Lecture 10

Now that we have established, work done for a general system,

$$\text{đ}W = \sum_i J_i \, dx_i$$
$$\text{đ}Q = \,?$$
$$\overline{dU = \sum_i J_i \, dx_i + \,?}$$

The questions that we ask is, can we write something for đQ similar to đW? If we can, which term might come up? Well, since we are dealing with equilibriums, in mechanical equilibrium, force is the same, on two systems if they are in equilibrium. Here, in thermal equilibrium, temperature plays the same role, and it might enter in the equation. We will have to verify this and find the generalized displacement term conjugated to temperature.

Heat capacity

In our previous mid lectures we introduced the

idea of heat capacity. It is the amount of heat needed to increase the temperature by 1 kelvin. But, we can do this in two process — at constant volume and constant pressure.

$$C_v = \left(\frac{dQ}{dT}\right)_V \qquad \text{and} \qquad C_p = \left(\frac{dQ}{dT}\right)_P$$

$$= \left(\frac{dU + PdV}{dT}\right)_V \qquad\qquad = \left(\frac{dU + PdV}{dT}\right)_P$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(P \frac{dV}{dT}\right)^{0}_V \qquad = \left(\frac{\partial U}{\partial T}\right)_P + \left(P \frac{\partial V}{\partial T}\right)_P$$

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

$$\therefore\ C_p = \left(\frac{\partial U}{\partial T}\right)_P + \left(P \frac{\partial V}{\partial T}\right)_P$$

$$\therefore\ C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Joule's expansion experiment

Consider the ideal gas expansion of the following.
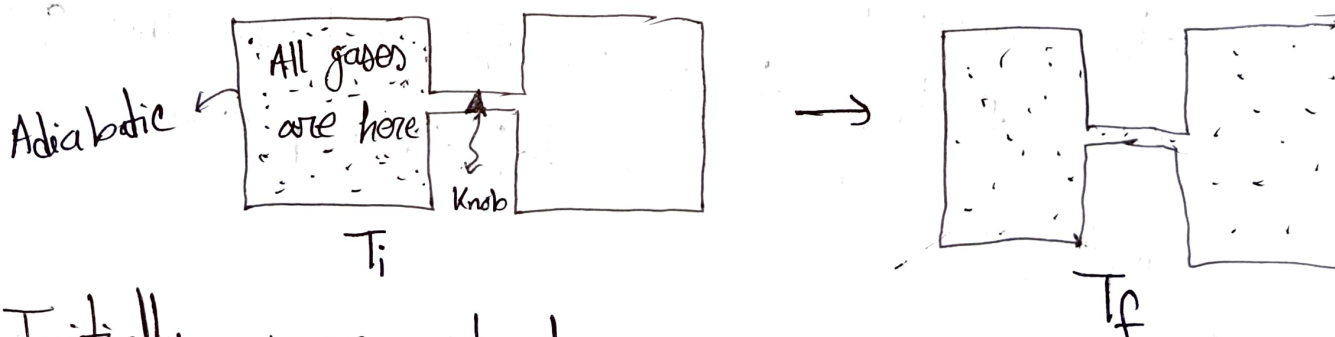
Initially some ideal gas was kept in the left chamber and a knob was restricting it to

but only a function of multiplication of them—
PV (since $PV \propto T$).

$$U = U(P,V) = U(PV) = U(T)$$

for ideal gases.

Now,
$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P + \left(P\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

Since U only depends on T and not individually on P and V, we conclude,

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

$$\therefore \quad C_p - C_v = \left(P\frac{\partial V}{\partial T}\right)_P$$

But again, since $PV = NK_BT$, at constant pressure,

$$V \propto T$$

$$V = \frac{NK_B}{P}T$$

and so, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}$

$$\Rightarrow \frac{\partial V}{\partial T} = \frac{NK_B}{P}$$

$$\therefore \quad C_p - C_v = \frac{PV}{T}$$

$$\therefore \quad C_p - C_v = NK_B$$

$$\therefore \quad C_p - C_v = R$$

This is true for ideal gas.

flow in the second chamber. The walls are adiabatic, so there can be no heat exchange.

$$\therefore \Delta Q = 0$$

And since no external work was done, $\Delta W = 0$

$$\therefore \Delta U = 0$$

It was found that, the temperatures before and after the expansion is same.

$$\therefore T_i = T_f = T$$

Now, internal energy U is surely $U(P, V)$, since these terms comes in dW and hence in dU. But we can exchange one of the variables with temperature T, since, for ideal gas, P and V are related to T by,

$$PV = NK_B T$$

$$\therefore \quad U = U(T, V)$$

But in this process, volume obviously changed, and the initial final and internal energies are the same. So, U can't be a function of V, but it has to be a function of T only. More explicitly its a function of P and V,

