Unit 1-10-S2: Adiabatic, Reversible, Quaistatic, etc., and Some Examples

In our weekly Discussion Session a student asked if "reversible" is the same as "adiabatic". This question brings up a number of points that I have until now swept under the rug.

When using the energy $E(S, V, N)$ as the fundamental thermodynamic potential, we had,

$$dE = TdS - pdV + \mu dN \tag{1.10.S2.1}$$

Formally, this means that if one varied the entropy by dS, and/or the volume by dV, and/or the number of particles by dN, then the resulting equilibrium state with $S + dS$, $V + dV$, and $N + dN$ would have a thermodynamic energy $E + dE$, with dE as given above. In the discussion below, let us imagine N is always kept fixed, so that the above simplifies to,

$$dE = TdS - pdV \qquad \text{or equivalently} \qquad dS = \frac{1}{T}dE + \frac{p}{T}dV \tag{1.10.S2.2}$$

Recognizing pdV as the mechanical work done by the system when its volume changes by dV, we then interpreted TdS as the heat added to the system, so that the above becomes a conservation of energy,

$$dE = \text{đ}Q - \text{đ}W, \qquad \text{(change in energy of system)} = \text{(heat inputed to system)} - \text{(work done by system)} \tag{1.10.S2.3}$$

We write $pdV = \text{đ}W$, and not dW, because pdV cannot in general be written as the total differential of some quantity $d(\cdot)$. Alternatively, the value of $\text{đ}W$ can depend on the path the system takes in going from (S, V) to $(S+dS, V+dV)$. Similarly with $TdS = \text{đ}Q$.

If we now try to interpret the above in the context of some physical process taking the system from one equilibrium state to another, then some complications arise.

Let us first imagine that the process that takes the system from equilibrium state (1) to equilibrium state (2) proceeds *quasistatically*. That means that the thermodynamic parameters are changing so slowly, that one can always assume that the system is instantaneously in equilibrium as it moves between states (1) and (2). It is in this case that we can interpret the heat absorbed by the system in this process as,

$$\text{đ}Q = TdS, \qquad \text{or} \qquad \Delta Q = \int_{(1)}^{(2)} T(S, V(S))\, dS \tag{1.10.S2.4}$$

And similarly the work done by the gas is,

$$\text{đ}W = pdV, \qquad \text{or} \quad \Delta W = \int_{(1)}^{(2)} p(S(V), V) dV \tag{1.10.S2.5}$$

In doing these integrals, we see that the integrands $T(S, V)$ and $p(S, V)$ depend on the pathway $V(S)$ (or equivalently $S(V)$) that one takes in going from (1) to (2). Such quasistatic processes are also said to be *reversible*. If in going from (1) to (2) the system has absorbed heat ΔQ and done work ΔW, then we can take the system from (2) back to (1) by having the system release heat ΔQ and absorb work ΔW. Such reversible processes are what we had in mind when discussed thermodynamic engines and the Carnot cycle or the Otto cycle. Any gas in a cylinder with a piston, where we control the position of the piston and move it only slowly, gives an example of a reversible process.

Formally, a process is said to be *adiabatic* if the system has neither absorbed nor released any heat ΔQ. For a reversible process, $\text{đ}Q = TdS$ and so $\Delta Q = 0 \;\; \Rightarrow \;\; \Delta S = 0$. A reversible, adiabatic, process is thus also *isentropic* – the entropy stays constant and $\Delta S = 0$.

However, not all processes that take a system between two equilibrium states (1) and (2) are quasistatic! And so not all such processes are reversible. The canonical example is when a constraint in a system is suddenly removed. For example, consider a gas in a box that is thermally isolated from its surroundings. In the box is a thermally insulating, immoveable, impermeable wall that separates the gas in the box into two regions. Each region is in thermal equilibrium with itself, but the two regions are not in thermal equilibrium with each other. Then one suddenly removes the wall and allows the gas in the two regions to mix. One can determine the new equilibrium state in the box from thermodynamic considerations. It will be the state that maximizes the entropy subject to the constraint that the total energy of the gas stays constant (and the total volume and the total number of particles similarly stays constant). However, as the gas goes from the initial state where the gases on the two sides of the wall are in equilibrium individually but not with each other, to the the final state where the two gases are mixed and in equilibrium with each other, the series of states that the gas passes through in this process of mixing are *not* equilibrium states. Hence one cannot do the integrals of Eqs. (1.10.S2.4) and (1.10.S2.5) since the thermodynamic quantities $T(S,V)$ and $p(S,V)$ are not even defined for these intermediary non-equilibrium states. And once the two gases have mixed and reached equilibrium, there is in general no thermodynamic process one can do that will take the system back to its initial state. The *sudden* process of removing the wall is therefore an *irreversible* process.

