Thermodynamics: Ideal Gases & Thermodynamic Laws (Solutions)

FIZIKA SPhO Training

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Contents

1 Notes

Now, we shall study how ideal gases behave and how energy flows.

Remark. Unless other specified, in this handout, take W to be the work done **on** the gas. To be clear, sometimes, it will be specified as W_{on}.

1.1 Ideal Gases

The **ideal gas model** is a simplified model for gas particles that is widely used in physics.

1.1.1 Macroscopic Properties: P, V, T

When we deal with gases, there are **three** macroscopic quantities we are concerned with:

1. **Pressure,** P exerted by gas particles as they collide with the walls of the container
2. **Volume,** V occupied by the gas
3. **Temperature,** T of the gas, a measure of how much energy it has

These three quantities are sufficient to uniquely describe any collection of ideal gas particles.

Remark. Sometimes, it doesn't make sense to talk about volume. For instance, when describing the atmosphere, volume isn't very well defined. We usually talk about density instead (alongside pressure and temperature).

1.1.2 Kinetic Theory of Gases

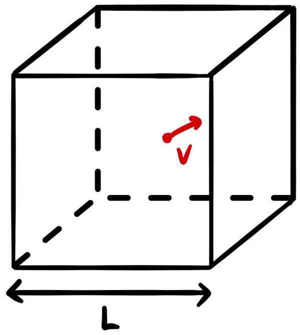
The **kinetic theory** is widely used to describe the motion and properties of ideal gases.

It is based on the following assumptions:

1. There are a **large number** of gas particles **constantly** in **random** motion.
2. The gas is **isotropic** (i.e. motion along the x, y and z directions are equal).
3. Potential energy between the gas particles is negligible.
4. All collisions (between particles or between particle and wall) are **elastic.**

Assumption 3 means that ideal gases have **no potential energy,** and hence their total energy is just their kinetic energy.

Assumption 4 is interesting to study, in terms of the momentum transfer during collisions. Consider a cubical box of length L, with $N >> 1$ ideal gas particles.



The number density is hence $n = \frac{N}{L^3}$. Now, consider a particle hitting a wall aligned with the $y - z$ plane. We can find $\Delta\ t$, the time between successive collisions, and Δp, the magnitude of momentum transferred per collision:

$$\Delta t = \frac{2L}{\langle v_x \rangle} \tag{1}$$

$$\Delta p = 2 \langle p_x \rangle \tag{2}$$

Hence, the average force contributed by each particle is

$$F_{\text{ave}} = \frac{\Delta p}{\Delta t} = \frac{\langle p_x v_x \rangle}{L} \tag{3}$$

and the total pressure contributed by all N particles is

$$P = \frac{N F_{\text{ave}}}{L^2} = \frac{N \langle p_x v_x \rangle}{L^3} = n \langle p_x v_x \rangle \tag{4}$$

Since the gas is isotropic, the x, y and z directions are equal. Hence,

$$\langle p_x v_x \rangle = \langle p_y v_y \rangle = \langle p_z v_z \rangle \tag{5}$$

Thus, we can relate $\langle p_x v_x \rangle$ (along one axis) to $\langle \mathbf{p} \cdot \mathbf{v} \rangle$:

$$\langle \mathbf{p} \cdot \mathbf{v} \rangle = \langle p_x v_x \rangle + \langle p_y v_y \rangle + \langle p_z v_z \rangle \quad \Rightarrow \quad \langle p_x v_x \rangle = \frac{1}{3} \langle \mathbf{p} \cdot \mathbf{v} \rangle \tag{6}$$

As a result, we obtain

$$P = \frac{1}{3} n \langle \mathbf{p} \cdot \mathbf{v} \rangle \tag{7}$$

This is a key result of kinetic theory. But more importantly, you should recognise how to use **isotropy arguments** to solve problems with kinetic theory.

1.1.3 Ideal Gas Law

The **ideal gas law** directly relates all three macroscopic properties:

$$PV = nRT \quad \text{or} \quad PV = N k_{\text{B}} T \tag{8}$$

where n is the number of moles, N is the number of particles, $R = 8.31\,\text{J/mol} \cdot \text{K}$ is the molar gas constant, and $k_{\text{B}} = 1.38 \times 10^{-23}\,\text{J/K}$ is the Boltzmann's constant.

From chemistry, you should also know that

$$N = n N_{\text{A}} \tag{9}$$

where $N_{\text{A}} = 6.02 \times 10^{23}\,\text{mol}^{-1}$ is the Avogadro's constant.

Either form of Equation (8) can be used, depending on whether you are more interested in the number of moles or the number of particles.

Remark. Equation (8) can only be applied for **ideal gases!** You may run into non-ideal gases sometimes in Olympiad problems. In such cases, the equation of state (the replacement for Equation (8) which takes into account non-ideal corrections) will be given to you. A famous example is the Van der Waals equation.

Sometimes, it may be more convenient to think in terms of density, ρ. Then, we can write:

$$PV = nRT = \frac{m}{\mu} RT \quad \Rightarrow \quad \frac{m}{V} = \frac{P\mu}{RT} \quad \Rightarrow \quad \rho = \frac{P\mu}{RT} \tag{10}$$

where μ is the molar mass of the gas.

From now on, our discussion will be restricted to ideal gases.

1.2 The First Law of Thermodynamics

The **first law** relates three important quantities: the internal energy, U, the work done, W, and the heat, Q:

$$\Delta U = \Delta Q + \Delta W \quad \text{or} \quad \mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \tag{11}$$

It is essentially a restatement of the conservation of energy. Any changes in internal energy could be due to work done on/by the gas or heat entering/leaving the gas.

1.2.1 Internal Energy, Work Done, Heat, Enthalpy

The **internal energy,** U, is the total KE and PE of a system of particles. (For an ideal gas, as PE $= 0$, this is just the total KE.)

For an ideal gas only,

$$U = nc_\mathrm{V}T \quad \text{or} \quad \mathrm{d}U = nc_\mathrm{V}\,\mathrm{d}T \tag{12}$$

where c_V is the molar heat capacity of the gas at constant volume. More on this later.

The **work done,** W, **on** a gas against a pressure P is given by

$$W_\mathrm{on} = -P\Delta V \quad \text{or} \quad \mathrm{d}W_\mathrm{on} = -P\,\mathrm{d}V \tag{13}$$

Remark. The **negative sign** in Equation (12) is very important! In contrast, if you were asked for work done **by** a gas, then there is no negative sign.

The **enthalpy,** H, is another useful quantity you may encounter. It is defined as

$$H = U + PV \quad \text{or} \quad \mathrm{d}H = \mathrm{d}U + \mathrm{d}\,(PV) \tag{14}$$

You should have learnt about heat capacities, C, and specific heat capacities (by mass), c:

$$\Delta Q = C\Delta T \quad \text{or} \quad \mathrm{d}Q = C\,\mathrm{d}T \tag{15}$$

$$\Delta Q = mc\Delta T \quad \text{or} \quad \mathrm{d}Q = mc\,\mathrm{d}T \tag{16}$$

However, in thermodynamics, we are more interested in the **molar heat capacity** (i.e. heat capacity per mole). More on this in Section 1.2.3.

1.2.2 State Functions

State functions are very useful quantities in thermodynamics. Essentially, these are quantities that are **path-independent** (i.e. their values only depend on the initial and final states).

It should be quite easy to see that Q and W are **not state functions,** since they depend on what you actually do to the gas.

However, T, U and H are **state functions!** These are quantities that measure the characteristics of a system at its current state, and don't depend on what you actually do to the gas.

State functions are important as they are much more easily calculated than non-state functions. Additionally, all state functions **are unchanged under a cyclic process.**

1.2.3 Relationship between c_P and c_V

There is a very important relationship between c_P, the molar heat capacity at constant pressure, and c_V, the molar heat capacity at constant volume.

Consider a **constant pressure** process. The molar heat capacity is c_P, so $\mathrm{d}Q = nc_\mathrm{P}\,\mathrm{d}T$. Using the first law,

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \quad \Rightarrow \quad nc_\mathrm{V}\,\mathrm{d}T = nc_\mathrm{P}\,\mathrm{d}T - P\,\mathrm{d}V \tag{17}$$

Using the ideal gas law, $P\,\mathrm{d}V = nR\,\mathrm{d}T$. Hence,

$$nc_\mathrm{V}\,\mathrm{d}T = nc_\mathrm{P}\,\mathrm{d}T - nR\,\mathrm{d}T \quad \Rightarrow \quad c_\mathrm{P} - c_\mathrm{V} = R \tag{18}$$

The final result of Equation (17) is very important!

We usually also define γ, the heat capacity ratio, to link c_P and c_V:

$$\gamma = \frac{c_\mathrm{P}}{c_\mathrm{V}} \tag{19}$$

It is useful to combine Equations (17) and (18) to get the relations

$$c_\mathrm{P} = \frac{\gamma R}{\gamma - 1}, \quad c_\mathrm{V} = \frac{R}{\gamma - 1} \tag{20}$$

Now, what exactly are the values of $c_\mathrm{P}, c_\mathrm{V}$ and γ? They depend on the **atomicity** of the gas:

1. **Monoatomic gases** (such as Ne, Ar): $c_\mathrm{P} = \frac{5}{2}R$, $c_\mathrm{V} = \frac{3}{2}R$, $\gamma = \frac{5}{3}$
2. **Diatomic gases** (such as N_2, O_2): $c_\mathrm{P} = \frac{7}{2}R$, $c_\mathrm{V} = \frac{5}{2}R$, $\gamma = \frac{7}{5}$

Remark. The derivation of the coefficients can be understood using the concept of degrees of freedom. However, this is not needed, and you can just memorise the coefficients. For this same reason, polyatomic gases are complicated to deal with in terms of their degrees of freedom, which is why we usually don't talk about them.

1.2.4 KE of Ideal Gases

As discussed previously, for ideal gases, the internal energy is just the kinetic energy.

We are usually interested in the **root-mean-square (RMS) speed** of gas particles. Mathematically, the RMS is defined as

$$v_\mathrm{RMS} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{\sum_{i=1}^{N} v_i^2}{N}} \tag{21}$$

Consider a monoatomic ideal gas. Equating the internal energy to the kinetic energy,

$$\frac{3}{2}nRT = \frac{1}{2}\mu n v_\mathrm{RMS}^2 \quad \Rightarrow \quad v_\mathrm{RMS} = \sqrt{\frac{3RT}{\mu}} \tag{22}$$

Equation (22) describes the RMS speed in terms of temperature. When we talk about the effective speed of gas particles, we are usually referring to this.

