

# Thermal physics — Extended example problems

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This document contains a selection of problems and their solutions that have been assigned in Phys 358, Thermal Physics, at the University of Waterloo. They correspond to the subject matter of Chapters 1 to 5 in Schroeder's *Introduction to Thermal Physics* (SITP).

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## 1 Introduction

It may be helpful to know that these problems were created for remote “open-book” tests given to students of Phys 358, Thermal Physics, at the University of Waterloo during the pandemic. During these tests students had access to textbooks, notes, etc... (but were not permitted to work together, except through public discussion on <https://piazza.com>). They typically had a few days to complete one or two of these problems (depending on their difficulty). I had the intention of making the questions a bit more open-ended than normal textbook questions, making use of the positive effects of the remote situation. For example, solving some of the problems requires writing a short computer program.

As such, these problems should be viewed as “food for thought”, not exercises to solve while preparing for in-person tests — primarily because of the time involved in solving (some) of them. Of course, if you *do* have the time, I think that they are worthwhile solving — I learned a lot by formulating them, answering students clarifying questions (sometimes giving small hints), and writing out full solutions.

For convenience, the “Questions” section contains links to the answers after each question, and the “Answers” section contains links to the question statement prior to the answer.

## 2 Question concepts

The following is a list of question titles (clickable links) followed by the corresponding course concepts:

- [Snowy mountain friend](#): multivariable calculus, triple product rule
- [Breaking rails](#): triple product rule, thermal expansion

- Kitchener coordinates: multivariable calculus
- Bursting balloons: buoyancy, ideal gas law
- Floating cities on Venus: buoyancy, ideal gas law
- Dancin' raisins: buoyancy
- Rally for Rayleigh: buoyancy, ideal gas law
- Nothing is perfect: ideal gas law, virial expansion
- Method of mixtures: heat capacities
- Jake braking the big rigs: adiabatic compression/expansion
- Compressed air energy storage: adiabatic compression/expansion
- Trangia trouble: combustion, enthalpy
- Shocking Schottky: entropy, temperature, two-state systems, data analysis
- Heat switch: heat conduction
- Kelvin was a flat earther: heat conduction, mathematical methods
- Sackur and Tetrode are gone: Sackur-Tetrode equation, Third law, data analysis, numerical methods
- Heist of the century or lame waste of time?: second law of thermodynamics, heat engines
- Demag and chill: two state systems, refrigeration, numerical methods
- Supercharging the dinosaur: internal combustion engines
- Cool under pressure: refrigeration, Stirling cycle
- An unpleasant subject?: Helmholtz free energy, Sackur-Tetrode equation
- Pockets for atoms: Helmholtz free energy, Sackur-Tetrode equation, surface physics
- Falling apart: Helmholtz free energy, Sackur-Tetrode equation

## 3 Questions

### 3.1 Snowy mountain friend

- (a) Suppose that you are on the south face of a mountain in a snow blizzard that limits your visibility. You must get to your friend who is on the east side of the mountain, and want to do so — if possible — without changing your elevation, hoping that this will be less tiring. The problem is that you don't know which direction to initially travel in so that your elevation remains constant. However, you have a compass to measure directions and a highly accurate

altimeter to measure changes in elevation. You make some measurements before setting out: You walk directly north for 100 steps and your elevation increases by  $\approx 10$  m. You return to your initial spot, and then travel directly to the east for 100 steps and find your elevation increases by  $\approx 6$  m. Again you return to your initial spot.

Based on these measurements, in what direction should you *initially* head to get to your friend, while keeping your elevation constant? Give your answer in degrees, as measured clockwise from north. (You may make any reasonable approximations.)

- (b) Now we will consider the generalization of your results from part (a), in a form that will be used frequently in this course. Call the elevation:  $h$ , distance north:  $y$ , and distance east:  $x$ . Your two measurements give estimates of  $(\partial h / \partial y)_x$  (the rate of change of elevation when travelling north  $y$ , while not changing your position to the east  $x$ ), and  $(\partial h / \partial x)_y$  (defined analogously). In the first part of this question you were asked to determine  $\theta$  such that  $\tan \theta = (\partial x / \partial y)_h$ ; i.e., how may both  $x$  and  $y$  be changed simultaneously while maintaining constant elevation?

Using the same argument that you used for part (a), write an expression for  $(\partial x / \partial y)_h$  in terms of  $(\partial h / \partial y)_x$  and  $(\partial h / \partial x)_y$ , and check that your answer to (a) is consistent with this expression.

[Answer.](#)

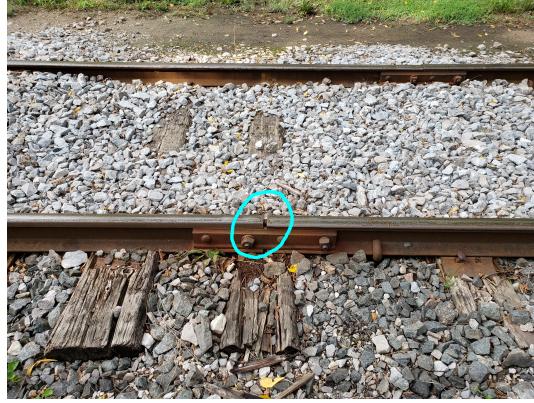
## 3.2 Breaking rails

Thermal expansion is dramatically illustrated by the formation of “sun-kinks”:



(From Transportation Safety Board of Canada, Railway Investigation Report R06T0153.)

In the past, small gaps were left between segments of rail to allow for thermal expansion. For example, on the older “[Spur line](#)” in KW:



But now rail is typically “continuously” welded; i.e., segments are welded together for improved reliability and lower maintenance. For example, if you look at the [LRT track next to UW](#), you will have a hard time finding any gaps in the rails. However, a disadvantage of continuous rail is that when the temperature goes up, the rail has “nowhere to go” but sideways; it may *buckle*. (The first picture above was taken during an investigation into a derailment in Oakville, Ontario.)

To help avoid buckling (“sun-kinks”), rail is typically welded together at a relatively high temperature ( $\approx 38^\circ\text{C}$ ), so that at typical outdoor temperatures, the rail is under *tension*, and when the rail is hotter, the *compressive* force is reduced and thus the potential for buckling. However, the opposite problem must also be considered: when it is cold, the rail can be put under too much tension and break:

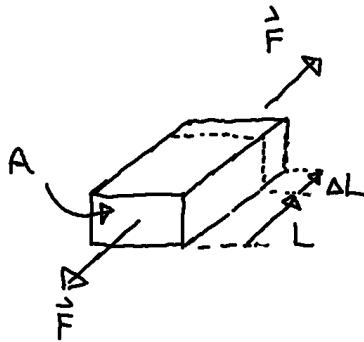


(From <https://www.networkrail.co.uk/stories/broken-rail-explained/>.)

It is possible to estimate the maximum tensile stress that continuously welded rail will experience, using two material properties of rail steel:

- (1) its Young’s modulus  $E \approx 200 \text{ GPa}$ , and
- (2) its coefficient of linear thermal expansion  $\alpha \approx 1.2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ .

The Young’s modulus  $E$  tells you the “springiness” of a material. Consider a length of a material of cross-sectional area  $A$ , put under tensile stress, at a constant temperature:



Its fractional elongation will be given by:

$$\frac{\Delta L}{L} \approx \frac{1}{E} \frac{F}{A}, \quad (1)$$

where  $F/A$  is the **stress**; i.e., force per unit area.

The coefficient of linear thermal expansion tells you how an object's dimensions will change with temperature, under constant stress:

$$\frac{\Delta L}{L} \approx \alpha \Delta T, \quad (2)$$

which is quite similar to the *volumetric* thermal expansion coefficient that is relevant to liquid-in-glass thermometers.

- (a) Estimate the maximum tensile stress (in Pa) that you could expect a steel rail to experience, on the coldest days in Canada, if it had been welded together at 38 °C.
- (b) Compare your estimate of the maximum tensile stress to typical ultimate tensile strengths of steel. Comment. (A few sentences will be fine.)

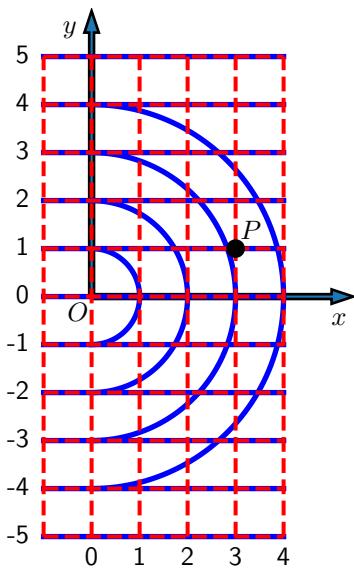
[Answer.](#)

### 3.3 Kitchener coordinates

Suppose that we are interested in the elevation over a geographical region (say Kitchener-Waterloo). We might use normal cartesian coordinates, so that the elevation may be written as  $h(x, y)$ , where  $x$  is the distance east of a reference point  $O$  (say Kitchener city hall), and  $y$  is the distance north of  $O$ .

Now let us consider a second way to describe the same elevations as a function of position. Assume that we are only interested in  $x > 0$ , and instead of using the  $x, y$  coordinates, we use  $r$  and  $y$ , where  $r$  is the radial distance from  $O$  ( $r := \sqrt{x^2 + y^2}$ ), and the meaning of  $y$  is the same as in the cartesian system.

As an example, here is the  $xy$  system (red-dashed) and the  $ry$  system (blue-solid) covering the same geographical area:



As example, consider point  $P$  in the diagram to the left. In the  $x, y$  system  $x = 3$  and  $y = 1$ . In the  $r, y$  system  $r = \sqrt{10} \approx 3.16$  and  $y = 1$ . Either of the two coordinate systems may be used to refer to the same location.

- (a) Suppose that we know  $(\partial h / \partial x)_y$  and  $(\partial h / \partial y)_x$  at a specific location. What is  $(\partial h / \partial y)_r$  in terms of  $r$ ,  $y$ ,  $(\partial h / \partial x)_y$ , and  $(\partial h / \partial y)_x$  at this point? (Since you will check your result in the next part, do not consult the solutions yet.)
- (b) Check your expression using a special case:

$$h(x, y) = h_0 e^{-\alpha x^2 - \beta y^2},$$

where  $h_0$ ,  $\alpha$ , and  $\beta$  are positive constants. Specifically:

- (i) Compute  $(\partial h / \partial y)_r$  using the expression you have found in part (a) i.e. get  $(\partial h / \partial x)_y$  and  $(\partial h / \partial y)_x$  from  $h(x, y)$  as given. Then express your final answer in terms of  $r$  and  $y$  (i.e. remove all explicit references to  $x$ ).
- (ii) Rewrite  $h(x, y)$  as a function of  $r$  and  $y$ , and then compute  $(\partial h / \partial y)_r$  directly, checking that it gives the same result that you found in (i).

Obviously this is only a sanity check — if you don't get agreement then your expression for part (a) is wrong.

- (c) Instead of considering elevation as a function of location, we might consider the properties of a material as a function of its volume  $V$  and temperature  $T$ , or perhaps instead its pressure  $P$  and temperature  $T$  (two different “coordinate systems”, either of which may be used to describe the “state” of the material, in the same sense that either  $x, y$  or  $r, y$  may describe location). Consider for example the energy  $U$  of the material. Suppose that we know  $(\partial U / \partial T)_V$  and  $(\partial U / \partial V)_T$ . Write an expression for  $(\partial U / \partial T)_P$  in terms of  $(\partial U / \partial T)_V$ ,  $(\partial U / \partial V)_T$ , and partial derivatives that may be computed provided that we know the **equation of state** of the material (the relationship between  $T$ ,  $P$  and  $V$  for a fixed amount of the material e.g.  $PV = NkT$  for an ideal gas).
- (d) Under what conditions do you expect  $(\partial U / \partial T)_V = (\partial U / \partial T)_P$ ? (Consider from both a mathematical and physical point of view.)
- (e) Using  $(\partial U / \partial T)_V$ ,  $(\partial U / \partial V)_T$ ,  $(\partial V / \partial P)_T$ , and  $(\partial P / \partial T)_V$ , write an expression for  $(\partial U / \partial T)_P$ .

[Answer.](#)

### 3.4 Bursting balloons

Consider a sealed balloon filled with hydrogen gas. The hydrogen is at the same temperature and pressure as the surrounding atmosphere (300 K and  $1 \times 10^5$  Pa). (Actually the hydrogen is at a slightly higher pressure  $\approx 0.1\%$  than the surrounding atmosphere due to the elasticity of the balloon material — but you can ignore this.) The total volume of the balloon is  $8 \text{ m}^3$ .

- (a) Estimate the maximum payload (in kg) that the balloon can lift. (The term **payload** refers to the *useful* mass — cameras, instruments, etc... — that can be lifted, and thus does not include the mass of the hydrogen.)
- (b) Such a balloon is released from the earth's surface and ascends. Why will the balloon grow in volume as it ascends and then eventually burst?

[Answer.](#)

### 3.5 Floating cities on Venus

On the wikipedia page: [Colonization of Venus](#), we find the statement:

Landis has proposed aerostat habitats followed by floating cities, based on the concept that breathable air (21:79 oxygen/nitrogen mixture) is a lifting gas in the dense carbon dioxide atmosphere, with over 60% of the lifting power that helium has on Earth.

- (a) Verify (or refute) the preceding quoted statement.
- (b) Let us consider the modest goal of a floating “hotel”, with a few occupants, like the International Space Station. A total payload mass (occupants, supplies, life support etc...) would be about  $10^5$  kg. Assume — for the comfort of its human occupants — that the air within the interior is at  $\approx 1 \text{ bar}$  and  $\approx 300 \text{ K}$ .
  - (i) *Estimate* what the volume of the station should be so as to float in the atmosphere of Venus, with a surrounding atmospheric pressure of  $\approx 1 \text{ bar}$ .
  - (ii) Compare your volume estimate to some other volumes, in a “useful” way. (There are many possible answers to this question, some more useful than others. e.g., I'm not so interested in the number of jelly beans that will be able to fit inside the hotel.)

All of the data that you need for this problem can be found on the wikipedia pages for: [Venus](#) and [the atmosphere of Venus](#).

(For the purposes of this question, I have linked to specific “revisions” of the wikipedia pages. The regular pages will (hopefully) be updated in the future.) [Answer.](#)

### 3.6 Dancin' raisins

We may *all* be a bit too old for this: <https://youtu.be/-1JIzf0-gF4>, but I found it fun!

The CO<sub>2</sub> that is dissolved in the ginger ale attaches — in the form of bubbles — to the side of the raisins, acting like a life preserver. But alas, their sugary fate is sealed, as the CO<sub>2</sub> escapes to air once the raisins reach the surface.

- (a) Estimate the total amount of CO<sub>2</sub> within the bubbles (in kg), that must be attached to the side of a raisin, for it to begin to float to the surface. (Some relevant numbers are given in the video description.)
- (b) Make (and describe) some checks on the reasonableness of your answer to the previous part.
- (c) Would you expect this demonstration to be better with smaller or larger raisins?
- (d) When I bought the ginger ale for this demonstration, I had the choice of “regular” or “diet” ginger ale. For better dancing raisins (and not necessarily my health), which should I have chosen, or does it matter?

Answer.

### 3.7 Rally for Rayleigh

Unless otherwise stated take  $P = 1 \text{ bar}$  and  $T = 300 \text{ K}$  as the “ambient” conditions of the surroundings in what follows. Assume that the ideal gas law may be used where relevant.

- (a) It is easy to forget about the buoyant force in situations where it is normally insignificant.

Estimate the buoyant force on an average human in air at the earth’s surface. Express as a fraction of the force of gravity on the same average human. (From your estimate it should be obvious why it would be ridiculous — although in principle necessary — to make a “buoyancy correction” when weighing yourself.)

- (b) Lord Rayleigh did extensive experiments involving the weighing of gases, ultimately leading to his discovery (with Ramsay) of argon.

A highly simplified description of his experiments is as follows:<sup>1</sup>

He had a hollow glass “globe”<sup>2,3</sup> with a valve that could be opened to let gas in and then closed to allow a weighing of the globe and its contents.

He would fill the globe with a specific gas at a well-defined pressure and temperature and then weigh the globe and its contents.

Then he would use a vacuum pump to remove all of the gas from the globe, eventually closing the valve to leave just “vacuum” inside. The empty globe would then be weighed.

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<sup>1</sup>I am simplifying some of the details of Rayleigh’s experiments.

<sup>2</sup>Nowadays we would probably refer to Rayleigh’s “globes” as “hollow spheres”.

<sup>3</sup>If you do not have access to youtube see the Microsoft stream [excerpt](#).

By taking the difference between the filled and empty globe weighings, the mass of the gas could be estimated (using the acceleration due to gravity  $g$ ). Through this differencing the mass of the globe itself cancels.

Of interest when Rayleigh began his gas weighing studies was the ratio of the mass of an oxygen atom to the mass of a hydrogen atom; i.e., he was interested in whether or not the ratio was *precisely* 16. By weighing both oxygen and hydrogen gases he could test this.

Show that if the masses of both the hydrogen and oxygen gases can be measured (separately, but using the same globe), and we know the temperature and pressure that the gases were at in the globe, we may experimentally determine the oxygen/hydrogen atomic mass ratio.

- (c) Should the ratio be precisely 16?
- (d) We might worry — and should (!) — about the effect of buoyancy on our measurements.

Compute the ratio between the buoyant force on the globe and the force of gravity on the hydrogen gas inside (the hydrogen case is more problematic than oxygen). You may assume that the hydrogen gas inside is at  $P = 1$  bar and  $T = 300$  K and that the walls of the globe are thin enough so that the volume inside is roughly the same as the volume of surrounding air that the entire globe displaces. (You may make this equal volume assumption for the rest of this test.)

- (e) Explain why — if ambient conditions remain constant — differencing the measured weights of the globe when it is filled and empty removes the effect of buoyancy, allowing the difference to be converted to the mass of the hydrogen (or oxygen) gas (using  $g$ ).
- (f) Atmospheric pressure is not constant but varies with the weather (e.g., a “high-pressure system”). What are the magnitude of typical fluctuations in atmospheric pressure? I am just looking for a ball-park number. Don’t forget to cite your sources.
- (g) Atmospheric pressure variations may spoil the cancellation of buoyancy obtained by differencing the two measured weights (i.e., part (e)). In Rayleigh’s experiments it took on the order of a day between the weighings of the filled and empty globe, during which time the atmospheric pressure could change. (Filling the globe with gas and evacuating it were not as easy as today).

Estimate the fractional uncertainty ( $\delta m/m$ ) in estimating the mass of the hydrogen gas  $m$  due to atmospheric pressure fluctuations (ignore temperature fluctuations). Would this uncertainty cause significant problems in observing that the ratio of the mass of oxygen atoms to the mass of hydrogen atoms was not precisely 16?

- (h) A solution to the problem of atmospheric variation is to use a second sealed globe (call it the “secondary globe”) that displaces the same volume of the atmosphere as the first “primary” globe (their masses do not have to be equal). For each of the two weighings of the primary globe (filled and under vacuum) to determine the mass of a given gas, we now measure the difference between its weight and that of the secondary globe (which remains unaltered) at the same time. (Using a [balance](#).)

Show that this procedure eliminates the influence of changing ambient air temperature and pressure, provided the secondary globe occupies the same amount of volume as the first. In this way the mass of the oxygen and hydrogen gases can be reliably determined.

- (i) After several *years* perfecting<sup>4</sup> his ability to make these mass measurements for hydrogen and

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<sup>4</sup>An interesting effect that Rayleigh recognized was the reduction in the volume of his primary globe when it was under vacuum as compared to when it was filled, due to compression by the pressure of the surrounding atmosphere. This effect requires additional corrections, but we will not consider them here.

oxygen (showing that the  $m_O/m_H \neq 16$ ) Rayleigh turned his attention to nitrogen gas. He compared the mass of “nitrogen gas” obtained two different ways: 1) from a chemical reaction in which he was fairly confident he was making pure nitrogen, and 2) from air after removing all of its oxygen. Explain why the average molar masses measured for these two samples of “nitrogen” would not be the same (be quantitative) and thereby what Rayleigh was able to conclude.

[Answer.](#)

### 3.8 Nothing is perfect

In “Rallying Rayleigh” you were allowed to use the ideal gas law to reason out how Rayleigh was able to experimentally determine  $m_{\text{single atom of O}}/m_{\text{single atom of H}} (=: r)$ .

Rayleigh’s weighings were done with the gases in the globe at  $P \approx 1 \text{ bar}$  and  $T \approx 285 \text{ K}$ . The relevant second virial coefficients at  $T = 285 \text{ K}$  are<sup>5</sup>

species	$B \text{ (m}^3/\text{mol)}$
$\text{O}_2$	$-1.91 \times 10^{-5}$
$\text{H}_2$	$1.40 \times 10^{-5}$

- (a) Estimate  $r_{\text{actual}}/r_{\text{assuming ideal}}$ ; i.e., the factor by which we should correct our answer to (b) from the previous test:

$$r_{\text{assuming ideal}} := \frac{T_{\text{O}_2}}{T_{\text{H}_2}} \frac{P_{\text{H}_2}}{P_{\text{O}_2}} \frac{m_{\text{O}_2}}{m_{\text{H}_2}} \quad (3)$$

to obtain the actual ratio of the atomic masses. You may assume that<sup>6</sup>  $T_{\text{O}_2} = T_{\text{H}_2} = 285 \text{ K}$  and  $P_{\text{O}_2} = P_{\text{H}_2} = 1 \text{ bar}$ , so that  $r_{\text{assuming ideal}} = m_{\text{O}_2}/m_{\text{H}_2}$ .

(You are encouraged — but are not required — to make use of approximations based on the fact that corrections to the ideal gas law are small.)

- (b) Was it important to account for the non-ideal gas behaviour in Rayleigh’s experiment?

[Answer.](#)

### 3.9 Method of mixtures

In the notes I describe a problem with naive calibration of the scale of liquid-in-glass thermometers: thermometers constructed using different liquids do not give consistent measurements when calibrated using the two fixed points of water ( $0^\circ\text{C}$  and  $100^\circ\text{C}$ ) and linear interpolation.

At one time it was thought that the **method of mixtures** offered a solution to thermometer calibration. The idea is the following: take equal masses of water at  $0^\circ\text{C}$  and  $100^\circ\text{C}$  and mix them

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<sup>5</sup>References will be supplied in the solutions.

<sup>6</sup>In practice the temperatures and pressures were not exactly the same, but making this assumption does not change the main point here.

to give water of “50 °C”; then use this mixture to mark 50 °C on the scale of the thermometer. The general idea is that by mixing different, non-equal, amounts of 0 °C and 100 °C water, water of *any* intermediate temperature can be obtained, and used to add an accurate scale to the thermometer.

The problem with this method is that it assumes a temperature-independent heat capacity of water — a good, but not perfect, assumption.

I want you to estimate the error in calibration by method of mixtures. You will use modern values of the enthalpy of liquid water between 0 °C and 100 °C to estimate the error (i.e., enthalpy as a function of “real temperature”).

More specifically, suppose that someone used the method of mixtures to make water at what they *thought* was 75 °C. What would the real temperature of this water be (based on modern tabulated enthalpy values)?

(You can find a \*.csv table of enthalpies and the Python program that I used to generate the table [here](#). You just need the table, but feel free to flex your Python muscles and write a short program to solve the problem using my `liquid_water_enthalpy` function.). [Answer](#).

### 3.10 Jake braking the big rigs

Trucks often make a distinctive loud noise when they are slowing down (e.g., <https://youtu.be/wRYMZmpkS5g?t=72>). The type of brakes that make this noise are known as **compression release engine brakes**, or more colloquially as “Jake brakes”. They are so loud that you often see road signs prohibiting their use near residential neighbourhoods.

Problem 1.37 of SITP (done as an example in the notes) asks for an estimate of the temperature increase that air (initially at room temperature) undergoes when compressed in volume by a factor of 20 (the **compression ratio**). In a Diesel engine, fuel is injected into this high temperature air, combustion occurs, increasing the temperature further, pushing the piston head back outwards, and doing more work in this expansion than was required for the compression (a net gain). There is a useful animation at the wikipedia page for [the four stroke engine](#). (The animation is actually illustrating a four-stroke *gasoline* engine, in which a mixture of fuel and air is compressed, and a spark plug causes ignition. In a Diesel engine, air is compressed, without fuel, and then fuel is squirted in at maximum compression, spontaneously igniting because of the high temperature.) We will discuss the thermodynamics of both regular gasoline engines and Diesels in Part III of the course.

The Jake braking mode of a Diesel engine allows the pistons to compress air, but acts like a brake by 1) not squirting any fuel into the cylinder, and 2) *releasing* the air at maximum compression by opening the exhaust valve (this valve would normally only open in the fourth stroke when the spent combustion products are forced out of the cylinder).

Suppose that we have a Diesel truck engine with a compression ratio of 18, an engine size of 15 litres, and with a *maximum* engine RPM of 2000 (rotations per minute).

- (a) If this engine is used for Jake braking, *estimate* the maximum deceleration (in m/s<sup>2</sup>) that may be obtained for a 30,000 kg truck travelling at 50 km/hr. Make sure to list all of your assumptions, and illustrate your solution using an indicator diagram.

- (b) Decide whether or not your estimate in (a) is reasonable by comparison to other accelerations/decelerations.

[Answer.](#)

### 3.11 Compressed air energy storage

One challenge with wind and solar energy sources, is their variation in availability (e.g., solar never works at night). For this reason it is helpful to have a means of storing energy, allowing it to be used later, when needed. One method, so-called [pumped storage hydroelectricity](#), pumps water uphill into a reservoir, and later when power is required, this water is used to drive a hydroelectric generator. But this approach is only suitable in locations with both water availability and large changes in elevation.

[Compressed air energy storage](#) (CAES) is another solution for locations with certain geologies. For example, salt mining caverns in [Goderich, On](#) are used to store compressed air in a prototype CAES installation (see <https://www.hydrostor.ca/>).

CAES systems are fairly complex, but the principles involved in their operation are an excellent illustration of some material in this module.

The basic idea of CAES is to use electrical power to compress air when that power is available (e.g., during the day for solar). Then later in time, when the power is required, use that compressed air to drive an electrical generator. That this should be possible, at least in principle, will be obvious to anyone who has inflated a bicycle tire.

Some questions immediately come to mind: how much energy can be stored this way, and how efficient is the storage and recovery process? i.e., how much of the energy that we put in do we get out?

Naively, you might expect to get all of the energy out that you put in. In expansion you would just retrace your compression path along an indicator diagram, but in the reverse direction. The problem is that in general, for *power* reasons, the compression and expansion steps are adiabatic. That's a problem because adiabatic compression leads to heating of the air. The stored compressed air will eventually reach the temperature of its container, so that when expanded back out again to atmospheric pressure, it will not return the same amount of energy that was used in compression.

Let's take a first-look at this problem, with numbers that are *not* typical of CAES systems, but give us an appreciation for some of the issues. Use 1 bar and 300 K for the available air and surroundings — so-called **ambient conditions**.

- (a) Suppose that at the end of the compression step, we do not wish the air temperature to exceed 100 °C. What is the maximum pressure that we may compress air to in the initial adiabatic quasi-static step? (Assume this is the pressure attained after the adiabatic compression step in all that follows.)
- (b) Draw an indicator diagram for a parcel of air (fixed amount) involved in a storage cycle consisting of adiabatic compression, followed by an isochoric process to return to the ambient

temperature (within the storage container), followed by adiabatic expansion (power generation) to ambient pressure, and then isobaric heating to the ambient temperature. All steps are quasi-static. (The diagram does need to be quantitative, but should include informative labels.)

- (c) What is the lowest temperature that the air will attain in this cycle (in °C)? Indicate any possible practical problems with this temperature.
- (d) Compute the efficiency of this simple system. i.e. what fraction of the energy that you put in will you get out? (Your answer should be a dimensionless number — but as is normal best practice, derive a formula before numerical evaluation.)
- (e) For this rudimentary CAES system, estimate the volume of compressed air that would need to be stored to provide an average household with a days worth of electricity. Compare this volume to some other volumes, in a “useful” way. (Unless it is blindingly obvious, in order for your comparisons to be useful, you must explain why you consider them to be so.)

[Answer.](#)

### 3.12 Trangia trouble

Simple liquid fuel stoves are useful for boiling water when camping: <https://web.microsoftstream.com/video/0e1824d6-4307-47bc-a95e-b6a8d34f26fa>

The stove uses the combustion of methanol:



for heating.

When bringing such a stove on a trip, it is useful to estimate the amount of fuel that you should bring as well.

- (a) Make a *naive* estimate of the amount of methanol (in kg) that would be required to bring 250 mL of room temperature water to a boil. Indicate your assumptions.
- (b) Compare your answer to the results of the video linked above. In particular, indicate possible reasons for the discrepancy, being as quantitative and precise as possible. e.g., it is insufficient to say “I didn’t include X. So maybe X is the problem.”

[Answer.](#)

### 3.13 Shocking Schottky

As mentioned in the notes, SITP uses three model systems to introduce entropy and temperature: 1) the Einstein solid, 2) the ideal gas, and 3) the two-state paramagnet. In this chunk, we’ve

focused on the Einstein solid, and in the next we will look at the ideal gas. In this question you'll consolidate your understanding of the general procedure by studying the two-state paramagnet.

The Einstein model consists of  $N$  oscillators, each having one of an infinite number of evenly spaced energies. The two-state paramagnet consists of  $N$  spins, each of which only has one of *two* possible energies.

The sequence of steps in our study of the Einstein solid was:

- (i) figure out expression an expression for the multiplicity  $\Omega$
- (ii) determine a good approximation for entropy  $S$ , suitable for large  $N$  (using Stirling's approximation).
- (iii) compute relationship between  $T$  and  $U$ .
- (iv) determine heat capacity  $C$
- (v) check the correspondence of  $C$  with experiment, possibly making use of approximate forms for  $C$  based on limiting high- and/or low- $T$  behaviour.

You should:

- (a) Start by explaining why

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} \quad (\text{SITP 3.27})$$

for the two state-paramagnet. Here  $N_\uparrow$  characterizes the macro-state (the number of sites with one of two possible energies), and as normal,  $\Omega$  corresponds to the number of contributing microstates.

Fill in the same steps (i)-(iv) in an analogous matter to the Einstein solid (the next part of problem will deal with (v), the “correspondence” aspect).

For the level of depth required, imagine making yourself making a “cheat-sheet” or summary for yourself in the future. A page or two should be sufficient.

Write your results in terms of  $\epsilon$ , the energy level difference between the two states.

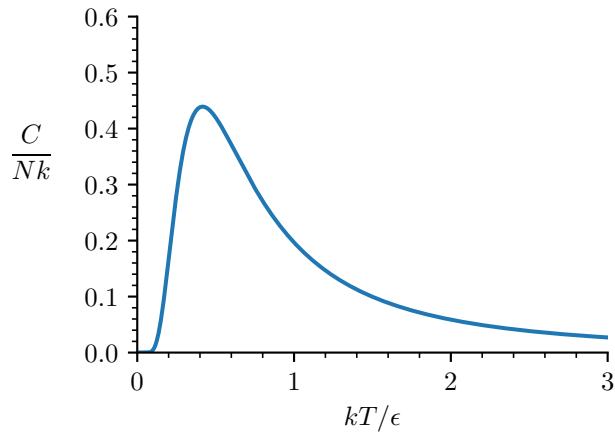
Your final result for the heat capacity (step (iv)) should be

$$C = Nk \left( \frac{\epsilon}{kT} \right)^2 \frac{\exp(-\epsilon/(kT))}{(1 + \exp(-\epsilon/(kT)))^2} \quad (4)$$

which exhibits what is known as a **Schottky peak** (or sometimes **Schottky anomaly**) — a peak in the heat capacity at a certain temperature:<sup>7</sup>

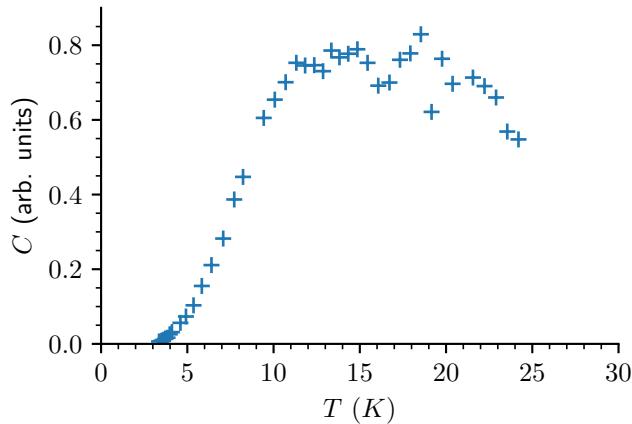
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<sup>7</sup>Admirers of the equipartition theorem should note that there is no limit where the theorem is valid in this “highly quantum” system.



- (b) A recent paper discusses how Schottky peaks might arise in the thermodynamics of black holes. The author states: “*like any other thermodynamic system, an examination of the specific heat as a function of temperature can provide valuable clues as to the nature of the available underlying degrees of freedom*”.

Let’s look at an example of this sort of reasoning, but in a laboratory-based situation for which we presently have data.<sup>8</sup> Shown below are some experimental measurements of the heat capacity of cerium magnesium nitrate (CMN) as a function of temperature:



This is experimental data, so it has noise, especially at the higher temperatures. However, one can discern that there is possibly a Schottky peak present. Just based on this data though, it’s hard to say. We really want more, less noisy, data at higher temperatures, to see if there is a peak.

But here is a common line of attack: hypothesize that there *is* a Schottky peak; then using the data determine the energy level difference  $\epsilon$ . Does this  $\epsilon$  make sense, given other things we know about this material? If it doesn’t, we can rule out the Schottky hypothesis.

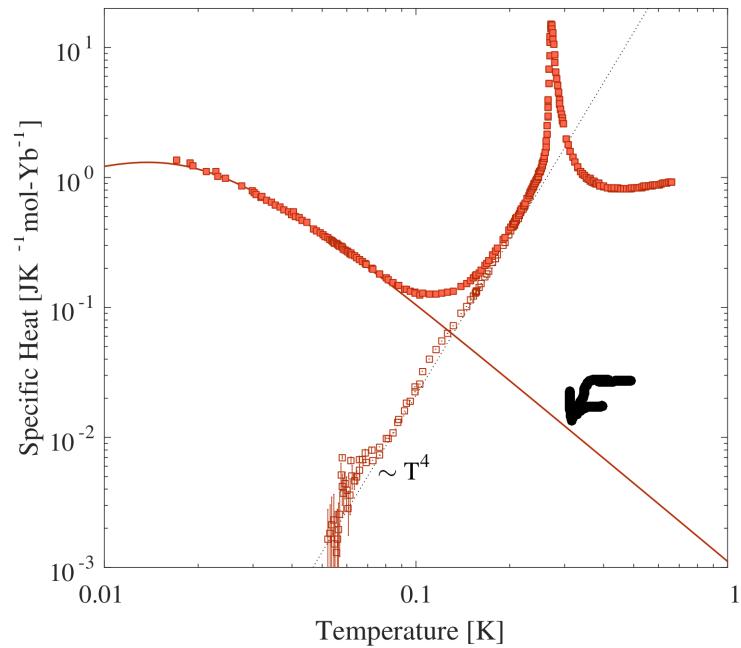
I want you to mimic the first step in this procedure: estimate  $\epsilon$  based on the data, assuming that there is a Schottky peak.

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<sup>8</sup>The data under discussion is from <https://iopscience.iop.org/article/10.1088/0370-1328/83/3/304>, but you do not need this paper to solve the problem.

The relative complexity of doing a non-linear fit of the full Schottky form for  $C$  doesn't seem warranted, given the noise. Instead, make your estimate using the low- $T$ , less noisy data (the full data is available at [here](#)). And instead of the full Schottky form given by Eq. 4, consider an asymptotic, low- $T$ , approximation to this expression. Express your answer in eV. (Aspiring experimentalists might consider the uncertainty in their estimates as well ;)

- (c) In this chunk, we have motivated the introduction of temperature by considering two Einstein solids that could exchange energy. Statistically speaking, they exchange energy until they reach the same temperature, maximizing the associated multiplicity (and entropy) of the joint system. This exchange of energy may also happen *within* a solid. More specifically, we may sometimes view a single solid as a combination of two systems, each of which we understand well. They can exchange energy until they are the same temperature. For example, a solid may consist of both spins (modelled as a two-state paramagnet), and vibrations (modelled as an Einstein solid). Normally these are in thermal equilibrium i.e., at the same temperature. Since the energies of these “sub-systems” are additive, so are their heat capacities. e.g.,  $C(T) = C_{\text{Einstein}}(T) + C_{\text{two-state}}(T)$ . It is frequently the case that one of the subsystems is well understood whereas the other is not. Then it is helpful to “disentangle” the different contributions to  $C$ , when trying to work out the “new physics”. Here is an example of this type of analysis from a [recent PhD thesis](#) of a student here at Waterloo:<sup>9</sup>



The peak at low temperature is believed to be a Schottky anomaly. By subtracting out this “known” behaviour from  $C$ , a clear  $T^4$  dependence may be observed. (The filled squares are the raw data for  $C$ ; the open squares are after “subtracting out” the Schottky anomaly.) The  $T^4$  structure at the higher temperatures is not well-understood at this time.