In an irreversible process one can still measure the work done ΔW by the gas on its surroundings since this can be defined in a purely mechanical way. And one can compute the energy difference between the initial and final states ΔE. And then one defines the heat absorbed by the system ΔQ by,

$$\Delta E = \Delta Q - \Delta W \tag{1.10.S2.6}$$

However, now one cannot relate ΔQ to the integral of Eq. (1.10.S2.4) because that integral is not defined and $đQ \neq TdS$. This is because in each step of the process, as the system absorbs heat $đQ$, it is *not* passing from one equilibrium state to another; only the initial and the final states are equilibrium states. In general one has $đQ \leq TdS$. This is because we know that when a constraint is lifted, the entropy will in general increase, so $dS > 0$, even if no heat is added to the system.

Similarly, in an irreversible process one in general has $đW \geq pdV$. This is because when the process is *not* quasistatic, there are finite velocities involved, and so the work the system does is not just due to the pressure of the gas acting on the walls of the container as the volume changes, but the gas also will do work against dissipative forces that might be involved, such as frictional forces in the bearings on which the wall slides, or the viscosity of the gas itself.

Because of this, in an irreversible process, adiabatic $\Delta Q = 0$ does not necessarily mean that $\Delta S = 0$. In fact, it generally doesn't. Consider the above example of a box, thermally insulated from its surroundings, in which we suddenly remove the internal wall and let the gases on the two sides mix and come into equilibrium. This is a adiabatic process with $\Delta Q = 0$ since the external walls of the box are thermally insulating – no heat goes into or out of the box. However we generally will have $\Delta S > 0$; maximizing S is what determines the new equilibrium state. Sudden, irreversible, adiabatic processes, generally do not have $\Delta S = 0$.

If, however, when the wall was still in place, the gases in the two sides of the box happened to be in thermal equilibrium with each other with equal temperature, volume, and number of particles (although there is no reason they needed to have been like that), then, as we calculated in class, once the wall is removed and the gases mix, we have $\Delta S = 0$. The wall can then be reinserted and we will return (at least in a thermodynamic sense) to the same equilibrium state we started with. In this special case, the process of removing the wall, although *sudden*, is still *reversible*.

So in general, adiabatic (i.e. $\Delta Q = 0$) does not mean reversible, nor does it mean $\Delta S = 0$. Adiabatic only means $\Delta Q = \Delta S = 0$ for quasistatic, reversible, processes.

To see the difference between reversible and irreversible, consider the following example. We have a box of total volume V that is thermally insulated from the surrounding environment. Inside the box there is a wall, partitioning the box into two volumes V_1 and $V_2 = V - V_1$. In the volume V_1 there is a gas of N particles in equilibrium at a temperature T_1. The volume V_2 is empty.

Reversible

Now imagine that the wall is slowly moved, so that V_1 gradually increases to contain all the volume V of the box, as in a piston. What is the final equilibrium state of the gas in the box? Assume an ideal gas.

This is a quasistatic process, and so it is reversible.

Since the box is thermally isolated from its surroundings, no heat flows in or out of the box, so $\Delta Q = 0$; the process is adiabatic. Since the process is adiabatic and *reversible*, we know that the entropy of the gas does not change $\Delta S = 0$. So this is an example of adiabatic expansion, where $p \sim 1/V^\gamma$ with $\gamma = 5/3$ for an ideal gas (see Problem Set 2, problem 1).

