Part II
First Law of Thermodynamics

Introduction

The **first law** deals with macroscopic properties, work, energy, enthalpy, etc. One of the most fundamental laws of nature is the conservation of energy principle. It simply states that

- during an interaction, energy can change from one form to another but the total amount of energy remains constant. That is, energy cannot be created or destroyed. Or,
- during an interaction between a system and its surroundings, the amount of energy gained by the system must be exactly equal to the amount of energy lost by the surroundings. A rock falling off a cliff, for example, picks up speed as a result of its potential energy being converted to kinetic energy.

The first law of thermodynamics is simply an expression of the conservation of energy principle, and it asserts that *energy* is a thermodynamic property.

Energy can cross the boundary of a closed system in two distinct forms: *heat* and *work*. It is important to distinguish between these two forms of energy. Therefore, they will be discussed first, to form a sound basis for the development of the first law of thermodynamics.

We can use the principle of conservation of energy to define a function U called the *internal energy.* When a closed system undergoes a process by which it passes from state A to state B, if the only interaction with its surroundings is in the form of transfer of heat Q to the system, or performance of work W *on* the system, the change in U will be

$$\Delta U = U_B - U_A = Q + W \qquad \text{2-1}$$

Note:

- In Equation 2-1 we have defined W as the work done on the system and Q is added to the system. If we had defined W as work done by the system, Equation 2-1 would become $\Delta U = Q - W$.
- For an isolated system there is no heat or work transferred with the surroundings, thus, by definition $W = Q = 0$ and therefore $\Delta U = 0$.
- The first law of thermodynamics states that this energy difference ΔU depends only on the initial and final states, and not on the path followed between them. Both Q and W have many possible values, depending on exactly how the system passes from A to B, but $Q + W = \Delta U$ is invariable and independent of the path. If this were not true, it would be possible, by passing from A to B along one path and then returning from B to A along another, to obtain a net change in the energy of the closed system in contradiction to the principle of conservation of energy.
- For a differential change, Equation 2-1 becomes

$$dU = dQ + dW \qquad \text{2-2}$$

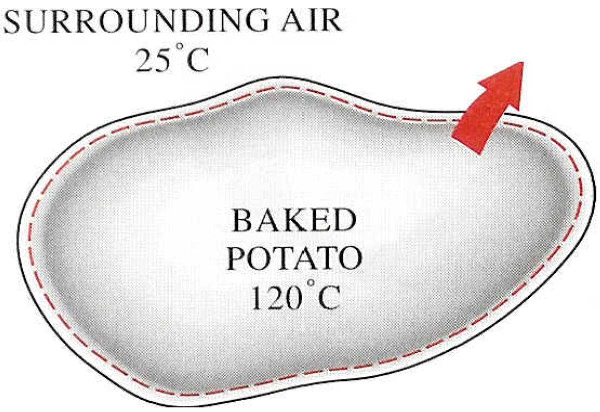
- For a cyclic process, A→B→A, when the system returns to state A, it has the same U, thus

$$\oint dU = 0 \qquad \text{2-3}$$

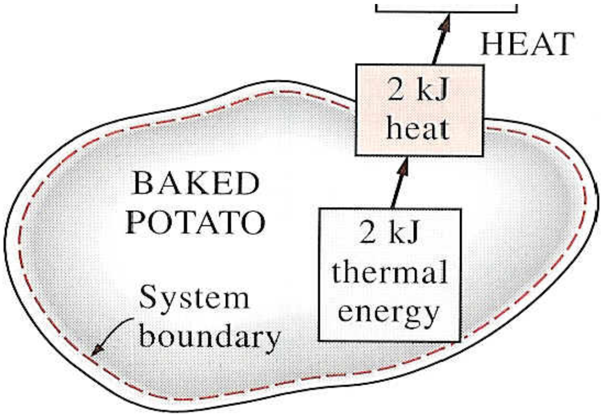
Next we will take a look separately at the heat transferred (dQ) and the work (dW) exchanged between the system and the surroundings.

2-1 Heat Transfer

Heat is defined as *the form of energy that* is *transferred between two systems (or a system and its surroundings) by virtue of a temperature difference.* That is, an energy interaction is heat only if it takes place because of a temperature difference. Then it follows that there cannot be any heat transfer between two systems that are at the same temperature



Heat is energy in transition. It is recognized only as it crosses the boundary of a system. Consider the hot baked potato. The potato contains energy, but this energy is **heat transfer** only as it passes through the skin of the potato (the system boundary) to reach the air, as shown below.



Once in the surroundings, the transferred heat becomes part of the internal energy of the surroundings. Thus, in thermodynamics, the term *heat* simply means *heat transfer*.

- A process during which there is no heat transfer is called an **adiabatic process**. There are two ways a process can be adiabatic:
    - Either the system is well insulated so that only a negligible amount of heat can pass through the boundary, or
    - both the system and the surroundings are at the same temperature and therefore there is no driving force (temperature difference) for heat transfer.
- An adiabatic process should not be confused with an ***isothermal process***. Even though there is no heat transfer during an adiabatic process, the

energy content and thus the temperature of a system can still be changed by other means such as work.

The amount of heat transferred during the process between two states (states 1 and 2) is denoted by Q_{12}, or just Q. Heat transfer *per unit mass* of a system is denoted q and is determined from

$$q = Q/m \qquad \text{2-4}$$

Sometimes it is desirable to know the *rate of heat transfer* (the amount of heat transferred per unit time) instead of the total heat transferred over some time interval. The heat transfer rate is denoted $\dot{Q}$, where the overdot stands for the time derivative, or "per unit time." The heat transfer rate $\dot{Q}$ has the unit kJ/s, which is equivalent to kW. When Q varies with time, the amount of heat transfer during a process is determined by integrating $\dot{Q}$ over the time interval of the process:

$$Q = \int_{t_1}^{t_2} \dot{Q}\,dt \qquad \text{2-5}$$

When $\dot{Q}$ remains constant during the process, the relation reduces to

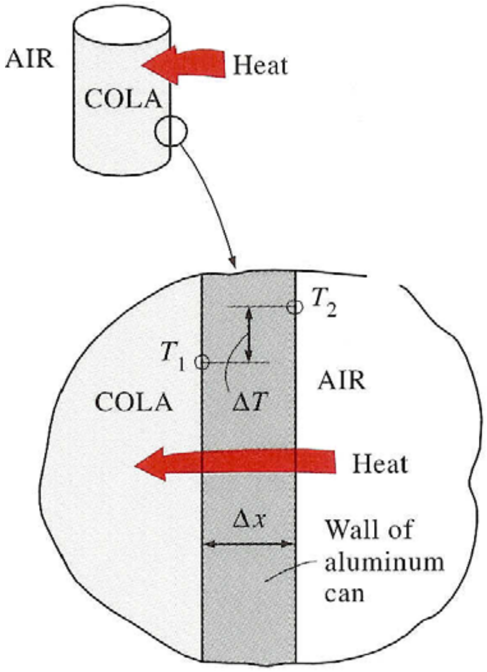
$$Q = \dot{Q}\,\Delta t \qquad \text{2-6}$$

Heat is a directional (or vector) quantity; the universally accepted sign convention for heat is as follows: *Heat transfer to a system is positive, and heat transfer from a system is negative*. That is, any heat transfer that increases the energy of a system is positive, and any heat transfer that decreases the energy of a system is negative.

Modes of Heat transfer

Heat can be transferred in three different ways: *conduction, convection,* and *radiation.* A detailed study of these heat transfer modes is given later. Below we will give a brief description of each mode to familiarize yourselves with the basic mechanisms of heat transfer. All modes of heat transfer require the existence of a temperature difference, and all modes of heat transfer are from the high-temperature medium to a lower-temperature one.

Conduction is the transfer of energy from the more energetic particles of a substance to the adjacent less energetic ones as a result of interactions between the particles. Conduction can take place in solids, liquids, or gases. In gases and liquids, conduction is due to the collisions of the molecules during their random motion. In solids, it is due to the combination of vibrations of the molecules in a lattice and the energy transport by free electrons. A cold canned drink in a warm room, for example, eventually warms up to the room temperature as a result of heat transfer from the room to the drink through the aluminum can by conduction.



It is observed that the rate of heat conduction $\dot{Q}_{cond}$ through a layer of constant thickness Δx is proportional to the temperature difference ΔT across the layer and the area A normal to the direction of heat transfer, and is inversely proportional to the thickness of the layer. Therefore,

$$\dot{Q}_{cond} = kA\frac{\Delta T}{\Delta x} \qquad 2\text{-}7$$

where the constant of proportionality k is the *thermal conductivity* of the material which is a measure of the ability of a material to conduct heat.. Materials such as copper and silver that are good electric conductors are also good heat conductors: $k_{copper} = 401$ W/(m.K), and therefore have high k values. Materials such as rubber, wood, and styrofoam are poor conductors of heat ($k_{urethane} = 0.026$), and therefore have low k values. Diamond has a very high thermal conductivity ($k = 2300$).

In the limiting case of $\Delta x \to 0$, the equation above reduces to the differential form

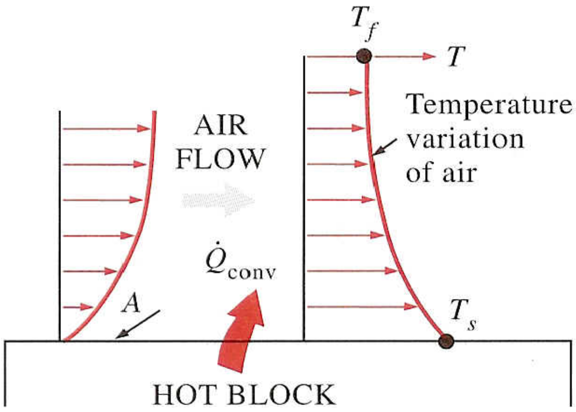
$$\dot{Q}_{cond} = -kA\frac{dT}{dx} \qquad 2\text{-}8$$

which is known as **Fourier's law of heat conduction**. It indicates that the rate of heat conduction in a direction is proportional to the *temperature gradient* in that direction. Heat is conducted in the direction of decreasing temperature, and the temperature gradient becomes negative when temperature decreases with increasing x. Therefore, a negative sign is added in Eq. 2-8 to make heat transfer in the positive x direction a positive quantity.

Note: Temperature is a measure of the kinetic energies of the molecules. In a liquid or gas, the kinetic energy of the molecules is due to the random motion of the molecules as well as the vibrational and rotational motions. When two molecules possessing different kinetic energies collide, part of the kinetic energy of the more energetic (higher-temperature) molecule is transferred to the less energetic (lower-temperature) particle, in much the same way as when two elastic balls of the same mass at different velocities collide, part of the kinetic energy of the faster ball is transferred to the slower one.

In solids, heat conduction is due to two effects: the lattice vibrational waves induced by the vibrational motions of the molecules positioned at relatively fixed positions in a periodic manner called a lattice, and the energy transported via the free flow of electrons in the solid. The thermal conductivity of a solid is obtained by adding the lattice and the electronic components. The thermal conductivity of pure metals is primarily due to the electronic component whereas the thermal conductivity of nonmetals is primarily due to the lattice component. The lattice component of thermal conductivity strongly depends on the way the molecules are arranged. For example, the thermal conductivity of diamond, which is a highly ordered crystalline solid, is much higher than the thermal conductivities of pure metals.