For your final (!) task, explain both: 1) why the part of the figure marked by the arrow ← is a straight line, and 2) why the value of the slope of that line is what it is. (It may make more sense to answer 2) first.)

### Answer.

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<sup>9</sup>For reference, this is Fig. 8.5 (pg 141) of the linked thesis. The material is Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. I do not intend for you to look up this thesis to answer this question.

### 3.14 Heat switch

Please view:

<https://web.microsoftstream.com/video/76f1d84b-d6ca-4e70-9fa3-a0729005e4a3>

Let us assume that both sides of the heat switch are at temperatures below 2 K so that we may assume that the thermal conductivity ( $\kappa_T$ ) of Pb *in the normal state* is temperature-independent.

First we will consider that the heat switch has been put in the thermally *conducting* state.<sup>10</sup>

- (a) Write a relationship between the heat flow rate  $\dot{Q}_{H \rightarrow C}$  across the bridge, using  $\kappa_T$  for Pb, the temperature difference between the hot and cold sides  $T_H - T_C$ , and the physical dimensions of the Pb “bridge”.
- (b) Numerically evaluate the rate of heat flow  $\dot{Q}_{H \rightarrow C}$  (in W) between the cold and hot sides for  $T_H = 2\text{ K}$  and  $T_C = 0.3\text{ K}$ .  
(Use de Haas and Rademakers’ paper to estimate the numerical value of the thermal conductivity that you need and the video to estimate the physical dimensions of the Pb bridge.)
- (c) Suppose that the cold side of the switch is made up of enough material so that its heat capacity may be effectively considered as infinite. However the hot side of the switch is made of 250 g of copper, which is known to have a low-temperature molar specific heat capacity of the form:

$$\frac{C}{n} \approx \alpha T \quad (5)$$

where  $\alpha \approx 0.7 \frac{\text{mJ}}{\text{mol} \cdot \text{K}^2}$ .

If the cold side is at 0.3 K and the hot side starts at 2 K, compute the time required (in s) for the hot side to get to within 10% of the absolute temperature of the cold side.

Now let us consider that the heat switch has been put in the thermally *non-conducting* (insulating) state. This situation is a bit more complicated than the conducting state because the thermal conductivity of Pb may no longer be considered to be temperature-independent.

The temperature-dependent resistivities measured by de Haas and Rademacher do not extend to low enough temperature to be directly useful here. However, at sufficiently low enough temperatures, theory says that the thermal conductivity in the superconducting state is proportional to  $T^3$ . You may estimate the “coefficient of proportionality” from the lowest temperature data of de Haas and Rademacher:<sup>11</sup> i.e., the  $D$  in  $\kappa_T(T) = DT^3$ .

- (d) Assuming that Fourier’s law of conduction holds *locally* at points within the bridge, with this temperature dependent  $\kappa_T(T)$ , derive an expression for  $\dot{Q}_{H \rightarrow C}$ , analogous to the one in part (a).
- (e) Numerically evaluate this  $\dot{Q}_{H \rightarrow C}$ , as in part (b), but for this thermally insulating state of the switch.

---

<sup>10</sup>Do not confuse the terms “thermal conductivity” and “superconductivity” in this question.

<sup>11</sup>The de Haas and Rademacher data is only applicable if the same magnetic field is used in the switch. We will assume that is the case.

- (f) Repeat the calculation that you did in part (c), but for this thermally insulating state of the switch. This calculation is not completely trivial. (You may want to consider various bounds as checks on your answer.)
- (g) Comment on the difference between the times computed in the previous part and part (c). Does the switch operate as expected?

[Answer.](#)

### 3.15 Kelvin was a flat earther

Well, not quite — but he did use a one-dimensional model of the earth to estimate its lifetime. In this problem you will reproduce his estimate as an application of the heat equation:

$$\frac{\partial T(x,t)}{\partial t} = K \frac{\partial^2 T(x,t)}{\partial x^2}. \quad (6)$$

In the suggested problems for this module, I verify that

$$T(x,t) = T_0 + \frac{A}{\sqrt{t}} e^{-x^2/(4Kt)}, \quad (7)$$

is a solution to the heat equation. Using superposition it is possible to combine solutions of this form to solve temperature variations in time for nearly arbitrary initial temperature distributions. To see this, it is useful to observe that as  $t \rightarrow 0^+$ , the heat equation solution:

$$d(x,t) = \frac{A}{\sqrt{t}} e^{-x^2/(4Kt)}, \quad (8)$$

acts like a **Dirac delta function** ( $\delta$ -fcn).

A  $\delta$ -fcn has the properties:

$$(i) \quad \int_{-\infty}^{\infty} dx \delta(x) = 1 \quad (9)$$

$$(ii) \quad \int_{-\infty}^{\infty} dx f(x) \delta(x-a) = f(a) \quad (10)$$

for any function  $f(x)$ .

- (a) Compute  $A$  so that  $d(x,t)$  satisfies (i). (Evaluate the integral from first principles — not a table.)
- (b) Explain why — intuitively — as  $t \rightarrow 0^+$ , the  $d(x,t)$  will show the behaviour of (ii).

- (c) Explain why

$$T(x, t) = \int_{-\infty}^{\infty} dx' g(x') d(x - x', t) \quad (11)$$

is a solution to the heat equation (for any given function  $g(x')$ ).

- (d) Using your answers to the previous parts, show that if we have an initial temperature distribution at  $t = 0$  given by  $T(x, 0)$ , then the temperature at any future time may be computed by:

$$T(x, t) = \frac{1}{2\sqrt{\pi Kt}} \int_{-\infty}^{\infty} dx' T(x', 0) \exp\left(-\frac{(x - x')^2}{4Kt}\right). \quad (12)$$

Kelvin considered the following model of a cooling earth: initially it was at a large homogeneous temperature ( $T_i \approx 3900^\circ\text{C}$ ). However, its surface is rapidly cooled to  $0^\circ\text{C}$  and stays there (due to rapid heat conduction into the atmosphere). Below the surface of the earth, the temperature increases as we head further into the earth.<sup>12</sup> However, this increase will become less pronounced as the earth cools with time. From observed values of this gradient  $dT/dx$  just below the surface, an estimated  $K$  (in the heat equation) for the earth, and an appropriate solution to the heat equation, the time elapsed since the homogeneous temperature condition may be estimated.<sup>13</sup>

It turns out — at least for “short” times — that “all of the action” occurs near the surface, so a one-dimensional model of heat conduction is fine. (You will verify this claim later.)

But we cannot apply Eq. 379 directly because  $K$  is not homogeneous (the same for all  $x$ ); i.e., we can only assume  $K$  is constant inside the earth ( $x \leq 0$ ); at the surface we need to apply the boundary condition:  $T(0, t) = 0^\circ\text{C}$ .

Here Kelvin employed a “method of images” type approach, to obtain the relevant solution:

$$T(x, t) = \frac{T_i}{2\sqrt{\pi Kt}} \left[ \int_{-\infty}^0 dx' \exp\left(-\frac{(x - x')^2}{4Kt}\right) - \int_0^{\infty} dx' \exp\left(-\frac{(x - x')^2}{4Kt}\right) \right]. \quad (13)$$

The [method of images](#)<sup>14</sup> is well-known in electrostatics: the simplest application being a point charge near a perfectly conducting surface.

- (e) Explain how — in analogy with the electrostatic example — Eq. 383 provides the relevant solution to Kelvin’s problem; namely it satisfies the heat equation, initial conditions, and boundary conditions.
- (f) Using the solution given by Eq. 383, determine an expression for  $dT/dx$  at the surface ( $x = 0$ ) that will allow you to estimate the time elapsed since the homogeneous temperature distribution.
- (g) For his estimate, Kelvin used  $K = 1.2 \times 10^{-6} \text{ m}^2/\text{s}$ .

Show that this not *too* unreasonable, based on the heat capacity and thermal conductivity of rock. (Do not forget to cite your sources.)

<sup>12</sup>Very near the surface (within a few metres) there is a seasonal fluctuation, but that is not relevant here.

<sup>13</sup>At least one problem with Kelvin’s model is that it neglects heat generated by radioactive decay within the earth, and thereby gives a lower bound on the lifetime of the earth. The actual lifetime of the earth is between one and two orders of magnitude greater than his estimate. But we are just concerned with Kelvin’s use of the heat equation in this problem, and not the limitations of his model.

<sup>14</sup>Section 3.2 of Griffiths’ *Introduction to Electrodynamics*, 4th ed. has a nice treatment of the method of images.

- (h) Kelvin used  $K$  from the previous part, a temperature gradient of  $dT/dx \approx -37^\circ\text{C}/\text{km}$ , and an initial temperature of  $T_i \approx 3900^\circ\text{C}$ . What was his estimate of the lifetime of earth (in years) (using your result from (f))?

(Making sure that the units work out will provide a check on your result from (f).)

- (i) Justify the “flat earth” approximation. (There is no need to be numerically precise; but be quantitative.)

Hint: does the estimated lifetime from the previous part give a length scale that can be compared to the radius of the earth?

[Answer.](#)

### 3.16 Sackur and Tetrode are gone

The validity of the Sackur-Tetrode equation may be tested by calorimetry measurements.

- (a) Compute the entropy (in J/K) of 1 mol of Ar gas at  $T = 85.67\text{ K}$  and  $P = 0.937\text{ bar}$  using the Sackur-Tetrode equation.
- (b) Starting with solid Ar at  $T = 2\text{ K}$ , Flubacher *et al.* <https://dx.doi.org/c8qtdv> measured the heat required to warm up Ar to its melting temperature, melt it into a liquid, heat it a bit further, and then vaporize it into gaseous form. This data can also be used compute the entropy of Ar gas for the conditions of part (a).

Their measured heat capacities of solid Ar between  $T = 2\text{ K}$  and  $83.8\text{ K}$  are posted [here](#).<sup>15</sup>

The latent heat associated with melting Ar at  $T = 83.8\text{ K}$  was measured to be  $L_m \approx 1190\text{ J}$  for 1 mol.

The heat capacity of the liquid Ar between  $T = 83.8\text{ K}$  and  $T = 85.67\text{ K}$  was measured to be  $C \approx 43.932\text{ J/K}$  for 1 mol.

The latent heat associated with vaporizing Ar at  $T = 85.67\text{ K}$  and  $P = 0.937\text{ bar}$  was measured to be  $L_v \approx 6544\text{ J}$  for 1 mol.

Assume that the entropy of the solid Ar is zero at  $T = 0\text{ K}$ .

Using this calorimetry data make a plot of entropy (in J/K) as a function of temperature (in K) from  $0\text{ K}$  to  $86\text{ K}$  (but make your axis run from  $0\text{ K}$  to  $100\text{ K}$ ). Label the discontinuities.

(Python is *my* weapon of choice here, but Excel will also work. You may use any software that you are comfortable with, but document your work.)

- (c) What entropy do you determine for the conditions of part (a) using this calorimetric data (without Sackur-Tetrode)? Compare with your Sackur-Tetrode value from part (a) and indicate the value of the entropy obtained from Sackur-Tetrode equation on your plot in the previous part.

---

<sup>15</sup>These heat capacities are neither  $C_V$ 's or  $C_P$ 's; however there is little error in assuming that all of the heat capacities and latent heats given in this question are at a constant pressure  $P = 0.937\text{ bar}$ .

- (d) If everything went well, you should have found reasonable agreement (on the order of 1%) between the values of entropy given by the Sackur-Tetrode equation and calorimetry. Suppose that instead of using this calorimetric data to test Sackur-Tetrode, we assume the Sackur-Tetrode equation to be true. Show that the value of the entropy derived from calorimetry may then be used to determine Planck's constant! Give a numerical value of Planck's constant  $h$  (in  $\text{J} \cdot \text{S}$ ) derived from the calorimetric entropy.
- (e) Imagine that — contrary to reality — water molecules consist of single atoms of atomic weight  $\approx 18 \text{ g/mol}$ . With this assumption, compute the entropy of 1 mol of water vapour at  $T = 300 \text{ K}$  and  $P = 1 \text{ bar}$  using the Sackur-Tetrode equation.
- (f) A generalization of the Sackur-Tetrode formula gives an entropy of  $S \approx 189.0 \text{ J/K}$  for 1 mol of water vapour at  $T = 300 \text{ K}$  and  $P = 1 \text{ bar}$ .
- Explain why this value is higher or lower than the one that you computed in the previous part; i.e., disagreement is expected, but is the disagreement in the expected direction?
- (g) Like for the case of Ar, we can independently check this computed entropy (from the generalized Sackur-Tetrode equation) using calorimetry data; i.e., from the heat capacities of ice, the latent heat of melting, the heat capacities of water and the latent heat of boiling. But this data gives  $S = 185.3 \text{ J/K}$  for 1 mol of water at  $T = 300 \text{ K}$  and  $P = 1 \text{ bar}$ , disagreeing by more than the estimated uncertainties. (Numbers are from <http://dx.doi.org/bv66rn>.)
- Briefly look over pg.'s 433-434 of Pauling's General Chemistry, 3rd ed., and pg.'s 94-95 of SITP (esp. **residual entropy**). Comment in a few sentences on why there is disagreement in the entropies for water vapour (from calorimetry and the generalized Sackur-Tetrode result), that does not occur in the Ar case.<sup>16</sup> It may be helpful to phrase your discussion in terms of *multiplicities* rather than entropies.
- (This type of analysis of residual entropy is important in modern research. See, for example, Fig. 4 of <http://dx.doi.org/f4z575>.)

[Answer.](#)

### 3.17 Heist of the century or lame waste of time?

Some apartment dwellers don't have to pay for hot water usage. But it's a resource that *could* be used to generate electrical power.

Residential hot water might typically be at about  $50^\circ\text{C}$ . A shower consumes about 8 litres/minute; so in a large building continuously using this amount of hot water probably wouldn't be noticed by building management.

Suppose that you make a device to generate electrical power using the hot water from your continuously flowing hot water tap.

You wouldn't want to try this in the summer (increasing the load on your air conditioning, which you probably *do* pay for). But in the winter, when you keep your apartment at  $\approx 20^\circ\text{C}$ , any extra

---

<sup>16</sup>Taking into account that Ar vapour is not an ideal gas reduces the difference between the calorimetric and Sackur-Tetrode entropies that you found in part (c).

heat load due to your secret device wouldn't be a problem. (Assume that you also don't pay for heating.)

- (a) Based on the laws of thermodynamics and some reasonable assumptions, compute a bound on the electrical power (in W) that you could expect to generate.
- (b) Compare with other powers (e.g., charging a cell phone). Is this a worthwhile scam?

[Answer.](#)

### 3.18 Demag and chill

In the problem "Shocking Schottky" you explored the properties of the two-state system (a set of  $N$  atoms, each having an energy of 0 or  $\epsilon$ ).

The two-state paramagnet is a special case, in which  $\epsilon$  is now a function of magnetic field  $B$ .

In this problem you will explore how by varying  $B$ , and thus  $\epsilon$ , a two-state paramagnet can be used for refrigeration.

- (a) Our primary goal in part (a) of "Shocking Schottky" was to determine the heat capacity  $C$  as a function of temperature  $T$ . However, we can use some of the intermediate results to determine the entropy  $S$ , as a function of  $T$ . Show (using any results from the solutions to "Shocking Schottky") that:

$$\frac{S}{Nk} = \frac{\alpha}{1 + e^\alpha} - \ln \left( 1 - \frac{1}{1 + e^\alpha} \right) \quad (14)$$

where  $\alpha = \epsilon/(kT)$ .

- (b) Plot (and include the plot in your solutions) the dimensionless scaled entropy per atom  $S/(Nk)$  as a function of dimensionless temperature  $T/(\epsilon/k)$ , from  $T/(\epsilon/k) = 0$  to  $T/(\epsilon/k) = 3$ .
- (c) What limits does  $S/(Nk)$  approach as  $T \rightarrow 0$  and  $T \rightarrow \infty$ ? Do these limits make physical sense?
- (d) Now we will consider the use of a magnetic field to control  $\epsilon$ . At low temperatures ( $< 1\text{ K}$ ) the material CMN acts like a two-state paramagnet where for each spin:

$$\epsilon = 2\mu B \quad (15)$$

with

$$\mu = 2 \frac{q}{2m} \frac{\hbar}{2} \quad (16)$$

where  $q/m$  is the charge to mass ratio of an electron, and  $\hbar$  is Planck's constant.

Suppose that we have a sample in thermal contact with a reservoir at  $T = 0.3\text{ K}$ . At zero magnetic field  $T/(\epsilon/k) \rightarrow \infty$  and the sample is **demagnetized** and has maximal entropy. However, as  $B$  is increased, and the sample remains at  $T = 0.3\text{ K}$  (since it is contact with reservoir), its entropy will *decrease* as it magnetizes.

- (i) At what  $B$  (in T) will 90% of all spins in the sample be in the ground state?
  - (ii) What is the scaled entropy per spin  $S/(Nk)$  with 90% of the spins in the ground state?
- (e) Suppose now, that these spins are taken *out* of thermal contact with the  $T = 0.3\text{ K}$  reservoir, and then the magnetic field is decreased to  $0.002\text{ T}$ . This is done in such a way that the number of spins in the ground state remains the same. (In general you would want to change the field rapidly so that heat doesn't "leak" into or out of the spin system due to imperfect thermal insulation.)
- (i) Does the entropy of the spins change? If so, by how much?
  - (ii) Does the temperature of the spins change? If so, by how much?

If you've reasoned everything out correctly, you should find that your spins have cooled. In general that might not be useful in and of itself, except for the fact that *you may now use this cold spin system to cool any other system, by putting it in thermal contact with these cold spins.*

- (f) As a numerical illustration of the preceding point, suppose that you have 2 mol of spins that you have cooled (as above). You place these spins in thermal contact with  $0.03\text{ mol}$  of liquid  $^3\text{He}$ , initially at  $0.3\text{ K}$ . What will the final temperature of the combined system be, after thermal equilibrium is reached? (In this step, the spins will demagnetize as they heat up while cooling the sample — so-called **demag cooling**.)

You will need the low temperature heat capacity for  $^3\text{He}$ . It has been empirically determined that the heat capacity  $C$  for  $^3\text{He}$  (in the relevant temperature range) is given by:

$$\frac{C}{nR} \approx bT + cT^2 + dT^3 \quad (17)$$

where  $n$  is the number of mols, and  $R$  is the gas constant, with

$$\begin{aligned} b &\approx 2.89\text{ K}^{-1} \\ c &\approx -7.8\text{ K}^{-2} \\ d &\approx 7.09\text{ K}^{-3}. \end{aligned}$$

(Ignore any possible volume change of the  $^3\text{He}$  and associated mechanical work.)

- (g) Demag cooling, at least using electron spins, fell out of vogue once other techniques (helium dilution refrigerators) became available. However, there is a new generation of demag coolers being used, or planned for use, in satellites for the observation of x-rays from astronomical sources. These demag coolers can cycle like the classic refrigerators discussed in SITP, and can get Carnot-like COPs when transferring heat away from cold x-ray sensors.

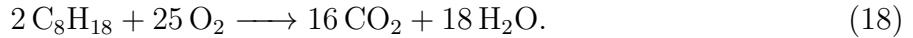
In a few sentences, indicate why cooling these x-ray detectors (to  $< 0.1\text{ K}$ ) is required, and what benefits demag cooling has over other methods in this application.

**Answer.**

### 3.19 Supercharging the dinosaur

In the following problem use  $P_0 \approx 1$  bar and  $T_0 = 300$  K for “ambient conditions” when appropriate.

- (a) The gasoline used as fuel in most automobiles is a mixture of various species. According to [wikipedia](#) a representative combustion reaction of gasoline is that of octane:



The standard enthalpy of formation for octane is  $\Delta_f H \approx -250$  kJ/mol.

Various sources indicate the “heat of combustion” of gasoline to be  $\approx 45$  MJ/kg for an optimal air:fuel ratio of 15 : 1 by mass.

Check the consistency of these two characterizations, by computing the “heat of combustion” in MJ/kg using the standard enthalpy of formation of octane (and other required quantities).

- (b) For the rest of problem, assume that for a given amount of air drawn into the cylinders of an internal combustion engine, the air:fuel ratio used is always optimal and that we can write:  $Q_H = q n_{\text{air}}$  where  $n_{\text{air}}$  is the number of moles of air. Using the “heat of combustion” number from the previous part what is the numerical value of  $q$  (in units of J/mol)?
- (c) There are two main contributions to the force required to maintain an automobile at constant speed:

- (i) air resistance:

$$F_d = \frac{1}{2} \rho C_d A v^2 \quad (19)$$

where  $\rho$  is the mass density of air,  $C_d$  is the “drag coefficient” (depends on “shape” of the car),  $A$  is the frontal area, and  $v$  is the speed.

- (ii) rolling resistance:

$$F_r = C_{rr} mg \quad (20)$$

where  $C_{rr} \approx 0.01$  is the coefficient of rolling resistance and  $mg$  is the weight of the car.

Some numbers typical for a Toyota Corolla are:  $C_d A \approx 0.6 \text{ m}^2$ ,  $m \approx 1500 \text{ kg}$ .

The compression ratio of the internal combustion engine in a Toyota Corolla is  $\approx 10.5$ .

Estimate the fuel consumption of a Corolla travelling at 100 km/hr, assuming use of a “perfect” Otto cycle. Express your answer in units of  $\ell/100\text{km}$ .

- (d) Compare your estimate from the previous part with published fuel efficiency numbers *from an authoritative source*, and briefly comment on the discrepancy (is it in the right direction?).
- (e) If the total engine capacity of the Corolla’s engine is  $1.8 \ell$  estimate the maximum power (in W) at 6100 rpm. Don’t forget that automobile engines are *four-stroke*.
- (f) The highest elevation on the Trans-Canada highway is  $\approx 1640$  m above sea level ([Kicking Horse Pass](#)). For this elevation estimate the fractional reduction in the Toyota’s maximum engine power compared to sea-level (e.g., “90% compared to sea-level”). Does the engine efficiency vary with elevation?

- (g) One possible way to increase the maximum power of an internal combustion engine, without increasing its cylinder volume (displacement), is to pressurize the air before it enters the cylinders. Of course, increasing the pressure above atmospheric will require some work, but that work can be extracted from the output of the engine itself. But is there a net win, a “replacement for displacement”?

Assuming *isothermal* compression from atmospheric pressure  $P_0$  to  $P_1$  prior to insertion of air in the engine cylinders, develop an expression for  $W/W_{\text{otto}}$ ; namely the boost in power over the standard Otto cycle (assuming that the engine can operate at the same rpm). Your expression should be in terms of  $e_{\text{otto}}$ ,  $RT_0/q$  and  $P_1/P_0$ . Numerically evaluate for  $P_1/P_0 = 2$  for the Corolla.

- (h) Develop an expression for  $e/e_{\text{otto}}$ ; namely the efficiency as fraction of the standard Otto cycle efficiency. Your expression should be in terms of  $e_{\text{otto}}$ ,  $RT_0/q$  and  $P_1/P_0$ . Numerically evaluate  $e/e_{\text{otto}}$  for  $P_1/P_0 = 2$  for the Corolla.
- (i) In real “supercharging”, it is not practical to perform the compression isothermally — instead there is heating as the gas is compressed. However prior reaching the cylinders, the compressed air is cooled (ideally to ambient) at the same pressure, using an *intercooler*. Why is this cooling done?

[Answer.](#)

### 3.20 Cool under pressure

Problem 4.21 of SITP concerns the **Stirling engine**. It is an example problem in my [notes](#) and I showed a Stirling engine variant in one of my [videos](#).

The Stirling engine was first demonstrated in the early 1800’s, but has taken a backseat to the internal combustion engine, except in certain niche applications. However in the 1940’s, it was noticed by workers at the Philips Laboratory that if instead of doing work, Stirling engines were driven by an external source of power, they could be quite effective refrigerators.<sup>17</sup>

Since that time, so-called **Stirling cryocoolers** have been extensively developed for low-temperature applications; e.g., for infrared sensors.

The analysis of the Stirling cryocooler is similar to that of the engine, except the cycle is traversed in reverse. In the following, use similar symbols as in SITP Problem 4.21 and my solution (but with the standard conventions for the signs of  $Q_H$ ,  $Q_C$  and  $W$  for a *refrigeration* cycle).

- (a) The use of a single indicator diagram for a Stirling cooler (or engine) is somewhat misleading, as not all of the gas is at the same temperature at all times. Consider operation as a cooler, and sketch three indicator diagrams: on the “hot” side, and one for the “cold” side, and the “combined” indicator diagram. Note that at any given time, we assume that the gas pressure is the same throughout the gas, but that the amount of gas on the hot and cold sides varies. The volume in the combined indicator diagram is the sum of the two volumes. Make sure

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<sup>17</sup>An interesting account of the early days of Stirling cryocoolers is given in Köhler, *The Stirling refrigeration cycle*, *Sci. Am.* **119**, 212 (1965) (posted to Learn).

to label the “direction” of the cycle in each of your diagrams, and the portion of the cycles that correspond to regeneration.

- (b) The regenerator is absolutely critical to operation as a refrigerator. As an illustration, imagine that the regenerator was *not* present, and the working gas must be cooled from  $T_H$  to  $T_C$  by the cold reservoir. This diminishes the cooling per cycle  $\dot{Q}_C$ . In fact, it can even prevent the device from working as a refrigerator. Write an equation determining the threshold for operation as a refrigerator; and from it numerically estimate the coldest reservoir temperature available with  $T_H = 300\text{ K}$ , He working gas, and a volume compression ratio of 2.
- (c) Show that the COP achieves the ideal Carnot value if the regenerator works perfectly. (This question is analogous to part (c) of SITP’s Problem 4.21.)

Relatively compact Stirling cryocoolers are available for purchase, through companies such as [Sunpower](#). To make things concrete, let us consider the Sunpower CryoTel CT cryocooler, with the performance data given on its [webpage](#). Some useful Sunpower terminology: “reject” temperature is  $T_H$ ; “cold-tip” temperature is  $T_C$ , and “lift” is  $\dot{Q}_C$ .

- (d) Check the webpage for consistency: at  $T_C = 77\text{ K}$  they give both “lift”, “% Carnot efficiency” and “input power”. Specifically, are the input power, cooling power, and temperatures consistent with the quoted “% Carnot efficiency”?
- (e) The webpage indicates that the % Carnot efficiency only gets up to about 20%. Suggest some reasons why.
- (f) Of course efficiency is important, especially for space-borne applications and so-on. But often what one really wants, especially in a laboratory setting, is just as high cooling power  $\dot{Q}_C$  as possible (for as little money as possible :)).

For a given physical Stirling cooler, there are two obvious ways of increasing the cooling power: 1) increasing the number of cycles per second, and 2) increasing the amount of working gas within the cooler.

The cycles per second are constrained in various ways: wear, mechanical strength and so-on. The Sunpower cooler operates at 60 Hz.

Increasing the amount of working gas increases the pressure within the system. Then the device has to be able to contain high pressures, which represent a safety hazard.<sup>18</sup>

Cryotel does not say what the pressure of the contained gas is, but we can *estimate* it.

More specifically, assume that the maximum volume that the gas occupies is  $5 \times 10^{-4}\text{ m}^3$ .<sup>19</sup> Grossly simplify Sunpower’s implementation of the Stirling process,<sup>20</sup> with the version that we have been studying (i.e., SITP Problem 4.21 “in reverse”). Assume a volume compression

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<sup>18</sup>An [article](#) by Walker notes that the compressed gas for cooling military night vision equipment was a major risk due to potential rupture by bullets and shrapnel. Imagine what happens to a balloon when you let the air out. But the thing ricocheting around is a metal cylinder.

<sup>19</sup>From  $V \approx 0.1\text{ m} \times \pi \times (0.08\text{ m}/2)^2$  using Sunpower’s drawings.

<sup>20</sup>Schroeder makes reference to leaving some of the fun to the engineers; i.e., how the pistons are moved. Actually it is not very complicated at all, at least in the earliest Stirling cryocoolers — see the figure on page 122 of the article by Köhler, *op. cit.* The not-so-straightforward part is analyzing the cycle with the non-ideal movement of the cylinders.

ratio of 2 and the usage of He gas. You can take any other parameters that you need from the webpage. What is the maximum pressure that the working gas will reach during a cycle (in bar)?

Answer.

### 3.21 An unpleasant subject?

Imagine a gas of hydrogen *atoms* confined to within a box of fixed volume. If the walls of the box are increased in temperature, we will eventually obtain a gas of separated electrons and protons; i.e., high energy collisions will ionize (split) hydrogen into free protons and electrons. One might *naively* think that it is only the temperature that dictates the degree (extent) of ionization of the gas, and that its density plays no role. That is not the case, as you will now show.

We may consider all three particle types — hydrogen atoms, electrons and protons — to be acting as ideal gases, and thus that the Sackur-Tetrode (ST) equation applies. In this problem, it will be useful to write the ST equation as:

$$S = Nk \left[ \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (21)$$

where instead of  $V_Q$ , as in the notes, we are now using the **thermal de Broglie wavelength**:

$$\lambda := \sqrt{\frac{2\pi\hbar^2}{mkT}}, \quad (22)$$

where  $m$  is the mass of the particle in equation.

At a given temperature there are three relevant thermal wavelengths:  $\lambda_H$ ,  $\lambda_{p^+}$  and  $\lambda_{e^-}$ . We will also define three corresponding **number densities**:<sup>21</sup>  $n_H := N_H/V$ ,  $n_{p^+} := N_{p^+}/V$  and  $n_{e^-} := N_{e^-}/V$ .

We will assume the total amounts of both protons and electrons in the box are fixed (and equal for electrical neutrality). We are interested in whether or not they are free, or in the form of hydrogen atoms. We may parameterize this degree of ionization by  $x$ :

$$x := \frac{n_{p^+}}{n_{p^+} + n_H}, \quad (23)$$

so that  $x = 0$  corresponds to hydrogen gas and  $x = 1$  corresponds to a fully ionized gas of electrons and protons. In the following, you will determine an expression for  $x$ .

- (a) In chunk 6, the textbook and notes discussed how the Gibbs free energy dictated the favoured state (e.g., graphite versus diamond). However, here we may use the *Helmholtz free energy* to determine the degree of ionization. Why? (A few sentences is fine.)
- (b) Assuming a fixed total number of protons and electrons ( $N$  each, overall neutral) write an expression for the Helmholtz free energy ( $F := U - TS$ ) as a function of  $T$ ,  $V$ ,  $N_H$ ,  $N$ ,  $\lambda_H$ ,  $\lambda_{p^+}$ ,  $\lambda_{e^-}$ , and relevant constants.

There will be an overall arbitrary constant in your definition of  $F$ ; but your expression *must* involve the ionization potential of hydrogen  $R \approx 13.6 \text{ eV}$  (the energy cost for ionization).

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<sup>21</sup>We are departing from the convention that  $n$  refers to mols.

- (c) To find the degree of ionization you should now differentiate  $F$  with respect to  $N_H$  while keeping  $T$ ,  $V$  and the total number of atoms constant. Set the derivative equal to zero (why?), to obtain an expression for

$$\frac{n_{p^+} n_{e^-}}{n_H} \quad (24)$$

in terms of temperature, thermal wavelengths, and the constants  $R$  and  $k$ .

- (d) You should be able to simplify your expression in the preceding part based on the fact that protons are much heavier than electrons. Make and justify this approximation, to obtain the **Saha equation** (or at least one of its variants):

$$\frac{n_{p^+} n_{e^-}}{n_H} \approx \frac{1}{\lambda_{e^-}^3} e^{-R/(kT)}. \quad (25)$$

If you are not able to obtain this approximate result, then you have most likely made an error earlier. Check your work.

- (e) Write the LHS of Eq. 25 in terms of  $x$  and  $n := n_H + n_{p^+}$  ( $= n_H + n_{e^-}$ ).

- (f) Now we can explore the physical consequences of the Saha equation. For that purpose it is useful to make something like — but not the same as — a phase diagram.

For a given number density  $n$ , the Saha equation dictates the temperature required to obtain a “half-ionized” gas:  $x = 0.5$ . On a log-log plot, with temperature as the vertical scale (in K) and number density  $n$  as the horizontal scale (ranging from  $\approx 1 \text{ m}^{-3}$  to  $\approx 10^{30} \text{ m}^{-3}$ ), split the parameter space into a neutral hydrogen “phase” and an ionized “phase” (these are not true phases) using a (curved) line corresponding to  $x = 0.5$ .

Include this plot in your answer.

- (g) We will now consider the physical context for Saha’s original work.

Recall that the density and temperature of the earth’s atmosphere decrease with altitude. We might also expect the same general behaviour in the sun: both density and temperature decrease as we move outwards.

Saha developed his equation to help explain the following observation: as one moved *away* from the sun within its chromosphere, spectral lines due to *ionized* calcium ( $\text{Ca}^+$ ) became more prominent, suggesting an increasing degree of ionization of neutral Ca. With the naive reasoning given at the start of this question, that observation seemed at odds with the likelihood that temperature was also decreasing as we moved away from the sun; i.e., contrary to the observations, we might naively expect *less* ionization as we moved away.

With direct reference to your diagram from part (f) (a particular manifestation of Saha’s equation) explain why there is not necessarily any inconsistency; i.e., explain why the degree of ionization may *increase* and the temperature may *decrease* as we move away from the centre of the sun.

(The relevant experimental observations have improved greatly since Saha’s time. There are also a variety of additional technical details required to accurately calculate the degree of ionization — obviously including replacing the ionization potential of H with that of Ca — but do not concern yourself with these details. Just use the plot that you have constructed for H in part (f) to make a qualitative argument.)

[Answer.](#)

## 3.22 Pockets for atoms

Imagine a porous solid material that has “pockets” that can store atoms. Each pocket may store a single atom or not. A pocket cannot store more than one atom. Let us suppose that this material is surrounded by a gas of atoms within a constant volume and both the material and gas are held at a constant temperature by thermal contact with a large reservoir. Some fraction of the gas molecules will go into the pockets and some will remain in the gas phase.

The fraction of pockets that are filled with atoms is determined by the relevant entropies:

- (1) Some energy is released when atoms go from the gas phase into a pocket; i.e., they tend to “stick” in the pockets. That energy is given up to the external reservoir in the form of heat and thus the entropy of the *external reservoir* goes up.
- (2) However when some of the atoms go from the gas into the pockets, the entropy of the *system* goes down. That makes intuitive sense — there seems to be more ways to distribute energy in the gas phase. Recall from the problem “Sackur and Tetrode are gone” that the entropy of Ar decreased from the gas phase to the liquid, and then to the solid.

The entropy of the universe is the sum of entropies of the reservoir and the system. Thus there is a competition between these two mechanisms for increasing the universe’s entropy. In this problem you will develop a simple model for the fraction of filled pockets based on this competition.

- (a) First let us consider the entropy of the pocketed atoms, ignoring the gas for now. Suppose that there are  $M$  pockets and  $A$  indistinguishable atoms. How many distinguishable ways can these atoms be distributed within the pockets?
- (b) Using Stirling’s approximation, show that the entropy of the pocketed atoms  $S_p$  may be approximated as:

$$\frac{S_p}{k} \approx M \ln M - A \ln A - (M - A) \ln(M - A) \quad (26)$$

- (c) The Helmholtz free energy of the system may be defined as:

$$F = U - TS \quad (27)$$

where  $U = U_p + U_g$  and  $S = S_p + S_g$ ; i.e., the total energy of the system is the sum of the energies associated with the pockets and the gas, and similarly for the entropies. For a fixed *total* number of atoms, number of pockets, and volume, we may consider  $F$  as a function of  $A$ , the number of atoms in pockets.

Explain why minimizing  $F$  will determine the fraction of filled pockets,  $A/M$ .

- (d) Determine the equilibrium fraction  $A/M$  by setting  $dF/dA = 0$ . Your answer should be written in terms of  $V$ ,  $N$ ,  $\lambda$ ,  $\epsilon$  and  $kT$ .

To determine the fraction, assume that the energy released when a pocket is occupied is  $\epsilon$ . Then the total energy of pockets may be then written as  $U_p = -A\epsilon$ , where a total energy of zero corresponds to all atoms being in the gas phase but not moving. You may also assume

that the gas is a monatomic ideal gas with an energy of  $U_g = (3/2)NkT$  and its entropy to be given by the Sackur-Tetrode equation:

$$S_g = Nk \left[ \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (28)$$

where instead of  $V_Q$ , as in the notes, we are now using the **thermal de Broglie wavelength**:

$$\lambda := \sqrt{\frac{2\pi\hbar^2}{mkT}}, \quad (29)$$

where  $m$  is the mass of the particle in equation.

- (e) Show that your result from the previous part may be written in terms of the pressure of the gas  $P$ :

$$\frac{A}{M} = \frac{1}{1 + \frac{P_0}{P}} \quad (30)$$

where

$$P_0 = (kT)^{5/2} \left( \frac{2\pi m}{h^2} \right)^{3/2} e^{-\epsilon/(kT)} \quad (31)$$

(If you do not get this result, check your result from the previous part.)