Remark. Be careful! The RMS speed **does not depend on the atomicity** of the gas particles/molecules. This is because only the translational degrees of freedom contribute to it, and every particle/molecule only has 3 translational degrees of freedom (x, y, z).

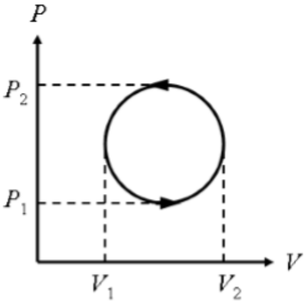
1.2.5 $P-V$ Diagrams (And How to Read Them)

To analyse processes, we usually plot them as $P-V$ diagrams on graphs, where P is the y-axis and V is the x-axis.

The reason why they are useful is because **work** can be easily calculated:

$$W = -\int P \, \mathrm{d}V = -\,(\text{area under the } P-V \text{ graph}) \tag{23}$$

Example 1.1 (SJPO 2009)**.** A thermodynamic system undergoes a cyclic process as shown in the figure below. What is the heat energy absorbed by the system over one complete cycle?



This is an easy example applying Equation (21). For a closed loop, since U is a state function, $\Delta U = 0$. Hence,

$$\Delta U = \Delta Q + \Delta W = 0 \quad \Rightarrow \quad \Delta Q = -\Delta W = \text{area under the } P-V \text{ graph}$$

The area is just the area of the ellipse (or circle), hence

$$\Delta Q = \pi \left(\frac{P_2 - P_1}{2}\right)\left(\frac{V_2 - V_1}{2}\right) = \frac{\pi}{4}\left(P_2 - P_1\right)\left(V_2 - V_1\right)$$

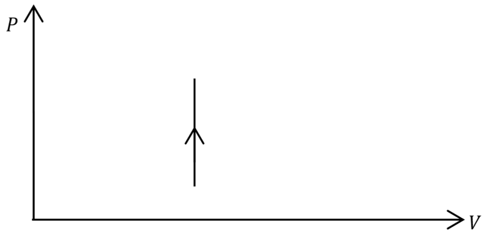
In reality, you aren't going to see circular $P-V$ diagrams. These processes are extremely contrived, but it is nonetheless important for you to know how to apply the area concept.

1.2.6 Common Processes: Isobaric, Isochoric, Isothermal, Adiabatic

There are **4 common processes** that you need to know how to deal with:

1. **Isobaric:** Constant pressure ($P = \text{constant}$)
2. **Isochoric:** Constant volume ($V = \text{constant}$)
3. **Isothermal:** Constant temperature ($T = \text{constant}$)
4. **Adiabatic:** No heat flow ($Q = 0$)

Let's start with an **isochoric process** (as it is the easiest):



From the ideal gas law, since $V = \text{constant}$,

$$\frac{P}{T} = \text{constant} \tag{24}$$

Using the first law,

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q \quad (\text{since } \mathrm{d}V = 0) \tag{25}$$

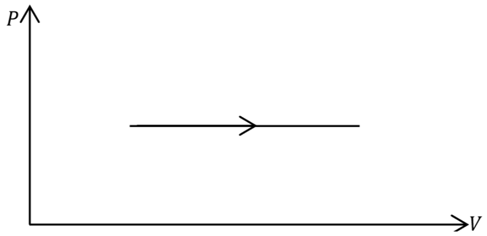
$$Q = \Delta U = nc_\mathrm{V}\Delta T \tag{26}$$

Finally, the enthalpy change is

$$\Delta H = \Delta\left(U + PV\right) = \Delta U + V\Delta P = \Delta U + nR\Delta T = n\left(c_\mathrm{V} + R\right)\Delta T = nc_\mathrm{P}\Delta T \tag{27}$$

Remark. Since U and H are state functions, $\Delta U = nc_\mathrm{V}\Delta T$ and $\Delta H = nc_\mathrm{P}\Delta T$ work for *any* process. However, $Q = nc_\mathrm{V}\Delta T$ does not work for non-isochoric processes, as it is path-dependent!

Next, we move on to an **isobaric process:**



From the ideal gas law, since $P = \text{constant}$,

$$\frac{V}{T} = \text{constant} \tag{28}$$

Using the first law,

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P\,\mathrm{d}V \tag{29}$$

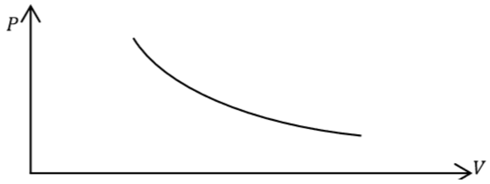
$$W = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -P\Delta V = -nR\Delta T \tag{30}$$

$$Q = nc_\mathrm{P}\Delta T \tag{31}$$

Finally, the enthalpy change is

$$\Delta H = nc_\mathrm{P}\Delta T \tag{32}$$

Then, we move on to an **isothermal process:**



From the ideal gas law, since $T = \text{constant}$,

$$PV = \text{constant} \tag{33}$$

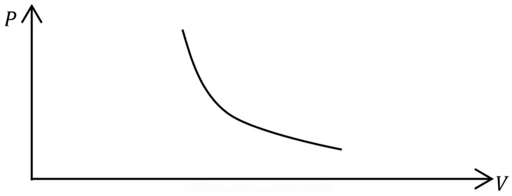
Using the first law,

$$\mathrm{d}U = 0,\ \Delta U = 0 \quad \Rightarrow \quad \mathrm{d}Q = -\,\mathrm{d}W = P\,\mathrm{d}V \tag{34}$$

$$Q = \int P \, \mathrm{d}V = \int_{V_1}^{V_2} \frac{nRT}{V} \, \mathrm{d}V = nRT \ln\left(\frac{V_2}{V_1}\right) \tag{35}$$

Finally, the enthalpy change is the same as Equation (27) or (32).

Lastly, we move on to an **adiabatic process:**



The fundamental relationships are:

$$PV^{\gamma} = \text{constant} \quad \text{or} \quad TV^{\gamma-1} = \text{constant} \quad \text{or} \quad P^{1-\gamma}T^{\gamma} = \text{constant} \tag{36}$$

Using the first law,

$$\mathrm{d}Q = 0, \; Q = 0 \quad \Rightarrow \quad \mathrm{d}U = \mathrm{d}W = -P \, \mathrm{d}V \tag{37}$$

$$W = \Delta U = nc_{\mathrm{V}} \Delta T \tag{38}$$

Finally, the enthalpy change is the same as Equation (27) or (32).

Now, let's apply these results to solve some problems.

Example 1.2 (Kalda)**.** Consider a balloon which has thick rigid walls from which all the air has been pumped out. Now, the valve of the balloon is slightly opened, and the balloon is slowly filled with the air from outside. Find the temperature of the air inside the balloon once the air flow has stopped (since a mechanical equilibrium has been reached). The room temperature is T, the balloon walls have low heat conductivity and capacity such that heat flux through the walls can be neglected. Treat air as diatomic.

Let the balloon have a volume V and let the atmospheric pressure be P_0. We shall consider our system as all the air that eventually makes it into the balloon.

Suppose this air has a volume V_0 when it is outside the balloon (before it enters). The chamber initially is a vacuum ($P = 0$), hence the work done **by** the rest of the atmosphere on this volume V_0 as it enters is P_0V_0.

The final internal energy of this air is hence

$$U = U_0 + W_{\mathrm{by}} = \frac{5}{2}nRT_0 + P_0V_0 = \frac{5}{2}nRT_0 + nRT_0 = \frac{7}{2}nRT_0$$

On the other hand, the final internal energy is also given by

$$U = \frac{5}{2}nRT_{\mathrm{f}}$$

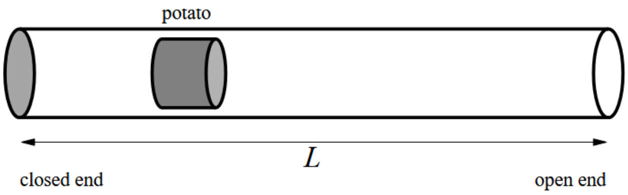
Hence, comparing the two expressions, the final temperature is

$$T_{\mathrm{f}} = \frac{7}{5}T_0$$

after which, the flow of air stops as a mechanical (pressure) equilibrium is reached.

Remark. You might suspect this violates COE, since the gas is increasing in temperature out of nowhere. Deep down, this extra energy is **gravitational;** the entire atmosphere must shrink down towards the Earth a little once a volume V_0 of air is removed from it, and this decrease in GPE compensates for the increase in internal energy of the gas.

Example 1.3 (USAPhO 2009, modified)**.** A potato gun fires a potato horizontally down a half-open cylinder of cross-sectional area A. When the gun is fired, the potato is at rest, the volume between the end of the cylinder and the potato is V_0, and the pressure of the gas in this volume is P_0. The atmospheric pressure is P_{atm}, where $P_0 > P_{\text{atm}}$. The gas in the cylinder is diatomic. The potato moves down the cylinder quickly enough so that no heat is transferred to the gas. Friction between the potato and the barrel is negligible and no gas leaks around the potato.



The parameters P_0, P_{atm}, V_0 and A are fixed, but the overall length L of the barrel may be varied. What is the maximum kinetic energy E_{max} with which the potato can exit the barrel, and at what length L does this occur?

The potato accelerates to the right as long as the pressure of the gas is greater than P_{atm}. Hence, our objective is to let the potato exit exactly when the pressures are equal.

