MZUZU UNIVERSITY
Faculty of Science, Technology and Innovation
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PHYS 4703

Classical and Statistical Thermodynamics

Laboratory Manual

A virtual laboratory of eleven experiments

Programme	Bachelor of Science
Subject	Physics
Level of study	3
Course code	PHYS 4703
Duration	16 weeks
Practical hours per week	3
Total course credits	12
Pre-requisites	PHYS 1101, PHYS 1201, STAT 2301

First edition. Prepared for face-to-face and ODeL delivery.
The laboratory is available at the address given by your lecturer; no account or sign-up is required.

How to use this manual

This manual is the authoritative document for the PHYS 4703 practical course. It contains everything you need in order to perform, analyse and write up the eleven experiments: the theory each one rests on, the derivation of every relation you are asked to use, the procedure, and a statement of exactly what you must report and how it will be marked.

The laboratory itself is a web application. That does not change what is being asked of you. You will still choose the conditions, take readings that scatter, find that your instrument has a zero error, decide how many points to take and where to take them, and defend your result with an uncertainty. What the computer removes is the queue for the equipment, not the thinking.

The structure of the manual

Part I concerns the conduct of the laboratory. Read Chapters 2 to 4 before your first session and keep returning to them: almost every mark lost in this course is lost on uncertainty and presentation rather than on physics. Chapter 5 sets out precisely what the simulated apparatus does, which models it obeys, and where those models break down. You are entitled to that information, and you will need it to answer some of the questions.

Part II contains the eleven experiments in the order in which they are normally taken. Each chapter has the same shape: aims, theory, apparatus, procedure, analysis, results to report, and questions.

A word on what is simulated

Every instrument in this laboratory is a mathematical model, and every model is documented in Chapter 5. Wherever a model has a limitation that could affect your result, this manual says so rather than hiding it. Two examples, both of which you will meet:

- The gas apparatus uses the virial equation truncated after the second coefficient. It is excellent at the pressures used here and wrong at high density, so the apparatus refuses to operate where it would be wrong rather than quietly returning a bad number.
- The specimens in Experiment 8 obey a Debye model with a weakly temperature-dependent Debye temperature. That model cannot reproduce both the room-temperature heat capacity and the standard entropy of a real metal. The resulting discrepancy of a few per cent has been left in place, because it is a genuine limitation of the Debye theory and one of the things the experiment is meant to expose.

Your bench

The laboratory gives you a *bench key*: a short code held in your browser. It seeds your apparatus, so your instrument has its own zero errors and its own unlabelled specimens, and it owns your measurements so that they survive a reload. Write it down. It is not a password, and anyone who has it can open your bench, which is deliberate so that laboratory partners can share one bench from two machines.

Contents

Part I

The conduct of the laboratory

CHAPTER 1

The course and its assessment

1.1 Aims

PHYS 4703 has two aims:

1. to develop your understanding of the principles of classical and statistical thermodynamics; and
2. to prepare you for further study in thermodynamics and related disciplines.

On successful completion you should be able to demonstrate understanding of the laws and principles of thermodynamics, explain the behaviour of thermodynamic systems, and analyse that behaviour quantitatively. The practical component exists because the third of those verbs cannot be learned from lectures. You analyse a system by measuring it, deciding what the numbers mean, and saying how confident you are.

1.2 The practical programme

The course carries three practical hours a week for sixteen weeks. The programme is eleven experiments occupying eighteen sessions, leaving time for introductory work, catch-up, and the practical examination.

No.	Experiment	Sessions
1	The zeroth law and the ideal-gas temperature scale	1
2	The first law: work, heat and the ratio of heat capacities	2
3	Calorimetry: heat capacity, latent heat and entropy change	2
4	The second law: heat engines, the Carnot cycle and efficiency	2
5	Entropy, irreversibility and the principle of increasing entropy	2
6	Thermodynamic potentials and the Clausius–Clapeyron equation	2
7	The Maxwell–Boltzmann distribution of molecular speeds	2
8	Heat capacity of solids: Einstein, Debye and the third law	2
9	Blackbody radiation and Bose–Einstein statistics	2
10	Fermi–Dirac statistics: thermionic emission from a metal	2
11	Joule–Thomson expansion and the Maxwell relations	1
	Total	**18**

Between them the eleven experiments touch every topic in the course outline, from the statement of the zeroth law to the Einstein and Debye theories of the heat capacity of a solid. The mapping is given at the head of each chapter.

1.3 Assessment

Assessment for PHYS 4703 as a whole is 40 % continuous and 60 % final examination. The practical work contributes to the continuous assessment through the laboratory reports, and there is a laboratory practical examination.

Each experiment carries marks in two categories.

Numerical results. The quantities you are asked to determine are checked automatically against the accepted value for your own apparatus. Two tolerances apply; the full schedule is in Appendix B. You see the outcome immediately, and you may revise and resubmit as often as you like before the deadline. Only the last submission counts.

Written answers. The discussion questions are marked by a demonstrator. The computer records them and shows you the marking points after you submit, so that you can assess your own answer first, but it does not award a mark for them. Judging an explanation is not something a tolerance check can do.

On getting the right answer

The tolerance check is a convenience, not the point of the exercise. A result inside the tolerance with no uncertainty attached, or with an uncertainty that does not cover the discrepancy, is not a good result. A result outside the tolerance that is honestly reported, with the discrepancy identified and explained, is worth far more in the written part than a lucky number. Do not adjust your data until the checker turns green: that is not physics, and it is easily detected.

1.4 Working in pairs

You may work in pairs. Share one bench key so that you share one set of apparatus and one data set; that is what a pair sharing a bench in a physical laboratory does. Each of you must write your own report in your own words.

1.5 Academic honesty

Your data are yours. Fabricating or altering a reading, copying another bench's data, or presenting an analysis you did not do is academic misconduct and is treated as such. Because every bench has a different apparatus – different zero errors, different unlabelled specimens – copied data is straightforward to detect.

CHAPTER 2

The laboratory notebook and the report

2.1 Why a notebook

A laboratory notebook is a contemporaneous record of what you did. It is not a fair copy, it is not tidy, and it is not written afterwards. Its value lies entirely in being written at the bench, at the time, including the things that went wrong.

Keep a notebook for this course even though the laboratory stores your readings for you. The application records numbers; it does not record why you chose a filling pressure of 60 kPa, why you discarded the third reading, or what you noticed about the shape of a curve. Those are the things you will need when you write the report, and they are the things that earn marks.

2.2 What to write

For each session:

- the date, the experiment and the part you are working on;
- your bench key, once, at the front;
- the apparatus constants shown on your bench, copied out — they differ from your neighbour's and you will need them in the analysis;
- for each set of readings: what you varied, what you held fixed, and why;
- every reading you take, including ones you later reject, with a note of why you rejected them;
- rough plots as you go. A graph drawn while you are still at the bench tells you whether you have enough points and whether they are in the right place. A graph drawn afterwards only tells you that you should have taken more.

Never erase. Rule a single line through anything you wish to discard so that it remains legible, and say why.

2.3 The report

A laboratory report is a scientific argument: here is what I set out to measure, here is how I measured it, here is what I got, here is how confident I am, and here is what it means. Everything in it should serve that argument.

The expected structure is:

Title and aims. One short paragraph. What quantity, by what method.

Theory. Only what your analysis actually uses, with the assumptions made explicit. Do not reproduce this manual. Do state, for instance, that you have neglected the molar volume of the liquid, and why that is justified.

Apparatus and procedure. Enough that a competent reader could repeat the measurement. Include the constants of *your* apparatus.

Results. Tabulated data with units and uncertainties in the column headings, and graphs. Raw data may go in an appendix if voluminous; the reduced data belong in the body.

Analysis. The path from your data to your answer, including the propagation of uncertainty. Show the working for one representative point and tabulate the rest.

Discussion. What the result means, how it compares with the accepted value, and whether the difference is significant given your uncertainty. This is where the marks are.

Conclusion. Your results, with uncertainties and units, in one place.

2.4 Presenting a result

Quote every result as

$$\text{value} \pm \text{uncertainty} \quad \text{unit},$$

with the uncertainty to one significant figure — two if the leading digit is a 1 — and the value rounded to the same decimal place. Thus

Write	**Not**
$\gamma = 1.401 \pm 0.012$	$\gamma = 1.40132 \pm 0.01214$
$L = 2.26 \pm 0.05 \times 10^{6}\,\mathrm{J/kg}$	$L = 2261482.3 \pm 51230.1$
$T = (273.4 \pm 1.7)\,\mathrm{K}$	$T = 273.4$

A number without a unit is meaningless, and a number without an uncertainty is not a measurement.

2.5 Comparing with an accepted value

Do not write "the percentage error was 3 %" and stop. That sentence contains no physics. Ask instead whether the difference is significant:

$$t = \frac{|x_{\mathrm{measured}} - x_{\mathrm{accepted}}|}{u(x_{\mathrm{measured}})}.$$

If $t \lesssim 2$ your result agrees with the accepted value. If $t \gtrsim 3$ it does not, and you must say what is responsible: an unmodelled systematic, an underestimated uncertainty, or a genuine discrepancy. That discussion is worth more than the number.

CHAPTER 3

Measurement and uncertainty

3.1 Two kinds of uncertainty

Every measurement has an uncertainty, and there are two ways of arriving at one.

Type A: evaluated statistically. You take the measurement N times and look at the scatter.

Type B: evaluated by other means. You reason from the instrument's resolution, its calibration certificate, or a physical argument.

Both are legitimate and both belong in a report. A common failure is to take ten readings, quote the standard error of their mean, and ignore the fact that the instrument has a 10 Pa resolution and a zero error you never checked.

3.2 Type A: the statistics of repeated readings

For N readings $x_1 \dots x_N$ of the same quantity, the best estimate is the mean

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i,$$

the spread of the individual readings is the sample standard deviation

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2},$$

and the uncertainty of the *mean* is the standard error

$$u(\bar{x}) = \frac{s}{\sqrt{N}}.$$

The $N-1$ matters and so does the distinction between s and $s/\sqrt{N}$. Quote s when you want to say how much a single reading scatters; quote $s/\sqrt{N}$ when you want to say how well you know the mean.

Note the $\sqrt{N}$: to halve your random uncertainty you must take four times as many readings. There is usually a point beyond which a systematic effect dominates and more readings buy nothing. Part of the skill of the laboratory is recognising where that point is.

3.3 Type B: resolution and calibration

A digital instrument reading to a least significant digit δ tells you the value lies in an interval of width δ. With no reason to prefer any part of that interval, the distribution is rectangular and its standard deviation is

$$u = \frac{\delta}{\sqrt{12}} \approx 0.29\,\delta.$$

For an analogue scale read to the nearest half-division, use half a division as δ.

If a manufacturer quotes a tolerance as $\pm a$ with no further information, the same rectangular assumption gives $u = a/\sqrt{3}$.

> **The instruments in this laboratory**
>
> Every simulated instrument has its resolution stated on the bench panel, and several have a zero error or a calibration factor that differs from bench to bench. Those are systematic: they do not average away, and in several experiments the procedure is designed so that they cancel. Where they do not, finding them is part of the exercise.

3.4 Propagating uncertainty

If $y = f(x_1, x_2, \ldots)$ and the x_i are independent, then

$$u^2(y) = \sum_i \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i). \tag{3.1}$$

This is the only formula you need; everything else is a special case.

Relation	Uncertainty	
$y = ax \pm bz$	$u^2(y) = a^2u^2(x) + b^2u^2(z)$	absolute in quadrature
$y = xz$ or x/z	$\left(\frac{u(y)}{y}\right)^2 = \left(\frac{u(x)}{x}\right)^2 + \left(\frac{u(z)}{z}\right)^2$	relative in quadrature
$y = x^n$	$\frac{u(y)}{y} = \lvert n\rvert \frac{u(x)}{x}$	
$y = \ln x$	$u(y) = \frac{u(x)}{x}$	
$y = \mathrm{e}^x$	$\frac{u(y)}{y} = u(x)$	

Two consequences are worth internalising. First, in a product the largest *relative* uncertainty dominates: improving anything else is wasted effort. Second, raising a quantity to a power multiplies its relative uncertainty by that power, so a quantity that enters as a cube — as θ_{D} does in Experiment 8 — needs three times the care.

3.4.1 When the variables are not independent

Equation (3.1) assumes independence. The gradient and intercept of a fitted line are *not* independent, and if you compute a quantity from both you must include the covariance:

$$u^2(y) = \left(\frac{\partial f}{\partial m}\right)^2 u^2(m) + \left(\frac{\partial f}{\partial c}\right)^2 u^2(c) + 2\,\frac{\partial f}{\partial m}\frac{\partial f}{\partial c}\,\mathrm{cov}(m, c).$$

You meet this in Experiment 2, where the dead volume is the ratio of an intercept to a gradient from the same fit.

3.5 Significant figures

Carry full precision through the arithmetic and round only at the end. Round the uncertainty first, to one significant figure — or two if it begins with a 1 — and then round the value to match. Writing more digits than the uncertainty supports is a claim you cannot defend.

3.6 Systematic error, and how to find it

A random error scatters your readings; a systematic error moves them all the same way, and no amount of repetition reveals it. The usual signatures are:

- a straight line that should pass through the origin but does not — the intercept is measuring your zero error;
- a result that changes when you change something that should not matter, such as the filling pressure in Experiment 1 or the slit width in Experiment 9;
- residuals that are not random but curve, indicating that the model you fitted is not the model the data obey.

The best defence is design. Where you can arrange for a systematic effect to cancel — by extrapolating to zero, by starting a calorimeter below room temperature and finishing above it, by measuring a difference rather than two absolutes — do so, and say in the report why you did.

CHAPTER 4

Graphs, fitting and the reduction of data

4.1 Why we straighten things

A straight line is the only functional form the eye can judge. Given $y = A\mathrm{e}^{-Bx}$ you cannot tell by looking whether the data obey it; given $\ln y$ against x you can see at a glance whether they lie on a line and where they depart from it.

Most of the analysis in this course consists of choosing the transformation that makes the expected relation linear, and then reading the physics off the gradient and the intercept.

