Thermodynamics

Unit: Thermodynamics

NGSS Standards/MA Curriculum Frameworks (2016): HS-PS2-6

AP® Physics 2 Learning Objectives/Essential Knowledge (2024): 9.3.A, 9.3.A.4, 9.4.A, 9.4.A.1, 9.4.A.1.i, 9.4.A.1.ii, 9.4.A.2, 9.4.B, 9.4.B.1, 9.4.B.1.i, 9.4.B.1.ii, 9.4.B.1.iii, 9.6.A, 9.6.A.1, 9.6.A.2, 9.6.A.2.i, 9.6.A.2.iii, 9.6.A.3, 9.6.A.3.i, 9.6.A.3.ii

Mastery Objective(s): (Students will be able to…)

- Calculate kinetic energy, internal energy and work done by the particles of a gas.

Success Criteria:

- Solutions have the correct quantities substituted for the correct variables.
- Algebra and rounding to appropriate number of significant figures is correct.

Language Objectives:

- Describe the different types of energy (kinetic, internal, work) and explain what they measure.

Tier 2 Vocabulary: internal, energy, work

Labs, Activities & Demonstrations:

- heat exchange dice game
- dice distribution game
- entropy (microstates) percentile dice game

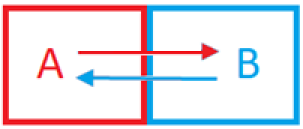
Notes:

thermodynamics: the study of heat-related (thermal) energy changes (dynamics)

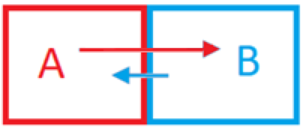
Thermodynamics is an application of the law of conservation of energy. In Physics 1, we studied changes between gravitational potential energy and kinetic energy. Thermodynamic changes involve the same principle; the details and the equations, however, are quite different.

As was the case with gas laws, the topic of thermodynamics is studied by both chemists and physicists. Chemists tend to be more concerned with the heat produced and consumed by chemical changes and reactions. Physicists tend to be more concerned with the conversion between thermal energy (regardless of how it is produced) and other forms of energy, particularly mechanical.

thermal equilibrium: if two systems "A" and "B" are in thermal equilibrium, heat is transferred from A to B at the same rate as heat is transferred from B to A.



Thermal equilibrium: equal amounts of heat transferred in each direction.



Not equilibrium: different amounts of heat transferred in each direction.

temperature: a measure of the average kinetic energy of the particles in a substance. (K)

$$K_{ave.} = \tfrac{1}{2} m v_{ave.}^2 = \tfrac{3}{2} k_B T$$

where:

$K_{ave.}$ = average kinetic energy (J)
m = mass of a particle (kg)
M = molar mass (mass of one mole of particles) $(\frac{\text{kg}}{\text{mol}})$[*]
$v_{ave.}$ = average velocity of a particle $(\frac{\text{m}}{\text{s}})$
k_B = Boltzmann's constant = $1.38 \times 10^{-23}\ \frac{\text{J}}{\text{K}}$
T = temperature (K)

The factor of $\frac{3}{2}$ is because there is an equal probability of a collision between particles in the *x*-, *y*-, and *z*-directions, and $(3)(\tfrac{1}{2}) = \tfrac{3}{2}$.

root mean square velocity (v_{rms}): the geometric mean (average) velocity of a particle. $(\frac{\text{m}}{\text{s}})$ The rms velocity is derived by solving $\frac{1}{2} m v_{ave.}^2 = \frac{3}{2} k_B T$ for the average velocity:

$$v_{rms} = \sqrt{v_{ave.}^2} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

[§§] Chemists express molar mass in $\frac{\text{g}}{\text{mol}}$ rather than $\frac{\text{kg}}{\text{mol}}$. Because we use the MKS system in physics, we need to express molar mass in $\frac{\text{kg}}{\text{mol}}$.

internal energy (U^*): the total thermal energy of a system due to the kinetic energy of its particles.

