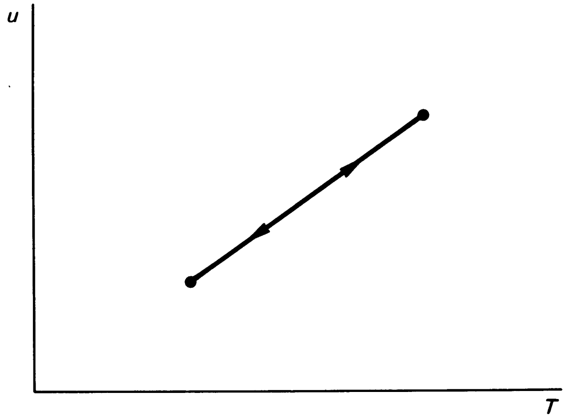

Figure H.5 *A Carnot cycle plotted on a graph of internal energy* U *against temperature* T *when the working substance is an ideal gas with constant specific heat capacities*

2 The fraction of the work recovered is 0.61.

3 The gravitational potential energy decrease as the ball-bearing falls a distance L is of magnitude MgL. The work done on the gas is

$$-\int_0^L (p - p_0) dV$$

where p is the pressure in the gas. Use pV^γ = constant to obtain

$$p\gamma \frac{dV}{V} + dp = 0$$

Assume that the variations in p and V are very small. Then

$$dV = -A dy$$

where y is measured from the initial position of the bearing, and

$$dp = -\frac{p_0\gamma}{V} dV = \frac{p_0\gamma A}{V} dy$$

so that, using the condition that $p = p_0$ when $y = 0$,

$$p - p_0 = \frac{p_0 \gamma A y}{V}$$

Substituting for dV and $(p - p_0)$ gives the result.

4 Use Equation (12.29), which integrates to give

$$\Delta T = -\frac{T}{C_L} A E \lambda \Delta L$$

provided that ΔT is small. If c_L is the specific heat capacity under constant load, $C_L = AL\rho c_L$, where ρ is the density of the material. Further, if the applied mass is M,

$$\frac{Mg}{A} = E\frac{\Delta L}{L}$$

Therefore,

$$\Delta T = -\frac{T\lambda Mg}{A\rho c_L} = -\ 0.014\ \mathrm{K}$$

5 Write $L = L(T, F)$ and apply the conditions that dF must be the same in both rods and that

$$\mathrm{d}L_1 + \mathrm{d}L_2 = 0$$

6 Use Equation (12.43), which, for an isentropic change, may be written

$$\mathrm{d}T = \frac{T}{C_{\mathrm{A}}}\frac{\mathrm{d}\sigma}{\mathrm{d}T}\mathrm{d}A$$

When the change in temperature is small, this equation may be written

$$\Delta T = \frac{T}{C_A}\frac{\mathrm{d}\sigma}{\mathrm{d}T}\Delta A$$

The value of $\mathrm{d}\sigma/\mathrm{d}T$ is -0.24 mJ m^{-2} K^{-1}, the value of ΔA is $-\ 125.5 \times 10^{-6}$m^2 and the value of C_A is 17.5×10^{-6} J K^{-1}. Substitution gives

$$\Delta T = 0.56\ \mathrm{K}$$

7 In the notation of Section 12.4

$$\mathrm{d}S_T = \frac{\mathrm{d}Q_T}{T} = V\left(\frac{\partial M}{\partial T}\right)_{B_\mathrm{a}} \mathrm{d}B_\mathrm{a}$$

$$\chi_m = \frac{a}{T - T_c}\text{(Curie–Weiss law)}$$

$$= \frac{\mu_0 M}{B_a}\text{(definition)}$$

Therefore,

$$\left(\frac{\partial M}{\partial T}\right)_{B_a} = -\frac{B_a a}{\mu_0 T^2}$$

and

$$\Delta S_T = -\frac{Va}{2\mu_0 T^2}(B_{af}^2 - B_{ai}^2)$$

8 Use Equation (12.74):

$$\frac{dE}{dT} = 0.00034 \text{ V K}^{-1}$$

and

$$E_{350} = 0.063 \text{ V}$$

This gives a value for ΔH_T of 5.4 kJ mol^{-1}.

9 (a)

$$\eta(\text{theoretical}) = \frac{T_1 - T_2}{T_1} = \frac{825 - 275}{825}$$

$$= 0.67$$

(b)

$$\eta = -\frac{W}{Q_1} = -\frac{dW/dt}{dQ_1/dt}$$

Therefore,

$$0.3 = -\frac{(-1.2 \times 10^6)}{dQ_1/dt}$$

so that

$$\frac{dQ_1}{dt} = 4.0 \times 10^6 \text{ W}$$

$$= 4.0 \text{ MW}$$

(c)

$$\frac{dQ_1}{dt} + \frac{dQ_2}{dt} + \frac{dW}{dt} = 0$$

Therefore,

$$4 \times 10^6 + \frac{dQ_2}{dt} + (-1.2 \times 10^6) = 0$$

and

$$\frac{dQ_2}{dt} = -2.8 \text{ MW}$$

(d)

$$\frac{dm}{dt} c_p \Delta T = 2.8 \text{ MW}$$

$$\frac{dm}{dt} = \frac{2.8 \times 10^6}{4.2 \times 10^3 \times 5}$$

$$= 0.13 \times 10^3 \text{ kg s}^{-1}$$

Chapter 13

1 (a) Valid; (b) valid; (c) invalid. Apply Equation (13.13)

2

$$V_c = 3b$$

$$p_c = \frac{RT_c}{2b} - \frac{a'}{9T_c b^2}$$

$$T_c^2 = \frac{8a'}{27Rb}$$

Use Equations (13.4).