Expected	Plot	against	Gradient	Intercept
$PV = nRT$	$1/P$	V	$1/nRT$	V_0/nRT
$PV^\gamma = \text{const}$	$\ln P$	$\ln V$	$-\gamma$	–
$P_{\text{sat}} = A\mathrm{e}^{-L/RT}$	$\ln P$	$1/T$	$-L/R$	$\ln A$
$C = \gamma T + \beta T^3$	C/T	T^2	β	γ
$J = AT^2\mathrm{e}^{-\phi/kT}$	$\ln(J/T^2)$	$1/T$	$-\phi/k$	$\ln A$
$M = \sigma T^n$	$\ln M$	$\ln T$	n	$\ln \sigma$

4.2 Least squares

Given points (x_i, y_i) with the x_i regarded as exact and the y_i carrying uncertainties σ_i, define the weights $w_i = 1/\sigma_i^2$ and the sums

$$S = \sum w_i, \quad S_x = \sum w_i x_i, \quad S_y = \sum w_i y_i, \quad S_{xx} = \sum w_i x_i^2, \quad S_{xy} = \sum w_i x_i y_i.$$

With $\Delta = SS_{xx} - S_x^2$, the best-fit line $y = c + mx$ has

$$m = \frac{SS_{xy} - S_x S_y}{\Delta}, \qquad u^2(m) = \frac{S}{\Delta}, \tag{4.1}$$

$$c = \frac{S_{xx}S_y - S_x S_{xy}}{\Delta}, \qquad u^2(c) = \frac{S_{xx}}{\Delta}, \tag{4.2}$$

and $\operatorname{cov}(m, c) = -S_x/\Delta$.

If you have no per-point uncertainties, set every $w_i = 1$. The gradient and intercept are unchanged, but the uncertainties must then be scaled by the observed scatter: multiply the variances above by

$$s^2 = \frac{1}{N-2}\sum_i (y_i - c - mx_i)^2.$$

The bench does exactly this, and tells you which of the two it has done.

Transforming the uncertainties too

If you plot $\ln y$ you must plot the uncertainty of $\ln y$, which is $u(y)/y$, not $u(y)$. A common and costly error is to carry the untransformed uncertainty into a logarithmic plot. Note in particular that constant *relative* uncertainty on y becomes constant *absolute* uncertainty on $\ln y$, so a log plot of such data should be fitted with equal weights.

4.3 Judging a fit

4.3.1 Residuals

Plot them. The residual $r_i = y_i - (c + mx_i)$ should scatter randomly about zero with no structure. Curvature in the residuals means the model is wrong, and no amount of staring at r^2 will tell you that: a badly curved data set can have $r^2 = 0.999$.

4.3.2 Chi-square

When you do have genuine per-point uncertainties,

$$\chi^2 = \sum_i \frac{(y_i - c - mx_i)^2}{\sigma_i^2}, \qquad \chi^2_\nu = \frac{\chi^2}{N-2},$$

and $\chi^2_\nu \approx 1$ indicates a fit consistent with the stated uncertainties. A value much greater than 1 means the model is wrong or the uncertainties are underestimated; much less than 1 means they are overestimated.

4.3.3 r^2

The coefficient of determination measures how much of the variance the line accounts for. It is worth reporting and worth almost nothing as evidence: report it, then look at the residuals.

4.4 Extrapolation

Several experiments in this course determine a quantity by extrapolating to a limit that cannot be reached: zero filling pressure, zero field, zero bandwidth, zero temperature. Extrapolation is legitimate and often the only way to remove a systematic, but it carries its own cost.

- The uncertainty of the intercept is larger than that of any data point, and grows the further the extrapolation reaches.
- It is only as good as the functional form. Extrapolating a straight line through data that curve is a guaranteed systematic error, so look at the residuals first.
- Where the physics gives a leading correction linear in some small parameter — as it does in Experiment 1 — extrapolate against that parameter and no other.

4.5 Tools

The bench has a plotting panel with a straight-line fit built in, including logarithmic axes. Use it while you are taking data, to see whether your points are where they need to be.

For the report you will usually want more, and every part of every experiment can be exported as CSV. Any tool is acceptable — a spreadsheet, Python with `numpy` and `scipy`, Origin, gnuplot — provided you say which you used and the analysis is yours.

CHAPTER 5

The simulated apparatus

5.1 What this chapter is for

You are entitled to know what the instruments in front of you actually do. This chapter states the physical model behind each class of apparatus, the data it uses, and where it stops being valid. Several of the discussion questions require this information.

Nothing here is a shortcut to the answers. The models are given; the apparatus constants that make your instrument yours — zero errors, calibration factors, the identity of the unlabelled specimens — are not, and they are generated from your bench key on the server and never sent to your browser.

5.2 Constants

The seven defining constants of the SI are exact:

$$\Delta\nu_{\mathrm{Cs}},\quad c,\quad h,\quad e,\quad k_{\mathrm{B}},\quad N_{\mathrm{A}},\quad K_{\mathrm{cd}}.$$

Everything derived from them — $R = N_{\mathrm{A}}k_{\mathrm{B}}$, the Stefan–Boltzmann constant $\sigma = 2\pi^5 k_{\mathrm{B}}^4/15h^3c^2$, the Wien constant, the Richardson constant $A_{\mathrm{G}} = 4\pi m e k_{\mathrm{B}}^2/h^3$ — is computed from them rather than typed in. Measured constants are the CODATA 2022 recommended values. Appendix A tabulates those you will need.

5.3 Gases

5.3.1 Equation of state

Every gas obeys the virial equation truncated after the second coefficient,

$$PV_{\mathrm{m}} = RT\left(1 + \frac{B(T)}{V_{\mathrm{m}}}\right). \tag{5.1}$$

$B(T)$ is not tabulated; it is computed from the Lennard-Jones (12–6) pair potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

through the classical expression

$$B(T) = -2\pi N_{\mathrm{A}}\int_0^\infty \left[\mathrm{e}^{-u(r)/k_{\mathrm{B}}T} - 1\right] r^2\,\mathrm{d}r, \tag{5.2}$$

evaluated by numerical quadrature to about twelve significant figures. The potential parameters σ and $\varepsilon/k_{\mathrm{B}}$ are those Hirschfelder, Curtiss and Bird obtained by fitting experimental second

virial coefficients, and they reproduce the measured B of the common gases to within about $1\,\mathrm{cm^3/mol}$ near room temperature.

The same $B(T)$ drives the gas thermometer of Experiment 1, the free expansion of Experiment 5 and the Joule–Thomson apparatus of Experiment 11. Those three experiments are therefore mutually consistent, and a result from one can legitimately be checked against another.

Where this stops working

Equation (5.1) is a two-term truncation of an infinite series. It is excellent while $|B|/V_\mathrm{m} \ll 1$ and meaningless when the density approaches the critical density. The apparatus refuses to operate where the truncation fails, rather than returning a plausible wrong number.

5.3.2 Heat capacity

Heat capacities come from the rigid-rotor, harmonic-oscillator model of the ideal gas evaluated from spectroscopic constants:

$$\frac{C_V}{R} = \underbrace{\frac{3}{2}}_{\text{translation}} + \underbrace{c_\mathrm{rot}}_{\text{rotation}} + \sum_j g_j \frac{x_j^2 \mathrm{e}^{x_j}}{(\mathrm{e}^{x_j}-1)^2}, \qquad x_j = \frac{\theta_j}{T}, \tag{5.3}$$

with $\theta_j = hc\tilde{\nu}_j/k_\mathrm{B}$ from the measured vibrational wavenumbers. The rotational term is 1 for a linear molecule and 3/2 for a non-linear one once $T \gg \theta_\mathrm{rot}$; where that does not hold — it does not for hydrogen, whose $\theta_\mathrm{rot} = 87.6\,\mathrm{K}$ — the rotational partition function is summed explicitly over J, with the nuclear spin weights of the frozen 1:3 para:ortho mixture found in a cylinder.

Equation (5.3) gives $\gamma = 5/3$ exactly for the monatomic gases, 1.400 for nitrogen at 300 K and 1.289 for carbon dioxide, matching the measured values.

5.4 Solids

The specimens of Experiment 8 obey

$$C_p(T) = \underbrace{3R\,\mathcal{D}\!\left(\frac{\theta_\mathrm{D}(T)}{T}\right)}_{\text{lattice}} + \underbrace{\gamma T}_{\text{electrons}} + \underbrace{\frac{T V_\mathrm{m} \alpha^2(T)}{\kappa_T}}_{C_p - C_V}, \tag{5.4}$$

where $\mathcal{D}$ is the Debye function, γ is the measured Sommerfeld coefficient and the last term is the exact thermodynamic difference between the principal heat capacities.

Two refinements make the model behave like a real solid.

A temperature-dependent Debye temperature. A real solid does not have a single θ_D: the value needed to reproduce the measured heat capacity falls by between 5 and 25 per cent between 0 K and room temperature, because the true phonon density of states is not the Debye parabola. The model applies a smooth softening that vanishes as T^2, so the exact T^3 law — and therefore the θ_D you obtain from a low-temperature C/T against T^2 plot — is preserved.

An expansivity that obeys the third law. Using the room-temperature expansivity at 2 K would make the $C_p - C_V$ term swamp the electronic term, which is physically wrong. The model ties α to the heat capacity through the Grüneisen relation $\alpha = \Gamma \kappa_T C_V / V_\mathrm{m}$ with Γ constant, so $\alpha \to 0$ as $T \to 0$ as it must.

An acknowledged limitation

A Debye spectrum with a single softening cannot reproduce both the measured C_p at 298 K and the measured standard entropy of a real metal. The model is calibrated on the heat capacity, and the entropy then comes out between about 1 and 13 per cent from the tabulated value depending on the material. This has deliberately *not* been tuned away: it is a real limitation of the Debye theory, and Experiment 8 asks you to quantify and account for it. Lead is a further special case, discussed there.

5.5 Phase equilibria

The saturation curve of water is the Wagner and Pruss equation adopted by IAPWS, valid from the triple point to the critical point; the organic liquids use their published Antoine constants over the stated range. The vapour is treated as ideal. That is an approximation of order a per cent, it is stated here, and Experiment 6 asks you to detect its consequences.

The melting curve of ice follows the Clapeyron equation integrated with the measured densities of ice and water.

5.6 Radiation

The cavity source of Experiment 9 emits Planck's spectrum with the emissivity engraved on the apparatus. The monochromator does *not* report the spectral radiance at the set wavelength: it reports the average over a triangular slit function of finite width,

$$L_{\mathrm{measured}}(\lambda_0) = \frac{\int W(\lambda - \lambda_0)\, L_\lambda(\lambda)\, \mathrm{d}\lambda}{\int W(\lambda - \lambda_0)\, \mathrm{d}\lambda},$$

which broadens the spectrum and shifts the apparent peak, exactly as a real instrument does. Detecting that shift is one of the objects of the experiment.

5.7 Kinetic theory

The relaxation study in Experiment 7 is a direct-simulation Monte Carlo of a hard-sphere gas. Pairs are chosen at random and accepted with a probability proportional to their relative speed, which reproduces the hard-sphere collision rate; the post-collision relative velocity is isotropic in the centre-of-mass frame, which is exact for hard spheres. Momentum and kinetic energy are conserved identically by construction, so the temperature is fixed and only the *distribution* evolves.

5.8 Noise, resolution and systematic error

Every reading passes through an instrument model before you see it:

- a random deviate, normally distributed, with the standard deviation appropriate to that instrument — often a fixed *fraction* of the reading, so that precision degrades at the bottom of the range;
- quantisation to the stated resolution;

- where appropriate, a zero error or calibration factor fixed for your bench and unknown to you;
- counting statistics where the quantity really is a count, so that the uncertainty is $\sqrt{N}$ and you can say so.

Repeating a reading under identical settings gives a genuinely new random deviate; it does not give a new zero error. That distinction is the whole content of Chapter 3, made concrete.

Part II

The experiments

EXPERIMENT 1

The zeroth law and the ideal-gas temperature scale

Aims

To establish an absolute temperature scale from first principles with a constant-volume gas thermometer; to show that a real gas indicates a temperature that depends on its density and on its identity, and that both dependences vanish in the limit of zero density; and to determine the Kelvin temperature of three unknown baths and the absolute zero of the Celsius scale.

Syllabus: statement of the zeroth law; the Kelvin temperature scale. **Sessions:** 1

1.1 Theory

1.1.1 The zeroth law

If body A is in thermal equilibrium with body C, and body B is in thermal equilibrium with body C, then A and B are in thermal equilibrium with each other. That is the zeroth law, and although it looks like a triviality it is what makes temperature exist. It says that "being in equilibrium with" partitions all bodies into equivalence classes, so a single number can be attached to each class, and a third body — a thermometer — can be used to compare two bodies that never touch.

The law does not tell us what number to attach. That requires a choice of thermometric property and a scale.

1.1.2 The constant-volume gas thermometer

Take a fixed quantity of gas in a fixed volume and use the pressure as the thermometric property. Define

$$T(P) = 273.16\,\mathrm{K} \times \frac{P}{P_{\mathrm{tp}}}, \tag{1.1}$$

where P_{tp} is the pressure the same gas exerts, in the same volume, at the triple point of water.[1]

If the gas were ideal, (1.1) would give the same answer whatever gas we used and however much of it we put in the bulb. It does not.

[1] Before the 2019 revision of the SI the triple point of water defined the kelvin exactly. It is now a measured quantity whose best value remains 273.16 K with a standard uncertainty of 0.1 mK, so (1.1) is unchanged in practice.

1.1.3 Why the answer depends on the filling pressure

Write the equation of state as a virial series in the molar density $\rho = 1/V_{\mathrm{m}}$:

$$P = \rho RT\,(1 + B(T)\rho + \cdots)\,.$$

At the triple point, $P_{\mathrm{tp}} = \rho RT_{\mathrm{tp}}(1 + B(T_{\mathrm{tp}})\rho)$; at the unknown temperature, $P = \rho RT(1 + B(T)\rho)$, with the *same* ρ because the volume and the amount of gas are fixed. Dividing,

$$T_{\mathrm{apparent}} \equiv T_{\mathrm{tp}}\frac{P}{P_{\mathrm{tp}}} = T\,\frac{1 + B(T)\rho}{1 + B(T_{\mathrm{tp}})\rho} \simeq T\Big[1 + (B(T) - B(T_{\mathrm{tp}}))\rho\Big]. \tag{1.2}$$

Two things follow immediately, and they are the whole experiment.

1. The apparent temperature is wrong by an amount *linear in the density*, and therefore linear in the filling pressure, since $\rho \simeq P_{\mathrm{tp}}/RT_{\mathrm{tp}}$ to the accuracy needed here. So a plot of T_{apparent} against P_{tp} is a straight line whose intercept is the true temperature.
2. The error depends on the gas only through $B(T) - B(T_{\mathrm{tp}})$, and that difference vanishes from the intercept. *Every* gas therefore extrapolates to the same value.

The common limit is the ideal-gas temperature. It can be shown from the second law — you will meet the argument in Experiment 4 — that it is identical to the thermodynamic temperature defined by a Carnot cycle, which is why it deserves the name Kelvin.

1.1.4 The sign of the correction

$B(T)$ is negative when attraction between the molecules dominates and positive when their repulsive cores do. Nitrogen at 273 K has $B \approx -10\,\mathrm{cm^3/mol}$; helium is positive, $B \approx +12\,\mathrm{cm^3/mol}$, over the whole range of this experiment because its well depth is only $\varepsilon/k_{\mathrm{B}} = 10.2\,\mathrm{K}$. You should be able to predict, before you take a reading, which way each gas will err.

