Statistical and Thermal Physics

Second year physics course: A1

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Problem Set 2

(A. T. Boothroyd)

Some useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Avogadro's number	N_A	$6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
Standard molar volume		$22.414 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$
Molar gas constant	R	$8.315\ \mathrm{J\,mol^{-1}\,K^{-1}}$
1 pascal (Pa)		$1\,\mathrm{N\,m^{-2}}$
1 standard atmosphere		$1.0132 \times 10^5\,\mathrm{Pa}\ (\mathrm{N\,m^{-2}})$
1 bar (= 1000 mbar)		$10^5\,\mathrm{N\,m^{-2}}$

PROBLEM SET 2: Basic Thermodynamics

Problem set 2 can be attempted in Week 6 or 7 of Michaelmas Term. There is about one-and-a-half tutorials or classes worth of material. The starred problem is more difficult.

Entropy Changes

2.1 In a free expansion of a perfect gas (also called a Joule expansion), we know U does not change, and no work is done. However, the entropy must increase because the process is irreversible. How are these statements compatible with $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$?

2.2 A mug of tea has been left to cool from 90°C to 18°C. If there is 0.2 kg of tea in the mug, and the tea has specific heat capacity $4200\,\mathrm{J\,K^{-1}\,kg^{-1}}$, show that the entropy of the tea has decreased by $185.7\,\mathrm{J\,K^{-1}}$. How is this result compatible with an increase in entropy of the Universe?

2.3 Calculate the changes in entropy of the Universe as a result of the following processes:

(a) A copper block of mass 400 g and heat capacity $150\,\mathrm{J\,K^{-1}}$ at 100°C is placed in a lake at 10°C;

(b) The same block, now at 10°C, is dropped from a height of 100 m into the lake;

(c) Two similar blocks at 100°C and 10°C are joined together (hint: save time by first realising what the final temperature must be, given that all the heat lost by one block is received by the other, and then re-use previous calculations);

(d) A capacitor of capacitance $1\,\mu$F is connected to a battery of e.m.f. 100 V at 0°C. (NB think carefully about what happens when a capacitor is charged from a battery.);

(e) The capacitor, after being charged to 100 V, is discharged through a resistor at 0°C;

(f) One mole of gas at 0°C is expanded reversibly and isothermally to twice its initial volume;

(g) One mole of gas at 0°C is expanded adiabatically to twice its initial volume;

(h) The same expansion as in (f) is carried out by opening a valve to an evacuated container of equal volume.

2.4 A block of lead of heat capacity $1\,\mathrm{kJ\,K^{-1}}$ is cooled from 200 K to 100 K in two ways:

(a) It is plunged into a large liquid bath at 100 K;

(b) The block is first cooled to 150 K in one bath and then to 100 K in another bath.

Calculate the entropy changes in the system consisting of block plus baths in cooling from 200 K to 100 K in these two cases. Prove that in the limit of an infinite number of intermediate baths the total entropy change is zero.

2.5 Two identical bodies of constant heat capacity C_p at temperatures T_1 and T_2 respectively are used as reservoirs for a heat engine. If the bodies remain at constant pressure, show that the amount of work obtainable is

$$W = C_p\left(T_1 + T_2 - 2T_\mathrm{f}\right),$$

where T_f is the final temperature attained by both bodies. Show that if the most efficient engine is used, then $T_\mathrm{f}^2 = T_1 T_2$. Calculate W for reservoirs containing 1 kg of water initially at 100°C and 0°C, respectively. (Ans: 32.7 kJ.)
(Specific heat capacity of water = 4,200 $\mathrm{J\,K^{-1}\,kg^{-1}}$).

2.6* Three identical bodies are at temperatures 300 K, 300 K and 100 K. If no work or heat is supplied from outside, what is the highest temperature to which any one of these bodies can be raised by the operation of heat engines?[1]
(Ans: 400 K)

Thermodynamic potentials and calculus

2.7 [*This question is just some bookwork practice and should only take a couple of minutes.*]

(a) Using the first law $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ to provide a reminder, write down the definitions of the four thermodynamic potentials U, H, F, G for a simple p-V system (in terms of U, S, T, p, V), and give $\mathrm{d}U$, $\mathrm{d}H$, $\mathrm{d}F$, $\mathrm{d}G$ in terms of T, S, p, V and their derivatives.
(b) Derive all the Maxwell relations.

