Chapter 3

Thermodynamics - Introduction and the First law

"A law is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. (..) It is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown." A. Einstein

Thermodynamics may be rightfully regarded as the crown jewel of theoretical sciences with reach and applications to every branches of physical, chemical, biological and engineering sciences. It may appear somewhat strange that such a universal theory grew out of a fairly mundane subject of estimating efficiency of a heat engine. Thermodynamics was developed between 1800-1850 during industrial revolution in Europe. This was just after James Watt perfected the steam engine in 1770-s. The subject grew out of the challenge as to how to get maximum amount of work done by spending minimum amount of heat.

Thermodynamics may be described in terms three laws, which in turn gave rise to our everyday concepts of internal energy, entropy, free energy, specific heat. In this and the next chapter, we present the developments of thermodynamics, both from a historical and conceptual basis. Our approach will be direct and minimalistic.

1. **Thermodynamics deals with inter-conversion of energies**

Thermodynamics, as the name suggests, deals with the inter-conversion of heat and mechanical work. In a machine (engine), the system absorbs heat to do work. The question is whether the work done (W) by a machine could be greater, equal or less than the heat absorbed (Q). The task of thermodynamics was to answer these questions. In a steam engine, heat is obtained from chemical energy (through burning of coal).

$$C + O_2 = CO_2 + \text{Heat}$$

In human body, the source of heat is the burning of carbohydrates (glucose, $C_6H_{12}O_6$).

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6\ H_2O + \text{Heat}$$

Thus thermodynamics also addresses conversion of chemical energy into heat. The discovery of electricity and magnetism by Michael Faraday (1791–1867), expanded the scope of the

James Watt, (1736-1819), a mechanical engineer, played a major role in ushering in the *Industrial Revolution*. He was not the first to invent the steam engine. He invented the most efficient steam engine. Since 1759, he started improving the Newcomen Engine (developed in 1712 by Thomas Newcomen). Watt obtained several patents on his engine between 1781 and 1784.

Sadi Carnot, (1796-1832), who lived for only 36 years, is often regarded as the *father of thermodynamics*. He was a French military engineer and physicist. In 1824, he published only one monograph, "*Reflections on the Motive Power of Fire*." Carnot gave the first successful theory of the maximum efficiency of heat engines. Carnot's work received little attention during his lifetime.

James Joule (1818-1889), first demonstrated the heating effect of electric current. This contradicted Lavoisier's caloric theory (that *heat can neither be created nor destroyed*) and hence, Joule faced severe criticism. Undaunted, Joule carried out a series of precise measurements, to establish the concept of inter-conversion of energy and mechanical equivalent of heat. This led to the law of conservation of energy and first law of thermodynamics.

subject. Conversion of chemical energy into electrical energy became part of thermodynamics. Eventually, thermodynamics started dealing with inter-conversion of all forms of energy.

1. Thermodynamics tells us what is possible

Thermodynamics goes much beyond mere conversion of energies. It tells us what is possible or not. For instance, we know burning a carbohydrate (glucose or cellulose in paper) into

CO_2 and water is easy and can be done also outside our body (you can burn glucose in a gas burner). But can we do the opposite process namely, absorb CO_2 and water from air and convert it into glucose? As you will see later, thermodynamics says it is not possible. If that be the case, how come the plants do it all the time during photosynthesis? Again note, glucose or paper does not burn in the presence of oxygen at room temperatures. Why do we have to heat them?

Such questions are, perhaps, the most important issues (food and energy) facing human civilizations at all times. This is why a solid foundation of thermodynamics is needed to solve fundamental issues in all scientific subjects irrespective of the discipline.

3.3 Thermodynamics is a logical and axiomatic science like geometry

Thermodynamics is, in certain sense, similar to geometry. Geometry is based on a few axioms (e.g. two parallel lines cannot cross). All theorems or other propositions are derived or disproved on the basis of these axioms. In thermodynamics, there are three laws (plus the zeroth law which defines temperature) that serve as axioms. Anything which violates these three laws is not possible. It is therefore, essential to learn the laws, logic and language of thermodynamics. We begin with the concept of temperature and Zeroth Law.

Zeroth Law: *If two bodies are at thermal equilibrium i.e. there is no net heat flow between them, they must have identical value of one property. This property is known as temperature.*

4. System and Surrounding

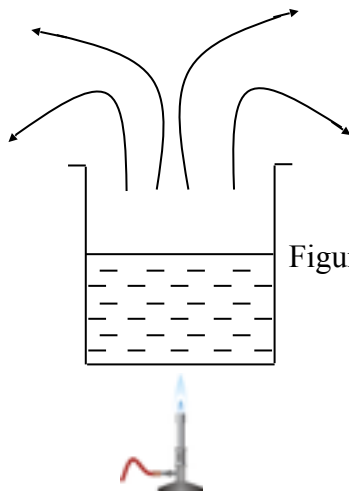These terms have definite meaning in thermodynamics and it is important to be precise about them.