We could do the whole thing from a more intuitive point of view. The internal energy in general a function of temperature and volume.

$$\therefore U = U(T, V)$$

$$\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From first law of thermodynamics, $dU = dQ + dW$

$$\Rightarrow dU = dQ - PdV$$

$$\therefore dQ = dU + PdV$$

$$\therefore dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)dV$$

$$\Rightarrow \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\frac{dV}{dT}$$

Now, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$ $\left\{ \begin{array}{l} \text{since at constant} \\ V, \;\; \frac{dV}{dT} = 0 \end{array} \right.$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

Specific heat capacities are defined as specific heat per unit mass.

$$\therefore c_V = \frac{C_V}{M} \qquad \text{and} \qquad c_P = \frac{C_P}{M}$$

Ratio of C_P and C_V is called the adiabatic index,

$$\gamma = \frac{C_P}{C_V}$$

Reversibility

In nature, there are processes that can be totally run backwards. Such processes are called reversible processes. However, there are processes that occurs only in one direction — the irreversible processes. For example, an egg might roll down from a table and then fall to the floor. The potential energy is being converted into kinetic energy, and then as the egg smashes on the floor, it shatters into pieces, and the kinetic energy is then converted into heat between the pieces of egg and the floor. Now, conservation of energy does not forbid the opposite process to occur — that is heat ~~energies~~ energies of shattered egg pieces to reassemble it, forming the kinetic energy and finally lifting it to the table, converting the kinetic energy to potential energy. But, this process never happens, meaning, its an irreversible process.

Think about another one. You have 100 coins in a box, ~~d~~ and you prepared them all facing heads up.

Now, if you shake the box for long time, you will see that the coins are randomly oriented now — some facing up, some facing down. However, if initially all of them were not facing down or up, rather were randomly oriented, the effect of shaking will not make all of them face up or down. So, the effect of shaking always cause the orientation to be in disordered state and its again an irreversible change.

In mechanics and thermodynamics, any process involving friction will eventually lead to an irreversible process, since it will convert some energy into heat which can't totally be pulled back. To have a reversible process in thermodynamics, you have to perform a process quasi-statically. If the equilibrium is maintained throughout a process, it can be carried out backwards too. Technically it will take an infinite amount of time to complete such a process, so in reality the reversible processes are really pseudo-reversible.

If it is not done in quasi-static manner, you do not really know about the thermodynamic

variables in between two equilibrium points. So, you don't really have any idea how the rever process is going to be the same if it has to be a reversible process.

Isothermal expansion of an ideal gas

Isothermal means at constant temperature. In a reversi ble isothermal expansion of an ideal gas, we want to calculate the heat change. For isothermal process.

$$\Delta T = 0.$$

For ideal gas, internal energy only depends on temperature and so,

$$\Delta U = 0$$

Since, $dU = đQ + đW$

$$\Rightarrow đQ = - đW$$

So, as we input heat to the system, the gas expands and while expanding, it does some work on the surrounding. That's why, even the gas is ~~geet~~ absorbing heat, its temperature remains constant.

Now, $đW = - PdV$ as per our definition.

So, the ~~work done~~ heat absorbed in the ~~isothermal~~

isothermal expansion of the gas from volume V_1 to V_2 of n

mole gas is given by,

$$\Delta Q = \int dQ = -\int dW = \int_{V_1}^{V_2} P\, dV$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V}\, dV = nRT\, \ln V \Big|_{V_1}^{V_2}$$

$$\therefore \Delta Q = nRT\, \ln\frac{V_2}{V_1}$$

The work done is then, $\Delta W = -nRT\, \ln\frac{V_2}{V_1}$

$V_2 > V_1$, and so $\Delta Q > 0$ and $\Delta W < 0$. Since the internal energy is the same, but the volume has ~~decrea~~ increased, the energy density is decreased. But, pressure, $P = \frac{2}{3}u$, where u is energy per unit volume. So, in this case, pressure will also decrease.