1.2 Apparatus

- A fused-silica bulb of engraved volume, connected through a capillary to a mercury manometer. The mercury is returned to a fiducial mark before every reading, so the volume is constant.
- Manometer resolution 10 Pa. Your instrument has a small zero error, fixed for your bench.
- A gas manifold: helium, neon, argon, nitrogen, oxygen, hydrogen and dry air.
- Baths at the defining fixed points of ITS-90, several practical baths, and three unknown thermostats labelled A, B and C.

The bulb is refilled at the triple point of water each time you change the filling pressure, and the apparatus records P_{tp} for you.

1.3 Procedure

Part A: the zero-pressure limit

1. Choose a gas and an unknown bath. Record P at five or more filling pressures spanning the range.

2. Plot $T_{\text{apparent}} = 273.16\,P/P_{\text{tp}}$ against P_{tp} and fit a straight line. The intercept is your answer.
3. Repeat with at least two more gases. The intercepts must agree within their uncertainties; if they do not, say so and investigate.
4. Repeat for all three unknown baths.

Helium works at every temperature available. The others condense: the apparatus will refuse, and tell you why.

Part B: absolute zero

1. At a single filling pressure, record P at every fixed point whose Celsius temperature you know.
2. Plot P against $t/^\circ\text{C}$ and extrapolate to $P = 0$. The intercept on the temperature axis is absolute zero.
3. Repeat at a much lower filling pressure and comment on the change.

1.4 Analysis

- Extrapolate; do not average. Averaging your five apparent temperatures gives you the value at the mean filling pressure, which is not what you want and is wrong by a knowable amount.
- Take the uncertainty of the intercept from the fit, and check it against the spread of the intercepts from your different gases. If they disagree, the fit uncertainty is the one to distrust.
- The manometer resolution is fixed at 10 Pa but the readings at low filling pressure are small, so the *fractional* uncertainty grows as you reduce the pressure. That is the trade-off the extrapolation is managing, and question 3 asks you to quantify it.

1.5 Results to report

The full schedule with tolerances is in Appendix B. In summary: the Kelvin temperature of each of the three unknown baths; absolute zero on the Celsius scale; and the amount of gas in your bulb when filled to 100.0 kPa at the triple point.

1.6 Questions

1. State the zeroth law and explain precisely which step of this experiment relies on it. [5]
2. Your extrapolated intercepts agree but the values at finite filling pressure do not. Explain the physical origin of the difference, and why the sign of the discrepancy differs between helium and nitrogen. [6]
3. Why is the ideal-gas temperature defined by an extrapolation rather than by a single very dilute filling? Answer with reference to your own uncertainties. [5]
4. Outline the argument that the ideal-gas scale and the thermodynamic scale coincide. [6]
5. ITS-90 does not use gas thermometry for routine work. What is used instead over the range of your unknown baths, and why? [4]

EXPERIMENT 2

The first law: work, heat and the ratio of heat capacities

Aims

To measure an isotherm and an adiabat for several gases; to determine the amount of gas confined and the dead volume of the apparatus from a single linear plot; to determine $\gamma = C_p/C_V$ by three independent methods; and to account for the measured values in terms of the degrees of freedom of the molecules.

Syllabus: heat, work and internal energy; statement and special cases of the first law; heat capacity at constant volume and constant pressure; isothermal and adiabatic changes for an ideal gas. **Sessions:** 2

2.1 Theory

2.1.1 The first law

The internal energy is a function of state, and

$$\mathrm{d}U = \delta Q - P\,\mathrm{d}V, \tag{2.1}$$

with $W = \int P\,\mathrm{d}V$ the work done *by* the system. The inexact differentials are the point: Q and W depend on the path, U does not.

2.1.2 Isothermal change

For an ideal gas U depends only on T, so an isothermal change has $\Delta U = 0$ and

$$Q = W = nRT \ln \frac{V_2}{V_1}. \tag{2.2}$$

All the heat absorbed appears as work.

2.1.3 Adiabatic change

With $\delta Q = 0$, (2.1) gives $nC_V\,\mathrm{d}T = -P\,\mathrm{d}V$. Substituting $P = nRT/V$ and using $C_p - C_V = R$,

$$\frac{\mathrm{d}T}{T} = -\frac{R}{C_V}\frac{\mathrm{d}V}{V} = -(\gamma - 1)\frac{\mathrm{d}V}{V},$$

which integrates to $TV^{\gamma-1} = \text{constant}$ and hence

$$PV^{\gamma} = \text{constant}, \qquad W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}. \tag{2.3}$$

2.1.4 What γ tells you

Equipartition gives $\frac{1}{2}k_{\mathrm{B}}T$ per quadratic degree of freedom, so

$$C_V = \tfrac{3}{2}R \ \text{(monatomic)}, \qquad C_V = \tfrac{5}{2}R \ \text{(diatomic, vibration frozen)},$$

and $\gamma = 5/3$ and $7/5$ respectively. Vibration is frozen when $\theta_{\mathrm{vib}} \gg T$, which is amply satisfied for nitrogen ($\theta_{\mathrm{vib}} = 3\,374\,\mathrm{K}$) at room temperature.

Carbon dioxide is the interesting case. It is linear, so rotation contributes R, but it has a doubly degenerate bending mode at only $\theta = 960\,\mathrm{K}$, which is substantially excited at $300\,\mathrm{K}$. Each mode contributes

$$\frac{C_{\mathrm{vib}}}{R} = \frac{x^2 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}, \qquad x = \frac{\theta}{T},$$

and summing over the four modes of CO_2 gives $C_V/R = 3.47$ and $\gamma = 1.289$ at $300\,\mathrm{K}$. You should be able to reproduce that number from the vibrational temperatures in Appendix A.

2.1.5 The dead volume

The gas does not occupy only the cylinder: there is a small extra volume V_0 in the connecting tube and the pressure gauge. What the scale reads is V; what the gas occupies is $V + V_0$. Then

$$P(V + V_0) = nRT \quad \Longrightarrow \quad \frac{1}{P} = \frac{V}{nRT} + \frac{V_0}{nRT},$$

so a plot of $1/P$ against the *indicated* volume is a straight line of gradient $1/nRT$ and intercept V_0/nRT. One graph gives you both n and V_0; and

$$V_0 = \frac{\text{intercept}}{\text{gradient}}$$

requires the covariance of the fit, because the two are strongly correlated.

2.1.6 Clément–Desormes

A large vessel is charged to P_1 slightly above atmospheric. The tap is opened; the gas expands adiabatically to P_0, cooling to $T_2 = T_0(P_0/P_1)^{(\gamma-1)/\gamma}$. The tap is closed and the gas warms back to room temperature at constant volume, reaching P_2. Eliminating T_2,

$$\gamma = \frac{\ln(P_1/P_0)}{\ln(P_1/P_2)} \simeq \frac{h_1}{h_1 - h_2}, \tag{2.4}$$

the last form holding when the manometer heads h are small compared with atmospheric pressure.

Equation (2.4) assumes the expansion is (i) complete and (ii) adiabatic. Leave the tap open too briefly and the pressure has not reached P_0; leave it open too long and heat has leaked in. Both bias the answer, in opposite directions. Finding the plateau between them is the exercise.

2.1.7 Rüchhardt's method

A ball of mass m sits in a precision tube of area A above a gas volume V. Displace it by x and the gas is compressed adiabatically: $\mathrm{d}P = -\gamma P\,\mathrm{d}V/V = \gamma P A x/V$. The restoring force is $-A\,\mathrm{d}P$, so

$$m\ddot{x} = -\frac{\gamma P A^2}{V}x \quad \Longrightarrow \quad \tau = 2\pi\sqrt{\frac{mV}{\gamma A^2 P}}, \qquad \gamma = \frac{4\pi^2 mV}{\tau^2 A^2 P},$$

with $P = P_{\mathrm{atm}} + mg/A$ the equilibrium pressure of the trapped gas.

The oscillation is not perfectly adiabatic: heat diffuses into the tube wall within a thermal diffusion length each cycle, softening the effective spring and lengthening the period. Rüchhardt's method therefore *under*estimates γ, typically by about one per cent.

2.2 Procedure

Four parts, described in full on the bench. In outline:

A. Isotherm. Eight or more indicated volumes at fixed temperature. Plot $1/P$ against V; extract n and V_0.

B. Adiabat. Eight or more final volumes from a common reference state. Plot $\ln P$ against $\ln(V + V_0)$; the gradient is $-\gamma$.

C. Clément–Desormes. Sweep the tap-open time over the whole available range at fixed h_1, then work at the best time for each gas.

D. Rüchhardt. Five timings of twenty oscillations for each ball-and-gas combination.

2.3 Analysis

- Part A is the only place you learn V_0, and Parts B and D both need it. Do it first and carry its uncertainty forward.
- In Part B, the abscissa is $\ln(V + V_0)$, not $\ln V$. Using the indicated volume alone biases γ downwards by a substantial amount: check for yourself how much.
- Compare your three values of γ for each gas with a proper weighted mean, and comment on their relative precision.
- For the first law: compute W, Q and ΔU for one isothermal and one adiabatic change and show the law is satisfied. For the adiabat, obtain ΔU twice — once as $-W$ from (2.3) and once as $nC_V\Delta T$ — and check that they agree.

2.4 Results to report

The dead volume; the amount of gas confined; γ for argon, nitrogen and carbon dioxide; C_V for carbon dioxide; C_p for nitrogen.

2.5 Questions

1. Plot your Clément–Desormes γ against the tap-open time. Explain the shape and justify the time you adopted. [8]
2. Account quantitatively for the values of γ you obtained for argon, nitrogen and carbon dioxide, using equipartition and the vibrational temperatures. [8]
3. Compute W, Q and ΔU for your isothermal expansion and your adiabatic compression, and show explicitly that the first law is satisfied in both. [7]
4. Why does Rüchhardt's method systematically underestimate γ, and how large is the effect in your data? [5]

EXPERIMENT 3

Calorimetry: heat capacity, latent heat and entropy

Aims

To determine specific heat capacities and latent heats by the method of mixtures; to apply a cooling correction and justify it; to test the Dulong–Petit rule and identify unlabelled specimens; and to compute the entropy generated in each irreversible process and confirm that it is positive.

Syllabus: heat, work and internal energy; heat capacity; measuring entropy and entropy changes; entropy and latent heat; the principle of increasing entropy. **Sessions:** 2

3.1 Theory

3.1.1 The method of mixtures

A body of mass m_s and specific heat capacity c_s, initially at T_h, is dropped into a calorimeter of heat capacity $C_w = m_{\text{cal}}c_{\text{cal}} + m_w c_w$ at T_i. If the calorimeter were isolated,

$$m_s c_s (T_h - T_f) = C_w (T_f - T_i). \tag{3.1}$$

The quantity $m_{\text{cal}}c_{\text{cal}}$ is the *water equivalent* of the calorimeter; omitting it is the single commonest error in this experiment.

3.1.2 The cooling correction

The calorimeter is not isolated. It loses heat to the laboratory at a rate proportional to the excess temperature,

$$C\frac{\mathrm{d}T}{\mathrm{d}t} = -U\,(T - T_{\text{env}}), \tag{3.2}$$

so the observed maximum $T_{\max}$ is below the equilibrium temperature (3.1) would predict. The correction to add back is the heat lost during the rise,

$$\Delta T_{\text{corr}} = \frac{U}{C}\int_0^{t_{\max}} (T(t) - T_{\text{env}})\,\mathrm{d}t,$$

and U/C is obtained directly from the gradient of the record before the addition and after the maximum, where nothing else is happening. In practice:

1. From the pre-period, measure $(\mathrm{d}T/\mathrm{d}t)_1$ at excess $\theta_1 = T_i - T_{\text{env}}$.
2. From the post-period, measure $(\mathrm{d}T/\mathrm{d}t)_2$ at excess $\theta_2 = T_{\max} - T_{\text{env}}$.
3. These give U/C twice; they should agree.

4. Evaluate the integral numerically from the recorded trace, or graphically by the area between the curve and the line $T = T_{\mathrm{env}}$.

> **Making the correction small**
>
> If you start the calorimeter as far below room temperature as it will finish above it, the heat gained during the first half of the rise nearly cancels the heat lost during the second, and the correction becomes a small residual rather than the dominant term. Design the run that way and say in your report that you did.

3.1.3 Latent heat

Adding ice of mass m_i at $0\,^{\circ}\mathrm{C}$:

$$m_i L_f + m_i c_w (T_f - T_0) = C_w (T_i - T_f), \tag{3.3}$$

with $T_0 = 273.15\,\mathrm{K}$. Condensing steam of mass m_s at the normal boiling point:

$$m_s L_v + m_s c_w (T_b - T_f) = C_w (T_f - T_i). \tag{3.4}$$

Note that the second term on the left of each equation is not negligible: the melt water still has to be warmed, and the condensate still has to be cooled.

3.1.4 Dulong and Petit

A classical solid has $3N$ vibrational degrees of freedom, each contributing $k_{\mathrm{B}}T$ (kinetic plus potential), so

$$C_{V,\mathrm{molar}} = 3R = 24.94\,\mathrm{J/(mol\,K)}.$$

At room temperature the common metals obey this to within about ten per cent, which is why $c \times M$ identifies a metal almost uniquely. The departures are instructive and are the subject of Experiment 8.

3.1.5 Entropy

Entropy is a function of state, so its change can be computed along any reversible path even though the actual process is violently irreversible. For a body of constant heat capacity taken from T_1 to T_2,

$$\Delta S = \int_{T_1}^{T_2} \frac{C\,\mathrm{d}T}{T} = C \ln \frac{T_2}{T_1},$$

and for an isothermal phase change, $\Delta S = mL/T$. The sum over all bodies is the entropy generated, and the second law requires

$$\Delta S_{\mathrm{universe}} = \sum_i \Delta S_i > 0. \tag{3.5}$$

3.2 Procedure

A. Specific heat capacity of three unlabelled specimens by the method of mixtures, at least twice each.

B. Latent heat of fusion of ice.

C. Latent heat of vaporisation of water, by condensing steam.

D. Two lagged blocks at different temperatures clamped together; follow both temperatures to the common final value.

Every run returns the complete temperature–time record with a sixty-second pre-period. Export it and do the correction properly.

3.3 Analysis

- Do not use the observed maximum. Correct it, and show the correction in your report.
- Propagate the uncertainties. In (3.1) the temperature *differences* carry the uncertainty, and $T_f - T_i$ is typically only a few kelvin, so its relative uncertainty dominates everything.
- In Part D, first check energy conservation: the energy lost by the hot block should equal that gained by the cold one, and any shortfall measures the residual heat leak.
- For the entropy generated in Part D, note that the first-order terms cancel by energy conservation, so $\Delta S_{\text{universe}}$ is second order in the temperature difference. Your two runs should show that.