Figure 3.1 A thermodynamic system

Let us consider a beaker containing water being heated by a gas burner. In this case our system is the beaker containing water (Fig. 3.1). It is getting heat from outside (i.e. the gas burner). As the water is getting heated water vapors escape our system and go outside. We call this outside world as surrounding. *To be precise, a system is that part of the universe*

which is under our consideration. The rest of the universe is surrounding. We thus describe this demarcation as follows,

System + Surrounding = Universe

Or, **Surrounding = Universe – System**

The system could vary from a small test tube containing a little water to as big as an entire galaxy containing many stars. Astrophysicists like S. Chandrasekhar (1910-1995) dealt with the latter systems.

If the system can exchange matter (mass) with the surrounding we call it an *open system*. An open beaker containing water is an open system because the vapors can escape to surrounding. If the system cannot exchange mass with surrounding (e.g. a sealed container) we call it a *closed system*. A system is called *isolated* if it can exchange neither matter nor energy with its surrounding.

4. Thermodynamic Variables and State of a System

Thermodynamics involves most macroscopic properties of a system. All these properties depend on four fundamental properties- pressure (P), volume (V), temperature (T) and mass (or number of moles, n). These four fundamental properties are called thermodynamic variables. A set of values of these four properties define a given *thermodynamic state* of the system. Thus (P_1, V_1, T_1, n_1) and (P_2, V_2, T_2, n_2) describes two different thermodynamic states. Any thermodynamic property, X, is a function of these four variables and may be written as,

$X = f(P, V, T, n)$ (1)

So that,

$$(2)$$

Properties like V that depends on mass are called *extensive property*. Those (e.g. P and T) which do not depend on mass are called *intensive property*.

The number of variables reduces if there is a relation between the four thermodynamic variables. A relation between these four variables is called an *equation of state*. For a gas, there are several equations of state. For instance, for an ideal gas the equation of state is PV=nRT. Such an equation of state can be complex for solids and liquids. This is the reason why most of the thermodynamic issues are explained in terms of gases (in particular, ideal gases) because the mathematical formulation is lot easier. *Sometimes this conveys a wrong impression that thermodynamics applies only to ideal gas*! *It is important to remember that thermodynamics applies to all kinds of gas, liquid and solid.*

5. First Law of Thermodynamics: Concept of Internal Energy, E

The first law of thermodynamics is essentially conservation of energy and may be stated as follows,

Energy can neither be created nor be destroyed but can be converted into other forms of energy.

Let us consider that a system absorbs Q amount of heat from surrounding and does W amount of work. Then according to the first law the difference of Q and W must be stored inside the system in some form of energy. This is called the internal energy (E). Thus

$$dE = Q-W \qquad (3)$$

E is a property of the state and is a function of (P, V, T, n). In other words, E is a state function whose value depends on the values of P, V, T and n. We will see in the next section that Q and W is not a state function and their values depend on the path i.e. how the state changes.

It helps to remember that dE is the change in internal energy which is a state function. When work is done on the system, internal energy increases and contribution of W must be positive. On the other hand, when work is done by the system, W is negative as dE must be negative.

6. Path: Reversible and Irreversible

When a system goes from one state (P_1, V_1, T_1, n_1) to another state (P_2, V_2, T_2, n_2) there are multitude of ways in which the state variables (P,V,T and n) may change. A thermodynamic path is defined as the way the values of P, V, T and n changes in a four dimensional space. We will now show that the amount of work done depends on whether the change or path is reversible or irreversible.

A reversible process is defined as the one that can be reversed easily. By necessity, this path is a sum of infinitesimal changes in the external conditions. An irreversible process, on the contrary, cannot be reversed by infinitesimal change in the external condition.

