The First Law of Thermodynamics: Closed Systems

The first law of thermodynamics can be simply stated as follows: 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 closed system can exchange energy with its surroundings through *heat* and *work* transfer. In other words, work and heat are the forms that energy can be transferred across the system boundary.

Based on kinetic theory, heat is defined as the energy associated with the random motions of atoms and molecules.

Heat Transfer

Heat is defined as the form of energy that is transferred between two systems by virtue of a *temperature difference*.

Note: there **cannot** be any heat transfer between two systems that are at the **same temperature**.

Note: It is the thermal (internal) energy that can be stored in a system. Heat is a form of energy in transition and as a result can only be identified at the system boundary.

Heat has energy units kJ (or BTU). Rate of heat transfer is the amount of heat transferred per unit time.

Heat is a directional (or vector) quantity; thus, it has magnitude, direction and point of action.

Notation:

– Q (*kJ*) amount of heat transfer

– $Q°$ (*kW*) rate of heat transfer (power)

– q (*kJ/kg*) - heat transfer per unit mass

– $q°$ (*kW/kg*) - power per unit mass

Sign convention: Heat Transfer *to a system is positive*, and heat transfer *from a system is negative*. It means any heat transfer that increases the energy of a system is positive, and heat transfer that decreases the energy of a system is negative.
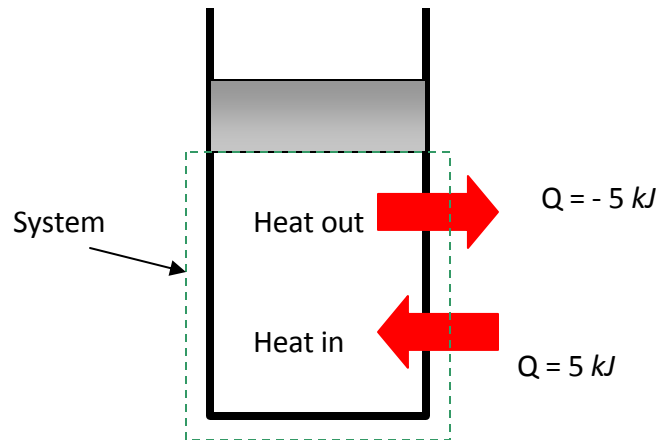
Fig. 1: Sign convention: positive if to the system, negative if from the system.

Modes of Heat Transfer

Heat can be transferred in three different modes *conduction, convection*, and *radiation*. All modes of heat transfer require the existence of a temperature difference.

Conduction: is the transfer of energy from the more energetic particles to the adjacent less energetic particles as a result of interactions between particles.

In solids, conduction is due to the combination of *vibrations* of the molecules in a *lattice* and the energy transport by *free electrons*.

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 (*advection*).

Convection is called *forced* if the fluid is forced to flow by external means such as a fan or a pump. It is called *free or natural* if the fluid motion is caused by buoyancy forces that are induced by density differences due to the temperature variation in a fluid.

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.

Work

Work is the energy interaction between a system and its surroundings. More specifically, work is the energy transfer associated with *force acting through a distance*.

 Notation:

– *W* (*kJ*) amount of work transfer

– *W°* (*kW*) power

– w (*kJ/kg*) - work per unit mass

– w° *(kW/kg)* - power per unit mass

<u>Sign convention</u>: work *done by* a system is *positive*, and the *work done on* a system is *negative*.
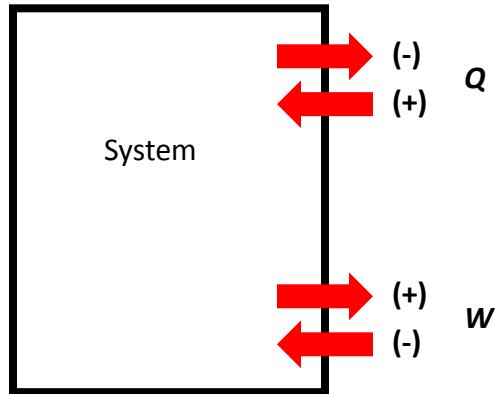

Fig. 2: Sign convention for heat and work.