The work done **by** the gas on the potato in this case is

$$W = \frac{c_V}{R}\left(P_0 V_0 - P_{\text{atm}} V_{\text{f}}\right)$$

However, remember that the potato is moving against air! Thus, we need to account for the work done by the atmospheric pressure. As such, the total energy given to the potato is

$$E_{\text{max}} = W - W_{\text{atm}} = \frac{c_V}{R}\left(P_0 V_0 - P_{\text{atm}} V_{\text{f}}\right) - P_{\text{atm}}\left(V_{\text{f}} - V_0\right)$$

Since no heat enters/leaves the gas, the expansion is adiabatic, hence

$$P_0 V_0^{\gamma} = P_{\text{atm}} V_{\text{f}}^{\gamma} \quad \Rightarrow \quad V_{\text{f}} = V_0 \left(\frac{P_0}{P_{\text{atm}}}\right)^{\frac{1}{\gamma}}$$

Combining all of these results, and using $c_V = \frac{5}{2}R$, we have

$$E_{\text{max}} = \frac{5}{2}P_0 V_0 - \frac{7}{2}P_{\text{atm}} V_{\text{f}} + P_{\text{atm}} V_0 = \left(\frac{5}{2}P_0 + P_{\text{atm}} - \frac{7}{2}P_{\text{atm}}^{\frac{2}{7}} P_0^{\frac{5}{7}}\right) V_0$$

For this to happen, the length of the tube is just

$$L = \frac{V_{\text{f}}}{A} = \frac{V_0}{A}\left(\frac{P_0}{P_{\text{atm}}}\right)^{\frac{5}{7}}$$

Many thermodynamics problems involving the 4 common processes also tie in to mechanics.

Example 1.4 (Kevin Zhou, modified)**.** Consider a cylinder of gas with adiabatic constant γ, cross-sectional area A and volume V. Assume all surfaces are frictionless and thermally insulating. A piston of mass m is placed snugly on top, and the entire set-up is inside an atmosphere with pressure P_{atm}. Suppose the system was initially in equilibrium. The piston is then given a small downward displacement. Find the angular frequency of small oscillations. (This set-up is known as the Rüchardt experiment, and can be used to determine γ.)

The equilibrium pressure of the gas is

$$P = P_{\text{atm}} + \frac{mg}{A}$$

by balancing forces on the piston.

When the piston has a displacement of x (defining positive x as downwards), let the gas pressure be P_x. Then, since the process is adiabatic (as all surfaces are thermally insulating),

$$PV^\gamma = P_x \left(V - Ax\right)^\gamma \quad \Rightarrow \quad P_x = P\left(\frac{V}{V - Ax}\right)^\gamma \approx P\left(1 + \frac{\gamma Ax}{V}\right)$$

Hence, writing N2L for the piston,

$$m\ddot{x} = -\left(P_x - P\right)A = -\frac{P\gamma A^2}{V}x \quad \Rightarrow \quad \ddot{x} + \frac{\gamma PA^2}{mV}x = 0$$

This is of the form of a SHM with angular frequency

$$\omega = \sqrt{\frac{\gamma PA^2}{mV}}$$

1.3 The Second Law of Thermodynamics

The **second law** has many equivalent formulations by different physicists:

1. **Clausius:** No process is possible whose sole result is the transfer of heat from a colder to a hotter body.
2. **Kelvin:** The efficiency of a thermodynamic cycle can never be 100%.
3. **Carnot:** Of all heat engines working between two fixed temperatures, none is more efficient than the Carnot engine.

It can be proven that these 3 statements all say the same thing.

1.3.1 Reversible vs Irreversible Processes

Before we discuss more about the second law, it is important for you to understand the difference between **reversible and irreversible** processes.

A **reversible** process is one where the system and environment can be restored to its initial state, by going backwards along the path of the process.

An **irreversible** process is the opposite – one where the system and environment will *not* return to its original state by going backwards along the path of the process.

This is important as we will define the **entropy,** S, later. The type of process influences how entropy changes:

1. **Reversible processes:** $\mathrm{d}S = 0$
2. **Irreversible processes:** $\mathrm{d}S > 0$
3. IMPOSSIBLE: $\mathrm{d}S < 0$

In addition, any **cyclic** process is reversible, since the system returns to its original state.

1.3.2 Macroscopic Formulation of Entropy

The **entropy,** S, is the measure of a system's thermal energy per unit temperature that is *unavailable* for doing useful work. It measures the level of **randomness or disorder** in a system.

For a **reversible process only,**

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \quad \text{or} \quad \Delta S = S_\mathrm{f} - S_\mathrm{i} = \int_\mathrm{i}^\mathrm{f} \frac{\mathrm{d}Q}{T} \tag{39}$$

Amazingly, even though heat is not a state function, **entropy is a state function!** This means entropy is extremely useful for solving problems involving cyclic processes, as the net entropy change will be 0! We will see how to apply entropy to solve such questions in Section 1.5.2.

First, let's deal with some simpler examples pertaining to entropy.

Example 1.5 (Ricardo)**.** A steel bar, whose heat capacity is h, is heated to temperature t and then plunged into a **large** oil bath at temperature T. Assume no heat loss from the system of the bar and the bath. Calculate the increase in entropy. Convince yourself that the system's entropy always increases no matter which initial temperature is higher.

Since the bath is large, its temperature will remain roughly constant at T throughout. As such, using Equation (39),

$$\Delta S_\mathrm{sys} = \Delta S_\mathrm{bar} + \Delta S_\mathrm{bath} = \int_t^T \frac{h\,\mathrm{d}t}{t} + \frac{h\,(t-T)}{T} = h\ln\left(\frac{T}{t}\right) + \frac{ht}{T} - h = h\left(\ln\left(\frac{T}{t}\right) + \frac{t}{T} - 1\right)$$

To prove that this quantity is always positive, define $x = \frac{t}{T}$. Then,

$$\Delta S_\mathrm{sys}\,(x) = h\,(x - \ln x - 1) \quad \Rightarrow \quad \frac{\mathrm{d}\,(\Delta S_\mathrm{sys})}{\mathrm{d}x} = h\left(1 - \frac{1}{x}\right)$$

Note that $\frac{\mathrm{d}(\Delta S_\mathrm{sys})}{\mathrm{d}x} > 0$ when $x > 1$, and $\frac{\mathrm{d}(\Delta S_\mathrm{sys})}{\mathrm{d}x} < 0$ when $x < 1$. This means that $x = 1$ corresponds to a local minimum, by the first derivative test.

But, $\Delta S_\mathrm{sys}\,(1) = 0$ is the minimum, and it is achieved when $T = t$. Hence, in general, when $T \neq t$, we have $x \neq 1$ and that means $\Delta S_\mathrm{sys} > 0$.

This example shows you that indeed, $\mathrm{d}S \geq 0$!

Example 1.6 (Kevin Zhou)**.** A container of volume V is divided in half by a partition. The two halves contain pure nitrogen and oxygen gas respectively, both of n moles at pressure P and temperature T. The partition is removed and the gases are allowed to mix. How much does the entropy increase?

Be careful with applying Equation (39) here! The gas is not in equilibrium through the process, and hence Equation (39) is not directly applicable.

However, since entropy is a state function, we are still allowed to apply Equation (39) through a process that only goes through equilibrium, reversible states!

Suppose we introduce a magical piston at one end, that is somehow transparent to oxygen. By moving it quasistatically and isothermally to the centre of the container, we move all the nitrogen back to where they started.

Since this process is isothermal, $Q = -W$. Hence,

$$\Delta S_{\mathrm{N}_2} = \frac{Q}{T} = -\frac{W}{T} = nR\ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right) = -nR\ln 2$$

By repeating a similar argument for oxygen, we also obtain

$$\Delta S_{\mathrm{O}_2} = -nR\ln 2$$

After these two processes, we get taken back to the original state. Since entropy is a state function, the increase in entropy when we allowed the gases to mix is hence

$$\Delta S = -\Delta S_{\mathrm{N}_2} - \Delta S_{\mathrm{O}_2} = 2nR\ln 2$$

which is positive, as expected!

1.4 Heat Engines And Heat Pumps

Heat engines and heat pumps are everywhere in daily life, and they run on cyclic processes.

In what follows, a **reservoir** is defined as a large heat source/sink that is maintained at a **constant temperature** throughout, regardless of how much heat was put in/taken away.

Heat engines transfer heat from a hot reservoir to a cold reservoir, and are used to **perform work.** In contrast, **heat pumps** transfer heat from a cold reservoir to a hot reservoir, and it **requires input work.**

1.4.1 Efficiency and Coefficient of Performance (COP)

The **efficiency** of a heat engine is defined as

$$\eta = \frac{|W|}{|Q_\mathrm{H}|} = 1 - \frac{|Q_\mathrm{C}|}{|Q_\mathrm{H}|} \tag{40}$$

Remark. Sometimes, the absolute values are left out. It should be understood, then, that signs are already accounted for, and all the values above are positive.

The **coefficient of performance (COP)** is defined differently for heat pumps and refrigerators! (Be careful with this!)

For a **heat pump,**

$$\mathrm{COP}_\mathrm{pump} = \frac{|Q_\mathrm{H}|}{|Q_\mathrm{H}| - |Q_\mathrm{C}|} \tag{41}$$

For a **refrigerator,**

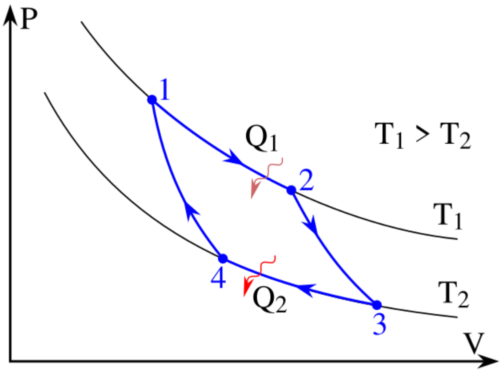
$$\mathrm{COP}_\mathrm{refrigerator} = \frac{|Q_\mathrm{C}|}{|Q_\mathrm{H}| - |Q_\mathrm{C}|} \tag{42}$$

Of course, high efficiency and high COP are desirable.

1.4.2 Carnot Cycle

The **Carnot cycle** consists of 4 stages:

1. Isothermal expansion
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression



It can be proven (by finding Q_H and Q_C) that for a Carnot cycle only,

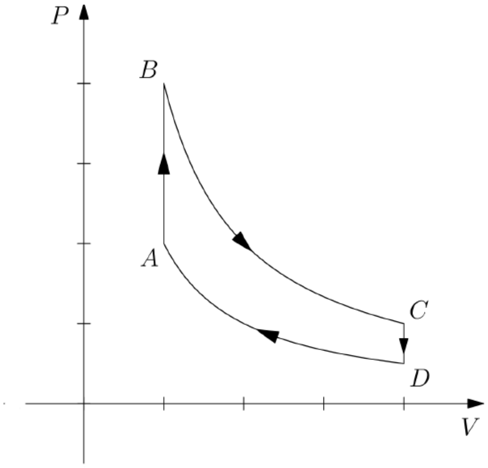
$$\eta_\mathrm{carnot} = 1 - \frac{T_\mathrm{H}}{T_\mathrm{C}} \tag{43}$$

This is also the **maximum possible** efficiency achieved between T_H and T_C.