(a). High jump, irreversible   (b). Stairs, reversible
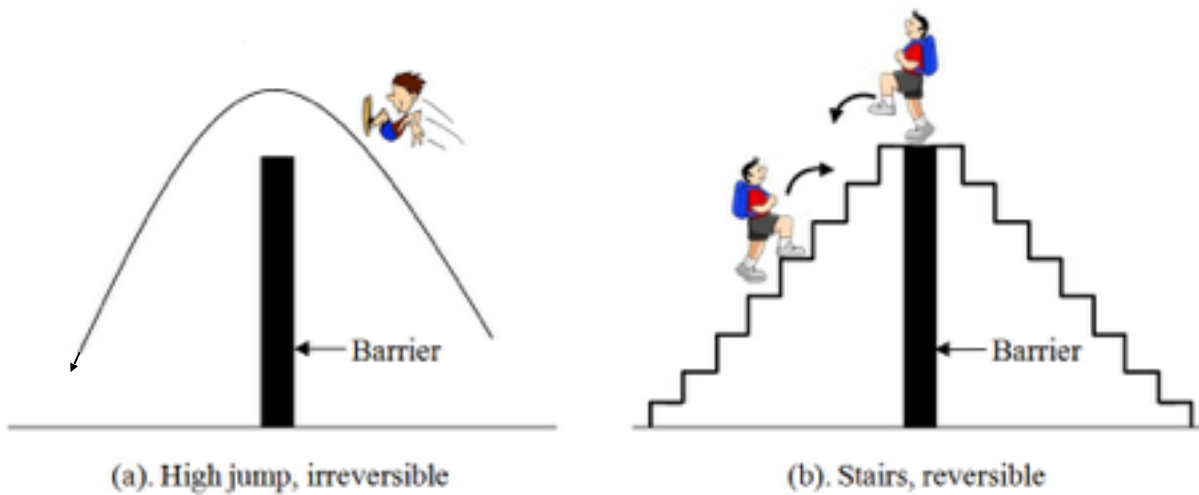
To understand this let us consider crossing of a 2 meter barrier. An athlete will cross it by making

a high jump (Fig. 3.2a). But he cannot change the direction of his motion at any point of his path.

On the other hand, if we place a stair case one can reverse the direction of motion at any point

during crossing the barrier (fig. 3.2b). For a truly reversible process, the height of each stair is

infinitesimally small.

3.6.1 Work done by expansion of a gas

Let us now calculate the work done in going from (P_1, V_1, T_1, n_1) to another state (P_2, V_2, T_2, n_2).

Let us consider that the gas is confined in closed cylinder by a piston of area A and external

pressure P_{ext} , with $P_{ext} < P_{int}$ (internal pressure). Obviously the gas will expand until the internal
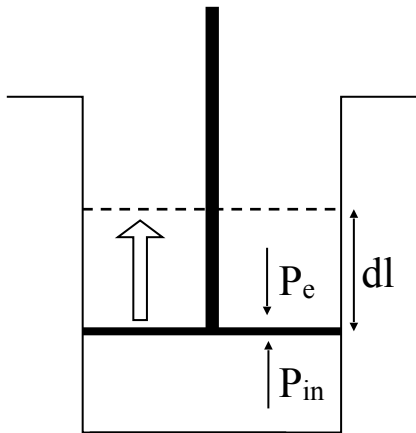
pressure decreases to be equal to external pressure.

Figure 3.3 Work done by expansion of a gas

Force on the gas F= pressure x area = P_{ext} x A

If the piston moves over a small distance dl, work done

$$dW = Fdl = P_{ext} Adl = P_{ext} dV \qquad (4)$$

Where dV = A dl.

a)   **Irreversible Work**

In the case of an irreversible process, the external pressure (P_{ext}) is kept constant and the gas expands in one step. Thus for an irreversible process, we can take the constant P_{ext} out of the integration sign as follows

$$W_{irrev} = \int dW = \int P_{ext} dV = P_{ext} \int dV = P_{ext}(V_2 - V_1) \tag{5}$$

Obviously, the external pressure will be equal to the final pressure so that $P_{ext}=P_2$. Thus,

$$W_{irrev} = P_2(V_2 - V_1) \tag{6}$$

b) Reversible Work

In a reversible process, the external pressure is not constant. The whole expansion is carried out in multiple small steps each time decreasing the external pressure by a small amount. This ensures that the process can be reversed by slight change in external pressure. In this case,

$$P_{ext} \approx P_{int} \tag{7}$$

Thus the for an reversible process

$$W_{rev} = \int dW = \int P_{ext} dV \approx \int P_{int} dV \tag{8}$$

The arguments presented so far is applicable to all gas, liquid and solid. We will now assume, for mathematical simplicity, that the system is one mole of an ideal gas so that

$$P_{int} V = RT$$,

so that $P_{int} = \dfrac{RT}{V}$ (9)

Substituting the value of P_{int} from equation (9) into equation (8) we get

$$W_{rev} = \int \left(\frac{RT}{V} \right) dV \quad (10)$$

We now make a further assumption that the process is isothermal i.e. temperature does not change during expansion. Thus $T_1 = T_2 = T$ (let).