- (f) [Banerjee et al.](#) describe a material with “pockets” suitable for capturing the Xe gas made in nuclear reactors. In particular, Fig. 4 of their paper shows how Xe atoms can be “pocketed”. Their Fig. 2a shows the amount of Xe gas absorbed in the pockets as a function of the surrounding gas pressure (at 298 K). Make a plot of their data (available [here](#)). Fit the data using the model of Eq. 30 and include the fit in your plot as well. (You may assume that a Xe uptake of 1.45 mmol/g corresponds to a filling of all the pockets.)
- (g) Determine  $\epsilon$  from your fit (in units of eV). Is your value reasonable? (Compare it to other relevant energies.)
- (h) If our model is correct, then it may be used to predict the influence of temperature on Xe uptake.

Suppose that we are interested in determining how increased temperature would worsen the Xe uptake. What temperature (in K) would result in an Xe uptake of only 1.0 mmol/g at  $P = 0.2$  bar?

[Answer.](#)

### 3.23 Falling apart

We normally assume that nitrogen gas at atmospheric pressure and room temperature consists solely of  $N_2$  molecules. We might anticipate that this is not true at higher temperatures, as collisions between  $N_2$  become more energetic, possibly leading to **dissociation** (“bond breaking”):

the formation of atomic N. But of course the amount of dissociation is a quantitative matter, and may be determined using thermodynamics. In this problem you will estimate the amount of dissociation of  $\text{N}_2$  at room temperature and pressure.

We will have to make some approximations:

- (i) both N and  $\text{N}_2$  act like ideal gases.
- (ii) we will assume that the entropy of both N and  $\text{N}_2$  are given by the Sackur-Tetrode equation. (That's brutal for  $\text{N}_2$ .)
- (iii) there is a single well-defined energy required to split  $\text{N}_2$  into two N atoms ( $= D$ ): specifically  $D = 9.8 \text{ eV}$ . We will ignore internal excitation of the  $\text{N}_2$  molecules; i.e., that they can rotate and vibrate.

We will imagine a certain amount of nitrogen to be in a box of fixed volume  $V$  and in thermal equilibrium with the surrounding environment at  $T = 300 \text{ K}$ . The total number of nitrogen atoms within the volume, in both molecular and atomic form, should be taken as the amount required to give a pressure of  $P = 1 \text{ bar}$  if all of the nitrogen was in molecular form  $\text{N}_2$ . We will call this total number of nitrogen atoms (in both molecular and atomic forms)  $N$ .

The strategy is the same as the example problem in the notes used to introduce the Helmholtz free energy  $F$ .<sup>22</sup> In that example,  $F$  is used to determine how gas was shared between two volumes at two different elevations. In this problem you will determine the amount of dissociation in a similar manner.

- (a) Explain qualitatively — in your own words — how the amount of dissociation involves the competition between maximizing the entropy of the system and the entropy of the surrounding reservoir. Your answer should be specific, and indicate how the definition of  $F$ , and its minimization decides this competition.<sup>23</sup>

In the problem of the notes,  $F$  is written as a function of  $\text{N}_2$  and then differentiated, and then the derivative set to zero to determine the minimum of  $F$ . Here the approach is similar. Let us use  $N_2$  for the number of  $\text{N}_2$  molecules within the volume and  $N_1$  for the number of N atoms in the volume. The total number of nitrogen atoms is then  $N = 2N_2 + N_1$  (see above for how  $N$  should be chosen). In the notes  $F$  is considered to be a function of  $N_2$ , then differentiated, etc... In this problem will use  $N_1$  (considering  $N_2$  in this problem to be a function of  $N$  and  $N_1$ ), and then differentiate, set to zero, etc...

- (b) Write  $U$ , the total energy of the system, as a function of  $N_1$ ,  $N$ ,  $D$ , and  $kT$ .
- (c) Write  $S$ , the total entropy of the system, as a function of  $k$ ,  $N_1$ ,  $N$ ,  $V$ ,  $\lambda_{\text{N}_2}$ , and  $\lambda_{\text{N}}$  (note that  $\lambda$  is different for N and  $\text{N}_2$  because of their mass difference).

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<sup>22</sup>You may also find it helpful to examine the problem: “An unpleasant subject” in the [extended example problems](#).

<sup>23</sup>Having confidence in your answer to this part of the question should help with the rest of this problem.

- (d) Combining the results of the previous two parts, write the expression for  $F$ , differentiate with respect to  $N_1$ , and then set the derivative equal to zero. You may then make the approximation that  $N_1/N \ll 1$ , to then derive a formula giving  $N_1/V$  as a function of  $D$ ,  $kT$ ,  $\lambda_{N_2}$ ,  $\lambda_N$ , and  $N/V$ .
- (e) Determine the numerical value of the fractional partial pressure of N in the box:  $P_N/(P_N + P_{N_2})$ . Does your answer make sense? (If you have the incorrect answer, you can obtain part marks by explaining why you think it might or might not be wrong, and what checks you have done.)

[Answer.](#)

## 4 Answers

### Snowy mountain friend — answer

[Question.](#) Answer:

- (a) This problem may be solved in a number of ways. The hint suggests an informal approach that gives some insight. Here we will use the more formal language of vector calculus.

The measurements provide an estimate of the **gradient** of elevation:

$$\vec{\nabla}h = \frac{6 \text{ m}}{100 \text{ steps}} \hat{x} + \frac{10 \text{ m}}{100 \text{ steps}} \hat{y} \quad (32)$$

at the point of observation, with  $\hat{x}$  representing east direction, and  $\hat{y}$ , the north.<sup>24</sup>

We may use the gradient to approximate changes in elevation  $\Delta h$  about the point of observation as we move in a certain direction  $\Delta\vec{r}$ :

$$\Delta h \approx \vec{\nabla}h \cdot \Delta\vec{r}. \quad (33)$$

The properties of the dot product give the gradient an intuitive interpretation: when expressed in cartesian coordinates, the gradient gives the direction that you should travel in for the largest rate of change in elevation. Here the problem is different, since we want *no change* in elevation as we move. Writing  $\Delta\vec{r} = \Delta x\hat{x} + \Delta y\hat{y}$  and setting  $\Delta h = 0$  on the LHS of Eq. 33:

$$0 \approx \frac{6 \text{ m}}{100 \text{ steps}} \Delta x + \frac{10 \text{ m}}{100 \text{ steps}} \Delta y. \quad (34)$$

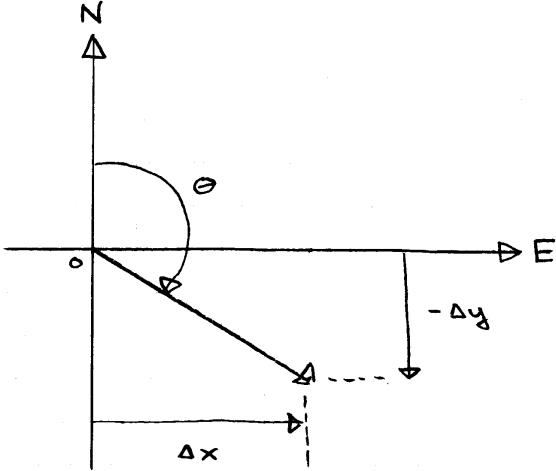
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<sup>24</sup>You may worry that the “steps” given are not distances projected onto a horizontal plane, but the distances travelled as measured along the slope. This is a problem in principle, but not for the numbers in this question (i.e., the “small-angle” hint). More specifically, since “a step” is about 0.75 m, a naive estimate of  $(\partial h/\partial y)_x$  gives  $\approx 10/75 \approx 0.133$ , whereas if the steps are measured along the slope, then  $\partial h/\partial y)_x \approx \tan(\sin^{-1}(10/75)) \approx 0.135$ , and thus ignoring this difference is completely reasonable given the precision to which the numbers have been stated i.e.  $\approx 10 \text{ m}$  etc...

Rearranging and simplifying gives:

$$\frac{\Delta x}{\Delta y} \approx -\frac{5}{3}. \quad (35)$$

The question asks for the direction that you should head, measured clockwise from north. Call this angle  $\theta$ :



and thus

$$\tan \theta = \frac{\Delta x}{\Delta y}. \quad (36)$$

But for a given value of  $\Delta x/\Delta y$  there are two solutions for  $\theta$  with  $-\pi < \theta \leq \pi$ , corresponding to opposite directions. In this problem:  $\theta \approx 121.0^\circ$  or  $\theta \approx -59.0^\circ$ .

Since you are on the south side of the mountain and your friend is on the east, the most direct route is probably to travel southeast ( $\theta \approx 121.0^\circ$ ) rather than northwest.

To make your way to your friend, while keeping your elevation constant, you should initially head in the direction  $\approx 121.0^\circ$  as measured clockwise from north.

(b) Following the strategy of the previous part, writing everything in symbolic form:

$$\Delta h \approx \vec{\nabla} h \cdot \Delta \vec{r}. \quad (37)$$

$$\approx \left[ \left( \frac{\partial h}{\partial x} \right)_y \hat{x} + \left( \frac{\partial h}{\partial y} \right)_x \hat{y} \right] \cdot [\Delta x \hat{x} + \Delta y \hat{y}]. \quad (38)$$

Setting the LHS to zero and rearranging gives:

$$\frac{\Delta x}{\Delta y} = -\frac{\left( \frac{\partial h}{\partial y} \right)_x}{\left( \frac{\partial h}{\partial x} \right)_y} \quad (39)$$

suggesting that

$$\left(\frac{\partial x}{\partial y}\right)_h = - \frac{\left(\frac{\partial h}{\partial y}\right)_x}{\left(\frac{\partial h}{\partial x}\right)_y}. \quad (40)$$

Equivalently, by rearrangement and use of the identity  $(\partial h / \partial y)_x = 1 / (\partial y / \partial h)_x$ , we have what is sometimes referred to as **the triple product rule**<sup>25</sup>:

$$\left(\frac{\partial x}{\partial y}\right)_h \left(\frac{\partial h}{\partial x}\right)_y \left(\frac{\partial y}{\partial h}\right)_x = -1. \quad (41)$$

I say “suggesting” because there are some additional constraints that must be satisfied. Roughly speaking we require that the function giving  $h$  in terms  $x$  and  $y$  be well-approximated by a “tangent plane” in a neighbourhood around the point of interest. In this course, this constraint will nearly always be satisfied.<sup>26</sup>

With this caveat, Eq. 41 is a general result, useful anytime that you have a function of two (or more) variables. Although in this problem both  $x$  and  $y$  measured distances, it is not at all necessary that the two variables have the same physical dimensions. The most trivial example that can be thought of involves the ideal gas law:

$$P = nRT/V. \quad (43)$$

With the correspondence  $P \rightarrow h$ ,  $T \rightarrow x$  and  $V \rightarrow y$ , we may verify that the triple product rule holds (see, for example, <https://youtu.be/uK-tSnrwpxM>) Okay, that might be a bit too trivial. But what about for the more elaborate van der Waals gas law:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}, \quad (\text{Eq. 5.49 of Schroeder})$$

where  $a$  and  $b$  are constants, specific to the gas in question? Naturally the rule works here as well (but it’s not a bad idea to check this).

The utility of the triple product rule is not for cases like the ideal and van der Waals gases, where a full functional relationship is known, but rather for cases like our “mountain” problem, where we have fragmentary information. For example, we may consider an experiment in which we can readily control and measure the volume and temperature of gas but are only able to measure pressure (and not control it). From measurements of the rate of change of pressure with volume at fixed temperature and the rate of change of pressure with temperature at fixed volume, the triple product rule will allow us to determine a quantity which we cannot easily measure: the rate of change of volume with temperature at fixed pressure.

<sup>25</sup>Application of the triple product rule yields what is **sometimes** called a **cyclic relation**

<sup>26</sup>Similarly we shall always assume equality of mixed partial derivatives e.g.

$$\frac{\partial^2}{\partial x \partial y} h(x, y) = \frac{\partial^2}{\partial y \partial x} h(x, y). \quad (42)$$

A physicist would consider exceptions to this rule and that of Eq. 41 as pathological. Nonetheless it is perhaps wise to keep the possibility of these exceptions in the back of your mind (for possible use beyond this course). A rigorous — but accessible — treatment of multivariable calculus is given by R. Courant and J. Fritz, *Introduction to calculus and analysis II/1* (Springer, Berlin, 2000).

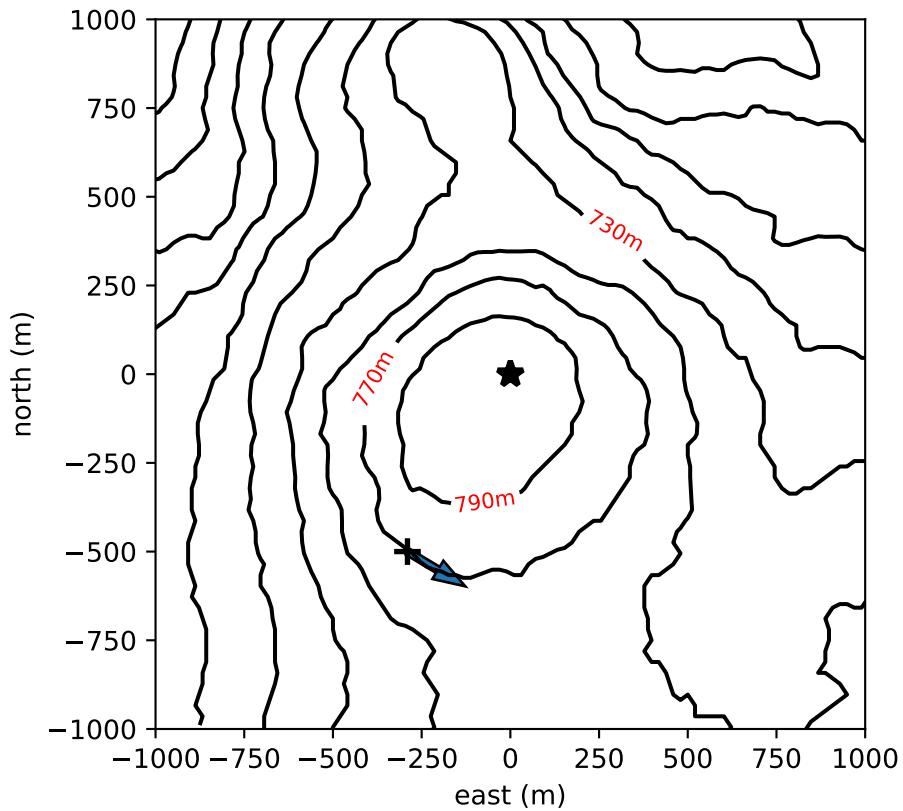
A stickler might say that we have ignored that  $P$  in the van der Waals gas law is actually a function of *more* than two variables i.e.  $P$  is a function of  $n$ ,  $b$ ,  $R$  and  $a$  in addition to  $V$  and  $T$ . Note that the reasoning that leads to triple product rule also holds for functions of more than two variables, *provided that when taking the three required derivatives, all other variables are held constant*. i.e. suppose that we had  $h(x, y, \text{other variables})$ , then we could write

$$\left( \frac{\partial x}{\partial y} \right)_{h, \text{other variables}} \left( \frac{\partial h}{\partial x} \right)_{y, \text{other variables}} \left( \frac{\partial y}{\partial h} \right)_{x, \text{other variables}} = -1, \quad (44)$$

meaning that as these three derivatives are taken, the “other variables” are held constant.

### For your interest only:

Admittedly, the mountain and snowstorm are a bit artificial. However, I’ve used real elevation data for [The Cabox](#), the highest mountain on the island of Newfoundland. Here is a contour plot of the elevation above sea level, centered around the Cabox peak (at about 810 m above sea-level, marked by  $\star$  below):



The + marker indicates the hypothetical initial location “on the south face”. The arrow indicates the initial direction one should travel to maintain the same elevation (770 m), as computed in part (a). This arrow is parallel with the 770 m contour line at the starting point, as we should expect. (I took a “step” to be 0.75 m; thus you may estimate from the separation of the contour lines that a gradient with magnitude on the order of 0.1 m/step is reasonable at the point of interest.)

## Breaking rails — answer

**Question.** Answer:

- (a) You are in essence being asked to apply the triple product rule. More specifically, you are given

$$\left(\frac{\partial \sigma}{\partial L}\right)_T = \frac{E}{L} \quad (45)$$

where  $\sigma := F/A$ .

Also, you are provided with

$$\left(\frac{\partial L}{\partial T}\right)_\sigma = \alpha L. \quad (46)$$

The derivative that we need to determine the change in stress with temperature for a fixed length is given by the triple product rule:

$$\left(\frac{\partial \sigma}{\partial T}\right)_L = - \left(\frac{\partial \sigma}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_\sigma \quad (47)$$

$$= -E\alpha. \quad (48)$$

So that we may estimate the change in stress  $\Delta\sigma$  for a given temperature change  $\Delta T$  for a rail of fixed length:

$$\Delta\sigma \approx \left(\frac{\partial \sigma}{\partial T}\right)_L \Delta T. \quad (49)$$

$$\approx -E\alpha\Delta T. \quad (50)$$

The rail will be stress free  $\sigma = 0$  at  $T = 38^\circ\text{C}$ . Let us take as an estimate of the coldest days  $\approx -40^\circ\text{C}$ , so that  $\Delta T \approx -78^\circ\text{C}$ , and thus

$$\Delta\sigma \approx -200 \times 10^9 \text{ Pa} \times 1.2 \times 10^{-5} \frac{1}{^\circ\text{C}} \times -78^\circ\text{C} \quad (51)$$

$$\approx 190 \text{ MPa} \quad (52)$$

(Note how the negative signs work out so that  $\Delta T < 0$  gives a *tensile* stress; i.e.,  $\sigma > 0$ .)

Assuming that the “coldest day” is  $\approx -40^\circ\text{C}$ , the tensile stress that the rail experiences will be  $\approx 190 \text{ MPa}$ .

It is an error to simply equate the two expressions for  $\Delta L$  given in the question, arriving at the incorrect expression:  $\Delta\sigma = E\alpha\Delta T$ , which is missing a negative sign. Equating these two expressions for  $\Delta L$  is unjustified; what is  $\Delta L$ ? After all the length doesn’t change.

An alternative to explicit use of the triple product rule, is to consider the two steps: 1) a thermal contraction at low temperatures, and then 2) an increase in tensile stress to restore the length. If you used this reasoning, or something similar, that is good — you have convinced yourself of the logic of the triple product rule, including the negative sign. (See the “you are on the south face of a mountain problem” and SITP’s Problem 1.46.)

(b) From [https://en.wikipedia.org/wiki/Ultimate\\_tensile\\_strength](https://en.wikipedia.org/wiki/Ultimate_tensile_strength) we see that although there is a wide variation in the ultimate tensile strength of steels, all are *greater than* our stress estimate from the previous part (including the uncertainty in estimating the “lowest temperature”). It is interesting to note that plain old cast iron would have insufficient strength  $\approx 200$  MPa. Steel was quite important in the development of railways (even before the use of continuously welded rail).

According to D. F. Cannon et al., “Rail defects: an overview”, *Fatigue & Fracture of Engineering Materials & Structures* **26**, 865–886 (2003), European Rail Standard grade 260 steel is typical of the steels used in many of the world’s rail systems, and has a ultimate tensile strength of 880 MPa.

Since we don’t see rail breaking all of the time in cold weather, all of this is reasonable. However, the closeness (with an order of magnitude), of the expected stresses to the maximum possible, suggest a few things:

- (a) inspection for defects in the steel is important, and
- (b) a more detailed analysis, considering the loading of trains on the rails is probably warranted.

Another thing to consider is the possibility of the steel permanently elongating — i.e., its **yield strength** is exceeded (for which the threshold stress is lower than for breakage). One might imagine that this elongation could be important once summer comes again — “stretched rail” may now be more susceptible to “sun-kinks”.

## Kitchener coordinates — answer

**Question.** Answer:

- (a) We have  $h(x, y)$  and want to know  $h$  as a function of  $r$  and  $y$ , so that we may differentiate as required. We may write  $x$  as a function of  $r$  and  $y$ , i.e.,  $x(r, y)$ , so that

$$h(x(r, y), y)$$

gives us  $h$  as a function of  $r$  and  $y$ . Now differentiate wrt  $y$ , while holding  $r$  constant, applying a variant of the chain rule to obtain:

$$\left(\frac{\partial h}{\partial y}\right)_r = \left(\frac{\partial h}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_r + \left(\frac{\partial h}{\partial y}\right)_x. \quad (53)$$

Since  $x = \sqrt{r^2 - y^2}$ , we have

$$\left(\frac{\partial x}{\partial y}\right)_r = -\frac{y}{\sqrt{r^2 - y^2}}, \quad (54)$$

so that

$$\left(\frac{\partial h}{\partial y}\right)_r = \left(\frac{\partial h}{\partial x}\right)_y \times \frac{-y}{\sqrt{r^2 - y^2}} + \left(\frac{\partial h}{\partial y}\right)_x,$$

(55)

and we cannot go any further without having an explicit form for  $h$ .

(b) (i) First evaluate the required partial derivatives appearing in Eq. 55; i.e.,

$$\left( \frac{\partial h}{\partial x} \right)_y = -\alpha 2xh(x, y) \quad (56)$$

and

$$\left( \frac{\partial h}{\partial y} \right)_x = -\beta 2yh(x, y). \quad (57)$$

Now substitute these derivatives into Eq. 55 to obtain:

$$\left( \frac{\partial h}{\partial y} \right)_r = -\alpha 2xh(x, y) \times \frac{-y}{\sqrt{r^2 - y^2}} + -\beta 2yh(x, y). \quad (58)$$

Recalling that  $x = \sqrt{r^2 - y^2}$ :

$$= \alpha 2yh(x, y) - \beta 2yh(x, y) \quad (59)$$

so that finally

$$\boxed{\left( \frac{\partial h}{\partial y} \right)_r = 2y(\alpha - \beta)h(x, y).} \quad (60)$$

(ii) Substituting  $x = \sqrt{r^2 - y^2}$  into  $h(x, y) = h_0 e^{-\alpha x^2 - \beta y^2}$  and remembering that  $x > 0$  gives

$$h(r, y) = h_0 e^{-\alpha r^2 - (\beta - \alpha)y^2}, \quad (61)$$

which may be differentiated wrt to  $y$  while holding  $r$  constant, to obtain

$$\boxed{\left( \frac{\partial h}{\partial y} \right)_r = 2y(\alpha - \beta)h(r, y),} \quad (62)$$

which is the same as Eq. 60, giving us some confidence in the answer to (a).

At this point I must call your attention to a common practice in thermodynamics, which is potentially confusing as it differs from normal mathematical convention. Specifically, the  $h$  as used in the expression  $h(x, y)$  is a *different function* of two variables than the  $h$  used in the expression  $h(r, y)$ . What do I mean? I mean that if I stick two numbers into one of these “function machines” that returns a single number — say the  $h$  in  $h(x, y)$  — this will *not* be the same number that I would obtain by sticking *the same* two numbers into the  $h$  which appears in  $h(r, y)$  (whereas the equality *would hold* in the normal convention of mathematics). However, by the thermodynamics convention (in this example)  $h(x, y) = h(r, y)$  where it is understood that  $x = \sqrt{r^2 - y^2}$  and it is generally not true that  $r = y$ . In the normal (sane) convention of mathematics, we would introduce a new function label, say  $g$ , so that  $h(x, y) = g(r, y)$ , whenever  $x = \sqrt{r^2 - y^2}$ .

Although the thermodynamic convention may seem confusing (even stupid), it does save time and is generally unproblematic, provided it is understood. Although I’m trying to be explicit about all of this, it is worth noting that had we swept the problem under the rug by simply using  $h$  in Eq.’s 60 and 62 instead of  $h(x, y)$  and  $h(r, y)$ , this difference might not be obvious at all. And in fact that is normally what is done in thermodynamics (note that even here we haven’t written the partial derivatives as explicit functions with arguments). Later in this answer I will discuss these differing conventions in a more physical context.

- (c) Only the quantities are different from part (a) ; the mathematics is the same. i.e., make the replacements:

$$\begin{aligned} h &\rightarrow U \\ x &\rightarrow V \\ y &\rightarrow T \\ r &\rightarrow P \end{aligned}$$

so that with  $U(V, T) = U(V(P, T), T)$  we obtain, in an analogous manner as Eq. 53:

$$\left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial U}{\partial T} \right)_V, \quad (63)$$

where the equation of state of the material gives  $V$  as a function of  $T$ ,  $P$  and the amount of material. e.g.,  $V = NkT/P$  for the ideal gas, which may be used to evaluate  $(\partial V/\partial T)_P$ .

- (d) From Eq. 63, we expect  $(\partial U/\partial T)_P = (\partial U/\partial T)_V$  if either (or both)  $(\partial U/\partial V)_T = 0$  or  $(\partial V/\partial T)_P = 0$ .

Physical speaking, although it is possible that  $(\partial V/\partial T)_P = 0$  — the most prominent example being water at 4 °C and 1 bar — we cannot expect this to happen generally. Nor would we normally expect that  $(\partial U/\partial V)_T = 0$ . However, as has been, or will be discussed in the lectures and notes, James Joule experimentally observed that for gases it is approximately true that  $(\partial T/\partial V)_U = 0$ , so that  $(\partial U/\partial V)_T = 0$  (make sure you understand this inference!). In fact we shall assume — justifying later from more fundamental principles — that  $(\partial U/\partial T)_P = (\partial U/\partial T)_V$  for ideal gases.

- (e) Given Eq. 63, we may replace  $(\partial V/\partial T)_P$  by  $-(\partial V/\partial P)_T(\partial P/\partial T)_V$  (i.e., the triple product rule) so that

$$\left( \frac{\partial U}{\partial T} \right)_P = - \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V + \left( \frac{\partial U}{\partial T} \right)_V, \quad (64)$$

as required. Variations on this usage of the triple product rule will occur repeatedly throughout this course.

Again, as in part (b) I point out that the function which gives  $U$  as a function of  $T$  and  $V$  is not — in the normal mathematical sense — the same function that gives  $U$  as a function of  $T$  and  $P$ . Underlying  $U(T, V) = U(T, P)$  (where  $U$  is a different function on both sides!) is the equation of state connecting  $T$ ,  $V$  and  $P$  (different “coordinates” for the same “location”, in the terminology of part (a)).

## Bursting balloons — answer

**Question.** Answer:

At 1 bar and 300 K, “hydrogen gas” is the *diatomic* molecule  $H_2$  (in the same way that “nitrogen and oxygen gases” consist of diatomic molecules at room temperature and pressure).

- (a) According to Archimedes’ principle, there will be a buoyant force equal to the weight of the air displaced from the surrounding atmosphere.

The total force, acting upwards on the balloon will be:

$$F_{\text{upwards}} = F_{\text{buoyant}} - F_{\text{weight of H}_2} - m_{\text{payload}}g \quad (65)$$

$$= \rho_{\text{air}} g V_{\text{balloon}} - \rho_{\text{H}_2} g V_{\text{balloon}} - m_{\text{payload}}g \quad (66)$$

$$= g V_{\text{balloon}} (\rho_{\text{air}} - \rho_{\text{H}_2}) - m_{\text{payload}}g. \quad (67)$$

(Note that we are ignoring the volume that the payload occupies, because the mass density of solids is much larger than that of gases at room temperature and pressure, i.e. a factor of  $\approx 10^3$ .)

The mass densities may be computed using the ideal gas law:

$$\rho = \frac{m}{V} \quad (68)$$

$$= \left\langle \frac{m}{n} \right\rangle n \frac{1}{V} \quad (69)$$

$$= \left\langle \frac{m}{n} \right\rangle \frac{PV}{RT} \frac{1}{V} \quad (70)$$

$$= \left\langle \frac{m}{n} \right\rangle \frac{P}{RT}. \quad (71)$$

$$(72)$$

Using this expression for the mass density in Eq. 67, gives:

$$F_{\text{upwards}} = \frac{gV_{\text{balloon}}P}{RT} \left( \left\langle \frac{m}{n} \right\rangle_{\text{air}} - \left\langle \frac{m}{n} \right\rangle_{\text{H}_2} \right) - m_{\text{payload}}g \quad (73)$$

$$(74)$$

The maximum payload corresponds to mechanical equilibrium,  $F_{\text{upwards}} = 0$ , and we rearrange, cancel the common  $g$  factors, and obtain:

$$m_{\text{payload}} = \frac{PV_{\text{balloon}}}{RT} \left( \left\langle \frac{m}{n} \right\rangle_{\text{air}} - \left\langle \frac{m}{n} \right\rangle_{\text{H}_2} \right) \quad (75)$$

and substitute the relevant quantities

$$= \frac{10^5 \text{ N/m}^2 \times 8 \text{ m}^3}{8.314 \text{ J/K/mol} \times 300 \text{ K}} \times (28.96 \text{ g/mol} - 2 \times 1.008 \text{ g/mol}) \times 10^{-3} \text{ kg/g} \quad (76)$$

$$= 8.64 \text{ kg}. \quad (77)$$

The maximum payload that the balloon can lift is 8.64 kg.

(Incorrectly using the mass of atomic hydrogen, instead of diatomic hydrogen, gives a wrong answer:  $m_{\text{payload}} \approx 8.965 \text{ kg}$ .)

- (b) Atmospheric pressure decreases with altitude. As the balloon rises, its pressure inside adjusts to match the external atmospheric pressure for mechanical equilibrium. Since the amount of gas in the balloon remains unchanged, the ideal gas law in the form:

$$V = \frac{1}{P} nRT \quad (78)$$

tells us that as  $P \downarrow$ , then  $V \uparrow$ . So the balloon increases in volume as it ascends.

(One might worry about the decrease of  $T$  with altitude. This has a smaller effect on  $V$  than the change in  $P$ . We know this because air density decreases with altitude and is proportional to  $P/T$ . Whereas  $V$  is *inversely* proportional to  $P/T$ , by Eq. 78. Lower air density is why long-distance aircraft flights are done at high altitude.)

As the volume of the balloon increases, its “envelope” material is stretched further and further. In the same way that a rubber band “snaps” when its elastic limit is reached, so will the balloon burst once its envelope has been stretched too much.

### For your interest only:

The numbers in this problem are typical for [weather balloons](#), which are an important part of the weather forecasting system. In this case, the “payload” consists of instruments to record temperature, pressure, humidity, etc..., as a function of altitude. If they transmit this information by radio, then they are also known as [radiosondes](#).

Both hydrogen and helium gases may be used in these balloons. But hydrogen is cheap and abundant — the only issue being its flammability.

## Floating cities on Venus — answer

[Question.](#) Answer:

- (a) Let’s *start* by interpreting “lifting power” as the weight of the maximum payload.

For Venus ( $\oplus$ ):

$$F_{\oplus} = g_{\oplus} V (\rho_{\oplus, \text{CO}_2} - \rho_{\text{air}}), \quad (79)$$

and for Earth ( $\oplus$ ):

$$F_{\oplus} = g V (\rho_{\oplus, \text{air}} - \rho_{\text{helium}}). \quad (80)$$

The 60% characterization suggests a fraction. i.e.,

$$\frac{F_{\oplus}}{F_{\oplus}} = \left( \frac{g_{\oplus}}{g} \right) \frac{(\rho_{\oplus, \text{CO}_2} - \rho_{\text{air}})}{(\rho_{\oplus, \text{air}} - \rho_{\text{helium}})}. \quad (81)$$

In the absence of any further information, I’ll assume that all gases are at the same temperature and pressure, so that by the ideal gas law,

$$\rho = \left\langle \frac{m}{n} \right\rangle \frac{P}{RT} \quad (82)$$

Substituting for the densities in Eq. 81 gives:

$$\frac{F_{\oplus}}{F_{\oplus}} = \left( \frac{g_{\oplus}}{g} \right) \left( \frac{\langle m/n \rangle_{\text{CO}_2} - \langle m/n \rangle_{\text{air}}}{\langle m/n \rangle_{\text{air}} - \langle m/n \rangle_{\text{He}}} \right) \quad (83)$$

The molecular masses can be found in a periodic table:<sup>27</sup>

$$\langle m/n \rangle_{\text{CO}_2} = (12.011 + 2 \times 15.999) \text{ g/mol} = 44.009 \text{ g/mol} \quad (84)$$

$$\langle m/n \rangle_{\text{air}} = 28.96 \text{ g/mol} \quad (85)$$

$$\langle m/n \rangle_{\text{He}} = 4.0026 \text{ g/mol} \quad (86)$$

On the [wikipedia page for Venus](#) we find that the surface gravity is  $0.904g$ , so that  $\frac{g_\oplus}{g} = 0.904$ .

Substituting these quantities into Eq. 81 gives:

$$\frac{F_\oplus}{F_\oplus} \approx 0.55. \quad (87)$$

If I (incorrectly) use  $\frac{g_\oplus}{g} = 1$  instead, then:

$$\frac{F_\oplus}{F_\oplus} \approx 0.60. \quad (88)$$

which must be the number referred to in the quote.

On the other hand, the ratio of the *weights* is probably not of primary interest, but rather ratio of the *masses* ( $F/g$ ) that can be lifted, on the respective planets. In that case ratio  $g_\oplus/g$  cancels out, so that:  $(F_\oplus/g_\oplus)/(F_\oplus/g) \approx 0.6$  (the Landis estimate). That must be what is meant by “lifting power”.

The assumption of the same pressure and temperature of CO<sub>2</sub> at Venus, as at the earth’s surface is rather drastic. Using the [wikipedia page for the atmosphere of Venus](#), an atmospheric pressure of 1 bar is reached at an altitude of about 50 km above its surface. The temperature at this altitude is on the order of 350 K. Assuming that the inside of the “aerostat” is to be maintained at 1 bar and 300 K, and that we are comparing with similar conditions on earth, the “lifting power” is now:

$$\frac{F_\oplus/m_\oplus}{F_\oplus/m_\oplus} = \frac{\langle m/n \rangle_{\text{CO}_2}^{\text{300 K}} - \langle m/n \rangle_{\text{air}}^{\text{350 K}}}{\langle m/n \rangle_{\text{air}} - \langle m/n \rangle_{\text{He}}} \quad (89)$$

which when evaluated gives

$$\frac{F_\oplus/m_\oplus}{F_\oplus/m_\oplus} \approx 0.35, \quad (90)$$

which is significantly less than the 60% number mentioned on wikipedia (!).

So although we can see where Landis’ estimate comes from, I conclude that the excerpt on wikipedia should definitely be qualified so as to indicate the assumptions regarding the temperature of the atmosphere of Venus.<sup>28</sup> It would also be helpful if a more precise description of “lifting power” was given.

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<sup>27</sup>I’ve assumed that the atmosphere of Venus is pure CO<sub>2</sub>. In fact, it is 96.5% carbon dioxide and 3.5% nitrogen by volume (<http://dx.doi.org/gc7b9n>). This composition corresponds to an average molar mass of 43.450 g/mol. Then  $\frac{F_\oplus}{F_\oplus} \approx 0.581$ .

<sup>28</sup>Some fairly recent information that I can find on the atmosphere of Venus is in the article:

<https://doi.org/10.1007/s11214-018-0525-2>

Figure 21 of this article confirms that 350 K is a good estimate for the temperature of Venus at an altitude with a pressure of 1 bar *in the equatorial region*. However, Fig. 16 shows that the atmospheric temperature decreases as one moves closer to the poles, at least at 55 km and higher (dropping by about 30 K). As a lower atmospheric temperature would be beneficial both to the lifting power and keeping the aerostat cool (for its occupants), it is possible that the Landis estimate corresponds to the polar regions. However, the polar regions have the disadvantage of reduced available solar power. Are there other relevant considerations?

(b) (i) Setting the lifting power of Eq. 79 equal to  $m_{\text{payload}}g_{\varphi}$  and rearranging to solve for the volume:

$$V = \frac{m_{\text{payload}}}{\rho_{\varphi} - \rho_{\text{air}}} \quad (91)$$

and using the ideal gas law

$$= \frac{m_{\text{payload}}}{\frac{P}{RT_{\varphi}} \left\langle \frac{m}{n} \right\rangle_{\varphi} - \frac{P}{RT_{\text{air}}} \left\langle \frac{m}{n} \right\rangle_{\text{air}}} \quad (92)$$

$$= \frac{m_{\text{payload}}R}{P} \frac{1}{\left( \frac{1}{T_{\varphi}} \left\langle \frac{m}{n} \right\rangle_{\varphi} - \frac{1}{T_{\text{air}}} \left\langle \frac{m}{n} \right\rangle_{\text{air}} \right)} \quad (93)$$

$$\approx \frac{10^5 \text{ kg} \times 8.314 \text{ J/K/mol}}{10^5 \text{ N/m}^2} \times \frac{1}{\left( \frac{1}{350 \text{ K}} \times 44 \times 10^{-3} \text{ kg} - \frac{1}{300 \text{ K}} \times 29 \times 10^{-3} \text{ kg} \right)} \quad (94)$$

$$\approx 290 \times 10^3 \text{ m}^3. \quad (95)$$

Recall our discussion from part (a) regarding the relevant temperature to use for Venus' atmosphere. If we set use 300 K instead of 350 K, we get  $V \approx 170 \times 10^3 \text{ m}^3$ .