If $\hat{T}$ is the reduced temperature and $\hat{V}_m$ is the reduced molar volume,

$$\left(p + \frac{3p_c}{\hat{T}\hat{V}_m^2}\right)\left(V - \frac{V_c}{3}\right) = RT$$

3 Use successive approximations for p, say, starting with $p = RT/V_m$

4

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{R}{1 - 2a(V_\mathrm{m} - b)^2/RTV_\mathrm{m}^3}$$

Use Equation (11.24).

5

$$\frac{T_\mathrm{B}}{T_\mathrm{c}} = \sqrt{6} = 2.45$$

Use the reduced equation of state and write as a series in $\hat{p}$. The Boyle temperature is that which makes the coefficient of the term in $\hat{p}$ equal to zero.

6

$$a'' = \frac{0.42748\ R^2T_\mathrm{c}^{2.5}}{p_\mathrm{c}}\ ;\ b'' = \frac{0.08664\ R\ T_\mathrm{c}}{p_\mathrm{c}}$$

7 Start with the equation

$$C_\mathrm{sat} = T\left(\frac{\partial S}{\partial T}\right)_\mathrm{sat}$$

and combine with a suitable differentiation of

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

8 Consider the isotherm ABKD of Figure 13.2. Let the volume of the system be V when it is in the state represented by the point K, let V_B be the volume corresponding to the state B, when all the substance is vapour, and V_D that corresponding to the state D, when all the substance is liquid.

Further, let c and $(1 - c)$ be the proportions by mass of the liquid phase and the vapour phase, respectively, in the state represented by the point K. Then,

$$V = c\ V_\mathrm{D} + (1 - c)\ V_\mathrm{B}$$

so that

$$c = \frac{V_\mathrm{B} - V}{V_\mathrm{B} - V_\mathrm{D}}$$

Now, $V_B - V$ is proportional to KB on Figure 13.2 and $V_\mathrm{B} - V_\mathrm{D}$ is proportional to DB. Therefore,

$$c = \frac{\mathrm{KB}}{\mathrm{DB}} \text{ and } (1 - c) = \frac{\mathrm{KD}}{\mathrm{DB}}$$

so that

$$\frac{c}{1 - c} = \frac{m_\mathrm{l}}{m_\mathrm{g}} = \frac{\mathrm{KB}}{\mathrm{KD}}$$

Chapter 14

1 Use

$$W = -\int p\mathrm{d}V$$

to show that the work done is about 7% of the enthalpy of vaporisation.

2 The triple temperature is determined from the intersection of the sublimation and vaporisation curves. $T_t = 195$ K. Equation (14.14) may be used to determine the enthalpy of vaporisation at the triple point. $H_{m,v} = 25.5$ kJ mol^{-1}.

3 Use Equation (14.19). c (saturated steam) $= -6.1$ kJ kg^{-1} K^{-1}.

4 29.2 kJ. Operate a Carnot refrigerator between the mass of water and a heat reservoir at a temperature of 20 °C.

5 Use Equation (14.12):

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\ 13.6 \text{ MPa K}^{-1}$$

6

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 3.6 \times 10^3 \text{ Pa K}^{-1}$$

$$= 3.55 \times 10^{-2} \text{ atm K}^{-1}$$

Therefore, $\Delta T = -18.3$ K, assuming that $\mathrm{d}p/\mathrm{d}T$ is a constant and the boiling point of water is 354.9 K or 82 °C.

7 Start with the first law of thermodynamics and remember that both T and p are constant in a first-order phase change. Combine with $\Delta S = H_{12}/T$ and Equation (14.12).

8 Start with Equation (14.11) and use reciprocity and reciprocal relations.

Chapter 15

1 (a) Use Equation (12.44).
(b) Use Equation (12.68).

2 The best refutation is probably that due to Einstein, who pointed out that thought experiments must at least be possible in principle. No real process

can be completely reversible nor can heat transfer be avoided altogether. In Nernst's cycle the slightest heat influx or irreversibility throws the system away from absolute zero.

3 Use Equation (M3) (page 113). Neither van der Waals' equation nor the ideal gas equation is in agreement with the result derived.

Chapter 16

1 Use Equation (16.2).
Joule coefficient = $-a/C_{V,\mathrm{m}}V_\mathrm{m}^2$

2 Examine the properties of Equation (16.19).

3 The result follows directly from Equation (16.11) and the definition of enthalpy. The first term in the square brackets indicates the departure from Joule's law and the second that from Boyle's law.

