$$\Delta H = U + PV$$
$$H + dH = (U + dU) + (P_{sys} + dP_{sys})(V + dV)$$
$$H + dH = U + dU + P_{sys}V + P_{sys}dV + VdP_{sys} + dP_{sys}dV$$
$$H + dH = (U + P_{sys}V) + dU + P_{sys}dV + VdP_{sys}$$
$$dH = -H + H + dU + P_{sys}dV + VdP_{sys}$$
$$dH = dU + P_{sys}dV + VdP_{sys}$$
$$dH = dq + dW + P_{sys}dV + VdP_{sys}$$
$$dH = dq - P_{ex}V + P_{sys}dV + VdP_{sys}$$
$$dH = dq - P_{sys}V + P_{sys}dV + VdP_{sys}$$
$$dH = dq + VdP_{ex}$$
$$dH = dq$$

dPdV is very small, so insignificant.

Reversible expansion. The system is mechanical equilibrium with the surroundings. $P_{ex} = P_{sys}$

Since Reversible expansion. $P_{ex} = P_{sys}$ and that P_{ex} is constant, then dP = 0. Here we are assuming that as the system heats up, the system expands instantly such that there is no increase in P_{sys} but there is an increase in V and thus $dP_{ex} = dP_{sys} = 0$.

Note of $P_{ext} = P_{sys}$: *only for this derivation, for example, think of box of gas molecules, as we heat it up, the molecules start moving faster; the pressure starts to increases. However, if we allow the system to expand such that the pressure is kept constant, then $dP_{sys} = 0$ but dV > 0. Now, if we withdraw heat from the system, molecules start to decelerate and loose energy; the pressure starts to drop. However, we allow the box to contract; this enables the P_{sys} to remain constant. This P_{sys} is trying to always be equal to P_{ext} and vice versa in order to be a reversible expansion.*

o **Heat capacity at constant Pressure (C_P):**
   ▪ when H = f(P,T), $(\partial H / \partial P)T\ dP = 0$ no work done; the important condition of the heat capacity is at constant pressure, because most experiments and processes are held at atmospheric pressure.
   ▪ This is called the Heat capacity at constant Pressure. This heat capacity is analogue to that at constant volume hence the explanation is the same as for the heat capacity for the internal energy.
   ▪ The molar heat capacity at constant pressure is given by C_P/n. this is the heat capacity per mole of substance and hence it is an intensive property.
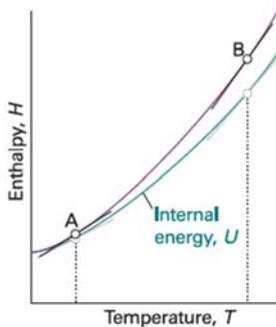

Fig. 2.14 The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different. For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{V,m}$.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P dT$$
$$C_P dT = dH = \Delta H = \int_{T1}^{T2} C_P dT$$
$$\Delta H = C_P(T_2 - T_1)$$

o **Enthalpy of Solids, liquid and gases:**
   ▪ solids and liquids have small molar volumes, for them PV_m is so small that the molar enthalpy and molar internal energy are almost identical ($H_m = U_m + PV_m \approx U_m$).
   ▪ Since there is hardly no change in V_m when heated, $P\Delta V_m = 0$.
   ▪ Consequently, sif a process involves only solids or liquids, the values of ΔH and ΔU are almost identical.
   ▪ In contrasts, the values of the ΔU and ΔH are very different for gases.
   ▪ The enthalpy for a perfect gas is thus $H = U + P_{sys}\Delta V = U + nR\Delta T$.
   ▪ Since $PV = nR\Delta T$. Whether the expansion is reversible or against constant pressure, if there is a change in $P\Delta V$, then $nR\Delta T$.

$$\Delta H_m = \Delta U_m + P\Delta V_m \approx \Delta U_m$$

$$\Delta H_m = \Delta U_m + \Delta nRT$$

Relating C_V and C_P:

- heat capacities at constant pressure is a function of Temperature and are thus expressed in polynomial form as given below, where the values of a, b and c are given in tables for each individual chemical compound.
- However, we can also derive expressions for the heat capacities at constant volumes from the thermodynamic relationships of $\Delta H = \Delta U + \Delta PV$.