Convection is the mode of energy transfer between a solid surface and the adjacent liquid or gas which is in motion, and it involves the combined effects of *conduction* and *fluid motion.* The faster the fluid motion, the greater the convection heat transfer. In the absence of any bulk fluid motion, heat transfer between a solid surface and the adjacent fluid is by pure conduction The presence of bulk motion of the fluid enhances the heat transfer between the solid surface and the fluid, but it also complicates the determination of heat transfer rates.



- Consider the cooling of a hot block by blowing of cool air over its top surface shown in figure above. The arrows in the figure indicate the velocity variation of air. Energy is first transferred to the air layer adjacent to the surface of the block by conduction. This energy is then carried away from the surface by convection; that is, by the combined effects of conduction within the air, which is due to random motion of air molecules, and the bulk or macroscopic motion of the air, which removes the heated air near the surface and replaces it by the cooler air.

Forced convection (left) and natural convection (right)

- Convection is called *forced convection* if the fluid is *forced* to flow in a tube or over a surface by external means such as a fan, pump, or the wind. In contrast, convection is called *free* (or *natural) convection* if the fluid motion is caused by buoyancy forces that are induced by density differences due to the variation of temperature in the fluid (see figure above). For example, in the absence of a fan, heat transfer from the surface of the hot block in figure will be by natural convection since any motion in the air in this case will be due to the rise of the warmer (and thus lighter) air near the surface and the fall of the cooler (and thus heavier) air to fill its place. Heat transfer between the block and the surrounding air will be by conduction if the temperature difference between the air and the block is not large enough to overcome the resistance of air to move and thus to initiate natural convection currents.
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- Heat transfer processes that involve *change of phase* of a fluid are also considered to be convection because of the fluid motion induced during the process such as the rise of the vapor bubbles during *boiling* or the fall of the liquid droplets during *condensation*.
- The rate of heat transfer by convection $\dot{Q}_{conv}$ is determined from **Newton's law of cooling**, which is expressed as

$$\dot{Q}_{conv} = hA\,(T_s - T_f) \qquad 2\text{-}9$$

where h is the *convection heat transfer coefficient, A* is the surface area through which heat transfer takes place, T_s is the surface temperature, and T_f is bulk fluid temperature away from the surface. (At the surface, the fluid temperature equals the surface temperature of the solid.)

Note: The convection heat transfer coefficient *h* is not a property of the fluid. It is an experimentally determined parameter whose value depends on all the variables that influence convection such as the surface geometry, the nature of fluid motion, the properties of the fluid, and the bulk fluid velocity. Typical values of *h,* in W /(m^2 . K), are 2-25 for the free convection of gases, 50-1000 for the free convection of liquids, 25-250 for the forced convection of gases, 50-20,000 for the forced convection of liquids, and 2500-100,000 for convection in boiling and condensation processes.

Radiation is the energy emitted by matter in the form of electromagnetic waves (or photons) as a result of the changes in the electronic configurations of the atoms or molecules. Unlike conduction and convection, the transfer of energy by radiation does not require the presence of an intervening medium. In fact, energy transfer by radiation is fastest (at the speed of light) and it suffers no attenuation in a vacuum. This is exactly how the energy of the sun reaches the earth.

- In heat transfer studies, we are interested in *thermal radiation,* which is the form of radiation emitted by bodies because of their temperature. It differs from other forms of electromagnetic radiation such as X-rays, gamma rays, microwaves, radio waves, and television waves which are not related to temperature. All bodies at a temperature above absolute zero emit thermal radiation.

- Radiation is a *volumetric phenomena,* and all solids, liquids, and gases emit, absorb, or transmit radiation to varying degrees. However, radiation is usually considered to be a *surface phenomenon* for solids that are opaque to thermal radiation such as metals, wood, and rocks since the radiation emitted by the interior regions of such material can never reach the surface, and the radiation incident on such bodies is usually absorbed within a few microns from the surface.

- The maximum rate of radiation that can be emitted from a surface at an *absolute* temperature T_s is given by the *Stefan-Boltzmann, law* as

$$\dot{Q}_{emit.max} = \sigma A T_s^4 \qquad 2\text{-}10$$

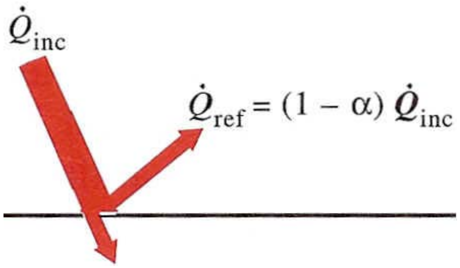
where A is the surface area and $\sigma = 5.67 \times 10^{-8}$ W / (m^2 . K^4) is the *Stefan-Boltzmann constant.* The idealized surface which emits radiation at this maximum rate is called a blackbody, and the radiation emitted by a blackbody is called *blackbody radiation*. The radiation emitted by all *real* surfaces is less than the radiation emitted by a blackbody at the same temperatures and is expressed as

$$\dot{Q}_{emit.max} = \varepsilon \sigma A T_s^4 \qquad 2\text{-}11$$

where ε is the *emissivity* of the surface. The property emissivity, whose value is in the range $0 \leq \varepsilon \leq 1$, is a measure of how closely a surface approximates a blackbody for which $\varepsilon = 1$. The human skin has an emissivity of 0.95, and aluminum foil 0.07.

- Another important radiation property of a surface is its *absorptivity, α,* which is the fraction of the radiation energy incident on a surface that is absorbed by the surface. Like emissivity, its value is in the range $0 \le \alpha \le 1$. A blackbody absorbs the entire radiation incident on it. That is, a blackbody is a perfect absorber $(\alpha = 1)$ as well as a perfect emitter.

- In general, both ε and α of a surface depend on the temperature and the wavelength of the radiation. Kirchhoff's law of radiation states that the emissivity and the absorptivity of a surface are equal at the same temperature and wavelength. In most practical applications, the dependence of ε and α on the temperature and wavelength is ignored, and the average absorptivity of a surface is taken to be equal to its average emissivity. The rate at which a surface absorbs radiation is determined from (see figure)



$$\dot{Q}_{abs} = \alpha\,\dot{Q}_{inc} \tag{2-12}$$

where $\dot{Q}_{inc}$ is the rate at which radiation is incident on the surface and α is the absorptivity of the surface. For opaque (nontransparent) surfaces, the portion of incident radiation that is not absorbed by the surface is reflected back.

  - The difference between the rates of radiation emitted by the surface and the radiation absorbed is the *net* radiation heat transfer. If the rate of radiation absorption is greater than the rate of radiation emission, the surface is said to be *gaining* energy by radiation. Otherwise, the surface is said to be *losing* energy by radiation. In general, the determination of the net rate of heat transfer by radiation between two surfaces is a complicated matter since it depends on the properties of the surfaces, their orientation relative to each other, and the interaction of the medium between the surfaces with radiation. However, in the special case of a relatively small surface of emissivity ε and surface area A at *absolute* temperature T_s that is completely enclosed by a much larger surface at *absolute* temperature T_{surr} separated by a gas (such as air) that does not interact with radiation (i.e., the amount of radiation emitted, absorbed, or scattered by the medium is negligible), the net rate of radiation heat transfer between these two surfaces is determined from

$$\dot{Q}_{rad} = \varepsilon\sigma A(T_s^{4} - T^{4}_{surr}) \qquad 2\text{-}13$$

Example 2-1 Consider a person standing in a breezy room at 20°C. Determine the total rate of heat transfer from this person if the exposed surface area and the average outer surface temperature of the person are 1.6 m^2 and 29°C, respectively, and the convection heat transfer coefficient is 6 W / (m^2 . ^{o}C) .

Solution

1. The heat transfer between the person and the air in the room will be by convection (instead of conduction) since it is conceivable that the air in the vicinity of the skin or clothing will warm up and rise as a result of heat transfer from the body, initiating natural convection currents. It appears that the experimentally determined value for the rate of convection heat transfer in this case is 6 W per unit surface area (m^2) per unit temperature difference (in K or ^{o}C) between the person and the air away from the person. Thus, the rate of convection heat transfer from the person to the air in the room is, from Eq. 2-9,

$$\dot{Q}_{conv} = hA\ (T_s - T_f) = 86.4\ \text{W}$$

2. The person will also lose heat by radiation to the surrounding wall surfaces. We take the temperature of the surfaces of the walls, ceiling, and the floor to be equal to the air temperature in this case for simplicity, but we recognize that this does not need to be the case. These surfaces may be at a higher or lower temperature than the average temperature of the room air, depending on the outdoor conditions and the structure of the walls. Considering that air does not intervene with radiation and the person is completely enclosed by the surrounding surfaces, the net rate of radiation heat transfer from the person to the surrounding walls, ceiling, and the floor is, from Eq. 2-13

$$\dot{Q}_{rad} = \varepsilon\sigma A(T_s^{4} - T^{4}_{surr}) = 81.7\ \text{W}$$

Note that we must use *absolute* temperatures in radiation calculations. Also note that we used the emissivity value for the skin and clothing at room temperature since the emissivity is not expected to change significantly at a slightly higher temperature.

Then the rate of total heat transfer from the body is determined by adding these two quantities to be

$$\dot{Q}_{total} = \dot{Q}_{conv} + \dot{Q}_{rad} = 168.1 \text{ W}$$

Note: The heat transfer would be much higher if the person were not dressed since the exposed surface temperature would be higher. In the above calculations, heat transfer through the feet to the floor by conduction, which is usually very small, is neglected. Heat transfer from the skin by perspiration, which is the dominant mode of heat transfer in hot environments, is not considered here.

2-2 Work

Work, like heat, is an energy interaction between a system and its surroundings. As mentioned earlier, energy can cross the boundary of a closed system in the form of heat or work. Therefore, *if the energy crossing the boundary of a closed system is not heat, it must be work.*

- Heat is easy to recognize: Its driving force is a temperature difference between the system and its surroundings. Then we can simply say that an energy interaction which is not caused by a temperature difference between a system and its surroundings is work. More specifically, *work is the energy transfer associated with a force acting through a distance.* A rising piston, a rotating shaft, and an electric wire crossing the system boundaries are all associated with work interactions.

- The work done during a process between states 1 and 2 is denoted W_{12}, or simply W. The work done *per unit mass* of a system is denoted w and is defined as

$$W = W/m \qquad 2\text{-}14$$

  - The work done *per unit time* is called **power** and is denoted $\dot{W}$. The unit of power is kJ/s, or kW.

  - The energy of a system decreases as it does work and increases as work is done on the system.

- Heat transfer and work are *interactions* between a system and its surroundings, and there are many similarities between the two:

  1. Both are recognized at the boundaries of the system as they cross them. That is, both heat and work are *boundary* phenomena.