Then equation (10) simplifies to

$$W_{rev} = RT \ln \left(\frac{V_2}{V_1} \right) \quad (11)$$

Under this condition i.e. isothermal expansion of an ideal gas from equation (6) for an irreversible process.

$$W_{irrev} = P_2 \left(V_2 - V_1 \right) = \frac{RT}{V_2} \left(V_2 - V_1 \right) \quad (12)$$

Problem 1. Using equations (11) and (12) show that $W_{rev} > W_{irrev}$.

From equations (11) and (12) it is obvious that work done in going from state (P_1, V_1, T) to (P_2, V_2, T) depends on the path and is different for reversible and irreversible processes. Difference in internal energy E between these two states are constant because E is state

function. Thus from equation (3) as dE is constant and W is path dependent, the heat absorbed Q=dE + W also depends on path.

In summary, Q and W are both path functions and depend on the path, but they combine via Eq.3 to produce a state function. This is the main outcome of the first law. It is utmost important to realize that work done by reversible and irreversible processes are different.

4. Heat Absorbed at constant volume is equal to dE

From equation (3)

$$dE = dQ - dW = dQ - P_{ext}dV \qquad (13)$$

in this equation we used a different symbol for change in Q and W to emphasize that they are path functions. If the change takes place at constant volume, dV=0. Then (15) reduces to

$$dE_V = dQ_v \qquad (14)$$

Here, the subscript, *V*, implies that the process takes place at constant volume. Eq.14 is an important conclusion. It says, if a process is *isochoric* (i.e constant volume) then the heat absorbed is equal to change in internal energy.

In general, heat absorbed in a process is equal to heat capacity, C (amount of heat needed to raise temperature by one degree) multiplied by change in temperature (dT).

$$dQ = CdT \qquad (15)$$

From (14) and (15)

$$dE_V = C_V \, dT \qquad\qquad (16)$$

The above equation may be rewritten as

$$\left(\frac{\partial E}{\partial T} \right)_V = C_V \qquad\qquad (17)$$

Equation (17) is an important and highly useful relation of thermodynamics. Note further the conclusions described by equations (15) and (17) are valid for all systems (gas, liquid or solid).

5. Concept of Enthalpy (H) as the Heat Absorbed at Constant Pressure

We just discussed the important result that the change in internal energy becomes equal to heat absorbed when the process occurs at constant volume. However, most chemical reactions and also physical transformations, occur under constant pressure and volume does not remain constant. Therefore, we need to know which thermodynamic function represents the heat absorbed at constant pressure. This turns out to be an important state function, termed enthalpy. We define enthalpy, H as follows

$$H = E + PV \qquad (18)$$

Obviously,

$$dH = dE + PdV + VdP \qquad (19)$$

For constant pressure, $dP=0$ and $P_{ext}=P_{int}=P$ so that

$$dH = dE + PdV$$

Now, PdV is the mechanical work due to volume change, and $PdV = dW_P$.

Thus using equation (3) we obtain

$$dH = dE + dW_p = dQ_P \qquad (20)$$

This is another important relation. It says that for an *isobaric* process (i.e. constant pressure) the heat change is equal to change in enthalpy. If dH_P ($=dQ_P$) is positive heat is absorbed by the system and the process or chemical reaction is *endothermic*. On the other hand, if dH_P ($=dQ_P$) is negative heat is released by the system and the process or chemical reaction is *exothermic*. In analogy to equations (15) to (17) one can write,

$$dH_P = C_p \, dT \qquad (21)$$

and $\left(\dfrac{dH}{dT} \right)_P = C_P \qquad (22)$

Where, C_P denotes heat capacity at constant pressure. Again note, equations (21) and (22) are applicable to solid, liquid and gases.

9. Relation between C_P and C_V

Since E is a state function, it depends on P, V, T and mass. Thus one can write for constant mass,

$$E=f(P, V, T, n) \quad (23)$$

For a fixed mass, n is constant. Thus

$$E= f(P,V,T) \quad (24)$$

At constant pressure,

$$E= f(T,V)$$

Thus $\quad\quad dE= (dE/dT)_V \, dT + (dE/dV)_T \, dV \quad (25)$

Then using equation (17) we obtain

$$dE= C_V dT + (dE/dV)_T \, dV \quad (26)$$

From equation (13) we obtain

$$dQ= dE + P_{ext} \, dV= C_V dT + (dE/dV)_T \, dV + P_{ext} \, dV \quad (27)$$

At constant pressure, $P_{ext} = P$, equation (27) may be rewritten as

$$dQ_P = C_V dT + [P + (dE/dV)_T]\, dV \qquad (28)$$

We divide both sides by dT and noting P is constant

$$C_P = (dQ/dT)_P = C_V + [P + (dE/dV)_T]\, (dV/dT)_P \qquad (29)$$

Except in the case of anomalous expansion of water between 0^0-4^0C for all materials with increase in temperature volume increases and hence, $(dV/dT)_P > 0$

Thus,

$$C_P > C_V \qquad\qquad\qquad (30)$$

The above inequality is valid universally and also from fundamental theory of thermodynamic fluctuations. Energy fluctuations are larger at constant pressure than at constant volume. However, this discussion is beyond the scope of this chapter.

