Thermodynamics I

Chapter 1

Heat, Work, System & State of the Working Fluid

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Introduction

Thermodynamics :

It is a science which deals with the energy and work of a system, the thermodynamics deals with the relations between heat and other forms of energy (such as mechanical, electrical, or chemical energy), and, by extension, of the relationships between all forms of energy.

Temperature :

Temperature is a measure of how fast the molecules within an object are moving. In fancier physics language, temperature is the average kinetic energy of the atoms that make up a substance, which we also call the internal energy of the system. It measures how fast, on average, a molecule in a substance is moving.

The most commonly used temperature scale is Celsius, which is based on the freezing and boiling points of water, assigning respective values of 0 degrees C and 100 degrees C , respectively. The Fahrenheit scale is also based on the freezing and boiling points of water which have assigned values of 32 F and 212 F, respectively.

Any object with at least one measurable property that changes as its temperature changes can be used as a thermometer. Most thermometers operate on the principle of thermal expansion:

Materials tend to occupy more volume at a given pressure when they are at a higher temperature. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual units for temperature we arbitrary assign 0 to the freezing point and 100 to the boiling or steam point of water. We then mark these two points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the Celsius (or centigrade) scale, by definition.

The *Kelvin scale* is an absolute temperature scale that measures temperature from absolute zero instead of from the freezing point of water. The relationship between these two temperature scales is given by :

$$T({}^0C) = T(K) - 273.15$$

By definition, the *Rankin scale*, is related to the *Kelvin scale* by a factor of 1.8:

$$T({}^0R) = 1.8\ T(K)$$

A degree of the same size as that on the Rankine scale is used in the *Fahrenheit scale* but the zero point is shifted according to the relation :

$$T({}^0F) = T({}^0R) - 459.67$$

From above equations the Fahrenheit scale can be related to the Celsius scale by :

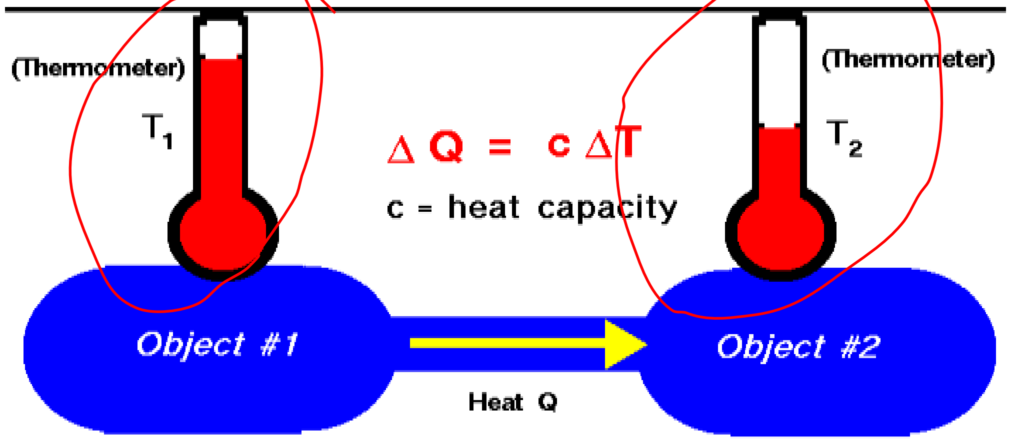
$$T({}^0F) = 1.8\ T({}^0C) + 32$$

Many of the equations of thermodynamics are correct only when you measure temperature on the absolute scale, Kelvin or Rankine. There will be no problem in using the Celcius and Fahrenheit scales when the *difference* between two temperatures is needed.

Heat

Heat is a form of energy associated with the kinetic energy of atoms or molecules and capable of being transmitted through solid and fluid media by conduction, through fluid media by convection, and through empty space by radiation.

OR , The transfer of energy from one body to another as a result of a difference in temperature or a change in phase.



In the process of reaching thermodynamic equilibrium, heat is transferred from the warmer object to the cooler object. At thermodynamic equilibrium heat transfer is zero.

When two objects are brought into contact and isolated from the surrounding, energy tends to move spontaneously from one to the other. The object that gives up energy is at a *higher* temperature, and the object that receives energy is at a *lower* temperature. We would be able to observe that the electrical resistance of the warmer object decreases with time, and that of the colder block increases with time; eventually there would be no change in the electrical resistances of these objects. The two objects are then in *thermal equilibrium*. They are at the same *Temperature*. We could then define temperature as a measure of the tendency of an object to spontaneously give up energy to its surroundings.