  2. Systems possess energy, but not heat or work. That is, heat and work are *transfer* phenomena.

  3. Both are associated with a *process,* not a state. Unlike properties, heat or work has no meaning at a state.

  4. Both are *path functions* (i.e., their magnitudes depend on the path followed during a process as well as the end states).

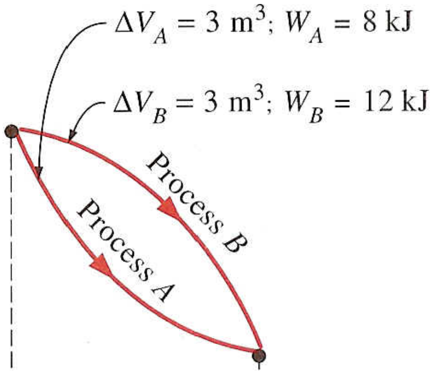
Path functions have inexact differentials designated by the symbol δ. Therefore, a differential amount of heat or work is represented by δQ or δW, respectively, instead of dQ or dW. Properties, however, are point functions (i.e., they depend on the state only, and not on how a system reaches that state), and they have exact differentials designated by the symbol *d.* A small change in volume, for example, is represented by dV and the total volume change during a process between states 1 and 2 is

$$\int_1^2 dV = V_2 - V_1 = \Delta V$$

That is, the volume change during process 1-2 is always the volume at state 2 minus the volume at state 1, regardless of the path followed (see figure below). The total work done during process 1-2, however, is

$$\int_1^2 \delta W = W_{12}$$

That is, the total work is obtained by following the process path and adding the differential amounts of work (δW) done along the way. The integral of δW *is not* $W_2 - W_1$ (i.e., the work at state 2 minus work at state 1), which is meaningless since work is not a property and systems do not possess work at a state.



Example 2-2

A candle is burning in a well-insulated room. Taking the room (the air plus the candle) as the system, determine *(a)* if there is any heat transfer during this burning process and *(b)* if there is any change in the internal energy of the system.

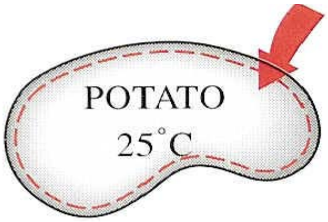
Solution

(a) The interior surfaces of the room form the system boundary. As pointed out earlier, heat is recognized as it crosses the boundaries. Since the room is well insulated, we have an adiabatic system and no heat will pass through the boundaries. Therefore, Q = 0 for this process.

(b) As discussed earlier, the internal energy involves energies that exist in various forms (sensible, latent, chemical, nuclear). During the process described above, part of the chemical energy is converted to sensible energy. That is, part of the internal energy of the system is changed from one form to another. Since there is no increase or decrease in the total internal energy of the system, $\Delta U = 0$ for this process.

Example 2-3

A potato that is initially at room temperature (25°C) is being baked in an oven which is maintained at 200°C. Is there any heat transfer during this baking process?



Solution

This is not a well-defined problem since the system is not specified. Let us assume that we are observing the potato, which will be our system. Then the skin of the potato may be viewed as the system boundary. Part of the energy in the oven will pass through the skin to the potato. Since the driving force for this energy transfer is a temperature difference, this is a heat transfer process.

Example 2-4
A well-insulated electric oven is being heated through its heating element. If the entire oven, including the heating element, is taken to be the system, determine whether this is a heat or work interaction.

Solution
For this problem, the interior surfaces of the oven form the system boundary. The energy content of the oven obviously increases during this process, as evidenced by a rise in temperature. This energy transfer to the oven is not caused by a temperature difference between the oven and the surrounding air. Instead, it is caused by the *electrons* crossing the system boundary and thus doing work. Therefore, this is a work interaction.

Example 2-5
Answer the question in Example 2-4 if the system is taken as only the air in the oven without the heating element.

Solution
This time, the system boundary will include the outer surface of the heating element and will not cut through it. Therefore, no electrons will be crossing the system boundary at any point. Instead, the energy generated in the interior of the heating element will be transferred to the air around it as a result of the temperature difference between the heating element and the air in the oven. Therefore, this is a heat transfer process.

For both cases, the amount of energy transfer to the air is the same. These two examples show that the same interaction can be heat or work depending on how the system is selected.

Electrical Work

It was shown above that electrons crossing the system boundary do electrical work on the system. In an electric field, electrons in a wire move under the effect of electromotive forces, doing work. When N coulombs of electrons move through a potential difference V, the electrical work done is

$$W_e = VN$$

Which can also be expressed in the rate form

$$\dot{W}_e = VI \qquad 2\text{-}14$$

where $\dot{W}_e$ is the electrical power and I the electric current. ($\dot{W}_e = VI = I^2R = V^2/R$)

In general, both V and I vary with time, and the electrical work done during a time interval Δt is expressed as

$$W_e = \int_1^2 VIdt \qquad 2\text{-}15$$

If both V and I remain constant during the time interval Δt, this equation will reduce to

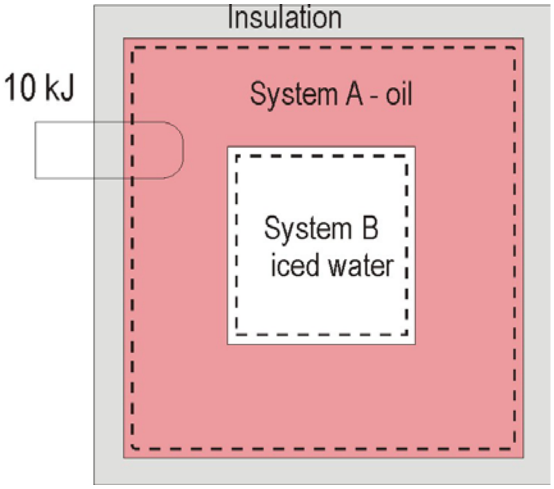
$$W_e = VI\Delta t \qquad 2\text{-}16$$

Example 2-6

A small tank containing iced water at 0°C is placed in the middle of a large, well-insulated tank filled with oil. The entire system is initially in thermal equilibrium at 0°C. The electric heater in the oil is now turned on, and 10 kJ of electrical work is done on the oil. After a while, it is noticed that the entire system is again at 0°C, but some ice in the small tank has melted. Considering the oil to be system *A* and the iced water to be system B, discuss the heat and work interactions for system A. system B, and the combined system (oil and iced water).

Solution

The boundaries of each system are indicated by dashed lines in the figure. Notice that the boundary of system B also forms the inner part of the boundary of system *A*.



System A: When the heater is turned on, electrons cross the outer boundary of system A, doing electrical work. This work is done on the system, and therefore $W_A = 10$ kJ. Because of this added energy, the temperature of the oil will rise, creating a temperature gradient, which results in a heat flow process from the oil to the iced water through their common boundary. Since the oil is restored to its initial temperature of 0 ^oC, the energy lost as heat must equal the energy gained as work. Therefore, $Q_A = 10$ kJ (or $Q_{A,out} = 10$ kJ).

System B: The only energy interaction at the boundaries of system B is the heat flow from system *A*.. All the heat lost by the oil is gained by the iced water. Thus, $W_B = 0$ and $Q_e = +10$ kJ.

Combined system: The outer boundary of system *A* forms the entire boundary of the combined system. The only energy interaction at this boundary is the electrical work. Since the tank is well insulated, no heat will cross this boundary. Therefore, $W_{comb} = 10$ kJ and $Q_{comb} = 0$. Notice that the heat flow from the oil to the iced water is an internal process for the combined system and, therefore, is not recognized as heat. It is simply the redistribution of the internal energy.

Mechanical forms of Work

There are several different ways of doing work, each in some way related to a force acting through a distance. In elementary mechanics, the work done by a constant force *F* on a body that is displaced a distance s in the direction of the force is given by

$$W = Fs \qquad \text{2-17}$$

- If the force *F* is not constant, the work done is obtained by adding (i.e., integrating) the differential amounts of work (force times the differential displacement *ds):*

$$W = \int_1^2 Fds \qquad \text{2-18}$$

- Obviously one needs to know how the force varies with displacement to perform this integration. Equations 2-17 and 2-18 give only the magnitude of the work. The sign is easily determined from physical considerations: The work done on a system by an external force acting in the direction of motion is positive, and work done by a system against an external force acting in the opposite direction to motion is negative.

- There are two requirements for a work interaction between a system and its surroundings to exist:

  1. there must be a *force* acting on the boundary, and
  2. the boundary must *move.* Therefore, the presence of forces on the boundary without any displacement of the boundary does not constitute a work interaction. Likewise, the displacement of the boundary without any force to oppose or drive this motion (such as the expansion of a gas into an evacuated space) is not a work interaction.

In many thermodynamic problems, mechanical work is the only form of work involved. It is associated with the movement of the boundary of a system or with the movement of the entire system as a whole .Some common forms of mechanical work are discussed below.

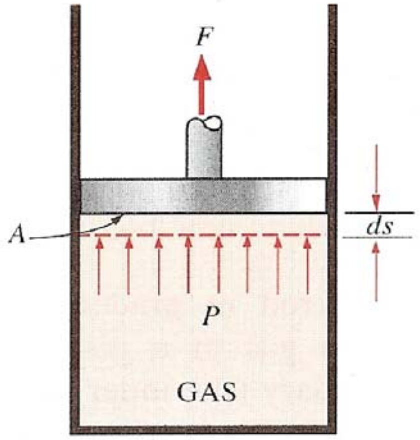
Moving Boundary Work

One form of mechanical work frequently encountered in practice is associated with the expansion or compression of a gas in a piston-cylinder device. During this process, part of the boundary (the inner face of the piston) moves back and forth. Therefore, the expansion and compression work is often called moving boundary work, or simply boundary work. Some prefer to call it the $P\,dV$ work for reasons explained below. Moving boundary work is the primary form of work involved in automobile engines. During their expansion, the combustion gases force the piston to move, which in turn forces the crank shaft to rotate.

The moving boundary work associated with real engines or compressors cannot be determined exactly from a thermodynamic analysis alone because the piston usually moves at very high speeds, making it difficult for the gas inside to maintain equilibrium. Then the states that the system passes through during the process cannot be specified, and no process path can be drawn. Work, being a path function, cannot be determined analytically without knowledge of the path. Therefore, the boundary work in real engines or compressors is determined by direct measurements.

In this section, we analyze the moving boundary work for a *quasi-equilibrium process,* a process during which the system remains in equilibrium at all times. A quasi-equilibrium process, also called a *quasi-static process,* is closely approximated by real engines, especially when the piston moves at low velocities. Under identical conditions, the work output of the engines is found to be a **maximum**, and the work input to the compressors to be a minimum, when quasi-equilibrium processes are used in place of non-quasi-equilibrium processes. Below, the work associated with a moving boundary is evaluated for a quasi-equilibrium process.

Consider the gas enclosed in the piston-cylinder device shown below.



