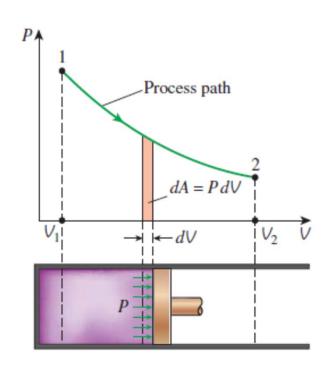
Slow expansion/compression of a gas to maintain mechanical equilibrium ($P_{ext} \approx P$): We will consider processes in which volume change is the only form of work.



Expansion/compression is sufficiently slow so that mechanical equilibrium is maintained throughout, i.e., $P_{\rm ext} \approx P$

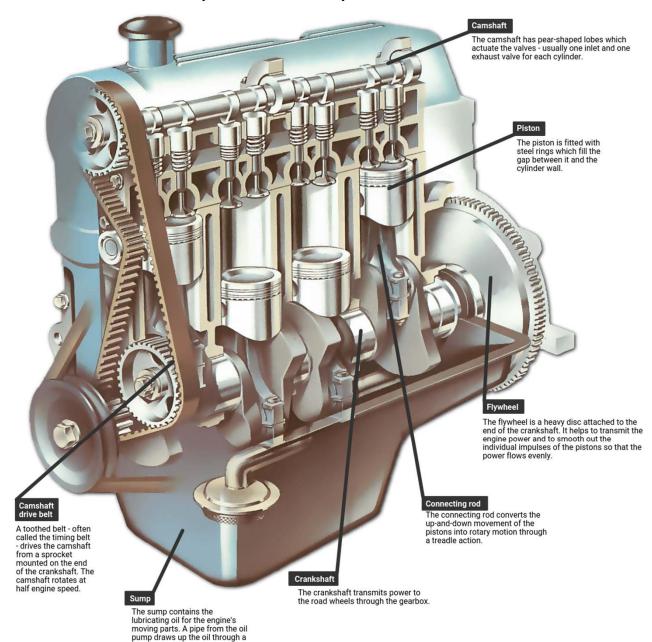
In practice##, it means that the velocity of piston needs to be small as compared to the speed of sound in the gas

$$W_{out} = \int_{1}^{2} P_{ext} \, dV$$

If
$$P_{\text{ext}} \approx P \implies W_{\text{out}} = \int_{1}^{2} P \, dV$$
 = Area under P-v curve (see figure)

##Reference: "Statistical Physics Part 1" – L.D.Landau and E.M.Lifshitz

Where is this process important?



Automobile engines

What happens due to **friction** during movement of piston in a cylinder?

Quasi equilibrium expansion/compression of a gas:

We will consider processes in which volume change is the only form of work. The expansion or compression must be sufficiently slow so as to maintain <u>internal equilibrium</u> throughout the process.

If the system (gas in the present case) can be considered to be in a state of internal equilibrium throughout the process then such as process is called as quasi-static or quasi-equilibrium process.

During a quasi-equilibrium process, system is in thermal equilibrium internally at any given time, i.e., temperature is uniform throughout the system, although temperature may vary with time. Moreover, mechanical equilibrium is also maintained throughout, i.e., $P_{\text{ext}} = P$ (internal pressure of gas)

Quasi equilibrium expansion/compression of a gas:

This is a more rigorous condition than the condition of slow expansion/compression required to maintain mechanical equilibrium. This is because internal equilibrium also entails thermal equilibrium for which much more time is required and therefore the process has to be a lot slower than that required for mechanical equilibration alone.

Quasi-equilibrium processes are easy to analyze since laws of thermodynamics (including state postulate) can be applied to the system.

Consider a sufficiently slow process of expansion or compression of an ideal gas the gas is in a state of internal equilibrium (quasi-equilibrium process)

Assuming that changes in kinetic and potential energies are insignificant, as per the first law of thermodynamics,

$$dU = \delta Q_{in} - \delta W_{out}$$

$$dU = (X - 1) \delta W_{out}$$

where we defined X (energy transfer ratio) as: $X = \frac{\delta Q_{in}}{\delta W_{out}}$

Since mechanical equilibrium is maintained ($P = P_{ext}$) throughout the process where P is the internal pressure of the ideal gas.

$$\delta W_{out} = P_{ext} dV = P dV$$

Therefore,
$$dU = (X - 1)PdV$$

OR
$$m C_V dT = (X - 1) PdV$$
 (A) (since $dU = m C_V dT$ for an ideal gas, $m = mass$ of ideal gas)

As per ideal gas equation of state mRT= PV

Hence,
$$mRdT = PdV + VdP$$
 (B)