Similarities between work and heat transfer:

➢ Both are recognized at the boundaries of the system as they cross them (boundary phenomena).

➢ Systems posses energy, but not heat or work (transfer phenomena).

➢ Both are associated with a process, not a state. Heat or work has no meaning at a state.

➢ Both are path functions, their magnitudes depend on the path followed during a process as well as the end states.

<u>Path functions</u>: have **inexact differentials** designated by symbol δ. Properties, on the other hand, are <u>point functions</u> which depend on the state only (not on how a system reaches that state), and they have **exact differentials**.

$$\int_{1}^{2} dV = V_2 - V_1 = \Delta V \qquad \text{(Point function)}$$

$$\int_{1}^{2} \delta W = W_{12} \qquad \text{(Path function, not } \Delta W \text{ nor } W_2 - W_1\text{)}$$

Electrical Work

The work that is done on a system by *electrons.* When N coulombs of electrons move through a potential difference V, the electrical work done is:

$$W_e = VN \quad (kJ)$$

Which can be explained in the rate form as

$$W_e^{\bullet} = VI \quad (kW)$$

Example 1: Electrical work

A well-insulated electrical oven is being heated through its heating element. Determine whether it is work or heat interaction. Consider two systems: a) the entire oven (including the heater), and b) only the air in the oven (without the heater) see Fig 3-3.

Solution:

The energy content of the oven is increased during this process.

a) The energy transfer to the oven is not caused by a temperature difference between the oven and air. Instead, it is caused by electrical energy crossing the system boundary and thus: **this is a work transfer process**.

b) This time, the system boundary includes the outer surface of the heater and will not cut through it. Therefore, no electrons will be crossing the system boundary. Instead, the energy transfer is a result of a temperature difference between the electrical heater and air, thus: **this is a heat transfer process.**
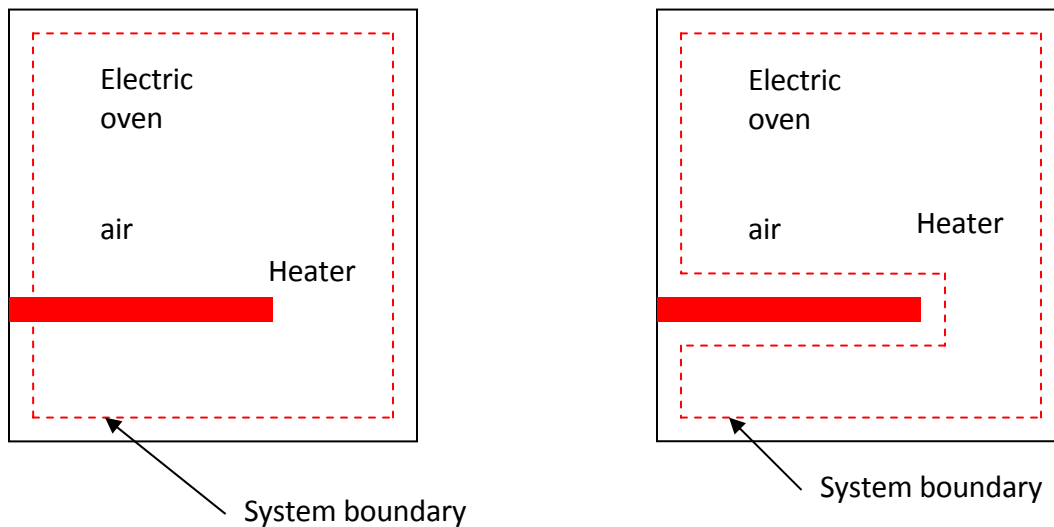

Fig. 3: Schematic for example 1.