$$C_p(T) = a + bT + cT^2 + dT^3$$

- **Ideal gases:**
  - the internal energy is independent of the volume for a perfect gas when $U = f(V,T)$ and hence ΔU is independent q. Since $\pi_T = 0$, there are not intermolecular interactions between the particles of the perfect gas.
  - However, if attractions are dominant in the gas, the internal energy increases with volume because the molecules become farther apart on average.
  - If repulsions are dominant, the internal energy decreases as the gas expands.
  - Now, we will consider cases where we want to tract down the enthalpy of a gas, that is when we vary the volume but keep the pressure constant of the system, Then:

$$H = U + PV$$
$$dH/dT = dU/dT + d(PV)/dT$$
$$dH/dT = dU/dT + d(RT)/dT$$

$$C_P = C_V + R$$

- **Liquids and solids:**
  - ΔU are nearly independent of pressure for liquids and solids because they undergo very small changes in volume when pressure changes.
  - We also know that, small changes in pressure will yield incredibly small changes in volumes, so then $\Delta PV \approx 0$, and thus $\Delta H \approx \Delta U$

$$\Delta H \approx \Delta U$$
$$dH/dT \approx dU/dT$$

$$C_P \approx C_V$$

Energy due to Heat flow:

- heat transfer is driven by the difference in temperature and friction due to flow of fluid through pipes and fittings. The concept of conduction, convection and radiation were learnt in CHNG2801. However, the formulas are given here:

| Conduction	Convection	Radiation
$\dot{Q} = -\dfrac{kA(T_{out} - T_{in})}{L}$	$\dot{Q} = -hA(T_{Wall} - T_\infty)$	$\dot{Q} = \sigma \varepsilon f A(T^4{}_{out} - T^4{}_{in})$

- Furthermore, heat could be lost from a fluid passing through pipes due to flow friction through fittings. This is given by the following equation:

$$\dot{q} = f\frac{L}{D}\left(\frac{V^2}{2g}\right) = K_L\left(\frac{V^2}{2g}\right)$$

f = friction factor
L = length of pipe
D = diameter of pipe
K_L = loss coefficient

Energy due to Work flow:

- work flow is an energy interaction that is not caused by a temperature difference between a system and its surroundings. Work is split into three parts.
- **Shaft work ($\dot{W}_s$):** shaft work occurs by a force acting on the shaft to turn it against a mechanical resistance. This is given by:
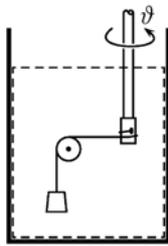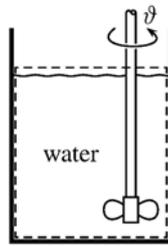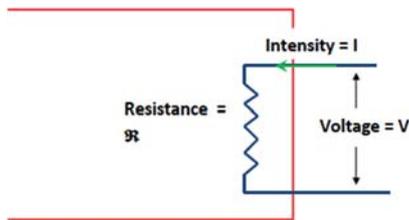

$$W_s = 2\pi \dot{n} T$$

$\dot{n}$ =is the number of revolutions per minute (1/s)
T =is the torque = F * r
r = radius of the rotating shaft (m)
F = force (N)

- **Electrical work ($\dot{W}_e$):** electrical work occurs when an electrical current passes through an electrical resistance in the circuit. This is given by:
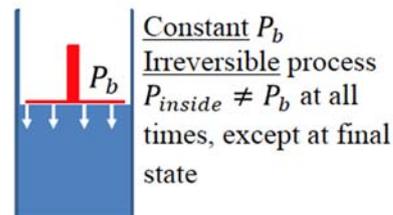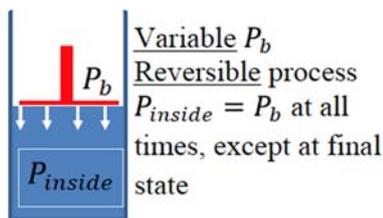

$$W_e = VI$$
$$W_e = I^2 R$$
$$W_e = \frac{V^2}{R}$$

- **Expansive or contractive work ($\dot{W}_b$):** this is expressed as boundary work. It occurs when a mechanical force moves the boundary of a system either expanding or contracting it. For instance, the pressure applied by a piston in a confined volume. This type of work can be categorized on how the work of the system changes based on whether which variable is kept constant. there are 2 types of work, they are reversible or irreversible work.


Variable P_b
Reversible process
$P_{inside} = P_b$ at all times, except at final state

Constant P_b
Irreversible process
$P_{inside} \neq P_b$ at all times, except at final state

Where P_b is the pressure at the boundary system, P_{inside} is the pressure inside piston, and dV is the change in volume inside the system.