4 T_c is obtained using Equation (13.4). T_B is obtained by expressing van der Waals' equation in the form

$$pV_\mathrm{m} = RT + \frac{RTb-a}{V_\mathrm{m}} - \frac{RTb^2}{V_\mathrm{m}^2} + \cdots$$

$T = T_\mathrm{B}$ when $RTb - a = 0$. Then show that the equation of the inversion curve is

$$T_\mathrm{i} = \frac{2a}{Rb}\left(1 - \frac{b}{V_\mathrm{m}}\right)^2$$

The maximum value of the inversion temperature is then $T_{\mathrm{imax}} = 2\,T_\mathrm{B}$.

5 Use Equation (16.19).

$$\Delta T = +\,5.8\ \mathrm{K}$$

6 The equation of the inversion curve is

$$\left(\frac{\partial \hat{V}_\mathrm{m}}{\partial \hat{T}}\right)_{\hat{p}} = \frac{\hat{V}}{\hat{T}}$$

Determine $(\partial \hat{V}_\mathrm{m}/\partial \hat{T})_p$ and substitute for this and for $\hat{T}$ in the above equation.

Chapter 17

1 Let 1 m^3 of ideal gas contain n moles of molecules. Then

$$pV = nRT$$

If N is the number of molecules, $N = nN_A$ and R/N_A is Boltzmann's constant k. Therefore,

$$N = \frac{pV}{kT}$$

$$= 2.68 \times 10^{25}\ \text{m}^{-3}$$

2

$$\text{Mean free path} = \frac{1}{N\pi\sigma^2}$$

where N is the mean number of molecules in 1 m^3. From Exercise 1, N is $2.68 \times 10^{25}\ \text{m}^{-3}$. Therefore, for nitrogen at s.t.p. the mean path is $3.96 \times 10^{-7}\text{m}$.

3

$$p = \frac{1}{3}\rho\overline{c^2}$$

The mass of 1 mol of nitrogen molecules is 28 g, which is 28×10^{-3} kg. Therefore,

$$\rho = \frac{28 \times 10^{-3}}{22.4 \times 10^{-3}} = 1.25\ \text{kg m}^{-3}$$

and $\overline{c^2}$ is $24.24 \times 10^4\ \text{m}^2\text{s}^{-2}$, so that the root mean square speed is 492 ms^{-1}.

4 The mean free path (fast molecule approximation) is equal to $1/n\pi\sigma^2$, where n is the number of molecules in unit volume and σ is the (hard sphere) molecular diameter. The average separation of the molecules is $1/n^{1/3}$ and so the result follows.

Chapter 18

1 308.4 K.

2 For a layer of insulation having internal and external radii R and R_0, respectively, the total heat transfer coefficient $\overline{U}$ is given by

$$\frac{1}{\overline{U}} = \frac{1}{2\pi R_0 h} + \frac{\ln (R_0/R)}{2\pi k}$$

This has a minimum value obtained by putting

$$\frac{\mathrm{d}\bar{U}}{\mathrm{d}R_0} = 0$$

giving $R_0 = k/h$.

3

$$r_0 = \sqrt{r_1 r_2}.$$

4 The dispersion produced by a prism is non-uniform, so that the thermometer bulb intercepts a greater range of wavelengths at the red end of the spectrum, and in the near infra-red, than it does elsewhere.

5 Use $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ to show that

$$S = \frac{16\sigma T^3 V}{3c} + \text{constant}$$

Then

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{16\sigma T^2 V}{c}$$

and

$$C_V = \frac{16\sigma T^3 V}{c}$$

6

$$T^4 - T_W^4 = (T^2 - T_W^2)(T^2 + T_W^2)$$

$$T^2 - T_W^2 = (T - T_W)(T + T_W)$$

$$\text{when } T \approx T_W,\ T + T_W \approx 2T_W$$

Then Equation (18.36) becomes

$$\frac{\mathrm{d}q}{\mathrm{d}t} = 4A\alpha(T)\sigma T_W^3(T - T_W)$$

7 When $c_2/\lambda T \gtrsim 5$, $\mathrm{e}^{c_2/\lambda T} \gg 1$.

Using this result and taking natural logarithims of both sides of the modified Equation (18.53) gives the result.

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Notes

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[2] Translated in Alembic Club Reprint No. 4 (Edinburgh: Livingstone, 1961) and also in *The Origins and Growth of Physical Science*, Volume 2, edited by D. L. Hurd and J. J. Kipling (Penguin Books, 1964)

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[5] Representative arguments from this book are in *The Origins and Growth of Physical Science*, Volume 2, edited by D. L. Hurd and J. J. Kipling (Penguin Books, 1964)

[6] N. Clément married the daughter of C. B. Désormes and, subsequently, often styled himself Clément-Désormes. This has sometimes led to confusion.

[7] A translation is given in *The Origins and Growth of Physical Science*, Volume 2, edited by D. L. Hurd and J. J. Kipling (Penguin Books, 1964)

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