Heat is energy can be converted from one form to another, or transferred from one object to another. For example, a stove burner converts electrical energy to heat and conducts that energy through the pot to the water. This increases the kinetic energy of the water molecules, causing them to move faster and faster. At a certain temperature (the boiling point), the atoms have gained enough energy to break free of the molecular bonds of the liquid and escape as vapour.

Relationship between heat and temperature :

Heat and temperature are two different but closely related concepts. Note that they have different units: temperature typically has units of degrees Celsius (°C) or Kelvin (K), and heat has units of energy, Joules (J). Temperature is a measure of the average kinetic energy of the atoms or molecules in the system. The water molecules in a cup of hot coffee have a higher average kinetic energy than the water molecules in a cup of iced tea, which also means they are moving at a higher velocity. Temperature is also an intensive property, which means that the temperature doesn't change no matter how much of a substance you have (as long as it is all at the same temperature!). This is why chemists can use the melting point to help identify a pure substance , means the temperature at which it melts is a property of the substance with no dependence on the mass of a sample.

Specific heat

The amount of heat required to increase the temperature of a certain mass of a substance by a certain amount is called specific heat, or specific heat capacity. The conventional unit for this is calories per gram per kelvin. The calorie is defined as the amount of heat energy required to raise the temperature of 1 gram of water by 1 degree.

Work :

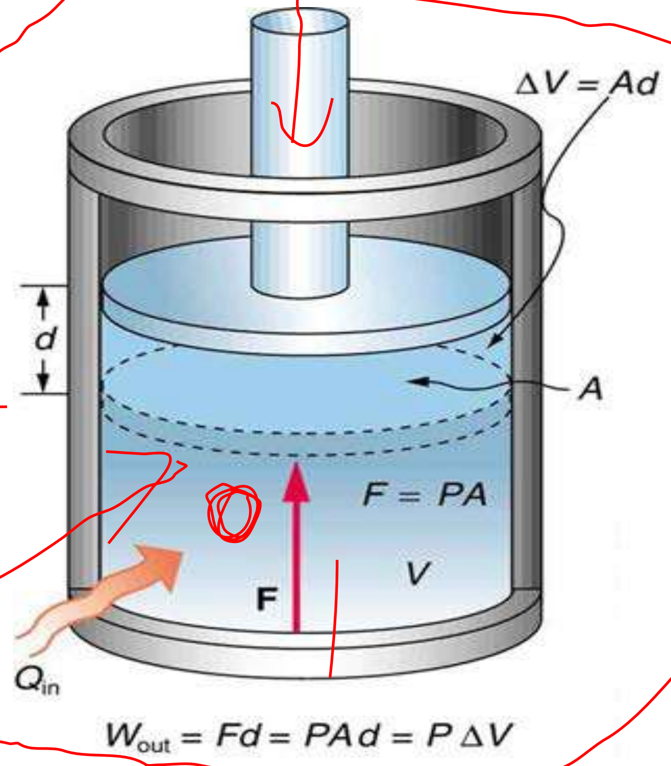
Commonly, the work defined as: The work done on a system by a constant force, is *the product of the component of the force in the direction of motion times the distance through which the force acts.*