Mechanical work

There are several ways of doing work, each in some way related to a force acting through a distance.

$$W = F.s \quad (kJ)$$

If the force is not constant, we need to integrate:

$$W = \int_1^2 F.ds \qquad (kJ)$$

There are two requirements for a work interaction:

➢ there must be a force acting on the boundary

➢ the boundary must move

Therefore, the displacement of the boundary without any force to oppose or drive this motion (such as expansion of a gas into evacuated space) is not a work interaction, W=0.

Also, if there are no displacements of the boundary, even if an acting force exists, there will be no work transfer W = 0 (such as increasing gas pressure in a rigid tank).

Moving Boundary Work

The expansion and compression work is often called moving boundary work, or simply *boundary work*.

We analyze the moving boundary work for a quasi-equilibrium process. Consider the gas enclosed in a piston-cylinder at initial P and V. If the piston is allowed to move a distance *ds* in a quasi-equilibrium manner, the differential work is:

$$\delta W_b = F.ds = PAds = PdV$$

The quasi-equilibrium expansion process is shown in Fig. 4. On this diagram, the differential area *dA* under the process curve in P-V diagram is equal to *PdV*, which is the differential work.

Note: a gas can follow several different paths from state 1 to 2, and each path will have a different area underneath it (work is path dependent).

The net work or cycle work is shown in Fig. 5. In a cycle, the net change for any properties (point functions or exact differentials) is zero. However, the net work and heat transfer depend on the cycle path.

$$\Delta U = \Delta P = \Delta T = \Delta(\text{any property}) = 0 \qquad \text{for a cycle}$$
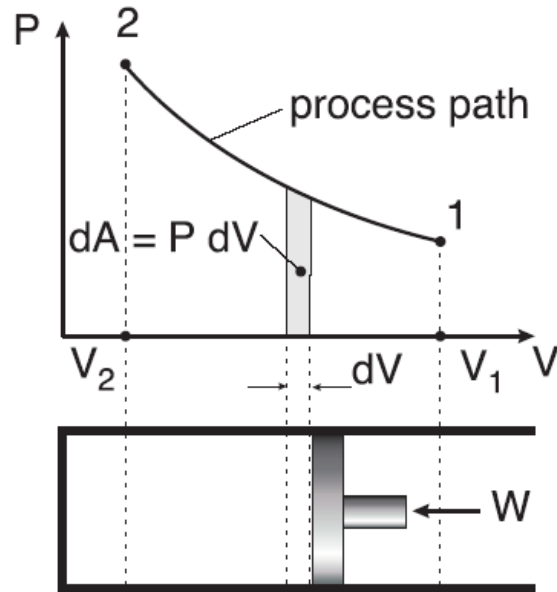
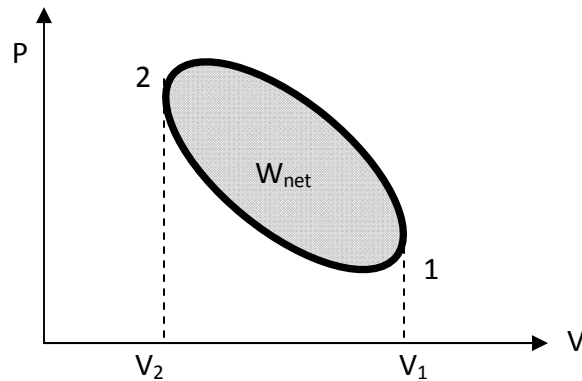Fig. 4: the area under P-V diagram represents the boundary work.

Fig. 5: network done during a cycle.