Dividing Eq. (B) by Eq. (A) on previous slide we get,

$$\frac{R}{Cv} = \frac{PdV + VdP}{(X-1)PdV}$$

$$\frac{Cp - Cv}{Cv} = \frac{1}{(X-1)} + \frac{VdP}{(X-1)PdV}$$

$$(X-1)(k-1) = 1 + \frac{VdP}{PdV}$$

$$Xk - k - X + 1 = 1 + \frac{VdP}{PdV}$$

$$\frac{-VdP}{PdV} = (1-k)X + k = n$$

$$-d(InP) = nd(InV)$$

Here $k = C_p / C_V$ is the ratio of specific heats

If we consider X (energy transfer ratio) and k (ratio of specific heats) as constant, then 'n' in above equation can also be considered as constant. Integrating both sides of above equation and rearranging we get,

$$PV^n = C (constant)$$

Thus, a polytropic process of an ideal gas is a quasi-static expansion or compression process in which X (energy transfer ratio) and k(specific heat ratio) are constant.

Now we can consider work done by the gas in a polytropic process as follows:

$$\begin{aligned} W_{out} &= \int_{1}^{2} P dV \\ &= \int_{1}^{2} \frac{C}{V^{n}} dV \\ &= C \left(\frac{V_{2}^{-n+1} - V_{1}^{-n+1}}{-n+1} \right) \qquad \text{for } n \neq 1 \\ &= \left(\frac{P_{2} V_{2}^{n} V_{2}^{-n+1} - P_{1} V_{1}^{n} V_{1}^{-n+1}}{-n+1} \right) \\ &= \left(\frac{P_{2} V_{2} - P_{1} V_{1}}{-n+1} \right) \end{aligned}$$

Special cases of polytropic process:

1. (Quasi-static) Isothermal expansion/compression:

When $\delta Q_{in} = \delta W_{out}$ througout the process, **X = 1**. This implies that $U_2 - U_1 = 0$, which means that temperature (T) remains constant throughout the process since for a given mass of an ideal gas U = U(T) as shown by Joule's experiments.

$$n = (1-k)X + k = 1$$
 (if $X = 1$) \rightarrow PV = C (constant)

The work done is given by
$$W_{out} = \int_{1}^{2} \frac{C}{V} dV = C \ln \left(\frac{V_2}{V_1} \right) = P_1 V_1 \ln \left(\frac{V_2}{V_1} \right)$$

2. (Quasi-static) Adiabatic expansion/compression:

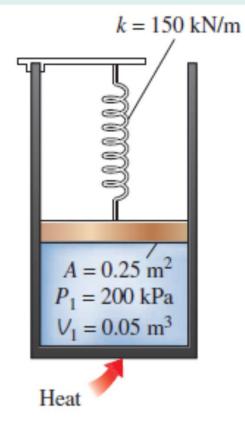
When $\delta Q_{in} = 0$ throughout the process, X = 0

$$n = (1-k)X + k = k$$
 (if $X = 0$) $\rightarrow PV^k = C$ (constant)

The work done is given by (see expression on last slide) $W_{out} = \left(\frac{P_2V_2 - P_1V_1}{-k+1}\right)$

Example problem 1:

A piston–cylinder device contains 0.05 m³ 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 0.25 m², 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.



(a) Final volume is twice the initial volume:

$$V_2 = 2V_1 = (2)(0.05 \text{ m}^3) = 0.1 \text{ m}^3$$

Displacement of the piston is:

$$\Delta x = \frac{\Delta V}{A} = \frac{(0.1 - 0.05) \text{ m}^3}{0.25 \text{ m}^2} = 0.2 \text{ m}$$

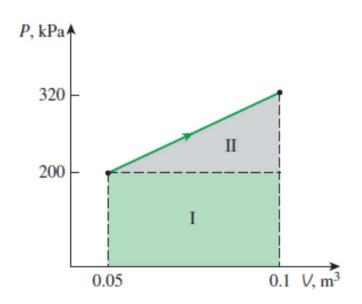
Force exerted by the piston in final position:

$$F = k\Delta x = \left(150 \frac{kN}{m}\right)(0.2 m) = 30 kN$$

(a) Therefore, the final pressure is calculated as:

$$P_2 = 200 \text{ kPa} + \frac{F}{A} = 200 \text{ kPa} + \frac{30 \text{kN}}{0.25 \text{ m}^2} = 320 \text{ kPa}$$