1.4.3 Otto Cycle

The **Otto cycle** also consists of 4 stages:

1. Isochoric process (increase in pressure)
2. Adiabatic expansion
3. Isochoric process (decrease in pressure)
4. Adiabatic compression



It can also be proven (by finding Q_H and Q_C) that for an Otto cycle only,

$$\eta_\text{otto} = 1 - \left(\frac{V_\text{min}}{V_\text{max}}\right)^{\gamma-1} \tag{44}$$

1.5 Ideas

Many tricky thermodynamics problems involve the use of the following ideas.

1.5.1 Dynamics Involving Ideal Gases

Problems involving ideal gases can become dynamics questions, because the first law is essentially a restatement of COE. We shall see a few examples below on how to deal with them.

Example 1.7 (Kevin Zhou)**.** A space station is a large cylinder of radius R_0 filled with air molecules of mass m. The cylinder spins about its axis at an angular velocity ω, and the air rotates along with it. If the temperature T is constant and uniform inside the station, what is the ratio of the air pressure at the centre of the station to that at the rim?

It is simplest to work in the rotating frame of the cylinder. In this case, the gas is at rest and experiences a centrifugal force.

By balancing forces on a thin parcel of air of radial thickness dr and area A,

$$A\,\mathrm{d}P = \rho A\omega^2 r\,\mathrm{d}r \quad\Rightarrow\quad \mathrm{d}P = \rho\omega^2 r\,\mathrm{d}r$$

since the pressure differential is balanced by the centrifugal force.

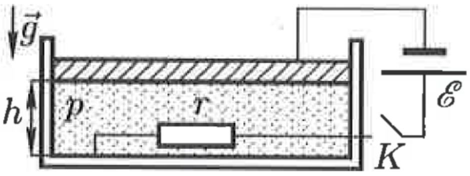
From the ideal gas law, $\rho = \frac{P\mu}{RT} = \frac{Pm}{k_\mathrm{B}T}$. Hence,

$$\frac{\mathrm{d}P}{P} = \frac{m\omega^2 r}{k_\mathrm{B}T}\,\mathrm{d}r \quad\Rightarrow\quad \int_{P(0)}^{P(R_0)} \frac{\mathrm{d}P}{P} = \int_0^{R_0} \frac{m\omega^2 r}{k_\mathrm{B}T}\,\mathrm{d}r \quad\Rightarrow\quad \frac{P\left(0\right)}{P\left(R_0\right)} = \exp\left(-\frac{m\omega^2 R_0^2}{2k_\mathrm{B}T}\right)$$

This example shows you that you can also perform infinitesimal analysis on ideal gases, just like you have been doing in mechanics and electromagnetism!

Remark. There is actually another (faster) way to solve this using statistical mechanics. More on this will be covered in the next handout.

Example 1.8 (Russia)**.** A cylinder with a metal bottom and insulating walls is underneath a thin massive metal piston located at a height h, which is much smaller than the cylinder diameter. A resistor of resistance r is placed inside and connected to an electric circuit with an emf E. The circuit is connected to the piston and cylinder bottom with light flexible wires.



Initially, the switch is open, the cylinder is filled with helium at a pressure $p \gg \frac{\varepsilon_0 E^2}{h^2}$. Treat helium as having a dielectric constant of 1. The system is thermally insulated, placed in a vacuum, and at thermal and mechanical equilibrium. Then, the switch K is closed. Find the height H of the piston after a long time.

A lot of things happen at once: the RC circuit, the expansion of the gas, and the movement of the piston. This would be a pain to analyse, but thankfully, we are only interested in the system's state after a long time – a hint to use COE!

The total energy added to the system is from the work done by the battery, Eq, where q is the final charge on the capacitor plates. Hence, the COE equation is

$$\frac{3}{2}pAh + mgh + Eq = \frac{3}{2}p_{\text{f}}AH + mgH + \frac{q^2}{2C}$$

The final charge is

$$q = CE = \frac{\varepsilon_0 AE}{H}$$

hence, the attractive force between the capacitor plates is

$$F = \frac{q^2}{2\varepsilon_0 A} = \frac{\varepsilon_0 AE^2}{2H^2}$$

Balancing forces on the piston, the final pressure is hence

$$p_{\text{f}} = p + \frac{F}{A} = p + \frac{\varepsilon_0 E^2}{2H^2}$$

Of course, force balance for the initial state gives

$$mg = pA$$

Combining all these results together carefully, and writing everything in terms of $\frac{H}{h}$, gives

$$\left(\frac{H}{h}\right)^2 - \frac{H}{h} = -\frac{\varepsilon_0 E^2}{10h^2 p} \quad \Rightarrow \quad H = h\left(\frac{1}{2} + \sqrt{\frac{1}{4} - \frac{\varepsilon_0 E^2}{10h^2 p}}\right) \approx h - \frac{\varepsilon_0 E^2}{10hp}$$

where we have taken the physically meaningful positive root.

1.5.2 Utilising Entropy

Entropy is immensely useful when it comes to cyclic processes.

Example 1.9. Prove Equation (43) using entropy.

Since a Carnot cycle is reversible, $\Delta S = 0$. As such,

$$\Delta S = \Delta S_{\text{C}} + \Delta S_{\text{H}} = \frac{Q_{\text{C}}}{T_{\text{C}}} - \frac{Q_{\text{H}}}{T_{\text{H}}} = 0 \quad \Rightarrow \quad \frac{Q_{\text{C}}}{Q_{\text{H}}} = \frac{T_{\text{C}}}{T_{\text{H}}} \quad \Rightarrow \quad \eta = 1 - \frac{Q_{\text{C}}}{Q_{\text{H}}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}$$

Here, we have been careful with the signs. $\Delta S_{\text{C}} > 0$ as the cold reservoir gains heat (and hence entropy), while $\Delta S_{\text{H}} < 0$ as the hot reservoir loses heat (and hence entropy).

Ultimately, this is so much more elegant than finding Q_{C} and Q_{H} and then finding the ratio!

Example 1.10. Two metal blocks A and B are thermally insulated from the environment, but are in good thermal contact with each other. They have heat capacities C_{A} and C_{B} respectively, and are initially at temperatures T_{A} and T_{B} respectively. A Carnot engine is run between the two blocks. What is the maximum work that can be extracted from the engine?

Again, we use the idea that $\Delta S = 0$. We know that the blocks must equilibrate (after a while) to some common temperature T. As such, we can find their corresponding entropy changes:

$$\Delta S_{\mathrm{A}} = \int_{T_{\mathrm{A}}}^{T} \frac{\mathrm{d}Q_{\mathrm{A}}}{T_{\mathrm{A}}} = \int_{T_{\mathrm{A}}}^{T} \frac{C_{\mathrm{A}}\,\mathrm{d}T_{\mathrm{A}}}{T_{\mathrm{A}}} = C_{\mathrm{A}} \ln\left(\frac{T}{T_{\mathrm{A}}}\right)$$

$$\Delta S_{\mathrm{B}} = \int_{T_{\mathrm{B}}}^{T} \frac{\mathrm{d}Q_{\mathrm{B}}}{T_{\mathrm{B}}} = \int_{T_{\mathrm{B}}}^{T} \frac{C_{\mathrm{B}}\,\mathrm{d}T_{\mathrm{B}}}{T_{\mathrm{B}}} = C_{\mathrm{B}} \ln\left(\frac{T}{T_{\mathrm{B}}}\right)$$

$$\Delta S = \Delta S_{\mathrm{A}} + \Delta S_{\mathrm{B}} = 0 \quad \Rightarrow \quad C_{\mathrm{A}} \ln\left(\frac{T}{T_{\mathrm{A}}}\right) + C_{\mathrm{B}} \ln\left(\frac{T}{T_{\mathrm{B}}}\right) = 0 \quad \Rightarrow \quad \ln\left(\frac{T^{C_{\mathrm{A}}+C_{\mathrm{B}}}}{T_{\mathrm{A}}^{C_{\mathrm{A}}} T_{\mathrm{B}}^{C_{\mathrm{B}}}}\right) = 0$$

$$\Rightarrow \quad T = T_{\mathrm{A}}^{\frac{C_{\mathrm{A}}}{C_{\mathrm{A}}+C_{\mathrm{B}}}} T_{\mathrm{B}}^{\frac{C_{\mathrm{B}}}{C_{\mathrm{A}}+C_{\mathrm{B}}}}$$

To calculate the total work extracted, we can just use COE.

The total heat extracted from A is

$$Q_{\mathrm{A}} = C_{\mathrm{A}} \left(T_{\mathrm{A}} - T\right)$$

and the total heat input into B is

$$Q_{\mathrm{B}} = C_{\mathrm{B}} \left(T - T_{\mathrm{B}}\right)$$

As such, the maximum work extracted is

$$W = Q_{\mathrm{A}} - Q_{\mathrm{B}} = C_{\mathrm{A}} \left(T_{\mathrm{A}} - T\right) + C_{\mathrm{B}} \left(T - T_{\mathrm{B}}\right) = C_{\mathrm{A}} T_{\mathrm{A}} + C_{\mathrm{B}} T_{\mathrm{B}} - \left(C_{\mathrm{A}} + C_{\mathrm{B}}\right) T_{\mathrm{A}}^{\frac{C_{\mathrm{A}}}{C_{\mathrm{A}}+C_{\mathrm{B}}}} T_{\mathrm{B}}^{\frac{C_{\mathrm{B}}}{C_{\mathrm{A}}+C_{\mathrm{B}}}}$$

1.5.3 Mean Free Path

The **mean free path,** λ, is important when we deal with the frequency of collisions of gas particles. It is the average distance a particle travels *before* colliding with another particle.