Polytropic Process

During expansion and compression processes of real gases, pressure and volume are often related by $PV^n=C$, where n and C are constants. The moving work for a polytropic process can be found:

$$W_{polytopic} = \int_1^2 PdV = \int_1^2 CV^{-n}dV = \frac{P_2V_2 - P_1V_1}{1-n}$$

Since $P_1V_1^n = P_2V_2^n = C$. For an ideal gas ($PV = mRT$) it becomes:

$$W_{polytropic} = \frac{mR(T_2 - T_1)}{1-n}, \quad n \neq 1 \quad (kJ)$$

The special case n =1 is the *isothermal* expansion $P_1V_1 = P_2V_2 = mRT_0 = C$, which can be found from:

$$W_{b,isothermal} = \int_1^2 PdV = \int_1^2 \frac{C}{V}dV = P_1V_1 \ln\left(\frac{V_2}{V_1}\right), \quad n = 1 \quad (kJ)$$

Since for an ideal gas, $PV = mRT_0$ at constant temperature T_0, or $P = C/V$.

Example 2: Polytropic work

A gas in piston-cylinder assembly undergoes a polytropic expansion. The initial pressure is 3 bar, the initial volume is 0.1 m³, and the final volume is 0.2 m³. Determine the work for the process, in *kJ*, if a) n=1.5, b) n=1.0, and c) n=0.

Solution:

Assume that i) the gas is a closed system, ii) the moving boundary is only work mode, and iii) the expansion is polytropic.

a) n =1.5

$$W = \int_{V1}^{V2} PdV = \frac{P_2V_2 - P_1V_1}{1-n}$$

We need P_2 that can be found from $P_1V_1{}^n = P_2V_2{}^n$:

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^n = (3bar)\left(\frac{0.1}{0.2}\right)^{1.5} = 1.06 \, bar$$

$$W = \left(\frac{(1.06bar)(0.2m^3) - (3)(0.1)}{1-1.5}\right)\left(\frac{10^5 \, N/m^2}{1 \, bar}\right)\left(\frac{1 \, kJ}{10^3 \, N.m}\right) = 17.6 \, kJ$$

b) n =1, the pressure volume relationship is PV = constant. The work is:

$$W = \int_1^2 PdV = P_1V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$W = (3bar)(0.1 \, m^3)\left[\frac{10^5 \, N/m^2}{1 \, bar}\right]\left(\frac{1 \, kJ}{10^3 \, N.m}\right)\ln\left(\frac{0.2}{0.1}\right) = 20.79 \, kJ$$

c) For n = 0, the pressure-volume relation reduces to P=constant (*isobaric process*) and the integral become W= P (V₂-V₁).

Substituting values and converting units as above, W=30 kJ.

Spring work

For linear elastic springs, the displacement x is proportional to the force applied:

$$F = k_s x$$

where k_s is the spring constant and has the unit *kN/m*. The displacement *x* is measured from the undisturbed position of the spring. The spring work is:

$$W_{spring} = \frac{1}{2} k_s \left(x_2^2 - x_1^2 \right) \quad (kJ)$$

Note: the work done on a spring equals the energy stored in the spring.

Non-mechanical forms of work

Non-mechanical forms of work can be treated in a similar manner to mechanical work. Specify a *generalized force F* acting in the direction of a *generalized displacement x*, the work transfer associated with the displacement *dx* is:

$$\delta W = F.dx$$

Example 3: Mechanical work

Calculate the work transfer in the following process:

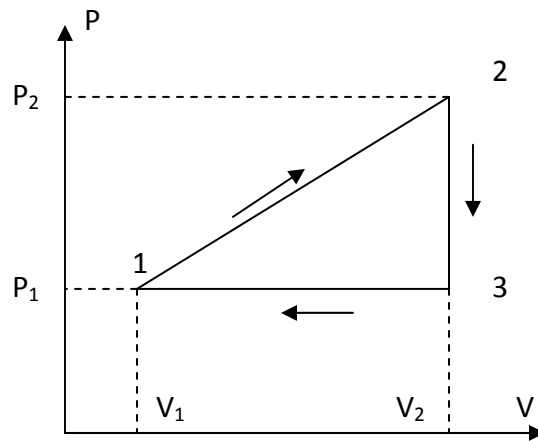
Fig. 6: Schematic P-V diagram for Example 3.

