ESO201A : THERMODYNAMICS
2021-22 Ist semester
IIT Kanpur

Instructor : P.A.Apte

Lecture 7

Quasi equilibrium expansion:

A process in which mechanical equilibrium is maintained throughout, i.e., $P_{ext} = P$ (internal pressure of gas)

The expansion must be sufficiently slow so as to maintain mechanical equilibrium 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.

Quasi-equilibrium processes are easy to analyze since equation of state can be applied throughout the process.

More on ideal gas :

According to state postulate, any intensive property including specific internal energy (u) can be considered as a function of (T,v) for a gas phase.

Joule performed an interesting experiment (see picture below) There are two rigid spherical containers connected through a valve and immersed in water.   One of the containers contains air at a certain pressure and the other container is evacuated. Water is in thermal equilibrium with air.

The valve is now opened and air expands into the other container. It is observed that there is no change in the temperature of water measured by the thermometer after the process is complete.

Ref. Cengel and Boles, 8th Edition (2015)
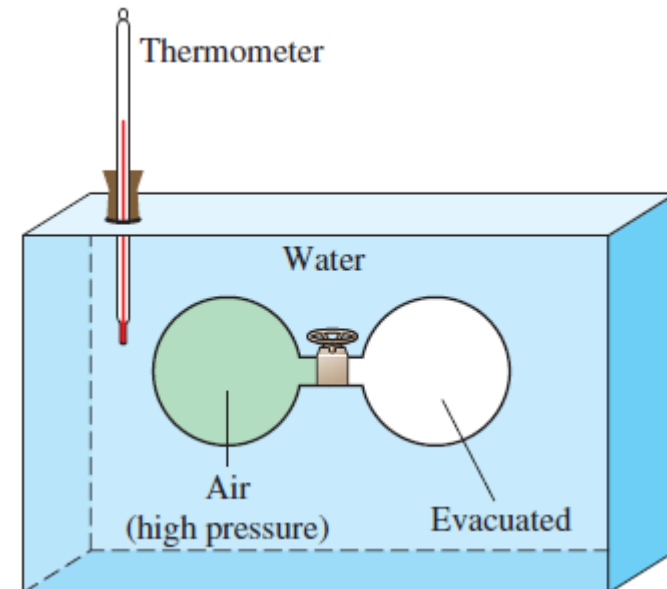
More on ideal gas :

Analysis of Joule's experiment:

Since containers are rigid, no work is done by air on the surroundings. Hence first law of thermodynamics takes the form: $\Delta U = Q_{in}$ [our system is the gas inside the container(s)]

Since water temperature does not change, there is no heat gained or lost by water. This means that $Q_{in} = 0$

This implies that $\Delta U = 0$

Thus, for a given mass of air, U is independent of volume.

However this is only true for gases which (at least) approximately behave as ideal gas !
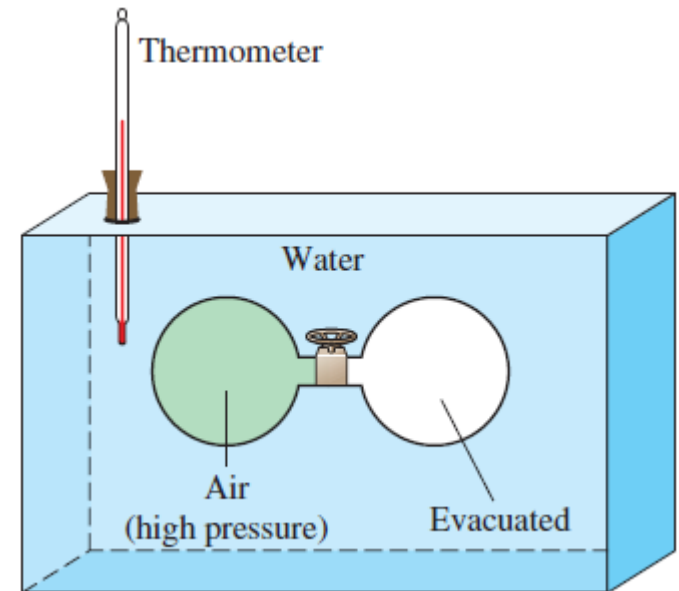
Thermometer

Water

Air
(high pressure)

Evacuated

Ref. Cengel and Boles, 8th Edition (2015)

More on ideal gas :

According to state postulate, any intensive property including specific internal energy (u) can be considered as a function of (T,v) for a gas phase.

Experimentally (for an ideal gas) it has been shown that for an ideal gas, internal energy U is independent of V. This implies that $u = u(T)$, i.e., u is independent of v

Since $h = u + Pv = u + RT$, $h = h(T)$ for an ideal gas

Note : if the same experiment (see previous slides) is performed for a <u>non-ideal gas</u>, there will be a heat exchange between gas and water which will result in a change of temperature. In Joule's experiment the temperature and pressure conditions were such that gas was closely approximating the ideal gas behavior.