The initial pressure of the gas is *P,* the total volume is *V,* and the cross-sectional area of the piston is *A*. If the piston is allowed to move a distance *ds* in a quasi-equilibrium manner, the differential work done during this process is

$$\delta W = F ds = PA\, ds = P\, dV \qquad 2\text{-}19$$

That is, the boundary work in the differential form is equal to the product of the absolute pressure *P* and the differential change in the volume *dV* of the system. This expression also explains why the moving boundary work is sometimes called the *P dV* work. In order to abide by the sign rule, for an expansion *dV* is positive, the pressure P is the absolute pressure which is always positive, thus, the work should be written as

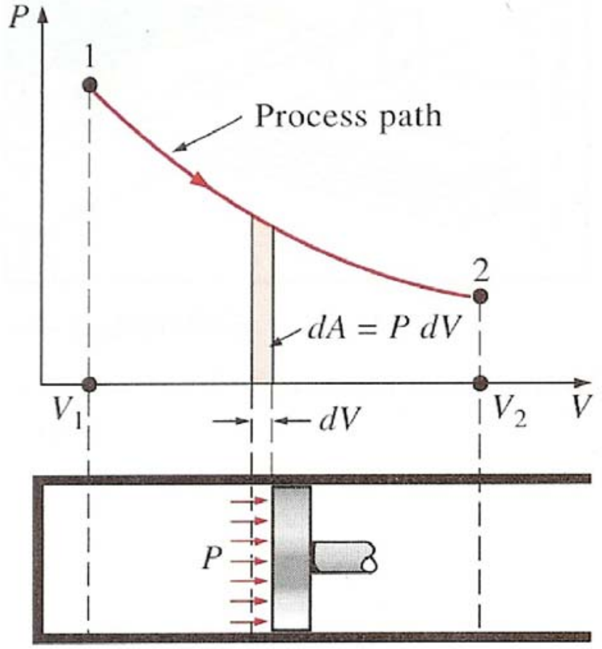
$$\delta W = -\, P\, dV \qquad 2\text{-}20$$

Thus, the boundary work is negative during an expansion process and positive during a compression process, which is consistent with the sign convention adopted for work. The total boundary work done during the entire process as the piston moves is obtained by adding all the differential works from the initial state to the final state:

$$W_b = -\int_1^2 P dV \qquad 2\text{-}21$$

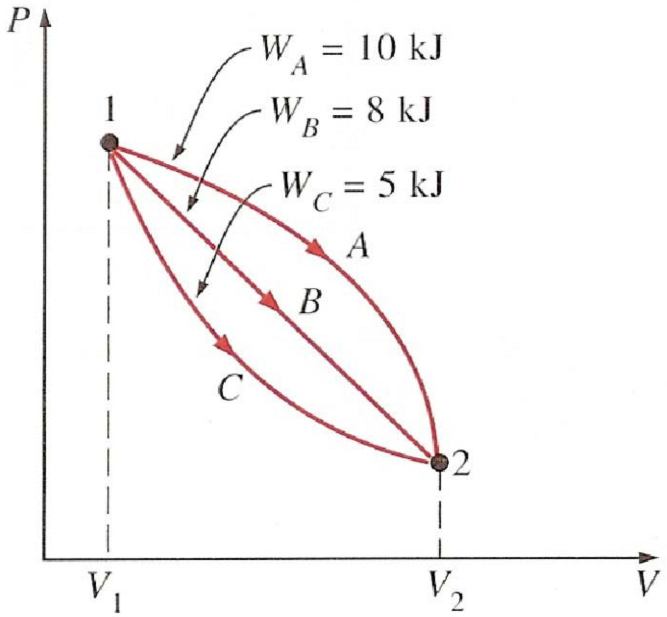
This integral can be evaluated only if we know the functional relationship between P and V during the process. That is, $P = f(V)$ should be available. Note that $P = f(V)$ is simply the equation of the process path on a P-V diagram.

The quasi-equilibrium expansion process described above is shown on a P-V diagram below. On this diagram, the differential area dA is equal to $P\,dV$, which is the differential work. The total area A under the process curve 1-2 is obtained by adding these differential areas:



The area under the process curve on a P-V diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression process of a closed system.

A gas can follow several different paths as it expands from state 1 to state 2. In general, each path will have a different area underneath it, and since this area represents the magnitude of the work, the work done will be different for each process.



This is expected, since work is a path function (i.e., it depends on the path followed as well as the end states). If work were not a path function, no cyclic devices (car engines, power plants) could operate as work-producing devices. The work produced by these devices during one part of the cycle would have to be consumed during another part, and there would be no net work output.

Note: If the relationship between *P* and *V* during an expansion or a compression process is given in terms of experimental data instead of in a functional form, obviously we cannot perform the integration analytically. But we can always plot the *P*-*V* diagram of the process, using these data points, and calculate the area underneath graphically to determine the work done.

Example 2-7

A frictionless piston-cylinder device contains 0.1 lb of water vapor at 20 psi and 320 ^{o}F. Heat is now added to the steam until the temperature reaches 400°F. If the piston is not attached to a shaft and its mass is constant, determine the work done by the steam during this process.

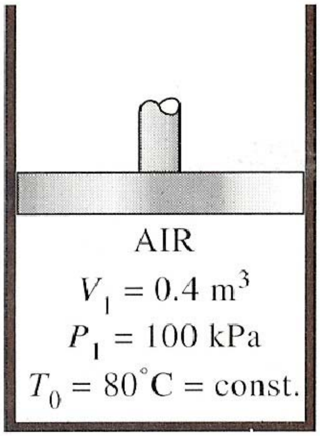
Hint: Even though it is not explicitly stated, the pressure of the steam within the cylinder remains constant during this process since both the atmospheric pressure and the weight of the piston remain constant. Therefore, this is a constant-pressure process.

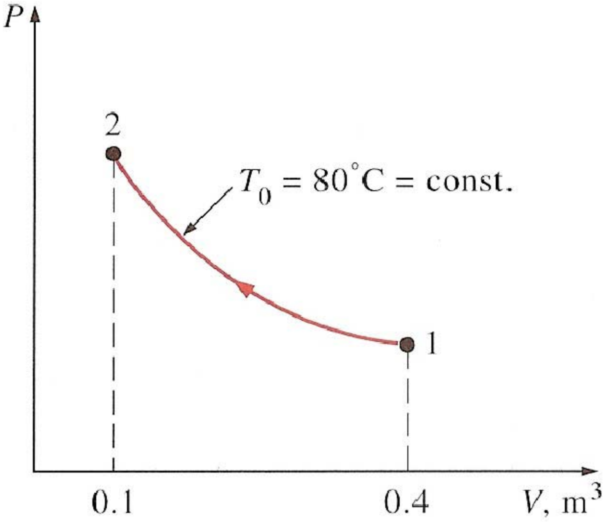
Example 2-8

A piston-cylinder device initially contains 0.4 m^3 of air at 100 kPa and 80°C. The air is now compressed to 0.1 m^3 in such a way that the temperature inside the cylinder remains constant. Determine the work done during this process.

Solution

A sketch of the system and the *P-V* diagram of the process are shown below. At the specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values (T_{cr} = -147°C, P_{cr} = 3390 kPa for nitrogen, the main constituent of air). For an ideal gas at constant temperature T_o,





$$P = C\ /\ V$$

where C is a constant. Eq. 2-21 becomes:

$$W_b = -\int_1^2 P dV = -\int_1^2 \frac{C}{V} dV = -C \ln\frac{V_2}{V_1} = -P_1 V_1 \ln\frac{V_2}{V_1}$$

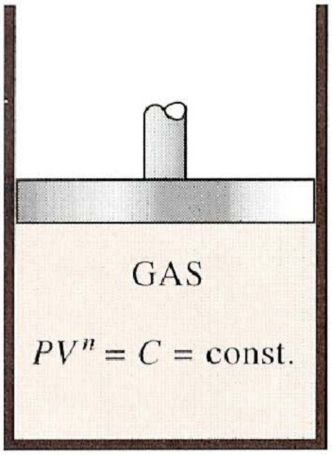
$$= 55.45 \text{ kJ}$$

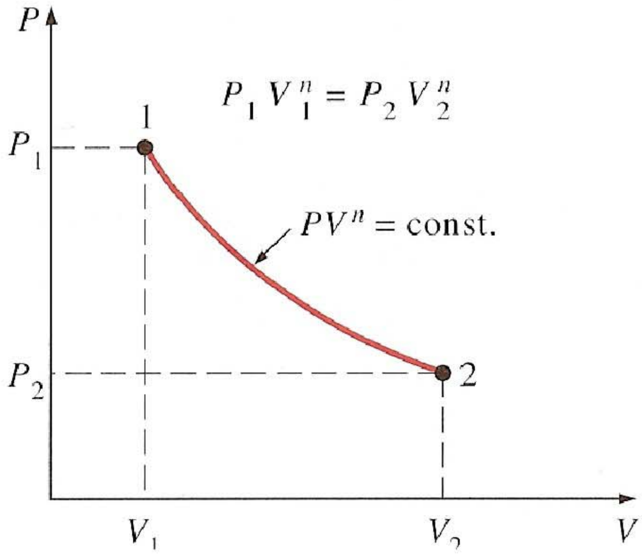
where $P_1\ V_1 = P_2\ V_2$

Polytropic Process

During expansion and compression processes of real gases, pressure and volume are often related by $P V^n = C$, where n and C are constants. A process of this kind is called a polytropic process. Below we develop a general expression for the work done during a polytropic process.

A sketch of the system and the *p*- *Y* diagram of the process are shown below





The pressure for a polytropic process can be expressed as

$$P = C V^{-n} \qquad \text{2-22}$$

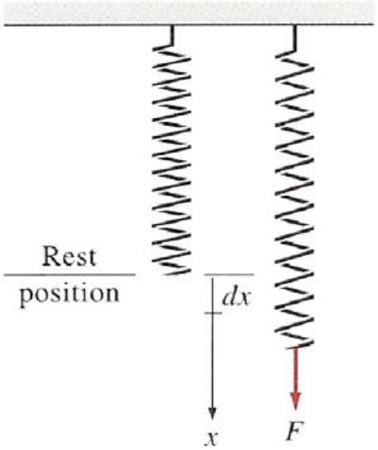
$$W_B = \int_1^2 P\,dV = \int_1^2 C V^{-n}\,dV = C\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} = \frac{P_2V_2 - P_1V_1}{1-n} \qquad \text{2-23}$$

$$W_B = \frac{mR[T_2 - T_1]}{1-n} \qquad \text{for } n \neq 1 \qquad \text{2-24}$$

The case for n = 1 is equivalent to the isothermal process already discussed.

Spring Work

It is common knowledge that when a force is applied on a spring, the length of the spring changes.



When the length of the spring changes by a differential amount *dx* under the influence of a force *F,* the work done is

$$\delta W_{spring} = F\,dx \qquad 2\text{-}25$$

To determine the total spring work, we need to know a functional relationship between F and x. For linear elastic springs, the displacement x is proportional to the force applied. That is,

$$F = k_s\,x \qquad 2\text{-}26$$

where k_s is the spring constant (in kN/m). Substituting in 2-25 and integrating we get

$$W_{spring} = ½\,k_s\,(x_2^{\,2} - x_1^{\,2}) \quad (\text{kJ}) \qquad 2\text{-}27$$

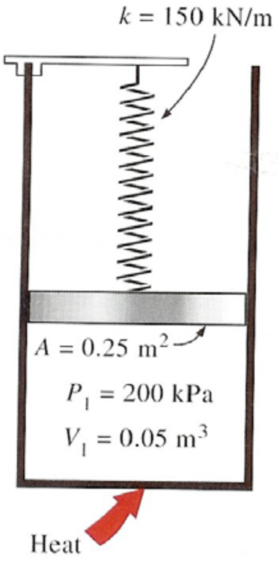
where x_1 and x_2 are the initial and the final displacements of the spring, respectively. Both are measured from the undisturbed position of the spring. Note that the work done on a spring equals the energy stored in the spring.