10. Value of $(dE/dV)_T$ for an ideal gas: Joule's Law

In order to determine $(dE/dV)_T$ for an ideal gas, James Joule (1818-1889) carried out a careful experiment in 1840s (fig).

Thermometer
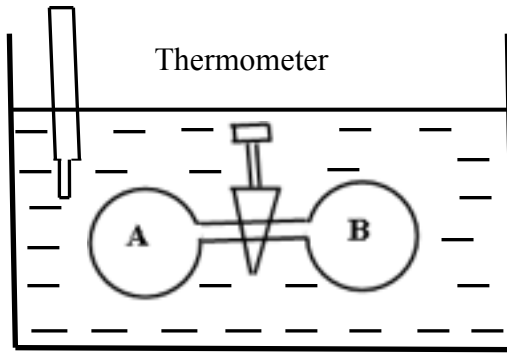
The apparatus consists of two vessels A and B connected by stop cock. Joule filled A with an ideal gas and evacuated B so that in B, pressure P=0. He then immersed the apparatus in reservoir of water. He opened the stopcock suddenly so that the gas in A undergoes irreversible expansion against zero pressure (P_{ext}=0). Under this condition equation 27 becomes

$$dQ = C_V dT + (dE/dV)_T \, dV \qquad (31)$$

Joule very carefully measured the temperature of the water in the reservoir and found that there is no change in the temperature ! That is, dQ=0 and dT=0.

Let us analyze this result in more detail. If both dQ and dT are zero in equation (31), we have

$$(dE/dV)_T \, dV = 0$$

Since $dV \neq 0$, we have the result that

$$(dE/dV)_T = 0 \qquad\qquad (32)$$

Equation (32) provides a mathematical definition of an ideal gas. According to equation (32) *for an ideal gas there is no change in internal energy when an ideal gas expands (dV>0) at constant temperature*. This is known as the *Joule's Law*.

This is clearly due to the absence of inter-molecular attraction in an ideal gas. *Thus no external energy is needed to be supplied to increase distance between the molecules during expansion.*

However, for all materials (real gas, liquid and solid) there is appreciable inter-molecular attraction. Thus for real systems, energy needs to be supplied for expansion if temperature to be kept constant. If we do not supply energy from outside during expansion the system will have to do work against the attractive force and this will result in a decrease in E and in temperature. In summary, for systems having intermolecular attraction

$$(dE/dV)_T > 0 \qquad\qquad (33)$$

11. Relation between C_P and C_V for an ideal gas

We just discussed that for an ideal gas,

$$(dE/dV)_T = 0$$

Further, for one mole of an ideal gas, PV=RT, so that $(dV/dT)_P = R/P$ (34)

Thus from equation (29), we obtain for one mole of an ideal gas

$$C_P = C_V + R \qquad (35)$$

$$\text{Or, } C_P - C_V = R.$$

The ratio of C_P and C_V is known as γ,

$$\gamma = C_P/C_V \qquad\qquad (36)$$

Since $C_P > C_V$,

$$\gamma > 1$$

12. Adiabatic processes

An adiabatic process is defined as one which does not involve exchange of heat with surrounding i.e. dQ=0. For an adiabatic process the system is thermally insulated from the surrounding. Otherwise the process is done is very quickly (suddenly) so that there is no time for heat flow. Thus for an adiabatic process, equation is written as

$$dE=-dW \qquad (37)$$

for ideal gas $dE=C_v\,dT$ so that (35) becomes

$$dW= -C_v dT \qquad (38)$$

For expansion of an ideal gas $dW=P_{ext}dV>0$. Then from equation (36) $dT<0$. Thus during an adiabatic expansion, temperature of an ideal gas decreases. Conversely, during adiabatic compression, temperature of an ideal gas increases.

