

**Thermodynamics**  
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**Lecture 59**

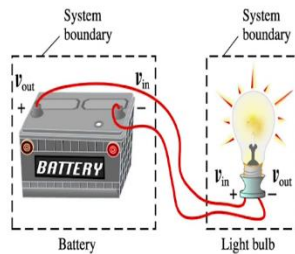
**Second Law of Thermodynamics: Limitations of the First Law of Thermodynamics**  
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Second Law of  
Thermodynamics



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First law given by:  $\frac{dE}{dt} = \dot{Q} - \dot{W}$



Figure 1.

For systems shown in Fig. 1, the rate equation of the first law is  $\frac{dE}{dt} = \dot{Q} - \dot{W}$ . If there are no changes in kinetic and potential energy during the process,  $E = U$ . (Refer Time Slide: 01:21)

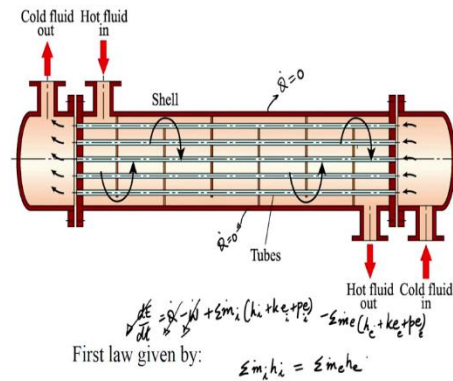


Figure 2.

For a heat exchanger as shown in Fig. 2, after making some assumptions, which were discussed in the previous lectures, the first law for a control volume reduces to,

$$\sum \dot{m}_i h_i = \sum \dot{m}_e h_e$$

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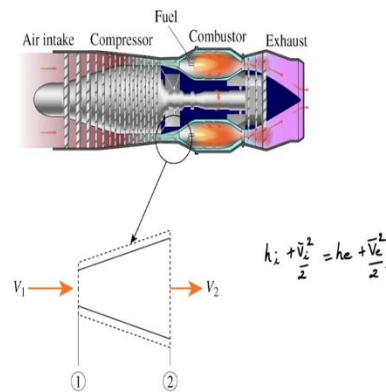


Figure 3.

For a nozzle or diffuser, the first law for a control volume reduces to,

$$h_i + \frac{\bar{V}_i^2}{2} = h_e + \frac{\bar{V}_e^2}{2} \text{ (see the previous lectures for assumptions made to reach this expression)}$$

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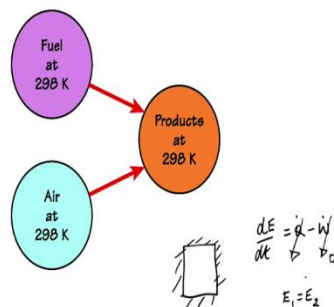
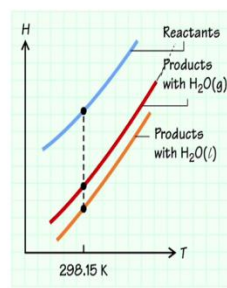


Figure 4.

Consider a closed rigid chamber (control volume) where we have air and fuel. There are no inlets and outlets. The air and fuel burn together to form products (assume the temperatures of the reactants and the products remain the same throughout the reaction). As the chamber is rigid, work interaction is 0. If the chamber is insulated, then heat interaction is also 0. In such a case, the first law for a control volume is  $\frac{dE}{dt} = 0$ , which implies  $E_1 = E_2$ . So, the energy content does not change.

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$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

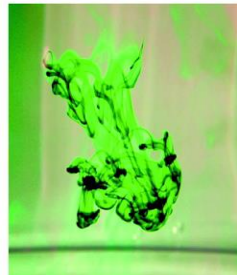
$$H_1 = H_2$$



Figure 5.

If the burning of a air-fuel mixture happens in an insulated piston-cylinder arrangement as shown in Fig. 5 and the piston is free to move, the work interaction is not 0. The process is a constant pressure process. Here,  $E = U$ . Hence,  $dU + pdV = 0$  ( $dU = \delta Q - pdV$  and  $\delta Q = 0$ ). Hence,  $dH = 0$ , which implies  $H_1 = H_2$ . During the process of burning, the temperature inside increases. Figure 5 shows the plot of enthalpy versus temperature for reactants and products. So, reactants and products can have the same enthalpy provided that the products are at higher temperature. Reactants can also form products at the same temperature if the heat transfer is allowed across the boundary of a system or control volume.