Specific heats :

Specific heat at constant volume (C_V) is (approximately) equal to the amount of energy required to raise the temperature of unit mass of a substance by one degree celcius at constant volume.
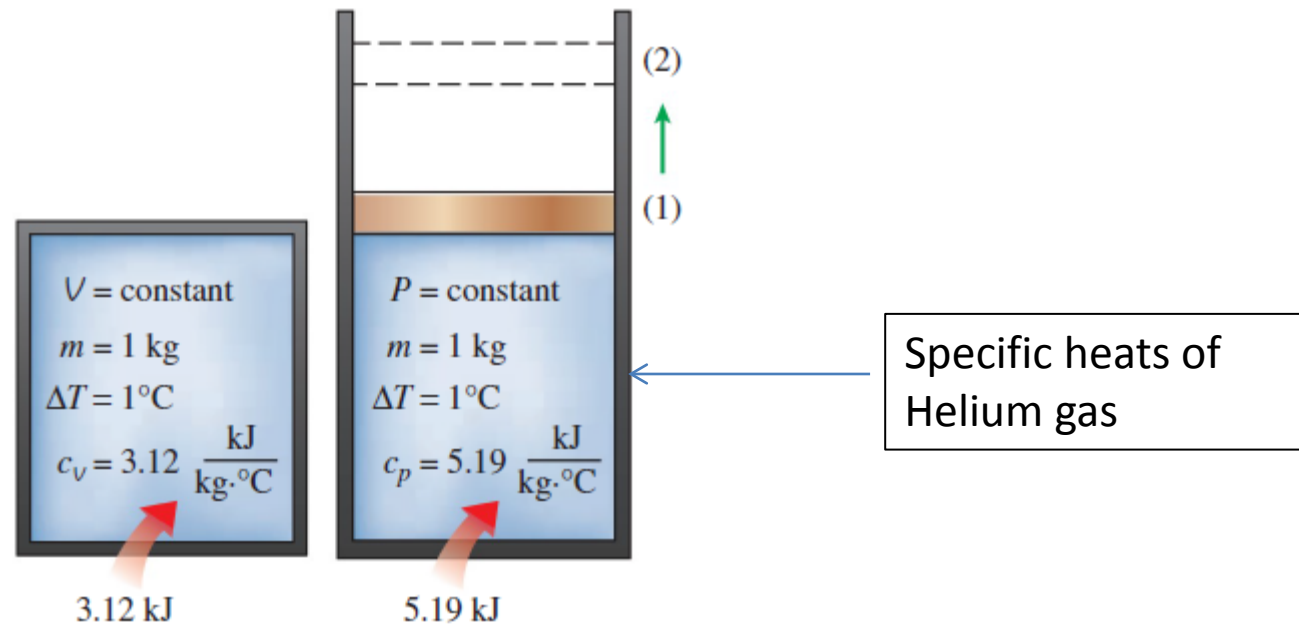
Specific heat at constant pressure (C_P) is (approximately) equal to the amount of energy required to raise the temperature of unit mass of a substance by one degree celcius at constant pressure.

Mathematically,

$$C_v = \frac{1}{m}\left(\frac{\partial Q_{in}}{\partial T}\right)_V$$

$$C_p = \frac{1}{m}\left(\frac{\partial Q_{in}}{\partial T}\right)_P$$

m = total mass
of substance

(2)

(1)

V = constant

m = 1 kg

ΔT = 1°C

$c_V = 3.12 \ \dfrac{kJ}{kg \cdot °C}$

P = constant

m = 1 kg

ΔT = 1°C

$c_p = 5.19 \ \dfrac{kJ}{kg \cdot °C}$

Specific heats of Helium gas

3.12 kJ

5.19 kJ

Ref. Cengel and Boles, 8th Edition (2015)

For a process at constant volume, work output is zero. Hence,

$$dU = dQ_{in}$$

As per the definition of C_V (last slide): $dQ_{in} = mC_V dT$ (at constant V)

By combining above two equations : $dU = mC_V dT$ (at constant V)

This leads to the following important relation :

$$C_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$$

u = specific internal energy

Fro a constant P process, it was shown : $dH = dQ_{in}$

From the definition of Cp (see last slide) : $dQ_{in} = mC_P dT$ (at constant P)

By combining the above two equations : $dH = mC_P dT$ (at constant P)

This implies that

$$C_P = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P$$

h = specific enthalpy

Note: A constant P process implies that mechanical equilibrium is maintained.
Because we can only control P_{ext} and we have no direct control over P. Hence constant P can ONLY be maintained by ensuring that P_{ext} is constant and mechanical equilibrium is maintained during the process

Specific heats of ideal gases :

Since u is a function only of T and is independent of v

$$C_v = \frac{1}{m}\left(\frac{dU}{dT}\right) = \frac{du}{dT}$$

For an ideal gas, there is NO requirement of constant V in the derivatives for C_P

Also, h is a function only of T and is independent of P for an ideal gas. Hence,

$$C_P = \frac{1}{m}\left(\frac{dH}{dT}\right) = \frac{dh}{dT}$$

For an ideal gas, there is NO requirement of constant P in the derivatives for C_P

Note that C_V and C_P are both functions only of T for an ideal gas. Many real gases approach ideal gas behavior at low pressures.   Hence the low pressure specific heats of gases are known as ideal gas specific heats or zero pressure specific heats and are denoted by adding a subscript '0' : C_{V0} and C_{P0}.

