Why evaporation causes coldness; a challenge to the second law of thermodynamics

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Abstract

In surface evaporation the liquid increases the potential energy of its molecules by taking heat while their kinetic energies remain unchanged. In such state the molecules are in the form of a gas (vapor). We know that in an isothermal system of a liquid and a gas adjacent to it, the temperature of the gas decreases due to the surface evaporation while some net heat is transferred from the gas to the liquid. So, if the temperature of the gas is lower than the temperature of the liquid only in a sufficiently small extent, some net heat will be still transferred from the gas to the liquid due to the surface evaporation and finally the gas and liquid (and vapor) will be isothermal (in a temperature lower than the initial temperature). This matter violates the Clausius (or refrigerator) statement of the second law of thermodynamics.

KEYWORDS: evaporation, surface, thermodynamics, second, law

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1 Introduction

Consider two particles that exert attraction force on each other. Suppose that these two particles are in an inertial coordinate system in such a manner that in the origin of time each has a specific speed and is going away from the other one. Now, imagine that beginning at the origin of time and under the influence of exertion of some forces these two particles go away from each other in the same line that they were going away from each other at the origin of time in such a manner that their speeds remain constant in the coordinate system while the distance between them increases. It is clear that the work done by these forces on this two-particle system (or in fact on these two particles) will not be conserved as increase in the kinetic energy of the particles because as we supposed their speeds won't change. Thus, inevitably, this work will be conserved as increase in the potential energy of the particles. Clearly, if, during their going away from each other, these two particles exert force on other bodies and move them (eg expand the elastic wall of the vessel containing them) in order for the kinetic energy of the particles to remain unchanged it will be necessary that more work to be done on these particles a part of which will be the same mentioned increase in their potential energies and the rest of it will be equal to the work done by the system on its surroundings (by exertion of the above force on the surrounding bodies and moving them (or expansion of the vessel containing them)). But, if we suppose that the expansion of the particles occurs without exertion of force on the surrounding bodies (probably because these surrounding bodies don't exist) such an additional work won't exist. In other words it is possible that the particles go away from each other under the influence of the work done on them in such a manner that this work is conserved totally as increase in the potential energy of the particles while the expansion of the particles (that eg can be done in vacuum) has not done any work on the surroundings.

2 Why wetness causes coldness

Now, considering the above introduction, let's proceed to the subject of evaporation of a liquid in its boiling point. (There are many textbooks about evaporation and the second law of thermodynamics, eg [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]) If in its boiling point we give a liquid some thermal energy, all of this energy will be spent in changing some liquid in its boiling point to some vapor in the same boiling point. Now, a question: “While we know temperature is proportional to the average kinetic energy of the molecules and then the average kinetic energy of the molecules in the liquid in its boiling point is equal to the average kinetic energy of the molecules in the vapor in its boiling point, where has gone the thermal energy given to the liquid or in fact the latent heat of the vaporization?” Answer is that we know where two particles attract each other and we separate them and increase the distance between them by doing work, this work is conserved as potential energy in them. Therefore, latent heat of vaporization is conserved as the potential energy of the molecules (which attract themselves in the liquid state).

Temperature is a quantity proportional to the average kinetic energy of the particles of matter. Imagine an isolated system consisting of some subsystems in contact with each other while this system is in thermal equilibrium ie each part of this system has the same constant temperature. So, we must conclude that the above-mentioned subsystems that are in contact with each other exchange equally kinetic energy with each other and then the net total of the kinetic energies of each subsystem will not change and its temperature will remain constant equal to the temperature of the system. But, if the situation changes in such a manner that in one or some of the subsystems the energy can also be conserved as potential energy, then the whole system, which we supposed it isolated ie without any thermal contact with other systems, will become involved in cooling because a part of exchanged kinetic energies now will be conserved as potential energy and then the sum of all the kinetic energies of the system will decrease and then the average kinetic energy of the particles will also decrease and then the temperature will decrease. Practical instance of the above-mentioned system is a liquid in the form of a layer which is in contact with another (sub)system (eg a solid) when this liquid layer becomes involved in surface evaporation by taking heat (or in fact kinetic energy) from this system. As we said, the liquid increases the potential energy of its particles by taking heat and changes into vapor without spending this heat in increasing the kinetic energy of the particles. So, we learn why wetness causes coldness.