3.4 Results to report

The specific and molar heat capacities of the three specimens; L_f and L_v; and the entropy generated in your largest Part D run (marked on its sign and method).

3.5 Questions

1. Derive the cooling correction from Newton's law and state the assumption that makes it valid. [8]
2. Compare your molar heat capacities with $3R$. Which specimen departs most, and why? [6]
3. Compute ΔS for the ice, for the water and for the universe. Explain the sign, and estimate how the answer would change if the ice were added slowly in many small pieces. [8]
4. Show that for small temperature differences the entropy generated in Part D grows as the square of that difference. [6]

EXPERIMENT 4

The second law: heat engines and the Carnot cycle

Aims

To take an indicator diagram from a Stirling engine and obtain the work per cycle from its area; to verify the first law for a cyclic device; to show that the thermal efficiency never exceeds the Carnot value and approaches it only as the power output vanishes; and to show that the efficiency at maximum power is close to $1 - \sqrt{T_c/T_h}$.

Syllabus: heat engines and the second law; Carnot's cycle and theorem. **Sessions:** 2

4.1 Theory

4.1.1 Cyclic devices

A heat engine takes Q_h from a hot reservoir, delivers work W and rejects Q_c to a cold reservoir. Over a complete cycle $\Delta U = 0$, so the first law gives $W = Q_h - Q_c$ and

$$\eta \equiv \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}. \tag{4.1}$$

4.1.2 The second law

Two statements, both denials:

Kelvin–Planck. No cyclic device can take heat from a single reservoir and convert it entirely into work.

Clausius. No cyclic device can transfer heat from a colder to a hotter body with no other effect.

They are equivalent: assuming a device that violates one, you can construct a device that violates the other, in both directions. Question 3 asks for the construction.

4.1.3 Carnot's theorem

No engine operating between two reservoirs can be more efficient than a reversible one, and all reversible engines between the same two reservoirs have the same efficiency.

Suppose an engine X were more efficient than a reversible engine R. Run R backwards as a refrigerator driven by X, sized so that the pair exchange the same heat with the hot reservoir. The composite device then extracts net heat from the cold reservoir and delivers net work, with

no other effect, violating Kelvin–Planck. Hence $\eta_X \le \eta_R$. Applying the argument with the roles exchanged, between two reversible engines, gives equality.

The consequence is that η_R cannot depend on the working substance, only on the two temperatures. Evaluating it for an ideal gas round a Carnot cycle gives

$$\eta_C = 1 - \frac{T_c}{T_h}, \tag{4.2}$$

and since the result is substance-independent, (4.2) defines the thermodynamic temperature ratio. That is the promised link back to Experiment 1.

4.1.4 Why a real engine cannot reach η_C

Reversible heat transfer requires an infinitesimal temperature difference, hence an infinite time, hence zero power. Any engine that actually delivers power must let heat cross a finite temperature drop, and is therefore irreversible.

Suppose *all* the irreversibility is confined to the two heat exchangers, the working fluid itself executing a reversible cycle between T_{hw} and T_{cw}. Such an engine is called *endoreversible*. With linear heat transfer,

$$\dot{Q}_h = \alpha(T_h - T_{hw}), \qquad \dot{Q}_c = \beta(T_{cw} - T_c),$$

and internal reversibility requires $\dot{Q}_h/T_{hw} = \dot{Q}_c/T_{cw}$. Writing $r = T_{cw}/T_{hw}$, the entropy balance fixes

$$T_{hw} = \frac{\alpha T_h + \beta T_c/r}{\alpha + \beta},$$

and the power is

$$\dot{W} = \dot{Q}_h(1 - r) = \frac{\alpha\beta}{\alpha + \beta}(1 - r)\left(T_h - \frac{T_c}{r}\right). \tag{4.3}$$

Setting $\mathrm{d}\dot{W}/\mathrm{d}r = 0$ gives $r = \sqrt{T_c/T_h}$, so the efficiency at maximum power is

$$\eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}}, \tag{4.4}$$

the Curzon–Ahlborn efficiency. The conductances have cancelled: the result depends only on the reservoir temperatures, which is why it applies remarkably well to real power stations.

For $T_h = 600\,\mathrm{K}$ and $T_c = 300\,\mathrm{K}$, $\eta_C = 0.500$ but $\eta_{CA} = 0.293$.

4.1.5 The indicator diagram

The work delivered per cycle is the area of the closed loop traced on a pressure–volume diagram:

$$W = \oint P\,\mathrm{d}V,$$

positive for a clockwise loop. This is the oldest measurement in engineering thermodynamics and still the most direct.

Your engine is a Stirling machine with sinusoidal piston motion and a regenerator dead volume, so its loop has rounded corners rather than the sharp ones of the two-isotherm, two-isochore idealisation. Comparing the two areas tells you what the idealisation costs.

4.2 Procedure

A. Capture indicator diagrams at three hot-end temperatures. Integrate each loop.

B. At fixed brake setting, sweep the hot-end temperature. Record T_h, T_c, the heater power $\dot{Q}_h$, the rate of heat rejection $\dot{Q}_c$ and the shaft power. Check the energy balance.

C. At fixed reservoir temperatures, sweep the brake from free running to stall in steps of five per cent.

4.3 Analysis

- Integrate the loop with the trapezium rule on the logged points, going once round in order. Check the sign.
- In Part B, plot η and η_C against $1 - T_c/T_h$ on the same axes. Your points must lie below the line of unit gradient; if any lie above, you have a systematic error, not a violation of the second law.
- In Part C, plot shaft power against measured efficiency. The result is a loop: zero power at both ends (free running, where friction consumes everything, and stall, where the engine does not turn) with a maximum between. Read η at the peak of the power.
- Compare that efficiency with both (4.2) and (4.4), at two different pairs of reservoir temperatures, so that agreement cannot be a coincidence.

4.4 Results to report

Work per cycle at $T_h = 600\,\mathrm{K}$, $T_c = 300\,\mathrm{K}$; the Carnot efficiency for those reservoirs; the measured efficiency at maximum power; and the maximum shaft power.

4.5 Questions

1. Show from your data that the efficiency approaches the Carnot value only as the power tends to zero, and explain why that must be so. [8]
2. Derive (4.4) for an endoreversible engine and compare it with your measurements at two pairs of reservoir temperatures. [10]
3. State the Kelvin–Planck and Clausius statements and prove that they are equivalent. [8]
4. Your loop is rounder than the ideal Stirling cycle. Identify the physical reasons and estimate the resulting loss of work. [6]

EXPERIMENT 5

Entropy, irreversibility and increasing entropy

Aims

To measure the Joule coefficient of a real gas in a free expansion; to show that the entropy change is the same for a free expansion and a reversible isothermal expansion between the same end states while the heat exchanged is not; to measure the entropy of mixing; and to show that dissipating work always increases the entropy of the universe.

Syllabus: concept of entropy; measuring entropy and entropy changes; entropy of an ideal gas; the principle of increasing entropy. **Sessions:** 2

5.1 Theory

5.1.1 Entropy

Entropy is defined by $\mathrm{d}S = \delta Q_{\mathrm{rev}}/T$ along a reversible path. Because S is a function of state, the same ΔS applies to any path between the same end states, reversible or not — but Q does not. The whole of this experiment is a working out of that one sentence.

5.1.2 Free expansion

A gas expands into an evacuated vessel. No work is done on the surroundings and no heat crosses the walls, so $\Delta U = 0$: the expansion is at constant internal energy. The temperature change is governed by the Joule coefficient

$$\mu_J \equiv \left(\frac{\partial T}{\partial V_{\mathrm{m}}}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_{V_{\mathrm{m}}} - P\right]. \tag{5.1}$$

For an ideal gas $T(\partial P/\partial T)_V = P$ exactly and $\mu_J = 0$: the temperature does not change. Any observed change is a direct measurement of non-ideality.

With the virial equation (5.1),

$$T\left(\frac{\partial P}{\partial T}\right)_{V_{\mathrm{m}}} - P = \frac{RT^2 B'(T)}{V_{\mathrm{m}}^2}, \qquad \text{so} \qquad \mu_J = -\frac{RT^2 B'(T)}{C_V V_{\mathrm{m}}^2}.$$

$B'(T) > 0$ for every gas over this range, so $\mu_J < 0$ and the gas *cools*. The effect is small — of order 0.2 K for nitrogen expanding from 1 MPa — which is why Joule himself, with a mercury thermometer in a water bath, could not detect it.

5.1.3 Entropy of expansion

For an ideal gas at constant temperature,

$$\Delta S = nR \ln \frac{V_2}{V_1} > 0. \tag{5.2}$$

In the free expansion, nothing else in the universe has changed, so $\Delta S_{\text{universe}} = \Delta S_{\text{gas}} > 0$ and the process is irreversible: running it backwards would decrease the entropy of an isolated system.

Carried out reversibly and isothermally between the same end states, ΔS_{gas} is exactly the same, but now the gas draws $Q = T\Delta S$ from the thermostat, whose entropy falls by precisely that amount. The total change is zero, as it must be for a reversible process.

5.1.4 Entropy of mixing

Two ideal gases at the same T and P, occupying volumes V_A and V_B, are allowed to mix. Each expands into the total volume, so

$$\Delta S_{\text{mix}} = -nR \sum_i x_i \ln x_i, \tag{5.3}$$

which contains no property of either species. It is positive for any mixture and maximal at equimolar composition.

The mixing can be done *reversibly* in a van 't Hoff cell, whose pistons carry membranes permeable to one species only. Then the work recovered is $W = T\Delta S_{\text{mix}}$, and measuring W is a measurement of the entropy.

If the two gases are the same, no such membrane exists, no work can be recovered, and no state has changed: $\Delta S = 0$. The discontinuity between "very nearly the same" and "the same" is Gibbs's paradox, and its resolution — that identical particles are indistinguishable, which appears in statistical mechanics as the $1/N!$ in the partition function — is one of the places where classical thermodynamics points unmistakably beyond itself.

5.1.5 The degradation of work

Falling masses drive a paddle wheel in a calorimeter. The work $W = Nmgh$ appears entirely as heat, raising the temperature from T_1 to T_2, and

$$\Delta S_{\text{universe}} = C \ln \frac{T_2}{T_1} > 0.$$

The reverse — the water cooling spontaneously and lifting the masses — conserves energy perfectly and never happens. Statistically, the ratio of the probabilities of the two directions is $\mathrm{e}^{-\Delta S/k_{\mathrm{B}}}$, and with ΔS of order joules per kelvin the exponent is of order 10^{23}.

5.2 Procedure

A. Free expansion of several gases at several initial pressures. Record the temperature before and immediately after.

B. The same expansion carried out reversibly and isothermally; the heat-flux meter integrates the heat drawn from the thermostat.

C. Reversible mixing at five mole fractions; record the work recovered. Try mixing a gas with itself.

D. The paddle wheel, at several values of $Nmgh$.

5.3 Analysis

- In Part A, plot ΔT against $\Delta(1/V_{\mathrm{m}})$ and take the gradient; a single pair of readings is not a measurement of a coefficient.
- Check that ΔS from Part A and Q/T from Part B agree. They should, to within the precision of the heat-flux meter; that agreement is the experimental content of "S is a function of state".
- In Part C, plot ΔS_{mix} against x_A and compare with (5.3). Note that the cell recovers slightly less than the ideal work: it is not perfectly reversible, and the shortfall is stated on the apparatus.
- In Part D, the paddle wheel loses a few per cent of the work to bearings and to sound. Say so; do not pretend the heat equals $Nmgh$ exactly.

5.4 Results to report

The Joule coefficient of carbon dioxide; the entropy generated in the free expansion; the entropy of mixing of an equimolar mixture; and the entropy generated by the paddle wheel (marked on sign and method).

5.5 Questions

1. Explain why ΔS is identical for the free and the reversible expansion although Q is not. What is ΔS of the surroundings in each case? [8]
2. Discuss Gibbs's paradox and its resolution. [8]
3. Explain why the paddle wheel never runs backwards, and estimate the probability of the reverse fluctuation for your apparatus. [8]

EXPERIMENT 6

Thermodynamic potentials and Clausius–Clapeyron

Aims

To measure the saturation vapour pressure of several liquids; to obtain the enthalpy of vaporisation both from the Clausius–Clapeyron straight line and from the exact Clapeyron equation, and to account for the difference; to test Trouton's rule; to identify an unknown liquid; and to measure the depression of the melting point of ice with pressure.

Syllabus: thermodynamic potentials — internal energy, enthalpy, Helmholtz and Gibbs functions; application of the Gibbs function to phase changes and the Clausius–Clapeyron equation; Helmholtz and Gibbs free energy. **Sessions:** 2

6.1 Theory

6.1.1 The four potentials

Starting from $\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$ and successively Legendre transforming,

$$U \qquad \mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V, \tag{6.1}$$

$$H = U + PV \qquad \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P, \tag{6.2}$$

$$F = U - TS \qquad \mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V, \tag{6.3}$$

$$G = H - TS \qquad \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P. \tag{6.4}$$

Each is the natural function of the variables that appear as differentials on the right. G is the one to use for phase equilibrium, because two phases in contact share a temperature and a pressure.

Equating mixed second derivatives gives the four Maxwell relations; the one from G,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{6.5}$$

reappears in Experiment 11.

6.1.2 The Clapeyron equation

Two phases in equilibrium have equal molar Gibbs functions, $g_1(T,P) = g_2(T,P)$. Move along the coexistence curve: the equality must persist, so $\mathrm{d}g_1 = \mathrm{d}g_2$, that is

$$-s_1\,\mathrm{d}T + v_1\,\mathrm{d}P = -s_2\,\mathrm{d}T + v_2\,\mathrm{d}P.$$

Rearranging, and using $\Delta s = L/T$ for an isothermal phase change,

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T\,(v_2 - v_1)}} \tag{6.6}$$

This is exact. It applies to any first-order phase transition.

6.1.3 The Clausius–Clapeyron approximation

For a liquid in equilibrium with its vapour, two approximations are usually made: $v_l \ll v_g$, and the vapour is ideal so $v_g = RT/P$. Then (6.6) becomes

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{LP}{RT^2} \quad\Longrightarrow\quad \frac{\mathrm{d}(\ln P)}{\mathrm{d}(1/T)} = -\frac{L}{R},$$

so

$$\ln P = -\frac{L}{RT} + \text{constant}. \tag{6.7}$$

A plot of $\ln P$ against $1/T$ is a straight line of gradient $-L/R$.