13. Reversible adiabatic process for an ideal gas: PV^γ=constant

Let us consider one mole of an ideal gas undergoing a reversible adiabatic change from state (P_1,V_1,T_1) to (P_2,V_2,T_2). We use the formula for reversible work (with $P_{ext}=P_{int}$) in equation (38) to obtain

$$P_{int}\,dV =- C_v dT \qquad (39)$$

For one mole of an ideal gas equation, $P_{int}=RT/V$. Therefore, (39) becomes

$$RdV/V=-C_v dT/T \qquad (40)$$

Integrating equation (40) from initial state (V_1,T_1) and final state (V_2,T_2)

$$R\ln(V_2/V_1)= -C_v\ln(T_2/T_1)= C_v\ln(T_1/T_2)$$

Or, $(V_2/V_1)^R = (T_1/T_2)^{C_v}$

Or, $(T_1/T_2) = (V_2/V_1)^{R/C_v} \qquad (41)$

Since $R = C_P - C_V$, and from equation (34) $R/C_V = \gamma - 1$,

Thus from (41)

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad (42)$$

For ideal gas $T_1 = P_1 V_1 / R$ and $T_2 = P_2 V_2 / R$

Thus from equations (41) and (42), we obtain

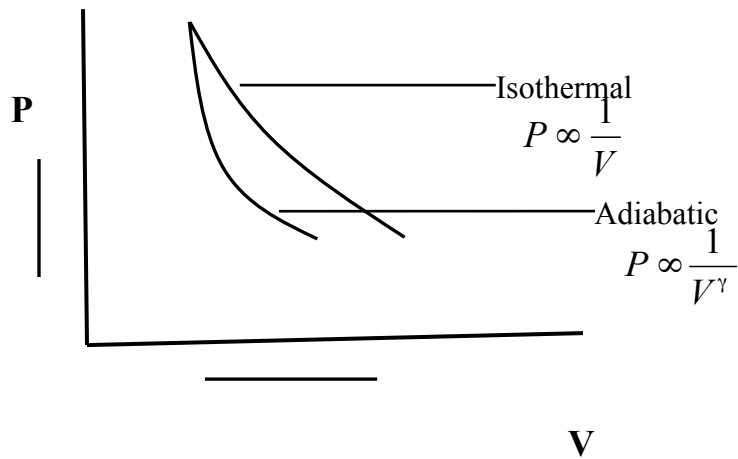$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \qquad (43)$$

Thus for a reversible adiabatic process of one mole of an ideal gas

$$PV^{\gamma} = constant \qquad (44)$$
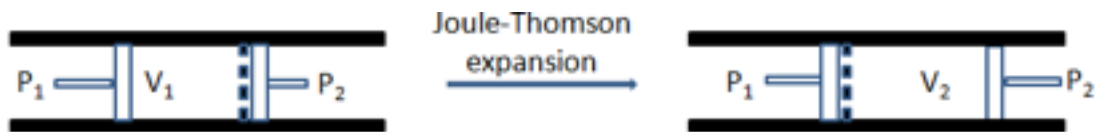
On the other hand, at constant temperature (i.e. for an isothermal process) for an ideal gas, according to Boyle's Law,

$$PV = Constant \qquad (45)$$

According to equation (44) for an adiabatic process, P is inversely proportional to V^{γ} and from equation (45) for an isothermal process, P is inversely proportional to V. In both cases, P decreases with increase in V. However, since $\gamma > 1$, P decreases faster in the case of adiabatic process. The P-V curve for an ideal gas in the two cases are shown in figure ?.

The graph shows curves with labels:

Isothermal $P \propto \dfrac{1}{V}$

Adiabatic $P \propto \dfrac{1}{V^{\gamma}}$

with axes P (vertical) and V (horizontal).

14. Joule-Thompson expansion: An iso-enthalpic process

Joule-Thomson expansion

P_1 — V_1 — P_2 → P_1 — V_2 — P_2

In 1852, James Joule and William Thomson (also known as Lord Kelvin, 1824-1907) carried out an important experiment on irreversible adiabatic expansion of a gas through a porous wall ("throttling"). For most gases, this causes substantial cooling of a gas resulting in liquefaction of gases. In this experiment, a gas is confined in a thermally insulated chamber and held on one side by a piston of pressure P_1 against a

porous wall. On the other side of the wall there is another piston of pressure P_2 with $P_2 < P_1$. Let the initial volume is V_1. The left piston rapidly and irreversibly pushes the gas through the hole into the other chamber so that the final volume of the gas is zero in the left chamber.

Thus the irreversible work done by left piston is $W_L = P_{ext}(0-V1) = -P_1 V_1$ (44)

In the case of the right piston, $P_{ext} = P_2$, initial volume is zero and final volume is V_2.