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$$dE=0$$



Figure 6.

Figure 6 shows a dye mixing in water in a beaker. The mixing process is adiabatic. There is no work interaction. For such a process, the first law implies  $E_1=E_2$ , i.e., the energy content does not change during the process. So, the first law allows us to tell something about the final state if we know something about the initial state.

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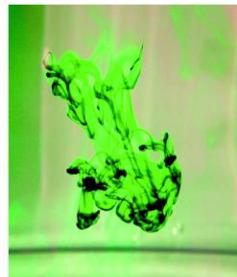


- First law
  - Relation between heat and work
  - Not about actual conversion
  - Analysis of feasibility and direction not given by 1<sup>st</sup> law



The first law is a relation between heat and work interaction. Knowing initial state of a system or a control volume, we can calculate its final state or vice versa. However, the first law does not say anything about the direction of the process. It does not talk about the feasibility of the process.

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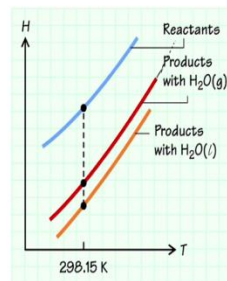


$dE=0$



In the example of mixing of the dye in water we considered above, the first law says  $E_1=E_2$ , i.e., the energy of the control volume/system does not change in the process of mixing. The first law is also valid for a process where the mixed dye in water separates out and agglomerates at one location. Here also,  $E_1=E_2$ . But, we do not see that happening naturally.

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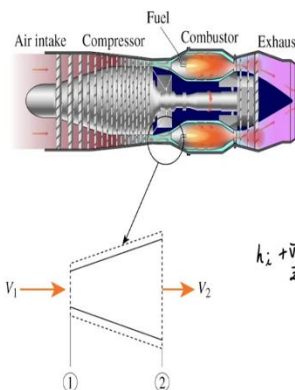
$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

$$H_1 = H_2$$



In the example of reactants burning into products (air-fuel mixture burning into products) in a piston-cylinder arrangement we considered above, the first law says  $H_1 = H_2$ , i.e., enthalpy of the reactants equals enthalpy of the products. The first law is also valid for a reaction where the products of the combustion in the above case form reactants. However, it doesn't happen spontaneously. We need to do something for this to happen. The first law does not say anything about the direction of a process.

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$$h_i + \frac{V_i^2}{2} = h_e + \frac{V_e^2}{2}$$



Figure 7.

The combustor in Fig. 7 burns a mixture of air and fuel and forms exhaust gases. If we send in the exhaust gases through the exit of the combustor, we do not get fuel and air. However, the first law is still valid for such a process (i.e. sending exhaust gases through the exit of the combustor and getting back fuel and air).

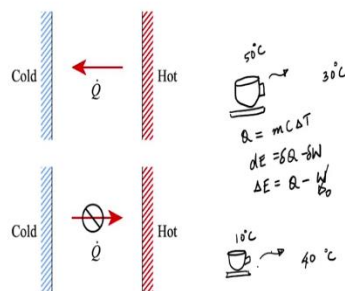
Hence, the analysis of feasibility and direction of a process is not given by the first law.

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- First law
  - Relation between heat and work
  - Not about actual conversion
  - Analysis of feasibility and direction not given by 1<sup>st</sup> law



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E.g. heat transfer from low temperature to high temperature

- First law valid
- But spontaneous heat transfer occurs only in one direction



Figure 8.



We know that heat transfer occurs from a hot substance to a cold substance. For example, a cup of hot coffee kept in an atmosphere whose temperature is lower than that of the coffee, cools down and achieves the temperature of the atmosphere after some time, and stays at that temperature. However, we do not see the reverse process happening, i.e., we do not see the coffee, which is at the atmospheric temperature now, becoming hot and attaining its initial temperature. However, the first law is valid for both the processes. It does not say anything about the direction in which the process tends to happen naturally. The first law can be used to calculate the heat transfer in the process where the hot coffee cools down from 50 °C to atmospheric temperature of 30 °C as well as the process where the coffee at 30 °C becomes hot and attains 50 °C naturally (work interactions are 0 for these processes).

We see spontaneous heat transfer happening from a hot substance to a cold substance, but not from a cold substance to a hot substance. A spontaneous process happens only in one direction. The first law is not enough to tell if a process will happen or not.