Three approximations have been made, and all three are detectable:

1. Neglecting v_l raises the deduced L by about 0.1 % at 1 atm. Small, but computable.
2. Treating the vapour as ideal. In this laboratory the apparatus itself uses an ideal vapour, so this one does *not* appear — and the manual says so, because pretending otherwise would be dishonest.
3. Treating L as constant. It is not: L falls with temperature and vanishes at the critical point. The straight-line fit therefore returns an average over your window, and the residuals of the fit will curve. That is the largest of the three effects and the one to look for.

6.1.4 Trouton's rule

At the normal boiling point,

$$\Delta S_{\mathrm{vap}} = \frac{L}{T_b} \approx 88\ \mathrm{J/(mol\,K)}$$

for most liquids. The reason is that the entropy change is dominated by the gain in translational freedom on going from a liquid of roughly fixed molar volume to a gas at 1 atm, and that is much the same for everybody.

The exceptions are informative. Water gives 109 J/(mol K) and ethanol about the same, because hydrogen bonding makes the liquid far more ordered than a normal liquid, so there is more order to lose. Benzene and propanone obey the rule closely.

6.1.5 The melting curve of ice

Water is anomalous: it contracts on melting, so $v_l - v_s < 0$ and (6.6) gives a *negative* $\mathrm{d}P/\mathrm{d}T$. Quantitatively,

$$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{T(v_l - v_s)}{L_f} \approx -7.4 \times 10^{-8}\ \mathrm{K/Pa} = -7.4 \times 10^{-3}\ \mathrm{K/bar}.$$

Ice therefore melts at a lower temperature under pressure — but only just. Question 4 asks you to weigh that against the popular explanation of ice skating.

6.2 Procedure

A. Saturation vapour pressure of at least three named liquids and the unlabelled sample U, twelve or more points each over the recommended window.

B. The temperature at which each liquid boils under a set external pressure, to locate the normal boiling point precisely.

C. The melting temperature of ice at eight or more pressures up to 150 bar.

Recommended windows: water 60 to 100 °C; ethanol 40 to 78 °C; methanol 27 to 64 °C; propanone 20 to 56 °C; benzene 60 to 80 °C. The marking tolerances assume you fit over these ranges.

6.3 Analysis

- Fit $\ln P$ against $1/T$ and take $L = -R \times$ gradient. Remember that plotting $\ln P$ requires the uncertainty $u(P)/P$.
- Then evaluate (6.6) directly at 373.15 K, using $v_g = RT/P$ and v_l from the density of water. Compare the two numbers and account for the difference.
- Look at the residuals of the straight-line fit. Curvature is the signature of a temperature-dependent L; quantify it.
- Identify sample U from its boiling point and its enthalpy of vaporisation together. Either alone is weaker evidence than both.
- For Part C, obtain L_f from the gradient using the accepted densities of ice and water, and compare with your calorimetric value from Experiment 3.

6.4 Results to report

L for water from the straight line and from Clapeyron; the normal boiling point of water; L and the boiling point of sample U; the entropy of vaporisation of benzene; the gradient of the ice melting curve; L_f from Clapeyron; and the molar mass of the liquid you identify sample U to be.

6.5 Questions

1. Derive the Clapeyron equation from the equality of the molar Gibbs functions, then state precisely the approximations that turn it into (6.7). [8]
2. Compare your two values of L for water. Which is larger, by how much, and which approximation is responsible? [6]
3. Trouton's rule holds for benzene and propanone but fails for water and ethanol. Explain, and say what the failure tells you about the liquid state. [6]
4. Derive the magnitude of the melting-point depression from your data and comment critically on the claim that this is why ice skates work. [6]

EXPERIMENT 7

The Maxwell–Boltzmann distribution

Aims

To measure the speed distribution of atoms in an effusive beam; to show that the beam distribution carries an extra factor of v relative to the distribution in the source, and to explain why; to determine an oven temperature from the shape of the distribution alone; and to watch a gas relax to equilibrium and confirm that the H-function decreases.

Syllabus: Maxwell–Boltzmann distribution; Boltzmann statistics and distribution; entropy, probability and disorder — the Boltzmann relation. **Sessions:** 2

7.1 Theory

7.1.1 The distribution

In equilibrium the probability of a molecule having velocity in $\mathrm{d}^3\mathbf{v}$ is proportional to the Boltzmann factor $\mathrm{e}^{-mv^2/2k_\mathrm{B}T}$. Normalising and converting to a distribution of speeds by integrating over the sphere $4\pi v^2\mathrm{d}v$,

$$F(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} v^2\mathrm{e}^{-mv^2/2k_\mathrm{B}T}\,\mathrm{d}v. \tag{7.1}$$

The two factors compete: the exponential falls, the v^2 from the volume of the shell in velocity space rises, and the product peaks at

$$v_\mathrm{mp} = \sqrt{\frac{2k_\mathrm{B}T}{m}} \equiv \alpha, \qquad \bar{v} = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}}, \qquad v_\mathrm{rms} = \sqrt{\frac{3k_\mathrm{B}T}{m}}, \tag{7.2}$$

so that

$$v_\mathrm{mp} : \bar{v} : v_\mathrm{rms} = 1 : \sqrt{4/\pi} : \sqrt{3/2} = 1 : 1.128 : 1.225.$$

Those ratios are universal: they contain neither T nor m, and measuring them is a test of the *shape* of the distribution independent of any calibration.

7.1.2 The beam is not the gas

This is the point of the experiment and the place where most students go wrong.

The flux of molecules through a small hole is proportional to v_z, the component of velocity along the hole. Integrating over the outward hemisphere, the number leaving per unit time with speed near v is proportional to $v\,F(v)$, not to $F(v)$. Physically: fast molecules reach the aperture more often. Hence the beam distribution

$$f_\mathrm{beam}(v)\,\mathrm{d}v = \frac{2}{\alpha^4}\,v^3\mathrm{e}^{-v^2/\alpha^2}\,\mathrm{d}v, \tag{7.3}$$

normalised over $v > 0$. The exponent of v is *three*, not two, and one of the marked results is that exponent, obtained by fitting $v^p \mathrm{e}^{-v^2/\alpha^2}$ with p free.

7.1.3 The rotating drum

A drum of radius R rotates at angular speed ω. An atom enters through a slit in the rim, crosses the diameter in time $2R/v$, and lands on the far wall displaced by

$$s = R\omega\,\frac{2R}{v} = \frac{2R^2\omega}{v} \quad\Longrightarrow\quad v = \frac{2R^2\omega}{s}.$$

Slow atoms land far round the drum, fast atoms land close to the entry point. To convert the deposit density $N(s)$ into a speed distribution you need the Jacobian:

$$f(v) = N(s)\left|\frac{\mathrm{d}s}{\mathrm{d}v}\right| = N(s)\,\frac{2R^2\omega}{v^2} = N(s)\,\frac{s^2}{2R^2\omega}. \tag{7.4}$$

Forgetting the Jacobian is the second commonest error, and it distorts the shape enough to change the fitted exponent by about one.

7.1.4 The velocity selector

Two slotted discs a distance ℓ apart on a common shaft, with their slots offset by ϕ, transmit only those atoms that cross in the time the shaft takes to turn through ϕ:

$$v = \frac{\omega\ell}{\phi} = \frac{2\pi\nu\ell}{\phi}.$$

The transmitted band has $\Delta v/v = \Delta\phi/\phi$, a constant fractional resolution, so the count rate at setting ν is proportional to $f_{\mathrm{beam}}(v)\,v$.

7.1.5 The H-theorem

Boltzmann defined

$$H = \int f \ln f \,\mathrm{d}^3\mathbf{v} \tag{7.5}$$

and proved that for a dilute gas evolving by binary collisions $\mathrm{d}H/\mathrm{d}t \le 0$, with equality only for the Maxwell–Boltzmann distribution. Since $S = -k_{\mathrm{B}} N H + \text{constant}$, this is the microscopic counterpart of the second law, and it connects directly to $S = k_{\mathrm{B}} \ln W$: the equilibrium distribution is the one realised by overwhelmingly the largest number of microstates at fixed energy and particle number.

The proof rests on the *Stosszahlansatz* — the assumption that the two molecules entering a collision are uncorrelated. That assumption is not time-reversal symmetric, which is how an irreversible conclusion can follow from reversible mechanics. Loschmidt's objection, and its resolution, are the subject of question 2.

7.2 Procedure

A. Expose the drum. Convert strip position to speed and counts to probability density, and fit (7.3). Repeat at three oven temperatures and with the unlabelled charge.

B. Step the velocity selector across its range and fit the same distribution to the count rate.

C. Relax a hard-sphere gas from a chosen non-equilibrium state. Inspect the final histogram against (7.1) and the H-function against the number of collisions.

Set the drum speed so that the deposit falls well inside the strip array; the apparatus tells you if it does not. Counts are Poisson distributed, so the uncertainty on a strip carrying N counts is $\sqrt{N}$ — use that as your weight in the fit and say so.

7.3 Analysis

- Fit with α and the exponent p both free. If p comes out near 3 you have the Jacobian right; if it comes out near 5 or near 1 you have applied it the wrong way round.
- Obtain T from $\alpha^2 = 2k_{\mathrm{B}}T/m$ and compare with the thermocouple. Your instrument has a calibration offset, so they will not agree exactly; the fitted value is the better one.
- Confirm $\alpha \propto \sqrt{T}$ over your three temperatures by plotting α^2 against T.
- For the unknown charge, $\alpha^2 \propto T/m$ identifies m once T is known from a species you have already characterised at the same oven setting.
- In Part C, run the same temperature from two different initial conditions and show that the final distributions coincide.

7.4 Results to report

The oven temperature from the shape of the distribution; the exponent p; the relative atomic mass of the unlabelled charge; the most probable speed; $\bar{v}/v_{\mathrm{mp}}$; and v_{rms} for argon at 300 K.

7.5 Questions

1. Derive (7.3) from (7.1) and explain physically why the extra factor of v appears. Quote your measured exponent. [8]
2. State the H-theorem, relate H to the entropy, and explain the apparent conflict with the time-reversibility of the collisions. [10]
3. Two runs from very different initial conditions at the same energy reached the same final distribution. What does this illustrate, and how does it connect to $S = k_{\mathrm{B}} \ln W$? [6]

EXPERIMENT 8

Heat capacity of solids and the third law

Aims

To measure the molar heat capacity of solids from 2 K to 300 K; to obtain the Debye temperature and the Sommerfeld coefficient from a low-temperature plot; to compare the Einstein and Debye models and show where the former fails; and to obtain the standard molar entropy by integration from absolute zero.

Syllabus: Einstein's and Debye's theory of the heat capacity of a solid; statements of the third law; microscopic and Simon formulations; consequences of the third law; quantum states and energy levels; density of quantum states. **Sessions:** 2

8.1 Theory

8.1.1 The classical result and its failure

A solid of N atoms has $3N$ vibrational degrees of freedom. Classically each contributes $k_{\mathrm{B}}T$, giving Dulong and Petit's $C = 3Nk_{\mathrm{B}} = 3R$ per mole, independent of temperature and of material. It is right at high temperature and badly wrong at low, where every measured C falls to zero.

8.1.2 Einstein

Einstein (1907) treated the solid as $3N$ independent quantum oscillators of a single frequency. The mean energy of one oscillator is $\hbar\omega/(\mathrm{e}^{\hbar\omega/k_{\mathrm{B}}T}-1)$, so

$$\frac{C}{3R} = \frac{x^2\mathrm{e}^x}{(\mathrm{e}^x-1)^2}, \qquad x = \frac{\theta_{\mathrm{E}}}{T}, \tag{8.1}$$

which tends to 1 at high temperature — recovering Dulong–Petit, and explaining it — and to $x^2\mathrm{e}^{-x}$ at low temperature. The exponential was a triumph in 1907 and is the model's undoing: real solids obey a cube law.

8.1.3 Debye

The failure is easy to locate. Einstein's solid has no low-frequency modes, but a real solid supports sound waves of arbitrarily low frequency. Debye (1912) replaced the single frequency with the acoustic spectrum, in which the number of modes with ω in $\mathrm{d}\omega$ is

$$g(\omega)\,\mathrm{d}\omega = \frac{3V\omega^2}{2\pi^2 c_s^3}\,\mathrm{d}\omega,$$

cut off at ω_D so that the total is exactly $3N$. Defining $\theta_\mathrm{D} = \hbar\omega_D/k_\mathrm{B}$,

$$C_V = 9R\left(\frac{T}{\theta_\mathrm{D}}\right)^3 \int_0^{\theta_\mathrm{D}/T} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x. \tag{8.2}$$

At high temperature this gives $3R$; at low temperature the upper limit may be taken to infinity, the integral becomes $4\pi^4/15$, and

$$C_V \to \frac{12\pi^4}{5} R\left(\frac{T}{\theta_\mathrm{D}}\right)^3 \equiv \beta T^3, \qquad \beta = \frac{12\pi^4 R}{5\theta_\mathrm{D}^3}. \tag{8.3}$$

8.1.4 The electrons

In a metal the conduction electrons add a term. Only those within about $k_\mathrm{B}T$ of the Fermi energy can be excited — a fraction $\sim T/T_F$ of the total — and each gains about $k_\mathrm{B}T$, so $C_\mathrm{el} \sim Nk_\mathrm{B}(T/T_F)$: linear in T, and small, because $T_F \sim 10^4\,\mathrm{K}$. The Sommerfeld expansion gives

$$C_\mathrm{el} = \gamma T, \qquad \gamma = \frac{\pi^2}{3} k_\mathrm{B}^2 g(E_F).$$

Adding the two, at low temperature

$$\boxed{\frac{C}{T} = \gamma + \beta T^2} \tag{8.4}$$

so a plot of C/T against T^2 gives γ from the intercept and θ_D from the gradient, both at once. This is the single most useful plot in low-temperature solid-state physics.

8.1.5 The third law

Because $C \to 0$ at least as fast as T, the integral

$$S(T) = \int_0^T \frac{C_p}{T'}\,\mathrm{d}T'$$

converges, and entropy has a definite value at $T = 0$.

Nernst. The entropy change of any isothermal reversible process tends to zero as $T \to 0$.

Planck. More strongly: $S \to 0$ for a perfect crystal.

Simon. The statement applies separately to each aspect of the system that is in internal equilibrium — which is why a glass, whose configurational degrees of freedom are frozen, retains a residual entropy.

Consequences you can check: the expansivity $\alpha \to 0$ (through the Grüneisen relation, since $\alpha \propto C_V$); $C_p - C_V \to 0$; and absolute zero is unattainable in a finite number of steps.

8.2 Procedure

A. $C_p(T)$ for several specimens from 2 K to 300 K: at least thirty points, closely spaced below 10 K.

B. Closely spaced points below 4 K for the entropy integration. Use the long-averaging option: it reduces the random error by about a factor of three, and below 4 K you need it.