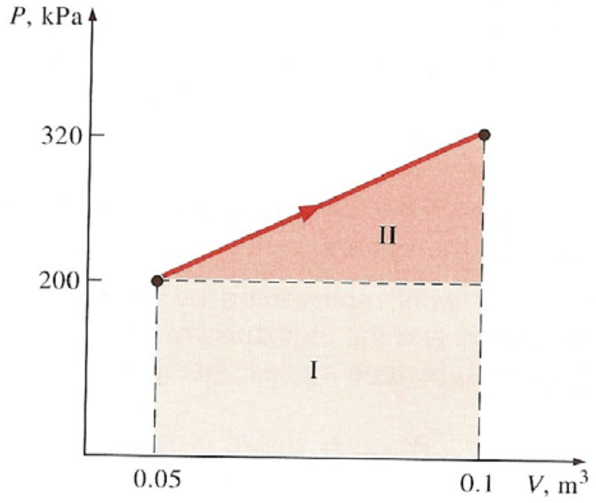
Example 2-9

A piston-cylinder device contains 0.05 m^3 of a gas initially at 200 kPa. At this state, a linear spring that has a spring constant of 150 kN/m is touching the piston but exerting no force on it. Now heat is transferred to the gas, causing the piston to rise and to compress the spring until the volume inside the cylinder doubles. If the cross-sectional area of the piston is 0.52 m^2, determine: a. the final pressure inside the cylinder; b. the total work done by the gas; and c. the fraction of this work done against the spring to compress it.

Solution

(a) A sketch of the system and the *P-V* diagram of the process are sown below.





The enclosed volume at the final state is

$$V_2 = 2\ V_1 = 0.1\ \text{m}^3$$

Then the displacement of the piston (and the spring) become

$$x = \Delta V\,/\,A = 0.2\ \text{m}$$

The force applied by the linear spring at the final state is

$$F = k_s\, x = 30\ \text{kN}$$

The additional pressure applied by the linear spring on the gas at this state is

$$P = F/A = 120\ \text{kPa}$$

Without the spring, the pressure of the gas would remain constant at 200 kPa while the piston is rising. But under the effect of the spring, the pressure rises linearly from 200 kPa to

$$200 + 120 = 320 \text{ kPa}$$

at the final state

(b) An easy way of finding the work done is to plot the process on a *P-V* diagram and find the area under the process curve. From figure above the area under the process curve (a trapezoid) is determined to be 13 kJ.

The sign of the work is determined, by inspection, to be negative since it is done by the system.

(c) The work represented by the rectangular area (region I) is done against the piston and the atmosphere, and the work represented by the triangular area (region II) is done against the spring. Thus $W_{spring} = 3$ kJ. The same result could have been obtained from Eq. 2-27.

Nonmechanical Forms of Work

Some work modes encountered in practice are not mechanical in nature. However, these nonmechanical work modes can be treated in a similar manner by identifying a *generalized force F* acting in the direction of a *generalized displacement* x. Then the work associated with the differential displacement under the influence of this force is determined from $\delta W = F.\, dx$

Some examples of nonmechanical work modes are **electrical work**, where the generalized force is the *voltage* (the electrical potential) and the generalized displacement is the *electrical charge* as discussed in the last section; **magnetic work**, where the generalized force is the *magnetic field strength* and the generalized displacement is the total *magnetic dipole moment;* and **electrical polarization work**, where the generalized force is the *electric field strength* and the generalized displacement is the *polarization of the medium* (the sum of the electric dipole rotation moments of the molecules). Detailed consideration of these and other nonmechanical work modes can be found in specialized books on these topics.

2-3 Energy

Chemical thermodynamics deals with the internal energy *U,* energy possessed by the system by virtue of the mass and motion of the molecules, intermolecular forces, chemical composition, etc. Any energy that the system possesses because of other considerations is ignored.

The internal energy is relative. ΔU in total internal energy is the difference between the energy in the final state and that in the initial state. The most significant aspect of this kind of relation is that the energy change depends only on the initial and final states and is independent of the path linking these states.

Thus:

(i) The change $\Delta.U$ in the internal energy of a system depends only on the initial and final states of the system and not on the path connecting those states. Although both Q and W depend on the path, $Q + W = \Delta U$ is independent of the path

(ii) The energy is an extensive state property of the system. Under the same conditions of temperature and pressure, 10 mol of the substance composing the system has ten times the energy of 1 mol of the substance. The energy per mole is an intensive state property of the system

(iii) Energy is conserved in all transformations. A perpetual-motion machine is a machine which by its action creates energy by some transformation of a system. The first law of thermodynamics asserts that it is impossible to construct such a machine.

2-4 The First Law of Thermodynamics

So far, we have considered various forms of energy such as heat Q, work *W,* and total energy *E* individually, and no attempt has been made to relate them to each other during a process. The *first law of thermodynamics,* also known as *the conservation of energy principle,* provides a sound basis for studying the relationships among the various forms of energy and energy interactions.

- Based on experimental observations, the first law of thermodynamics states that *energy can be neither created nor destroyed; it can only change forms*. Therefore, every bit of energy should be accounted for during a process.

- The first law cannot be proved mathematically, but no process in nature is known to have violated the first law, and this should be taken as sufficient proof.

- Consider a system undergoing a series of *adiabatic* processes from a specified state 1 to another specified state 2. Being adiabatic, these processes obviously cannot involve any heat transfer but they may involve several kinds of work interactions. Careful measurements during these experiments indicate the following: *For all adiabatic processes between two specified states of a closed system, the net work done is the same regardless of the nature of the closed system and the details of the process*. Considering that there are an infinite number of ways to perform work interactions under adiabatic conditions, the statement above appears to be very powerful, with a potential for far-reaching implications. This statement, which is largely based on the experiments of Joule in the first half of the nineteenth century, cannot be drawn from any other known physical principle, and is recognized as a fundamental principle. This principle is called the **first law of thermodynamics** or just the first law.

- A major consequence of the first law is the existence and the definition of the property *total energy* *E.* Considering that the net work is the same for all adiabatic processes of a closed system between two specified states, the value of the net work must depend on the end states of the system only, and thus it must correspond to a change in a property of the system. This property is the *total energy.* Note that the first law makes no reference to the value of the total energy of a closed system at a state. It simply states that the *change* in the total energy during an adiabatic process must be equal to the net work done. Therefore, any convenient arbitrary value can be assigned to total energy at a specified state to serve as a reference point.

- Implicit in the first law statement is the conservation of energy. Although the essence of the first law is the existence of the property *total energy,* the first law is often viewed as a statement of the *conservation of energy* principle. Below we develop the first law or the conservation of energy relation for closed systems with the help of some familiar examples using intuitive arguments.

A. Let us consider first some processes that involve heat transfer but no work interactions. Take the example with the potato in the oven. As a result of heat transfer to the potato, the energy of the potato will increase. If we disregard any mass transfer (moisture loss from the potato), the increase in the total energy of the potato becomes equal to the amount of heat transfer. This and other similar examples can be summarized as follows: *In the absence of any work interactions between a system and its surroundings, the amount of net heat transfer is equal to the change in energy of a closed system.* That is,

$$Q = \Delta E \quad \text{when } W = 0$$

B. Now consider a well-insulated (i.e., adiabatic) room heated by an electric heater as the system. As a result of electrical work done, the energy of the system will increase. Since the system is adiabatic and cannot have any heat interactions with the surroundings ($Q = 0$), the conservation of energy principle dictates that the electrical work done on the system must equal the increase in energy of the system. That is, $W_e = \Delta E$.

We know that the temperature of air rises when it is compressed (think of the example of the air in a cylinder with a piston). This is because energy is added to the air in the form of boundary work. In the absence of any heat transfer ($Q = 0$), the entire boundary work will be stored in the air as part of its total energy. The conservation of energy principle again requires that $W_b = \Delta E$.

.

Thus, *for adiabatic processes, the amount of work done is equal to the change in the energy of a closed system.* That is,

$$W = \Delta E. \text{ when } Q = 0$$

C. Now we are in a position to consider simultaneous heat and work interactions. When a system involves both heat and work interactions during a process, their contributions are simply added. That is, if a system receives 12 kJ of heat while a paddle wheel does 6 kJ of work on the system, the net increase in energy of the system for this process will be 18 kJ.

To generalize our conclusions, the first law of thermodynamics, or the conservation of energy principle for a closed system or a fixed mass, may be expressed as follows:

Net energy transfer to (or from) the system as heat and work = net change in the total energy of the system:

$$Q + W = \Delta E \qquad \text{(in kJ)} \qquad 2\text{-}28$$

Here $\boldsymbol{Q}$ = net heat transfer across system boundaries $\boldsymbol{(= \Sigma Q_{in} - \Sigma Q_{out})}$
$\boldsymbol{W}$ = net work done in all forms $\boldsymbol{(= \Sigma W_{in} - \Sigma W_{out})}$
$\boldsymbol{\Delta E}$ = net change in total energy of the system $\boldsymbol{E_2 - E_1}$

$$\Delta E = \Delta U + \Delta KE + \Delta PE \qquad 2\text{-}29$$

Most closed systems encountered in practice are stationary, i.e., they do not involve any changes in their velocity or the elevation of their center of gravity during a process. Thus, for stationary closed systems, the changes in kinetic and potential energies are negligible, and the first-law relation reduces to

$$Q + W = \Delta U \qquad \text{(in kJ)} \qquad 2\text{-}30$$

Sometimes it is convenient to consider the work term in two parts: W_{olher} and W_b, where W_{other} represents all forms of work except the boundary work. (This distinction has important bearings with regard to the second law of thermodynamics, as is discussed in later chapters.) Then the first law takes the following form:

$$Q + W_{other} + W_b = \Delta E \qquad \text{(in kJ)} \qquad 2\text{-}31$$

> Note: It is extremely important that the *sign convention* be observed for heat and work interactions. Heat flow into and work done to a system are positive, and heat flow from a system and work done by a system are negative. A system may involve more than one form of work during a process. The only form of work whose sign we do not need to be concerned with is the boundary work W_b as defined by Eq. 2-21. Boundary work calculated by using Eq. 2-21 will always have the correct sign. The signs of other forms of work are determined by inspection.