We saw that some water in an isolated container becomes involved in surface evaporation and its temperature decreases. We repeat the question: Why does the temperature of the isolated water decrease due to the surface evaporation? The answer we find in textbooks is ambiguously that the liquid loses its latent heat of vaporization due to the surface evaporation and its temperature decreases. The ambiguity existent in this answer is that latent heat of vaporization is related to the boiling point of the liquid and is given to the liquid from outside of it until the liquid changes into vapor while the temperature remains constant in the boiling point, and this is not so related to surface evaporation which doesn't take place in the boiling point and during it neither any heat is given to the liquid from outside of it nor the temperature remains constant. There is of course an intention of stating a fact hidden in the purport of this answer which we try to make it clear here.

Why does the water in an earthen pitcher become cool in summer? The reason presented is that the water penetrates into the wall of the pitcher and so the outer surface of it remains damp; and this damp evaporates in the summer heat and takes the heat necessary for evaporation of itself from the water in the pitcher causing this water to become cool. There are two questions: Firstly, is there any reason that the damp on the outer surface of the pitcher takes the heat necessary for its evaporation from the water inside the pitcher, not from the hot weather of the summer? Secondly, what is the mechanism of this taking heat from the water inside the pitcher? The answers we will find here for these questions will be that firstly, this damp (on the outer surface) does not take the whole necessary heat from the water inside the pitcher but a part of this heat is taken from the water inside the pitcher and the rest of it is taken from the outside heat, and, secondly, the reason why this part of heat can be taken from the water is that, as we will see here, a part of the kinetic energies of the particles of the water (which is the same heat of the water) can be conserved as the potential energy of them (in the form of vapor) and then the average kinetic energy of the particles of the water, which is the same temperature of the water, will decrease.

Let place some liquid, which is initially in a thermal equilibrium at a constant temperature, inside a closed vacuum container having adiabatic walls. What happens? Due to surface evaporation the temperature of the total system of the liquid and its vapor in the space above it in the container (which was previously a vacuum space) decreases in comparison with the above-mentioned constant temperature. Note that in any state, or in fact in any instant of the process of surface evaporation, both the liquid and the vapor above it in the container have the same relevant decreased temperature and they are in thermal equilibrium (in the same temperature). In fact if we consider one specified instant of the above-mentioned process we will see that we have both a number of liquid molecules, that the sum of their kinetic energies divided by their number yields the average kinetic energy of the liquid molecules which is the same temperature of the liquid, and a number of vapor molecules, that the sum of their kinetic energies divided by their number yields the average kinetic energy of the vapor molecules which is the same temperature of the vapor, and in this instant the above-mentioned average kinetic energy or the temperature of the liquid molecules is equal to the above-mentioned average kinetic energy or the temperature of the vapor molecules.

As we reasoned, due to the above-mentioned surface evaporation, the temperature of the total system decreases because a part of the kinetic energies of the liquid molecules is conserved as the potential energy of the vapor molecules and then altogether the sum of the kinetic energies of the molecules of the system decreases which means that the temperature of the system decreases. Unfortunately, instead of this straightforward reasoning (related to surface evaporation) there is a current wrong reasoning presented in those textbooks which proceed with this subject as follows: “In surface evaporation (or generally in evaporation) the faster molecules of the liquid escape from it as vapor, and then the average kinetic energy of the molecules of the liquid, or its temperature, decreases (since only the slower molecules remain in the liquid).” Such a reasoning necessitates accepting that thus the temperature of the vapor adjacent to the liquid is greater than the liquid temperature because it has faster molecules (escaped from the liquid), and since the vapor and liquid are in thermal contact with each other, the heat is again transferred from the vapor to the liquid until they reach the same temperature which is higher than the above-mentioned decreased temperature as reasoned in the current reasoning. So, such a reasoning necessitates no decrease in temperature due to evaporation! (This reasoning has no application to boiling either, because, in principle, when boiling, the temperature of the liquid and vapor remain constant and the same, and this means that the average kinetic energy of the molecules escaped from the liquid is equal to the average kinetic energy of the liquid molecules and this is contrary to the supposition of the reasoning. Note that the above-mentioned textbooks also accept the above wrong reasoning for boiling by stating that when some heat is given to a liquid to help it to evaporate more, indeed some energies sufficient for escape are given to more molecules of the liquid.)