8.3 Analysis

- Fit (8.4) below about 6 K. Both γ and θ_{D} come from that one fit; note that $\theta_{\mathrm{D}} \propto \beta^{-1/3}$, so its relative uncertainty is one third of β's.
- Silicon has no measurable electronic term. Fit it anyway and report what you get: an intercept consistent with zero is a result.
- Fit both (8.1) and (8.2) to copper over the whole range, and plot the ratio of model to data. Say where the Einstein model departs and by how much.
- For the entropy: integrate your fit analytically from zero to your lowest measured point — $\int(\gamma + \beta T^2)\mathrm{d}T = \gamma T + \beta T^3/3$ — then integrate the data numerically to 298.15 K.

Two honest caveats

Your integrated entropy will differ from the tabulated standard entropy by a few per cent. That is not a mistake in your arithmetic: a single Debye temperature cannot describe the real phonon spectrum over the whole range, and Chapter 5 explains what the specimen model does and does not reproduce. Quantify the discrepancy and account for it — that is question 3.

Lead is a further special case. Its low-temperature γ is strongly enhanced by electron–phonon coupling that has disappeared by room temperature, so its accepted parameters cannot be made mutually consistent, and the model reproduces its room-temperature C_p only to about three per cent. Its low-temperature behaviour, which is what you are asked to measure, is exact.

8.4 Results to report

θ_{D} and γ for copper; θ_{D} for the unlabelled specimen; γ for silicon; the high-temperature limit of the lattice heat capacity; C_p of diamond at 298 K; the standard molar entropy of copper from your integration; and C_V of copper at 298 K.

8.5 Questions

1. Fit both models to your copper data. Show where the Einstein model fails, quantify the failure, and explain its origin. [10]
2. State the third law in the Nernst and Simon forms, explain how your integration tests it, and say what would go wrong if C did not tend to zero. [8]
3. Quantify the discrepancy between your integrated entropy and the tabulated value, and discuss which assumption is responsible. [8]
4. Explain why C_p and C_V differ, derive the expression you used, and state which Maxwell relation it rests on. [6]

EXPERIMENT 9

Blackbody radiation and Bose–Einstein statistics

Aims

To measure the spectrum of a cavity radiator and fit Planck's law, obtaining h and k_{B}; to show where the Rayleigh–Jeans and Wien forms fail; to verify Wien's displacement law and the Stefan–Boltzmann law; and to relate all of these to the Bose–Einstein occupation of photon modes.

Syllabus: Bose–Einstein distribution; density of quantum states; quantum states and energy levels. **Sessions:** 2

9.1 Theory

9.1.1 Counting the modes

Standing electromagnetic waves in a cube of side L have $\mathbf{k} = (\pi/L)(n_x, n_y, n_z)$ with positive integers n_i. Counting the states in $|\mathbf{k}| \to |\mathbf{k}| + \mathrm{d}k$ in the positive octant, doubling for the two polarisations, and using $\omega = ck$ gives the density of modes per unit volume

$$g(\nu)\,\mathrm{d}\nu = \frac{8\pi\nu^2}{c^3}\,\mathrm{d}\nu. \tag{9.1}$$

9.1.2 Occupying them

Photons are bosons, so any number may occupy one mode. Crucially, photon number is *not* conserved: the walls create and destroy them freely. The equilibrium condition is that the free energy be stationary with respect to N as well as E, which forces the chemical potential to vanish:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0.$$

The Bose–Einstein distribution then reduces to the Planck occupation

$$\bar{n}(\nu) = \frac{1}{\mathrm{e}^{h\nu/k_{\mathrm{B}}T} - 1}. \tag{9.2}$$

That $\mu = 0$ is the single feature that makes the photon gas the simplest Bose system there is.

9.1.3 Planck's law

Multiplying (9.1) by (9.2) and by $h\nu$ gives the energy density; converting to the spectral radiance of a blackbody surface, and transforming from frequency to wavelength with the Jacobian

$|\mathrm{d}\nu/\mathrm{d}\lambda| = c/\lambda^2$,

$$L_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5\left(\mathrm{e}^{hc/\lambda k_\mathrm{B}T} - 1\right)}. \tag{9.3}$$

9.1.4 The two classical limits

For $h\nu \ll k_\mathrm{B}T$, expand the exponential: $\mathrm{e}^x - 1 \to x$, and

$$L_\lambda \to \frac{2ck_\mathrm{B}T}{\lambda^4}, \tag{9.4}$$

the Rayleigh–Jeans law. It is what equipartition gives — $k_\mathrm{B}T$ per mode regardless of frequency — and integrating it over all wavelengths diverges: the ultraviolet catastrophe. Quantisation cures it because modes with $h\nu \gg k_\mathrm{B}T$ have exponentially small occupation.

For $h\nu \gg k_\mathrm{B}T$ the -1 is negligible and $L_\lambda \to (2hc^2/\lambda^5)\mathrm{e}^{-hc/\lambda k_\mathrm{B}T}$, Wien's 1896 form. It fits the short-wavelength data and fails at long wavelength.

9.1.5 Wien's displacement law

Setting $\partial L_\lambda/\partial\lambda = 0$ and writing $x = hc/\lambda k_\mathrm{B}T$ gives the transcendental equation $x = 5(1 - \mathrm{e}^{-x})$, whose root is $x_W = 4.965114\ldots$, so

$$\lambda_\mathrm{max}T = \frac{hc}{x_W k_\mathrm{B}} = 2.8978 \times 10^{-3}\,\mathrm{m\,K}. \tag{9.5}$$

9.1.6 The Stefan–Boltzmann law

Integrating (9.3) over all wavelengths and over the hemisphere,

$$M = \sigma T^4, \qquad \sigma = \frac{2\pi^5 k_\mathrm{B}^4}{15h^3c^2} = 5.6704 \times 10^{-8}\,\mathrm{W/(m^2\,K^4)}. \tag{9.6}$$

The integral that produces the $\pi^4/15$ is $\int_0^\infty x^3/(\mathrm{e}^x - 1)\,\mathrm{d}x = 6\zeta(4)$, and the same family of integrals gives the photon number density $n = 16\pi\zeta(3)(k_\mathrm{B}T/hc)^3 \approx 2.03 \times 10^7\,T^3\,1/\mathrm{m}^3$.

9.1.7 What the instrument actually measures

Your monochromator does not sample L_λ at a point. It averages over a triangular slit function of full width $\Delta\lambda$:

$$L_\mathrm{measured}(\lambda_0) = \frac{\int W(\lambda - \lambda_0)L_\lambda(\lambda)\,\mathrm{d}\lambda}{\int W(\lambda - \lambda_0)\,\mathrm{d}\lambda}.$$

Because the Planck curve is asymmetric about its peak — it rises steeply on the short-wavelength side and falls slowly on the long — convolution shifts the apparent maximum towards longer wavelengths, by an amount proportional to $(\Delta\lambda)^2$. Detecting that shift, and dealing with it, is part of the experiment.

9.2 Procedure

A. The spectrum at three cavity temperatures, more finely sampled near the peak. Subtract the dark signal and divide by the responsivity given on the apparatus.

B. Locate the peak at a series of temperatures, with the wide slit and then with the narrow one.

C. Total exitance over the whole temperature range with the pyrometer.

9.3 Analysis

- Fit (9.3) with h and k_{B} free and c and T fixed. The two are strongly correlated — the fit is much better determined in the combinations hc/k_{B} and hc^2 — so quote the correlation, and expect k_{B} to be the less well determined.
- Overlay the Rayleigh–Jeans and Wien forms on your data and mark where each departs by more than your uncertainty.
- For (9.5), use the narrow slit or extrapolate to zero bandwidth. Then deduce h from $\lambda_{\max}T$ given c and k_{B}, and compare with your spectral fit.
- For Part C, fit $\ln M$ against $\ln T$ and report the exponent with its uncertainty before assuming it is 4. Then fix it at 4 and extract σ, correcting for the cavity emissivity.
- Fit the spectrum once more with T free and h, k_{B} fixed at their accepted values. The difference from the indicated temperature is the calibration offset of your cavity thermometer.

9.4 Results to report

h and k_{B} from the spectral fit; the Wien displacement constant; the exponent in the Stefan–Boltzmann law; σ; the calibration offset of your cavity thermometer; and the photon number density at $1\,000\,\mathrm{K}$.

9.5 Questions

1. Derive Planck's law from the Bose–Einstein distribution and the density of modes, and explain why $\mu = 0$ for the photon gas. [10]
2. Show that your data are inconsistent with Rayleigh–Jeans at short wavelength, and explain why the classical result diverges. [8]
3. Explain why the apparent peak shifts with slit width, and say which measurement you used for the displacement constant and why. [6]

EXPERIMENT 10

Fermi–Dirac statistics: thermionic emission

Aims

To measure the characteristic of a vacuum diode and identify the space-charge-limited and saturated regions; to verify the Child–Langmuir law; to obtain the work function of several cathodes from a Richardson plot; and to detect the Schottky lowering of the barrier by the applied field.

Syllabus: the Fermi–Dirac distribution; quantum states and energy levels; density of quantum states. **Sessions:** 2

10.1 Theory

10.1.1 The electron gas

Electrons are fermions, so at most one occupies each state and the mean occupation is

$$f(E) = \frac{1}{\mathrm{e}^{(E-\mu)/k_{\mathrm{B}}T} + 1}. \tag{10.1}$$

At $T = 0$ this is a step: every state below $\mu = E_F$ is full, every state above is empty. At finite T the step is rounded over a width of a few $k_{\mathrm{B}}T$, and since $E_F \sim 5\,\mathrm{eV} \approx k_{\mathrm{B}} \times 60\,000\,\mathrm{K}$, even a filament at $2\,500\,\mathrm{K}$ is strongly degenerate.

Far above the Fermi level, $E - \mu \gg k_{\mathrm{B}}T$, the $+1$ is negligible and

$$f(E) \simeq \mathrm{e}^{-(E-\mu)/k_{\mathrm{B}}T},$$

a Boltzmann tail. Emission samples only that tail, which is why a quantum gas produces a classical-looking exponential.

10.1.2 The Richardson–Dushman law

An electron escapes if the kinetic energy associated with motion normal to the surface exceeds the barrier. Integrating $e v_z f(E)$ over the outward-moving states, with the density of states $2/h^3$ per unit volume of phase space,

$$J = A_{\mathrm{G}} T^2 \mathrm{e}^{-\phi/k_{\mathrm{B}}T}, \qquad A_{\mathrm{G}} = \frac{4\pi m e k_{\mathrm{B}}^2}{h^3} = 1.2017 \times 10^6\,\mathrm{A/(m^2\,K^2)}, \tag{10.2}$$

where ϕ is the work function, the height of the barrier above the Fermi level. The T^2 comes from the two-dimensional integral over the transverse momenta; the exponential from the Boltzmann tail.

Real surfaces emit less than (10.2) predicts, because a fraction of the electrons approaching the barrier are reflected by it quantum-mechanically. The measured prefactor is written $\lambda_R A_\mathrm{G}$ with $\lambda_R < 1$; for clean tungsten it is about 0.5.

Taking logarithms,

$$\ln\!\left(\frac{J}{T^2}\right) = \ln(\lambda_R A_\mathrm{G}) - \frac{\phi}{k_\mathrm{B}} \cdot \frac{1}{T}, \tag{10.3}$$

so a plot of $\ln(J/T^2)$ against $1/T$ — a Richardson plot — gives ϕ from the gradient.

The intercept is very badly conditioned

The intercept of (10.3) is at $1/T = 0$, an enormous extrapolation from data taken between 1 800 K and 2 500 K. A change in the gradient of one per cent moves the intercept by a factor of order $\mathrm{e}^{0.01\phi/k_\mathrm{B}T} \sim \mathrm{e}^{0.25}$. Quote $\lambda_R A_\mathrm{G}$ with an honest — large — uncertainty; the tolerance in the marking schedule reflects this.

10.1.3 Space charge

At low anode voltage the emitted electrons form a cloud in front of the cathode whose own field repels further emission. The current is then limited not by emission but by transport. Solving Poisson's equation with the boundary condition that the field at the cathode vanishes gives the Child–Langmuir law

$$J = \frac{4}{9}\varepsilon_0 \sqrt{\frac{2e}{m}}\,\frac{V^{3/2}}{d^2} = 2.334 \times 10^{-6}\,\mathrm{A/V^{1.5}} \times \frac{V^{3/2}}{d^2}. \tag{10.4}$$

The three-halves power is the signature, and it is independent of temperature.

A Richardson plot taken while the diode is space-charge limited measures nothing about the work function. Establish where saturation begins before you take Part B; the apparatus will warn you when you have not.

10.1.4 The Schottky effect

Even in saturation the current creeps up with anode voltage. The applied field $E = V/d$ adds a term $-eEx$ to the potential seen by an escaping electron, which combined with its image charge lowers the barrier by

$$\Delta\phi = \sqrt{\frac{e^3 E}{4\pi\varepsilon_0}}. \tag{10.5}$$

Hence

$$\ln I = \text{constant} + \frac{1}{k_\mathrm{B}T}\sqrt{\frac{e^3}{4\pi\varepsilon_0 d}}\,\sqrt{V},$$

and a plot of $\ln I$ against $\sqrt{V}$ is a straight line whose intercept gives the zero-field work function.

10.1.5 The filament temperature

There is no thermometer on the filament. Its temperature is deduced from its resistance, using the accepted resistivity of tungsten (tabulated in Appendix A): measure R, form R/R_{293}, and read T off the tabulated ratio. Because $\phi/k_\mathrm{B}T$ is large, a one per cent error in T produces a twenty-five per cent error in the current — so the temperature determination, not the current measurement, sets the precision of this experiment.

10.2 Procedure

A. Sweep the anode voltage from 1 V to 300 V at fixed filament current. Plot $\log I$ against $\log V$ and identify the region of gradient $3/2$ and the onset of saturation.

B. With the anode voltage well into saturation, step the filament current and record R, T and I. At least twelve points.

C. At fixed filament temperature, record the saturation current from 50 V to 300 V and plot $\ln I$ against $\sqrt{V}$.

10.3 Analysis

- Convert current to current density with the emitting area given on the apparatus before comparing prefactors.
- The gradient of the Richardson plot is $-\phi/k_{\mathrm{B}}$; convert to electron-volts and quote the uncertainty from the fit.
- Because the Part B data are taken at a fixed non-zero anode voltage, the ϕ they give is field-lowered. Correct it using your Part C intercept and say how large the correction is.
- Repeat for the other cathodes, and identify the unlabelled one from its work function.

10.4 Results to report

The work function of tungsten and of the unlabelled cathode; the effective Richardson constant of tungsten; the universal constant A_{G} computed from the fundamental constants; the exponent of V in the space-charge region; and the coefficient of $\sqrt{V}$ in the Schottky plot.