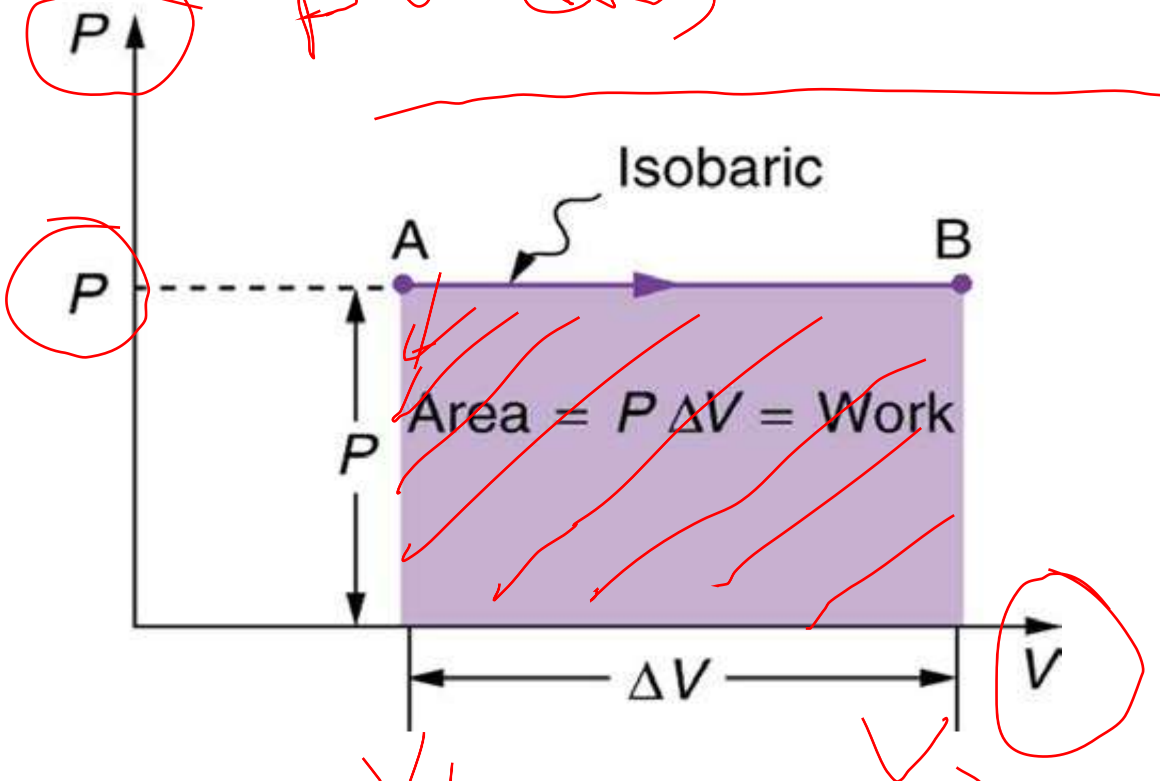
- In the SI system of measurement, work is measured in joules (symbol: J). The rate at which work is performed is power.
- Pressure – volume work (or PV work) occurs when the volume V of a system changes.
- PV work SI system units, which measures P in Pascal (Pa), V in m^3, and PV in Joule (J), where 1 J = 1 Pa·m^3.
- PV work is an important topic in Thermodynamics. Work, denoted W and measured in J; specific work (normalized to mass), denoted w and measured in J kg^{-1}

For example : A process by which a gas does work on a piston at constant pressure is called an **isobaric process**. Since the pressure is constant, the force exerted is constant and the work done is given as exerted is constant and the work done is given as

$$\mathbf{W = F\,d = P\,A\,d = P\,\Delta V}$$

An isobaric expansion of a gas requires heat transfer to keep the pressure constant. Since pressure is constant, the work done is $P\Delta V$. Because the volume of a cylinder is, its cross-sectional area A times its length d , we see that $Ad = \Delta V$, the change in volume.





It is not surprising that W = PΔV , since we have already noted in our treatment of fluids that pressure is a type of potential energy per unit volume and that pressure in fact has units of energy divided by volume. We also noted in our discussion of the ideal gas law that PV has units of energy. In this case, some of the energy associated with pressure becomes work.

Figure shows a graph of pressure versus volume (that is, a PV diagram for an isobaric process. You can see in the figure that the work done is the area under the graph.

This property of PV diagrams is very useful and broadly applicable. The work done on or by a system in going from one state to another equals the area under the curve on a PV diagram. I general, the wok can be found by :