Thus the work done on the right piston

$W_R = P_2(V_2-0) = P_2 V_2$ (46)

Thus the total work done is

$W = W_L + W_R = P_2 V_2 - P_1 V_1$ (47)

Let the initial internal energy of the gas is E_1 and final internal energy is E_2 so that

change in internal energy $= E_2 - E_1$ (48)

From equation (3) since for Joule-Thompson process is adiabatic, $Q=0$,

Thus $dE = -W$ and hence from equations (47) and (48) we get

$E_2 - E_1 = P_2 V_2 - P_1 V_1$

Or, $E_2 + P_2 V_2 = E_1 + P_1 V_1$

Or, $H_2 = H_1$ (49)

In other words, final enthalpy equals initial enthalpy. Thus, during Joule-Thompson expansion enthalpy remains constant i.e. the process is iso-enthalpic. Note that this conclusion is valid irrespective of whether the gas is real or ideal.

In Joule-Thompson expansion change in pressure, $dP=P_2-P_1<0$ i.e. negative. The change in temperature dT depends on the overall sign of the Joule-Thompson coefficient, μ_{JT} which is defined as,

$$\mu_{JT}= (d\mathrm{T}/d\mathrm{P})_{\mathrm{H}} \qquad (50)$$

The subscript *H* indicates the iso-enthalpic condition. Evidently, dT is negative if $\mu_{JT}>0$ (i.e. positive) and this results in cooling of the gas. if $\mu_{JT}<0$ (i.e. negative), dT is positive and as a result heating occurs during Joule-Thompson expansion. The value of μ_{JT} depends on the nature of the gas and the initial temperature.

At room temperature, for hydrogen and oxygen Joule-Thompson expansion causes tremendous increase in temperature leading to explosion. However, if hydrogen and oxygen are initially cooled down below a certain temperature (called *inversion temperature*) they also cool like all other gases during Joule-Thompson expansion. We will later derive an expression for the value of if μ_{JT}.

15. Carnot Cycle: Efficiency of an engine

An engine converts absorbed heat into useful work. In an engine, the system undergoes a cyclic process in which the final state is same as the initial state so that there is no change in the system, and the cycle is repeated. If such a cyclic machine absorbs Q amount of heat and does W amount of work, the efficiency (ε) is defined as,

$$\varepsilon = W/Q \qquad\qquad (51)$$

Naturally one aims for an engine with high efficiency. Ideal case will be an engine with efficiency unity but that is not possible. But one can look for an engine with *maximum efficiency.* Such a machine was conceived by Sadi Carnot (1796 –1832).

In Carnot cycle, the system consists of one mole of an ideal gas. It undergoes, following four *reversible* steps.

a) **Reversible isothermal expansion** at temperature T_1 from the state A (P_1, V_1, T_1) to the state B (P_2, V_2, T_1).

For this reversible step, work done, $W_1 = RT_1 \ln(V_2/V_1)$ $\qquad\qquad$ (52)

Since the system is an ideal gas, $dE = C_v dT = 0$

As a result, heat absorbed $Q_1 = dE + W_1 = W_1 = RT_1 \ln(V_2/V_1)$ $\qquad$ (53)

The heat (Q_1) is supplied by a *source* (called a heat reservoir or bath) which is so large that its temperature (T_1) does not change after the transfer (fig).
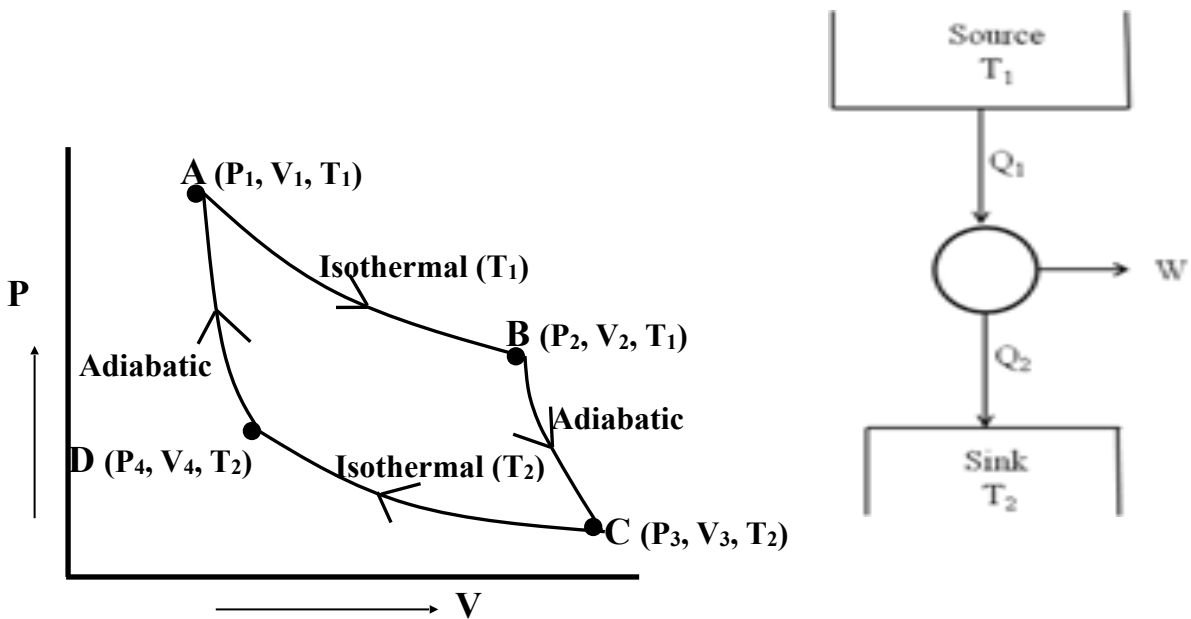
b) In the next step, the system under goes **reversible adiabatic expansion** during which the temperature drops from T_1 to T_2 as the system goes from state B (P_2,V_2,T_1). to state C (P_3,V_3,T_2). In this case, Q=0 so that,