If the kinetic energy of a single particle is $K_{ave.} = \frac{3}{2}k_BT$, then the total kinetic energy in a system that has N particles would be:

$$U = NK_{ave.} = \frac{3}{2}Nk_BT$$

Because it is generally unwieldy to perform calculations for systems with large numbers of particles, it is more convenient to use moles. Substituting nR for Nk_B gives the equation for the internal energy of a system that has n moles of particles:

$$U = \frac{3}{2}nRT$$

Similarly, a *change* in internal energy (ΔU) is related to the corresponding *change* in temperature (ΔT):

$$\Delta U = \frac{3}{2}nR\Delta T \quad (= \frac{3}{2}Nk_B\Delta T)$$

heat (Q): thermal energy transferred into or out of a system. (J)

work (W): mechanical energy (such as the application of a force over a distance) transferred into or out of a system. (J)

The work that a gas can do comes from its ability to move an object by applying a force on it as it expands. If the pressure is constant:

$$W = Fd = F\Delta x$$

$$P = \frac{F}{A} \quad \rightarrow \quad F = PA$$

$$\therefore\ W = (PA)\Delta x$$

$$\Delta V = A\Delta x$$

$$\therefore\ W = P\Delta V$$

If a gas does work by expanding, the energy is transferred from the gas (the system) to the object that the gas is pushing against (the surroundings). This means that when the volume increases (ΔV is positive), energy is leaving the system (W is negative). Conversely, if work is done to compress a gas, energy is entering the system in order to compress the gas (W is positive), and the volume decreases (ΔV is negative). This means that W and $P\Delta V$ must have opposite signs, which gives the equation:

$$W = -P\Delta V$$

assuming that pressure is constant.

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[*] Chemistry textbooks often use the variable E instead of U.

If pressure is not constant, then $W = -\Delta(PV)$, which means you would need to calculate PV at each point, taking the limit as the distance between the data points shrinks to zero, and add them up. In calculus, this is the integral: $W = -\int P\,\mathrm{d}V$, where P is a function of V.

In an algebra-based course, we will limit ourselves to problems where the pressure is constant, or where the pressure change is linear and you can use the average pressure, giving:

$$W = -P_{ave.}\Delta V$$

entropy (S): "unusable" thermal energy in a system. Energy in the form of entropy is unavailable because it has "escaped" or "spread out". (Entropy will be discussed further in the Second Law of Thermodynamics.)

Laws of Thermodynamics

The laws of thermodynamics describe the behavior of systems with respect to changes in heat energy.

For historical reasons, the laws are numbered from 0–3[*] instead of 1–4, because the 0 law was added after the others, and the laws are often referred to by their number.

0. If a system is at thermal equilibrium, every component of the system has the same temperature. ("You have to play the game.")
1. Heat always flows from a region of higher internal energy to a region of lower internal energy. Because internal energy is directly proportional to temperature, this is equivalent to saying that heat flows from a region of higher temperature to a region of lower temperature. This means you can't get more heat out of a system than you put in. ("You can't win.")
2. In almost every change, some energy is irretrievably lost to the surroundings. Entropy is a measure of this "lost" energy. The entropy of the universe is always increasing, which means on any practical scale, you will always get out less energy than you put in. ("You can't break even.")
3. Conservation of energy always applies. In any closed system, the total energy (internal energy + entropy + work) remains constant. If energy was "lost," it turned into an increase in entropy. ("You can't get out of the game.")

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[*] There is one type of person in the world: those who start counting from zero and those who start counting from one.

Zeroth Law (or Zero Law)

The zeroth law says that if you have multiple systems in thermal equilibrium (the heat transferred from "A" to "B" is equal to the heat transferred from "B" to "A"), then the systems must have the same temperature. The consequences of this are:

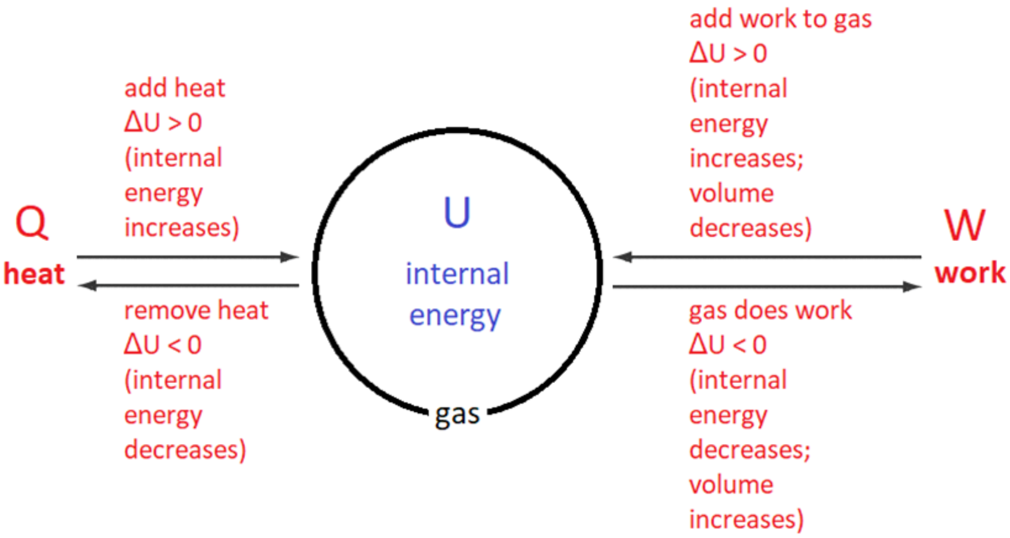
- If we have three (or more) systems "A," "B," and "C," and A is in thermal equilibrium with B, and B is in thermal equilibrium with C, this means that A, B, and C must all have the same temperature, and A is therefore in thermal equilibrium with C. (This is akin to the transitive property of equality in mathematics.)
- If an object with a higher temperature (a "hotter" object) is in contact with an object with a lower temperature (a "colder" object), heat will flow from the object with higher temperature to the object with lower temperature until the temperatures are the same (the objects are in thermal equilibrium).