(b) Total work done by the gas:



$$W_{\text{out}} = \int_{1}^{2} P_{\text{ext}} dV$$

$$= \frac{(P_1 + P_2)}{2} \quad (V_2 - V_1)$$

$$= \frac{(200 + 320)}{2} (0.1 - 0.05)$$

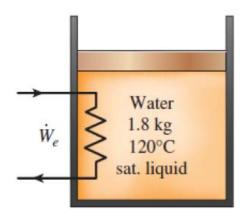
$$= 13 \text{ kJ}$$

(c) Work done on the spring:

$$W_{\text{spring}} = \frac{1}{2}k(x_2^2 - x_1^2) = \frac{1}{2}(150 \text{ kN/m})[(0.2 \text{ m})^2 - 0^2] = 3 \text{ kJ}$$

Example problem 2:

An insulated piston-cylinder device initially contains 1.8 kg of saturated liquid water at 120 °C. Now an electrical resistor placed in the tank is turned on until the volume becomes 4 times the initial volume. Determine (a) the final volume of the tank (b) the final temperature and (c) the electrical work done by the resistor (in kJ).



Solution: We shall assume that changes in kinetic and potential energies of water are negligible. Further, we shall assume that process is slow so that external pressure is same as internal pressure. The total pressure exerted on water is due to the weight of the piston divided by area plus the atmospheric pressure. Since piston is resting on water and is not connected to any other mechanical device such as spring or a rod, **the pressure exerted on water will be constant** during the process.

To calculated initial volume : At 120 $^{\circ}$ C, $v_f = 0.00106 \text{ m}^3/\text{kg}$ $V_1 = (1.8 \text{ kg})(0.00106 \text{ m}^3/\text{kg}) = 0.001908 \text{ m}^3$ Psat @ 120 $^{\circ}$ C = 198.67 kPa

Example problem 2:

Final volume : $V_2 = 4 V_1 = 0.007632 \text{ m}^3$ Final specific volume $v_2 = (0.007632)/1.8 = 0.00424 \text{ m}^3/\text{kg}$ At P= 198.67 kPa, $v_g = 0.89133 \text{ m}^3/\text{kg}$

Since $v_f < v_2 < v_g$ the final mixture must be a saturated liquid-saturated vapor mixture and hence the **final temperature is 120** $^{\circ}$ C.

The quality in the final state is computed from $v_2 = (1-x) v_f + x v_g$. Solving this equation for x, we get x = 0.00357

Applying first law of thermodynamics, $Q_{in} + W_{e,in} - W_{b,out} = (U_2 - U_1)$ $W_{b,out} = \int_{1}^{2} P_{ext} dV = \int_{1}^{2} P dV = P(V_2 - V_1)$

Substituting moving boundary work in 1st law equation, we get

$$W_{e,in} = (U_2 - U_1) + P(V_2 - V_1)$$

$$= (H_2 - H_1)$$

$$= m(h_2 - h_1)$$

$$h_1 = h_f (120 \, ^{0}\text{C}) = 503.81 \, \text{kJ/kg}$$

$$h_2 = (1-x) \, h_f + x \, h_g = (1-0.00357)(503.81) + (0.00357)(2706) = 511.676$$

$$W_{e,in} = (1.8)(511.676 - 503.81) = 14.16 kW$$

Specific heats of solids and liquids:

For any simple compressible substance, the following relation between Specific heats can be derived

$$c_p - c_V = -T \left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial V}\right)_T$$

This is a general relation valid for gases, liquids, and stress-free solids.

Solids and liquids are generally considered as incompressible substances. This is because the volume of a solid or a liquid does not change significantly upon application of pressure (i.e., compression). Therefore the second derivative on the RHS of the above equation is close to zero. Also the value of the first derivative is relatively small in solids and liquids. Therefore the right hand side (RHS) of above equation is negligible.

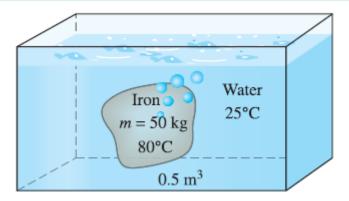
Thus

$$C_p \approx C_V = C$$

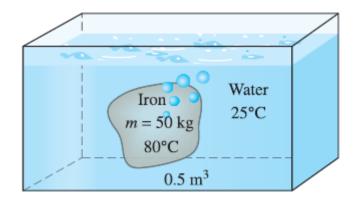
Thus the specific heats are nearly equal and therefore specific heat of a solid or liquid is denoted by symbol C.

Example problem 3:

A 50-kg iron block at 80°C is dropped into an insulated tank that contains 0.5 m³ of liquid water at 25°C. Determine the temperature when thermal equilibrium is reached.



SOLUTION An iron block is dropped into water in an insulated tank. The final temperature when thermal equilibrium is reached is to be determined. **Assumptions** 1 Both water and the iron block are incompressible substances. 2 Constant specific heats at room temperature can be used for water and the iron. 3 The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. 4 There are no electrical, shaft, or other forms of work involved. 5 The system is well-insulated and thus there is no heat transfer.