- **Reversible constant Volume process (<u>Isochoric, V = constant</u>):**
  - Volume does not change during a process.
  - Another name is reversible constant volume. In a constant volume process the working substance is contained in a rigid vessel, hence the boundaries of the system are immovable and no work can be done on or by the system.
  - Hence, if there is no change in volume, then constant volume implies zero work. See "internal energy" section.

Fig. 4.5 shows the system and states before and after the heat addition at constant volume.

$W = 0$

(a)   (b)
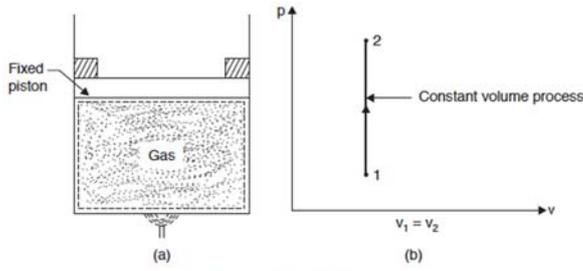
Fig. 4.5. Reversible constant volume process.

o **Reversible constant Pressure process (Isobaric, P = constant):**
  - Pressure is constant during a process. another name is eversible constant pressure.
  - When the boundary of the system is inflexible (constant volume), then the pressure rises when heat is supplied.
  - Hence, for a constant pressure process, the boundary must move against an external resistance as heat is supplied in order to maintain the same pressure inside.
  - As a result, work is done by the gas on its surroundings.

Fig. 4.6 shows the system and states before and after the heat addition at constant pressure.
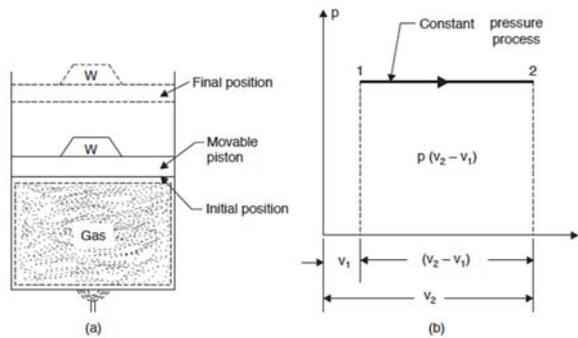

(a)   (b)

Fig. 4.6. Reversible constant pressure process.

  - This is called Expansion against constant pressure.
  - Expansion work is the work required to move an object a distance dz against an opposing force of magnitude $|F|$ is given by $dw = -|F|dz$. That is, if dz is positive (motion to positive z) then dw is negative, and the internal energy decreases since the system is doing work unto the surroundings (the change is negative).
  - Now consider the arrangement shown in Fig. 2.6, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A.
  - If the external pressure is P_{ex}, the magnitude of the force acting on the outer face of the piston is $F = P_{ex}A$. When the system expands through a distance dz against an external pressure P_{ex}, it follows that the work done is $dw = -P_{ex}Adz$. But Adz is the change in volume, dV, in the course of the expansion. Therefore, the work done when the system expands by dV against a pressure P_{ex}, when pressure is the same throughout the expansion (This is equal to the area beneath the horizontal line at P = P$_{ex}$ lying between the initial), is:
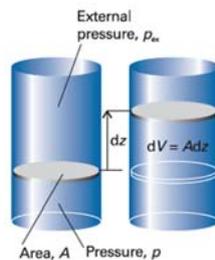
$$dw = -P_{ex}dV$$

$$w = -P\int_{v1}^{v2} dV$$

Fig. 2.6 When a piston of area A moves out through a distance dz, it sweeps out a volume dV = Adz. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.
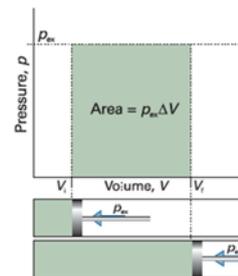

Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

- o **Reversible constant temperature process (<u>Isothermal, T = constant, PV = constant</u>):**
  - temperature is constant during a process.
  - when a working substance in a cylinder behind a piston expands from a high pressure to a low pressure there is a tendency for the temperature to fall.
  - In an isothermal expansion heat must be added continuously in order to keep the temperature the same to the initial value.
  - Similarly, in an isothermal compression heat must be removed from the working substance continuously during the process.
  - The work done is the area under the curve where P is a function of V. Now for a perfect gas, we have the perfect gas equation given by $PV = nRT$.
  - We know that n and R are constants, and since T is also constant then $PV = T = constant$. This is a rectangular hyperbola in a PV graph:
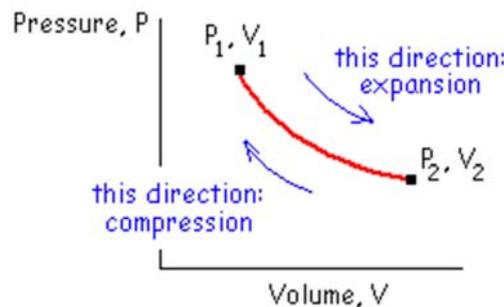
  - The work done can either be an expansion or contraction against a varying pressure.
  - This is called a Reversible expansion; a reversible change in thermodynamics is a change that can be reversed.
  - This is the case for equilibrium. Suppose a gas is confined by a piston and that the external pressure, P_{ex}, is set equal to the pressure, P_{in}, of the confined gas.
  - Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions of the system.
  - If the external pressure is reduced infinitesimally, then the gas expands slightly in order for the pressure of the gas to equate the external pressure.
  - To achieve reversible expansion, we set P_{ex} equal to P_{in} at each stage of the expansion so that the downward force due to the weights always matched the changing upward force, P_{in}, due to the pressure of the gas. When we set $P_{ex} = P_{in}$ we obtain:

$$Constant = PV$$
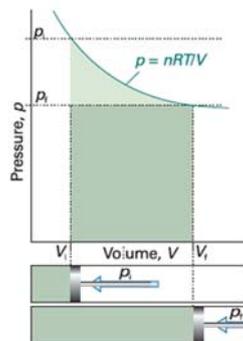$$C = PV$$
$$P = C/V$$
$$Where\ Constant = nRT$$

Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

$$dw = -P_{ex}dV = -PdV$$
$$w = -\int_{v1}^{v2} PdV$$
$$w = -nRT \int_{v1}^{v2} \frac{dV}{V}$$
$$w = -nRTln\left(\frac{V2}{V1}\right)$$

- Superimposed on the diagram is the rectangular area obtained for irreversible expansion against constant external pressure fixed at the same final value as that reached in the reversible expansion.
- More work is obtained when the expansion is reversible (the area is greater) because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted.
- Because some pushing power is wasted when $P > P_{ex}$ (that is when P_{ex} is constant).
- We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression.

Note: for any ideal gas that undergoes isothermal expansion or contraction, the we know that $P_1V_1 = P_2V_2$ is true. In the case above, P is a function of V that is why it is included in the integral, since it will vary as the volue varies in order to keep PV = constant, being true. However, we always write that W = PdV, since even though P varies, it will always vary with respect to the change in volume, hence we need to replace P for an expression in terms of V.

- o **Reversible adiabatic process ($\underline{PV^\gamma = constant}$):**
    - Is one which no heat is transferred to or from the fluid during the process. Such a process can be reversible or irreversible.
    - <u>This process should not be called polytropic process</u> like Alejandro calls it in the lectures because polytropic is a general term for all reversible process (see below under "general process for ideal gasses").
    - This process involves <u>changes in pressure, volume and temperature</u> but no heat transfer.
    - We know that $\Delta U = \Delta Q - \Delta W$, since $Q = 0$, then we can obtain that

    $$\Delta U = - \Delta W$$

    - The above equation is true for an adiabatic process whether the process is reversible or not. In an adiabatic expansion, the work done W by the gas is at the expense of a reduction in the internal energy because there is a lower internal energy.
    - Similarly, in an adiabatic compression all the work done on the gas goes to increase the internal energy of the gas.
    - The relationship between P and V for a perfect gas is given by:

    $$dU = -dW$$
    $$dU = -PdV$$
    $$0 = dU + \frac{RT}{v}dV$$

    - let $U = C_V T$ or $dU = C_V dT$

    $$0 = C_V dT + \frac{RT}{v}dV$$
    $$0 = C_V \frac{dT}{T} + \frac{R}{v}dV$$
    $$constant = C_V \ln(T) + R\ln(V)$$

    - Substituting $T = \frac{PV}{R}$

    $$constant = C_V \ln\left(\frac{PV}{R}\right) + R\ln(V)$$
    $$constant = \ln\left(\frac{PV}{R}\right) + \frac{R}{C_V}\ln(V)$$

    - Substitute $C_V = \frac{R}{\gamma - 1}$ or $\frac{R}{C_V} = \gamma - 1$ (see book "Engineering thermodynamics" page 109, under the heading of "relationship between two specific heats" for derivation).