First Law

Consider an isolated system—*i.e.,* a system where heat and other forms of energy cannot enter nor leave the system. This system is doing no work, but it has internal energy.

Internal energy is similar to potential energy—it is a property of a system that is not doing work currently, but has the potential to do work in the future.

According to the First Law, the internal energy of a system increases $(\Delta U > 0)$ if energy is added in the form of heat $(Q > 0)$ or work $(W > 0)$. The internal energy decreases if energy is removed from the system, by removing heat $(Q < 0)$ or by using the internal energy of the system (the gas) to do work on the surroundings ($W < 0$ because work is going out of the system).



In equation form, the First Law looks like this:

$$\Delta U = Q + W^{*}$$

The First Law is simply the law of conservation of energy—the change in internal energy comes from the heat added to or removed from the system combined with the work done on or by the system.

Combining the First Law with the definition of internal energy gives:

$$\Delta U = \tfrac{3}{2} nR\Delta T = Q + W$$

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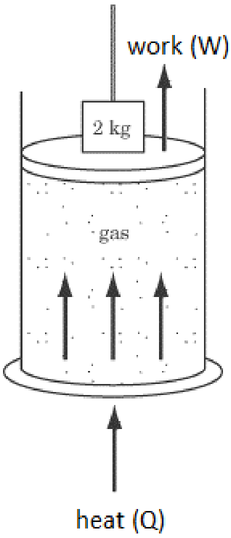
[*] Some textbooks define work exclusively as work done ***by*** the system ***on*** the surroundings (*i.e.,* energy ***leaving*** the system). Using this definition would reverse the sign of W in the equation, giving:

$$\Delta U = Q - W$$

Sample Problem:

Q: A cylinder containing 1.8 mol of an ideal gas with a temperature of 275 K has a piston with a weight on top. The combined mass of the piston plus the weight is 2.0 kg, and the cross-sectional area of the piston is 0.01 m^2. The volume of the gas in the cylinder is 0.033 m^3.



Heat is added, and the volume of the gas increases to 0.040 m^3. How much heat was added to the gas?

A: When the gas is heated, the following occur:

1. In order to increase the volume, the gas has to expand, which means the temperature needs to increase. We know how much the volume increased, and the pressure remains constant (the piston pushes the same amount throughout the process). We can use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ to find the final temperature of the gas.

$$\frac{\cancel{P_1}V_1}{T_1} = \frac{\cancel{P_2}V_2}{T_2} \rightarrow \frac{0.033}{275} = \frac{0.040}{T_2} \rightarrow T_2 = 333\,\text{K}$$

2. The increase in temperature means the internal energy of the gas has increased. We can use $\Delta U = \frac{3}{2}nR\Delta T$ to find out how much the internal energy of the gas increased (ΔU). The equation $\Delta U = Q + W$ tells us that some of the heat energy needed to be used for the increase in internal energy, and the rest of it was used to do the work of raising the piston.

$$\Delta U = \tfrac{3}{2}nR\Delta T \rightarrow \Delta U = (\tfrac{3}{2})(1.8)(8.31)(333-275) = 1301\,\text{J}$$

3. We can calculate the work used to raise the piston from the work equation from physics 1: $W = mg\Delta h$ (Note that $\Delta V = A\Delta h$.)

$$W = -mg\Delta h = -mg\frac{\Delta V}{A} = -(2)(10)\frac{0.007}{0.01} = -14\,\text{J}$$

The work is negative because the energy is going out of the system (remember that the system is the gas) and into the surroundings.