Adiabatic expansion of ideal gas

Adiabatic means without the flow of any heat. Here, a process will be adiabatic if its performed without any heat input and is reversible. So, here,

$$dQ = 0$$

$$~~dU = dW~~ \qquad \therefore dU = dW$$

For ideal gas, $dU = C_v dT$ and $dW = -P dV$

$$\therefore C_v dT = -P dV = -\frac{nRT}{V} dV$$

$$\Rightarrow \frac{dT}{T} = -\frac{nR}{C_v} \frac{dV}{V}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = -\frac{nR}{C_v} \ln \frac{V_2}{V_1}$$

If one wants to calculate for 1 mole gas, then $n=1$, and we can work with molar heat capacities (C_v is per mole).

$$C_p = C_v + R$$

and, $\gamma = \frac{C_p}{C_v} = 1 + \frac{R}{C_v}$ $\Rightarrow -\frac{R}{C_v} = 1-\gamma$

$$\therefore \ln \frac{T_2}{T_1} = (1-\gamma) \ln \frac{V_2}{V_1}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

$$\Rightarrow \cancel{\ln \left(\frac{T_2/T_1}{}\right)} \Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

$$\therefore T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\boxed{\therefore TV^{\gamma-1} = \text{constant}}$$

Since, $PV \propto T$, you can also show,
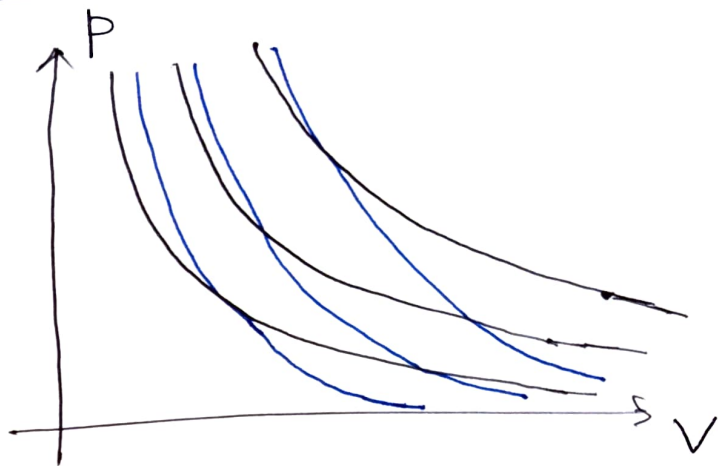
$\boxed{P^{1-\gamma} T^{\gamma} = \text{constant}}$ and $\boxed{PV^{\gamma} = \text{constant}}$

For an isothermal process, temperature is constant.

$$\therefore PV = constant$$

— isotherms

— adiabats

Isotherms are lines of constant temperature as followed in isothermal expansion and adiabats are lines followed in an adiabatic expansion where heat can't ~~ento~~ enter or leave. At each points, adiabats has steeper gradients than isotherms.

Adiabatic atmosphere

Consider a layer of gas between height z and $z+dz$. If n is number of molecules per unit volume, ~~then~~ then ndz is the number of molecules per unit area in this layer. So, the exerted pressure is,

$$dP = -ndz\, mg$$

where each molecule has a mass of m.

If mass density, $\rho = nm$, then,

$$dP = -\rho g\,dz$$

which is called the hydrostatic equation.

Now, $P = nk_BT$ and $\rho = nm$

$$\therefore \rho = \frac{mP}{k_BT}$$

$$\therefore \frac{dP}{dz} = -\frac{mPg}{k_BT}$$

$$\Rightarrow T\frac{dP}{P} = -\frac{mg}{k_B}\,dz \qquad —①$$

If we assume the atmosphere to be adiabatic, that is they do not exchange heat while the expand, then, $P^{1-\gamma}T^{\gamma} = $ constant.

$$\Rightarrow \frac{d}{dT}\left(P^{1-\gamma}T^{\gamma}\right) = 0$$

$$\Rightarrow T^{\gamma}(1-\gamma)P^{-\gamma}\frac{dP}{dT} + P^{1-\gamma}\gamma T^{\gamma-1} = 0$$

$$\Rightarrow (1-\gamma)\frac{dP}{dT} = -P\gamma T^{-1}$$

$$\therefore (1-\gamma)\frac{dP}{P} + \gamma\frac{dT}{T} = 0$$

① $\Rightarrow$

$$\therefore T\cdot\left(-\frac{\gamma}{1-\gamma}\right)\frac{dT}{T} = -\frac{mg}{k_B}\,dz$$

$$\therefore \frac{dT}{dz} = -\left(\frac{\gamma-1}{\gamma}\right)\frac{mg}{k_B}$$

which gives up the expression relating the rate of decrease of temperature with height, which is linear. We can write,

$$\frac{\gamma - 1}{\gamma} = \frac{R}{C_p} = \frac{N_A k_B}{C_p}$$

$$\therefore \quad \frac{dT}{dz} = - \frac{N_A m \, g}{C_p}$$

$$\boxed{\therefore \quad \frac{dT}{dz} = - \frac{M_{molar} \, g}{C_p}}$$

The quantity $\frac{M_{molar} \, g}{C_p}$ is known as adiabatic lapse rate, for dry air (nitrogen mostly) it is $9.7 \, K/km$.