

# Lecture 6: Work, Heat, Energy, and First Law of Thermodynamics II

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Winter 2023

## 2.2 Work

**Example 2.1.** A greatly simplified model of an internal combustion engine is as follows. At the start of the power stroke the ignited gases exert a pressure of 20 atm, and drive the piston back against a constant force equivalent to 5.0 atm. In so doing, the piston sweeps out  $250 \text{ cm}^3$ . What is the power output of a six-cylinder engine working at 2000 RPM (with one power stroke from each cylinder every second revolution)?

*Solution 2.1.* Given  $P = 5.0 \text{ atm}$ ,  $V_1 = 0 \text{ L}$  and  $V_2 = 0.250 \text{ L}$  First, we determine the work done per one stroke.

$$\begin{aligned} W &= - \int_{V_1}^{V_2} P_{ext} dV = - \int_0^{0.250} 5.0 dV = - [5.0V]_0^{0.250} = -1.25 \text{ L atm} \\ &= -1.25 \text{ L atm} \times 101.325 \text{ J/L atm} = -1.3 \times 10^2 \text{ J} \end{aligned}$$

Let  $\omega$  represent the number of revolutions per minute. Then since we have 6 cylinders, then the six such cylinders produce

$$W_6 = \omega \times 6 \times W \times \frac{1}{2} = 7.8 \times 10^5 \text{ J}$$

Finally, the rate of production is given by the power output:  $P = \frac{W_6}{t}$ , where  $t$  is in seconds.

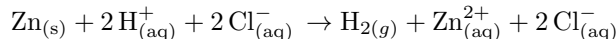
$$P = \frac{7.8 \times 10^5}{60} = 13 \text{ kW}$$

as required. □

**Example 2.2** (Expansion Work). (a) How much work has been done if 5 g of Zn have completely reacted according to the following reaction if the external pressure is 1 atm and  $T = 298 \text{ K}$ ?

(b) What is the work per 1 mol of Zn consumed?

*Solution 2.2.* (a) Consider the chemical equation below:



First calculating the number of moles of Zn, which can be calculated by calculating the number of moles of  $\text{H}_2$ .

$$n(\text{H}_2) = n(\text{Zn}) = \frac{5 \text{ g}}{65.38 \text{ g/mol}} = 0.0765 \text{ mol}$$

Then the change in volume is calculated by using the ideal gas law:

$$\Delta V = \frac{n(\text{H}_2)RT}{P} = \frac{(0.0765)(0.08206)(298)}{1} = 1.87 \text{ L}$$

Then the work done against the external pressure of 1 atm:

$$W = - \int_{V_1}^{V_2} P_{ext} dV = - \int_0^{1.87} dV = -1.87 \text{ J}$$

(b) The work per mole of Zn is:

$$\theta = \frac{W}{n} = \frac{-1.87}{0.0765} = 24.4 \text{ J/mol}$$

as required □

There are four types of work that we observe in physics and chemistry:

- Volume Expansion:  $W = - \int_{\Omega} P_{ext} dV$
- Stretching:  $W = - \int_{\Omega} F dL$
- Surface Expansion:  $W = - \int_{\Omega} \gamma d\sigma$
- Electrical:  $W = \int_{\Omega} \phi dQ$

**Question 2.1** (Compression/Expansion). *How is the work related to the electrical work done by the surroundings and on the system? What about PV graphs?*

**Answer 2.1.** *For any compression or expansion, we know that*

$$W = \int_{\Omega} F dL = - \int_{\Omega} P_{ext} dV$$

*Then the electrical work  $W_e$  done by the surrounds on the system is given by:*

$$W_e = Q\phi = I\eta t$$

where  $I$  is the current,  $\eta$  is the voltage, and  $t$  is the time.

For PV graphs: the work done by the system on the surroundings is

$$W_{PV} = - \int_{\Omega} P_{ext} dV$$

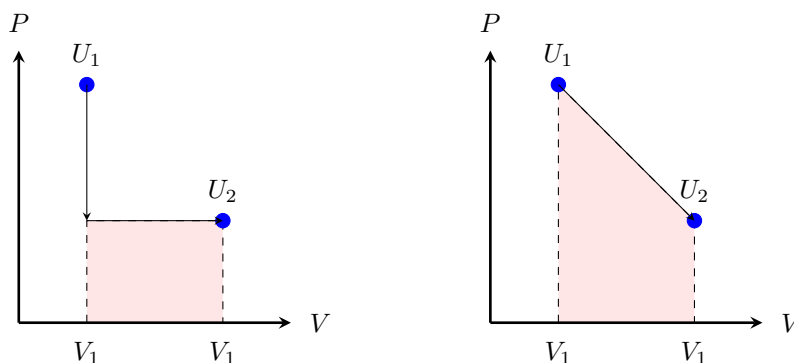
Then the total work is:

$$W = I\eta t - \int_{\Omega} P_{ext} dV = I\eta t - P_{ext}\Delta V$$

## 2.6 State Functions and Path Independence

Interval energy  $U$  is a state function (path independent), so we are only interested in the final  $U_2$  and the initial  $U_1$  states.

To find  $\Delta U = U_2 - U_1$  we pick a convenient path to get from the initial state  $A$  to the final state  $B$  to find  $W$  and  $q$  along this path.



For ideal gases:

$$\Delta U = f(T) \quad \Delta U \neq f(V) \quad \Delta U = f(P)$$

But as a result:

$$\frac{\partial U}{\partial V} = 0$$

## 2.3 Heat

Heat is the transfer of energy between two entities that are at different temperatures. Heat however is *not* a state function, because it is path dependent.