Consider two random particles numbered 1 and 2. The expectation value of the square of the relative velocity is

$$\left\langle \mathbf{v}_{\mathrm{rel}}^2 \right\rangle = \left\langle (\mathbf{v}_1 - \mathbf{v}_2)^2 \right\rangle = \left\langle |\mathbf{v}_1|^2 + |\mathbf{v}_2|^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2 \right\rangle = \left\langle |\mathbf{v}_1|^2 + |\mathbf{v}_2|^2 \right\rangle \tag{45}$$

whereby the last equality holds because $\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = 0$, since the velocities of random particles must not be correlated due to the random nature.

Therefore, the magnitude of the relative speed is just

$$v_{\mathrm{rel}} = \sqrt{|\mathbf{v}_1|^2 + |\mathbf{v}_2|^2} = \sqrt{2} v \tag{46}$$

This means that the frequency of collisions is $\sqrt{2}$ times of that compared to if a particle was striking a stationary target.

We have established the existence of a factor of $\sqrt{2}$. The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\sigma n} = \frac{k_{\mathrm{B}} T}{\sqrt{2}\pi d^2 P} \tag{47}$$

where σ is the effective cross-sectional area of collisions, and n is the number density of particles. Assuming spherical particles of diameter d, it can be shown that $\sigma = \pi d^2$.

While the mean free path is rarely tested in Olympiad problems, it is good to know Equation (47), and it also provides some intuition for Section 1.5.4.

1.5.4 Effusion

Effusion is the process whereby gas particles escape from a container through a small hole. In this regime, the hole is so small that the diameter of the hole $d \ll \lambda$.

Qualitatively, during effusion, particles fly out of the hole without encountering others at all. Therefore, we shouldn't think about the average gas pressure or flow velocity, but rather just analyse each individual particle.

Effusion obeys **Graham's Law:**

$$\frac{r_1}{r_2} = \sqrt{\frac{\mu_2}{\mu_1}} \tag{48}$$

where r is the rate of effusion and μ is the molar mass. This provides a quantitative way to compare effusion rates between two gases.

Example 1.11 (Kalda)**.** Natural uranium consists of mainly two isotopes, ^{238}U and ^{235}U, and the relative concentration of the latter is 0.7%. Uranium is enriched by a multi-stage process, where at each stage, evaporated UF_6 is led through a porous wall. The porous wall is a thin film with microscopic holes, much smaller than the mean free path of the molecules, but larger than the dimension of the molecules. How many stages are needed to increase the ^{235}U content to 1.4%? The molar mass of fluorine is 19 g/mol.

The key observation is that since the average translational KE of particles is $\frac{3}{2}k_\mathrm{B}T$, both types of UF_6 have the same average translational KE.

Suppose the two types of UF_6 have molecular masses M_1 and M_2 respectively. Then, equating the average translational KE,

$$\frac{1}{2}M_1v_1^2 = \frac{1}{2}M_2v_2^2 \quad \Rightarrow \quad \frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

Hence, the ratio of rates at which ^{238}U and ^{235}U leave is

$$\frac{r_{238}}{r_{235}} = \sqrt{\frac{M_{235}}{M_{238}}} \approx 0.9957$$

Throughout the process, almost all the uranium is ^{238}U, hence the proportion of it falls by approximately $\frac{r_{238}}{r_{235}}$ per stage. Therefore, the number of stages N is

$$0.9957^N = \frac{0.7}{1.4} = \frac{1}{2} \quad \Rightarrow \quad N \approx 160$$

2 Problems

Problems are arranged in roughly increasing difficulty.

Problem 2.1 (SPhO 2005)**.** In a cylinder of an automobile engine just after combustion, the gas is confined to a volume of $50.0\,\mathrm{cm}^3$ and has an initial pressure of $3.00 \times 10^6\,\mathrm{Pa}$. The piston moves outwards to a final volume of $300\,\mathrm{cm}^3$ and the gas expands without energy loss by heat. (i) If the adiabatic constant is $\gamma = 1.40$ for the gas, what is the final pressure? (ii) Determine the amount of work done by the gas during the expansion.

Solution. (i) This is a very simple application of the adiabatic condition:

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \Rightarrow \quad P_2 = P_1 \left(\frac{V_1}{V_2}\right)^\gamma = 2.44 \times 10^5\,\mathrm{Pa}$$

(ii) You can approach this via integrating $W_{\mathrm{by}} = \int P\,\mathrm{d}V$. However, an easier way is to just apply the first law for an adiabatic process:

$$\Delta W_{\mathrm{adiabatic,by}} = -\Delta U = \frac{5}{2}\left(P_1 V_1 - P_2 V_2\right) = 192\,\mathrm{J}$$

Problem 2.2 (SPhO 2009)**.** A certain amount of steam initially at 130°C is used to warm $200\,\mathrm{g}$ of water in a $100\,\mathrm{g}$ glass container from 20.0°C to θ. Calculate the mass of steam required if the temperature is (i) $\theta = 100°\mathrm{C}$ (ii) $\theta = 50°\mathrm{C}$.

You may use the following data:

1. Specific heat capacity of glass, $c_{\mathrm{glass}} = 837\,\mathrm{J\,kg^{-1}\,K^{-1}}$
2. Specific heat capacity of steam, $c_{\mathrm{steam}} = 2.01 \times 10^3\,\mathrm{J\,kg^{-1}\,K^{-1}}$
3. Specific heat capacity of water, $c_{\mathrm{water}} = 4.19 \times 10^3\,\mathrm{J\,kg^{-1}\,K^{-1}}$
4. Specific latent heat of vaporisation of water, $L_{\mathrm{water}} = 2.26 \times 10^6\,\mathrm{J\,kg^{-1}}$

Solution. The amount of heat needed to warm mass m_{water} of water and mass m_{glass} of glass from $\theta_{\mathrm{water},0} = 20.0°\mathrm{C}$ to θ is

$$Q = \left(m_{\mathrm{water}} c_{\mathrm{water}} + m_{\mathrm{glass}} c_{\mathrm{glass}}\right)\left(\theta - \theta_{\mathrm{water},0}\right)$$

The amount of heat lost to cool mass m_{steam} of steam from $\theta_{\mathrm{steam},0} = 130°\mathrm{C}$ to θ is

$$Q = m_{\mathrm{steam}} c_{\mathrm{steam}}\left(\theta_{\mathrm{steam},0} - \theta_{\mathrm{boil}}\right) + m_{\mathrm{steam}} L_{\mathrm{water}} + m_{\mathrm{steam}} c_{\mathrm{water}}\left(\theta_{\mathrm{boil}} - \theta\right)$$

whereby $\theta_{\mathrm{boil}} = 100°\mathrm{C}$, and $\theta \leq \theta_{\mathrm{boil}}$ (meaning all the steam condenses).

Equating these two, we obtain

$$m_{\mathrm{steam}} = \frac{\left(m_{\mathrm{water}} c_{\mathrm{water}} + m_{\mathrm{glass}} c_{\mathrm{glass}}\right)\left(\theta - \theta_{\mathrm{water},0}\right)}{c_{\mathrm{steam}}\left(\theta_{\mathrm{steam},0} - \theta_{\mathrm{boil}}\right) + L_{\mathrm{water}} + c_{\mathrm{water}}\left(\theta_{\mathrm{boil}} - \theta\right)}$$

Evaluating this expression at the two required temperatures, we obtain (i) $m_{\mathrm{steam}} = 31.8\,\mathrm{g}$ and (ii) $m_{\mathrm{steam}} = 10.9\,\mathrm{g}$.

Problem 2.3 (SPhO 2015)**.** You have 2 reservoirs, one at $900\,\mathrm{K}$ and another at $300\,\mathrm{K}$. (i) What is ΔS of transferring $100\,\mathrm{J}$ of heat from the $900\,\mathrm{K}$ to the $300\,\mathrm{K}$ reservoir? (ii) For a reversible engine between the two reservoirs, find Q_{out} and W per $100\,\mathrm{J}$ input. (iii) Find ΔS of the above engine. (iv) If an actual engine is placed between the two reservoirs, what can we say about ΔS?

Solution. (i) Since the reservoirs remain at constant temperature, this part is simple:

$$\Delta S = \Delta S_{\mathrm{C}} + \Delta S_{\mathrm{H}} = -\frac{Q}{T_{\mathrm{H}}} + \frac{Q}{T_{\mathrm{C}}} = 0.222\,\mathrm{J/K}$$

(ii) This is just a Carnot cycle. We can just calculate the efficiency and find the respective quantities:

$$\eta = 1 - \frac{T_{\mathrm{C}}}{T_{\mathrm{H}}} = \frac{2}{3} \quad \Rightarrow \quad W = \eta Q_{\mathrm{in}} = 66.7\,\mathrm{J},\ Q_{\mathrm{out}} = Q_{\mathrm{in}} - W = 33.3\,\mathrm{J}$$

(iii) Since this is a Carnot cycle, $\Delta S = 0$.

(iv) For a non-ideal heat engine, $\Delta S > 0$ by the second law.

Problem 2.4 (SPhO 2019)**.** A mass of $0.25\,\mathrm{kg}$ is hung from a spring of spring constant $20\,\mathrm{N\,m^{-1}}$, starting from zero extension. It is then released, and air resistance damps the motion until it reaches equilibrium. Given that the surroundings remain at a constant temperature of $298\,\mathrm{K}$, find the entropy change of the surroundings.

Solution. The mass comes at rest at its equilibrium position at $x = \frac{mg}{k}$. As such, the total energy lost is

$$\Delta E = mgx - \frac{1}{2}kx^2 = \frac{m^2g^2}{2k}$$

We assume that energy transfer to the surroundings is perfect. As such,

$$\Delta S = \frac{\Delta Q}{T} = \frac{\Delta E}{T} = \frac{m^2g^2}{2kT} = 5.01 \times 10^{-4}\,\mathrm{J/K}$$

Problem 2.5 (SPhO 2007)**.** To account for the finite size of molecules and the attractive forces between molecules, Van der Waal devised an equation to describe the gas law for "real" gases:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Here, P, V, T are the pressure, volume and temperature of the gas respectively, and R is the universal gas constant. (i) What are the dimensions of the constants a and b? (ii) Show that the critical point temperature and pressure are given by

$$T_{\mathrm{c}} = \frac{8a}{27Rb} \quad \text{and} \quad P_{\mathrm{c}} = \frac{a}{27b^2}$$

Note: The definition of "critical point" was not provided in the original SPhO problem, but that made it impossible to solve this problem if you didn't know what it was beforehand.