The first-law relation for closed systems can be written in various forms. Dividing Eq. 2-28 by the mass of the system, for example, gives the first-law relation on a **unit-mass** basis as

$$q + w = \Delta e \qquad 2\text{-}32$$

The rate form of the first law is obtained by dividing Eq. 2-28 by the time interval Δt and taking the limit as $\Delta t \rightarrow 0$. This yields

$$\dot{Q} + \dot{W} = \frac{dE}{dt} \qquad \text{(in kW)} \qquad 2\text{-}33$$

where dQ/dt is the rate of net heat transfer, dW/dt is the power, and dE/dt is the rate of change of total energy.

Equation 2-28 can be expressed in **differential form as**

$$\delta Q + \delta W = dE \qquad 2\text{-}34$$

For a cyclic process, the initial and final states are identical, and therefore $\Delta E = E_2 - E_1 = 0$. Then the first-law relation for a cycle simplifies to

$$Q + W = 0$$

That is, the net heat transfer and the net work done during a cycle must be equal.

Note: As energy quantities, heat and work are not that different, and you probably wonder why we keep distinguishing them. After all, the change in the energy content of a system is equal to the amount of energy that crosses the system boundaries, and it makes no difference whether the energy crosses the boundary as heat or work. It seems as if the first-law relations would be much simpler if we had just one quantity which we could call *energy interaction* to represent both heat and work. Well, from the first-law point of view, heat and work are not different at all, and the first law can simply be expressed as

$$E_{in} - E_{out} = \Delta E \qquad 2\text{-}35$$

where E_{in} and E_{out} are the total energy that *enters* and *leaves* the system, respectively, during a process. But from the second-law point of view, heat and work are very different, as you will see in later chapters.

Example 2-10

Consider the quasi-equilibrium expansion or compression of a gas in piston cylinder device. Show that the boundary work W_b and the change internal energy ΔU in the first law relation can be combined into one term, ΔH, for such a system undergoing a constant-pressure process.

Solution

Neglecting the changes in kinetic and potential energies and expressing the work as in Eq. 2-31,

$$Q + W_{other} + W_b = U_2 - U_1$$

For a constant-pressure process, the boundary work is given by $W_b = - P_0 (V_2 - V_1)$. The – sign preserves the sign convention that when the surroundings do work on the system, the final volume is less than the initial and the net work is positive. Substituting this into the above relation gives

$$Q + W_{other} - P_0 (V_2 - V_1) = U_2 - U_1$$

But $P_0 = P_2 = P_1$ thus $Q + W_{other} = (U_2 + P_2V_2) - (U_1 + P_1V_1)$

Taking $H = U + PV$, leads to

$$Q + W_{other} = H_2 - H_1 \qquad 2\text{-}36$$

which is the desired relation. *This equation is very convenient to use in the analysis of closed systems undergoing a constant-pressure quasi-equilibrium process since the boundary work is automatically taken care of by the enthalpy terms, and one no longer needs to determine it separately.*

Some Consequences of the First Law

2-5 Heat Capacity

We have already defined heat capacity as the amount of heat required to raise the temperature of a mass of a system by 1°C. It is denoted by *C*.

$$Q = C\,\Delta T \qquad 2\text{-}37$$

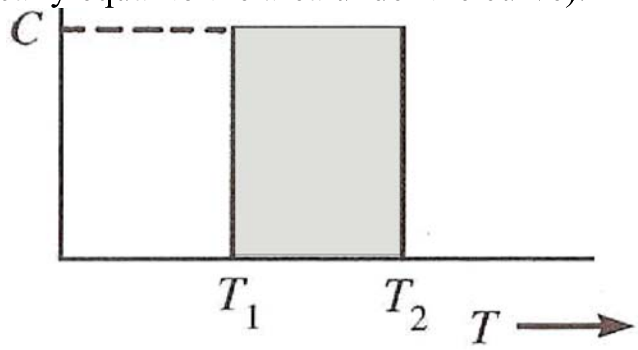
Where Q is in kJ, C in kJ/kg.^{0}C.

Equation 2-37 is a general definition of heat capacity and it implies that the heat capacity of a system depends not only on the heat-absorbing ability but also, in a simple way, on the amount of substance present.

- When defining heat capacity in terms of material in the system, we have:
    - *Specific heat capacity*. Heat absorbed by 1 kg of material that undergoes a rise in temperature of 1°C.
    - *Molar heat capacity*. Heat absorbed by 1 kg mol of material that undergoes a rise in temperature of 1°C.
- When the heat capacity is essentially constant between the two temperatures T_1 and T_2,

$$Q = C\,\Delta T = C\,(T_2 - T_1) \qquad 2\text{-}37a$$

See figure (it is numerically equal to the area under the curve).



If C varies significantly with temperature, then:

$$Q = \int_1^2 C[T]dT \qquad \text{2-38}$$

and again, it is numerically equal to the area under the curve.

- We can express C by an empirical power series such as $C=a+bT+cT^{-2}$ Then,

$$Q = \int_{T_1}^{T_2} (a + bT + cT^{-2})\mathrm{d}T = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note: If the heat capacity cannot be expressed analytically as a function of temperature and experimental data is available, Q can be evaluated from the C vs T graph. If a suitable function is available, the integration can be performed numerically by the use of integration rules.

2-6 Specific Heat Capacity

We already know that the quantity of heat exchange with a system depends on the path, thus, for different paths, C will be different.

(i) At ***constant volume***, over a temperature range in which the heat capacity is constant, Equation 2-37 becomes

$$Q_V = C_V \Delta T \qquad \text{2-39}$$

And because the volume is constant, $Q_V = \Delta U$, thus

$$\Delta U = C_V \Delta T \qquad \textit{2-40}$$

If C_V is the molar heat capacity, then for n moles,

$$\Delta U = n\, C_V\, \Delta T \tag{2-41}$$

If, over the temperature range concerned, C_V is not constant

$$\Delta U = Q_V = \int_1^2 C_V(T)\, dT \tag{2-42}$$

(ii) At ***constant pressure***, we have similarly

$$Q_P = C_P\, \Delta T \tag{2-43}$$

If in Eq 2-36 there is no other types of work involved except boundary work, then $Q_P = \Delta H$

And thus, for a constant C_P

$$\Delta H = C_P\, \Delta T \tag{2-44}$$

and for n moles

$$\Delta H = nC_P\, \Delta T \tag{2-45}$$

$$\Delta H = C_P\, \Delta T \tag{2-44}$$

and if C_P varies, then

$$\Delta H = Q_V = \int_1^2 C_V(T)\, dT \tag{2-46}$$

(iii) Relationship between ***constant pressure*** C_P and ***constant volume*** $C_{V.}$

For the molar heats, we have

$$C_P = C_V + R. \tag{2-47}$$

The ratio of the 'heat capacities' is given by

$$\gamma = C_P / C_V \qquad \text{2-48}$$

For monatomic gases γ =1.67.

Eq. 2-47 holds approximately for dia- and polyatomic gasses

Heat capacity ratio of some important gases at 0.1 MPa pressure

Gas	Specific heat (kJ kg^{-1} K^{-1})		Molar heat capacity (Jmol^{-1} K^{-1})		Cp-Cv (Jmol^{-1} K^{-1})	γ
	Cv	Cp	C_v	C_p		
Monatomic						
He	3.138	4.812	12.468	20.794	8.326	1.67
Ne	0.619	1.029	12.468	20.794	8.326	1.67
A						1.67
Hg						1.67
Na						1.67
Diatomic						
H_2		0.014				1.40
N_2	0.740	1.038	20.753	29.079	8.326	1.40
Air	0.718	1.005	20.8	29.114	8.314	1.4
O_2	0.648	0.912	21.046	29.413	8.368	1.40
Triatomic						
CO_2	0.640	0.833	28.451	36.945	8.494	1.30
H_20	1.464	2.017	25.941	34.309	8.368	1.32
Polyatomic						
C_2H_6	1.435	1.724	43.095	51.672	8.577	1.20

Example 2-11

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using *(a)* the functional form of the specific heat and *(b)* the average specific heat value.

Solution

At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values (T_{cr} = -147°C, P_{cr} = 3390 kPa for nitrogen, the main constituent of air). The internal energy change Δu of ideal gases depends on the initial and final temperatures only, and not on the type of process. Thus, the solution given below is valid for any kind of process

(a) The change in internal energy of air, using the functional form of the specific heat, is determined as follows. The *Cp(T)* of air is given in the form of a third-degree polynomial expressed as

$$C_P\,(T) = a + bT + cT^2 + dT^3$$

where a = 28.11, $b = 0.1967 \times 10^{-2}$, $C = 0.4802 \times 10^{-5}$, and $d = -1.966 \times 10^{-9}$. Next we have

$$C_V\,(T) = C_P - R_{molar} = (a - R_{molar}) + bT + cT^2 + dT^3$$

Replacing it in Eq. 2-42 and performing the integral, we get

$$\Delta U = 6447.15 \text{ kJ / kmol}$$

The molar mass of air is 28.97 kg /kmol, thus, the change in internal energy per unit mass is:

$$\Delta u = \Delta U / M = 225.55 \text{ kJ / kg}$$

(b) The average value of the constant-volume specific heat $C_{v.av}$ is determined from the values at 300 and 600 K. At the average temperature 450 K tables give the value Table A-2b at the average temperature (~ + 7;)/2 = 450 K to be

$$C_{v.av} = C_V@450\text{K} = 0.733 \text{ kJ/(kg . K)}$$

Thus $\Delta u = C_{v.av}\ (T_2 - T_1) = 219.9 \text{ kJ / kg}$

This answer differs from the above result by only 1.2 percent. This close agreement is not surprising since the assumption that C_v varies linearly with temperature is a reasonable one at temperature intervals of only a few hundred degrees. If we had used the C_v value at $T_1 = 300$ K instead of at T_{av}, the result would be 215.4 kJ/kg, which is in error by about 3 percent. Errors of this magnitude are acceptable for most engineering purposes.

Example 2-12

A piston-cylinder device initially contains 0.5 m^3 of nitrogen gas at 400 kPa and 27°C. An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of

2800 J occurs during the process. Determine the final temperature of the nitrogen

Solution

This time, we take the nitrogen in the piston-cylinder device as our system. At the specified conditions, the nitrogen gas can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values (T_{cr} = -147°C, P_{cr}, = 3390 kPa).

First, let us determine the electrical work done on the nitrogen:

$$W_e = V\, I\, \Delta t = 72 \text{ kJ}$$

The mass of nitrogen is determined from the ideal-gas relation

$$M = PV / RT = 2.25 \text{ kg}$$

The conservation of energy gives:

$$Q + W_e + W_b = \Delta U$$

For a constant pressure process of a closed system,

$$Q + W_e = \Delta H = mC_P\,(T_2 - T_1)$$

Using the value of C_P from the table, we get $T_2 = 56.6\ ^0\text{C}$

2-7 Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids

The difference between C_P and C_V for liquids and solids is rather small, and, except for where high accuracy is required, it is sufficient to take $C_P = C_V$. The reason for this is that the thermal expansion coefficients of liquids and solids are very small, so that the volume change on increasing the temperature by 1°C is very small; correspondingly the work produced by the expansion is small and little energy is required for the small increase in the spacing of the molecules.