The volume of the station to float in the atmosphere of Venus at an altitude of corresponding to an atmospheric pressure of 1 bar should be  $V \approx 290 \times 10^3 \text{ m}^3$ , assuming an atmospheric temperature of 350 K.

The lower volume for 300 K *could* be an acceptable answer, if some justification was given for assuming 300 K. (Again, see the discussion in part (a).)

(ii) There is one killer answer here: a comparison with the largest airship ever flown, the [Hindenberg](#), which had a volume of  $200 \times 10^3 \text{ m}^3$ , which is surprisingly close to our estimate. I think that this is a useful comparison, because the type of structure is quite similar to that which would be required for the Venus hotel. (These airships were quite similar to hotels in many ways.)

Venus has the problem of corrosion due to sulphuric acid clouds (∴ The Vega balloons that the Soviets used in the atmosphere of Venus (amazing experiments) were made using PTFE (teflon) for corrosion resistance. Apparently this material may be used for large tents; e.g., <https://alfaqaertents.com/ptfe-fiber-glass/> For that reason, I believe that another useful comparison to make is with the volume of large tents. A volume of  $V \approx 290 \times 10^3 \text{ m}^3$  corresponds to a  $L \times L \times L$  box with  $L \approx 66 \text{ m}$ . A reference that I consult for all my important research, the “Guinness Book of Superlatives: The original book of fascinating facts”, says that the largest tent ever made was for the annual show of the Royal Horticultural Society in London in 1951 (the equivalent to our CNE (?)), and had dimensions 95 m by 146 m (no height given). Thus we clearly know (or did know) how to make structures of linear dimensions  $\approx 100 \text{ m}$  out of fabric; i.e., similar to those required for our Venus hotel. (The airship comparison is a better one though.)

Unless it is blindingly obvious, I think that in order for your comparisons to be *useful*, you must explain why you consider them to be so.

## Dancin' raisins — answer

**Question.** Answer:

From the video description:

Before pouring all of the ginger ale out of the can, I measured that the can and its contents had a mass of 383 g. The empty can was measured to have a mass of 15 g. There was (supposedly) 355 mL of ginger ale in the can. The raisin package had about 70 raisins with a total mass of 30 g. The density of raisins is estimated from the literature, to be about 1.3 g/cm<sup>3</sup> (Karimi et al., Int. Agrophys., 2011, 25, 141-147). (I'll probably check this number for these type of raisins over the next few days — I don't have an accurate way to measure volume at home.) This density is not out of line with other references that I found.

- (a) We will make use of Archimedes' principle to compute the buoyant force on the raisins and attached CO<sub>2</sub>. For that we need the density of the ginger ale:

$$\rho_{ga} \approx \frac{383 \text{ g} - 15 \text{ g}}{355 \text{ cm}^3} \quad (96)$$

$$\approx 1.04 \text{ g/cm}^3 \times 10^3 \text{ kg/m}^3 \quad (97)$$

$$\approx 1040 \text{ kg/m}^3, \quad (98)$$

which is less dense than the estimated raisin density  $\rho_r = 1300 \text{ kg/m}^3$ , as expected, since the raisins sink in the ginger ale (without the help of CO<sub>2</sub>).

We will also need the density of CO<sub>2</sub> within the bubbles, which we will assume are at atmospheric pressure.<sup>29</sup>

$$\rho_b = \frac{m}{V} \quad (99)$$

$$= \frac{m}{n} \frac{n}{V} \quad (100)$$

and assuming the ideal gas law:

$$= \frac{m}{n} \frac{P}{RT}. \quad (101)$$

The quantity  $m/n$  is the molar mass of CO<sub>2</sub>, which is  $m/n \approx (12 + 2 \times 16) \text{ g/mol} \approx 44 \text{ g/mol}$ .

Thus

$$\rho_b \approx 0.044 \text{ kg/mol} \times \frac{10^5 \text{ Pa}}{\frac{\text{J}}{\text{mol} \cdot \text{K}}} \times \frac{1}{300 \text{ K}} \quad (102)$$

$$\approx 1.76 \frac{\text{kg}}{\text{m}^3}. \quad (103)$$

For the raisin to begin to float to the surface the buoyant force must exceed the force of gravity:

$$\vec{0} = \vec{F}_b + \vec{F}_g \quad (104)$$

$$0 = g\rho_{ga}(V_r + V_b) - gm_r - gm_b \quad (105)$$

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<sup>29</sup>The pressure increase from the top to the bottom of the glass of ginger ale is on the order of 1%.

Substitute  $V_r = m_r/\rho_r$  and  $v_b = m_b/\rho_b$ , to obtain:

$$0 = \rho_{ga} \left( \frac{m_r}{\rho_r} + \frac{m_b}{\rho_b} \right) - m_r - m_b \quad (106)$$

$$= m_r \left( \frac{\rho_{ga}}{\rho_r} - 1 \right) + m_b \left( \frac{\rho_{ga}}{\rho_b} - 1 \right). \quad (107)$$

Rearrange to give:

$$m_b = m_r \frac{\left( 1 - \frac{\rho_{ga}}{\rho_r} \right)}{\left( \frac{\rho_{ga}}{\rho_b} - 1 \right)} \quad (108)$$

and substitute the relevant quantities, to obtain:

$$m_b \approx 0.43 \times 10^{-3} \text{ kg} \times \frac{\left( 1 - \frac{1040}{1300} \right)}{\left( \frac{1040}{1.76} - 1 \right)} \quad (109)$$

$$\boxed{m_b \approx 1.5 \times 10^{-7} \text{ kg}} \quad (110)$$

- (b) There are many checks that can be made here. One check is an estimate of the volume of the CO<sub>2</sub> bubbles corresponding to the mass estimate:

$$V_b \approx \frac{m_b}{\rho_b} \quad (111)$$

$$\approx \frac{1.5 \times 10^{-7} \text{ kg}}{1.76 \text{ kg/m}^3} \quad (112)$$

$$\approx 8.5 \times 10^{-8} \text{ m}^3 \quad (113)$$

$$\approx 0.085 \text{ cm}^3 \quad (114)$$

whereas each raisin has a volume

$$V_r \approx \frac{0.43 \text{ g}}{1.3 \text{ g/cm}^3} \quad (115)$$

$$\approx 0.33 \text{ cm}^3, \quad (116)$$

so that  $V_r/V_b \approx 0.33/0.085 \approx 4$ .

Judging by the video, it seems that the volume of the raisins is significantly more than a factor of 4 larger than volume of the bubbles.

I suspect that the estimated raisin density might be off — it should be measured.

- (c) The amount of CO<sub>2</sub> that can be attached to the surface of the raisin should be proportional to its surface area, whereas the amount of CO<sub>2</sub> required for flotation should be proportional to its volume. Volume grows “more quickly” than surface area as an object gets bigger; i.e., consider a sphere:  $\frac{4}{3}\pi r^3$  versus  $4\pi r^2$ . Thus, smaller raisins are more likely to float, and would most likely give a better demo.

A student reported cutting raisins into smaller parts and observing that in fact the smaller raisins were better dancers.

(d) There is a well-known phenomena, in which *diet* coke cans float in water, whereas *regular* coke cans sink, the cause of which is the greater density of regular coke due to the dissolved sugar. Thus, in principle, assuming the same amount of carbonation, we might expect less CO<sub>2</sub> to be required for flotation of the raisins in regular ginger ale. The raisins might be expected to rise up more frequently than for diet ginger ale.

But do the numbers support a *significant* difference? The regular ginger ale in this experiment had a density of 1.04 g/cm<sup>3</sup>. That is not *too* different from the density of water 1.00 g/cm<sup>3</sup>.

Furthermore, a student pointed out that, due to the sugar, regular coke is more viscous than diet coke, and increased viscosity reduces the rate of bubble formation. Increased bubble formation in diet ginger ale would lead to better dancing raisins. A related anecdote is the [apparent dislike](#) by flight attendants of diet coke requests from passengers.

It is difficult, without a quantitative treatment, to decide if the differences in densities, viscosities, or other properties of the diet and regular ginger ales would be more significant in giving better dancing raisins. Experimentation is the most expedient approach here.

## Rally for Rayleigh — answer

[Question.](#) Answer:

(a) By Archimedes' principle, the upwards buoyant force on a body submersed in a fluid is:

$$F_b = g\rho_{\text{air}}V_h, \quad (117)$$

where  $\rho_{\text{air}}$  is the mass density of the air displaced by the volume of the human body  $V_h$ . The mass density of air may be estimated from the ideal gas equation:

$$\rho_{\text{air}} = \langle m/n \rangle_{\text{air}} \frac{P_{\text{air}}}{RT_{\text{air}}} \quad (118)$$

where the average molar mass of air is given by Problem 1.14 of Schroeder  $\langle m/n \rangle_{\text{air}} \approx 29 \text{ g/mol}$ .

We are asked for the ratio  $F_b/(m_hg)$ , where  $m_h$  is the mass of the human body. This ratio simplifies to:

$$\frac{F_b}{m_hg} = \frac{g\rho_{\text{air}}V_h}{m_hg} \quad (119)$$

$$= \frac{\rho_{\text{air}}}{\rho_h} \quad (120)$$

with the introduction of the mass density of the human body  $\rho_h$ .

Thus we do not need to *independently* know the average mass and volume for a person, but instead, the average mass density for a person:  $\rho_h \approx 1.1 \text{ g/mL}$ . [https://en.wikipedia.org/wiki/Body\\_composition](https://en.wikipedia.org/wiki/Body_composition) (There are many independent studies in support of this number. See for example Ref. [3].)

Combining Eq. s 118 and 119 gives:

$$\frac{F_b}{m_h g} = \frac{\rho_{\text{air}}}{\rho_h} \quad (121)$$

$$= \frac{1}{\rho_h} \langle m/n \rangle_{\text{air}} \frac{P_{\text{air}}}{R T_{\text{air}}} \quad (122)$$

$$\approx \frac{1}{1100 \text{ kg/m}^3} \times \frac{10^5 \text{ Pa}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times 300 \text{ K}} \times 0.029 \text{ kg/mol} \quad (123)$$

$$\boxed{\frac{F_b}{m_h g} \approx 1.1 \times 10^{-3}} \quad (124)$$

supporting the assertion that accounting for buoyancy when weighing yourself would be a bit silly.

- (b) If we can measure the temperature, pressure, volume and mass  $m$  of a gas, then — assuming the ideal gas equation is valid — we can compute the molar mass of a gas using:

$$\left\langle \frac{m}{n} \right\rangle = \frac{RT}{PV} m. \quad (125)$$

Applying this formula twice, assuming that the gases were measured in the same volume (inside the same “globe”), and cancelling common factors we obtain:

$$\frac{\langle m/n \rangle_{\text{O}_2}}{\langle m/n \rangle_{\text{H}_2}} = \frac{T_{\text{O}_2}}{P_{\text{O}_2}} m_{\text{O}_2} \frac{P_{\text{H}_2}}{T_{\text{H}_2}} \frac{1}{m_{\text{H}_2}} \quad (126)$$

Since the mass of single atom of oxygen is:

$$m_{\text{single atom of O}} = \langle m/n \rangle_{\text{O}_2} \frac{1}{2} \frac{1}{N_A} \quad (127)$$

and similarly for hydrogen, we have:

$$\boxed{\frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}} = \frac{T_{\text{O}_2}}{T_{\text{H}_2}} \frac{P_{\text{H}_2}}{P_{\text{O}_2}} \frac{m_{\text{O}_2}}{m_{\text{H}_2}}} \quad (128)$$

as required. Note that if we guarantee that we make the measurements of oxygen and hydrogen gases at the same temperature and pressure, we don't even need to know that temperature and pressure.

- (c) We may consult a modern compilation of molar masses [4] to find that

$$\langle m/n \rangle_O \approx 15.9994 \text{ mol}^{-1} \quad (129)$$

and

$$\langle m/n \rangle_H \approx 1.007,94 \text{ mol}^{-1} \quad (130)$$

from which we obtain:

$$\frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}} \approx 15.8734. \quad (131)$$

No, we do not expect the ratio  $\frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}}$  to be precisely 16.

There are several reasons why this ratio is not precisely 16 (a violation of Prout's hypothesis):

- (i) there are different isotopes and the atomic masses of unenriched samples will be weighted averages of natural abundances
  - (ii) the mass of a proton is not the same as the mass of a neutron
  - (iii) there are binding energies associated with nuclei i.e., the mass of an nucleus is not just the sum of the masses of its isolated constituent protons and neutrons,  $E = mc^2$ .
- (d) We are asked to determine the ratio of the buoyant force on the gas to the force of gravity:  $F_b/(m_{H_2}g)$ . Using Archimedes' principle:

$$\frac{F_b}{m_{H_2}g} = \frac{\rho_{\text{air}} V g}{m_{H_2}g} \quad (132)$$

The mass of the hydrogen gas can be computed using the ideal gas law:

$$m = \left\langle \frac{m}{n} \right\rangle_{H_2} n_{H_2} \quad (133)$$

$$= \left\langle \frac{m}{n} \right\rangle_{H_2} \frac{PV}{RT}. \quad (134)$$

Likewise, the density of air may also be computed using the ideal gas law and the known molar mass of air:

$$\rho_{\text{air}} = \left\langle \frac{m}{n} \right\rangle_{\text{air}} \frac{P}{RT} \quad (135)$$

Substituting both of these results into Eq. 132 and considering that  $P$  and  $T$  are the same and that globe displaces (approximately) the same volume of air that it holds as contents ("thin-walled"):

$$\frac{F_b}{m_{H_2}g} = \frac{\rho_{\text{air}}}{\rho_{H_2}} \quad (136)$$

$$\approx \frac{29 \text{ g/mol}}{2 \text{ g/mol}} \quad (137)$$

$$\frac{F_b}{m_{H_2}g} \approx 14 \quad (138)$$

Buoyancy may be a cause for concern!

- (e) The buoyant force depends on the volume of air displaced and the mass density of the surrounding air. Thus if the globe displaces the same volume of air during the two weighings and the atmospheric pressure and temperature are the same then the buoyant force in the filled and empty weighings will be the same and thus cancel when we take the weight differences, together with the weight of the globe itself.
- (f) I found some nice histograms of atmospheric pressure fluctuations at:  
[http://www.victoriaweather.ca/pressure\\_pdf.php?id=16](http://www.victoriaweather.ca/pressure_pdf.php?id=16)  
from which I guesstimate that pressure variations are on the order of 20 mbar = 2 kPa. (It would be better to look at histograms of the pressure differences between consecutive days.) A wide range of values would be considered acceptable answers to this question: 1 mbar → 100 mbar (?).

- (g) If the atmospheric pressure changes (as per previous part) and temperature remains constant (Rayleigh did his experiments in a cellar), then the air density will vary and thus the buoyant force. It will not cancel.

The buoyant force is given by:

$$F_b = gV\rho_{\text{air}} \quad (139)$$

$$= gV \left\langle \frac{m}{n} \right\rangle_{\text{air}} \frac{P}{RT} \quad (140)$$

So the error in the buoyant force due to fluctuations in pressure  $\delta P$  will be:

$$\delta F_b = gV \left\langle \frac{m}{n} \right\rangle_{\text{air}} \frac{1}{RT} \delta P \quad (141)$$

This error in the buoyant force shows up additively in the determination of the estimate of the force of gravity  $F_g$  on  $H_2$  (which we use to determine the mass). Thus:

$$\frac{\delta m}{m} = \frac{\delta F_b}{F_g} \quad (142)$$

$$= \frac{\delta F_b}{gm_{H_2}} \quad (143)$$

$$= \frac{gV \left\langle \frac{m}{n} \right\rangle_{\text{air}} \frac{\delta P}{RT}}{g \left\langle \frac{m}{n} \right\rangle_{H_2} \frac{PV}{RT}} \quad (144)$$

$$= \frac{\left\langle \frac{m}{n} \right\rangle_{\text{air}} \frac{\delta P}{P}}{\left\langle \frac{m}{n} \right\rangle_{H_2}}. \quad (145)$$

Substituting numbers gives:

$$\frac{\delta m}{m} \approx \frac{29 \text{ g/mol}}{2 \text{ g/mol}} \frac{20}{1000} \quad (146)$$

$$\frac{\delta m}{m} \approx 0.3$$

(147)

(This number is of course dependent on the pressure variations that you assume.)

This relative error in the mass measurements then shows up in the mass ratio (there will be an error in the oxygen measurement as well, but it is less due to the larger molar mass).

This relative error would cause us to not be able to distinguish

$$\frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}} \approx 15.8734 \quad (148)$$

from

$$\frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}} \approx 16 \quad (149)$$

which would require a much better relative error  $\approx (16 - 15.8734)/16 \approx 0.01$ .

(h) Let's briefly restate the procedure: The weights of the primary and secondary globe are measured at the same time, on opposite sides of a balance, so that we obtain their difference. This weighing is done twice:

- 1) with gas in the primary globe, and then day or so later:
- 2) with "vacuum" in the primary globe.

The secondary globe is left sealed between these weighings. Its mass, volume and so-on remains constant between 1) and 2).

In 1) we measure:

$$\underbrace{m_p g + m_{H_2} g - F_{b_1}}_{\text{filled primary globe "weight"} } - \underbrace{[m_s g - F_{b_1}]}_{\text{secondary globe "weight"} } = m_p g + m_{H_2} g - m_s g \quad (150)$$

were  $p$  and  $s$  refer to the primary and secondary globes. Note that the buoyancy forces  $F_{b_1}$  cancel because the primary and secondary globes displace the same volume of air.

In 2) we measure:

$$\underbrace{m_p g - F_{b_2}}_{\text{empty primary globe "weight"} } - \underbrace{[m_s g - F_{b_2}]}_{\text{secondary globe "weight"} } = m_p g - m_s g \quad (151)$$

Again the buoyancy forces on the two globes  $F_{b_2}$  cancel, but they can be different from day 1 due to a different density of the surrounding air (due to temperature and/or pressure variations).

Differencing the results from day 1 and 2 (Eq.'s 150 and 151):

$$\underbrace{m_p g + m_{H_2} g - m_s g}_{\text{day 1}} - \underbrace{[m_p g - m_s g]}_{\text{day 2}} = m_{H_2} g, \quad (152)$$

giving us  $m_{H_2}$ , free from the influence of varying buoyancy between the days  $\square$ .

- (i) The key point is that removing the oxygen from air does *not* give pure nitrogen. Recall Problem 1.14 from Schroeder (a suggested problem): *Calculate the mass of a mole of dry air, which is a mixture of  $N_2$  (78% by volume),  $O_2$  (21%), and argon (1%).* from which we obtained the average molar mass of air: 29 g/mol. But argon was unknown when Rayleigh began his experiments.

After removing oxygen from air we will be left with nitrogen *and* argon (and some trace gases such as  $CO_2$  which are not quantitatively important here).

What will the average molar mass of the nitrogen argon mixture be?

Taking molar masses from a modern compilation [4]:

element	molar mass (g/mol)
N	14.0067
A	39.948

we get:

$$\left\langle \frac{m}{n} \right\rangle_{N_2} = 2 \times 14.0067 \text{ g/mol} \quad (153)$$

$$= 28.0134 \text{ g/mol} \quad (154)$$

and for air with oxygen removed

$$\left\langle \frac{m}{n} \right\rangle_{\text{N}_2} = \frac{28.0134 \text{ g/mol} \times 0.78 + 39.948 \text{ g/mol} \times 0.01}{0.78 + 0.01} \quad (155)$$

$$= 28.16 \text{ g/mol.} \quad (156)$$

Rayleigh detected this (unexpected) small mass difference  $\approx 0.5\%$  (using the same techniques as he did for the oxygen to hydrogen mass ratio).

But here is the key thing (a moral of the tale?). Rayleigh followed up on this discrepancy, even writing a letter to Nature asking for help [5]:

I am much puzzled by some recent results as to the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values.

Eventually, together with Ramsay, he was able to isolate and study the properties of this previously unknown element, argon — for which he was [awarded the Nobel Prize](#). As attributed to Isaac Asimov (possibly apocryphal):

The most exciting phrase to hear in science, the one that heralds new discoveries, is not “Eureka” (I found it!) but “That’s funny ...”

### For your interest:

Rayleigh's presents his experiments on the nitrogen to oxygen atomic mass ratio in Ref. 's [6] and [7]. Note that “Rayleigh” is a peerage title; “Strutt” was his name.

An [informative biography](#) of Rayleigh was written by his son.

### Nothing is perfect — answer

**Question.** Answer:

- (a) On the previous test, we assumed that the ideal gas equation was valid, to obtain:

$$r_{\text{assuming ideal}} = \frac{m_{\text{O}_2}}{m_{\text{H}_2}} \quad (157)$$

Let us rewrite the RHS *without* the ideal gas assumption:

$$\frac{m_{\text{O}_2}}{m_{\text{H}_2}} = \frac{n_{\text{O}_2} \left\langle \frac{m}{n} \right\rangle_{\text{O}_2}}{n_{\text{H}_2} \left\langle \frac{m}{n} \right\rangle_{\text{H}_2}} \quad (158)$$

$$= \frac{n_{\text{O}_2}}{n_{\text{H}_2}} \frac{m_{\text{single atom of O}}}{m_{\text{single atom of H}}} \quad (159)$$

$$= \frac{n_{\text{O}_2}/V}{n_{\text{H}_2}/V} r_{\text{actual}} \quad (160)$$

We can rearrange to obtain an expression for what the problem statement asks for

$$\frac{r_{\text{actual}}}{r_{\text{assuming ideal}}} = \frac{n_{\text{H}_2}/V}{n_{\text{O}_2}/V}. \quad (161)$$

The quantities  $n_{\text{O}_2}/V$  and  $n_{\text{H}_2}/V$  are called **molar densities**. We can compute their values for a specific gas at a given temperature and pressure using the truncated virial expansion (e.g., Problem 1.17 of SITP):

$$PV = nRT \left( 1 + \frac{B(T)}{(V/n)} \right). \quad (162)$$

where the temperature dependent  $B(T)$  is specific to the gas concerned.

Let us write this equation in terms of molar density of the gas ( $=: x$ ):

$$x_{\text{ideal}} = x(1 + xB(T)) \quad (163)$$

where  $x_{\text{ideal}} := P/RT$ .

Rearranging gives a quadratic in  $x$ :

$$0 = B(T)x^2 + x - x_{\text{ideal}}. \quad (164)$$

Let us rewrite using the dimensionless variables:  $\alpha := x/x_{\text{ideal}}$  and  $\beta := B(T)x_{\text{ideal}}$ :

$$0 = \beta\alpha^2 + \alpha - 1 \quad (165)$$

which has the standard solutions:

$$\alpha = \frac{-1 \pm \sqrt{1 + 4\beta}}{2\beta} \quad (166)$$

As mentioned in the problem statement, approximations are fine, even encouraged! Thus, since  $|\beta| \ll 1$  we make use of the Taylor expansion:

$$\sqrt{1 + 4\beta} \approx 1 + \frac{1}{2}(4\beta) - \frac{1}{8}(4\beta)^2 + \dots \quad (167)$$

substituting it into Eq. 166, selecting the +ve root, so that:

$$\alpha \approx \frac{1}{2\beta} \left( \frac{1}{2}(4\beta) - \frac{1}{8}(4\beta)^2 + \dots \right) \quad (168)$$

$$\approx 1 - \beta + \dots \quad (169)$$

Converting back to the “dimensionfull” variables (using  $\alpha := x/x_{\text{ideal}}$ ,  $\beta := B(T)x_{\text{ideal}}$ , and  $x := n/V$ ):

$$\frac{n}{V} = \frac{P}{RT} \left( 1 - B(T) \frac{P}{RT} \right) \quad (170)$$

We may use this result for the molar densities in Eq. 161, to obtain:

$$\frac{r_{\text{actual}}}{r_{\text{assuming ideal}}} \approx \frac{1 - B_{\text{H}_2} \frac{P}{RT}}{1 - B_{\text{O}_2} \frac{P}{RT}} \quad (171)$$

$$\approx 1 - B_{\text{H}_2} \frac{P}{RT} + B_{\text{O}_2} \frac{P}{RT} \quad (172)$$

$$\approx 1 + \frac{P}{RT} (B_{\text{O}_2} - B_{\text{H}_2}). \quad (173)$$

Substituting numbers gives:

$$\frac{r_{\text{actual}}}{r_{\text{assuming ideal}}} \approx 1 + \frac{10^5 \text{ J/m}^3}{8.314 \text{ J/mol/K} \times 285 \text{ K}} (-1.91 - 1.40) \times 10^{-5} \text{ m}^3/\text{mol} \quad (174)$$

$$\approx 1 - 0.0014 \quad (175)$$

$$\frac{r_{\text{actual}}}{r_{\text{assuming ideal}}} \approx 0.9986$$

(176)

In words: assuming ideal gases gives a fractional error on the order of  $10^{-3}$ .

- (b) Your reasoning here is more important than your answer. We really have to consider the error in the context of Rayleigh's goal: checking whether or not  $m_{\text{single atom of O}}/m_{\text{single atom of H}} = 16$ .

In reality  $m_{\text{single atom of O}}/m_{\text{single atom of H}}/16 \approx 15.8734/16 \approx 0.992$ . This is a fractional difference of order  $10^{-3} \rightarrow 10^{-2}$ . That is not *too* much different from the fractional error in using the ideal gas assumption that we found in the previous part. So do we have to account for the non-ideal gas behaviour? Probably not for the purposes of concluding  $m_{\text{single atom of O}}/m_{\text{single atom of H}} \neq 16$ . But we are reaching that conclusion based on modern, well-known virial coefficients. It is worth noting that Rayleigh *did* attempt to correct for the non-ideal gas behaviour (i.e., “Professor Morley’s ratio of volumes” in Ref. [7]).

### For your interest only:

The virial coefficients for  $\text{O}_2$  and  $\text{H}_2$  given in the problem statement are from Ref. [8].

## Method of mixtures — answer

### Question.

Answer: We assume that no heat flows out of or into the mixture so that the heat that flows into the cold water is the same as the heat that leaves the hot water.

$$Q_{\text{cold water}} = -Q_{\text{hot water}}. \quad (177)$$

Since the only work that can be done is expansion/compression work against the surrounding constant pressure atmosphere at 1 bar, differences in enthalpies give us the heat flows, so that Eq. 177 becomes:

$$H_c(T) - H_c(0^\circ\text{C}) = H_h(100^\circ\text{C}) - H_h(T) \quad (178)$$

where  $T$  is the final temperature of the mixture, and  $h$  and  $c$  indicate the “hot” and “cold” water respectively. Let us rewrite in terms of  $H$  normalized by mass (an intensive quantity):

$$m_c \left( \frac{H(T)}{m} - \frac{H(0^\circ\text{C})}{m} \right) = m_h \left( \frac{H(100^\circ\text{C})}{m} - \frac{H(T)}{m} \right) \quad (179)$$

and rearranging gives:

$$\frac{H(T)}{m} (m_c + m_h) = m_h \frac{H(100^\circ\text{C})}{m} + m_c \frac{H(0^\circ\text{C})}{m} \quad (180)$$

Although it is not necessary, it simplifies things a bit if we adopt the convention that  $H(0^\circ\text{C}) = 0$ , so that:

$$\frac{H(T)}{m}(m_c + m_h) = m_h \frac{H(100^\circ\text{C})}{m} \quad (181)$$

The simplest (but inaccurate) model of water would be that of a constant temperature-independent heat capacity, with corresponding enthalpy:

$$H(T) \approx \frac{T}{100^\circ\text{C}} H(100^\circ\text{C}) \quad (182)$$

where  $T$  should be taken in  $^\circ\text{C}$ . Substituting into Eq. 181 gives:

$$T \approx \frac{m_h}{m_c + m_h} 100^\circ\text{C} \quad (183)$$

So the general strategy of the “method of mixtures” indicates that in order to get  $75^\circ\text{C}$  we should mix a mass of hot water  $m_h$  and cold water  $m_c$  such that  $m_h/(m_c + m_h) = 0.75$ .

The question is: what is the temperature of this mixture when using the *real* temperature dependence of the enthalpy?

Rearranging Eq. 181 gives:

$$H(T) = \frac{m_h}{m_c + m_h} H(100^\circ\text{C}) \quad (184)$$

and substituting the relevant numbers gives:

$$H(T) \approx 0.75 \times 419.105 \text{ kJ} \quad (185)$$

$$\approx 314.329 \text{ kJ}. \quad (186)$$

Examination of the table of enthalpies indicates this value of enthalpy between  $T = 75.05^\circ\text{C}$  and  $75.10^\circ\text{C}$ . In other words an error of between  $0.05^\circ\text{C}$  and  $0.10^\circ\text{C}$ . To refine this estimate using the table we could use some form of interpolation between these two temperatures.

Alternately, with a simple python program and the provided enthalpy function, we can compute the temperature using “root finding”:

```

1 import scipy.optimize as so
2 from liquid_water_enthalpy import liquid_water_enthalpy as enthalpy
3
4 if __name__ == "__main__":
5     t_desired = 75.0
6     def f(x): return (t_desired / 100 * enthalpy(100) - enthalpy(x))
7     t_actual = so.brentq(f, 0.1, 99)
8     print("actual temperature: ", t_actual)
9     print("actual error: ", t_actual-t_desired)

```

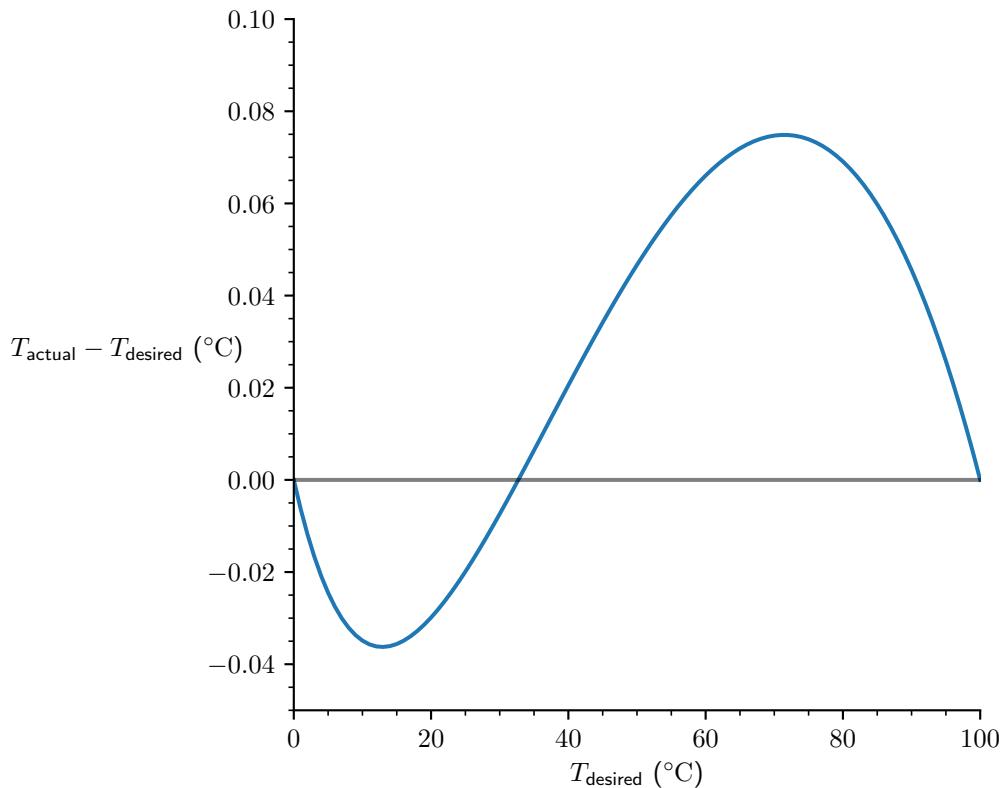
which gives:  $T_{\text{actual}} \approx 75.07^\circ\text{C}$ . Thus:

Calibration by the method of mixtures at 75 °C gives a thermometer scale that would read too low by  $\approx 0.074$  °C.

Incidentally, I'm not sure that any sort of percent or fractional error characterization makes sense, at least using the °C scale, as its zero is somewhat arbitrary; i.e., why should an error of 0.1 °C be more significant near 0 °C as compared to 100 °C?

### For your interest only:

It is straightforward to compute the error over the entire relevant temperature range:



It is surprising and interesting that at around 30 °C the error goes to zero. But I don't think that there is any deep significance in this occurrence.

The excellent book by Chang [9] discusses the early history of thermometer calibration by the method of mixtures.

### Jake braking the big rigs — answer

**Question.** Answer:

- (a) As suggested by Problem 1.37 of SITP, in normal operation air is adiabatically compressed

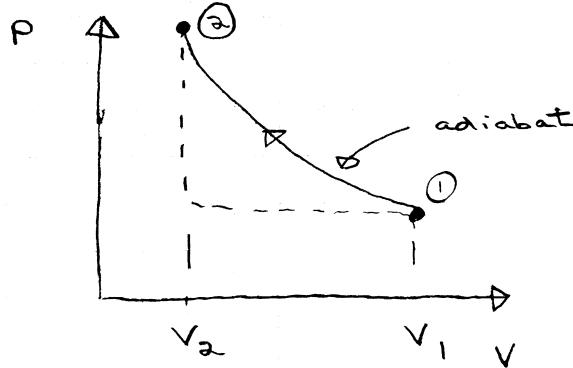
in one of the “strokes” of the four-stroke power generation cycle of the Diesel engine. It seems reasonable to assume that the compression is adiabatic in the Jake braking mode.

For the air we will assume that

$$C_V = \frac{f}{2} Nk \quad \text{with } f = 5. \quad (187)$$

and thus  $\gamma = 1 + 2/f = 7/5$ .

On an indicator diagram the compression stroke looks like:



where  $V_1/V_2 = 20$  (i.e., the compression ratio). The return from 2 to 1 is somewhat ill-defined — certainly the drop in pressure after the valve opens is not a “quasi-static” process. And the return of the piston back to  $V_1$  while the chamber is filling at  $P_1$ , doesn’t contribute to braking (the atmospheric pressure is the same on both sides of the piston).

We want to know the work done on the gas in compressing the gas in the compression stroke.

By the first law

$$\Delta U = W + Q \quad (188)$$

and this is an adiabatic process ( $Q = 0$ ) so that

$$\Delta U = W. \quad (189)$$

Recall that for an ideal gas, energy is a function of temperature only, so that

$$\Delta U = C_V \Delta T \quad (190)$$

(Imagine the heat that flows in a hypothetical constant volume process — no work done — but the temperature is changed).

Writing  $\Delta T = T_2 - T_1$ , we have

$$W = C_V(T_2 - T_1) \quad (191)$$

$$= C_V T_1 \left( \frac{T_2}{T_1} - 1 \right) \quad (192)$$

From the notes, or SITP’s Eq. (1.38) (recalling  $f = 2/(\gamma - 1)$ ):

$$\frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{\gamma-1} \quad (193)$$

so that

$$W = C_V T_1 \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] \quad (194)$$

Substituting  $C_V = Nk/(\gamma - 1)$ , and recognizing that  $NkT_1 = P_1 V_1$ , gives:

$$W = \frac{P_1 V_1}{\gamma - 1} \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right]. \quad (195)$$

(Aside: an equally valid, perhaps better way to determine  $W$  is by integration:

$$W = - \int P dV \quad (196)$$

$$= - \int_{V_1}^{V_2} dV P_1 \left( \frac{V_1}{V} \right)^\gamma \quad (197)$$

$$= -P_1 V_1^\gamma \int_{V_1}^{V_2} dV V^{-\gamma} \quad (198)$$

$$= -P_1 V_1^\gamma \frac{V^{-\gamma+1}}{-\gamma+1} \Big|_{V_1}^{V_2} \quad (199)$$

$$= \frac{P_1 V_1}{\gamma - 1} \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right], \quad (200)$$

which agrees with Eq. 195, as it should.)

There is an interesting subtlety here though: the surrounding atmosphere helps push the piston in, contributing  $W = P_1(V_1 - V_2)$  towards the effort, so that the effective braking work is

$$W_{\text{brake}} = \frac{P_1 V_1}{\gamma - 1} \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] - P_1 V_1 (1 - V_2/V_1). \quad (201)$$

Make no mistake though:  $W$  as given by Eq. 195 is the work done on the gas — it's just not *all* done by slowing the truck. As we shall see below, neglecting the “atmospheric” contribution does not result in a large error.

The average braking power is:

$$\dot{W}_{\text{brake}} = \frac{W}{\Delta t} \quad (202)$$

where  $\Delta t$  is the time between successive compression strokes.

Let's denote the frequency of revolution of the crank shaft by  $F$  ( $= 2000$  rpm). We might expect  $\Delta t$  to be  $1/F$ , but write  $\Delta t = q/F$ , with either<sup>30</sup>  $q = 1$  or  $q = 2$ .

Thus, the braking power becomes:

$$\dot{W}_{\text{brake}} = \frac{F}{q} \left\{ \frac{P_1 V_1}{\gamma - 1} \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] - P_1 V_1 (1 - V_2/V_1) \right\}. \quad (203)$$

---

<sup>30</sup>Recall that Diesel operation is normally “four-stroke” and only one of those strokes involves adiabatic compression. The earliest and most straightforward implementation of Jake braking just adds “release” at the end of this one compression stroke. Thus  $\Delta t = 2/F$ , for this so-called “four-stroke” braking cycle. If, as more recently, *two* of the four strokes are used for compression and release then for this “two-stroke braking cycle”, as it is known,  $\Delta t = 1/F$ . To incorporate both cases into our formulae, we will write  $\Delta t = q/F$ , evaluating with  $q = 1$  or  $2$ , as appropriate.