Solution. (i) We perform simple dimensional analysis. We can see that a has the units of pressure $\times$ volume^2, which in SI units is $\left(\mathrm{kg\ m^{-1}s^{-2}}\right)\left(\mathrm{m^3}\right)^2 = \mathrm{kg\ m^5\,s^{-2}}$. And, we can see that b has the units of volume, which is SI units is $\mathrm{m^3}$.

(ii) The definition of critical point is that

$$\frac{\partial P}{\partial V} = 0 \quad \text{and} \quad \frac{\partial^2 P}{\partial V^2} = 0$$

We first re-express P in terms of V to make our life easier:

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

As such, we can take the partial derivative of both sides with respect to V, giving us:

$$\frac{\partial P}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$

It becomes a matter of algebra to obtain

$$T = \frac{3a\,(V-b)^3}{RV^4},\ V = 3b \quad \Rightarrow \quad T_\mathrm{c} = \frac{8a}{27Rb},\ P_\mathrm{c} = \frac{a}{27b^2}$$

Remark. Hopefully, you can see why this problem is not well-set. The reason why we set both partial derivatives to 0 is, literally, by definition, and if you didn't know about it, there is also no way for you to derive it.

Problem 2.6 (SPhO 2019)**.** A well-lagged uniform cylindrical copper rod is 30.0 cm long and has a diameter of 2.00 cm. One end of it is in thermal contact with a hot reservoir maintained at a temperature of 200°C while the other end is in thermal contact with a cold reservoir at temperature 0°C. Calculate the rate of entropy of the system comprising the hot and cold reservoirs and the copper rod.

Solution. The heat conduction at steady-state is given by Fourier's Law:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = kA\left(\frac{T_\mathrm{H} - T_\mathrm{C}}{L}\right)$$

The rate of entropy changes of the hot and cold reservoir are

$$\dot{S_\mathrm{H}} = -\frac{\dot{Q}}{T_\mathrm{H}},\ \dot{S_\mathrm{C}} = \frac{\dot{Q}}{T_\mathrm{C}}$$

Hence, the total rate of change of entropy is

$$\dot{S_\mathrm{total}} = \dot{S_\mathrm{H}} + \dot{S_\mathrm{C}} = \dot{Q}\left(\frac{1}{T_\mathrm{C}} - \frac{1}{T_\mathrm{H}}\right) = \frac{kA\,(T_\mathrm{H} - T_\mathrm{C})}{L}\left(\frac{1}{T_\mathrm{C}} - \frac{1}{T_\mathrm{H}}\right) = 0.130\,\mathrm{J/K\cdot s}$$

Problem 2.7 (SPhO 2014)**.** At low temperatures, the heat capacity of a substance is dependent on its temperature. A thermally insulated piece of the substance is heated under atmospheric pressure by an electric current so that it receives electric energy at a constant power P. This leads to an increase of the absolute temperature T of the substance with time t as

$$T\,(t) = T_0\,(1 + \alpha\,(t - t_0))^{\frac{1}{3}}$$

where α, t_0, T_0 are constants. Determine the heat capacity at constant pressure C_P of the substance as a function of temperature T.

Solution. Since the aforementioned process takes place at constant pressure (atmospheric pressure), $\mathrm{d}Q = C_\mathrm{P}\,\mathrm{d}T$. By definition as well, $\mathrm{d}Q = P\,\mathrm{d}t$. Hence,

$$C_\mathrm{P} = \frac{P}{\frac{\mathrm{d}T}{\mathrm{d}t}} = \frac{P}{\frac{1}{3}\alpha T_0\,(1 + \alpha\,(t - t_0))^{-\frac{2}{3}}} = \frac{3PT^2}{\alpha T_0^3}$$

Problem 2.8 (IZhO 2022)**.** One mole of ideal monoatomic gas initially has volume $V_0 = 1\,\mathrm{m}^3$ and pressure $P_0 = 10^5\,\mathrm{Pa}$. It then undergoes a quasistatic process. At every moment in this process, the rate of work done is proportional to the rate of change of the internal energy of the gas. At the end of the process, the gas has volume $4V_0$ and pressure $\frac{P_0}{2}$. Find the total work done by the gas.

Solution. We go back to the infinitesimal form of the first law. Let the proportionality constant between the work done and the change in internal energy be k, i.e. $\mathrm{d}W = k\,\mathrm{d}U$, where k is to be determined. Then,

$$-P\,\mathrm{d}V = \frac{3}{2}kR\,\mathrm{d}T = \frac{3}{2}k\left(P\,\mathrm{d}V + V\,\mathrm{d}P\right) \quad \Rightarrow \quad \frac{3}{2}kV\,\mathrm{d}P = \left(-\frac{3}{2}k - 1\right)P\,\mathrm{d}V$$

$$\frac{\mathrm{d}P}{P} = \left(-1 - \frac{2}{3k}\right)\frac{\mathrm{d}V}{V} \quad \Rightarrow \quad \int_{P_0}^{\frac{P_0}{2}}\frac{\mathrm{d}P}{P} = \left(-1 - \frac{2}{3k}\right)\int_{V_0}^{4V_0}\frac{\mathrm{d}V}{V}$$

$$-\ln 2 = -\left(1 + \frac{2}{3k}\right)\ln 4 \quad \Rightarrow \quad 1 + \frac{2}{3k} = \frac{1}{2} \quad \Rightarrow \quad k = -\frac{4}{3}$$

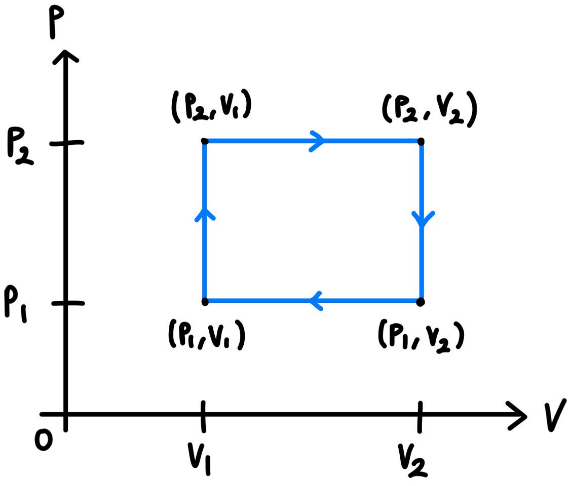
With this, the total work done **by** the gas is

$$W_{\text{by}} = \int \mathrm{d}W_{\text{by}} = -k\int \mathrm{d}U = \frac{4}{3}\left(\frac{3}{2}\right)\left(\left(\frac{P_0}{2}\right)(4V_0) - P_0V_0\right) = 2P_0V_0 = 2\times 10^5\ \mathrm{J}$$

Problem 2.9 (Ricardo)**.** An ideal gas engine using one mole of gas with adiabatic constant γ operates in a cycle which, when represented on a $P-V$ diagram, is a rectangle. Let P_1, P_2, V_1, V_2 be the lower and higher pressures and volumes respectively. The cycle goes from (P_1, V_1) to (P_2, V_1), to (P_2, V_2), to (P_1, V_2) and finally back to (P_1, V_1). (i) Calculate the work done in one cycle. (ii) Calculate the heat taken in during one cycle. (c) Show that the efficiency is

$$\eta = \frac{\gamma - 1}{\frac{\gamma P_2}{P_2 - P_1} + \frac{V_1}{V_2 - V_1}}$$

Solution. (i) Let's first draw out the points on a $P-V$ diagram:



(i) The work done in one cycle is simply the area bounded by the graph, and is hence

$$W = (P_2 - P_1)(V_2 - V_1)$$

(ii) Heat is taken in by the processes that move further away from the origin in the $P-V$ diagram. Hence,

$$(P_1, V_1) \to (P_2, V_1):\ Q = nc_{\mathrm{V}}\Delta T = \frac{V_1(P_2 - P_1)}{\gamma - 1}$$

$$(P_2, V_1) \to (P_2, V_2):\ Q = nc_{\mathrm{P}}\Delta T = \frac{\gamma P_2(V_2 - V_1)}{\gamma - 1}$$

$$Q_{\text{in,net}} = \frac{V_1 (P_2 - P_1)}{\gamma - 1} + \frac{\gamma P_2 (V_2 - V_1)}{\gamma - 1}$$

where we note that $n = 1$.

(iii) The efficiency is found using the previous two parts:

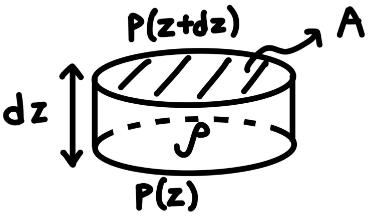
$$\eta = \frac{W}{Q_{\text{in,net}}} = \frac{(P_2 - P_1)(V_2 - V_1)}{\frac{V_1(P_2-P_1)+\gamma P_2(V_2-V_1)}{\gamma-1}} = \frac{(\gamma - 1)(P_2 - P_1)(V_2 - V_1)}{V_1 (P_2 - P_1) + \gamma P_2 (V_2 - V_1)} = \frac{\gamma - 1}{\frac{\gamma P_2}{P_2-P_1} + \frac{V_1}{V_2-V_1}}$$

Problem 2.10 (USAPhO 2014, Problem A2)**.** A nice exercise on a Carnot cycle.

Solution. See the official solutions here.

Problem 2.11 (Kevin Zhou, modified)**.** (i) Assume the atmosphere to be an ideal gas at constant temperature T in mechanical equilibrium, with gas molecules of mass m. Find the expression for the pressure in terms of height, $P(z)$. (ii) Suppose instead now that the atmosphere is adiabatic and not isothermal. Assume that air molecules are diatomic. Find the expression for the temperature in terms of height, $T(z)$.

Solution. (i) Consider a parcel of gas of cross sectional area A and thickness dz.