A substance whose specific volume (or density) is constant is called an incompressible

substance. The specific volumes of solids and liquids essentially remain constant during a process. Therefore, liquids and solids can be approximated as incompressible substances without sacrificing much in accuracy. The constant-volume assumption should be taken to imply that the energy associated with the volume change, such as the boundary work, is negligible compared with other forms of energy. Otherwise, this assumption would be ridiculous for studying the thermal stresses in solids (caused by volume change with temperature) or analyzing liquid-in-glass thermometers.
For solids and liquids,

$$C_P = C_V = C \qquad 2\text{-}49$$

Example: C_P for asphalt is 0.920 kJ / kg . ^{0}C

Like those of ideal gases, the specific heats of incompressible substances depend on temperature only.

$$dU = C_v\, dT = C(T)\, dT \qquad 2\text{-}50$$

The change in the internal energy between two states is

$$\Delta U = U_2 - U_1 = \int_1^2 C[T]dT \qquad 2\text{-}51$$

For small temperature intervals, we can use an average value for *C*

$$\Delta U \approx C_{av}(T_2 - T_1) \qquad 2\text{-}52$$

For the enthalpy, by using its definition, we get

$$\Delta H = \Delta U + V\Delta P \qquad (\text{kJ}) \qquad 2\text{-}53$$

The second term in the above equation is often small compared with the first term and can be neglected without significant loss of accuracy.

2-7 Heat Conduction

We have seen that the for a temperature gradient *dT / dx* the heat flows as

$$\dot{Q}_{cond} = -kA\frac{dT}{dx} \qquad (2\text{-}8)$$

where k is the thermal conductivity of the material (in W/m ^{0}C).

A substance with a large thermal conductivity is known as a *thermal conductor,* and one with a small value of *k* as a *thermal insulator.* The numerical value of *k* depends on a number of factors, one of which is the temperature. If the temperature difference between parts of a substance is small, *k* can be considered to be almost constant throughout the substance.

Examples of practical situations. In all cases, we shall assume that *k* is constant throughout the conducting substance.

(a) *Linear flow of heat perpendicular to the faces of a slab.* If the temperature difference $T_1 - T_2$ and the thickness *d* are small, then

$$\dot{Q} = kA\frac{T_1 - T_2}{d}$$

(b) *Radial flow of heat between two coaxial cylinders.* If the conducting material lies between an inner cylinder of radius r_l kept at temperature T_1 and an outer cylinder of radius r_2, and temperature T_2 both of length *1, then* there will be a steady radial flow of heat at the constant rate.

The area through which heat flows depends on the distance from the cylinders. For a distance r from the axis of the cylinders, the area is $A = 2\pi rl$ and for a thickness *dr*, the temperature gradient is dT/dr. Thus,

$$\dot{Q} = -k2\pi rl\frac{dT}{dr}$$

$$dT = -\frac{\dot{Q}}{2\pi lk}\frac{dr}{r}$$

and after integration:

$$T_1 - T_2 = \frac{\dot{Q}}{2\pi lk} \ln\left(\frac{r_2}{r_1}\right)$$

(c) *Radial flow of heat between two concentric spheres.* If the conducting material lies between an inner sphere of radius r_1 held at constant temperature T_1 and an outer sphere of radius r_2 held at constant temperature T_2 there will be a steady radial flow of heat at a constant rate. In this case by following a procedure similar to the concentric cylinders we get:

$$T_1 - T_2 = \frac{\dot{Q}}{4\pi k} \ln\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

2-8 Reversible and irreversible processes

Reversible isothermal process

An ideal gas is placed in a cylinder with a piston, and expands very slowly and keeps the temperature constant all the time by either withdrawing heat from or supplying heat to the system. Let $P_1\ V_1\ T_1$ be the initial state and $P_2,\ V_2,\ T_2$ be the final state.

For a perfect gas, $\Delta U = C_V \Delta T = 0$, and from the first law we have $Q + W = 0$

The work done by the gas for a small increase in volume dV is $dW = -P\,dV$
The total work between the two states is

$$W = -Q = -\int_1^2 P dV \qquad \text{2-54}$$

which for ideal gases can be written as

$$W = -Q = -nRT\int_1^2 \frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

Since at constant temperature $P_1 V_1 = P_2 V_2$

$$W = -Q = -nRT\int_1^2 \frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right)$$

This equation can be also written as

$$P_2 = P_1 \exp\left(\frac{W}{nRT}\right) \tag{2-55}$$

Irreversible isothermal process

The numerical value of the work done on the surroundings, whether positive or negative, is always a maximum in reversible process. This is, in fact, true for any kind of work and for any path. Since only irreversible processes are observable (the reversible processes are the hypothetical processes) we conclude that *all observable processes produce less work than the maximum work, and result in dissipation of work as heat.*

Adiabatic irreversible process (Q = 0)

In this case

$$\Delta U = W \tag{2-56}$$

The change ΔU can be calculated by considering that each individual small adiabatic change $(\Delta U)_A$ is the sum of an isocoric $(\Delta U)_V$ and an isothermal process $(\Delta U)_T$, thus

$$(\Delta U)_A = (\Delta U)_V + (\Delta U)_T$$

For an isothermal process $(\Delta U)_T = 0$

$$(\Delta U)_V = n\int_1^2 C_V(T)\,dT \tag{2-57}$$

thus

$$[\Delta U]_A = n\int_1^2 C_V\,dT$$

so the general equation for the adiabatic change gives

$$\Delta U = n\int_1^2 C_V\,dT = -\int_1^2 P\,dV = W \qquad 2\text{-}58$$

Example 2-13

5 mol of an ideal monatomic gas, with the specific heat at constant volume being 20.92 J mol^{-1} K^{-1}, expands irreversibly but adiabatically from an initial pressure of 2.02 MPa against a constant external pressure of 0.101 MPa until the temperature drops from the initial value of 27°C to a final value of 7°C. How much work has been done in the process? What is the final volume?

Solution

Eq. 2-58 gives $\Delta U = n\,C_V(T_2 - T_1)$ = -2.09 kJ which is equal to the work done W.

The final volume can be found as follows:

$$W = -P_{ext}(V_2 - V_1) = -2.09 \text{ kJ}$$

so

$$(V_2 - V_1) = 0.02 \text{ m}^3$$

$P_1 V_1 = nRT_1$, that give for $V_1 = 0.006 \text{ m}^3$, so $V_2 = 0.026 \text{ m}^3$

Adiabatic reversible process (Q = 0)

For ideal gases, the adiabatic processes are described by (see Part I page 101)

$$PV^{\gamma} = \text{a constant} \qquad 2\text{-}59$$

$$TV^{\gamma-1} = \text{a constant} \qquad 2\text{-}60$$

Where $\gamma = C_P / C_V$, and $\gamma - 1 = R / C_V$.

For van der Waals gases, the above equation becomes:

$$T\,(V - b)^{\gamma-1} = \text{a constant} \qquad 2\text{-}61$$

For ideal gases, by replacing V with nRT/P in Eq.2-59 we get

$$T^{\gamma} P^{1-\gamma} = \text{const} \qquad 2\text{-}62$$

or

$$T\,P^{1/\gamma - 1} = \text{a constant} \qquad 2\text{-}63$$

For real gases, some of the adiabatic expansion forms are:

$$T(V - b)^{\gamma-1} = const.$$

$$T\left(P + \frac{a}{V^2}\right)^{1/\gamma-1} = const. \qquad 2\text{-}64$$

$$\left(P + \frac{a}{V^2}\right)(V - b)^{\gamma} = const$$

The work done in a adiabatic expansion can be calculated from

$$W = -\int_1^2 PdV \qquad 2\text{-}65$$

where P is (const. x $V^{-\gamma}$) which gives

$$W = -\frac{1}{1-\gamma}\left[CV^{1-\gamma}\right]_{V_1}^{V_2} \qquad 2\text{-}66$$

where C is a constant. This becomes

$$W = -\frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \qquad 2\text{-}67$$

In adiabatic processes, from $\Delta U = Q + W$, $Q = 0$, we get $W = \Delta U$

But $\Delta U = C_V\, \Delta T$,

So

$$W = -\ C_V\, \Delta T \qquad 2\text{-}68$$

And for a real gas

$$W = -\ C_V\, \Delta T + a\, \Delta\, (1/V) \qquad 2\text{-}69$$

Enthalpy (*H = U + PV*)

For an isobaric process the first law can be written as

$$\Delta U = Q + W = Q_P - P\,(V_2 - V_1)$$

rearranging, we get

$$\Delta H = Q_P \qquad 2\text{-}70$$

Thus,

- *The heat absorbed in any reversible isobaric process is equal to the difference between the enthalpies of the system in the end states of the process.*
- *Enthalpy, like energy U or temperature T, is a function of state of the system alone and is independent of the path through which that state is reached.*

Because $Q_P = C_P\, \Delta T = \Delta H$

We get

$$C_P = (\partial H / \partial T)_P \qquad 2\text{-}71$$

Consider a stationary closed system undergoing a constant-volume process ($W_b = 0$). The first-law relation for this process can be expressed in the differential form as

$$\delta Q - \delta W_{other} = dU$$

The left-hand side of this equation represents the amount of energy transferred to the system in the form of heat and/or work. From the definition of C_V, this energy must be equal to $C_V\,dT$, where dT is the differential change in temperature. Thus,

$$C_V\,dT = dU \text{ at constant volume}$$

In other words,

$$C_V = (\partial U / \partial T)_V \qquad \text{2-72}$$

For ideal gases, the work done in an isothermal process is given by (see Part I)

$$W = -\int_1^2 P dV \qquad \text{(2-65)}$$

$$W = -\int_i^f P_{ext} dV = -nRT\int_i^f \frac{dV}{V} = -nRT \ln\frac{V_f}{V_i}$$

For real gases, in order to calculate the work in an **isothermal process**

From the van der Waals equation for $n = 1$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

we take the pressure out and get

$$W = -\left[RT\ln\left(\frac{V_2 - b}{V_1 - b}\right) + \frac{a}{V_2} - \frac{a}{V_1}\right] \qquad \text{2-73}$$

Van der Waals equation gives

$$PV = \frac{RTV}{V-b} - \frac{a}{V}$$

It can be shown that for real gases there is a small change in the internal energy with the change in the volume at constant temperature:

$$(\partial U / \partial V)_T = a / V^2$$

Thus, for an isothermal process,

$$\Delta H = \Delta U + \Delta(PV)$$

which leads to

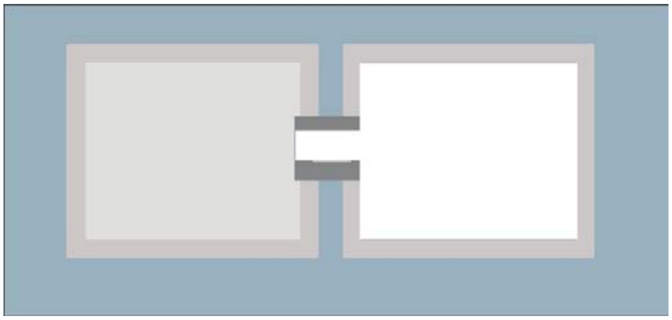
$$\Delta H = bRT\left(\frac{1}{V_2 - b} - \frac{1}{V_1 - b}\right) - \frac{2a}{V_2} + \frac{2a}{V_1} \qquad \text{2-74}$$

Joule and Joule – Thomson experiment

It is interesting to see how the energy of a gas depends on its volume, or how the enthalpy of a gas depends on pressure. For this purpose, Joule and Gay-Lussac carried out a series of experiments and later Joule and Thomson carried out another set of experiments. These two experiments are now known as the Joule experiment and the Joule-Thomson experiment.