To obtain the deceleration we equate the rate of change of kinetic energy with braking power:

$$\frac{d}{dt} \left( \frac{1}{2} mv_x^2 \right) = -\dot{W}_{\text{brake}} \quad (204)$$

$$mv_x \dot{v}_x = -\dot{W}_{\text{brake}} \quad (205)$$

and rearrange to obtain:

$$\dot{v}_x = -\frac{1}{mv_x} \dot{W}_{\text{brake}} \quad (206)$$

It is now just a matter of substituting the numbers into this expression and that of Eq. 203. Using, what I will call the “canonical” values:

$$m = 30,000 \text{ kg} \quad (207)$$

$$v_x = 50 \text{ km/hour} \times 10^3 \text{ m/km} \times 1/3600 \text{ hour/s} \quad (208)$$

$$F = 2000 \text{ rpm} \times 1/60 \text{ minutes/s} \quad (209)$$

$$q = 1 \quad (210)$$

$$V_1 = 15 \text{ litre} \times 10^{-3} \text{ m}^3/\text{litre} \quad (211)$$

$$P_1 = 10^5 \text{ N/m}^2 \quad (212)$$

$$V_1/V_2 = 18 \quad (213)$$

$$\gamma = 7/5 \quad (214)$$

I get

$$\boxed{\dot{v}_x \approx -0.58 \text{ m/s}^2} \quad (215)$$

If instead of  $W_{\text{brake}}$  I neglect the “push of the atmosphere”, and use  $W$ , as given by Eq. 195, I get  $\dot{v}_x \approx -0.69 \text{ m/s}^2$ . Both these decelerations should be halved for a “four-stroke” braking cycle ( $q = 2$ ).

(b) Obviously there are a multitude of possible “correct” answers to this question.

But there is one acceleration that is so overwhelmingly important to earthlings that we use it as a universal “scale”, namely  $g \approx 9.8 \text{ m/s}^2$ .

A braking deceleration of  $0.58 \text{ m/s}^2$  is a meagre  $0.06g$ . I don’t think that tells us much by itself (?). However, because so many accelerations are quoted as fractions of  $g$ , we will follow that convention in the following comparisons.

My choice for comparisons is:

### Aircraft braking

Although we all have experienced rapid decelerations in automobiles, those don’t typically occur over sustained periods. On the other hand, when airplanes brake after landing, we often experience a relatively high deceleration over a longer duration (because of their high initial speed).

The maximum braking deceleration that aircraft can typically achieve is  $\approx 0.5g$  (required in a rejected take-off scenario).

Landing on a short runway — say Toronto Island airport — you might typically experience  $\approx 0.35g$  after landing.

A deceleration of  $\approx 0.2g$  or less is considered desirable for passenger comfort.

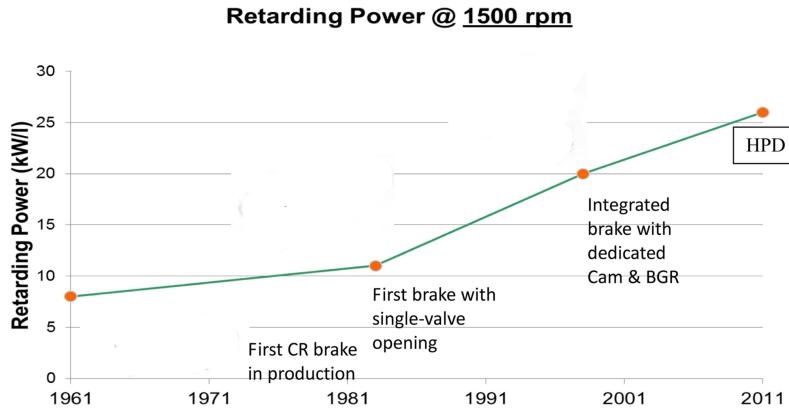
On the basis of these comparisons it appears likely that an estimate of  $0.06g$  for truck braking is not an over-estimate. It may be an under-estimate. It certainly neglects other contributions to the deceleration, such as friction, air resistance, and the use of the “service” brakes. In any case, our estimate is certainly not orders of magnitude off in either direction.

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## For your interest only:

How does our estimate for the braking power of Jake brakes compare to their actual performance? Our naive estimate seems a bit low, based on our deceleration comparisons.

The Jacobs company has summarized the improvements in braking power with time:



From N. Fuchs et al., “Development of a High Performance Two-Cycle Engine Brake for Medium and Heavy Duty Diesel Engines”, [SAE Int. J. Commer. Veh. 6, 34–46 \(2013\)](#). The vertical axis has units of kW/litre.

With the canonical values (replacing 2000 rpm by 1500 rpm), I get 5.6 kW/litre for a four-stroke braking cycle ( $k = 2$ ), which is satisfying close to the 1961 value of 8 kW/litre.

From my cursory reading — I’m not looking at becoming an expert on truck braking — it appears that the improvement over time has been partially due to the switch from 4-stroke to 2-stroke braking cycles. But by itself that only gives you a factor of two improvement.

A second reason for the increase is instructive: we assumed that the air that entered the piston chambers was at atmospheric pressure. But by deriving power from the flow through the exhaust using a turbine, air may be compressed *prior* to being drawn into the piston. So-called **turbocharging** is done for increased engine power, but a residual benefit is enhanced Jake braking. Analysis of the effect of turbocharging on Jake braking would take us well out of the realm of the fundamental principles of thermodynamics. However, it is interesting to note that the [wikipedia page for turbochargers](#) discusses **adiabatic efficiency**, “*a measure of a compressor’s ability to compress air without adding excess heat to that air*”. That’s not the best wording when we consider that isothermal compression is the ideal, which actually requires drawing heat *out* of the air as it is compressed.

Here is a nice [video](#) discussing Jake brakes from an experienced truck driver’s perspective.

## Compressed air energy storage — answer

**Question.** Answer:

I will assume a temperature independent heat capacity for air at temperatures not too far from room temperature, so for numerical evaluation we will use  $C_V \approx \frac{5}{2}Nk$ , from which it follows from  $C_P = C_V + Nk$  that  $\gamma := C_P/C_V \approx 7/5$ .

I will repeatedly use some results regarding adiabatic quasi-static expansion processes:

- (i) Since  $Q = 0$ , by the first law

$$\Delta U = C_V \Delta T. \quad (216)$$

- (ii) From the notes, if states labelled by 1 and 2 are connected by an adiabatic quasi-static process:

$$\frac{P_1}{P_0} = \left( \frac{V_1}{V_0} \right)^{-\gamma} \quad (217)$$

$$\frac{T_1}{T_0} = \left( \frac{V_1}{V_0} \right)^{-(\gamma-1)} \quad (218)$$

$$\frac{P_1}{P_0} = \left( \frac{T_1}{T_0} \right)^{\frac{\gamma}{\gamma-1}} \quad (219)$$

Note that any one of these equations may be derived from another, using the ideal gas law.

- (a) We may compute the pressure  $P_1$  after the initial compression using Eq. 219:

$$P_1 = P_0 \left( \frac{T_1}{T_0} \right)^{\frac{\gamma}{\gamma-1}} \quad (220)$$

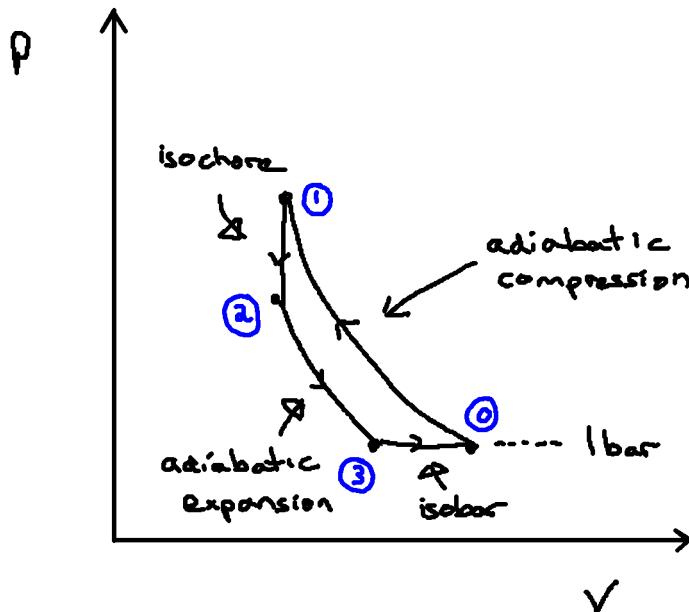
$$\approx 1 \text{ bar} \left( \frac{273 \text{ K} + 100 \text{ K}}{300 \text{ K}} \right)^{\frac{7/5}{7/5-1}} \quad (221)$$

$$\approx 1 \text{ bar} \left( \frac{373 \text{ K}}{300 \text{ K}} \right)^{7/2} \quad (222)$$

$P_1 \approx 2.14 \text{ bar}$

(223)

- (b) Indicator diagram:



I'll use the labels 0, 1, 2, 3 extensively in what follows.

- (c) The adiabatic expansion ( $2 \rightarrow 3$ ) begins at ambient temperature ( $T_2 = T_0$ ). Thus we will be able to determine  $T_3$  using Eq. 219, provided we have  $P_2$ , since  $P_3$  is just ambient pressure ( $= P_0$ ).

The isochoric process  $1 \rightarrow 2$  allows us to determine  $P_2$  using the ideal gas law:

$$P_2 = P_1 \frac{T_2}{T_1} \quad (224)$$

$$= P_1 \frac{T_0}{T_1} \quad (225)$$

and as in part (a),  $P_1$  is given by the step  $0 \rightarrow 1$ , so that by Eq. 220:

$$P_2 = P_0 \left( \frac{T_1}{T_0} \right)^{\frac{1}{\gamma-1}} \frac{T_0}{T_1} \quad (226)$$

$$= P_0 \left( \frac{T_1}{T_0} \right)^{\frac{1}{\gamma-1}} \quad (227)$$

Now considering the expansion process  $2 \rightarrow 3$ , we rearrange Eq. 219 into a form suitable for  $2 \rightarrow 3$  giving:

$$\frac{T_3}{T_2} = \left( \frac{P_3}{P_2} \right)^{\frac{\gamma-1}{\gamma}} \quad (228)$$

and recalling that  $P_3 = P_0$  and that  $T_2 = T_0$ :

$$T_3 = T_0 \left( \frac{P_0}{P_2} \right)^{\frac{\gamma-1}{\gamma}} \quad (229)$$

and we may substitute for  $P_2/P_0$  using Eq. 227:

$$T_3 = T_0 \left( \frac{T_1}{T_0} \right)^{\frac{-1}{\gamma-1} \frac{\gamma-1}{\gamma}} \quad (230)$$

$$= T_0 \left( \frac{T_1}{T_0} \right)^{-\frac{1}{\gamma}} \quad (231)$$

and substituting the relevant numbers:

$$T_3 = 300 \text{ K} \times \left( \frac{373 \text{ K}}{300 \text{ K}} \right)^{-\frac{1}{7/5}} \quad (232)$$

$$\approx 257 \text{ K} \quad (233)$$

$$T_3 \approx -16^\circ\text{C} \quad (234)$$

Any vapour water in the air (humidity) might condense and freeze, causing problems for the machinery (turbines) extracting work in the adiabatic expansion.

(Real CAES systems do not rely on a single adiabatic expansion, for precisely this reason.)

- (d) I'll start by ignoring an important subtlety here relating to the role of atmospheric pressure in "helping" and "hindering" the compression and expansion steps, but will return to this issue.

The work done on the air in quasi-static adiabatic compression ( $Q = 0$ ) is:

$$W_c = \Delta U \quad (235)$$

$$= C_V \Delta T \quad (236)$$

$$= C_V(T_1 - T_0). \quad (237)$$

Likewise, the work done on the air in expansion is:

$$W_e = C_V(T_3 - T_2) \quad (238)$$

and since  $T_2 = T_0$ ,

$$W_e = C_V(T_3 - T_0) \quad (239)$$

which will be negative, i.e.,  $T_3 < T_0$ , since the gas will be doing work in expansion.

So naively, the efficiency of energy recovery is

$$e = \frac{-W_e}{W_c} \quad (240)$$

$$= -\frac{T_3 - T_0}{T_1 - T_0} \quad (241)$$

and substituting numbers gives:

$$e \approx -\frac{257 \text{ K} - 300 \text{ K}}{373 \text{ K} - 300 \text{ K}} \quad (242)$$

$$e \approx 0.59. \quad (243)$$

Now let's make sure that this is the number that we actually want. There is no work done in the isochoric step  $1 \rightarrow 2$ . However, work *is* done by the gas in the isobaric  $3 \rightarrow 0$  step. Do we need to account for this work in the efficiency calculation? No, because this work is required to "make room" for the air in the atmosphere. We don't get to use it. This work done *by* the trapped gas in expanding goes into *doing* work on the atmosphere. And therein lies the issue with our naive approach to  $e$  – we've neglected the role of atmospheric pressure — it helps compress the gas but also must be overcome when expanding the gas.

Writing  $W = W_e + W_{atm}$ , where  $W_{atm} = -P_0\Delta V$ , we have for the electrical work that must be done

$$W_e = W - W_{atm} \quad (244)$$

$$= W + P_0\Delta V \quad (245)$$

where  $W$  remains unchanged; i.e., Eq.'s 239 and 237.

So for compression:

$$W_{e,c} = C_V(T_1 - T_0) + P_0(V_1 - V_0) \quad (246)$$

and for expansion:

$$W_{e,e} = C_V(T_3 - T_2) + P_0(V_3 - V_2). \quad (247)$$

Before evaluating  $e = -W_{e,e}/W_{e,c}$  we need to rewrite these expressions in a more suitable form, allowing the amount gas to "cancel", in a similar manner as  $C_V$  did in Eq. 240.

For compression:

$$W_{e,c} = Nk \frac{C_V}{Nk}(T_1 - T_0) + \frac{NkT_0}{V_0}(V_1 - V_0) \quad (248)$$

$$= Nk \left[ \frac{C_V}{Nk}(T_1 - T_0) + T_0 \left( \frac{V_1}{V_0} - 1 \right) \right] \quad (249)$$

$$= Nk \left[ \frac{C_V}{Nk}(T_1 - T_0) + T_0 \left( \left( \frac{T_1}{T_0} \right)^{\frac{-1}{\gamma-1}} - 1 \right) \right]. \quad (250)$$

Note that the [] bracketed expression is independent of the *amount* of gas. Numerical evaluation gives  $W_{e,c}/(Nk) \approx 56.5$  K.

For expansion, we have the same goal, namely to "factor out" the amount of gas:

$$W_{e,e} = Nk \frac{C_V}{Nk}(T_3 - T_2) + P_0(V_3 - V_2) \quad (251)$$

$$= Nk \frac{C_V}{Nk}(T_3 - T_0) + \frac{NkT_0}{V_0}(V_3 - V_1) \quad (252)$$

$$= Nk \left[ \frac{C_V}{Nk}(T_3 - T_0) + \frac{T_0V_1}{V_0}(V_3/V_1 - 1) \right]. \quad (253)$$

We don't know the volume ratios, but write them in terms of the known temperature ratios using Eq. 218. i.e.,

$$\frac{V_1}{V_0} = \left( \frac{T_1}{T_0} \right)^{\frac{-1}{\gamma-1}} \quad (254)$$

and

(255)

$$\frac{V_3}{V_1} = \frac{V_3}{V_2} \quad (256)$$

$$= \left( \frac{T_3}{T_2} \right)^{\frac{-1}{\gamma-1}} \quad (257)$$

$$= \left( \frac{T_3}{T_0} \right)^{\frac{-1}{\gamma-1}} \quad (258)$$

Substituting these results into Eq. 253, we get:

$$W_{e,e} = Nk \left[ \frac{C_V}{Nk} (T_3 - T_0) + T_0 \left( \frac{T_1}{T_0} \right)^{\frac{-1}{\gamma-1}} \left( \left( \frac{T_3}{T_0} \right)^{\frac{-1}{\gamma-1}} - 1 \right) \right] \quad (259)$$

as desired, namely that the bracketed term is independent of the amount of gas as with Eq. 250. Numerical evaluation gives  $W_{e,e}/(Nk) \approx -25.3 \text{ K}$ .

Using both Eq. 250 and 259, we may evaluate the efficiency, accounting for the role of atmospheric pressure in helping and hindering the expansion and compression steps:

$$e = \frac{-W_{e,e}}{W_{e,c}} \quad (260)$$

$$= \frac{-W_{e,e}/(Nk)}{W_{e,c}/(Nk)} \quad (261)$$

$$\approx 25.3/56.6 \quad (262)$$

$$\boxed{e \approx 0.45} \quad (263)$$

which is a bit smaller than the result ignoring atmospheric pressure  $e \approx 0.59$ .

- (e) Customizing the table at <https://doi.org/10.25318/2510006001-eng> to show only electricity energy usage (it shows *total* energy usage by default) we find that in 2015, the average Canadian household consumed an average of  $41.8 \times 10^9 \text{ J}$  annually, corresponding to  $E = 41.8 \times 10^9 \text{ J}/365 \approx 1.1 \times 10^8 \text{ J}$  in a day. (A commonly used unit for electrical energy usage is a “kilowatt hour” ( $\text{kW} \cdot \text{hr}$ ) which is  $\approx 3.6 \times 10^6 \text{ J}$ , so the average daily consumption  $E \approx 32 \text{ kW} \cdot \text{hr}$ , which is consistent with other sources that I found; e.g., <https://www.eia.gov/tools/faqs/faq.php?id=97&t=3>)

From the previous question part, we know  $W_{e,e}/(Nk)$ , so we equate  $E = -W_{e,e}$ , obtaining:

$$Nk = \frac{E}{-W_{e,e}/(Nk)} \quad (264)$$

which using the ideal gas law, we may rewrite as:

$$V_0 = \frac{T_0}{P_0} \frac{E}{(-W_{e,e}/(Nk))} \quad (265)$$

For the volume *after compression* we have:

$$V_1 = V_0 \left( \frac{T_1}{T_0} \right)^{\frac{-1}{\gamma-1}} \quad (266)$$

and substitute  $V_0$  as we have just determined (Eq. 265):

$$V_1 = \frac{T_0}{P_0} \frac{E}{(-W_{e,e}/(Nk))} \left(\frac{T_1}{T_0}\right)^{\frac{-1}{\gamma-1}} \quad (267)$$

which substituting quantities gives:

$$V_1 \approx \frac{300 \text{ K}}{10^5 \text{ J/m}^3} \frac{1.1 \times 10^8 \text{ J}}{25.3 \text{ K}} \left(\frac{373 \text{ K}}{300 \text{ K}}\right)^{\frac{-1}{7/5-1}} \quad (268)$$

$$V_1 \approx 7.6 \times 10^3 \text{ m}^3 \quad (269)$$

Alternately (but incorrectly), if one ignores the atmospheric pressure consideration, we obtain:

$$V_1 = \frac{T_0}{P_0} \frac{E}{(-W_e/(Nk))} \left(\frac{T_1}{T_0}\right)^{\frac{-1}{\gamma-1}} \quad (270)$$

which after substituting quantities gives:

$$V_1 \approx 1.7 \times 10^3 \text{ m}^3 \quad (271)$$

Let's consider the volume of a swimming pool for comparison, as that's a reasonably common residential excavation. The typical volume of such a pool might be about  $V \approx 4 \text{ m} \times 8 \text{ m} \times 2 \text{ m} \approx 64 \text{ m}^3$ . That's quite a bit smaller than our estimate, so at least as it stands, these particular numbers do not seem feasible. In *real* CAES systems, the pressure of the compressed air is much higher  $> 50$  bar reducing the volume requirements.

### For your interest:

The best general treatment of CAES that I have found is R. L. Jaffe and W. Taylor, *The physics of energy* (Cambridge University Press, Cambridge, United Kingdom ; New York, NY, 2018), which contains references to the specialist literature.

## Trangia trouble — answer

**Question.** Answer:

- (a) Compute  $\Delta H$  per mole of methanol ( $\text{CH}_3\text{OH}$ ) consumed. Use Hess' law and the enthalpies of formation (from the Reference Data for the course):

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad (272)$$

$$= \frac{1}{2} [2\Delta_f H(\text{CO}_2) + 4\Delta_f H(\text{H}_2\text{O(g)}) - 3\Delta_f H(\text{O}_2) - 2\Delta_f H(\text{CH}_3\text{OH(l)})] \quad (273)$$

$$\approx \frac{1}{2} [2 \times -393.51 \text{ kJ} + 4 \times -241.82 \text{ kJ} - 3 \times 0 \text{ kJ} - 2 \times -238.66 \text{ kJ}] \quad (274)$$

$$\approx -638.49 \text{ kJ} \quad (275)$$

(There is some question about whether or not we should take the heat of formation for *liquid* or *gaseous* water. See comments at end.)

So for  $m_{\text{CH}_3\text{OH}}$

$$Q = m_{\text{CH}_3\text{OH}} \frac{1}{\langle \frac{m}{n} \rangle_{\text{CH}_3\text{OH}}} \Delta H \quad (276)$$

To heat the water, we require:

$$Q = C_P \Delta T \quad (277)$$

$$= \frac{C_P}{m_{\text{H}_2\text{O}}} m_{\text{H}_2\text{O}} \Delta T \quad (278)$$

$$= \frac{C_P}{m_{\text{H}_2\text{O}}} \rho_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} \Delta T \quad (279)$$

Equating with Eq. 276 and rearranging we obtain:

$$m_{\text{CH}_3\text{OH}} = \frac{C_P}{m_{\text{H}_2\text{O}}} \times \frac{\rho_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} \Delta T \langle \frac{m}{n} \rangle_{\text{CH}_3\text{OH}}}{\Delta H} \quad (280)$$

and substituting the relevant numbers gives:

$$m_{\text{CH}_3\text{OH}} \approx \frac{4.2 \text{ J}/(\text{g°C}) \times 1 \text{ g/cm}^3 \times 250 \text{ cm}^3 \times (373 - 288) \text{ K} \times (12 + 4 + 16) \text{ g/mol}}{640 \times 10^3 \text{ J}} \quad (281)$$

$$\boxed{m_{\text{CH}_3\text{OH}} \approx 4.5 \text{ g}} \quad (282)$$

Note that I took the change in enthalpy based on the product water being in gaseous form, since without the pan present, the combustion flame does not show an evidence of the presence of liquid water (“steam” droplets). However, when the pan is placed directly over the flame, some water from combustion may condense on the bottom surface of the pan, contributing to heating. This condensation would be more significant when the pan is cold; i.e.,  $\ll 100^\circ\text{C}$ . If we assume that the product water is left in liquid form, as appropriate if the water condenses and contributes to the heating, then  $\Delta H \approx -726.51 \text{ kJ}$  per mol of methanol, and the amount of methanol required decreases to about  $m_{\text{CH}_3\text{OH}} \approx 4.0 \text{ g}$ . (For a general discussion of the water condensation issue, see the discussion of “high” and “low” heating values at [https://en.wikipedia.org/wiki/Heat\\_of\\_combustion](https://en.wikipedia.org/wiki/Heat_of_combustion).)

- (b) In the video, 17 g of methanol were required. To explain the discrepancy with our estimate, there are few candidates to consider:
- (i) incomplete heat transfer (hot air rises)
  - (ii) heating of the pan, the stove itself, etc...
  - (iii) evaporation of the water before boiling is reached.

All of these would contribute to *increasing* the amount of fuel required. The first candidate is difficult to estimate, but the contributions of the second two can be bounded to some extent.

## Shocking Schottky — answer

**Question.** Answer:

1. With a total of  $N$  spins, consisting of two groups:

- (i)  $N_\uparrow$  indistinguishable symbols, and
- (ii)  $N_\downarrow = N - N_\uparrow$  indistinguishable symbols,

there are  $N!/(N_\uparrow!N_\downarrow!) = \binom{N}{N_\uparrow}$  *distinguishable* ways that we can arrange these spins in a line (exactly same argument as for the stars and bars of the Einstein solid model). Thus the number of microstates corresponding to a given macrostate, namely the multiplicity, is  $\Omega = \binom{N}{N_\uparrow}$ .

Now let us consider an expression for the entropy  $S$ , in the case of a large number of spins:

$$\frac{S}{k} = \ln \Omega \quad (283)$$

$$= \ln \left( \frac{N!}{N_\uparrow!(N - N_\uparrow)!} \right) \quad (284)$$

$$= \ln N! - \ln N_\uparrow! - \ln(N - N_\uparrow)! \quad (285)$$

and apply Stirling's approximation ( $\ln n! \approx n \ln n - n$ , for large  $n$ ) so that

$$\frac{S}{k} \approx N \ln N - N - N_\uparrow \ln N_\uparrow + N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) + N - N_\uparrow \quad (286)$$

$$\approx N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow). \quad (287)$$

Note that the same expression with  $N_\uparrow$  replaced by  $N_\downarrow$  is also valid.

Now we must make the connection between  $N_\uparrow$  and the energy of the system. Let us suppose that  $\uparrow$  refers to the lower energy state (consistent with Fig. 3.7 of SITP), and that all spins in the lowest energy corresponds to  $U = 0$  (this choice is arbitrary). Then,

$$U = \epsilon(N - N_\uparrow) \quad (288)$$

$$= \epsilon N_\downarrow \quad (289)$$

When combined with Eq. 287 we now have the relationship between entropy and energy for the system (however remember the arbitrariness in the zero of energy). From this relationship we may now determine the temperature as a function of energy.

Using the chain rule:

$$\frac{d}{dU} \left( \frac{S}{k} \right) = \frac{1}{\epsilon} \frac{d}{dN_\downarrow} \left( \frac{S}{k} \right) \quad (290)$$

$$= \frac{1}{\epsilon} \left( -\ln N_\downarrow - \frac{N_\downarrow}{N_\downarrow} + \ln(N - N_\downarrow) + \frac{N - N_\downarrow}{N - N_\downarrow} \right) \quad (291)$$

$$= \frac{1}{\epsilon} \ln \left( \frac{N - N_\downarrow}{N_\downarrow} \right) \quad (292)$$

$$= \frac{1}{\epsilon} \ln (N/N_\downarrow - 1) \quad (293)$$

so that using the definition of temperature, we have:

$$T = \frac{1}{dS/dU} \quad (294)$$

$$= \frac{\epsilon}{k \ln(N/(U/\epsilon) - 1)}. \quad (295)$$

Rearrange to solve for  $U$  as a function of  $T$  (in preparation for differentiation to determine  $C$ ):

$$\ln\left(\frac{N}{U/\epsilon} - 1\right) = \frac{\epsilon}{kT} \quad (296)$$

$$\frac{N}{U/\epsilon} - 1 = e^{\epsilon/(kT)} \quad (297)$$

$$\frac{N}{U/\epsilon} = 1 + e^{\epsilon/(kT)} \quad (298)$$

$$U = N\epsilon(1 + e^{\epsilon/(kT)})^{-1}. \quad (299)$$

For low- $T$  this expression gives  $U \rightarrow 0$ , which makes sense — all spins will be in the lower energy state. At high- $T$ , we have  $U \rightarrow N\epsilon/2$ , which also makes sense — the spins will be in a 50/50% mixture of the two energy states.

Now we may determine the heat capacity:

$$C = \frac{dU}{dT} \quad (300)$$

$$= N\epsilon \times \frac{-1}{(1 + e^{\epsilon/(kT)})^2} \times e^{\epsilon/(kT)} \times \frac{-\epsilon}{k} \times \frac{1}{T^2} \quad (301)$$

$$= k \frac{\epsilon^2}{(kT)^2} \frac{e^{\epsilon/(kT)}}{(1 + e^{\epsilon/(kT)})^2} \quad (302)$$

Equivalently, if we multiply the numerator and denominator by a factor of  $e^{-2\epsilon/(kT)}$ :

$$\boxed{\frac{C}{Nk} = \left(\frac{\epsilon}{kT}\right)^2 \frac{e^{-\epsilon/(kT)}}{(1 + e^{-\epsilon/(kT)})^2}} \quad (303)$$

- At low- $T$ , the exponent  $-\epsilon/(kT)$  in Eq. 303 is a large negative number, so that  $|e^{-\epsilon/(kT)}| \ll 1$  and thus

$$\frac{C}{Nk} \approx \left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/(kT)}. \quad (304)$$

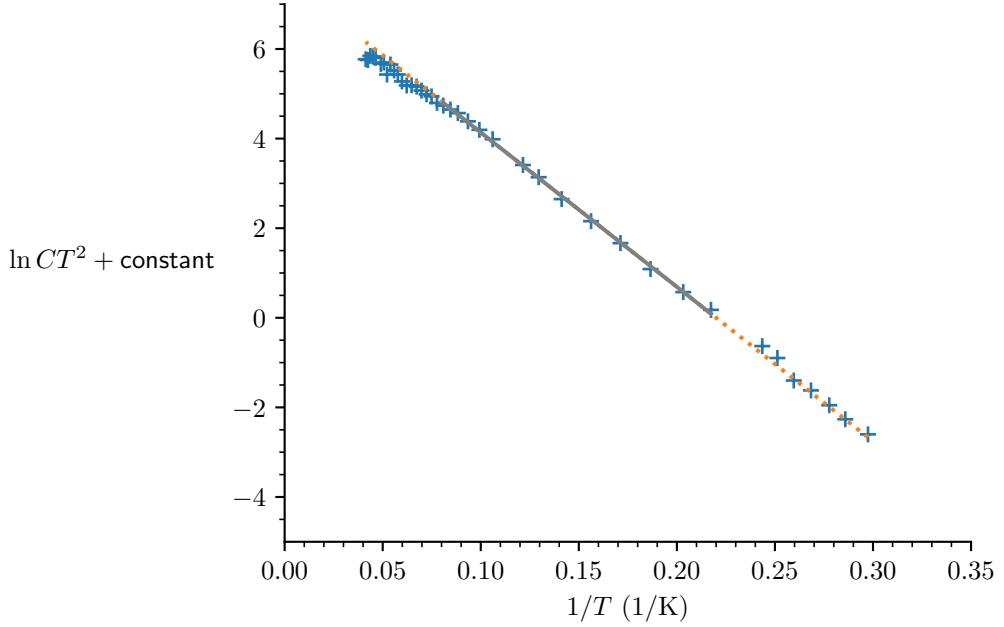
Rearrange slightly, to give

$$CT^2 = Nk \left(\frac{\epsilon}{k}\right)^2 e^{-\epsilon/(kT)}. \quad (305)$$

Take the  $\ln$  of both sides, giving:

$$\ln CT^2 = \ln \left(Nk \left(\frac{\epsilon}{k}\right)^2\right) - \frac{\epsilon}{kT}. \quad (306)$$

Thus, a plot of  $CT^2$  vs  $1/T$  will be a straight line with a slope of  $-\epsilon/k$ :



At the highest temperatures (to the left in the plot), there is a systematic deviation from the straight-line behaviour (as we might expect based on our approximation). At the lowest temperatures (to the right in the plot), the data seems noisier. Thus the data is fitted in the range  $0.08 \text{ K}^{-1} < 1/T < 0.23 \text{ K}^{-1}$  (indicated with grey line), giving a slope  $-34.5(3) \text{ K}$ . (The error has been estimated using the procedure at <https://stackoverflow.com/a/38957633>.) To get  $\epsilon$ :

$$\epsilon \approx -\frac{\epsilon}{k} \times -k \quad (307)$$

$$\approx 34.5(3) \text{ K} \times 1.38 \times 10^{-23} \text{ J/K} \times 6.24 \times 10^{18} \text{ eV/J} \quad (308)$$

$$\approx 2.97(3) \text{ meV} \quad (309)$$

Thus, if the heat capacity vs temperature is a Schottky peak, then the energy between the two levels is  $\boxed{\epsilon \approx 2.97(3) \text{ meV}}$ .

3. At high- $T$ ,

$$e^{-\epsilon/(kT)} \approx 1 \quad (310)$$

so that

$$\frac{C}{Nk} \approx \left(\frac{\epsilon}{kT}\right)^2 \frac{1}{4} \quad (311)$$

i.e.,  $C \propto 1/T^2$ .

In this high- $T$  regime a factor of 10 increase in  $T$  (e.g., 0.1 K to 1 K) corresponds to a factor of 100 decrease in heat capacity, which is roughly what is observed on the plot.

From Eq. 311, we have:

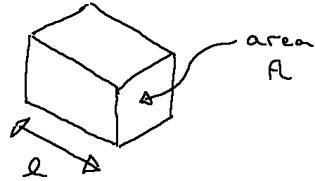
$$\log_{10} \frac{C}{Nk} = -2 \log_{10} T + \log_{10} \left( \left(\frac{\epsilon}{k}\right)^2 \frac{1}{4} \right), \quad (312)$$

so that the “slope” of the log-log plot in this high- $T$  regime is  $-2$ .

## Heat switch — answer

**Question.** Answer:

- (a) Let us define some geometric quantities for the Pb bridge:



Fourier's law of heat conduction

$$\dot{Q}_x = -\kappa_T A \frac{dT}{dx} \quad (313)$$

may be integrated over the length of the bridge to give:

$$\boxed{\dot{Q}_{H \rightarrow C} = \kappa_T A \frac{(T_H - T_C)}{\ell}} \quad (314)$$

for the heat flow from the hot to cold side of the bridge. Note that we have assumed a temperature-independent thermal conductivity  $\kappa_T$ .

- (b) From Fig. 3 and Table II of Ref. [12] for the *normal* state (not superconducting), the thermal resistivity at 2 K is estimated to be

$$\rho \approx 0.04 \frac{\text{cm} \cdot \text{K}}{\text{W}} \quad (315)$$

and thus

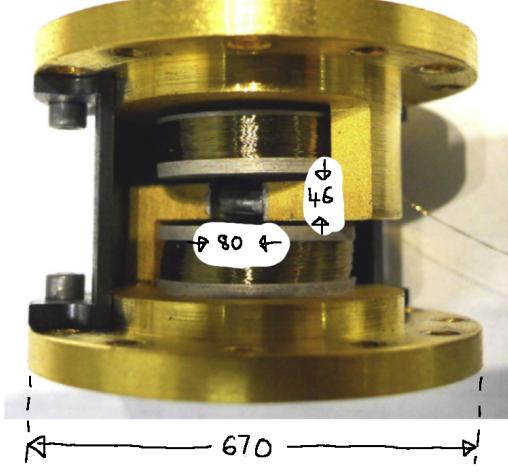
$$\kappa_T = \frac{1}{\rho} \quad (316)$$

$$\approx \frac{1}{0.04 \text{ cm} \cdot \text{K}} \frac{\text{W}}{\text{cm}} \times 10^2 \frac{\text{cm}}{\text{m}} \quad (317)$$

$$\approx 2500 \frac{\text{W}}{\text{m} \cdot \text{K}}, \quad (318)$$

which, incidentally, is quite high compared to the room temperature value  $\kappa_T \approx 35 \frac{\text{W}}{\text{m} \cdot \text{K}}$  (from [13]).

Here are some relevant measurements of the photograph of the heat switch from Ref. [14] in pixels (pix):



We are told in the paper (and video) that the width across is 38 mm. That sets the scale of the image and allows us to estimate the bridge dimensions.