4. Once we have ΔU and W, we can find Q by applying the first law:

$$\Delta U = Q + W$$
$$1301 = Q + (-14)$$
$$1315\,\text{J} = Q$$

Alternatively, we could calculate the work using $W = -P\Delta V$, but we would need to use gauge pressure rather than absolute pressure. (See the explanation below.)

The first two steps are the same as above.

1. This step is the same as step #1 above—we need to find the temperature change necessary to produce the change in volume.

2. This step is the same as step #2 above—we need to calculate the change in internal energy of the gas caused by the change in temperature.

3. Instead of calculating the work using equations from physics 1, we can use $W = -P\Delta V$. However, pressure needs to be the amount of pressure that is doing the work, which is the difference in pressure between the inside of the piston and the outside of the piston. (This would be the gauge pressure inside the cylinder.) We can calculate this using the pressure equation from fluids in physics 1:

   $$P = \frac{F}{A} = \frac{(2)(10)}{0.01} = 2\,000\ \text{Pa}$$

   This is the pressure at which the gas needs to do work.

   Once we have the pressure, the work is given by:

   $$\begin{aligned}&W = -P\Delta V\\&\Delta V = 0.040 - 0.033 = 0.007\ \text{m}^3\\&W = -(2000)(0.007) = -14\ \text{J}\end{aligned}$$

4. Once we have ΔU and *W*, we can find Q by applying the first law:

   $$\begin{aligned}\Delta U &= Q + W\\1301 &= Q + (-14)\\1315\ \text{J} &= Q\end{aligned}$$

Second Law

The Second law tells us that heat energy cannot flow from a colder system to a hotter one unless work is done on the system. This is why your coffee gets cold and your ice cream melts.

One consequence of this law is that no machine can work at 100% efficiency; all machines generate some heat, and some of that heat is always lost to the surroundings.

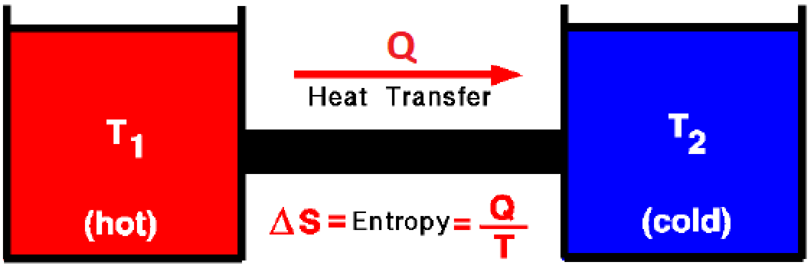
Entropy

Because energy must be conserved, we have to account for energy that still exists, but has "gotten lost" ("escaped" or "spread out") and is no longer usable by the system. Energy that has spread out and cannot be recovered is called entropy.

For example, when an egg falls to the floor and breaks, gravitational potential energy is converted to a combination of internal energy (the measurable increase in the temperature of the egg), and entropy (heat energy that is radiated to the environment and "lost"). Over time, the internal energy in the egg is also radiated to the environment and "lost" as the egg cools off. Ultimately, all of the gravitational potential energy ends up converted to entropy, which is the heat energy that is dissipated and cannot be recovered.

Entropy is sometimes called "disorder" or "randomness", but in the thermodynamic sense this is not correct. The entropy of your room is a *thermodynamic* property of the heat energy in your room, not a commentary on the amount of dirty laundry on the floor!

Whenever heat is transferred from an object with a higher temperature to an object with a lower temperature, the heat "spreads out" as it warms the colder object. The amount of energy that goes into this "spread" is called entropy.



If the heat could be transferred in a way that is completely reversible (which is impossible and would take an infinite amount of time), then you would be able to recover the energy that was converted to entropy when transferring it back to the hotter object. We call this fictitious heat "reversible heat," denoted Q_{rev}.

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$$\Delta S = \frac{Q_{rev}}{T}$$

Real energy transfers that take place in finite amounts of time can never recover all of the energy that was turned into entropy. This means the actual increase in entropy is always more than the amount that would occur in a reversible process:

$$\Delta S = \frac{Q_{rev}}{T} \geq \frac{Q}{T}$$

In other words, the energy that is lost to entropy by transfer of an amount of heat Q would be exactly $\frac{Q}{T}$ for a completely reversible process (*i.e.,* $Q = Q_{rev}$), and more than that for any real process.

