Do you really understand Thermodynamics?

--- A quick note to the fundamentals of thermodynamics

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Who are supposed to read this note? If you just begin with this new course or if you just finish studying the basic principles in thermodynamics but find yourself rather confused, this note may be helpful.

First law in Thermodynamics

The first law comes from conservation of energy and is actually one way of expressing this universal law in physics. The first law itself can be expressed in many different ways. Here is one of the most general forms which is mainly used for open systems or control voloum:

$$\Delta E_{sys} = W + Q + \sum m_i (h + gz + \frac{C^2}{2})_i - \sum m_e (h + gz + \frac{C^2}{2})_e \quad (1)$$

In this expression, the LHS *delta_E_sys* refers to the total change of energy in the system, including the change of kinetic energy, potential energy, and internal energy. For most cases we are interested in, change of kinetic energy *delta_KE* and change of potential energy *delta_PE* can be neglected. That's to say, we are considering systems which are under conservation of mechanical energy. In these cases, we can replace the LHS simply with *delta_U* which refers to change of internal energy in the system. On the RHS, *W* refers to the net input work **to** the system, and *Q* refers to the net heat transfer **to** the system. Be careful with the directions of work and heat transfer here! If the net work or heat transfer turns out to be from the system, we should have minus signs before the terms or we have to use negative values for these terms. The subscript *i* in the sigma terms means inlets and *e* means exits. Basically, the sigma terms mean the energy that is transfer into the system by mass flows.

Now we could develop a basic idea of the physical meaning of this equation. Essentially we have 3 ways of changing the energy in a system: work, heat transfer and mass transfer. If work is input into the system, or heat is transferred to the system, or mass carrying energy is transferred to the system, the energy of the system will increase.

So for a close system, since we don't have change of mass, that is we don't have any mass transfer, we simply have

$$\Delta U = W + Q \quad (2)$$

That's the form we are most familiar with. But you have to note that we are neglecting *delta_KE* and *delta_PE* (we are assuming the conservation of mechanical energy) and be careful with the signs before *W* and *Q*. (Many textbook defines *W* as the work done by the system to the surroundings, so no wonder they have a minus sign before *W*. The reason why I prefer the form I mentioned above is that I don't have to memorize the definitions since I can always do the things correctly if I have the physical meaning in my mind.)

Taking derivatives of Eq (1) with respect to time, we can get the rate form of energy conservation:

$$\Delta \dot{E}_{sys} = \dot{W} + \dot{Q} + \sum \dot{m}_i (h + gz + \frac{C^2}{2})_i - \sum \dot{m}_e (h + gz + \frac{C^2}{2})_e \quad (3)$$

For steady state systems, the energy of the system is not changing with time so we have zero for the LHS of Eq (3) and we can simply have that RHS of the Eq (3) is zero.

For many cases in engineering, we can have more assumptions: the steady-state devices are well-insulated (Q is zero), the mass flow rate is constant, and the kinetic and potential effects are negligible, so we will have very simple a expression for steady-state devices such as turbines, compressors and pumps:

$$w = \frac{\dot{W}}{\dot{m}} = \Delta h \quad (4)$$

Second law in Thermodynamics

The second law in Thermodynamics also has many different statements. One of the most famous inequalities derived directly from the second law is the *Clausius* inequality

$$\oint \frac{\delta Q}{T} \le 0 \quad (5)$$

where the equality only holds for totally or internally **reversible** process.

From Clausius inequality we can introduce a new thermodynamic property called entropy:

$$dS = \left. \frac{\delta Q}{T} \right|_{rev} \quad (6)$$

Note that we can not directly define entropy but can only define the differentiation or change of entropy in a macroscopic view.

From (5) and (6) we can get another famous inequality known as the **increase of entropy principle** which can be expressed as:

$$\sigma \ge 0 \quad (7)$$

where σ is known as **entropy generation** or product of entropy during the process. The equality holds for a totally or internally reversible process.

Finally, we come to the entropy balance which can be expressed in a general form very similar to Eq (1):

$$\Delta S_{sys} = \sum \frac{Q}{T} + (\sum m_i s_i - \sum m_e s_e) + \sigma \quad (8)$$

The LHS of Eq (8) is the total change of entropy of the system. The RHS means the change of entropy is due to three effects: entropy introduced by heat transfer, entropy introduced by mass transfer and the entropy generated during the irreversible process. The signs of heat transfer terms and the subscripts in the mass transfer terms keep the same as that in Eq (1).

From Eq (8), we can also get the close system from, the rate form, and the steady state form respectively, just as we do in the first law.

Some terms may cause confusions
isothermal – constant temperature
isobaric – constant pressure
isochoric – constant volume or specific volume
adiabatic – well insulated so the heat transfer is negligible
reversible – can be restored to the in situ (original) states
isentropic – constant entropy

From Eq (8), for a close system, we don't have mass transfer, and if it is both adiabatic and reversible, then the RHS turns out to be zero so that it is an isentropic process. So for a close system, *adiabatic* + *reversible* = *isentropic*.

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