It looks as if the bridge has been photographed from an angle at 45 degrees with respect to its length, and thus:

$$\ell \approx \sqrt{2} \times 80 \text{ pix} \times \frac{0.038 \text{ m}}{670 \text{ pix}} \quad (319)$$

$$\approx 6.4 \times 10^{-3} \text{ m} \quad (320)$$

and

$$A \approx \left( 46 \text{ pix} \times \frac{0.038 \text{ m}}{670 \text{ pix}} \right)^2 \quad (321)$$

$$\approx 6.8 \times 10^{-6} \text{ m}^2 \quad (322)$$

Substituting the numerical quantities into Eq. (b):

$$\dot{Q}_{H \rightarrow C} = \kappa_T A \frac{(T_H - T_C)}{\ell} \quad (323)$$

$$\approx 2500 \frac{\text{W}}{\text{m} \cdot \text{K}} \times 6.8 \times 10^{-6} \text{ m}^2 \times \frac{(2 \text{ K} - 0.3 \text{ K})}{6.4 \times 10^{-3} \text{ m}} \quad (324)$$

$$\boxed{\dot{Q}_{H \rightarrow C} = 4.5 \text{ W}} \quad (325)$$

(c) By the chain rule:

$$\frac{dT_H}{dt} = -\frac{\dot{Q}}{C(T)} \quad (326)$$

$$= -\frac{\kappa_T A}{\ell} \frac{(T_H - T_C)}{n\alpha T_H}. \quad (327)$$

Introduce a dimensionless temperature  $\tilde{T} = T_H/T_C$  and dimensionless time  $\tilde{t} = t/\tau$  where

$$\tau := \frac{T_c n \alpha \ell}{\kappa_T A} \quad (328)$$

so that we may write the rewrite Eq. 327 as:

$$\frac{d\tilde{T}}{d\tilde{t}} = -\frac{\tilde{T} - 1}{\tilde{T}} \quad (329)$$

Rearrange and integrate:

$$-\int d\tilde{t} = \int d\tilde{T} \frac{\tilde{T}}{\tilde{T} - 1} \quad (330)$$

$$-\tilde{t} = \int d\tilde{T} \frac{\tilde{T} - 1 + 1}{\tilde{T} - 1} \quad (331)$$

$$= \int d\tilde{T} \left[ 1 + \frac{1}{\tilde{T} - 1} \right] \quad (332)$$

$$= \left[ \tilde{T} + \ln(\tilde{T} - 1) \right] \Big|_{\tilde{T}_I}^{\tilde{T}_F} \quad (333)$$

$$\tilde{t} = \left[ \tilde{T} + \ln(\tilde{T} - 1) \right] \Big|_{\tilde{T}_F}^{\tilde{T}_I} \quad (334)$$

$$= \tilde{T}_I - \tilde{T}_F + \ln \left( \frac{\tilde{T}_I - 1}{\tilde{T}_F - 1} \right) \quad (335)$$

Returning to unscaled time

$$t = \tau \left[ \tilde{T}_I - \tilde{T}_F + \ln \left( \frac{\tilde{T}_I - 1}{\tilde{T}_F - 1} \right) \right] \quad (336)$$

and substituting values:

$$t \approx \frac{0.3 \text{ K} \times 250 \text{ g}/(63.5 \text{ g/mol}) \times 0.7 \times 10^{-3} \frac{\text{J}}{\text{mol} \cdot \text{K}^2} \times 6.4 \times 10^{-3} \text{ m}}{2500 \frac{\text{W}}{\text{m} \cdot \text{K}} \times 6.8 \times 10^{-6} \text{ m}^2} \times \left[ 2/0.3 - 1.1 + \ln \left( \frac{(2/0.3 - 1)}{(1.1 - 1)} \right) \right] \quad (337)$$

$$\boxed{t \approx 0.003 \text{ s}} \quad (338)$$

(d) Fourier's law applies at each cross-section along the length of the bridge:

$$\dot{Q}_x = -\kappa_T A \frac{dT}{dx} \quad (339)$$

but with a temperature-dependent thermal conductivity:

$$\dot{Q}_x = -DT^3 A \frac{dT}{dx}. \quad (340)$$

Integrating along the length gives:

$$\int_0^\ell dx = -\frac{DA}{\dot{Q}_x} \int_{T_H}^{T_C} dT T^3 \quad (341)$$

$$\ell = \frac{DA}{\dot{Q}_{\text{H} \rightarrow \text{C}}} \left( \frac{T_H^4 - T_C^4}{4} \right) \quad (342)$$

and rearranging gives:

$$\boxed{\dot{Q}_{H \rightarrow C} = \frac{DA}{4\ell}(T_H^4 - T_C^4)} \quad (343)$$

- (e) A numerical value of  $D$  can be determined from Fig. 3 of de Haas and Rademakers [12]. Specifically, at 2 K, the thermal resistivity is  $\rho \approx 0.5 \frac{\text{cm} \cdot \text{K}}{\text{W}}$ , and thus

$$\kappa_T \approx \frac{1}{\rho} \quad (344)$$

$$\approx \frac{1}{0.5 \frac{\text{cm} \cdot \text{K}}{\text{W}}} \times 10^2 \frac{\text{cm}}{\text{m}} \quad (345)$$

$$\approx 200 \frac{\text{W}}{\text{m} \cdot \text{K}}, \quad (346)$$

So with  $\kappa_T(T) = DT^3$ , we have

$$D \approx \frac{\kappa_T(T)}{T^3} \quad (347)$$

$$\approx \frac{200 \frac{\text{W}}{\text{m} \cdot \text{K}}}{(2 \text{ K})^3} \quad (348)$$

$$\approx 25 \frac{\text{W}}{\text{m} \cdot \text{K}^4} \quad (349)$$

And thus we may evaluate Eq. 343:

$$\dot{Q}_{H \rightarrow C} = \frac{DA}{4\ell}(T_H^4 - T_C^4) \quad (350)$$

$$= \frac{25 \frac{\text{W}}{\text{m} \cdot \text{K}^4} \times 6.8 \times 10^{-6} \text{ m}^2}{4 \times 6.4 \times 10^{-3} \text{ m}} ((2 \text{ K})^4 - (0.3 \text{ K})^4) \quad (351)$$

$$\boxed{\dot{Q}_{H \rightarrow C} \approx 0.11 \text{ W}} \quad (352)$$

(f)

$$\frac{dT_H}{dt} = -\frac{\dot{Q}_{H \rightarrow C}}{C(T)} \quad (353)$$

$$= -\frac{DA}{4\ell} \frac{(T_H^4 - T_C^4)}{n\alpha T_H} \quad (354)$$

Introduce a dimensionless temperature  $\tilde{T} := T_H/T_C$  and dimensionless time  $\tilde{t}/\tau$  where  $\tau := 4n\alpha\ell/(DAT_C^2)$ , so that Eq. 354 simplifies to:

$$\frac{d\tilde{T}}{d\tilde{t}} = -\frac{(\tilde{T}^4 - 1)}{\tilde{T}} \quad (355)$$

and may be integrated

$$-\int d\tilde{t} = \int d\tilde{T} \frac{\tilde{T}}{\tilde{T}^4 - 1} \quad (356)$$

$$-\tilde{t} = \frac{1}{4} \ln \left( \frac{\tilde{T}^2 - 1}{\tilde{T}^2 + 1} \right) \Big|_{\tilde{T}_I}^{\tilde{T}_F} \quad (357)$$

$$\tilde{t} = \frac{1}{4} \ln \left( \frac{(\tilde{T}_I^2 - 1)}{(\tilde{T}_I^2 + 1)} \frac{(\tilde{T}_F^2 + 1)}{(\tilde{T}_F^2 - 1)} \right) \quad (358)$$

Reverting to the original unscaled variables for numerical evaluation:

$$t = \tau \frac{1}{4} \ln \left( \frac{(\tilde{T}_I^2 - 1)}{(\tilde{T}_I^2 + 1)} \frac{(\tilde{T}_F^2 + 1)}{(\tilde{T}_F^2 - 1)} \right) \quad (359)$$

$$= \frac{4n\alpha\ell}{DAT_C^2} \frac{1}{4} \ln \left( \frac{(\tilde{T}_I^2 - 1)}{(\tilde{T}_I^2 + 1)} \frac{(\tilde{T}_F^2 + 1)}{(\tilde{T}_F^2 - 1)} \right) \quad (360)$$

$$\approx \frac{4 \times 250 \text{ g}/(63.5 \text{ g/mol}) \times 0.7 \times 10^{-3} \frac{\text{J}}{\text{mol} \cdot \text{K}^2} \times 6.4 \times 10^{-3} \text{ m}}{25 \frac{\text{W}}{\text{m} \cdot \text{K}^4} \times 6.8 \times 10^{-6} \text{ m}^2 \times (0.3 \text{ K})^2} \times \frac{1}{4} \ln \left( \frac{((2/0.3)^2 - 1)}{((2/0.3)^2 + 1)} \frac{(1.1^2 + 1)}{(1.1^2 - 1)} \right) \quad (361)$$

$$t \approx 2.66 \text{ s} \quad (362)$$

- (g) There is a dramatic difference (three orders of magnitude) between the times for the hot side to come to within 10% of  $T_C$  when the switch the thermal switch is in conducting versus non-conducting state.

The switch is operating as expected.

## Kelvin was a flat earther — answer

**Question.** Answer:

- (a) Apply the constraint:

$$1 = \int_{-\infty}^{\infty} dx \frac{A}{\sqrt{t}} e^{-\frac{x^2}{4Kt}}. \quad (363)$$

Make a change of variables:  $\alpha = x/\sqrt{4Kt}$  and  $dx = d\alpha\sqrt{4Kt}$ , so that:

$$1 = \int_{-\infty}^{\infty} d\alpha \sqrt{4Kt} \frac{A}{\sqrt{t}} e^{-\alpha^2}. \quad (364)$$

Rearranging and simplifying gives:

$$A = \frac{1}{\sqrt{4K}} \left[ \int_{-\infty}^{\infty} d\alpha e^{-\alpha^2} \right]^{-1} \quad (365)$$

Note that  $A$  is independent of  $t$ .

So, the problem is to evaluate

$$G := \int_{-\infty}^{+\infty} d\alpha e^{-\alpha^2} \quad (366)$$

Note that  $e^{-\alpha^2}$  has no elementary anti-derivative. But here is a nice trick:<sup>31</sup> introduce a second coordinate  $y$  and instead of  $G$  consider  $G^2$ :

$$G^2 = \int_{-\infty}^{+\infty} dx e^{-x^2} \int_{-\infty}^{+\infty} dy e^{-y^2} \quad (367)$$

$$= \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy e^{-(x^2+y^2)} \quad (368)$$

and now switch to polar coordinates, recognizing that the integrand only has an  $r$  (and not  $\phi$ ) dependence:

$$G^2 = \int_0^{\infty} dr 2\pi r e^{-r^2}. \quad (369)$$

This integral may be readily evaluated. Make a change of variables  $u = r^2$ ,  $dr = du/(2r)$ :

$$G^2 = \int_0^{\infty} du/(2r) 2\pi r e^{-u} \quad (370)$$

$$= \pi \int_0^{\infty} du/e^{-u} \quad (371)$$

$$= \pi (-e^{-u})|_0^{\infty} \quad (372)$$

$$= \pi \quad (373)$$

Thus  $G = \sqrt{\pi}$ , which we substitute into Eq. 365 to give:

$$A = \frac{1}{2\sqrt{\pi K}}$$

(374)

- (b) As  $t \rightarrow 0^+$ , the function  $d(x - a, t)$  becomes narrower and narrower (spike-like) around  $a$ , while still retaining the same area. Thus in the range that  $d(x - a, t)$  is non-zero, we can approximate  $f(x) \approx f(a)$ . Thus

$$\int_{-\infty}^{\infty} dx f(x)\delta(x - a) \approx \int_{-\infty}^{\infty} dx f(a)\delta(x - a) \quad (375)$$

$$\approx f(a) \int_{-\infty}^{\infty} dx \delta(x - a) \quad (376)$$

which by property (i) gives

$$\approx f(a), \quad (377)$$

as required. (This is obviously not a rigorous argument.)

---

<sup>31</sup>A summary of a variety of techniques to evaluate  $G$  may be found at <https://math.stackexchange.com/q/9286>.

- (c) The heat equation exhibits translational invariance (provided  $K$  does not depend on location). Thus, if  $d(x, t)$  is a solution, so is  $d(x - x', t)$ , where  $x'$  is any constant (you can verify by direct substitution into the heat equation).

Furthermore, the heat equation is a linear partial differential equation. For example, if we have two solutions,  $d_1(x, t)$  and  $d_2(x, t)$ , to the heat equation, then  $k_1 d_1(x, t) + k_2 d_2(x, t)$  is also a solution, where  $k_1$  and  $k_2$  are any two constants. The integral in the given expression:

$$T(x, t) = \int_{-\infty}^{\infty} dx' g(x') d(x - x', t) \quad (378)$$

is just a superposition of an infinite number of solutions,  $d(x - x', t)$ , parameterized by  $x'$ , with the different “coefficients” given by  $g(x')$ . Since *any* linear superposition of individual solutions satisfies the heat equation, this particular superposition does as well.

- (d) The solution

$$T(x, t) = \frac{1}{2\sqrt{\pi Kt}} \int_{-\infty}^{\infty} dx' T(x', 0) \exp\left(-\frac{(x - x')^2}{4Kt}\right). \quad (379)$$

is of the same form as Eq. 378, and thus by construction is a solution to the heat equation. We have also shown that as  $t \rightarrow 0^+$ , the function

$$d(x, t) = \frac{1}{2\sqrt{\pi Kt}} \exp\left(-\frac{x^2}{4Kt}\right) \quad (380)$$

acts like a  $\delta$ -fcn.

Thus, we have as  $t \rightarrow 0^+$ , the solution of Eq. 379 giving

$$T(x, 0) = \int_{-\infty}^{\infty} dx' T(x', 0) \delta(x - x') \quad (381)$$

$$= T(x, 0), \quad (382)$$

showing that as  $t \rightarrow 0^+$ , the initial conditions are satisfied.

- (e) The solution:

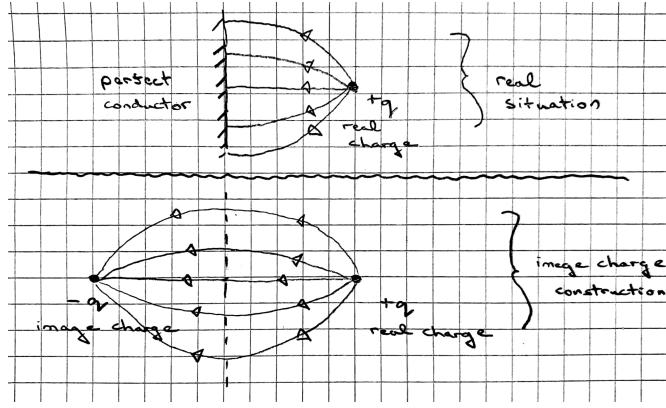
$$T(x, t) = \frac{T_i}{2\sqrt{\pi Kt}} \left[ \int_{-\infty}^0 dx' \exp\left(-\frac{(x - x')^2}{4Kt}\right) - \int_0^{\infty} dx' \exp\left(-\frac{(x - x')^2}{4Kt}\right) \right]. \quad (383)$$

is just a special case of Eq. 379, where the initial conditions are:

$$T(x, 0) = \begin{cases} T_i, & \text{for } x < 0 \\ -T_i, & \text{for } x > 0 \end{cases} \quad (384)$$

Obviously the solution is not applicable to the actual physical situation for  $x > 0$ . Nonetheless, pretending that we are solving a the heat equation with  $K$  the same everywhere (both  $x < 0$  and  $x > 0$ ) allows us to satisfy the boundary condition  $T(0, t) = 0$  for all  $t$ . You can verify that this condition is satisfied by evaluating Eq. 383 at  $x = 0$ . The two integrals cancel.

This is more less exactly what we are doing in the image charge situation. To solve for the potential (and thus field) of a point charge above a conducting plane, we imagine an image charge:



Poisson's equation is then solved everywhere, but the solution is only relevant for  $x > 0$ . The image charge allows us to satisfy the boundary conditions ( $\vec{E}$  normal to surface, or equivalently, the surface is an equipotential).

- (f) Evaluate the derivative with respect to  $x$  of the solution Eq. 383:

$$\frac{\partial T(x, t)}{\partial x} = \frac{T_i}{2\sqrt{\pi Kt}} \left[ \int_{-\infty}^0 dx' \exp\left(-\frac{(x-x')^2}{4Kt}\right) \times \frac{-1}{4Kt} 2(x-x') - \int_0^\infty dx' \exp\left(-\frac{(x-x')^2}{4Kt}\right) \times \frac{-1}{4Kt} 2(x-x') \right] \quad (385)$$

Substituting  $x = 0$  and simplifying gives

$$\frac{\partial T(x, t)}{\partial x} \Big|_{x=0} = -\frac{T_i}{2\sqrt{\pi Kt}} \frac{1}{Kt} \int_0^\infty dx' \exp\left(-\frac{x'^2}{4Kt}\right) x'. \quad (386)$$

Make a change of variables  $\theta = x'/\sqrt{4Kt}$ ,  $dx'/d\theta = \sqrt{4Kt}$ , so that:

$$\frac{\partial T(x, t)}{\partial x} \Big|_{x=0} = -\frac{T_i}{2\sqrt{\pi Kt}} \frac{1}{Kt} 4Kt \int_0^\infty d\theta e^{-\theta^2} \theta \quad (387)$$

$$= -\frac{2T_i}{\sqrt{\pi Kt}} \int_0^\infty d\theta e^{-\theta^2} \theta \quad (388)$$

and noting that  $de^{-\theta^2}/d\theta = -2\theta e^{-\theta^2}$ , we have:

$$\frac{\partial T(x, t)}{\partial x} \Big|_{x=0} = -\frac{2T_i}{\sqrt{\pi Kt}} \frac{1}{(-2)} e^{-\theta^2} \Big|_0^\infty \quad (389)$$

$$\boxed{\frac{\partial T(x, t)}{\partial x} \Big|_{x=0} = \frac{-T_i}{\sqrt{\pi Kt}}} \quad (390)$$

- (g) As shown in Problem 1.62 of SITP [15] (one of the suggested problems):

$$K = \frac{k_t}{(C/m)\rho} \quad (391)$$

where  $k_t$  is the thermal conductivity that appears in Fourier's law of heat conduction,  $C/m$  is the specific heat capacity, and  $\rho$  is the mass density.

We can look up estimates of all of these for the earth's crust and thus check to see the value that Kelvin used is reasonable.

Reference [16] says that the *thermal conductivity of rocks falls usually in the range*  $0.40 - 7.00 \text{ W}/(\text{m} \cdot \text{K})$ .

From Table 3 in Ref. [17],  $C/m \approx 1 \text{ kJ}/(\text{kg} \cdot \text{K})$  seems like a reasonable estimate.

At [https://en.wikipedia.org/wiki/Structure\\_of\\_Earth](https://en.wikipedia.org/wiki/Structure_of_Earth) it is stated that *the average density of surface material is only around  $3.0 \text{ g}/\text{cm}^3$* .

Substituting numbers into Eq. 391, we obtain:

$$K \approx \frac{k_t}{(C/m)\rho} \quad (392)$$

$$\approx \frac{1 \text{ W}/(\text{m} \cdot \text{K})}{10^3 \text{ J}/(\text{kg} \cdot \text{K}) \times 3 \times 10^3 \text{ kg}/\text{m}^3} \quad (393)$$

$$K \approx 3 \times 10^{-7} \text{ m}^2/\text{s}, \quad (394)$$

suggesting that Kelvin's  $K \approx 1.18 \times 10^{-6} \text{ m}^2/\text{s}$  is not completely unreasonable (less than an order of magnitude off).

(h) Rearranging Eq. 390 to solve for  $t$  gives:

$$t = \frac{1}{\pi K} \left( \frac{T_i}{-\frac{\partial T(x,t)}{\partial x} \Big|_{x=0}} \right)^2 \quad (395)$$

and substituting the relevant quantities gives:

$$t \approx \frac{1}{\pi \times 1.2 \times 10^{-6} \text{ m}^2/\text{s}} \times \left( \frac{3900 \text{ }^\circ\text{C}}{3.7 \times 10^{-2} \text{ }^\circ\text{C}/\text{m}} \right)^2 \quad (396)$$

$$\approx 2.95 \times 10^{15} \text{ s} \times \frac{1}{3.154 \times 10^7 \text{ s/year}} \quad (397)$$

$$t \approx 90 \times 10^6 \text{ years} \quad (398)$$

(i) The form of the dimensionless exponents in the solution Eq. 383 indicates that we can get a length scale  $\ell$  for the temperature variations at a given time by rearranging  $1 = \ell^2/(4Kt)$  to give:

$$\ell \approx \sqrt{4Kt} \quad (399)$$

$$\approx \sqrt{4 \times 1.2 \times 10^{-6} \text{ m}^2/\text{s} \times 2.95 \times 10^{15} \text{ s}} \quad (400)$$

$$\approx 1 \times 10^5 \text{ m} \quad (401)$$

The radius of the earth  $\approx 6 \times 10^6 \text{ m}$  is significantly greater than  $\ell$ , justifying the flat earth model.

It should be said that treating this as a spherical problem adds little to the physics, and does not change the estimate significantly, especially considering the various uncertainties. However, it is a useful exercise in mathematical physics.

## For your interest only:

Kelvin's<sup>32</sup> original paper [18] is very readable. As his paper makes clear, the idea of this sort of estimate originates in the work of Fourier.

There are many accounts of how Kelvin's estimate was received by other physicists, geologists and so-on [19, 20]. For a mathematically respectable presentation of the details, see Ref. [21].

## Sackur and Tetrode are gone — answer

**Question.** Answer:

- (a) Starting with the Sackur-Tetrode equation:

$$S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right], \quad (\text{Eq. 2.49 of SITP})$$

we can replace  $V/N$  by  $kT/P$  (the ideal gas law),  $U$  by  $\frac{3}{2}NkT$  (the energy of a monatomic gas), and  $Nk$  by  $nR$  (where  $R$  is the ideal gas constant) giving:

$$S = nR \left[ \ln \left( \frac{(kT)^{5/2}}{P} \left( \frac{2\pi m}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right]. \quad (402)$$

Note that the mass that appears here is the mass of a single atom. To obtain  $m$  we will take the “molecular mass”  $\approx 40 \text{ g/mol}$  and divide by Avogadro’s number  $N_A \approx 6 \times 10^{23} \text{ mol}^{-1}$ .

Substituting the numbers of this problem:

$$\begin{aligned} S &\approx 1 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \left[ \ln \left( (1.38 \times 10^{-23} \text{ J/K} \times 85.67 \text{ K})^{5/2} \times \frac{1}{0.937 \times 10^5 \text{ Pa}} \right. \right. \\ &\quad \times \left. \left. \left( \frac{2\pi \times 39.95 \times 10^{-3} \text{ kg/mol}}{(6.6 \times 10^{-34} \text{ J} \cdot \text{s})^2 \times 6.02 \times 10^{23} \text{ 1/mol}} \right)^{3/2} \right) + 5/2 \right] \end{aligned} \quad (403)$$

$$S \approx 129.46 \text{ J/K} \quad (404)$$

- (b) To derive  $S$  versus  $T$  from the calorimetric data we make use of two important results. Firstly in both the solid and liquid phases, the changes in entropy between different temperatures are given by:

$$\Delta S_{1 \rightarrow 2} = \int_{T_1}^{T_2} \frac{C}{T} dT \quad (405)$$

which arises from  $Q = CdT$  and  $Q = TdS$ . We are assuming everything is at constant pressure here.

Secondly, at the two phase transitions, we assume that the changes in entropy are related to the latent heats  $L$  by

$$\Delta S = \frac{L}{T}. \quad (406)$$

---

<sup>32</sup>“Kelvin” is a title. “Thomson” was his proper surname.

All of these entropy changes accumulate, so that in the final vapour state:

$$S = \int_0^{T_m} \frac{C_s}{T} dT + \frac{L_m}{T_m} + \int_{T_m}^{T_v} \frac{C_\ell}{T} dT + \frac{L_v}{T_v} \quad (407)$$

Computing the change in entropy as the liquid is heated is straightforward, since we are given a *temperature independent* heat capacity for the liquid phase, so that the integral is readily evaluated analytically:

$$\int_{T_m}^{T_v} \frac{C_\ell}{T} dT = C_\ell \ln \left( \frac{T_v}{T_m} \right). \quad (408)$$

However, computing the entropy change of the heated solid is a bit more complicated as we are supplied with a *temperature dependent* heat capacity at some specific temperatures. There are a variety of valid ways to perform the integration. One sensible approach is to interpolate the data with a simple function and then integrate that function analytically. Or fit the data and integrate the fitted function. Even just assuming that  $C$  is constant between the sampled temperatures is reasonable as a first stab. I used Scipy's "Simpson's rule" integrator (all of my code can be [downloaded](#)):

```

1 import csv
2 import numpy as np
3 import scipy.integrate as si
4
5 def ar_entropy_as_a_function_of_temperature():
6     """Compute entropy of 1 mol of Ar as a function of temperature using
7     calorimetry data from Flubacher et al., https://dx.doi.org/c8qtdv
8
9     Return two arrays: temperatures (K) and the corresponding entropies (J/K)
10    """
11
12    t_m = 83.8 # melting temperature (K)
13    l_m = 1190.0 # latent heat of melting (J)
14    t_v = 85.67 # vaporization temperature (K)
15    l_v = 6544.0 # latent heat of vaporization (J)
16    c_l = 43.932 # heat capacity of liquid (J/K)
17
18    # read in heat capacity data for solid from the *.csv file:
19    with open('ts_and_cs_generated.csv', newline='') as f:
20        reader = csv.reader(f)
21        raw_rows = [r for r in reader]
22        rows = [[float(c) for c in row] for row in raw_rows[1:]]
23        first_row = rows[0]
24        ts, cjs = (np.array(column) for column in
25                    ([row[column_index] for row in rows]
26                     for column_index, _ in enumerate(first_row)))
27
28    part_a_ts = ts
29    part_a_ss = np.zeros_like(ts)

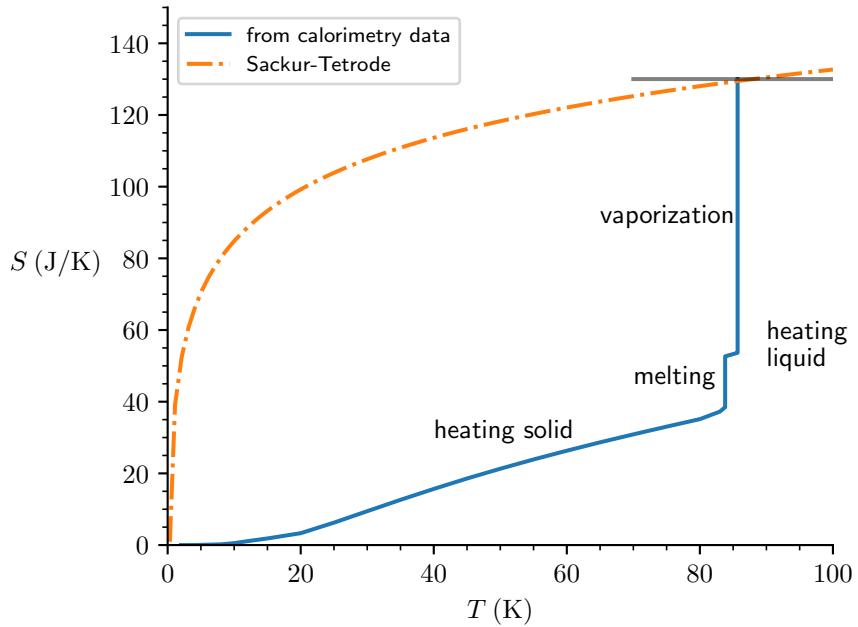
```

```

30     part_a_ss[0] = 0.0 # the third law!
31
32     # integrate C/T for the solid:
33     for i in range(1, len(part_a_ts)):
34         part_a_ss[i] = si.simps(cjs[0:i] / ts[0:i] , ts[0:i])
35
36     # add L_m/T for melting and integrate C/T for liquid:
37     part_b_ts = np.linspace(t_m, t_v, 10)
38     part_b_ss = part_a_ss[-1] + l_m / t_m + np.zeros_like(part_b_ts)
39     part_b_ss += c_l * np.log(part_b_ts/ t_m)
40
41     # add L_v/T for vaporization:
42     part_c_ts = np.array([t_v,])
43     part_c_ss = np.array([part_b_ss[-1] + l_v / t_v,])
44
45     return (np.concatenate([part_a_ts, part_b_ts, part_c_ts]),
46             np.concatenate([part_a_ss, part_b_ss, part_c_ss]))

```

The entropy versus temperature may then be plotted:



(I've also superimposed what Sackur-Tetrode would give over the same temperature range, but that's not necessary.)

- (c) The entropy derived from calorimetry is the highest temperature entropy computed in the last part (at the end of the arrays):

$$S \approx 130.0 \text{ J/K} \quad (409)$$

which is quite close to the  $S \approx 129.46 \text{ J/K}$  computed in part a) from the Sackur-Tetrode equation.

(d) We may rearrange Eq. 402 to obtain  $h$  in terms of the entropy derived from  $S_{\text{calorimetry}}$ :

$$h = \sqrt{2\pi m} \frac{(kT)^{5/6}}{P^{1/3}} \exp\left(\frac{1}{3}\left(\frac{5}{2} - \frac{S_{\text{calorimetry}}}{nR}\right)\right). \quad (410)$$

Substituting  $S_{\text{calorimetry}} \approx 130.0 \text{ J/K}$  gives:

$$h \approx 6.5 \times 10^{-34} \text{ J} \cdot \text{s} \quad (411)$$

compared to  $h \approx 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$  (see <https://physics.nist.gov/cuu/Constants/index.html>).

Of course, this is not viable technique to determine Planck's constant to great precision. But I personally find it quite surprising that "plain-old calorimetry" could determine Planck's constant at all.

(e) We may evaluate Eq. 402 using  $P = 10^5 \text{ Pa}$ ,  $T = 300 \text{ K}$  with a molecular mass of  $18 \text{ g/mol}$ :

$$\begin{aligned} S &\approx 1 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \left[ \ln\left(\left(1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}\right)^{5/2} \times \frac{1}{10^5 \text{ Pa}} \right. \right. \\ &\quad \times \left. \left. \left( \frac{2\pi \times 18 \times 10^{-3} \text{ kg/mol}}{(6.6 \times 10^{-34} \text{ J} \cdot \text{s})^2 \times 6.02 \times 10^{23} \text{ 1/mol}} \right)^{3/2} \right) + 5/2 \right] \end{aligned} \quad (412)$$

$$S \approx 145.0 \text{ J/K} \quad (413)$$

(f) As the question problem notes, the *actual* entropy of water vapour under these conditions is  $S \approx 189.0 \text{ J/K}$ , which is higher than the Sackur-Tetrode value.

The resolution of this discrepancy is the entropy associated with the internal motion of the water molecule. Water molecules rotate and vibrate. There is entropy associated with these motions that is not accounted for in Sackur-Tetrode, which assumes that the only contribution to entropy is translational motion. The neglect of the additional molecular motions in Sackur-Tetrode is consistent with the entropy that it predicts being *lower* than more sophisticated calculations.

(g) At low temperatures the water molecules in ice become "locked into" certain orientations with respect to neighbours. However, there is not a unique arrangement of molecular orientations; there is an entropy associated with the possibilities. Although there may be some energy splitting associated with these different arrangements, it occurs at temperatures too low to observe, and the time-scales for conversion between these forms is exceedingly long. To all intents and purposes there is effectively a multiplicity greater than one at the lowest energies/temperatures.

This type of randomness does not occur in crystals of Ar, where each atom has no orientation to speak of. Some statements of the 3<sup>rd</sup> law attempt to incorporate this idea by saying something to the effect of  $S = 0$  at  $T = 0$  for a perfect crystal.

### For your interest:

The "classic" test of the Sackur-Tetrode equation is with Hg and described in E. Fermi, *Thermodynamics* (Dover Publications, New York, 1986). I found out about the noble gas comparisons from F. J. Paños and E. Pérez, "Sackur-Tetrode equation in the lab", *Eur. J. Phys.* **36**, 055033 (2015).

## Heist of the century or lame waste of time? — answer

**Question.** Answer:

(a) Define:

$T_C$ : room temperature (absolute)  $\approx 20 + 273 \text{ K} = 293 \text{ K}$

$T_{IW}$ : initial water temperature (absolute)  $\approx 50 + 273 \text{ K} = 323 \text{ K}$

$T_{FW}$ : final water temperature (absolute) (not sure of value yet)

We will start by considering how much work may be done by a fixed mass of water, entering and leaving the apartment, with temperature-independent heat capacity  $C_P$ .

The entropy change of this water is

$$\Delta S_W = - \int_{T_{FW}}^{T_{IW}} \frac{C_P}{T} dT \quad (414)$$

$$= -C_P \ln \left( \frac{T_{IW}}{T_{FW}} \right) \quad (415)$$

The entropy change of the cold reservoir (the room) is

$$\Delta S_C = \frac{Q_C}{T_C} \quad (416)$$

where we have assumed  $Q_C$  is positive for heat flow *into* the room.

The 2<sup>nd</sup> law tells us that:

$$\Delta S_W + \Delta S_C \geq 0 \quad (417)$$

which by Eq.'s 415 and 416 means:

$$-C_P \ln \left( \frac{T_{IW}}{T_{FW}} \right) + \frac{Q_C}{T_C} \geq 0. \quad (418)$$

Equivalently, in a form that will be useful shortly:

$$-Q_C \leq -T_C C_P \ln \left( \frac{T_{IW}}{T_{FW}} \right). \quad (419)$$

Defining  $Q_W$  as the heat that *leaves* the water, the 1<sup>st</sup> law gives:

$$W = Q_W - Q_C \quad (420)$$

$$= C_P(T_{IW} - T_{FW}) - Q_C. \quad (421)$$

Rearrange, in a way that we may use the inequality of Eq. 419:

$$W - C_P(T_{IW} - T_{FW}) = -Q_C \quad (422)$$

$$\leq -T_C C_P \ln \left( \frac{T_{IW}}{T_{FW}} \right). \quad (423)$$

Rearrange, to obtain a bound on the maximum work done by this water:

$$W \leq C_P \left[ T_{IW} - T_{FW} - T_C \ln \left( \frac{T_{IW}}{T_{FW}} \right) \right] \quad (424)$$

We may now determine what  $T_{FW}$  should be for *maximum*  $W$ . Differentiate wrt  $T_{FW}$  and set = 0, obtaining  $T_{FW} = T_C$ , which we might expect; i.e., the water should leave at room temperature.

The maximum bound is:

$$W \leq C_P \left[ T_{IW} - T_C - T_C \ln \left( \frac{T_{IW}}{T_C} \right) \right]. \quad (425)$$

Remember that this is the maximum work that can be done by a specific amount of water of heat capacity  $C_P$ . We can convert this to a power, by considering the flow rate of the water  $\dot{V}$ . With a mass density of  $\rho$ , the power is:

$$\dot{W} = \rho \dot{V} \frac{C_P}{m} \frac{W}{C_P}. \quad (426)$$

So finally, with  $W/C_P$  bounded by Eq. 425, we have:

$$\dot{W} \leq \rho \dot{V} \frac{C_P}{m} (T_{IW} - T_C) \alpha, \quad (427)$$

where the dimensionless factor:

$$\alpha := \left[ 1 - \frac{T_C}{T_{IW} - T_C} \ln \left( \frac{T_{IW}}{T_C} \right) \right] \quad (428)$$

has been introduced to allow easy comparison to a (wrong) solution (*vide infra*).

Substituting some numbers:

$$\rho \dot{V} \frac{C_P}{m} (T_{IW} - T_C) = 1 \text{ kg/litre} \times 8 \text{ litres/minute} \times \frac{1}{60} \text{ minute/s} \times 4.2 \text{ kJ/kg} \times 30 \text{ K} \quad (429)$$

$$= 16.8 \times 10^3 \text{ kW} \quad (430)$$

and

$$\alpha = 1 - \frac{T_C}{T_{IW} - T_C} \ln \left( \frac{T_{IW}}{T_C} \right) \quad (431)$$

$$= 1 - \frac{293}{30} \ln \left( \frac{323}{293} \right) \quad (432)$$

$$= 0.0479 \quad (433)$$

which when combined with Eq. 430 gives

$$\boxed{\dot{W} \leq 806 \text{ W}} \quad (434)$$

For a discussion of common wrong bound and a more conservative, realistic bound, see the notes title “For your own interest” at end.

(b) A typical cell-phone charging rate might be on the order of 10 W (for USB-C, see [https://en.wikipedia.org/wiki/USB\\_hardware#Power](https://en.wikipedia.org/wiki/USB_hardware#Power)). Charging on the order of 80 cell phones seems pretty good.

A report of the Ontario Energy Board states that “The overall Ontario three-year average residential monthly consumption is 753 kWh” corresponding to

$$\dot{W} \approx 753 \text{ kW} \cdot \text{hrs/month} \times \frac{1000 \text{ W/kW}}{30 \times 24 \text{ hrs/month}} \quad (435)$$

$$\approx 1050 \text{ W} \quad (436)$$

So if you were able to get close to the maximum thermodynamic efficiency, you could nearly supply average household energy use. That seems pretty good.

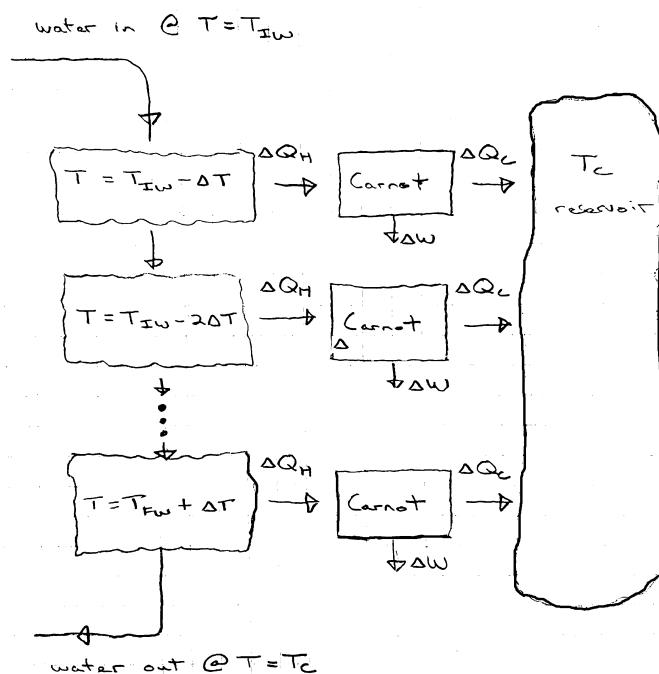
My most recent electricity bill gives a rate of \$0.13 / (kW · hr). Thus being able to produce 800 W continuously, corresponds to about  $0.8 \text{ kW} \times \$0.13 / (\text{kW} \cdot \text{hr}) \times 24 \times 30 \text{ hr} \approx \$75$  per month.