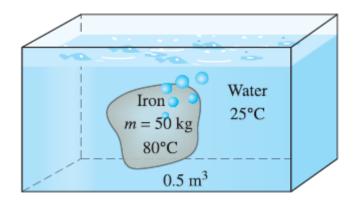
We consider (Iron + Water) as our system (closed mass). Since system is enclosed in a rigid container (tank), there is **no work done** by surroundings on the sytem. Since container is insulated there is **no heat transfer** between system and surroundings. Hence according to first law total change in internal energy must be zero.

$$0 = \Delta U$$

The total internal energy U is an extensive property, and therefore it can be expressed as the sum of the internal energies of the parts of the system. Then the total internal energy change of the system becomes

$$\Delta U_{\rm sys} = \Delta U_{\rm iron} + \Delta U_{\rm water} = 0$$

$$[mc(T_2 - T_1)]_{iron} + [mc(T_2 - T_1)]_{water} = 0$$



The specific volume of liquid water at or about room temperature can be taken to be 0.001 m³/kg. Then the mass of the water is

$$m_{\text{water}} = \frac{V}{V} = \frac{0.5 \text{ m}^3}{0.001 \text{ m}^3/\text{kg}} = 500 \text{ kg}$$

The specific heats of iron and liquid water are determined from Table A–3 to be $c_{\text{iron}} = 0.45 \text{ kJ/kg} \cdot ^{\circ}\text{C}$ and $c_{\text{water}} = 4.18 \text{ kJ/kg} \cdot ^{\circ}\text{C}$. Substituting these values into the energy equation, we obtain

$$(50 \text{ kg})(0.45 \text{ kJ/kg} \cdot ^{\circ}\text{C})(T_2 - 80 ^{\circ}\text{C}) + (500 \text{ kg})(4.18 \text{ kJ/kg} \cdot ^{\circ}\text{C})(T_2 - 25 ^{\circ}\text{C}) = 0$$

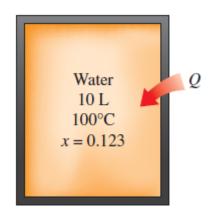
$$T_2 = 25.6 ^{\circ}\text{C}$$

Therefore, when thermal equilibrium is established, both the water and iron will be at 25.6°C.

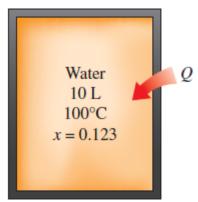
Discussion The small rise in water temperature is due to its large mass and large specific heat.

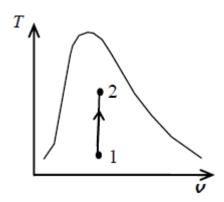
Example problem 4:

A rigid 10-L vessel initially contains a mixture of liquid water and vapor at 100°C with 12.3 percent quality. The mixture is then heated until its temperature is 150°C. Calculate the heat transfer required for this process.



<u>Solution</u>: Since the system is stationary, changes in kinetic and potential energies are negligible. Since the vessel is rigid there is no work done on the system. Since the process occurs at constant volume and inititially contains a mixture of saturated liquid and saturated vapor, the process can be depicted pictorially as: T_{A}





Due to absence of work term, the first law takes the form : $Q_{in} = \Delta U = m(u_2 - u_1)$ The properties at the initial and final states are (Table A-4)

$$T_1 = 100^{\circ}\text{C}$$
 $v_1 = v_f + x v_{fg} = 0.001043 + (0.123)(1.6720 - 0.001043) = 0.2066 \text{ m}^3 / \text{kg}$
 $x_1 = 0.123$ $u_1 = u_f + x u_{fg} = 419.06 + (0.123)(2087.0) = 675.76 \text{ kJ/kg}$
 $T_2 = 150^{\circ}\text{C}$ $v_2 = \frac{v_2 - v_f}{v_{fg}} = \frac{0.2066 - 0.001091}{0.39248 - 0.001091} = 0.5250$
 $v_2 = v_1 = 0.2066 \text{ m}^3 / \text{kg}$ $u_2 = u_f + x_2 u_{fg}$
 $v_3 = 631.66 + (0.5250)(1927.4) = 1643.5 \text{ kJ/kg}$

The mass in the system is

$$m = \frac{V_1}{v_1} = \frac{0.100 \,\mathrm{m}^3}{0.2066 \,\mathrm{m}^3/\mathrm{kg}} = 0.04841 \,\mathrm{kg}$$

Substituting,

$$Q_{\text{in}} = m(u_2 - u_1) = (0.04841 \,\text{kg})(1643.5 - 675.76) \,\text{kJ/kg} = 46.9 \,\text{kJ}$$