2.8 (a) Derive the following general relations

$$\begin{array}{lrcl} \text{(i)} & \left(\dfrac{\partial T}{\partial V}\right)_U & = & -\dfrac{1}{C_V}\left[T\left(\dfrac{\partial p}{\partial T}\right)_V - p\right] \\ \text{(ii)} & \left(\dfrac{\partial T}{\partial V}\right)_S & = & -\dfrac{1}{C_V}T\left(\dfrac{\partial p}{\partial T}\right)_V \\ \text{(iii)} & \left(\dfrac{\partial T}{\partial p}\right)_H & = & \dfrac{1}{C_p}\left[T\left(\dfrac{\partial V}{\partial T}\right)_p - V\right] \end{array}$$

In each case the quantity on the left hand side is the appropriate thing to consider for a particular type of expansion. State what type of expansion each refers to.

(b) Using these relations, verify that for an ideal gas $\left(\frac{\partial T}{\partial V}\right)_U = 0$ and $\left(\frac{\partial T}{\partial p}\right)_H = 0$, and that $\left(\frac{\partial T}{\partial V}\right)_S$ leads to the familiar relation $pV^\gamma = \text{constant}$ along an isentrope.

2.9 Use the First Law of Thermodynamics to show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\beta_p} - p$$

where β_p is the coefficient of volume expansivity and the other symbols have their usual meanings.

[1] If you set this problem up correctly you may have to solve a cubic equation. This looks hard to solve but in fact you can deduce one of the roots [hint: what is the highest temperature of the bodies if you do nothing to connect them?]

Thermodynamics of non p–V systems

2.10 For a stretched rubber band, it is observed experimentally that the tension f is proportional to the temperature T if the length L is held constant. Prove that:

(a) the internal energy U is a function of temperature only;

(b) adiabatic stretching of the band results in an increase in temperature;

(c) the band will contract if warmed while kept under constant tension.

[You may assume that $\left(\frac{\partial L}{\partial f}\right)_T > 0$.]

2.11 For a fixed surface area, the surface tension of water varies linearly with temperature from $75 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 5°C to $70 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 35°C. Calculate the surface contributions to the entropy per unit area and the internal energy per unit area at 5°C.
[Ans: $\left(\frac{\partial S}{\partial A}\right)_T = 0.167 \times 10^{-3}\,\mathrm{J\,K^{-1}\,m^{-2}}$, $\left(\frac{\partial U}{\partial A}\right)_T = 121.3 \times 10^{-3}\,\mathrm{J\,m^{-2}}$]

An atomizer produces water droplets of diameter $0.1\,\mu$m. A cloud of droplets at 35° C coalesces to form a single drop of water of mass 1 g. Estimate the temperature of the drop assuming no heat exchange with the surroundings. What is the increase in entropy in this process? (Specific heat capacity of water $c_p = 4,200\,\mathrm{J\,K^{-1}\,kg^{-1}}$.)
[Ans: $\Delta T = 1.73\,\mathrm{K}$, $\Delta S = 13.6 \times 10^{-3}\,\mathrm{J\,K^{-1}}$]

2.12 The magnetization M of a paramagnetic material is given by $M = \chi B/\mu_0$, where B is the magnetic flux density and the susceptibility χ follows Curie's law $\chi = C/T$ with C a constant.

If the heat capacity per unit volume at constant M is $c_M = a/T^2$, show that the heat capacity per unit volume at constant B is

$$c_B = \frac{a}{T^2}\left(1 + \frac{B^2 C}{\mu_0 a}\right).$$

If a sample is initially at temperature T_1 in an applied field of flux density B_1, show that the temperature after adiabatic reduction of the field to zero is

$$T_2 = \frac{T_1}{\left(1 + \frac{B_1^2 C}{\mu_0 a}\right)^{1/2}}.$$