10.5 Questions

1. Derive (10.2) from (10.1), stating clearly where the Boltzmann approximation is justified. [10]
2. Explain why the electrons obey Fermi–Dirac statistics inside the metal but a Boltzmann distribution once emitted, and estimate the degeneracy parameter in each region. [8]
3. Compare your work function from the Richardson plot with the zero-field value from the Schottky plot. Which is the true work function, and how large is the correction? [6]

EXPERIMENT 11

Joule–Thomson expansion and the Maxwell relations

Aims

To measure the Joule–Thomson coefficient of several gases; to locate the inversion temperature of nitrogen and show that helium warms on throttling at room temperature; and to test the identity $\mu C_p = T(\partial V/\partial T)_P - V$ and hence the Maxwell relation from which it follows.

Syllabus: Maxwell's relations; application of Maxwell's relations; thermodynamic potentials.
Sessions: 1

11.1 Theory

11.1.1 Throttling is isenthalpic

Gas is forced steadily through a porous plug from P_1 to $P_2 < P_1$. The upstream gas does work P_1V_1 on the parcel; the parcel does P_2V_2 on the gas downstream. The process is adiabatic, so

$$U_2 - U_1 = P_1V_1 - P_2V_2 \quad \Longrightarrow \quad H_1 = H_2.$$

The enthalpy is conserved. Note that the process is nevertheless violently irreversible: it is isenthalpic, not isentropic, and the intermediate states are not equilibrium states at all.

11.1.2 The coefficient, and the Maxwell relation behind it

Take $H = H(T, P)$:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P = C_p\,\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P.$$

For the second coefficient, use $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P$:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V.$$

Now $(\partial S/\partial P)_T$ is not directly measurable — but the Maxwell relation obtained from the Gibbs function, by equating the mixed second derivatives of $G(T, P)$,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{11.1}$$

converts it into something you can measure with a dilatometer. Setting $\mathrm{d}H = 0$,

$$\boxed{\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]} \tag{11.2}$$

This is the whole point of Maxwell's relations, and it is worth stating plainly: they take a derivative involving entropy, which no instrument reads, and replace it by derivatives of P, V and T, which every instrument reads.

For an ideal gas $T(\partial V/\partial T)_P = RT/P = V$ exactly, so $\mu = 0$. Any measured effect is a measurement of departure from ideality.

11.1.3 The sign, and the inversion temperature

With the virial equation $V_\mathrm{m} = RT/P + B(T)$,

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_P = \frac{R}{P} + B'(T),$$

and substituting into (11.2) the ideal parts cancel exactly, leaving

$$\mu\, C_p = T\, B'(T) - B(T). \tag{11.3}$$

Everything follows from the shape of $B(T)$.

At low temperature B is large and negative (attraction dominates) and B' is large and positive, so $\mu > 0$: the gas cools. At high temperature B flattens off at a positive value and $B' \to 0$, so $\mu < 0$: the gas warms. Between them lies the *inversion temperature*,

$$T_\mathrm{inv}: \quad TB'(T) = B(T), \tag{11.4}$$

equivalently the temperature at which B/T is stationary.

Physically: expansion increases the mean separation. Work done against the attractive tail cools the gas; the loss of repulsive potential energy heats it. Which wins depends on how closely the molecules approach, and therefore on temperature.

The consequence is practical. Nitrogen has $T_\mathrm{inv} \approx 620\,\mathrm{K}$, so it cools on throttling at room temperature and can be liquefied by a Linde cycle directly. Helium has $T_\mathrm{inv} \approx 43\,\mathrm{K}$ and hydrogen about 205 K: both *warm* at room temperature and must be pre-cooled below their inversion temperatures before throttling will do anything useful. That is why liquid helium was so long in coming.

11.2 Procedure

A. At fixed inlet temperature and pressure, record ΔT for a series of outlet pressures. Repeat for at least four gases at room temperature.

B. With a small pressure drop — so that μ is measured essentially at the inlet temperature — step the inlet temperature across the whole range and locate the sign change.

C. With the dilatometer, measure $V_\mathrm{m}(T)$ at fixed pressure around 300 K and form $(\partial V/\partial T)_P$ numerically.

11.3 Analysis

- In Part A, plot ΔT against ΔP and take the gradient as $\Delta P \to 0$. A single pair of readings gives an average over the pressure range, not the coefficient.

- In Part B, plot μ against T and find the zero crossing by interpolation, with an uncertainty from the fit.
- In Part C you are subtracting two nearly equal numbers: $T(\partial V/\partial T)_P$ and V differ by less than one per cent of either. The uncertainty of the difference is therefore enormously larger than that of either term, and managing it is the whole difficulty of the comparison. Say so explicitly in your report, with numbers.
- Identify the unlabelled cylinder from the magnitude and sign of its coefficient at two temperatures.

11.4 Results to report

μ for nitrogen, carbon dioxide and helium at 300 K; the inversion temperature of nitrogen; $T(\partial V/\partial T)_P - V$ for nitrogen at 300 K and 1.0 MPa; C_p of nitrogen; and the molar mass of the gas in the unlabelled cylinder.

11.5 Questions

1. Derive (11.2) from $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P$, identifying the Maxwell relation used and the potential it comes from. Show that $\mu = 0$ for an ideal gas. [10]
2. Explain physically why some gases cool and others warm on throttling at room temperature, and why every gas has an inversion temperature. [8]
3. Compare μC_p from Part A with $T(\partial V/\partial T)_P - V$ from Part C. Quantify the agreement and discuss the dominant uncertainty. [8]
4. The process is isenthalpic but irreversible. Compute the entropy generated per mole in one of your runs and explain why the process cannot be reversed by raising the downstream pressure. [6]

Part III

Reference

APPENDIX A

Physical constants and material data

All values used by the laboratory software are those given here. The seven defining constants of the SI are exact; the remainder are the CODATA 2022 recommended values or accepted tabulated data as noted.

A.1 Defining constants of the SI (exact)

Constant	Symbol	Value
Caesium hyperfine frequency	$\Delta\nu_{\mathrm{Cs}}$	$9\,192\,631\,770\,\mathrm{Hz}$
Speed of light in vacuum	c	$299\,792\,458\,\mathrm{m/s}$
Planck constant	h	$6.62607015 \times 10^{-34}\,\mathrm{J\,s}$
Elementary charge	e	$1.602176634 \times 10^{-19}\,\mathrm{C}$
Boltzmann constant	k_{B}	$1.380649 \times 10^{-23}\,\mathrm{J/K}$
Avogadro constant	N_{A}	$6.02214076 \times 10^{23}\,\mathrm{/mol}$
Luminous efficacy	K_{cd}	$683\,\mathrm{lm/W}$

A.2 Derived and measured constants

Constant	Symbol	Value
Molar gas constant	$R = N_{\mathrm{A}} k_{\mathrm{B}}$	$8.314462618\,\mathrm{J/(mol\,K)}$
Stefan–Boltzmann constant	σ	$5.670374419 \times 10^{-8}\,\mathrm{W/(m^2\,K^4)}$
Wien displacement constant	b	$2.897771955 \times 10^{-3}\,\mathrm{m\,K}$
Second radiation constant	$c_2 = hc/k_{\mathrm{B}}$	$1.438776877 \times 10^{-2}\,\mathrm{m\,K}$
Richardson constant	A_{G}	$1.20173 \times 10^{6}\,\mathrm{A/(m^2\,K^2)}$
Child–Langmuir constant		$2.3339 \times 10^{-6}\,\mathrm{A/V^{1.5}}$
Electron mass	m_e	$9.1093837139 \times 10^{-31}\,\mathrm{kg}$
Atomic mass constant	m_u	$1.66053906892 \times 10^{-27}\,\mathrm{kg}$
Vacuum permittivity	ε_0	$8.8541878188 \times 10^{-12}\,\mathrm{F/m}$
Standard gravity (defined)	g_n	$9.80665\,\mathrm{m/s^2}$
Standard atmosphere (defined)		$101\,325\,\mathrm{Pa}$
Ice point (defined)		$273.15\,\mathrm{K}$
Triple point of water		$273.16\,\mathrm{K}$
Apéry constant	$\zeta(3)$	1.2020569032

A.3 Gases

Lennard-Jones parameters are those fitted to second virial coefficients by Hirschfelder, Curtiss and Bird. Characteristic temperatures are $\theta = hc\tilde{\nu}/k_{\mathrm{B}}$ from measured vibrational wavenumbers;

degeneracies in parentheses.

Gas	M / g/mol	σ / Å	ε/k_B / K	θ_rot / K	θ_vib / K
He	4.0026	2.556	10.22	–	–
Ne	20.180	2.749	35.60	–	–
Ar	39.948	3.405	119.8	–	–
H_2	2.0159	2.928	37.00	87.6	6332
N_2	28.013	3.698	95.05	2.88	3374
O_2	31.999	3.580	117.5	2.08	2256
Air	28.965	3.617	97.0	2.7	3200
CO	28.010	3.590	110.0	2.78	3103
CO_2	44.010	4.486	189.0	0.561	960 (2), 1997, 3380
CH_4	16.043	3.817	148.2	7.54	1879 (3), 2207 (2), 4197, 4344 (3)

A.4 Solids

θ_D and γ from Kittel; the remainder from the CRC Handbook.

Solid	M / g/mol	ρ / kg/m^3	c_p / J/(kg K)	θ_D / K	γ / mJ/(mol K^2)	S° / J/(mol K)
Cu	63.546	8960	385	343	0.695	33.15
Al	26.982	2700	897	428	1.35	28.30
Ag	107.868	10490	235	225	0.646	42.55
Au	196.967	19300	129	165	0.729	47.40
Pb	207.2	11340	129	105	2.98	64.80
Fe	55.845	7874	449	470	4.98	27.32
Zn	65.38	7140	388	327	0.64	41.63
W	183.84	19250	132	400	1.3	32.64
Si	28.086	2329	712	645	0	18.81
Diamond	12.011	3515	509	2230	0	2.377
Brass	64.09	8500	380	330	0.68	35.6

A.5 Water and phase-change data

Specific latent heat of fusion of ice at 0 °C	333.55 kJ/kg
Specific latent heat of vaporisation at 100 °C	2 256.4 kJ/kg
Specific heat capacity of water at 25 °C	4 181.6 J/(kg K)
Specific heat capacity of ice at 0 °C	2 093 J/(kg K)
Density of water at 0 °C	999.84 kg/m^3
Density of ice at 0 °C	916.7 kg/m^3
Normal boiling point of water	373.124 K
Critical temperature of water	647.096 K

The specific heat capacity of liquid water is represented by a quartic passing exactly through the IAPWS-95 values at 0, 25, 50, 75 and 100 °C; the density by Kell's equation, which reproduces the maximum at 3.98 °C.

A.6 Liquids

Antoine constants for $\log_{10}(P/\mathrm{bar}) = A - B/(T/\mathrm{K} + C)$. Water uses the Wagner and Pruss equation instead.

Liquid	M / g/mol	T_b / K	L / kJ/mol	A	B	C
Water	18.015	373.124	40.65	Wagner–Pruss		
Ethanol	46.068	351.44	38.56	5.24677	1598.673	−46.424
Methanol	32.042	337.7	35.21	5.20409	1581.341	−33.50
Propanone	58.079	329.2	29.10	4.42448	1312.253	−32.445
Benzene	78.112	353.24	30.72	4.72583	1660.652	−1.461

A.7 Resistivity of tungsten

Used to deduce the filament temperature in Experiment 10. Form the ratio R/R_{293} from your measured resistance and interpolate.

T / K	ρ / $10^{-8}\,\Omega\,\mathrm{m}$	R/R_{293}	T / K	ρ / $10^{-8}\,\Omega\,\mathrm{m}$	R/R_{293}
293	5.28	1.000	1800	52.8	10.00
500	10.3	1.951	2000	60.7	11.50
800	18.6	3.523	2200	69.0	13.07
1000	24.9	4.716	2400	77.7	14.72
1200	31.3	5.928	2600	86.7	16.42
1400	38.0	7.197	2800	96.2	18.22
1600	45.2	8.561	3000	106.0	20.08

A.8 ITS-90 defining fixed points used in Experiment 1

Fixed point	T / K	Fixed point	T / K
Triple point of e-H_2	13.8033	Triple point of water	273.16
Triple point of Ne	24.5561	Melting point of Ga	302.9146
Triple point of O_2	54.3584	Freezing point of In	429.7485
Triple point of Ar	83.8058	Freezing point of Sn	505.078
Triple point of Hg	234.3156	Freezing point of Zn	692.677

Practical baths: boiling nitrogen 77.355 K, subliming carbon dioxide 194.686 K, ice point 273.15 K, steam point 373.124 K, all at 1 atm.

APPENDIX B

Marking schedule

Every numerical result you report is compared with the accepted value for *your* apparatus, which the laboratory computes from your bench key. Two tolerances are applied: a result inside the first earns the full mark for that quantity, a result inside the second earns half, and anything outside earns nothing. A few quantities are judged on their sign alone, because the physics being tested is the sign.

Written answers are not marked by the computer. They are recorded with your submission and assessed by a demonstrator against the marking points, which the laboratory shows you after you submit so that you can check your own work first.

This appendix is generated directly from the laboratory software, so it cannot disagree with the tolerances actually applied.

B.1 Experiment 1: The Zeroth Law and the Ideal-Gas Temperature Scale

Automatically checked: **36** marks. Written answers: **26** marks. Total: **62** marks.

Quantity	Unit	Tolerance	Marks
Kelvin temperature of Unknown bath A	K	0.4 % / 1 %	8
Kelvin temperature of Unknown bath B	K	0.4 % / 1 %	8
Kelvin temperature of Unknown bath C	K	0.4 % / 1 %	8
Absolute zero on the Celsius scale	degC	0.4 % / 2 %	8
Amount of gas in the bulb when filled to 100.0 kPa at the triple point	mmol	2 % / 5 %	4
Total			**36**

Written questions

1. State the zeroth law of thermodynamics and explain precisely which step of this experiment relies on it. [5]
2. Your extrapolated intercepts for different gases agree, but the values at finite filling pressure do not. Explain the physical origin of the difference and why the sign of the discrepancy differs between helium and nitrogen. [6]
3. Why is the ideal-gas temperature defined by an extrapolation rather than by a measurement with a single, very dilute filling? Answer with reference to your uncertainties. [5]
4. The ideal-gas scale is defined operationally, whereas the Kelvin scale is defined from the second law using a Carnot engine. Outline the argument that the two coincide. [6]
5. ITS-90 does not use gas thermometry directly for routine work. What is used instead over the range of your unknown baths, and why? [4]

B.2 Experiment 2: The First Law: Work, Heat and the Ratio of Heat Capacities

Automatically checked: **38** marks. Written answers: **28** marks. Total: **66** marks.