Heat is a transitory, i.e. it only appears during energy flow. Heat is transferred from a hot entity to a cold entity if the two are in contact through a diathermic wall. If the two entities have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall. This condition corresponds to thermal equilibrium.

Conservation of energy requires that:

$$q_{sys} + q_{sur} = 0 \Rightarrow q_{sys} = -q_{sur}$$

The sign convention of heat is as follows:

- If heat is *added to the system*, then  $q > 0$ , since  $T_2 > T_1$ .
- If heat is *removed from the system*, then  $q < 0$ , since  $T_1 > T_2$ .

**Example 2.3.** How much heat is transferred in raising the temperature of a beaker of water (50 g) from 25°C to 35°C, while keeping constant pressure of 1 atm?

*Solution 2.3.* Given  $m = 50$  g,  $\Delta T = 10^\circ\text{C}$ , and  $C = 4.184$  J/C°, then

$$q = mC\Delta T = (50)(4.184)(10) = 2092 \text{ J}$$

The system may be heated by sonicating or mixing on a stir plate in which case mechanical work is used to increase temperature and heat. Or could increase  $T$  by combination of heating in water bath and mechanical mixing then ...?

## 2.4 Heat Capacity

Heat capacity is the amount of heat needed to change temperature of a substance by a given amount. For a closed system with no phase changes and no chemical reactions:

$$q = \int_{T_1}^{T_2} C dT = \int_{T_1}^{T_2} m\bar{C} dT$$

where

- $C$  is the heat capacity of the system.
- $\bar{C}$  is the specific heat capacity.
- $m$  is the mass of the system.

$C$  is constant whenever the temperature range is between  $T_2$  and  $T_1$ . That is

$$q = m\bar{C}(T_2 - T_1)$$

Some important equations to keep in mind:

$$C = \frac{q}{\Delta T} \quad \bar{C} = \frac{C}{n} = \frac{q}{n\Delta T} \quad C_s = \frac{q}{m\Delta T}$$

where the first question is the general form of the heat capacity,  $\bar{C}$  is the molar heat capacity, and  $C_s$  is the specific heat capacity.

When heat is added to a substance, its temperature will rise. How much the temperature will rise depends on:

1. The amount of heat delivered.
2. The amount of substance present.
3. The chemical nature and physical state of the substance.
4. The conditions under which heat is added to the system.

Heat capacity is a quantity that can be measured directly, and can be measured at constant volume or constant pressure.

- At constant volume:  $C_V = \frac{\Delta U}{\Delta T} = \frac{q_V}{\Delta T}$ 
  - At constant  $V$  the heat absorbed by the system is equal to the change in internal energy.
- At constant pressure:  $C_P = \frac{\Delta H}{\Delta T} = \frac{q_P}{\Delta T}$ 
  - At constant  $P$ , the heat absorbed is equal to the change in enthalpy.

It follows that:

$$\begin{cases} \Delta U = C_V \Delta T = n\bar{C}_V \Delta T \\ \Delta H = C_P \Delta T = n\bar{C}_P \Delta T \end{cases}$$

In general,  $C_V$  and  $C_P$  for a substance are not equal...but why? This is because a constant pressure process, volume is changing (expansion!) so work must be done on the surroundings.

**Question 2.2.** *How are  $C_P$  and  $C_V$  related for a gas?*

**Answer 2.2.** *The equations are related for a gas as follows:*

$$C_P - C_V = nR \quad C_{P,m} - C_{V,m} = R$$

*this is true mainly for gases only, because the volume of liquids and solids doesn't change much with temperature, so work done on the surroundings is very small.*

**Question 2.3.** *How does the heat capacity  $C$  of a gas differ from that of a liquid?*

**Answer 2.3.** *Remember that calculating heat capacity for gases:  $C = \frac{\Delta U}{\Delta T}$ , where*

$$U = E_{tr} + E_{ro} + E_{vib} + E_{ele}$$

*Heat capacity of liquids are much greater than gases, and can't be accounted for just by considering translational, rotational, and vibrational contributions. There are weak interactions present between molecules in the liquid and solid state, which contribute to the increase in  $C$ .*

**Question 2.4.** *If  $C = \lim_{\Delta T \rightarrow 0} \frac{q}{\Delta T}$ , what kind of variable is heat capacity?*

**Answer 2.4.** *Extensive.*

## 2.6 State Functions and Path Independence (Revisited)

The total change in internal energy from initial state  $A$  to final state  $B$ :

1. Depends on the intermediate state.
2. **Does not depend on the intermediate state.**

State function depends on state of system, and not path to reach that state:

$$\Delta U = \int_A^B dU = U_B - U_A$$

we say that  $dU$  is an *exact differential*. As well,

$$\oint_C dU = U_B - u_A = 0$$

(integral over a closed path) for any closed curve  $C \subset \Omega$ , where  $\Omega$  is an open subset in  $\mathbb{R}^3$ .

**Remark 2.1.** *Every closed differential is an exact differential. But the converse is not exactly true.*

Assume  $T_1 < T_2 < T_3$ . If  $P_{ext}$  depend on the mass, then  $W$  would always differ. That is,

$$W = - \int_{V_1}^{V_2} P_{ext} dV = -P_{ext} \Delta V$$

and as well,

$$\Delta U = U(T_3, V_2) - U(T_1, V_1) = q + W$$

We can choose a different path from  $V_1, T_1$  to  $V_2, T_3$ , and a different path from  $V_2, T_2$  to  $V_1, T_1$ . Since  $W$  is different for each path, the integral of a closed path of work is not 0. Since  $\Delta U$  is the and  $W$  always differs, then  $q$  will be different as well. Hence, both  $q$  and  $W$  are path functions.