Because actual heat transfer in a finite amount of time cannot be completely reversible, some heat is lost to the surroundings and the actual entropy change is always greater than the actual heat change at a given temperature. The concept of a reversible process is an idealization that represents the maximum amount of work that could theoretically be extracted from the process.

Consequences of the Second Law

- The total entropy of an isolated system can never decrease and is constant only when all of the thermodynamic processes are reversible.
- Localized energy will tend to disperse (spread out). When this happens, thermal energy is lost to the surroundings, and the entropy of the system increases.
- Entropy is a state function, which means the entropy of a system does not depend on the energy pathway the system follows.
- Closed systems spontaneously move toward thermodynamic equilibrium (*i.e.,* all parts of the system have the same temperature). When a system has reached thermodynamic equilibrium, the system's entropy is maximized.
- Because the universe is a closed system, the entropy of the universe is always increasing.
- The entropy of an open system can be decreased through a transfer of energy into the system from the surroundings.

In physics, there is a hierarchy of thinking. Conservation of energy, conservation of momentum, and the Second Law are at the top of the hierarchy. Just as special relativity tells us that time, distance and mass all need to be changeable in order to maintain conservation of energy and momentum, the Second Law explains why time cannot move backwards—to do so would require a decrease in the entropy of the universe.

Third Law

The Third Law tells us that in an isolated system, the total energy of the system must be constant. (An isolated system is a system for which it is not possible to exchange energy with the surroundings.) This makes intuitive sense; because energy must be conserved, if no energy can be added or taken away, then the total energy cannot change.

Thermodynamic Quantities and Equations

Because energy is complex and exists in so many forms, there are many thermodynamic quantities that can be calculated in order to quantify the energy of different portions of a system. The following is a list of some of the more familiar ones:

Selected Thermodynamic Quantities

Variable	Name	Description
Q	heat	Thermal energy (heat) transferred into or out of a system due to a difference in temperature.
W	work	Mechanical energy transferred into or out of a system through the action of a force applied over a distance. $W = \vec{\boldsymbol{F}} \bullet \vec{\boldsymbol{d}} = -P\Delta V$
U^*	internal energy	Total thermal (non-chemical) energy contained within the particles of a system because of their kinetic energy. $U = \frac{3}{2}nRT \qquad \Delta U = Q + W = \frac{3}{2}nR\Delta T$
S	entropy	Energy that is "lost" (inaccessible) because it has spread to the surroundings or has spread to separate microstates and cannot be utilized by the particles of the system.
A	Helmholtz free energy	Useful work that could theoretically be obtained from a system. $A = U - TS \qquad \Delta A = \Delta U - T\Delta S$
H	enthalpy	Heat energy available in a chemical reaction. $H = U + PV \qquad \Delta H = \Delta U + P\Delta V = \Delta U - W$
G	Gibbs free energy	Total energy available in a chemical reaction. $G = H - TS \qquad \Delta G = \Delta H - T\Delta S$

Because this is a physics course, we will leave enthalpy and Gibbs free energy to the chemists.

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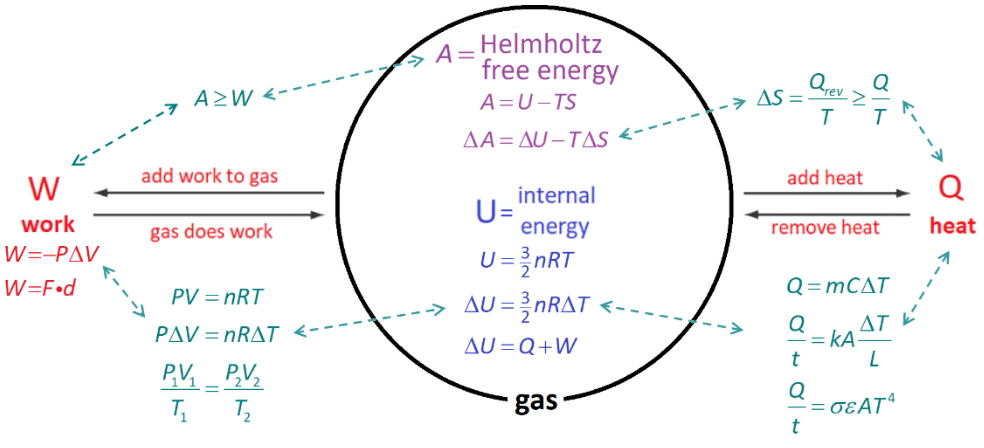
[*] Some chemistry textbooks use the variable *E* instead of *U*.