Solution:

Process 1-2 is an expansion ($V_2 > V_1$) and the system is doing work ($W_{12} > 0$), thus:

$W_{12} = P_1 (V_2 - V_1) + [0.5(P_1 + P_2) - P_1] (V_2 - V_1)$

$\quad = (V_2 - V_1) (P_1 + P_2) / 2$

Process 2 - 3 is an isometric process (constant volume $V_3 = V_2$), so $W_{23} = 0$

Process 3 - 1 is a compression ($V_3 > V_1$), work is done on the system, ($W_{31} < 0$)

$W_{31} = - P_1 (V_2 - V_1)$

$W_{cycle} = W_{net} = W_{12} + W_{23} + W_{31} = (V_2 - V_1)(P_2 - P_1) / 2$

Note that in a cycle $\Delta U = \Delta P = \Delta T = \Delta$(any property) = 0

First Law of Thermodynamics

First law, or the *conservation of energy principle*, states that energy can be neither created nor destroyed; it can only *change forms*.

The first law <u>cannot be proved mathematically,</u> it is based on *experimental* observations, i.e., there are no process in the nature that violates the first law.

The first law for a closed system or a fixed mass may be expressed as:

net energy transfer to (or from) = net increase (or decrease) in the total
the system as heat and work   energy of the system

$$Q - W = \Delta E \quad (kJ)$$

where

Q = net heat transfer $(= \Sigma Q_{in} - \Sigma Q_{out})$

W= net work done in all forms $(= \Sigma W_{in} - \Sigma W_{out})$

ΔE= net change in total energy $(= E_2 - E_1)$

The change in total energy of a system during a process can be expressed as the sum of the changes in its internal, kinetic, and potential energies:

$$\Delta E = \Delta U + \Delta KE + \Delta PE \quad (kJ)$$

$$\Delta U = m \left(u_2 - u_1 \right)$$

$$\Delta KE = \frac{1}{2} m \left(V_2^2 - V_1^2 \right)$$

$$\Delta PE = mg \left(z_2 - z_1 \right)$$

Note: for stationary systems *$\Delta PE = \Delta KE = 0$*, the first law reduces to

$$Q - W = \Delta U$$

The first law can be written on a unit-mass basis:

$$q - w = \Delta e \quad (kJ/kg)$$

or in *differential form*:

$$\delta Q - \delta W = dU \quad (kJ)$$

$$\delta q - \delta W = du \quad (kJ/kg)$$

or in the rate form:

$$Q° - W° = dE / dt \qquad (kW)$$

For a cyclic process, the initial and final states are identical, thus $\Delta E = 0$. The first law becomes:

$$Q - W = 0 \qquad (kJ)$$

Note: from the *first law* point of view, there is no difference between *heat transfer* and *work*, they are both *energy interactions*. But from the *second law* point of view, heat and work are *very different*.