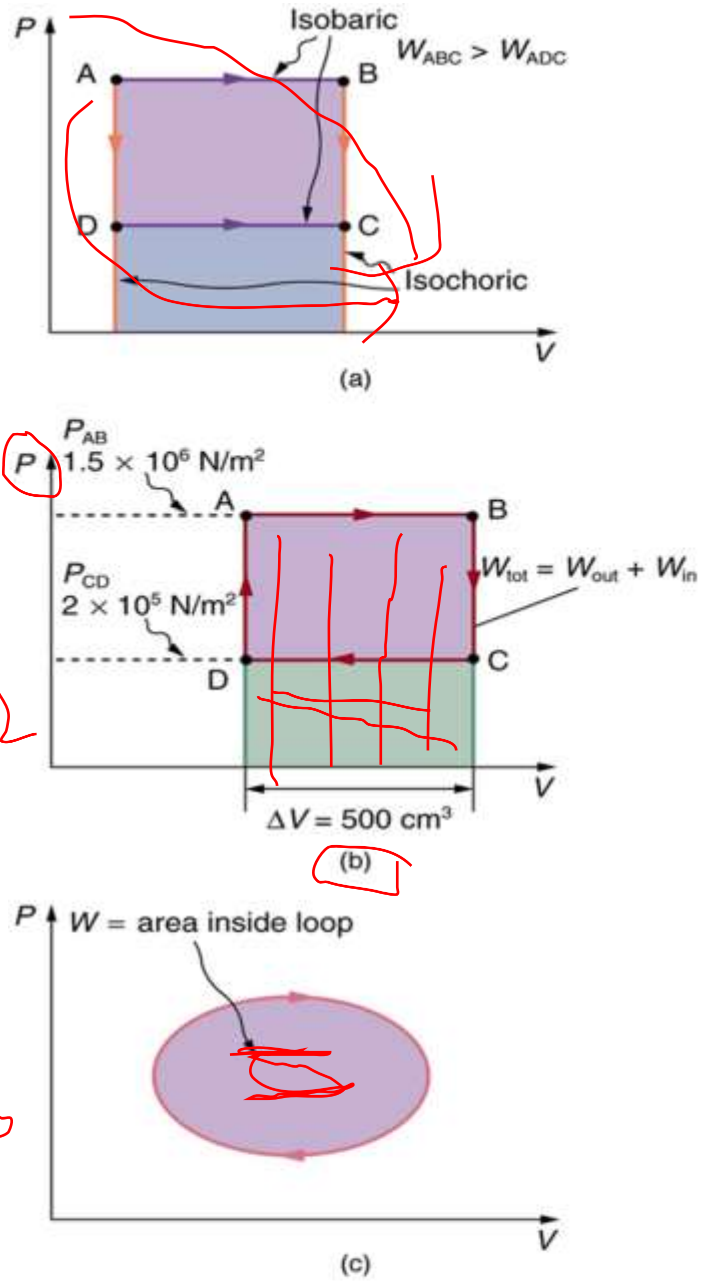
$$W = \int_A^B P\,dV$$

The result, the work is equal to the area under the curve of the process.

The work done for each interval is, its average pressure times the change in volume, or the area under the curve over that interval. Thus the total area under the curve equals the total work done.

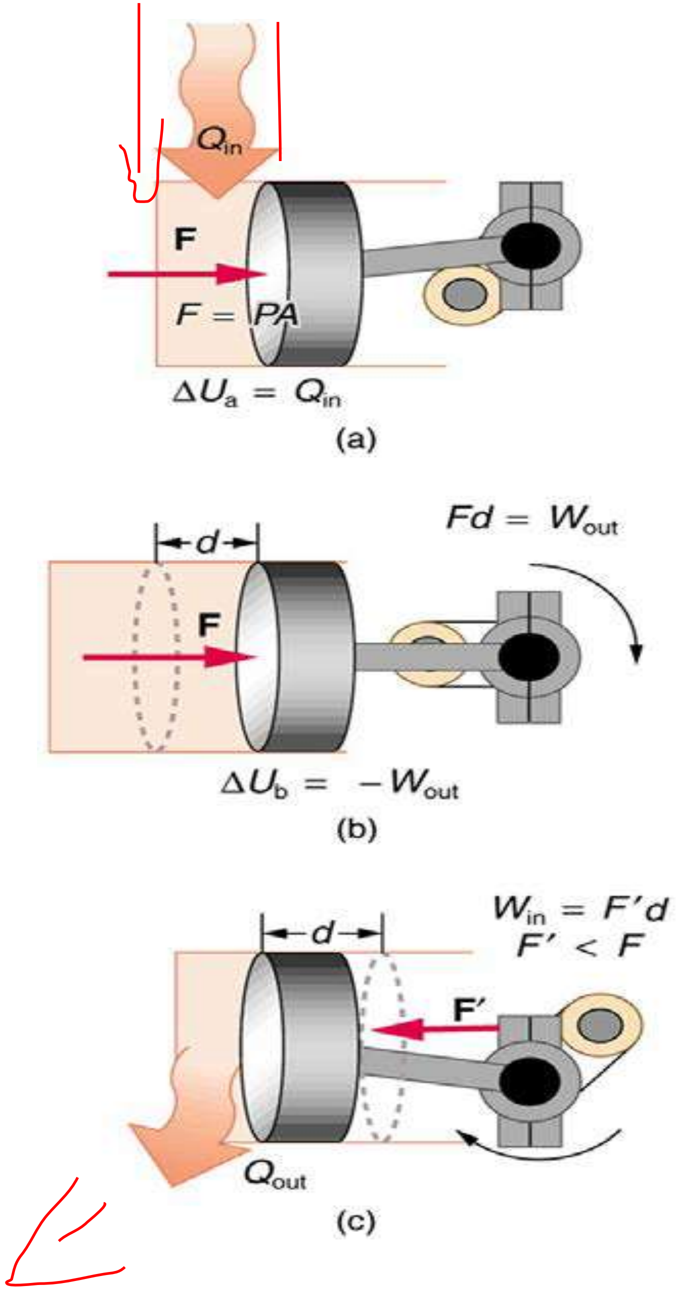
Work must be done on the system to follow the reverse path. This is interpreted as a negative area under the curve. If the path is reversed, as in Figure (b), then work is done on the system. The area under the curve in that case is negative, because ΔV is negative.