The condition for mechanical equilibrium is

$$\rho g A \, \mathrm{d}z = (P(z) - P(z + \mathrm{d}z)) A \quad \Rightarrow \quad \frac{\mathrm{d}P}{\mathrm{d}z} = -\rho g$$

This is called the **hydrostatic equation.**

We can substitute $\rho = \frac{Pm}{k_{\mathrm{B}} T}$ into the hydrostatic equation:

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\frac{Pmg}{k_{\mathrm{B}} T} \quad \Rightarrow \quad \frac{\mathrm{d}P}{P} = -\frac{mg}{k_{\mathrm{B}} T} \mathrm{d}z$$

$$\Rightarrow \quad \int_{P_0}^{P} \frac{\mathrm{d}P}{P} = -\frac{mg}{k_{\mathrm{B}} T} \int_0^z \mathrm{d}z \quad \Rightarrow \quad P(z) = P_0 \exp\left(-\frac{mgz}{k_{\mathrm{B}} T}\right)$$

where P_0 is the pressure at $z = 0$.

(ii) For an adiabatic atmosphere, the temperature T is now no longer constant. However, it doesn't make sense to talk about volume for an atmosphere. Thus, we shall resort to using temperature and pressure, related by

$$P^{1-\gamma} T^{\gamma} = \text{constant} \quad \Rightarrow \quad \gamma T^{\gamma - 1} P^{1-\gamma} \, \mathrm{d}T + (1 - \gamma) P^{-\gamma} T^{\gamma} \, \mathrm{d}P = 0$$

$$\Rightarrow \quad (\gamma - 1) \frac{\text{constant}}{P} \mathrm{d}P = \gamma \frac{\text{constant}}{T} \mathrm{d}T \quad \Rightarrow \quad \frac{\mathrm{d}P}{P} = \frac{\gamma}{\gamma - 1} \frac{\mathrm{d}T}{T}$$

The hydrostatic equation still holds as each infinitesimal gas parcel is in mechanical equilibrium. Hence, using a similar approach as part (i), we have

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\rho g = -\frac{mg}{k_{\mathrm{B}}T}P \quad \Rightarrow \quad \frac{\mathrm{d}P}{P} = -\frac{mg}{k_{\mathrm{B}}T}\,\mathrm{d}z = \frac{\gamma}{\gamma-1}\frac{\mathrm{d}T}{T} \quad \Rightarrow \quad \frac{\gamma}{\gamma-1}\,\mathrm{d}T = -\frac{mg}{k_{\mathrm{B}}}\,\mathrm{d}z$$

$$\mathrm{d}T = -\frac{\gamma-1}{\gamma}\frac{mg}{k_{\mathrm{B}}}\,\mathrm{d}z = -\frac{2mg}{7k_{\mathrm{B}}}\,\mathrm{d}z \quad \Rightarrow \quad \int_{T_0}^{T}\mathrm{d}T = -\frac{2mg}{7k_{\mathrm{B}}}\int_0^z \mathrm{d}z \quad \Rightarrow \quad T(z) = T_0 - \frac{2mg}{7k_{\mathrm{B}}}z$$

Problem 2.12 (Ricardo)**.** A gas-tight, thermally isolated cylinder of volume V is divided into two parts A and B by the piston, movable from outside the cylinder, and made of a conducting material. Initially, A and B are of equal volume; they contain each 1 mole of an ideal monoatomic gas, all at temperature T_0. The piston is then moved to such a position that A and B have volumes $\frac{V}{3}$ and $\frac{2V}{3}$ respectively. This is done sufficiently slowly for the temperature of the two samples of gas to remain uniform throughout the process. Find an expression for the final temperature of the system. Neglect the heat capacity of the cylinder and the piston.

Solution. The temperatures of the two compartments are always equal, because the piston is a good conductor of heat. However, the pressures aren't equal! This is because you are applying an external force on the piston, enabling a pressure difference to be possible.

The work done by you is

$$\mathrm{d}W_{\mathrm{on}} = -P_{\mathrm{A}}\,\mathrm{d}V_{\mathrm{A}} - P_{\mathrm{B}}\,\mathrm{d}V_{\mathrm{B}} = -RT\left(\frac{\mathrm{d}V_{\mathrm{A}}}{V_{\mathrm{A}}} + \frac{\mathrm{d}V_{\mathrm{B}}}{V_{\mathrm{B}}}\right)$$

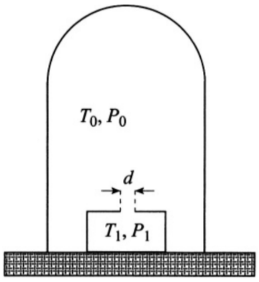
Since everything is insulated, no heat can enter or leave the system, hence the process is adiabatic. Hence, being careful that the total number of moles of gas in the system is 2, we have

$$\mathrm{d}U = \frac{3}{2}nR\,\mathrm{d}T = 3R\,\mathrm{d}T = \mathrm{d}W_{\mathrm{on}}$$

Combining these two results, we get

$$\frac{3\,\mathrm{d}T}{T} = -\frac{\mathrm{d}V_{\mathrm{A}}}{V_{\mathrm{A}}} - \frac{\mathrm{d}V_{\mathrm{B}}}{V_{\mathrm{B}}} \quad \Rightarrow \quad 3\int_{T_0}^{T_{\mathrm{f}}}\frac{\mathrm{d}T}{T} = -\int_{\frac{V}{2}}^{\frac{V}{3}}\frac{\mathrm{d}V_{\mathrm{A}}}{V_{\mathrm{A}}} - \int_{\frac{V}{2}}^{\frac{2V}{3}}\frac{\mathrm{d}V_{\mathrm{B}}}{V_{\mathrm{B}}} \quad \Rightarrow \quad T_{\mathrm{f}} = \frac{3^{\frac{2}{3}}}{2}T_0$$

Problem 2.13 (Cahn)**.** A small vessel with a tiny hole of diameter d is placed inside a chamber, where the pressure is so low that the mean free path is $\lambda \gg d$. The temperature of the gas in the chamber is T_0, and the pressure is P_0. The temperature in the vessel is kept at a constant $T_1 = 4T_0$. What is the pressure inside the vessel when steady state is reached? *Hint: It is not P_0! Mechanical equilibrium is not reached. Can you explain why?*



Solution. First, let's start with explaining why the answer is **not** P_0.

Since the chamber is much larger than the vessel, a small amount of gas entering/leaving the vessel will not affect the temperature of the chamber very much. Since we are in the effusive regime of $\lambda \gg d$, if a particle is near a hole and is heading towards it, it is very likely for it to pass through without hitting anything at all. This means that even if the pressures equilibrate, the particles that were meant to pass through the hoe are too unlikely to collide with one another to change their paths.

Instead, equilibrium is achieved when the rate of particles going from the chamber to the vessel is the same as that going from the vessel in the chamber. The rate is proportional to the number density times the average speed, hence

$$n_0 \langle v_0 \rangle = n_1 \langle v_1 \rangle$$

By setting total KE equal to the total internal energy, we know that $\langle v_i \rangle \propto \sqrt{T_i}$. Therefore,

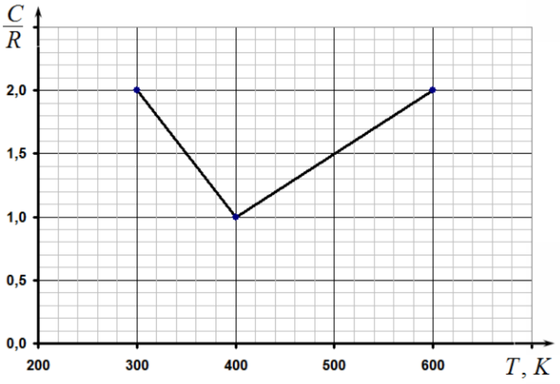
$$n_1 = \frac{n_0 \langle v_0 \rangle}{\langle v_1 \rangle} = n_0 \sqrt{\frac{T_0}{T_1}} = \frac{n_0}{2}$$

Lastly, the ideal gas law gives $P \propto nT$, hence

$$\frac{P_0}{n_0 T_0} = \frac{P_1}{n_1 T_1} \quad \Rightarrow \quad P_1 = \frac{P_0 n_1 T_1}{n_0 T_0} = 2P_0$$

Remark. If you are not convinced, you can use dimensional analysis. Clearly, the rate of particles going through the hole must only depend on the number density n, the average speed $\langle v \rangle$, and the area of the hole A. The only combination that is dimensionally correct is $nA \langle v \rangle$.

Problem 2.14 (IZhO 2023)**.** One mole of an ideal monatomic gas, located in the cylinder under the piston, is quasi-statically heated from the temperature $T_1 = 300\,\mathrm{K}$ to $T_2 = 600\,\mathrm{K}$, changing its volume in such a way that the dependence of the heat capacity C of the gas on its temperature has the form shown in the figure below. Find the work done (in J) on the gas from the state in which the graph of its volume versus temperature reaches a local maximum, to the state in which the same graph reaches a local minimum.



Solution. First, let's understand what the local maximum and minimum here mean.

Since we are dealing with an ideal monoatomic gas, $c_V = \frac{3}{2}R$. There are 2 distinct points on the graph where $\frac{C}{R} = \frac{3}{2}$ (note that $C = nc = c$ as $n = 1$), at $T = 350\,\mathrm{K}$ and $T = 500\,\mathrm{K}$. The graph of $\frac{C}{R}$ against T also reaches a local minimum at $T = 400\,\mathrm{K}$.

By the definition of heat capacity,

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} \quad \Rightarrow \quad \mathrm{d}Q = C\,\mathrm{d}T \quad \Rightarrow \quad Q = \int C\,\mathrm{d}T = \text{area under the } C - T \text{ graph}$$

so now, we know how to utilise the provided graph.

The problem boils down to calculating the work done on the gas between the temperatures $T = 350\,\text{K}$ and $T = 500\,\text{K}$, because these two points correspond to the local extrema of volume (constant volume). Hence,

$$Q_{350-500} = \frac{R}{2}(1.5 + 1.0)(50) + \frac{R}{2}(1.0 + 1.5)(100) = 187.5R$$

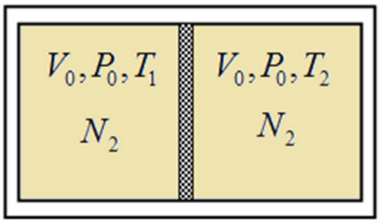
The change in internal energy is easy:

$$\Delta U_{350-500} = \frac{3}{2}nR\Delta T = \frac{3}{2}R(500 - 350) = 225R$$

As such, the work done on the gas is

$$W_{\text{on}} = \Delta U - Q = 225R - 187.5R = 37.5R = 312\,\text{J}$$

Problem 2.15 (IZhO 2024)**.** A thermally insulated vessel with a volume of $2V_0 = 2.00\,\text{L}$ is divided by a thin weightless movable heat-conducting partition into two equal parts, each containing nitrogen N_2 at a pressure $P_0 = 100\,\text{kPa}$. The initial temperature of nitrogen in one half of the vessel is $T_1 = 240\,\text{K}$, and it is $T_2 = 360\,\text{K}$ in the other. As a result of heat exchange, the partition begins to move slowly without friction. (i) Determine the amount of heat that will be exchanged between parts of the vessel by the time complete thermodynamic equilibrium is established. (ii) Calculate the minimum work W' that must be done to return the partition to its original position. Neglect the heat capacities of the vessel and partition.