Joule experiment

- Two containers, one containing a gas at a given pressure and temperature and the other evacuated, joined by a tube provided with a stopcock are immersed in a calorimeter bath



- The stopcock is opened, the gas is allowed to expand freely from one container into the other and then the net temperature change attending the process is measured after reaching thermal equilibrium.

- It is observed that, when ordinary gases at moderate pressures are subjected to the Joule experiment, the net temperature change is very small so that we can assume that the temperature change is actually zero.

- There is no work done by the system against an external pressure, thus $W = 0$

- There no heat exchanged with the environment, thus $Q = 0$

- In conclusion,

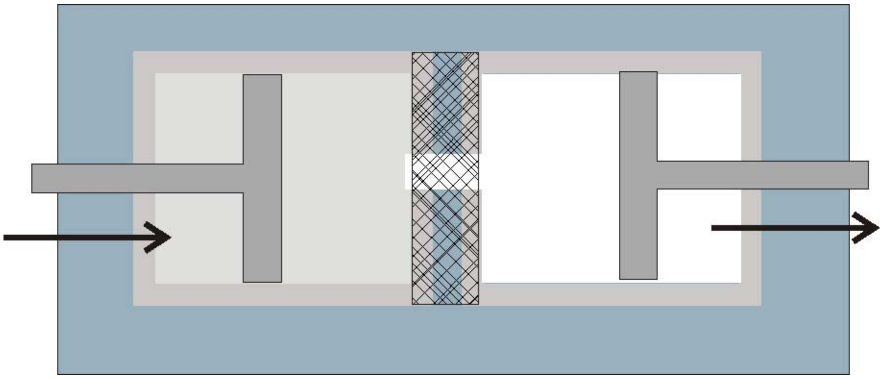
$$\Delta U = Q + W = 0$$

and the energy of an ideal gas is a function of temperature only and it does not depend on its volume. It follows that C_V depends on T only.

$$dU = C_V(T)\, dT$$

Joule – Thomson experiment

Joule and Thomson devised another experiment in such a way that the temperature change due to expansion of a gas would much more accurately be measured.



Note: The results of this experiment provide information about intermolecular forces. This information can be used to in the liquefaction of gases such as hydrogen and helium.

A cylindrical tube, insulated to prevent any transfer of heat to the surroundings, is fitted with two pistons and a porous plug which is capable of allowing gas to flow slowly through it. The left tube is initially filled with a certain amount of a gas at temperature T_1, volume V_1 and pressure P_1 ; the right tube is empty. The gas is then allowed to flow slowly through the plug in such a way that its pressure in left tube is kept constant at P_1 by the movement of the piston towards the plug. At the same time the right piston is adjusted in such a way that the low pressure P_2 ($< P_1$) is kept constant. The final volume in right tube after all the gas has streamed through the porous plug, is V_2 and its temperature T_2. The significant datum obtained in this experiment is the change in temperature due to flow of the gas through the porous plug. This can be obtained by measuring temperatures T_1 and T_2.

In this experiment:

- $Q = 0$
- The change in the internal energy of the system is due to the work done

$$W = P_1 V_1 - P_2 V_2$$

But

$$\Delta U = U_2 - U_1 = P_1 V_1 - P_2 V_2$$

By rearranging we get

$$\Delta H = 0$$

This shows that the Joule-Thomson experiment is carried out under constant-enthalpy conditions.

Note:

- When the gas involved is perfect, H is a function of T only, and therefore $\Delta H = 0$ implies that $\Delta T = 0$, thus no temperature change for a perfect gas.
- For a real gas it generally depends on whether T_2 is greater or smaller than T_1. At the critical temperature (called the *Joule-Thomson inversion temperature*). Above this temperature there will be heating; below this temperature there will be cooling upon Joule-Thomson expansion.

The *Joule-Thomson coefficient (μ)* is defined as the change in temperature per unit change in pressure when the enthalpy is constant. In terms of partial derivatives

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H .$$

2-75

The sign of the coefficient indicates if the gas cools or warms up upon expansion.

- if the gas cools in the process of streaming through the plug, $\mu > 0$. Conversely, when $\mu < 0$ there is an increase in temperature.

If we consider H as a function of temperature and pressure, the total differential of H is given by

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP.$$

It can be shown that if C_p remains constant over a small temperature range, then (see text page 100)

$$\Delta T = \frac{T(\partial V/\partial T)_P - V}{C_P}\Delta P. \qquad \text{2-76}$$

This is the equation for the differential Joule-Thomson effect, ΔT being the increase in temperature for a change ΔP in pressure in the proximity of the temperature T. In their experiment, Joule and Thomson found that the decrease in temperature was proportional to the difference in pressure on the two sides of the porous plug.

For a van der Waals gas, U is not a function of temperature only, whereas for an ideal gas, U is a function only of temperature. It can be shown (see text page 102) that

$$U = U_0 + C_V T - a / V \qquad 2.77$$

Where U_0 is a constant.

Similarly, the enthalpy for van der Waals gases is expressed as

$$H = U_0 + (C_V + R)T + P\left(b - \frac{2a}{RT}\right). \qquad \text{2-78}$$

For a small pressure change, the expansion should still be at constant enthalpy, thus

$$H(P + dP,\ T + dT) = H(P,\ T). \qquad \text{2-79}$$

By differentiating with respect to P, we get

$$\left(\frac{\partial H}{\partial P}\right)_T = b - \frac{2a}{RT}$$

The left-hand side of Eq. 2-79 can be expanded by Taylor expansion as

which leads to

Combining with 2-79 we get

$$H(P + \mathrm{d}P,\ T + \mathrm{d}T) \simeq H(P, T) + \left(\frac{\partial H}{\partial P}\right)_T \partial P + \left(\frac{\partial H}{\partial T}\right)_P \partial T.$$

$$\frac{\partial T}{\partial P} \simeq -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P.$$

Where the term at the denominator is C_P. *Thus we have for the Joule-Thomson coefficient*

$$\frac{\partial T}{\partial P} = -\frac{b - 2a / RT}{C_P} \qquad 2\text{-}80$$

At the inversion temperature $\mu = 0$, so we can find $T_i = 2a / Rb$

- At this temperature the Joule-Thomson effect is zero; no change in temperature occurs on expansion. Below T_i there is cooling and above it heating for Joule-Thomson expansion

- Evidently the Joule-Thomson effect depends on both *a* and *b,* even though it may depend only on *a* as it is the cohesion force a/V^2 against which work is to be done.

- By differentiating Eq. 2-78 with respect to T, and replacing ($\partial H / \partial T$) by C_P, we get

$$C_P - C_V = R + 2aP / RT^2 \qquad 2\text{-}81$$

This shows that in the case of a van der Waals gas the difference between *Cp* and *Cv* is greater than that in the case of an ideal gas.

Some Applications of the First Law

The first law of thermodynamics is

$$dU = dQ + dW \qquad \text{2-82}$$

The energy equation of a system is the relation between the internal energy U and the state variables of the system: pressure, volume and temperature.

$U = f(T, V)$ and $dW = -P\, dV$

The quantity of heat dQ becomes

$$\mathrm{d}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \mathrm{d}V. \qquad \text{2-83}$$

This equation is a general equation and can be applied to <u>any substance and to any reversible process</u>.

A. $V = constant$ $\quad (\mathrm{d}Q)_V = C_V(\mathrm{d}T)_V$

And from Eq, 2-83 we obtain the eq. for C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

B. $P = constant$ $\quad (\mathrm{d}Q)_P = C_P(\mathrm{d}T)_P.$

And Eq. 2-83 becomes

$$C_P(\mathrm{d}T)_P = C_V(\mathrm{d}T)_P + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] (\mathrm{d}V)_P. \qquad \text{2-84}$$

or

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P. \qquad \text{2-85}$$

C. T = constant

Eq. 2-83 becomes

$$(dQ)_T = P(dV)_T + \left(\frac{dU}{dV}\right)_T (dV)_T \qquad \text{2-86}$$

D. Q = 0

Eq. 2-83 becomes

$$C_V\ \mathrm{d}T = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\mathrm{d}V. \qquad \text{2-87}$$

or

$$C_V \frac{\partial T}{\partial V} = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]. \qquad \text{2-88}$$

U = f(T, P)

Differentiating dV

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P. \qquad \textit{2-89}$$

and similarly dU, the first law can be written as

$$\mathrm{d}Q = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]\mathrm{d}T + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\mathrm{d}P.$$

P = constant $(\mathrm{d}Q)_P = C_P(\mathrm{d}T)_P.$

$$C_P = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] \tag{2-90}$$

and Eq. 2-89 becomes

$$dQ = C_P dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial V}{\partial P}\right)_T\right] dP \tag{2-91}$$

V = constant $(\mathrm{d}Q)_V = C_V(\mathrm{d}T)_V$

$$C_V(\mathrm{d}T)_V = C_P(\mathrm{d}T)_V + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right](\mathrm{d}P)_V \tag{2-92}$$

or

$$C_V = C_P + \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_V. \tag{2-93}$$

Similar equations can be obtained for $U = f\,(P,V)$

Internal Energy of Gases

It will be shown later that for any substance

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V. \tag{2-94}$$

we can compute $(dU / dV)_T$

For one mole of ideal gas, from $PV = RT$ we get $(dP / dT)_V = R / V$, thus

$$(dU / dV)_T = -P + TR / V = P - P = 0$$

This shows that at constant temperature the internal energy of an ideal gas is independent of volume or density.
By differentiating with respect to P, we also get;

$$(dU / dP)_T = 0.$$

In conclusion, the internal energy of an ideal gas depends on temperature only. Thus

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

becomes

$$C_V = \frac{dU}{dT} \qquad \text{2-95}$$

and in general

$$U = U_0 + \int_{T_0}^{T} C_V \, dT \qquad \text{2-96}$$

where U_0 is a constant.

For a mole of van der Waals gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}.$$

By differentiating with respect to T at constant volume

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

and substituting in Eq.2-94, we get

$$\left(\frac{dU}{dV}\right)_T = \frac{a}{V^2}$$

We have

$$dU = \left(\frac{dU}{dT}\right)_V + \left(\frac{dU}{dV}\right)_T dV$$

becomes

$$dU = C_V\, dT + (a / V^2)\, dV$$

Thus

$$U = U_0 + \int_{T_0}^{T} C_V\, dT + \left(\frac{a}{V_0} - \frac{a}{V}\right) \qquad \text{2-97}$$

This shows that *the internal energy of a van der Waals gas depends on its volume and temperature.* Since the van der Waals constant b is a measure of molecular diameter only, it does not affect the energy, and hence it does not appear in the energy equation.