Work done $W_2 = -dE = -C_v(T_2-T_1)$ (54)

For this adiabatic process, $T_1 V_2{}^{\gamma-1} = T_2 V_3{}^{\gamma-1}$

Or, $T_1/T_2 = (V_3/V_2)^{\gamma-1}$ (55)

c) The third step is **reversible isothermal compression** at temperature T_2 from the state C (P_3, V_3, T_2) to the state D (P_4, V_4, T_2).

In this step, work done, $W_3 = RT_2 \ln(V_4/V_3)$ (56)

Since the system is an ideal gas, $dE = C_v dT = 0$

As a result, heat absorbed $Q_2{}' = dE + W_3$

$$= RT_2 \ln(V_4/V_3) = -RT_2 \ln(V_3/V_4)   (57)$$

Since $V_3 > V_4$, Q_2 is negative i.e. heat is given out from system. In this case the heat is given to a *sink* (a heat reservoir). Let us write the heat released

$$Q_2 = -Q_2{}' = -W_3   (58)$$

d) In the fourth step, the system undergoes **reversible adiabatic compression** when temperature decreases from T_2 to T_1 and the system goes from D (P_4,V_4,T_2) back to initial state A(P_1,V_1,T_1). In analogy to equation (55)

$$W_4 = -dE = +C_v(T_2-T_1) \qquad (59)$$

While from equation (55), $T_2V_4^{\gamma-1} = T_1V_1^{\gamma-1}$

Or, $\qquad\qquad\qquad\qquad T_1/T_2 = (V_4/V_1)^{\gamma-1} \qquad (60)$

From (55) and (60), $(V_3/V_2)^{\gamma-1} = (V_4/V_1)^{\gamma-1}$,

Or $\qquad\qquad\qquad (V_3/V_4) = (V_2/V_1) \qquad (61)$

The total work done in the Carnot Cycle, $W = W_1 + W_2 + W_3 + W_4$

$$\text{Thus } W = Q_1 - Q_2 \qquad (62)$$

$$\text{Or, } W = (T_1-T_2)\, R\ln(V_2/V_1) \qquad (63)$$

Thus, the efficiency of the engine is obtained by,

$$\varepsilon = \text{(total work done)/heat absorbed}$$

$$= W/Q_1$$

$$\text{or, } \varepsilon = (T_1-T_2)/T_1 = 1 - (T_2/T_1) \qquad (64)$$

One can also rewrite (64) as

$$\varepsilon = 1 - (Q_2/Q_1) \qquad\qquad (63)$$

According to equation (64) or equation (62), $\varepsilon < 1$ i.e. total work done (W) is less than heat absorbed (Q_1) because $T_2 \neq 0$ (according to third Law of thermodynamics). From equation (60), a part (Q_2) of the total heat absorbed (Q_1) can not be converted into work.

Finally, it should be emphasized that the maximum efficiency of Carnot engine is due to the reversible processes invoked in each step. If any of the steps is irreversible, the efficiency will decrease.

Problem 2. Draw the H against T curve for the Carnot cycle.

Problem 3. Suppose, the source and sink are not large reservoirs so that their temperature changes every time heat is absorbed and released by the system. Show in this case the final temperature of both the source and sink is $\sqrt{(T_1 T_2)}$.