Solution. (i) When complete thermodynamic equilibrium is reached, both sides of the vessel have the same temperature. Let the number of moles on the left and right be n_1 and n_2 respectively. Then,

$$n_1 = \frac{P_0V_0}{RT_1}, \ n_2 = \frac{P_0V_0}{RT_2}$$

Since the entire vessel is thermally insulated, energy is conserved. By COE, we have

$$\frac{5}{2}n_1RT_1 + \frac{5}{2}n_2RT_2 = \frac{5}{2}(n_1 + n_2)RT$$

$$\implies \quad T = \frac{n_1T_1 + n_2T_2}{n_1 + n_2} = \frac{\frac{P_0V_0}{R} + \frac{P_0V_0}{R}}{\frac{P_0V_0}{RT_1} + \frac{P_0V_0}{RT_2}} = \frac{2T_1T_2}{T_1 + T_2} = 288\,\text{K}$$

Now, it is important to realise that mechanical equilibrium exists from the start, since both pressures began at P_0. There is no reason for the pressures to change and for mechanical equilibrium to be broken. Therefore, the process within each gas is isobaric.

As such, considering the left side,

$$\frac{V}{T} = \text{constant} \quad \implies \quad \frac{V_0}{T_1} = \frac{V_f}{T} \quad \implies V_f = \frac{2V_0T_2}{T_1 + T_2}$$

Hence, the amount of heat exchanged (taking magnitude) is

$$Q = \Delta U - W_{\text{on}} = \frac{5}{2}P_0\Delta V + P_0\Delta V = \frac{7}{2}P_0\Delta V = \frac{7}{2}P_0V_0\left(\frac{T_2 - T_1}{T_1 + T_2}\right) = 70.0\,\text{J}$$

(ii) The easiest way to do this is using entropy.

If the partition can be returned to its original position, the system can be restored back to its original state. This means that the overall process is reversible. As such, $\Delta S = 0$.

We start using the infinitesimal forms:

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} = \frac{\mathrm{d}U - \mathrm{d}W_{\text{on}}}{T} = \frac{nc_{\text{v}}\,\mathrm{d}T + P\,\mathrm{d}V}{T} = nc_{\text{v}}\frac{\mathrm{d}T}{T} + nR\frac{\mathrm{d}V}{V}$$

$$\implies \quad \Delta S = nc_{\text{v}}\ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) + nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)$$

This holds for any general process with an ideal gas. We can then find the total entropy change and set it to 0:

$$\Delta S_{\text{net}} = \frac{5}{2}n_1R\ln\left(\frac{T'}{T}\right) + n_1R\ln\left(\frac{V_0}{V_1}\right) + \frac{5}{2}n_2R\ln\left(\frac{T'}{T}\right) + n_2R\ln\left(\frac{V_0}{V_2}\right) = 0$$

where T' is the final temperature of the system after the work has been done (to be determined), and V_1 and V_2 are the volumes of the left and right side respectively after the initial thermodynamic equilibrium is reached.

Using the isobaric relation, we can determine V_1 and V_2:

$$V_1 = \frac{2V_0T_2}{T_1 + T_2},\ V_2 = \frac{2V_0T_1}{T_1 + T_2}$$

The equation can then be (rather tediously) solved to obtain T':

$$T' = T\left(\frac{T}{T_1}\right)^{\frac{T}{5T_1}}\left(\frac{T}{T_2}\right)^{\frac{T}{5T_2}} = 290\,\text{K}$$

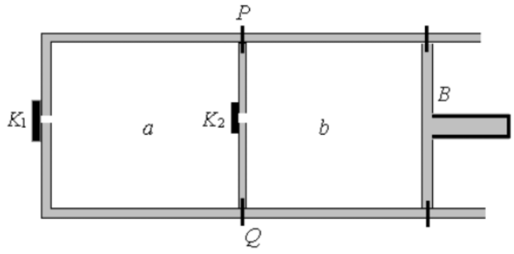
The work done is used to change the internal energy, hence

$$W' = \Delta U = (n_1 + n_2)\,c_{\text{v}}\,(T' - T) = 4.04\,\text{J}$$

3 Advanced Problems

These problems are way too difficult to be tested in a modern-day SPhO. If you have completed all the previous problems and are down for a challenge, try these!

Problem 3.1. As shown in the figure below, a container has two plugs K_1 and K_2. Compartments a and b are separated by a negligibly thin wall. A piston B is placed at the right of compartment b. The container, wall, plugs and piston are all insulating. The wall and piston can be fixed by nails, and once the nails are removed they can move freely to the left and right, without friction or gas leakage. The entire container is placed in an atmosphere with pressure P_0 and temperature T_0.



Initially, the piston is at the location shown and the wall is at PQ. The compartments both have volume V_0, and K_1 and K_2 are both closed. Compartment b is in vacuum and compartment a has pressure $\frac{4}{5}P_0$ and temperature T_0. The molar heat capacity C_V of the ideal gas is known.

(a) Now, K_1 is opened. When the pressures outside and inside compartment a are equalised, K_1 is immediately closed. Assume no heat is exchanged in this process. Find the temperature of a at equilibrium.

(b) Now, K_2 is opened. When the two compartments reach equilibrium, K_2 is closed. The nails in the in the wall and piston are removed, and the piston is pushed slowly until it reaches position PQ. Determine the work done by the wall on the gas in compartment a. It is known that during the pushing process, PV^γ is constant.

Solution. Part (a) of the problem is hard because it is not clear what to define as our system in this case. Thus, we present an idea called "low work" which involves analyzing the work done by the atmosphere.
(a) When dn moles of gas are inserted from the outside reservoir (P_0, T_0) into the rigid, adiabatic tank, the outside *atmosphere* must push them across the boundary. The atmosphere performs "low work"

$$\delta W_{\text{atm}\to\text{tank}} = P_0\, dV_{\text{res}} = P_0\, v_{\text{res}}\, dn = (RT_0)\, dn$$

and the entering moles carry their own internal energy

$$\delta U_{\text{carried}} = u_{\text{in}}\, dn = (C_v T_0)\, dn$$

Thus the total energy delivered to the tank by the small influx dn is

$$\delta E_{\text{in}} = (C_v T_0 + RT_0)\, dn = (C_p T_0)\, dn$$

Because the tank is rigid and insulated, this is the *only* energy input, so the change of the tank's internal energy satisfies

$$d(nC_vT) = C_pT_0\, dn \quad\Longrightarrow\quad C_v(n_2T_2 - n_1T_1) = C_pT_0\,(n_2 - n_1)$$

Initially $P_1 = \frac{4}{5}P_0,\ T_1 = T_0,\ V_0$; finally $P_2 = P_0,\ V_0$ (equalized with the atmosphere). Hence

$$n_1 = \frac{\frac{4}{5}P_0V_0}{RT_0}, \qquad n_2 = \frac{P_0V_0}{RT_2}$$

Insert these into the previous equation and use $C_p = C_v + R$:

$$T_2 = T_0\,\frac{5C_p}{4C_p + C_v} = T_0\,\frac{5(C_v + R)}{5C_v + 4R}$$

$$\boxed{T_a = T_0\,\frac{5\,(C_v + R)}{5C_v + 4R}}$$

(b) With K_2 open and the middle wall still fixed, the gas in a freely expands into the vacuum of b at constant total volume $2V_0$ and with no heat/work; hence T remains T_2 and the common pressure becomes

$$P = \frac{n_2RT_2}{2V_0} = \frac{P_0}{2}$$

Close K_2, remove the nails, and push the right piston *slowly*. The separating wall is frictionless and massless, so $P_a = P_b$ throughout; each side undergoes a *reversible adiabatic* with the same constant, hence $V_a(t) = V_b(t)$ at all times. When the right piston reaches PQ, the total gas volume is V_0, giving

$$V_a^{(f)} = V_b^{(f)} = \frac{V_0}{2}, \qquad T_f = T_2\Big(\frac{V_0}{V_0/2}\Big)^{\gamma-1} = T_2\,2^{\gamma-1}$$

where $\gamma = 1 + \frac{R}{C_v}$

The work done *by the wall on* the gas in a during this slow adiabatic compression equals the internal-energy increase of gas a:

$$W_{\text{wall}\to a} = \Delta U_a = n_aC_v(T_f - T_2)$$

At the start of the push, each side contains

$$n_a = \frac{\frac{1}{2}P_0V_0}{RT_2}$$

Therefore

$$W_{\text{wall}\to a} = \frac{P_0V_0}{2RT_2}\,C_v\Big(T_2\,2^{\gamma-1} - T_2\Big) = \frac{P_0V_0}{2}\,\frac{C_v}{R}\Big(2^{\gamma-1} - 1\Big) = \frac{P_0V_0}{2}\,\frac{C_v}{R}\Big(2^{R/C_v} - 1\Big)$$

$$\boxed{W_{\text{wall}\to a} = \frac{P_0V_0}{2}\,\frac{C_v}{R}\Big(2^{R/C_v} - 1\Big)}$$

Problem 3.2 (EuPhO 2017, T2)**.** An excellent kinetic theory problem.

Solution. See the official solutions here.

Problem 3.3 (APhO 2010, T3B)**.** An excellent problem on an adiabatic process.

Solution. See the official solutions here.

Problem 3.4 (Physics Cup 2019, Problem 2)**.** An excellent problem on the second law.

Solution. See the many solutions submitted by contestants here.

Remark. All the problems here are exceptionally hard, at the level of international Olympiads or even beyond. Don't be too discouraged if you have no idea what is happening!