Quantity	Unit	Tolerance	Marks
Dead volume of the apparatus	cm^3	6 % / 15 %	6
Amount of gas confined in the cylinder	mmol	2 % / 5 %	5
gamma for argon	–	2 % / 4 %	6
gamma for nitrogen	–	2 % / 4 %	6
gamma for carbon dioxide	–	2 % / 5 %	6
Molar heat capacity at constant volume of carbon dioxide	$\mathrm{J\ mol^{-1}\ K^{-1}}$	5 % / 12 %	5
Molar heat capacity at constant pressure of nitrogen	$\mathrm{J\ mol^{-1}\ K^{-1}}$	5 % / 12 %	4
Total			**38**

Written questions

1. Plot your Clement-Desormes value of gamma against the tap-open time. Explain the shape of the curve and justify the open time you finally adopted. [8]
2. Argon and nitrogen have gamma close to 5/3 and 7/5 respectively, but carbon dioxide gives about 1.29. Account for all three values quantitatively using equipartition and the vibrational temperatures of the molecules. [8]
3. For your isothermal expansion between the first and last volumes of Part A, compute W, Q and dU. Do the same for the adiabatic compression of Part B. Show explicitly that the first law is satisfied in both cases. [7]
4. Why does Ruchhardt's method systematically underestimate gamma, and how large is the effect in your data? [5]

B.3 Experiment 3: Calorimetry: Heat Capacity, Latent Heat and Entropy Change

Automatically checked: **49** marks. Written answers: **28** marks. Total: **77** marks.

Quantity	Unit	Tolerance	Marks
Specific heat capacity of specimen X	$\mathrm{J\ kg^{-1}\ K^{-1}}$	4 % / 10 %	6
Specific heat capacity of specimen Y	$\mathrm{J\ kg^{-1}\ K^{-1}}$	4 % / 10 %	6
Specific heat capacity of specimen Z	$\mathrm{J\ kg^{-1}\ K^{-1}}$	4 % / 10 %	6
Molar heat capacity of specimen X	$\mathrm{J\ mol^{-1}\ K^{-1}}$	5 % / 12 %	3
Molar heat capacity of specimen Y	$\mathrm{J\ mol^{-1}\ K^{-1}}$	5 % / 12 %	3
Molar heat capacity of specimen Z	$\mathrm{J\ mol^{-1}\ K^{-1}}$	5 % / 12 %	3
Specific latent heat of fusion of ice	$\mathrm{J\ kg^{-1}}$	4 % / 9 %	8
Specific latent heat of vaporisation of water	$\mathrm{J\ kg^{-1}}$	4 % / 9 %	8
Entropy generated in your Part D run with the largest temperature difference	$\mathrm{J\ K^{-1}}$	sign only (positive)	6
Total			**49**

Written questions

1. Explain the cooling correction you applied. Derive it from Newton's law of cooling and state the assumption that makes it valid. [8]
2. Compute the molar heat capacity of each specimen and compare with 3R. Which specimen departs most from the Dulong-Petit value, and why? [6]
3. For your ice experiment, compute the entropy change of the ice, of the water and of the universe. Explain why the last is positive, and estimate how it would change if the ice were added in many small pieces over a long time. [8]
4. Your two determinations of the entropy generated in Part D used different initial temperature differences. Show that for small differences the entropy generated grows as the square of the temperature difference. [6]

B.4 Experiment 4: The Second Law: Heat Engines, the Carnot Cycle and Efficiency

Automatically checked: **27** marks. Written answers: **32** marks. Total: **59** marks.

Quantity	Unit	Tolerance	Marks
Work per cycle from the indicator diagram at T_h = 600 K, T_c = 300 K	J	6 % / 15 %	8
Carnot efficiency for T_h = 600 K and T_c = 300 K	–	1 % / 3 %	3
Measured efficiency at maximum power for T_h = 600 K, T_c = 300 K	–	8 % / 20 %	10
Maximum shaft power at T_h = 600 K and T_c = 300 K	W	8 % / 20 %	6
Total			**27**

Written questions

1. Your measured efficiency never reaches the Carnot value. Show from your data that it approaches it only as the power output tends to zero, and explain why that must be so. [8]
2. Compare your efficiency at maximum power with 1 - sqrt(T_c/T_h) for at least two pairs of reservoir temperatures. Derive that expression for an endoreversible engine. [10]
3. State the Kelvin-Planck and Clausius statements of the second law and prove that they are equivalent. [8]
4. Your indicator loop is noticeably rounder than the ideal Stirling cycle of two isotherms and two isochores. Identify the physical reasons and estimate the resulting loss of work. [6]

B.5 Experiment 5: Entropy, Irreversibility and the Principle of Increasing Entropy

Automatically checked: **30** marks. Written answers: **24** marks. Total: **54** marks.

Quantity	Unit	Tolerance	Marks
Joule coefficient of carbon dioxide at 2.0 MPa and the thermostat temperature	K m^{-3} mol	15 % / 35 %	8
Entropy generated in the free expansion of carbon dioxide from 2.0 MPa	J K^{-1}	5 % / 12 %	8
Entropy of mixing for an equimolar mixture of 0.100 mol in total	J K^{-1}	4 % / 10 %	8
Entropy generated by the paddle wheel in your longest run	J K^{-1}	sign only (positive)	6
Total			**30**

Written questions

1. Explain why the entropy change is identical for the free expansion and the reversible isothermal expansion, although the heat exchanged is not. What is the entropy change of the surroundings in each case? [8]
2. The entropy of mixing does not depend on which gases are mixed, provided they are different, yet it vanishes when they are the same. Discuss this discontinuity (Gibbs's paradox) and its resolution. [8]
3. Your paddle-wheel experiment converts work entirely into heat. Explain in terms of the second law why the reverse never happens, and estimate the probability of the reverse fluctuation for your apparatus. [8]

B.6 Experiment 6: Thermodynamic Potentials, the Gibbs Function and the Clausius-Clapeyron Equation

Automatically checked: **56** marks. Written answers: **26** marks. Total: **82** marks.

Quantity	Unit	Tolerance	Marks
Molar enthalpy of vaporisation of water from ln P against 1/T over 60–100 °C	J mol^{-1}	3 % / 8 %	8
Molar enthalpy of vaporisation of water at 373.15 K from the exact Clapeyron equation	J mol^{-1}	3 % / 8 %	6
Normal boiling point of water from your fit (at 101.325 kPa)	K	0.3 % / 1 %	5
Molar enthalpy of vaporisation of the unlabelled liquid	J mol^{-1}	4 % / 10 %	8
Normal boiling point of the unlabelled liquid	K	0.4 % / 1 %	6
Entropy of vaporisation of benzene at its boiling point	J mol^{-1} K^{-1}	5 % / 12 %	5
Gradient of the ice melting curve, dT/dP	K Pa^{-1}	5 % / 12 %	8
Specific latent heat of fusion of ice from the Clapeyron equation	J kg^{-1}	5 % / 12 %	6

Quantity	Unit	Tolerance	Marks
Molar mass implied by identifying the unlabelled liquid (report the molar mass of your identification)	g mol^{-1}	2 % / 5 %	4
Total			**56**

Written questions

1. Derive the Clapeyron equation from the equality of the molar Gibbs functions of two coexisting phases, and then state precisely the two approximations that turn it into the Clausius-Clapeyron equation. [8]
2. Compare your two values of L for water. Which is larger, by how much, and which of the approximations is responsible? [6]
3. Trouton's rule holds for benzene and propanone but fails badly for water and ethanol. Explain, and say what the failure tells you about the liquid state. [6]
4. Ice melts at a lower temperature under pressure. Derive the magnitude of the effect from your data and comment critically on the common claim that this is why ice skates work. [6]

B.7 Experiment 7: The Maxwell-Boltzmann Distribution of Molecular Speeds

Automatically checked: **40** marks. Written answers: **24** marks. Total: **64** marks.

Quantity	Unit	Tolerance	Marks
Oven temperature obtained from the shape of the beam distribution at a nominal setting of 700 K	K	3 % / 8 %	10
Power of v in the beam distribution, obtained by fitting v^p exp(-v^2/alpha^2)	–	8 % / 20 %	8
Relative atomic mass of the unlabelled charge	–	6 % / 15 %	8
Most probable speed of the unlabelled species in the oven at a nominal 700 K	m/s	4 % / 10 %	5
Ratio of the mean speed to the most probable speed in the gas	–	2 % / 6 %	5
Root-mean-square speed of argon at 300 K	m/s	2 % / 5 %	4
Total			**40**

Written questions

1. Derive the beam distribution from the Maxwell-Boltzmann distribution and explain physically why the extra factor of v appears. Quote the value of the exponent you measured. [8]
2. Your H-function falls monotonically and then flattens. State the H-theorem, relate H to the entropy, and explain the apparent conflict with the time-reversibility of the underlying collisions. [10]
3. Two runs of Part C started from very different initial conditions at the same total energy and reached the same final distribution. What does this illustrate, and how does it connect

to S = k ln W? [6]

B.8 Experiment 8: Heat Capacity of Solids: the Einstein and Debye Theories, and the Third Law

Automatically checked: **52** marks. Written answers: **32** marks. Total: **84** marks.

Quantity	Unit	Tolerance	Marks
Debye temperature of copper	K	3 % / 8 %	8
Sommerfeld coefficient of copper	mJ mol^{-1} K^{-2}	6 % / 15 %	8
Debye temperature of the unlabelled specimen	K	4 % / 10 %	8
Sommerfeld coefficient of silicon	mJ mol^{-1} K^{-2}	±0.03 / ±0.1 mJ mol^{-1} K^{-2}	4
High-temperature limit of the lattice heat capacity	J mol^{-1} K^{-1}	3 % / 8 %	5
Molar heat capacity of diamond at 298.15 K	J mol^{-1} K^{-1}	4 % / 10 %	4
Standard molar entropy of copper from your integration of C/T	J mol^{-1} K^{-1}	5 % / 12 %	10
C_V of copper at 298.15 K, after correcting C_p	J mol^{-1} K^{-1}	3 % / 8 %	5
Total			**52**

Written questions

1. Fit both the Einstein and the Debye models to your copper data over the whole range. Show where the Einstein model fails, quantify the failure, and explain its physical origin. [10]
2. State the third law in both the Nernst and the Simon forms. Explain how your entropy integration tests it, and what would go wrong if C did not tend to zero. [8]
3. Your integrated entropy differs from the tabulated standard entropy. Quantify the discrepancy and discuss which of your assumptions is responsible. [8]
4. Explain why C_p and C_V differ, derive the expression you used to convert between them, and state which Maxwell relation it rests on. [6]

B.9 Experiment 9: Blackbody Radiation and Bose-Einstein Statistics

Automatically checked: **50** marks. Written answers: **24** marks. Total: **74** marks.

Quantity	Unit	Tolerance	Marks
Planck constant from your fit to the spectrum	J s	4 % / 10 %	10
Boltzmann constant from your fit to the spectrum	J K^{-1}	5 % / 12 %	8
Wien displacement constant	m K	3 % / 8 %	8
Exponent in the Stefan-Boltzmann law	–	2 % / 4 %	6
Stefan-Boltzmann constant, corrected for the cavity emissivity	W m^{-2} K^{-4}	4 % / 10 %	8
Calibration offset of the cavity thermometer, from your Planck fits	K	±0.6 / ±1.8 K	5

Quantity	Unit	Tolerance	Marks
Photon number density inside the cavity at 1000 K	$\mathrm{m^{-3}}$	6 % / 15 %	5
Total			**50**

Written questions

1. Derive Planck's law from the Bose-Einstein distribution and the density of electromagnetic modes. Explain why the chemical potential of the photon gas is zero. [10]
2. Show that your data are inconsistent with the Rayleigh-Jeans law at short wavelength, and explain why the classical result diverges. [8]
3. The apparent peak of your spectrum shifts when you change the slit width. Explain, and state which measurement you used for the displacement constant and why. [6]

B.10 Experiment 10: Fermi-Dirac Statistics: Thermionic Emission from a Metal

Automatically checked: **41** marks. Written answers: **24** marks. Total: **65** marks.

Quantity	Unit	Tolerance	Marks
Work function of pure tungsten	eV	4 % / 10 %	10
Work function of the unlabelled cathode	eV	5 % / 12 %	8
Effective Richardson constant of pure tungsten from the intercept	$\mathrm{A\ m^{-2}\ K^{-2}}$	40 % / 80 %	6
The universal Richardson constant 4 pi m e $\mathrm{k^2/h^3}$	$\mathrm{A\ m^{-2}\ K^{-2}}$	0.1 % / 1 %	3
Exponent of V in the space-charge-limited region	–	5 % / 12 %	8
Coefficient of sqrt(V) in the Schottky plot, ln I against sqrt(V_a)	V^-1/2	12 % / 30 %	6
Total			**41**

Written questions

1. Derive the Richardson-Dushman law from the Fermi-Dirac distribution, stating clearly where the approximation exp(-(E-mu)/kT) is justified. [10]
2. Explain why the electrons obey Fermi-Dirac statistics inside the metal but a Boltzmann distribution once emitted. Estimate the degeneracy parameter in each region. [8]
3. Compare your work function from the Richardson plot with the zero-field value obtained by extrapolating the Schottky plot. Which is the true work function, and what is the size of the correction? [6]

B.11 Experiment 11: Joule-Thomson Expansion and the Maxwell Relations

Automatically checked: **50** marks. Written answers: **32** marks. Total: **82** marks.

Quantity	Unit	Tolerance	Marks
Joule-Thomson coefficient of nitrogen at 300 K	K MPa^{-1}	6 % / 15 %	8
Joule-Thomson coefficient of carbon dioxide at 300 K	K MPa^{-1}	6 % / 15 %	6
Joule-Thomson coefficient of helium at 300 K	K MPa^{-1}	12 % / 30 %	6
Inversion temperature of nitrogen	K	5 % / 12 %	10
T (dV/dT)_P - V for nitrogen at 300 K and 1.0 MPa, from your dilatometer data	cm^3 mol^{-1}	10 % / 25 %	10
Molar heat capacity of nitrogen at constant pressure at 300 K	J mol^{-1} K^{-1}	4 % / 10 %	4
Molar mass of the gas in the unlabelled cylinder, from your identification	g mol^{-1}	3 % / 8 %	6
Total			**50**

Written questions

1. Derive the Joule-Thomson coefficient from dH = T dS + V dP, identifying the Maxwell relation used and the potential it comes from. Show that it vanishes for an ideal gas. [10]
2. Explain physically why some gases cool and others warm on throttling at room temperature, and why every gas has an inversion temperature. [8]
3. Compare mu C_p from Part A with T(dV/dT)_P - V from Part C. Quantify the agreement and discuss the dominant source of uncertainty. [8]
4. The Joule-Thomson process is isenthalpic but irreversible. Compute the entropy generated per mole for one of your runs and explain why the process cannot be reversed by simply raising the downstream pressure. [6]