Not the heist of the century, but possibly not a lame waste of time either. Maybe the better, more productive message, is not to waste hot water.

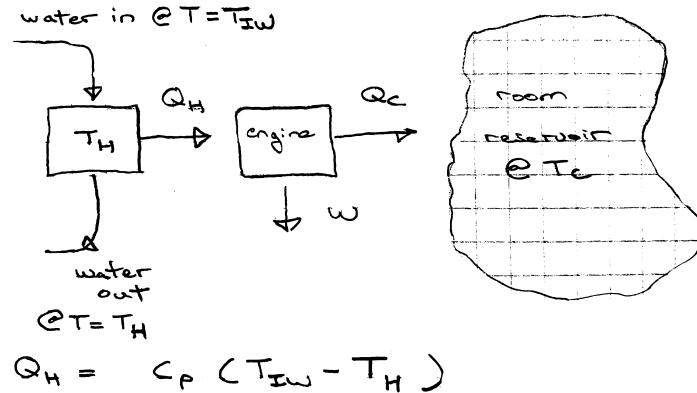
### For your interest:

It is *wrong* to use  $\alpha = 1 - T_C/T_{IW} \approx 0.093$  in Eq. 427, giving the more optimistic  $\dot{W} \leq 1560 \text{ W}$ . You might use this  $\alpha$  based on the standard heat engine configuration discussed in the notes and Schroeder. But ultimately, a correct analysis must consider that water leaves your apartment at the same rate that it comes in. If your engine is doing work, this water *must* leave at a lower temperature. (If you were somehow allowed to dump water into some sort of infinite reservoir in your apartment, then this  $1 - T_C/T_H$  factor might be correct. But for obvious reasons you can't do that.)

What sort of engine *would* obtain the correct bound (Eq. 434)? One possible approach is a string of Carnot engines, each having a lower and lower hot reservoir temperature:



This particular arrangement seems impractical — particularly for the last stages where the hot reservoir temperatures approach room temperature. Instead as a more practical alternative, you might consider a *single* Carnot engine with a high temperature reservoir at  $T_H$ , *intermediate* between the incoming water temperature and room temperature:



By the standard Carnot engine efficiency formula:

$$\frac{W}{Q_H} = 1 - \frac{T_C}{T_H} \quad (437)$$

and thus

$$W = Q_H \left( 1 - \frac{T_C}{T_H} \right) \quad (438)$$

$$= C_P(T_{IW} - T_H) \left( 1 - \frac{T_C}{T_H} \right) \quad (439)$$

As before we may obtain the power from the water flow:

$$\dot{W} = \rho \dot{V} \frac{C_P}{m} (T_{IW} - T_H) \left( 1 - \frac{T_C}{T_H} \right). \quad (440)$$

I find this single Carnot engine case quite insightful, as it illustrates the trade off between extracting heat from the water and the efficiency of the heat engine. More specifically, the lower  $T_H$  is, the more heat we extract from water (the  $T_{IW} - T_H$  factor), but the lower its thermodynamic efficiency (the  $1 - T_C/T_H$  factor). Extracting the maximum power balances these two competing factors.

Again you can maximize  $\dot{W}$ , by differentiating wrt to  $T_H$ , and setting the derivative equal to zero. The result is  $T_H = \sqrt{T_C T_{IW}}$ . Substituting this back into the expression for  $\dot{W}$  gives

$$\dot{W} = \rho \dot{V} \frac{C_P}{m} (T_{IW} - T_C) \alpha, \quad (441)$$

where we have written in a form similar to Eq. 427, but in this case

$$\alpha = \left( \frac{T_{IW}}{T_{IW} - T_C} \right) \left( 1 - \sqrt{\frac{T_C}{T_{IW}}} \right)^2 \quad (442)$$

where substitution of the relevant numbers gives

$$\alpha = \left( \frac{323 \text{ K}}{30 \text{ K}} \right) \left( 1 - \sqrt{\frac{293 \text{ K}}{323 \text{ K}}} \right)^2 \quad (443)$$

$$= 0.0244 \quad (444)$$

so that when combined with Eq. 430, we have  $\dot{W} = 409 \text{ W}$ . Note that — as necessary — this single Carnot engine power is lower than the bound  $\dot{W} \leq 806 \text{ W}$ . (Since we are using a Carnot engine — which doesn't produce any excess entropy — the entropy “creation” step is throwing the incoming hot water into the lower temperature reservoir, which is the high temperature reservoir for our Carnot engine.)

I suspect that  $\dot{W} \approx 400 \text{ W}$  is a reasonable estimate of what might be expected in practice. But regardless,  $\dot{W} \leq 806 \text{ W}$  is the upper bound dictated by solely by the laws of thermodynamics.

## Demag and chill — answer

**Question.** Answer:

- (a) From the solutions to “Shocking Schottky”, we find that the entropy is:

$$\frac{S}{k} = N \ln N - N_{\downarrow} \ln N_{\downarrow} - (N - N_{\downarrow}) \ln(N - N_{\downarrow}), \quad (445)$$

and the total energy is:

$$U = \epsilon N_{\downarrow} \quad (446)$$

$$= N \epsilon (1 + e^{\alpha})^{-1}. \quad (447)$$

where  $\alpha = \epsilon/(kT)$ .

Rewriting the entropy in terms of the energy:

$$\frac{S}{k} = N \ln N - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} - (N - \frac{U}{\epsilon}) \ln(N - \frac{U}{\epsilon}), \quad (448)$$

and now  $\alpha$

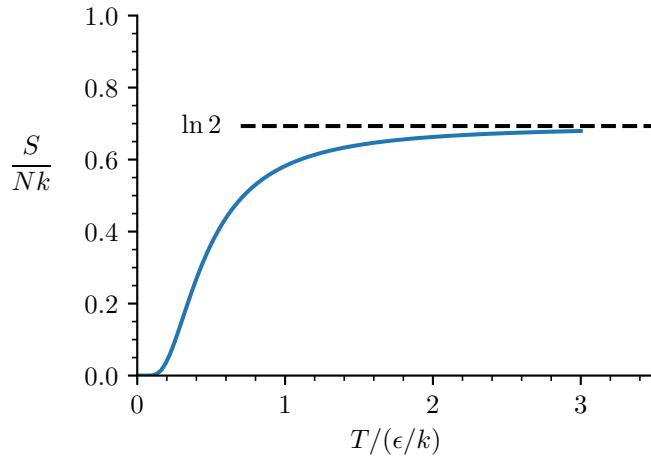
$$\frac{S}{k} = N \ln N - \frac{N}{1 + e^{\alpha}} \ln \frac{N}{1 + e^{\alpha}} - (N - \frac{N}{1 + e^{\alpha}}) \ln(N - \frac{N}{1 + e^{\alpha}}), \quad (449)$$

and simplifying gives

$$\frac{S}{Nk} = \frac{\alpha}{1 + e^{\alpha}} - \ln \left( 1 - \frac{1}{1 + e^{\alpha}} \right) \quad (450)$$

as required.

- (b) Using the expression for entropy from the preceding part:



- (c) At low temperatures,  $S/(Nk) \rightarrow 0$ , corresponding to  $\Omega = 1$ , which we expect, as there is a single ground state (all “atoms” in the lower state).

High temperature  $S/(Nk) \rightarrow \ln 2 \approx 0.7$ . This is the result that we would obtain from a multiplicity of  $\Omega = 2^N$ . This is actually the total number of possible states of *all* energies, not just those with the correct energy ( $U = N\epsilon/2$ ), which is a bit surprising (at least to me). It reflects the fact that most of the possibilities *do* correspond to a 50/50 mixture of the two states.

- (d) (i) We need to compute  $\alpha$ , such that

$$\left(1 - \frac{N_\uparrow}{N}\right) N\epsilon = \frac{N\epsilon}{1 + e^\alpha} \quad (451)$$

where  $N_\uparrow = 0.9$ . Solving gives  $\alpha \approx 2.2$ .

We can compute what  $B$  field is required:

$$B = \frac{kT\alpha m}{q\hbar} \quad (452)$$

$$\approx \frac{1.38 \text{ J/K} \times 0.3 \text{ K} \times 2.2 \times 9.1 \times 10^{-31} \text{ kg}}{1.6 \times 10^{-19} \text{ C} \times 10^{-34} \text{ J} \cdot \text{S}} \quad (453)$$

$$B \approx 0.52 \text{ T} \quad (454)$$

- (ii) To obtain the entropy, we may substitute  $\alpha \approx 2.2$  into Eq. 450, giving:

$$\boxed{\frac{S}{Nk} \approx 0.33} \quad (455)$$

- (e) (i) As the magnetic field is decreased, the entropy stays the same, since  $N_\downarrow/N$  stays the same; i.e., Eq. 445.  
(ii) The dimensionless  $\alpha = \epsilon/(kT)$  stays the same, since  $S$  remains the same. However, since  $\epsilon$  has been changed (since the magnetic field is now lower), the temperature is changed. The temperature deceases by the same factor that the magnetic field decreases by (for the same  $\alpha$ ):

$$T_{\text{after}} = T_{\text{before}} \frac{B_{\text{after}}}{B_{\text{before}}} \quad (456)$$

$$\approx 0.3 \text{ K} \frac{0.002 \text{ T}}{0.52 \text{ T}} \quad (457)$$

$$\boxed{T_{\text{after}} \approx 0.0012 \text{ K}} \quad (458)$$

- (f) The basic idea is that heat flows from  $^3\text{He}$  to the spins. For both systems, spins and the  $^3\text{He}$ , we know how their internal energies depend on temperature. We find the corresponding final temperature, such that the gain in energy of the spins is matched by the loss of energy by  $^3\text{He}$ .

You can do all of this by hand, except for the very last part, where you have to use some type of numerical equation solver (graphical solution is fine as well). But it's easier to write a simple program (in Python here):

```

1 import os
2 import numpy as np
3 import matplotlib.pyplot as plt
4 import scipy.constants as sc
5 import scipy.optimize

6
7 import he_heat_capacity # supplies  ${}^3\text{He}$  heat capacity given in problem
8
9 init_t = 0.3 # initial temperature (in Kelvin)
10 spin_pol = 0.90 # ground state spin polarization (as fraction of total spins)
11 b_min = 0.002 # magnetic field after adiabatic reduction (in T)
12 nmol_spins = 2.0 # number of spins (in mols)
13 nmol_he = 0.03 # amount of  ${}^3\text{He}$  (in mols)

14
15 # compute epsilon/B:
16 epsilon_div_b = sc.hbar * sc.e / sc.m_e

17
18 # compute magnetic field required to get polarization:
19 alpha = np.log(1.0 / (1.0 - spin_pol) - 1.0)
20 b0 = sc.k * init_t * alpha / epsilon_div_b

21
22 # entropy
23 entropy = (alpha / (1.0 + np.exp(alpha))
24             - np.log(1.0 - 1.0 / (1 + np.exp(alpha))))
25 print("entropy: ", entropy)

26
27 # compute spin temperature after reduction of magnetic field:
28 t_spin = init_t * b_min / b0
29 print("t_spin", t_spin)
30 epsilon = epsilon_div_b * b_min
31 alpha0 = epsilon / (sc.k * t_spin)

32
33 # Now consider temperature after spins and  ${}^3\text{He}$  thermally equilibrate.
34 # Define functions that give  $U$  of each, relative to their initial  $U$ 
35 # as a function of temperature. That helps us to determine the temperature
36 # for which the energy gained by the spins is equal to the energy lost
37 # by the  ${}^3\text{He}$ :

38
39 def u_spins(temperature):
40     return (nmol_spins * sc.Avogadro * epsilon * (
41         1/(1 + np.exp(epsilon / sc.k / temperature)))

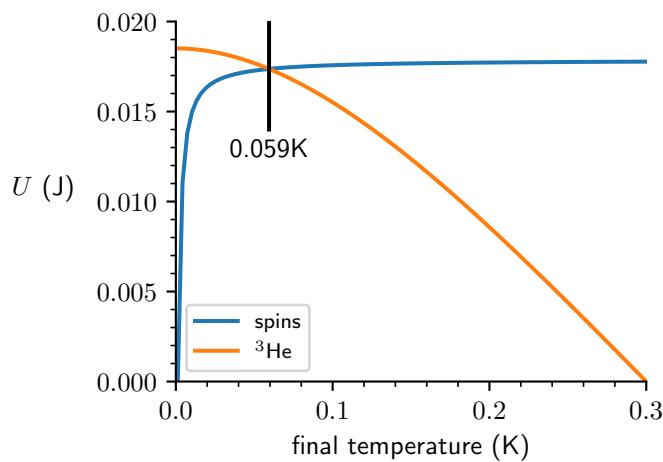
```

```

42     - 1/(1 + np.exp(alpha))))
43
44 def u_3He(temperature):
45     return nmol_he * sc.R * (he_heat_capacity.u(temperature) -
46                               he_heat_capacity.u(init_t))
47
48 # solve numerically for final temperature:
49 t_final = scipy.optimize.brentq(
50     lambda temperature: u_spins(temperature) + u_3He(temperature),
51     t_spin, init_t)
52 print("final temperature: ", t_final)
53
54 # plot graphically as a sanity check:
55 base_filename = os.path.splitext(__file__)[0]
56 with plt.style.context(base_filename + ".mplstyle"):
57     fig = plt.figure()
58     ax = fig.add_axes([0.25, 0.2, 0.70, 0.75])
59     ax.set_xlim([0.0, 0.3])
60     ax.set_ylim([0.0, 0.02])
61     temps = np.linspace(t_spin, init_t, 100)
62     ax.plot(temps, u_spins(temps), label="spins")
63     ax.plot(temps, -u_3He(temps), label="$^3$He")
64     ax.axvline(t_final, 0.7, 1.0, color="black")
65     ax.text(t_final, 0.0125, ("%.3fK" % t_final),
66             horizontalalignment="center")
67     ax.set_ylabel("$U$ (J)", rotation=0.0, labelpad=20)
68     ax.set_xlabel("final temperature (K)")
69     ax.legend(loc="lower left")
70     plt.savefig(base_filename + "_generated.pdf")

```

which produces:



The final equilibrium temperature is  $\approx 0.059$  K.

- (g) An important class of photon detectors are those of the **bolometric** type: they measure the *heating* due to photons being absorbed by the detector. If this can be done for *each* absorbed

photon — requiring a relatively low rate of absorption — determination of  $Q = h\nu$  due to each photon measures the spectrum of the incident light.

Bolometric detectors benefit from and often require cooling. One specific type, the “[transition-edge sensor](#)” relies on keeping the absorber, or a material in close thermal contact with the absorber, at a temperature “on the edge” of a superconducting transition.

As a particular example, the planned [ATHENA](#) satellite will use transition edge sensors to detect x-rays of up to 12 keV photon energy, which our atmosphere would completely absorb, making detection from the ground impossible.

As mentioned above, the transition edge sensors are required to be at a low temperature because they employ superconductivity. Furthermore, heat must be constantly drawn away from these detectors due to both the absorbed photons and the electronics associated with read-out.

The cooling of bolometric detectors on a spacecraft is a complicated, multi-stage affair, where different technologies are employed in stages to shuttle heat up to a temperature where it is efficiently radiated away into space.

The coldest stage of refrigeration should not create any more  $Q_H$  than required, as this ends up as a  $Q_C$  for the next stage at so on, eventually impacting  $W$  required for refrigeration at the highest temperature stage. The  $W$  of the last stage can be quite large when compared to  $Q_H$  for the lowest temperature stage. The second law and the bounds it places on the COP for refrigeration can be quite insightful here.

The adiabatic demagnetization refrigerator (ADR) may approach Carnot-like efficiencies. It is also relatively simple, doesn’t use liquid helium, and is insensitive to gravity. So although helium dilution refrigerators largely replaced ADRs for cooling to the millikelvin range, ADRs have made a comeback, at least in the niche area of refrigeration of bolometric sensors in spacecraft.

The recent [Hitomi satellite](#) employed three successive stages of ADR for detector cooling. Unfortunately Hitomi [failed](#) (shortly after launch in 2016 but not due to its cooling system). Although a replacement mission is planned I have not been able to find much on its cooling system. The planned [ATHENA](#) mission will use a single ADR for its coldest stage.

## For your interest:

The idea for this question comes from: R. Baierlein and B. Bertman, “Reversibility in Magnetic Cooling”, [American Journal of Physics 37, 101–102 \(1969\)](#) (Unfortunately I don’t recommend reading this paper. If you are interested in ADR, I would instead recommend one of the generic books on low-temperature techniques, such as F. Pobell, *Matter and methods at low temperatures*, 3rd, rev. and expanded ed (Springer, Berlin ; New York, 2007).)

The  $^3\text{He}$  heat capacity equations are from: A. C. Anderson et al., “Specific Heat, Entropy, and Expansion Coefficient of Liquid Helium-Three”, [Phys. Rev. 130, 495–501 \(1963\)](#).

A technical description of the ADR system for the Hitomi mission (also known as ASTRO-H), is given in: P. J. Shirron et al., “Performance Testing of the Astro-H Flight Model 3-stage ADR”, [Physics Procedia, Proceedings of the 25th International Cryogenic Engineering Conference and International Cryogenic Materials Conference 2014 67, 250–257 \(2015\)](#).

It is worth noting that a predecessor to the failed Hitomi mission, [Suzaku](#), experienced an inadvertent leak of its liquid He, disabling one of its x-ray calorimeter systems (R. L. Kelley et al., “The

Suzaku High Resolution X-Ray Spectrometer”, Publ Astron Soc Jpn **59**, S77–S112 (2007)). This undoubtedly influenced the design of Hitomi’s refrigeration system, which was less susceptible to cryogen loss.

## Supercharging the dinosaur — answer

**Question.** Answer:

- (a) Compute  $\Delta H$  per mole of octane consumed. Use Hess’ law and the enthalpies of formation (from the Reference Data for the course):

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad (459)$$

$$= \frac{1}{2} [16\Delta_f H(\text{CO}_2) + 18\Delta_f H(\text{H}_2\text{O(g)}) - 25\Delta_f H(\text{O}_2) - 2\Delta_f H(\text{C}_8\text{H}_{18(l)})] \quad (460)$$

$$\approx \frac{1}{2} [16 \times -393.51 \text{ kJ} + 18 \times -241.82 \text{ kJ} - 25 \times 0 \text{ kJ} - 2 \times -250 \text{ kJ}] \quad (461)$$

$$\approx -5.07 \text{ MJ} \quad (462)$$

And 1 mol of octane is  $\approx 5 \times 0.012 \text{ kg} + 18 \times 0.001 \text{ kg} \approx 0.114 \text{ kg}$ .

Thus the heat released per kg of octane is:

$$Q_H \approx \frac{5.07 \text{ MJ}}{0.114 \text{ kg}} \quad (463)$$

$$\boxed{Q_H \approx 44 \text{ MJ/kg}} \quad (464)$$

which is in reasonable agreement with the 45 MJ/kg “heat of combustion” quoted in the problem statement.

(If we consider liquid water as a product, instead of vapour, we get  $\approx 48 \text{ MJ/kg}$ . However, it is water vapour that is produced. Condensation of this vapour is what you see on cold days as the “white” smoke emerging from automobile exhausts.)

(b)

$$q = \frac{Q_H}{n_{\text{air}}} \quad (465)$$

$$\approx \frac{45 \times 10^6 \text{ J}}{\frac{15 \text{ kg}}{0.029 \text{ kg/mol}}} \quad (466)$$

$$\boxed{q \approx 8.7 \times 10^4 \frac{\text{J}}{\text{mol}}} \quad (467)$$

- (c) The work done in travelling  $x = 100 \text{ km}$  will be:

$$W = -\vec{F} \cdot x \quad (468)$$

$$= \left( \frac{1}{2} \rho_{\text{air}} C_d A v^2 + C_{rr} m g \right) x \quad (469)$$

where the density of air is

$$\rho_{\text{air}} = \frac{P}{RT} \left\langle \frac{m}{n} \right\rangle_{\text{air}} \quad (470)$$

$$\approx \frac{1 \times 10^5 \text{ J/m}^3}{8.314 \text{ J/mol/K} \times 300 \text{ K}} \times 0.029 \text{ kg/mol} \quad (471)$$

$$\approx 1.16 \text{ kg/m}^3. \quad (472)$$

and thus

$$W \approx (0.5 \times 1.16 \text{ kg/m}^3 \times 0.6 \text{ m}^2 \times (100 \times 10^3 / 3600 \text{ s})^2) \quad (473)$$

$$+ 0.01 \times 1500 \text{ kg} \times 9.8 \text{ m/s}^2 \times 100 \times 10^3 \text{ m} \quad (474)$$

$$\approx 4.16 \times 10^7 \text{ J}. \quad (475)$$

From the definition of heat engine efficiency

$$Q_H = \frac{W}{e_{\text{otto}}} \quad (476)$$

where from SITP Eq. 4.10:

$$e_{\text{Otto}} = 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} \quad (477)$$

$$\approx 1 - \left( \frac{1}{10.5} \right)^{7/5-1} \quad (478)$$

$$\approx 0.605 \quad (479)$$

The mass of fuel used will be

$$m_{\text{fuel}} = \frac{Q_H}{Q_H/m_{\text{fuel}}} \quad (480)$$

where, as given in the problem statement  $Q_H/m_{\text{fuel}} \approx 45 \text{ MJ/kg}$ .

To get the volume of the fuel:

$$V_{\text{fuel}} = \frac{m_{\text{fuel}}}{\rho_{\text{fuel}}} \quad (481)$$

where  $\rho_{\text{fuel}} \approx 0.755 \text{ kg/L}$  from <https://en.wikipedia.org/wiki/Gasoline#Density>.

Putting everything together:

$$V_{\text{fuel}} = \frac{1}{\rho_{\text{fuel}}} \frac{1}{(Q_H/m_{\text{fuel}})} \frac{1}{e_{\text{otto}}} \left( \frac{1}{2} \rho_{\text{air}} C_d A v^2 + C_{rr} m g \right) x \quad (482)$$

$$\approx \frac{1}{0.755 \text{ kg/L}} \times \frac{1}{45 \text{ MJ/kg}} \times \frac{1}{0.605} \times 4.16 \times 10^7 \text{ J} \quad (483)$$

$$\approx 2.02L \quad (484)$$

Thus a (naive) estimate of the fuel consumption is  $\approx 2.02 \text{ L/100km}$ .

- (d) From Toyota's web-site we find that a 2021 "L CVT" Corolla has a fuel consumption (highway) of 6.1 L/100km.

That the *real* fuel consumption is higher than our estimate is expected. We have neglected various inefficiencies, and the Otto cycle is not a particularly accurate idealization.

- (e) A nice animation of the four-stroke engine is [here](#). The key point for us is that one Otto cycle is executed for every *two* revolutions of the crankshaft at the bottom.

To get the power  $\dot{W}$  that the engine can produce, we need to combine the work done per Otto cycle, with the number of Otto cycles per second:

$$\dot{W} = W_{\text{otto}} f_{\text{otto}} \quad (485)$$

$$= Q_H e_{\text{otto}} f_{\text{otto}}. \quad (486)$$

From part b) we write:

$$Q_H = n_{\text{air}} q \quad (487)$$

$$= \frac{PV}{RT} q \quad (488)$$

so that

$$\dot{W} = \frac{PV}{RT} q e_{\text{otto}} f_{\text{otto}}. \quad (489)$$

Substituting numbers gives:

$$\dot{W} \approx \frac{10^5 \text{ J/m}^3 \times 1.8 \times 10^{-3} \text{ m}^3}{8.314 \text{ J/mol/K} \times 300 \text{ K}} \times 8.7 \times 10^4 \text{ J/mol} \times 0.605 \times \frac{6100}{2 \times 60} \text{ s}^{-1} \quad (490)$$

$$\boxed{\dot{W} \approx 190 \text{ kW}} \quad (491)$$

(As a point of interest, Toyota's [web-site](#) quotes the "horsepower" as 139 kW at 6100 RPM, which is a smaller discrepancy than we found for the fuel efficiency.)

- (f) Since air density decreases with elevation, we also expect the power of the engine to decrease. i.e., if we draw in a fixed *volume* of air, but at a lower density, then there are less oxygen molecules available for combustion.

Recall from earlier in the course (Problem Set 1) that if we assume an isothermal atmosphere, the mass density of the atmosphere  $\rho$  decreases with elevation  $z$  like

$$\rho = \rho_0 e^{-\frac{g}{RT} \langle \frac{m}{n} \rangle_{\text{air}} z} \quad (492)$$

where  $\rho$  is the mass density at sea-level ( $z = 0$ ),  $\langle \frac{m}{n} \rangle_{\text{air}}$  is the average molar mass of air,  $g$  is the gravitational constant, and  $R$  the gas constant.

Substituting the relevant numbers here:

$$\frac{\rho}{\rho_0} \approx \exp \left( \frac{-9.8 \text{ m/s}^2}{8.314 \text{ J} \cdot \text{mol/K} \times 300 \text{ K}} \times 0.029 \text{ kg/mol} \times 1640 \text{ m} \right) \quad (493)$$

$$\approx 0.83 \quad (494)$$

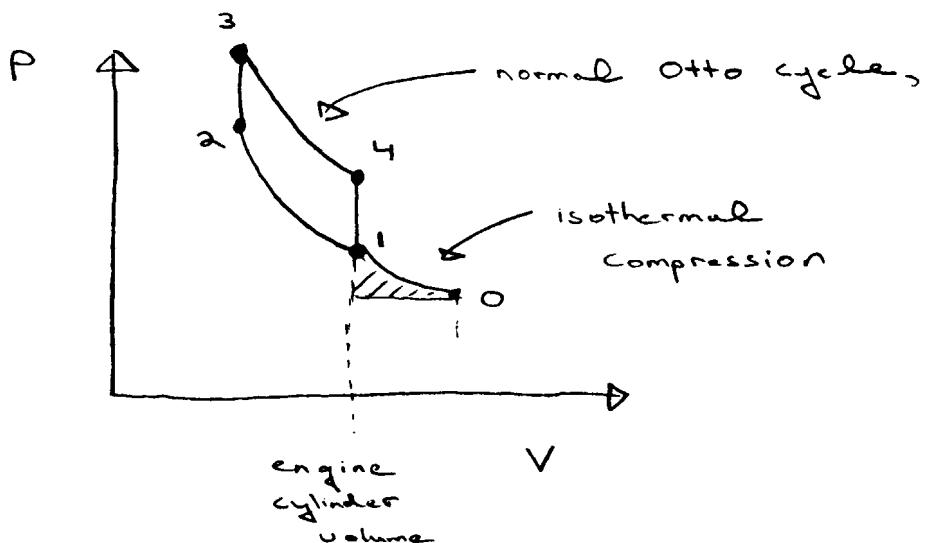
The Otto cycle efficiency doesn't depend on the density of the air. Thus we do not expect efficiency to change at the higher elevation, at least in the most naive picture. We will make less power, but we will also be burning less fuel.

At an elevation of 1640 m engine power is expected to decrease to about 80% of its sea-level value. No change in efficiency is expected.

- (g) See next page.

- (h) See next page.

(g)



$$W = Q_H \text{ otto} - W_{0 \rightarrow 1} \quad \begin{matrix} \text{work done in} \\ \text{compressing air} \end{matrix}$$

$$Q_H = \gamma \frac{P_1 V_1}{R T_1}$$

$$W_{0 \rightarrow 1} = P_1 V_1 \ln\left(\frac{P_1}{P_0}\right) - P_0 (V_0 - V_1)$$

$$\text{So } W = P_1 V_1 \left[ \frac{\gamma}{R T_1} \text{ otto} - \ln\left(\frac{P_1}{P_0}\right) + \frac{P_0 (V_0 - V_1)}{P_1 V_1} \right]$$

$$W_{\text{otto}} = \text{otto} \gamma \frac{P_0 V_1}{R T_1}$$

$$\begin{aligned} \frac{W}{W_{\text{otto}}} &= \frac{R T_1}{\gamma P_0 V_1 \text{ otto}} \left[ \frac{\gamma}{R T_1} \text{ otto} - \ln\left(\frac{P_1}{P_0}\right) + \frac{P_0 (V_0 - V_1)}{P_1 V_1} \right] \\ &= \frac{P_1}{P_0} \left[ 1 - \frac{R T_1}{\gamma \text{ otto}} \left( \ln\left(\frac{P_1}{P_0}\right) + 1 + \frac{P_0}{P_1} \right) \right] \end{aligned}$$

$$\begin{aligned} \frac{W}{W_{\text{otto}}} &\approx 2 \left[ 1 - \frac{\frac{8.314 \frac{J}{mol \cdot K} * 300K}{8.7 * 10^4 \frac{J}{mol}} * 0.605}{\left( \ln 2 + 1 + \frac{1}{2} \right)} \right] \\ \boxed{\frac{W}{W_{\text{otto}}} \approx 1.98} \end{aligned}$$

$$(h) \quad e = \frac{w}{Q_H}$$

$$= \frac{RT_1}{q} \left[ \frac{2}{RT_1} e_{otto} - \ln \left( \frac{P_1}{P_0} \right) + \frac{P_0 (v_0 - v_1)}{P_1 v_1} \right]$$

$$\frac{e}{e_{otto}} = 1 - \frac{RT_1}{q_{otto}} \left( \ln \left( \frac{P_1}{P_0} \right) - 1 + \frac{P_0}{P_1} \right)$$

$$\approx 1 - \frac{8.314 * 300K}{8.7 * 10^4 \frac{J}{mol} * 0.605} \left( \ln 2 - 1 + \frac{1}{2} \right)$$

$$\frac{e}{e_{otto}} \approx 0.99$$

(i) The goal in supercharging is to increase the amount of air ingested by the cylinders, thereby increasing power. At a given pressure, we can increase the density of air by reducing the temperature. So by “intercooling” we can increase the intake of air and thus the engine power.

It is also of some benefit to reduce the temperature of air to avoid pre-ignition during compression.

**For your interest only:**

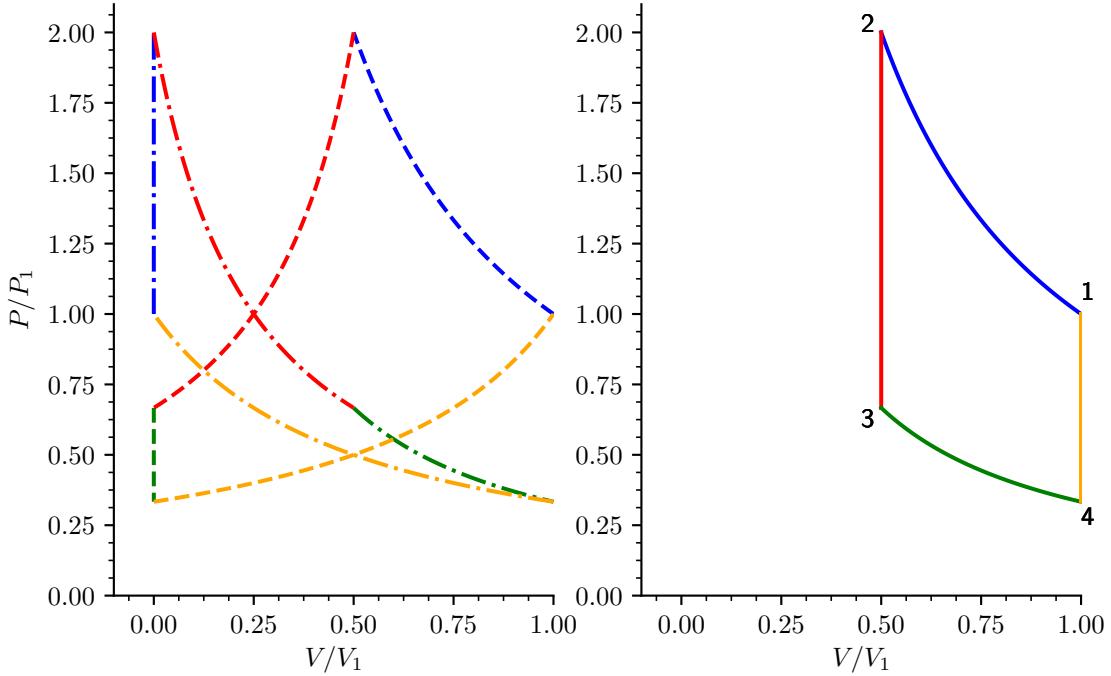
An interesting history of supercharging in aircraft is given here: <https://youtu.be/ULLsIo1VzTw>.

**Cool under pressure — answer**

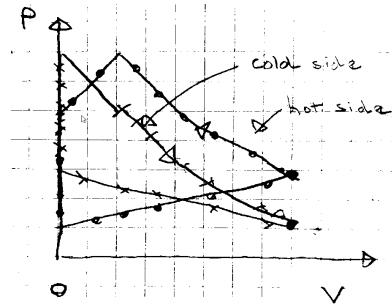
**Question.** Answer:

(a) The indicator diagrams for the hot side (dashed line) and cold side (dot dashed line) are shown on the left below. The right side shows the combined cycle. The “directions” are indicated by the coloring: blue → red → green → yellow. I’ve chosen  $T_H/T_C = 3$ . The fundamental relation used to generate the “transfer” lines is:

$$Nk = P \left( \frac{V_H}{T_H} + \frac{V_C}{T_C} \right) \quad (495)$$



A simple hand-drawn sketch was all that was required. Here is my effort before making the computer generated plot (with  $T_H/T_C$  closer to one than above):



Yes, I am no artist.

(b) The  $Q_C$  obtained in the isothermal expansion step is reduced by the requirement to cool the gas from  $T_H$  to  $T_C$ , and thus

$$Q_C = NkT_C \ln \left( \frac{V_1}{V_2} \right) - C_V(T_H - T_C) \quad (496)$$

For cooling  $Q_C > 0$ , and thus

$$NkT_C \ln \left( \frac{V_1}{V_2} \right) - C_V(T_H - T_C) > 0, \quad (497)$$

For the requested numerical estimate, we set  $C_V = (3/2)Nk$  (i.e., He gas), giving:

$$NkT_C \ln \left( \frac{V_1}{V_2} \right) - \frac{3}{2}Nk(T_H - T_C) > 0, \quad (498)$$

$$T_C \left[ \ln \left( \frac{V_1}{V_2} \right) + \frac{3}{2} \right] > \frac{3}{2}T_H. \quad (499)$$

Rearranging gives:

$$T_C > \frac{T_H}{\frac{2}{3} \ln \left( \frac{V_1}{V_2} \right) + 1} \quad (500)$$

$$> \frac{300 \text{ K}}{\frac{2}{3} \ln (2) + 1} \quad (501)$$

$$T_C > 205 \text{ K} \quad (502)$$

(c) For  $1 \rightarrow 2$  the heat released into the hot reservoir is:

$$Q_H = NkT_H \ln \left( \frac{V_1}{V_2} \right), \quad (503)$$

and for  $3 \rightarrow 4$ , the heat absorbed from the cold reservoir is:

$$Q_C = NkT_C \ln \left( \frac{V_1}{V_2} \right). \quad (504)$$

Due to the presence of the regenerator, we do not need to consider the heat released or absorbed by during  $2 \rightarrow 3$  and  $4 \rightarrow 1$  (these are the same for an ideal gas with a temperature independent heat capacity).

The COP is given by:

$$COP := \frac{Q_C}{W} \quad (505)$$

which by the first law can be written as:

$$= \frac{1}{\frac{Q_H}{Q_C} - 1}. \quad (506)$$

Substituting our  $Q_H$  and  $Q_C$  from above:

$$= \frac{1}{\frac{T_H}{T_C} - 1}, \quad (507)$$

$$(508)$$

which is the same as for the Carnot cycle.

- (d) At 77 K, we can estimate the COP from the data on the webpage (take 23 °C “reject” temperature:

$$\text{COP} \approx \frac{\dot{Q}_C}{\dot{W}} \quad (509)$$

$$\approx \frac{11 \text{ W}}{160 \text{ W}} \quad (510)$$

$$\approx 0.06875 \quad (511)$$

The Carnot value is

$$\text{COP}_{\text{Carnot}} = \frac{1}{T_H/T_C - 1} \quad (512)$$

$$\approx \frac{1}{296 \text{ K}/77 \text{ K} - 1} \quad (513)$$

$$\approx 0.351 \quad (514)$$

and thus

$$\eta = \text{COP}/\text{COP}_{\text{Carnot}} \quad (515)$$

$$\approx 0.06875/0.351 \quad (516)$$

$$\approx 0.2. \quad (517)$$

This roughly agrees with the “Percent Carnot Efficiency” plot on the webpage, which gives 19% at 77 K and 23 °C “reject” temperature.

- (e) Some possible reasons for not obtaining 100% Carnot efficiency are:

- imperfect regeneration — the regenerator heats up due to imperfect thermal insulation.
- the efficiency of the electric motor drive
- not perfect flow; i.e., turbulence and so-on, which leads to heating.

- (f) Essentially we need to determine the *amount* of gas. Then the ideal gas law will give us the pressure, since we know the relevant volume and temperature.