The work done by the gas on the moving wall is,

$$\Delta W = \int_{V_1}^{V} p\,dV = \int_{V_1}^{V} cV^{-\gamma}\,dV = \left[\frac{c}{(1-\gamma)}V^{(1-\gamma)}\right]_{V_1}^{V} = \frac{3c}{2}\left[V_1^{-2/3} - V^{-2/3}\right] \tag{1.10.S2.7}$$

The constant c is determined by the initial condition, $p_1 = Nk_BT_1/V_1 = c/V_1^{5/3}$, so

$$c = Nk_BT_1V_1^{2/3} \tag{1.10.S2.8}$$

and

$$\Delta W = \frac{3}{2}Nk_BT_1\left[1 - \left(\frac{V_1}{V}\right)^{2/3}\right] \tag{1.10.S2.9}$$

The energy of the gas changes according to $\Delta E = \Delta Q - \Delta W$. We have $\Delta Q = 0$ since this is an adiabatic, reversible, process. Hence $\Delta E = -\Delta W$. Since $E = \frac{3}{2}Nk_BT$, the temperature of the gas thus must decrease. We therefore have for the final equilibrium temperature T_f,

$$T_f = \frac{2}{3}\frac{E}{Nk_B} = \frac{2}{3}\frac{E_i - \Delta W}{Nk_B}, \quad \text{where } E_i = \frac{3}{2}Nk_BT_1 \text{ is the initial energy of the gas before the wall starts to move.} \tag{1.10.S2.10}$$

$$T_f = T_1\left\{1 - \left[1 - \left(\frac{V_1}{V}\right)^{2/3}\right]\right\} = T_1\left(\frac{V_1}{V}\right)^{2/3} \tag{1.10.S2.11}$$

So the final equilibrium state is characterized by having volume V, number of particles N, and,

$$T_f = T_1\left(\frac{V_1}{V}\right)^{2/3}, \quad p_f = \frac{Nk_BT_f}{V}, \quad E_f = \frac{3}{2}Nk_BT_f, \quad \text{and no change in entropy, } \Delta S = 0 \tag{1.10.S2.12}$$

Irreversible

Now imagine that, instead of the wall moving, the wall is suddenly removed, and the gas is free to expand and fill the entire box. What is the final equilibrium state of the gas in the box in this case?

The process is still adiabatic with $\Delta Q = 0$. But now the gas does no work as it expands (there is no wall to push against), so $\Delta W = 0$. The change in energy is therefore, $\Delta E = \Delta Q - \Delta W = 0$. Since $E = \frac{3}{2}Nk_BT$, and E and N stay constant, we conclude that the temperature of the gas does not change and the final equilibrium temperature is $T_f = T_1$. This process is isothermal expansion.

If we were to now put back the wall, we would not return to the initial state of the box, since there would still be gas on both sides of the wall. This process is therefore irreversible. Since this process is irreversible, the fact that it is adiabatic with $\Delta Q = 0$ does *not* imply that $\Delta S = 0$. We can now compute ΔS.

The entropy of an ideal gas is,

$$S(E,V,N) = \left(\frac{N}{N_0}\right)S_0 + Nk_B\ln\left[\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right] \tag{1.10.S2.13}$$

where N_0, S_0, E_0, and V_0 are constants. Since N and E do not change when we remove the wall, we have,

$$\Delta S = S_f - S_i = S(E,V,N) - S(E,V_1,N) = Nk_B \ln\left[\frac{V}{V_1}\right] > 0 \tag{1.10.S2.14}$$

We thus have $\Delta S > 0$ as expected, even though $\Delta Q = 0$.

Below is the problem that stimulated the above discussion.

Consider a box of total volume V, thermally insulated from the surrounding environment. Inside, the box is partitioned into two regions. In region 1 there is a gas of N particles in a volume V_1 in equilibrium at temperature T_1. In region 2 there is a gas of N particles in a volume $V_2 = V - V_1$ in equilibrium at temperature T_2. The two gases are the same type of gas. The wall separating them is thermally insulating, immoveable, and impermeable. The gases in the two regions are therefore each in equilibrium, but they are not in equilibrium with each other because of the separating wall.

Now we suddenly remove the partitioning wall and allow the gases in the two regions to mix. When the system comes back into equilibrium, what is the final temperature T_f, the final pressure p_f, and what is the change in entropy ΔS?

We will assume that the gases can be treated as ideal gases.