3 More analytical proof

Thermal equilibrium is a dynamic process, ie while in thermal equilibrium temperatures of the subsystems, being in contact with each other, are the same, they are exchanging heat with each other but of course the net heat transferred to each subsystem is zero in each instant. Now, consider a liquid and a gas adjacent to and in contact with it which both have the same temperature at a point under the boiling point of the liquid. In a time interval, some kinetic energies of the gas molecules are transferred to the liquid. For simplicity suppose that all of these energies are spent on surface evaporation of the liquid, ie in the same mentioned temperature all of these transferred energies only increase the potential energy of some molecules of the liquid changing them into the molecules of vapor without any alteration to the temperature (of liquid (and vapor)). Therefore, average kinetic energy of the gas molecules (and so the gas temperature) decreases while average kinetic energy of the molecules of the liquid and its (newly produced) vapor (and so their temperature) remains constant. Some heat is transferred from the molecules of the vapor (and liquid), the temperature of which being now more than of the gas, to the gas molecules. For simplicity suppose that all the heat the vapor loses in this manner causes decrease in the temperature of the vapor (without any change of it into liquid). The amount of heat the gas molecules receive in this manner is less than the heat they lost at first, because according to our supposition the whole heat the gas molecules lost at first was spent to increase the potential energy of some of the liquid molecules (through their change into vapor) while this potential energy, according to the supposition of the problem, is not restored to the gas molecules at all and only some (heat as) kinetic energy is transferred from the molecules of the vapor (and liquid) to the molecules of the gas the amount of which is less than the mentioned increase in the potential energy, because this increase is equal to the total of the kinetic energies of some certain number of the initial gas molecules (which their kinetic energies have been absorbed afterwards by the liquid causing its evaporation), and in thermal equilibrium with the molecules of the vapor and liquid, each of which has on average the same average energy of the initial gas molecules (before giving their kinetic energies to the liquid), if this certain number of the gas molecules have no kinetic energies they will gain some energy less than the total of the kinetic energies of the same number of molecules each having the average kinetic energy of the initial gas molecules (ie, contrary to the case of boiling point, some net heat is taken from the gas causing its cold (after which, because of its touch to the liquid, the whole system cools)). Therefore, altogether, some of the kinetic energies of the molecules of the above-mentioned isolated system of gas-liquid-vapor have changed into potential energy and then the average of the kinetic energies of the molecules of the system, ie its temperature, decreases.

The following procedure can also take place: Consider a liquid in an isothermal contact with a gas. At a point, under the boiling point, some of the liquid molecules undergo surface evaporation, ie because of some collisions of the liquid molecules, beyond the average collisions of the molecules with one molecule of the liquid this molecule conserves additional kinetic energy it receives as increase in the potential energy (by changing into vapor) while its kinetic energy remains unchanged equal to the average kinetic energy of the molecules of the liquid (and gas). This causes the temperature of the liquid to decrease because of the change of a part of the kinetic energies of the liquid molecules into the potential energy of the vapor molecules (previously being the liquid molecules) each having the same previous average kinetic energy. Created vapor has the same temperature of the gas adjacent to the liquid. The cooled liquid takes heat from these two (gas and vapor) until its temperature increases to a new equilibrium temperature of the system of gas-liquid-vapor which will be less than the initial equilibrium temperature of the system (of gas-liquid) because of the change of a part of the kinetic energies of the particles of the system into potential energy.