The heat taken from the cold reservoir by the isothermal expansion is:

$$Q_C = NkT_C \ln \left( \frac{V_1}{V_2} \right) \quad (518)$$

The web-page gives us  $\dot{Q}_C \approx 11 \text{ W}$  at  $T_C = 77 \text{ K}$ , from which, together with the cycle frequency  $f \approx 60 \text{ Hz}$ , we can determine  $Q_C$ . Rearranging Eq. 518, then gives us the amount of gas:

$$Nk = \frac{\dot{Q}_C/f}{T_C \ln \left( \frac{V_1}{V_2} \right)} \quad (519)$$

Using this result in the ideal gas law gives:

$$P_2 = \frac{NkT_H}{V_2} \quad (520)$$

$$= \frac{1}{V_1} \left( \frac{V_1}{V_2} \right) \left( \frac{T_H}{T_C} \right) \frac{\dot{Q}_C/f}{\ln \left( \frac{V_1}{V_2} \right)} \quad (521)$$

and substituting numbers:

$$P_2 \approx \frac{1}{5 \times 10^{-4} \text{ m}^3} \times 2 \times \frac{300 \text{ K}}{77 \text{ K}} \times 11 \text{ W}/60 \text{ Hz} \times \frac{1}{\ln 2} \quad (522)$$

$$\approx 4 \times 10^3 \text{ J/m}^3 \times 10^{-5} \text{ bar/Pa} \quad (523)$$

$$P_2 \approx 4 \times 10^{-2} \text{ bar} \quad (524)$$

This is quite a bit lower than I expected. If anything this pressure represents an *implosion* — not explosion — risk.

### For your interest only:

Apparently you get these cryocoolers on e-bay. See <https://youtu.be/dCXkaQa53QQ?t=40>.

## An unpleasant subject? — answer

**Question.** Answer:

- (a) When a system under constant pressure and temperature conditions lowers its Gibbs free energy ( $G = U + PV - TS$ ), the total entropy of the universe increases. Therefore the second law favours minimization of the Gibbs free energy.

The Helmholtz free energy ( $F = U - TS$ ) is relevant under conditions of constant volume (not pressure) and temperature. Lowering the Helmholtz free energy under these conditions corresponds to increasing the total entropy of the universe. Thus, for a “box” of hydrogen in thermal equilibrium with a wall at a certain temperature, the favoured conditions may be determined by minimization of the Helmholtz free energy.

- (b) The total energy is given by the kinetic energy of the three gases and the energy associated with ionization.<sup>33</sup>

$$U = N_H \frac{3}{2}kT + N_{e^-} \frac{3}{2}kT + N_{p^+} \frac{3}{2}kT - N_H R$$

which we may rewrite using  $N_{e^-} = N_{p^+} = N - N_H$  as:

$$= N_H \frac{3}{2}kT + 2 \times (N - N_H) \frac{3}{2}kT - N_H R. \quad (525)$$

The total entropy is given by:

$$S = S_H + S_{e^-} + S_{p^+} \quad (526)$$

where the entropy for each of the three gases may be evaluated using the expression given in the problem statement, so that

$$\frac{S}{k} = N_H \left[ \ln \left( \frac{V}{N_H} \frac{1}{\lambda_H^3} \right) + \frac{5}{2} \right] + N_{p^+} \left[ \ln \left( \frac{V}{N_{p^+}} \frac{1}{\lambda_{p^+}^3} \right) + \frac{5}{2} \right] + N_{e^-} \left[ \ln \left( \frac{V}{N_{e^-}} \frac{1}{\lambda_{e^-}^3} \right) + \frac{5}{2} \right] \quad (527)$$

---

<sup>33</sup>One might also write the ionization term as  $R(N - N_H)$ .

Again, we may also rewrite using  $N_{e^-} = N_{p^+} = N - N_H$ .

Combining our expressions for the total energy and entropy, in  $F = U - TS$ :

$$\begin{aligned} F = -N_H R + kT & \left\{ \frac{3}{2}N_H + 3(N - N_H) \right. \\ & - N_H \left[ \ln \left( \frac{V}{N_H} \frac{1}{\lambda_H^3} \right) + \frac{5}{2} \right] \\ & - (N - N_H) \left[ \ln \left( \frac{V}{(N - N_H)} \frac{1}{\lambda_{p^+}^3} \right) + \frac{5}{2} \right] \\ & \left. - (N - N_H) \left[ \ln \left( \frac{V}{(N - N_H)} \frac{1}{\lambda_{e^-}^3} \right) + \frac{5}{2} \right] \right\} \end{aligned} \quad (528)$$

- (c) To differentiate the expression for  $F$  with respect to  $N_H$ , it is first useful to start with the general expression for  $S$  for a monatomic ideal gas:

$$\frac{S}{k} = N \left[ \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (529)$$

and differentiate with respect to  $N$ :

$$\frac{d}{dN} \left( \frac{S}{k} \right) = \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} - \frac{N}{N} \quad (530)$$

$$= \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{3}{2}. \quad (531)$$

By using this result together with  $d/dN_H = -d/dN_{p^+} = -d/dN_{e^-}$  we may avoid some of the tedium (and possible errors) in differentiating  $F$  wrt  $N_H$ :

$$\begin{aligned} \left( \frac{\partial F}{\partial N_H} \right)_{V,T} = -R + kT & \left\{ \frac{3}{2} - 3 \right. \\ & - \frac{3}{2} - \ln \left( \frac{V}{N_H} \frac{1}{\lambda_H^3} \right) \\ & + \frac{3}{2} + \ln \left( \frac{V}{N_{p^+}} \frac{1}{\lambda_{p^+}^3} \right) \\ & \left. + \frac{3}{2} + \ln \left( \frac{V}{N_{e^-}} \frac{1}{\lambda_{e^-}^3} \right) \right\} \end{aligned} \quad (532)$$

To find the extremum (minimum, but probably we should probably show this), set equal to zero, rearrange, and simplify using number densities:

$$\frac{R}{kT} = \ln \left( \frac{\lambda_H^3 n_H}{\lambda_{p^+}^3 n_{p^+} \lambda_{e^-}^3 n_{e^-}} \right) \quad (533)$$

Rearranging to solve for the requested quantity:

$$\boxed{\frac{n_{p^+} n_{e^-}}{n_H} = \frac{\lambda_H^3}{\lambda_{e^-}^3 \lambda_{p^+}^3} e^{-R/(kT)}} \quad (534)$$

- (d) Since  $m_{e^-}/m_{p^+} \approx 1/1800$ , we have  $m_H/m_p \approx 1 + 1/1800$ , so that  $\lambda_{p^+} \approx \lambda_H$ , and so we can “cancel” these factors in Eq. 534 to give:

$$\boxed{\frac{n_{p^+}n_{e^-}}{n_H} \approx \frac{1}{\lambda_{e^-}^3} e^{-R/(kT)}} \quad (535)$$

as required.

- (e) From the definition of  $x$  (Eq. 23),  $x = n_{p^+}/n$ , and since  $n_{e^-} = n_{p^+}$ , we also have  $x = n_{e^-}/n$ . Also

$$n_H = n - n_p \quad (536)$$

$$= n - xn \quad (537)$$

$$= n(1 - x). \quad (538)$$

Using these results, we may rewrite the LHS of Eq. 535 as:

$$\frac{n_{p^+}n_{e^-}}{n_H} = \frac{n^2 x^2}{n(1-x)} \quad (539)$$

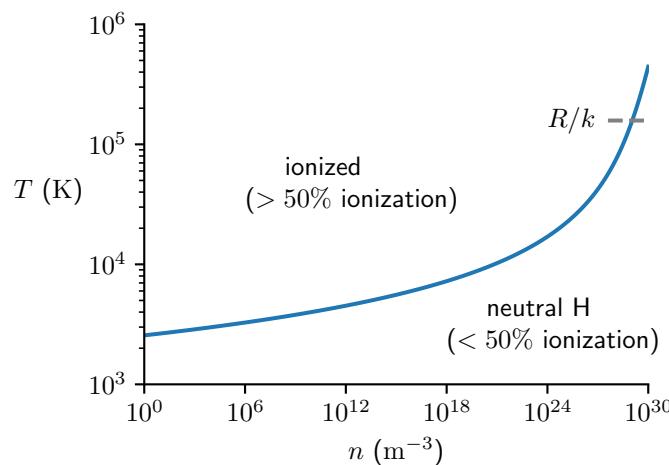
$$= n \frac{x^2}{1-x}. \quad (540)$$

So we may write Eq. 535 as:

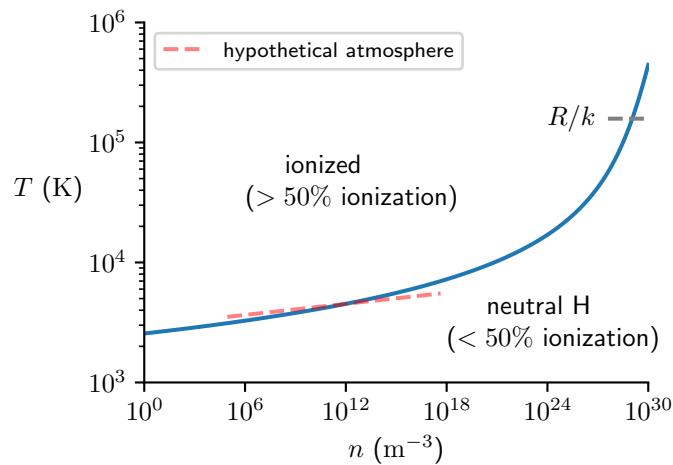
$$\boxed{n \frac{x^2}{1-x} \approx \frac{1}{\lambda_{e^-}^3} e^{-R/(kT)}} \quad (541)$$

- (f) To obtain the line which divides the “phases”, we set  $x = 0.5$  in Eq. 541. However, it is difficult (impossible?) to explicitly solve for  $T$  given  $n$ , since  $T$  appears both in the exponent and in  $\lambda_{e^-}$ . But if given  $T$ , solving for  $n$  is straightforward. We just need an appropriate range of temperatures. We can start with a range of temperatures around “the natural scale”  $T \approx R/k$  and then repeatedly enlarge the temperature range until we get the requested number density range.

(An alternate approach is to *numerically* solve Eq. 541 for the maximum and minimum  $T$  given the maximum and minimum  $n$  required.)



- (g) Consider a possible way in which both number density and temperature can decrease as we travel away from the sun's centre (dashed red line):



As one moves to the left along the red line to lower density, the temperature decreases. As we travel along this line, we also pass from less than 50% ionization to more than 50% ionization.

This example shows that as we travel outwards from the sun it *is* possible for both the temperature to decrease and the extent of ionization to *increase*, provided that the density drops sufficiently quickly.

(That lowering the density encourages ionization is an example of Le Chatelier's Principle, albeit in a less familiar context.)

### For your interest:

Saha summarizes his results nicely in the short letter: M. N. Saha, “Ionisation in the Solar Chromosphere”, [Nature 105, 232–233 \(1920\)](#) with more details in: M. N. Saha, “LIII. Ionization in the solar chromosphere”, [The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 40, 472–488 \(1920\)](#). The form of his equations are slightly different and instead of number density he refers to pressure, but in essence is the same as the treatment here.

The details of the chromosphere of the sun are not the important point here. In fact, if you examine this [figure](#) you will see that temperature decreases and then increases as we travel outwards through the chromosphere. However, Saha went on to apply his equation to the photosphere and the determination of the surface temperatures of different stars, which *is* important. Later Fowler and Milne incorporated the internal levels of the atoms into the theory. (Notice that we ignored the fact that hydrogen has energy levels (!) You will be able to account for these once you study statistical mechanics in Phys 359.) More of the history of Saha and his equation are given in <http://arxiv.org/abs/1810.10898> and the book: G. Venkataraman, *Saha and his formula* (Universities Press, Hyderabad, 1995). Besides some interesting biographical material, one also sees that physicists learned something from chemists — the chemist Nernst in particular.

The Saha equation is also relevant in cosmology, since there is a special significance to the time at which electrons and protons become cool enough so that they combine to make hydrogen (confusingly referred to as **recombination**). Don't forget the importance of density! After

recombination, electromagnetic radiation travels much more freely and interacts less with matter. Although recombination is discussed in all cosmology texts, non-specialists may wish to look at Chapter 9, *Thermodynamics of the early universe*, in R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed (Elsevier/Academic Press, Amsterdam ; Boston, 2011), <https://archive.org/details/PathriaR.K.BealeP.D.StatisticalMechanics>.

You will find a “phase diagram”, similar to the one you have computed in this question, but with more physical phenomena indicated, in Fig. 20.1 of K. S. Thorne and R. D. Blandford, *Modern classical physics: optics, fluids, plasmas, elasticity, relativity, and statistical physics* (Princeton University Press, Princeton, 2017). You can find a pre-publication version of the figure on page 7 of <http://www.pmaweb.caltech.edu/Courses/ph136/yr2012/1220.1.K.pdf>.

## Pockets for atoms — answer

**Question.** Answer:

- (a) Suppose initially, for the sake of argument, that we sequentially place *A distinguishable* atoms in *M* locations. Then the first atom has *M* possible locations, the second has *M* – 1 and so-on, so that the total number of ways to place the distinguishable atoms is  $M \times (M - 1) \times \dots \times (M - (A - 1)) = M!/(M - A)!$ . If we now consider that the atoms are in fact *indistinguishable* we will have over-counted by a factor of *A*!, as each arrangement of atoms may be rearranged in *A*! ways. Thus we divide by this factor, so that the multiplicity associated with the pocketed atoms is:

$$\Omega_p = \frac{M!}{(M - A)!A!} \quad (542)$$

which is conventionally written as

$$\boxed{\Omega_p = \binom{M}{A}} \quad (543)$$

(You must provide justification for this result; but that could be as straightforward as noting the similarity to other systems, such as the two-state paramagnet — see pg 99 of SITP.)

- (b) Starting with

$$S_p = k \ln \Omega_p \quad (544)$$

and taking  $\Omega_p$  from the previous part we have:

$$\frac{S_p}{k} = k \ln \Omega_p \quad (545)$$

$$= \ln M! - \ln(M - A)! - \ln A! \quad (546)$$

to which we apply Stirling’s approximation ( $\ln n! \approx n \ln n - n$ ) to obtain:

$$\frac{S_p}{k} \approx M \ln M - M - (M - A) \ln(M - A) + (M - A) - A \ln A + A \quad (547)$$

$$\boxed{\frac{S_p}{k} \approx M \ln M - (M - A) \ln(M - A) - A \ln A} \quad (548)$$

as required.

- (c) The quantity  $F = U - TS$  has been constructed “by design” for this purpose. i.e., minimizing  $F$  for a constant volume system in thermal equilibrium with a constant temperature reservoir will maximize the *total* entropy of the universe: i.e., that of the system *and* the reservoir.

I'll briefly justify this assertion (mainly following SITP Section 5.2). Consider the total entropy given by:

$$S_{\text{total}} = S + S_R \quad (549)$$

where  $S$  corresponds to the system of interest and  $S_R$  is the entropy of the reservoir. Since it is a constant temperature reservoir:

$$dS_R = \frac{dU_R}{T}. \quad (550)$$

But the energy gained by the reservoir is obtained from the system, so that  $dU_R = -dU$ , and we may write the change in the total entropy as

$$dS_{\text{total}} = dS + dS_R \quad (551)$$

$$= -\frac{1}{T}(dU - TdS) \quad (552)$$

and since  $F = U - TS$ , we have  $dF = dU - TdS$ , so that

$$dS_{\text{total}} = -\frac{dF}{T}. \quad (553)$$

Thus, maximizing entropy of the *universe* (not just the system) is equivalent to minimizing the Helmholtz free energy of a fixed volume system that is in thermal equilibrium with its surrounding environment.

- (d) The total free energy of the system, which includes the pocketed atoms and surrounding gas, may be obtained from the associated energies and entropies:

$$F = U - TS \quad (554)$$

$$= U_p + U_g - T(S_p + S_g) \quad (555)$$

$$= U_p - TS_p + U_g - TS_g \quad (556)$$

Let us take the derivative wrt to  $A$ , the number of pocketed (absorbed) atoms. We will initially consider the derivatives of each of the four terms of Eq. 556 separately:

- (i) As stated in question:

$$U_p = -\epsilon A \quad (557)$$

and thus

$$\frac{dU_p}{dA} = -\epsilon. \quad (558)$$

- (ii) From part (b):

$$\frac{S_p}{k} = M \ln M - A \ln A - (M - A) \ln(M - A) \quad (559)$$

$$= M \ln M - A \ln A - M \ln(M - A) + A \ln(M - A) \quad (560)$$

so that

$$\frac{1}{k} \frac{dS_p}{dA} = -\ln A - 1 + \frac{M}{M - A} + \ln(M - A) - \frac{A}{M - A} \quad (561)$$

$$= \ln \left( \frac{M - A}{A} \right) \quad (562)$$

(iii) For a monatomic ideal gas:

$$U_g = \frac{3}{2} N k T. \quad (563)$$

Since the total number of atoms  $A + N$  is fixed,  $U_g$  has an implicit dependence on  $A$ . By the chain rule:

$$\frac{dU_g}{dA} = -\frac{dU_g}{dN} \quad (564)$$

$$= -\frac{3}{2} k T \quad (565)$$

(iv) From the problem statement:

$$S_g = N k \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right]. \quad (566)$$

Again, as with  $U_g$ ,  $S_g$  depends implicitly on  $A$ , so that

$$\frac{1}{k} \frac{dS_g}{dA} = -\frac{1}{k} \frac{dS_g}{dN} \quad (567)$$

$$= - \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right] - N \left( -\frac{1}{N} \right) \quad (568)$$

$$= -\ln \left( \frac{V}{N \lambda^3} \right) - \frac{3}{2}. \quad (569)$$

Using the results of Eq.'s 558, 562, 565, and 569 to take the derivative of Eq. 556 gives:

$$\frac{dF}{dA} = \frac{dU_p}{dA} - T \frac{dS_p}{dA} + \frac{dU_g}{dA} - T \frac{dS_g}{dA} \quad (570)$$

$$= -\epsilon - kT \ln \left( \frac{M-A}{A} \right) - \frac{3}{2} kT + kT \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{3}{2} \right] \quad (571)$$

$$= -\epsilon - kT \ln \left( \frac{M}{A} - 1 \right) + kT \ln \left( \frac{V}{N \lambda^3} \right) \quad (572)$$

$$= -\epsilon - kT \ln \left( \left[ \frac{M}{A} - 1 \right] \frac{V}{N \lambda^3} \right). \quad (573)$$

Setting this derivative equal to zero and rearranging to solve for  $M/A$  gives:

$$\frac{M}{A} = 1 + \frac{V}{N \lambda^3} e^{-\epsilon/(kT)} \quad (574)$$

and thus the fraction of the pockets with atoms is

$$\boxed{\frac{A}{M} = \frac{1}{1 + \frac{V}{N \lambda^3} e^{-\epsilon/(kT)}}} \quad (575)$$

(e) Using the ideal gas law in the form  $V/N = kT/P$  we have

$$\frac{A}{M} = \frac{1}{1 + \frac{kT}{P \lambda^3} e^{-\epsilon/(kT)}}. \quad (576)$$

Equivalently

$$\frac{A}{M} = \frac{1}{1 + \frac{P_0}{P}}, \quad (577)$$

where

$$P_0 = \frac{kT}{\lambda^3} e^{-\epsilon/(kT)} \quad (578)$$

$$= kT \left( \frac{2\pi\hbar^2}{MT} \right)^{3/2} e^{-\epsilon/(kT)} \quad (579)$$

$$P_0 = (kT)^{5/2} \left( \frac{2\pi m}{h^2} \right)^{3/2} e^{-\epsilon/(kT)} \quad (580)$$

as was required.

(f) It is convenient to rearrange Eq. 577 to solve for  $P$  in terms of  $A/M =: f$ :

$$P = P_0 \frac{f}{1-f}, \quad (581)$$

so that we have a **linear least squares** problem. More specifically, given the  $P_i$ ,  $f_i$  data points, we can ask: what  $P_0$  minimizes the error

$$e = \sum_i \left( P_i - P_0 \frac{f_i}{1-f_i} \right)^2 ? \quad (582)$$

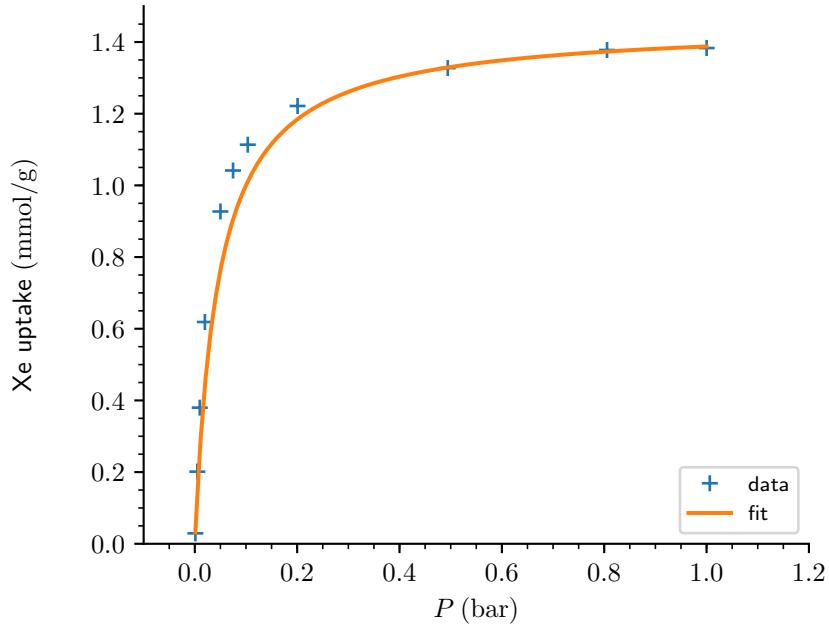
Differentiating wrt to  $P_0$ , setting the derivative equal to zero, and then rearranging gives:

$$P_0 = \frac{\sum_i P_i f_i / (1-f_i)}{\sum_i (f_i / (1-f_i))^2}, \quad (583)$$

which when evaluated using the data points gives:

$$P_0 \approx 0.0450 \text{ bar}. \quad (584)$$

There are many equally valid ways to go about this fitting; e.g., direct fitting of Eq. 577, using canned functions from Python, etc... The most important thing is to *check* your fit graphically:



There does seem to be a systematic difference between the data and the fitted model, suggesting that something has been overlooked; i.e., the model is either too simple or that there are problems with the data.

(g) To determine  $\epsilon$ , we may rearrange Eq. 578, giving:

$$\epsilon = kT \ln \left( \frac{1}{P_0} (kT)^{5/2} \left( \frac{2\pi m}{h^2} \right)^{3/2} \right) \quad (585)$$

for which substituting the relevant numbers gives:

$$\epsilon \approx 0.54 \text{ eV} \quad (586)$$

(If I was a better person, I would do an error estimate.)

The eV scale is the energy scale associated with “atomic” and “molecular” phenomena. Recall that the Rydberg constant is given by fundamental constants:

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}, \quad (587)$$

which is  $\approx 13.6$  eV. This sets the energy scale for ionization, chemical bonds and so-on.

More precisely, chemical bonds correspond to the range of about 1.5 eV to 10 eV (source: [https://en.wikipedia.org/wiki/Bond-dissociation\\_energy](https://en.wikipedia.org/wiki/Bond-dissociation_energy)). As Xe is *inert* we would expect it to stick to the pockets with less than a typical bond energy. So  $\epsilon \approx 0.5$  eV is unlikely to be a significant *underestimate*; i.e., it is good that our estimate is not higher as that would correspond to typical chemical bonding energies, which we do not expect for Xe sticking to a surface.

On the other hand, it turns out that two Xe atoms may form a weak **van der Waals** bond in the gas phase.<sup>34</sup> It takes about 0.023 eV to break this bond [34]. We would expect the “bond” of a single Xe atom to a surface to be a bit stronger than this.

---

<sup>34</sup>It turns out that the “lazy” gases are not so lazy after all.

Thus,  $\epsilon \approx 0.5$  eV is certainly reasonable, at least to within an order of magnitude or so. Furthermore, Fig. 1b of Banerjee *et al.* [35] indicates that the “average energy of Xe adsorption” (indicated by the colour yellow in the diagram) for the “pocket” material here, SBMOF-1, is  $\approx 40$  kJ/mol  $\approx 0.4$  eV which is surprisingly close to our fitted estimate.

(There are other good answers to this question.)

- (h) Given a certain pressure  $P$ , we may compute the  $P_0$  required to give any fractional uptake  $A/M =: f$  by rearranging Eq. 577 to give:

$$P_0 = P \frac{1-f}{f}. \quad (588)$$

From that  $P_0$  we may use Eq. 580 to determine the required temperature, making use of the  $\epsilon$  determined in the previous part of this question. The only slight issue is that the equation cannot be rearranged to directly solve for  $T$  — instead we must numerically solve this equation:

```

1  """Determine temperature required for uptake"""
2
3  from scipy import optimize as so, constants as sc
4  import numpy as np
5
6  p = 0.2e5  # pressure
7  f = 1.0 / 1.45  # fractional uptake
8  p_0_target = p * (1.0 / f - 1.0)  # target value of p_0
9  epsilon = 0.539507 * sc.e  # from previous part
10
11 def p_0(t):
12     """P_0 corresponding to temperature t"""
13     m = 131.293 * 1e-3 / sc.N_A
14     return ((sc.k * t)**2.5 *
15             (2 * np.pi * m / sc.h**2)**1.5 * np.exp(-epsilon/(sc.k * t)))
16
17 def error(t):
18     return p_0_target - p_0(t)
19
20 # solve for temperature to give the target value of p_0:
21 print("temperature (K): ", so.brentq(error, 250.0, 350.0))

```

From this program we compute that for an uptake of 1.0 mmol/g at 0.2 bar:

$$T \approx 307 \text{ K}. \quad (589)$$

But this estimate is fairly sensitive to the determined  $\epsilon$ . For example, the also reasonable  $\epsilon \approx 0.55$  eV gives  $T \approx 312$  K.

### For your interest only:

The curve of uptake versus pressure is known more generally as an **isotherm**. Instead of “pockets” one normally refers to **adsorption sites**.

A nice recent review of the area is Ref. [36], from which pointed me to the article by Banerjee *et al.* [35].

There are obviously many ways to generalize the theory, particularly if we are dealing with sites on planar surfaces. For example, we could include motion on the surface, interactions between the adsorbed atoms, and so-on. And of course, the more general case is for *molecules*, for which the Sackur-Tetrode equation does not apply.

But those are all just complications. You would still need to minimize the Helmholtz free energy and that is the important point here.

(This problem is also solved using the “grand partition function” formalism on pg 174 of Ref. [37].)

## Falling apart — answer

**Question.** Answer:

- (a) When a nitrogen molecule dissociates into two atoms, the entropy of the *system* increases.

On the other hand, for a constant temperature, this energy for dissociation must come from the surrounding reservoir, which will *decrease* its entropy as heat flows out of it.

As the course notes explain, the definition of the Helmholtz free energy  $F := U - TS$ , reflects this competition between these two entropies. The  $U$  term relates to the entropy of the reservoir, whereas the  $-TS$  term relates to the entropy of the system. Minimizing  $F$ , will maximize the total entropy (of the system and surrounding reservoir), for constant volume, constant temperature systems.

- (b) The energy of the system is

$$U = -DN_2 + \frac{3}{2}kT(N_1 + N_2). \quad (590)$$

Substituting  $N_2 = (N - N_1)/2$  gives:

$$U = -D \frac{(N - N_1)}{2} + \frac{3}{2}kT \left( N_1 + \frac{N - N_1}{2} \right) \quad (591)$$

Note that I have taken the “zero energy” as corresponding to a sample of all N atoms ( $N_2 = 0$ ), not moving ( $T = 0$ ). A constant offset, independent of  $N_1$ , is fine — it will disappear upon differentiation wrt  $N_1$ .

- (c) The total entropy of the system is just the sum of the entropy of both gas components:

$$S = S_{\text{N}} + S_{\text{N}_2} \quad (592)$$

$$= S(N_2, V, T, m_{\text{N}_2}) + S(N_1, V, T, m_{\text{N}}) \quad (593)$$

where

$$S(N, V, T, m) = Nk \left[ \ln \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad \text{with} \quad \lambda := \sqrt{\frac{2\pi\hbar^2}{mkT}}, \quad (594)$$

Substituting  $N_2 = (N - N_1)/2$  gives:

$$S = S\left(\frac{N - N_1}{2}, V, T, m_{N_2}\right) + S(N_1, V, T, m_N) \quad (595)$$

- (d) I find it useful to differentiate  $U$  and  $S$  in  $F = U - TS$  separately. Otherwise it is a bit too much to fit everything on a single line (and error-prone). To differentiate the entropies it is helpful to start with the form given in Eq. 594, and determine that:

$$\frac{1}{k} \frac{dS}{dN} = \ln\left(\frac{V}{N\lambda^3}\right) + \frac{3}{2}. \quad (596)$$

We apply this result twice to our system. i.e.,

$$\frac{dS}{dN_1} = \frac{dS_{N_2}}{dN_2} \frac{dN_2}{dN_1} + \frac{dS_N}{dN_1} \quad (597)$$

by the chain rule, where  $dN_2/dN_1 = -1/2$ . So we have

$$\frac{1}{k} \frac{dS}{dN_1} = -\frac{1}{2} \left[ \ln\left(\frac{V}{N_2 \lambda_{N_2}^3}\right) + \frac{3}{2} \right] + \ln\left(\frac{V}{N_1 \lambda_N^3}\right) + \frac{3}{2}. \quad (598)$$

which simplifies to

$$\frac{1}{k} \frac{dS}{dN_1} = \ln\left(\frac{V}{N_1} \frac{1}{\lambda_N^3} \sqrt{\frac{\lambda_{N_2}^3 N_2}{V}}\right) + \frac{3}{4} \quad (599)$$

We will use this result in  $dF/dN_1$  shortly; now let us turn to  $dU/dN_1$ . Starting from our expression in Eq. 591, and differentiating wrt to  $N_1$  gives:

$$\frac{dU}{dN_1} = \frac{D}{2} + \frac{3}{4}kT. \quad (600)$$

Using this together with entropy derivative gives:

$$\frac{1}{k} \frac{dF}{dN_1} = \frac{D}{2k} + \frac{3}{4}T - T \times \left[ \ln\left(\frac{V}{N_1} \frac{1}{\lambda_N^3} \sqrt{\frac{\lambda_{N_2}^3 N_2}{V}}\right) + \frac{3}{4} \right]. \quad (601)$$

Setting equal to zero and simplifying gives

$$\frac{D}{2k} = T \ln\left(\frac{V}{N_1} \frac{1}{\lambda_N^3} \sqrt{\frac{\lambda_{N_2}^3 N_2}{V}}\right) \quad (602)$$

Equivalently:

$$\frac{N_1}{V} = \frac{1}{\lambda_N^3} \sqrt{\frac{\lambda_{N_2}^3 N_2}{V}} \times \exp\left(-\frac{D}{2kT}\right) \quad (603)$$

and with the approximation  $N_2 \approx N/2$ :

$$\frac{N_1}{V} \approx \frac{1}{\lambda_N^3} \sqrt{\frac{\lambda_{N_2}^3 N}{2V}} \times \exp\left(-\frac{D}{2kT}\right) \quad (604)$$

(e) By the ideal gas law:

$$\frac{P_N}{P_N + P_{N_2}} = \frac{N_1}{N_1 + N_2} \quad (605)$$

but we again assume  $N_1 \ll N_2$  so that

$$\frac{P_N}{P_N + P_{N_2}} \approx \frac{N_1}{N_2} \quad (606)$$

$$\approx \frac{N_1/V}{N/(2V)}. \quad (607)$$

Substituting the expression for  $N_1/V$  from the previous part of this question gives:

$$\frac{P_N}{P_N + P_{N_2}} \approx 2 \sqrt{\frac{1}{2} \frac{\lambda_{N_2}^3}{\lambda_N^6} \frac{V}{N}} \times \exp\left(-\frac{D}{2kT}\right) \quad (608)$$

Note that the prefactor is dimensionless as is the argument to exp. That is good.

As per the problem statement, the factor  $V/N$  is given by the ideal gas law:

$$\frac{V}{N} = \frac{1}{2} \frac{kT}{P} \quad (609)$$

where  $T = 300\text{ K}$  and  $P = 1\text{ bar}$ . (Recall that there are *two* nitrogen atoms per nitrogen molecule.) Thus:

$$\frac{P_N}{P_N + P_{N_2}} \approx \sqrt{\frac{kT}{P} \frac{\lambda_{N_2}^3}{\lambda_N^6}} \times \exp\left(-\frac{D}{2kT}\right) \quad (610)$$

Numerical evaluation is rather tedious. Here is something that might be useful to you in the future: usage of python, with automatic "units" / checking of dimensions:

```

1 import numpy as np
2 import pint # handy for checking units and physical constants
3 ureg = pint.UnitRegistry(auto_reduce_dimensions=True)
4
5 def thermal_de_broglie(amu, t):
6     """Compute the thermal deBroglie wavelength given atomic mass
7     and absolute temperature (K)"""
8     k = ureg("boltzmann_constant").to("J / K")
9     hbar = ureg("planck_constant").to("J * s") / (2.0 * np.pi)
10    m = amu * ureg("amu").to("kg")
11    return np.sqrt(2.0 * np.pi * hbar**2 / (m * k * t))
12
13 if __name__ == "__main__":
14     k = ureg("boltzmann_constant").to("J / K")
15     t = 300.0 * ureg("K")
16     lambda_n = thermal_de_broglie(14, t).to("m")
17     lambda_n2 = thermal_de_broglie(28, t).to("m")
18     kt_div_p = (k * t / (1e5 * ureg("Pa"))).to("m^3")
19     d = 9.8 * ureg("eV").to("J")

```

```

20     p_ratio = (np.sqrt(kt_div_p * lambda_n2**3 / lambda_n**6)
21             * np.exp(-d / (2 * k * t)))
22     print("lambda_n:", lambda_n)
23     print("lambda_n2:", lambda_n2)
24     print("kt_div_p:", kt_div_p)
25     print("partial pressure ratio:", p_ratio)

```

which outputs:

```

1 lambda_n: 2.6938616683594083e-11 meter
2 lambda_n2: 1.9048478532754438e-11 meter
3 kt_div_p: 4.1419464000000006e-26 meter ** 3
4 partial pressure ratio: 4.177180061658617e-80 dimensionless

```

So that

$$\boxed{\frac{P_N}{P_N + P_{N_2}} \approx 4 \times 10^{-80}} \quad (611)$$

This very low fraction certainly supports the common assumption that nitrogen gas at room temperature and pressure consists of solely of N<sub>2</sub>. Of course, we should check some of the assumptions regarding the entropy of N<sub>2</sub>. But the principle of the calculation will remain the same.

### For your interest only:

In some sense this process is a simple chemical reaction and thus is amenable to the standard approaches discussed in Section 5.6 of SITP (not normally covered in Phys 358). But I think that there is a significant pedagogical advantage to *not* using those standard techniques when first approaching the subject. Those techniques tend to be used in a cookbook fashion. Concentrating on the Helmholtz free energy for a fixed volume system — as we have done here — makes the role of the second law clear. With that appreciation instilled, the slick procedures of the chemists may then be adopted!

It is interesting to do a quick calculation using the standard techniques, because it quickly tells us how bad using the Sackur-Tetrode equation for N<sub>2</sub> was.

The fundamental result that we need is an adaptation of Eq. 5.105 of SITP:

$$RT \ln \left( \frac{P_{N_2} P_0}{P_N^2} \right) = \Delta G^0 \quad (612)$$

corresponding to the “reaction”:



From the literature [38] we find  $\Delta G_f^0(N) \approx 455.56 \text{ kJ}$  (this is to make 1 mol of N at  $T = 298 \text{ K}$  and  $P = 1 \text{ bar}$ ). So for the reaction of Eq. 613, we have  $\Delta G^0 \approx 455.56 \text{ kJ} \times 2 \approx 911.12 \text{ kJ}$ .

We may rearrange Eq. 612 to obtain the quantity of interest (assuming  $P_N \ll P_{N_2}$ ):

$$\frac{P_N}{P_{N_2}} = \sqrt{\frac{P_0}{P_{N_2}}} \times e^{-\Delta G^0/(2RT)} \quad (614)$$

and substitute numbers to obtain:

$$\frac{P_N}{P_{N_2}} \approx \exp\left(-\frac{911.12 \text{ kJ} \times 1000 \text{ J/kJ}}{2 \times 8.314 \text{ J/K} \times 298 \text{ K}}\right) \quad (615)$$

$$\approx 1.4 \times 10^{-80} \quad (616)$$

in quite reasonable agreement with the naive estimate that we made.

It is also possible to compute a “naive” value of  $\Delta G^0$  using the assumptions of the problem (i.e., that the entropy of  $N_2$  is given by the Sackur-Tetrode equation and that there is no internal excitation of  $N_2$ ). This approximate  $\Delta G^0$  may then be substituted into Eq. 614, which gives precisely the estimate of Eq. 611, as expected.

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