Example 4: Fist law

Air is contained in a vertical piston-cylinder assembly fitted with an electrical resistor. The atmospheric pressure is 100 *kPa* and piston has a mass of 50 *kg* and a face area of 0.1 m^2. Electric current passes through the resistor, and the volume of air slowly increases by 0.045 m^3. The mass of the air is 0.3 kg and its specific energy increases by 42.2 kJ/kg. Assume the assembly (including the piston) is insulated and neglect the friction between the cylinder and piston, g = 9.8 m/s^2. Determine the heat transfer from the resistor to air for a system consisting a) the air alone, b) the air and the piston.
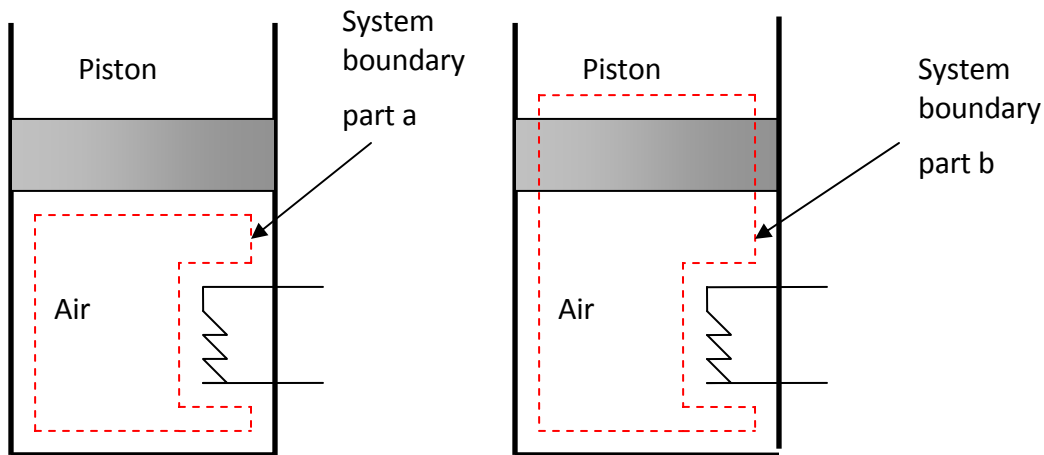

Fig. 7: Schematic for problem 4.

Assumptions:

➢ Two closed systems are under consideration, as shown in schematic.

➢ The only heat transfer is from the resistor to the air. $\Delta KE = \Delta PE = 0$ (for air)

➢ The internal energy of the piston is not affected by the heat transfer.

a) Taking the air as the system,

$$(\Delta KE + \Delta PE + \Delta U)_{air} = Q - W$$

$$Q = W + \Delta U_{air}$$

For this system work is done at the bottom of the piston. The work done by the system is (at constant pressure):

$$W = \int_{V1}^{V2} PdV = P(V_2 - V_1)$$

The pressure acting on the air can be found from:

$$PA_{piston} = m_{piston}\, g + P_{atm}\, A_{piston}$$

$$P = \frac{m_{piston}\, g}{A_{piston}} + P_{atm}$$

$$P = \frac{(50kg)(9.81m/s^2)}{(0.1m^2)}\left(\frac{1Pa}{1N/m^2}\right)\left(\frac{1kPa}{1000Pa}\right) + 100kPa = 104.91\ kPa$$

Thus, the work is

$$W = (104.91\ \text{kPa})(0.045\text{m}^3) = 4.721\ \text{kJ}$$

With $\Delta U_{air} = m_{air}\, \Delta u_{air}$, the heat transfer is

$$Q = W + m_{air}\, \Delta u_{air} = 4.721\ \text{kJ} + (0.3\ \text{kg})(42.2\ \text{kJ/kg}) = 17.38\ \text{kJ}$$

b) system consisting the air and the piston. The first law becomes:

$$(\Delta KE + \Delta PE + \Delta U)_{air} + (\Delta KE + \Delta PE + \Delta U)_{piston} = Q - W$$

where $(\Delta KE = \Delta PE)_{air} = 0$ and $(\Delta KE = \Delta U)_{piston} = 0$. Thus, it simplifies to:

$$(\Delta U)_{air} + (\Delta PE)_{piston} = Q - W$$

For this system, work is done at the top of the piston and pressure is the atmospheric pressure. The work becomes

$$W = P_{atm}\, \Delta V = (100\ \text{kPa})(0.045\text{m}^3) = 4.5\ \text{kJ}$$

The elevation change required to evaluate the potential energy change of the piston can be found from the volume change:

$$\Delta z = \Delta V / A_{piston} = 0.045\ \text{m}^3 / 0.1\ \text{m}^2 = 0.45\ \text{m}$$

$$(\Delta PE)_{piston} = m_{piston}\, g\, \Delta z = (50\ \text{kg})(9.81\ \text{m/s}^2)(0.45\ \text{m}) = 220.73\ \text{J} = 0.221\ \text{kJ}$$

$$Q = W + (\Delta PE)_{piston} + m_{air}\, \Delta u_{air}$$

$$Q = 4.5\ \text{kJ} + 0.221\ \text{kJ} + (0.3\ \text{kg})(42.2\ \text{kJ/kg}) = 17.38\ \text{kJ}$$

Note that the heat transfer is identical in both systems.