Temperature

Since the box is isolated from the surrounding environment, the total energy $E = E_1 + E_2$ is conserved. Initially,

$$E_1 = \frac{3}{2}Nk_BT_1 \qquad \text{and} \qquad E_2 = \frac{3}{2}Nk_BT_2 \qquad \text{so} \qquad E = E_1 + E_2 = \frac{3}{2}Nk_B(T_1+T_2) \tag{1.10.S2.15}$$

After the wall is removed, we have a single gas with $2N$ particles filling the volume V at temperature T_f, so

$$E = \frac{3}{2}(2N)k_BT_f = \frac{3}{2}Nk_B(T_1+T_2) \qquad \Rightarrow \qquad \boxed{T_f = \frac{T_1+T_2}{2}} \tag{1.10.S2.16}$$

Pressure

The final pressure of the gas is obtained by the ideal gas law,

$$p_f = \frac{(2N)k_BT_f}{V} = \frac{Nk_B(T_1+T_2)}{V_1+V_2} \tag{1.10.S2.17}$$

To relate that to the initial pressures before the wall was removed,

$$p_1 = \frac{Nk_BT_1}{V_1} \quad \text{and} \quad p_2 = \frac{Nk_BT_2}{V_2} \qquad \Rightarrow \qquad V_1 = \frac{Nk_BT_1}{p_1} \quad \text{and} \quad V_2 = \frac{Nk_BT_2}{p_2} \tag{1.10.S2.18}$$

Using that in Eq. (1.10.S2.17) we get,

$$\boxed{p_f = \frac{T_1+T_2}{\frac{T_1}{p_1}+\frac{T_2}{p_2}} = \frac{p_1p_2(T_1+T_2)}{p_2T_1+p_1T_2}} \tag{1.10.S2.19}$$

Suppose, to simplify the problem, we had initially that $T_1 = T_2$. Then $T_f = T_1 = T_2$ and the above becomes

$$p_f = \frac{2p_1p_2}{p_1+p_2} \qquad \text{or} \qquad \frac{1}{p_f} = \frac{1}{2}\left(\frac{1}{p_1}+\frac{1}{p_2}\right) \tag{1.10.S2.20}$$

The inverse of the final pressure is the average of the inverses of the initial pressures!

In this case, is p_f less than or greater than the average of the initial pressures? Define,

$$\bar{p} \equiv \frac{p_1 + p_2}{2} \quad \text{and} \quad \delta p = \frac{p_1 - p_2}{2} \qquad \text{so that} \qquad p_1 = \bar{p} + \delta p \quad \text{and} \quad p_2 = \bar{p} - \delta p \tag{1.10.S2.21}$$

Then

$$p_f = \frac{2(\bar{p} + \delta p)(\bar{p} - \delta p)}{\bar{p} + \delta p + \bar{p} - \delta p} = \frac{2(\bar{p}^2 - \delta p^2)}{2\bar{p}} = \bar{p} - \frac{\delta p^2}{\bar{p}} < \bar{p} \tag{1.10.S2.22}$$

and the final pressure is *less* than the average of the initial pressures.

Entropy

Initially, the entropy of the system is,

$$S_i = S(E_1, V_1, N) + S(E_2, V_2, N) \qquad \text{since entropy is additive} \tag{1.10.S2.23}$$

After the wall is removed, we have a single gas of $2N$ particles in a volume V at energy $E = E_1 + E_2$, so,

$$S_f = S(E, V, 2N) \tag{1.10.S2.24}$$

The change in entropy $\Delta S = S_f - S_i$.

Assuming we are dealing with ideal gases, the entropy of an ideal gas is,

$$S(E, V, N) = \left(\frac{N}{N_0}\right) S_0 + N k_B \ln \left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right] \tag{1.10.S2.25}$$

where N_0, S_0, E_0, and V_0 are constants. We then have,

$$S_f = \left(\frac{2N}{N_0}\right) S_0 + 2N k_B \ln \left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{2N}{N_0}\right)^{-5/2} \right] = \left(\frac{2N}{N_0}\right) S_0 + N k_B \ln \left[\left(\frac{E}{E_0}\right)^{3} \left(\frac{V}{V_0}\right)^{2} \left(\frac{2N}{N_0}\right)^{-5} \right] \tag{1.10.S2.26}$$

while

$$S_i = \left(\frac{N}{N_0}\right) S_0 + N k_B \ln \left[\left(\frac{E_1}{E_0}\right)^{3/2} \left(\frac{V_1}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right] + \left(\frac{N}{N_0}\right) S_0 + N k_B \ln \left[\left(\frac{E_2}{E_0}\right)^{3/2} \left(\frac{V_2}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right] \tag{1.10.S2.27}$$

so

$$\Delta S = S_f - S_i = N k_B \ln \left[\left(\frac{E^2}{E_1 E_2}\right)^{3/2} \left(\frac{V^2}{V_1 V_2}\right) 2^{-5} \right] \tag{1.10.S2.28}$$