PV diagrams clearly illustrate that *the work done depends on the path taken and not just the endpoints*. This path dependence is seen in Figure (a), where more work is done in going from A to C by the path via point B than by the path via point D. The vertical paths, where volume is constant, are called **isochoric** processes. Since volume is constant, $\Delta V = 0$, and no work is done in an isochoric process. Now, if the system follows the cyclical path ABCDA, as in Figure (b), then the total work done is the area inside the loop.



The negative area below path CD subtracts, leaving only the area inside the rectangle. In fact, the work done in any cyclical process (one that returns to its starting point) is the area inside the loop it forms on a PV diagram, as Figure (c) illustrates for a general cyclical process. Note that the loop must be traversed in the clockwise direction for work to be positive—that is, for there to be a net work output.

Figure (a) The work done in going from A to C depends on path. The work is greater for the path ABC than for the path ADC, because the former is at higher pressure. In both cases, the work done is the area under the path. This area is greater for path ABC. The total work done in the cyclical process ABCDA is the area inside the loop, since the negative area below CD subtracts out, leaving just the area inside the rectangle. The area inside any closed loop is the work done in the cyclical process. If the loop is traversed in a clockwise direction, W is positive—it is work done by the system on the outside environment. If the loop is traversed in a counter-clockwise direction, W is negative—it is work done on the system by the surrounding.



Example

Calculate the total work done in the cyclical process ABCDA shown in Figure (b) by the following two methods to verify that work equals the area inside the closed loop on the *PV* diagram. (Take the data in the figure to be precise to three significant figures.)

(1) Calculate the work done along each segment of the path and add these values to get the total work.

(2) Calculate the area inside the rectangle ABCDA.

Strategy

To find the work along any path on a *PV* diagram, you use the fact that work is pressure times change in volume, or

$$W = P\Delta V$$

So, this value is calculated for each leg of the path around the closed loop.

Solution for (a)

The work along path AB is

$$W_{AB} = P_{AB}\,\Delta V_{AB} = (1.5\times10^{6}\ \frac{N}{m^{2}})(500\times10^{-6}\ m^{3}) = 750\ J$$

Since the path BC is isochoric, $\Delta V_{BC} = 0$, and so $W_{BC} = 0$.

The work along path CD is negative, since ΔV_{CD} is negative (the volume decreases). The work is

$$W_{CD} = P_{CD} \Delta V_{CD} = (2 \times 10^5 \frac{N}{m^2})(-500 \times 10^{-6} m^3) = -100 J$$

Again, since the path DA is isochoric, $\Delta V_{DA} = 0$, and so $W_{DA} = 0$.

Now the total work is

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$W = 750 J + 0 + (-100J) + 0 = 650 J$$

Solution for (b)

The area inside the rectangle is its height times its width, or

$$\text{area} = (P_{AB} - P_{CD}) \Delta V$$

$$\text{area} = [(1.5 \times 10^6 \frac{N}{m^2}) - (2 \times 10^5 \frac{N}{m^2})](500 \times 10^{-6} m^3) = 650 J$$

Thus, $\text{area} = 650 J = W$