Specific Heats

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree. There are two kinds of specific heats:

> ➢ specific heat at constant volume, C_v (the energy required when the volume is maintained constant)

> ➢ specific heat at constant pressure, C_p (the energy required when the pressure is maintained constant)

The specific heat at constant pressure C_p is **always higher than** C_v because at constant pressure the system is allowed to expand and energy for this expansion must also be supplied to the system.

Let's consider a stationary closed system undergoing a constant-volume process ($w_b = 0$). Applying the first law in the differential form:

$$\delta q - \delta w = du$$

at constant volume (no work) and by using the definition of C_v, one can write:

$$C_v dT = du$$

$$or$$

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Similarly, an expression for the specific heat at constant pressure Cp can be found. From the first law, for a constant pressure process ($w_b + \Delta u = \Delta h$). It yields:

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

> ➢ specific heats (both C_v and C_p) are properties and therefore independent of the type of processes.

> ➢ C_v is related to the changes in *internal energy u,* and C_p to the changes in *enthalpy, h*.

It would be more appropriate to define: C_v is the change in specific internal energy per unit change in temperature at constant volume. C_p is the change in specific enthalpy per unit change in temperature at constant pressure.

Specific heats for ideal gases

It has been shown mathematically and experimentally that the internal energy is a function of temperature only.

$$u = u(T)$$

Using the definition of enthalpy ($h = u + Pv$) and the ideal gas equation of state ($Pv = RT$), we have:

$$h = u + RT$$

Since R is a constant and u is a function of T only:

$$h = h(T)$$

Therefore, at a given temperature, u, h, C_v and C_p of an ideal gas will have fixed values regardless of the specific volume or pressure. For an ideal gas, we have:

$$du = C_v(T) dT$$
$$dh = C_p(T) dT$$

The changes in internal energy or enthalpy for an ideal gas during a process are determined by integrating:

$$\Delta u = u_2 - u_1 = \int_1^2 C_v(T) dT \qquad (kJ/kg)$$

$$\Delta h = h_2 - h_1 = \int_1^2 C_p(T) dT \qquad (kJ/kg)$$

As low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only. The specific heats of real gases at low pressures are *called ideal-gas specific heats (*or *zero-pressure specific heats)* and are often denoted by C_{p0} and C_{v0}. To carry out the above integrations, we need to know $C_v(T)$ and $C_p(T)$. These are available from a variety of sources:

➢ Table A-2a: for various materials at a fixed temperature of T = 300 K

➢ Table A-2b: various gases over a range of temperatures 250 ≤ T ≤ 1000 K

➢ Table A-2c: various common gases in the form of a third order polynomial

For an ideal gas, we can write:

$$RT = h(T) - u(T)$$
$$R = \frac{dh}{dT} - \frac{du}{dT}$$
$$R = C_p - C_v$$

The ratio of specific heats is called the *specific heat ratio $k = C_p/C_v$*:

➢ varies with temperature, but this variation is very mild.

➢ for monatomic gases, its value is essentially constant at 1.67.

➢ Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

Specific heats for solids and liquids

A substance whose specific volume (or density) is constant is called *incompressible substance*. The specific volumes of solids and liquids (which can be assumed as incompressible substances) essentially remain constant during a process.