We can now use, $E_1 = \frac{3}{2} N k_B T_1$, $E_2 = \frac{3}{2} N k_B T_2$, and $E = \frac{3}{2}(2N) k_B T_f$ to get $\frac{E^2}{E_1 E_2} = \frac{4 T_f^2}{T_1 T_2} = \frac{(T_1 + T_2)^2}{T_1 T_2}$, and so,

$$\Delta S = N k_B \ln \left[\left(\frac{(T_1 + T_2)^2}{T_2 T_2}\right)^{3/2} \left(\frac{(V_1 + V_2)^2}{V_1 V_2}\right) 2^{-5} \right] = N k_B \ln \left[\frac{\left(\frac{T_1 + T_2}{2}\right)^3 \left(\frac{V_1 + V_2}{2}\right)^2}{(T_1 T_2)^{3/2}\, V_1 V_2} \right] \tag{1.10.S2.29}$$

$$= N k_B \ln \left[\left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right)^3 \left(\frac{V_1 + V_2}{2\sqrt{V_1 V_2}}\right)^2 \right] \tag{1.10.S2.30}$$

Now note that each term in a parenthesis within the logarithm is ≥ 1. For example,

$$\frac{V_1+V_2}{2\sqrt{V_1V_2}} = \frac{1}{2}\left(\sqrt{\frac{V_1}{V_2}}+\sqrt{\frac{V_2}{V_1}}\right) = \frac{1}{2}\sqrt{\left(\sqrt{\frac{V_1}{V_2}}+\sqrt{\frac{V_2}{V_1}}\right)^2} = \frac{1}{2}\sqrt{\frac{V_1}{V_2}+\frac{V_2}{V_1}+2} \geq \frac{1}{2}\sqrt{2+2} \geq 1 \tag{1.10.S2.31}$$

In the last step we used that the function $f(x) = x + 1/x$ has a minimum value of 2 at $x = 1$.

So we conclude that $\boxed{\Delta S \geq 0}$. Note, we will have $\Delta S = 0$ only when $V_1 = V_2$ and $T_1 = T_2$, i.e. when the two gases on either side of the wall already happened to be in equilibrium with each other. Otherwise, we have $\Delta S > 0$.

As we expect, the entropy increases when the wall is removed. Note that $\Delta S > 0$ even though removing the wall is an adiabatic process, i.e. there is no heat added or removed from the box, so $\Delta Q = 0$. We can have $\Delta S > 0$ even though $\Delta Q = 0$ because this is an irreversible process. If we let the gases mix and reach equilibrium, and then we reinserted the wall, we do not come back to the initial state.

If we did have the special case that $V_1 = V_2$ and $T_1 = T_2$, then we would have $\Delta S = 0$, and this would be a reversible process. If we let the gases mix and reach equilibrium, and then reinserted the wall, we do wind up with a state that is indistinguishable from the initial state.

Note, when we say the above is a reversible process, we mean in the thermodynamic sense. The initial and final states are both described by saying the gases on each side of the wall have the same equal values of T, V, and N, and specifying the values of T, V, and N are sufficient to uniquely describe the equilibrium state of the gas. But one might think that this process is *not* reversible in a microscopic sense, since after we reinsert the wall, the particular particles that are on a given side of the wall is not the exact same set of particles that were on that side of the wall initially. This observation is what led to Gibbs' Paradox for the entropy of mixing – see Notes 2-6. Gibbs concluded that the only way to reconcile this paradox is to assume that all particles in the gas are indistinguishable from each other – even for a gas of *classical* particles obeying Newtonian mechanics – and so the final configuration is indeed indistinguishable from the initial configuration and the process is reversible!