4 Challenge to the second law of thermodynamics

The above result, that (surface) evaporation under the boiling point decreases the temperature of the gas adjacent to a liquid, has the following important consequence: As we saw, if we have an isolated gas and separately an isolated liquid and the temperatures of these gas and liquid are the same and we touch them together, we will observe, according to the above reasonings, that (due to surface evaporation) some net heat will be transferred from the gas to the liquid and then the temperature of the gas and subsequently the equilibrium temperature of the whole system (of gas and liquid (and vapor)) will decrease. Now, if the above-mentioned isolated gas has initially a temperature smaller than the initial temperature of the above-mentioned isolated liquid but its temperature is only very little smaller than the liquid temperature, it is quite clear by intuition that after their touch together yet some net heat (although being smaller than ago) will be transferred from the gas to the liquid and the final equilibrium temperature of the whole system will be smaller than the initial temperature of the gas. This means that we have a system in which some net heat is transferred spontaneously from a cold object to a hot object, and this violates the Clausius (or refrigerator) statement of the second law of thermodynamics.

Now, let's see if this example violates the precise statement of this law. First, analytic form of this statement:

When a system is in contact with another system (or a hot source), heat is exchanged mutually between these two systems, ie some heat is transferred from the second system (or the source) to the first system and some (not necessarily equal) heat is transferred from the first system to the second system (or the hot source), and this is due to the conductivity between these two systems (or the system and the hot source) (through which kinetic energies of the molecules can be transferred from one side to the other side). The second law of thermodynamics states that no fresh heat is possible to be transferred from the second system (or the source) to the first system without restoring any part of it to the second system (or the source); and this seems apparently natural since transfer of the kinetic energies of the particles of the second system to the first system causes increase in the kinetic energies of the particles of the first system which in turn causes more transfer of the kinetic energies from the first system to the second system. In simpler words, if two systems are in isothermal contact with each other and have only two passages for exchanging energy between each other, it is clear that the net kinetic energy transferred through one of these passages is zero (ie the same gone energy comes back). Now, if a large amount of kinetic energies rush through the other passage from one of these systems to the other one, it is natural that the average kinetic energy of the molecules of the system being rushed will increase relative to the other system and so the net kinetic energy transferred through the above-mentioned passage no longer will be zero but is from the rushed system to the other one.

In this manner, according to this law, if an additional heat is transferred to a system, it is not the case that the whole of it is conserved as increase in the kinetic energies of the particles of the system or the (regular) work done by the system on its surroundings, but a part of it is conserved as the additional heat taken from the system. (In this discussion the second system (or the hot source or surroundings) can be several-piece (eg as so-called hot and cold sources).)

The whole of what stated above for the definition of the second law of thermodynamics are on this base that the heat transferred from a system (surroundings) to another (considered) system is conserved as work or change in the kinetic energies of the particles. If this transferred heat can also be conserved as change in the potential energies of the particles, this law cannot be established any longer with such mentioned decisive statement, because we can think about a system in which the additional heat, given to it, is conserved as increase in the potential energies of its particles without any change in the average kinetic energy of its particles or its temperature (relative to the temperature of the surroundings) and so without any exit of any net heat from it (due to any difference between temperatures). Such a system can be a liquid being in contact with an adjacent gas (as its surroundings) such that the gas has a calculated temperature higher than the liquid temperature. In this system, according to what stated about surface evaporation, some heat is taken from the gas for surface evaporation of the liquid without any change in the temperature of the liquid (and its newly created vapor) while the temperature of the gas decreases until it becomes equal to the liquid (and vapor) temperature. Here, the heat taken from the gas has been only spent on increasing the potential energies of some liquid molecules without restoring of any fraction of it.

According to the Kelvin-Planck (or heat engine) statement of the second law of thermodynamics it is impossible that the whole heat given to a system by the source is changed into (or conserved as) the work done by that system (on its surroundings) without restoring of any fraction of it to the (cold part of the) source. And the above example shows a system that changes the whole of such a heat into the potential energies of the particles of the system (without restoring of any fraction of it). And then, the discussion concludes with this question that whether it is possible to construct a device which changes a part of the potential energy of an isolated system into work (and not heat) without any change in its temperature.

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