The constant volume assumption means that the volume work (boundary work) is negligible compared with other forms of energy. As a result, it can be shown that the constant-volume and constant-pressure specific heats are identical for incompressible substances:

$$C_p = C_v = C$$

Specific heats of incompressible substances are only a function of temperature,

$$C = C(T)$$

The change of internal energy between state 1 and 2 can be obtained by integration:

$$\Delta u = u_2 - u_1 = \int_1^2 C(T)\,dT \qquad (kJ/kg)$$

For small temperature intervals, a C at averaged temperature can be used and treated as a constant, yielding:

$$\Delta u \approx C_{ave}(T_2 - T_1)$$

The enthalpy change of incompressible substance can be determined from the definition of enthalpy *(h = u + Pv)*

$$h_2 - h_1 = (u_2 - u_1) + v(P_2 - P_1)$$

$$\Delta h = \Delta u + v\Delta P \quad (kJ/kg)$$

The term *vΔP* is often small and can be neglected, so *Δh = Δu*.

Example 5: Specific heat and first law

Two tanks are connected by a valve. One tank contains 2 kg of CO_2 at 77°C and 0.7 bar. The other tank has 8 kg of the same gas at 27°C and 1.2 bar. The valve is opened and gases are allowed to mix while receiving energy by heat transfer from the surroundings. The final equilibrium temperature is 42°C. Using ideal gas model, determine a) the final equilibrium pressure b) the heat transfer for the process.

Assumptions:

➢ The total amount of CO_2 remains constant (closed system).

➢ Ideal gas with constant C_v.

➢ The initial and final states in the tanks are equilibrium. No work transfer.
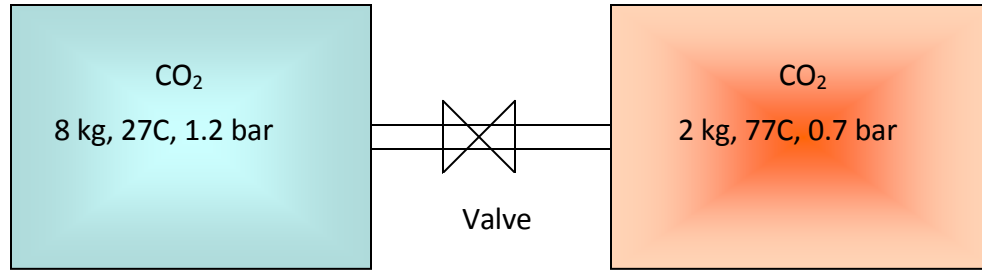
The final pressure can be found from ideal gas equation of state:

$$P_f = \frac{m_t RT_f}{V_1 + V_2} = \frac{(m_1 + m_2)RT_f}{V_1 + V_2}$$

For tank 1 and 2, we can write: $V_1 = m_1 RT_1/P_1$ and $V_2 = m_2 RT_2/P_2$. Thus, the final pressure, P_f becomes:

$$P_f = \frac{(m_1 + m_2)RT_f}{\left(\frac{m_1 RT_1}{P_1}\right) + \left(\frac{m_2 RT_2}{P_2}\right)} = \frac{(m_1 + m_2)T_f}{\left(\frac{m_1 T_1}{P_1}\right) + \left(\frac{m_2 T_2}{P_2}\right)}$$

$$P_f = \frac{(10kg)(315K)}{\frac{(2kg)(350K)}{0.7bar} + \frac{(8kg)(300K)}{1.2bar}} = 1.05 bar$$

b) The heat transfer can be found from an energy balance:

$$\Delta U = Q - W$$

With W = 0,

$$Q = U_f - U_i$$

where initial internal energy is: $U_i = m_1 u(T_1) + m_2 u(T_2)$

The final internal energy is: $U_f = (m_1 + m_2) u(T_f)$

The energy balance becomes:

$$Q = m_1 [u(T_f) - u(T_1)] + m_2 [u(T_f) - u(T_2)]$$

Since the specific heat C_v is constant

$$Q = m_1 C_v [T_f - T_1] + m_2 C_v [T_f - T_2]$$

$$Q = (2kg)\left(0.745\frac{kJ}{kg.K}\right)(315K - 350K) + (8kg)\left(0.745\frac{kJ}{kg.K}\right)(315K - 300K) = 37.25kJ$$

The plus sign indicates that the heat transfer is *into the system*.