Thermodynamics Equations Used in This Course

Most of the thermodynamics problems encountered in this course are applications of the following equations:

Equation	Quantities that are Changing
$U=\frac{3}{2}nRT$	internal energy *vs.* temperature
$\Delta U=\frac{3}{2}nR\Delta T$	
$\Delta U=Q+W$	internal energy *vs.* heat & work
$PV=nRT$	pressure & volume *vs.* temperature
$P\Delta V=nR\Delta T$	
$W=-P\Delta V$ *	work *vs.* volume

What makes thermodynamics challenging is that there are many relationships between the quantities in these equations, as shown in the following thermodynamics equation map:



It is often necessary to combine equations. For example:

$$\Delta U=\frac{3}{2}nR\Delta T=Q+W$$

$$-W=P\Delta V=nR\Delta T$$

(Note that we moved the negative sign from $W=-P\Delta V$ to the other side of the equation.)

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* In an algebra-based course, we need to restrict ourselves to problems in which the pressure remains constant during volume changes. In a calculus-based course, this equation would be $W=-\int P\,dV$, where *P* is a function of *V*.

The problems that you will encounter will involve a change in a measurable state variable (pressure, volume and/or temperature). To solve these problems, you will need to:

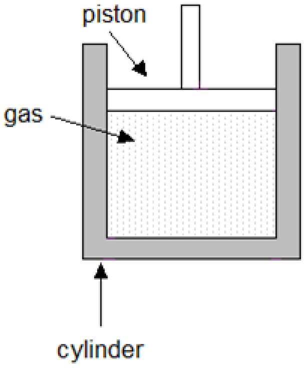
1. Determine what the change involves:
    - heat transfer (Q)
    - work (W) resulting from a change in volume (ΔV).
    - a change in internal energy (ΔU) resulting from a change in temperature (ΔT).

   (There can be more than one of these happening at the same time.)

2. If necessary, determine initial and/or final values of these state variables in relation to other variables using equations such as:
    - $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
    - $PV = nRT$

3. Apply algebraic combinations of these equations to find each of the necessary quantities to answer the question.

Homework Problems



Each of the problems below consists of a gas in a cylinder, as shown in the diagram to the right.

The gas in the cylinder has an initial volume of 0.01 m^3 and an initial temperature of 300 K. The piston has an area of 0.2 m^2, moves freely (with negligible friction), and has a weight of 250 N. Atmospheric pressure outside the cylinder is 100 000 Pa.

You may assume that the cylinder is perfectly insulated, which means the amount of heat that escapes from the cylinder in each situation is negligible.

1. **(M)** What is the initial pressure inside the cylinder? (*This is a fluids problem.*)

   Answer: 101 250 Pa

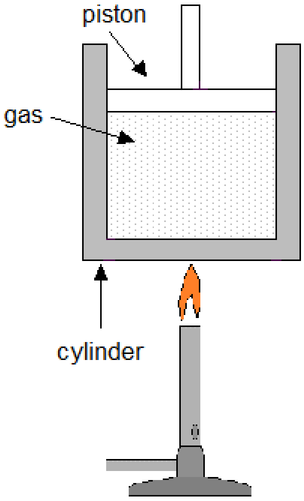
2. **(M)** How many moles of gas are in the cylinder?

   Answer: 0.406 mol

3. **(M)** What is the internal energy of the gas in the cylinder?

   Answer: 1 519 J

4. **(M)** A Bunsen burner is placed below the cylinder and is turned on. Heat is added to the gas (with the pressure remaining constant) until the volume increases to 0.012 m^3.



   a. What is the new temperature of the gas?

   Answer: 360 K

   b. What is the new internal energy of the gas?

   Answer: 1822.5 J

   c. How much work was done to raise the piston? (If you use $W = P\Delta V$, remember to use gauge pressure by subtracting the atmospheric pressure that is pushing down on the piston.)

   Answer: 2.5 J

   d. How much total heat was added to the gas?

   Answer: 306.25 J

5. **(M)** Suppose instead that the piston from problem #4 above was fixed in position and was not allowed to move, so the volume remains constant at 0.01 m^3 while the 306.25 J of heat from question 4d was added.
    a. What is the new temperature of the gas?

       Answer: 360.5 K

    b. What is the new pressure of the gas?

       Answer: 121 667 Pa

    c. If the piston is then released and allowed to move freely, what will the new pressure be inside the cylinder?

       Answer: 101 250 Pa (the same as in problem #1 above)