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :
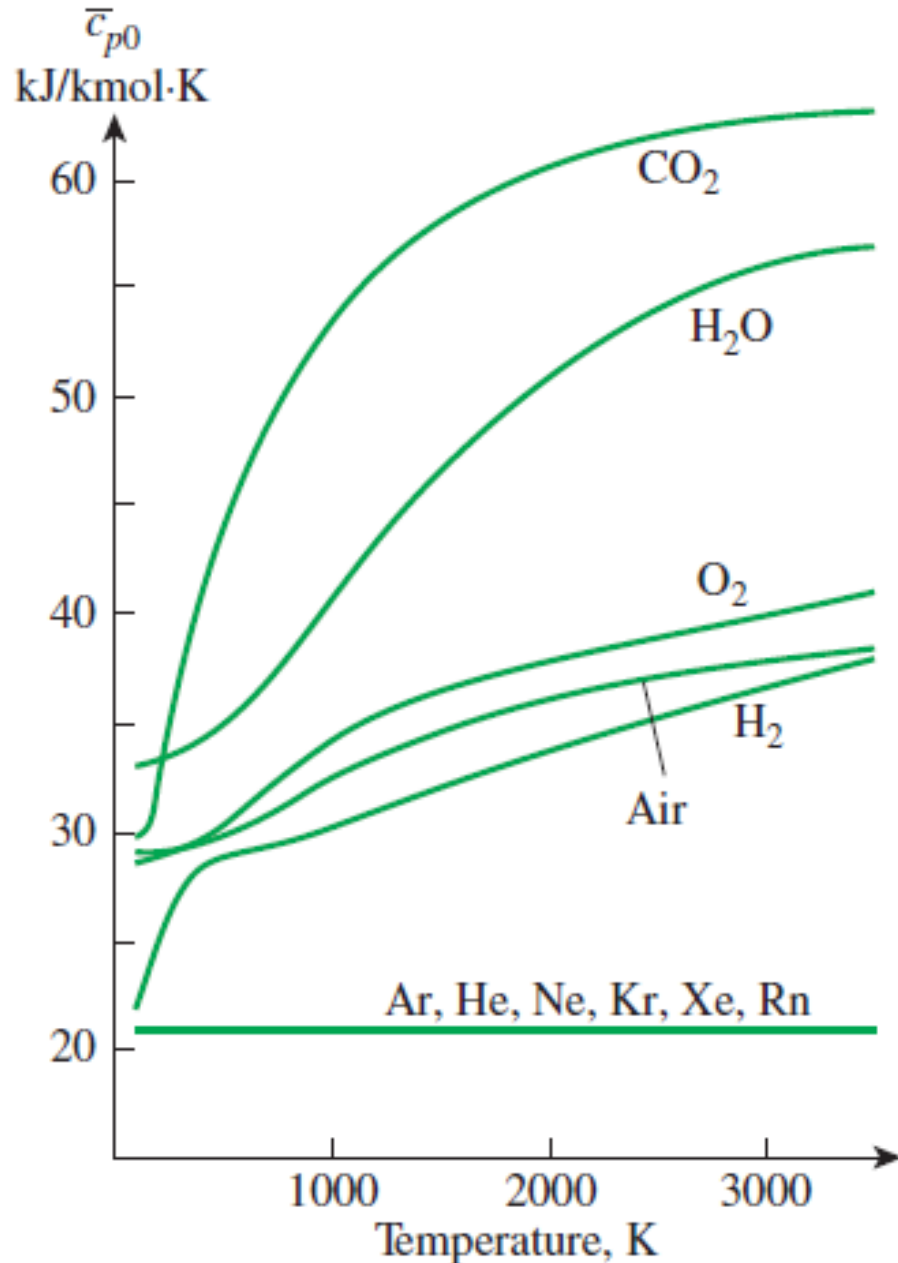
The "bar" on the $\overline{C_{P0}}$ indicates that specific heat is on per mole basis

Since Ar, He, Ne, Kr, Xe, Rn are monatomic gases, the ideal gas or zero pressure specific heats of these gases remain constant.

For polyatomic gases, the specific heats increase with temperature due to translational, rotational and vibrational components of kinetic energy

Ref. Cengel and Boles, 8th Edition (2015)

Relations between specific heats of ideal gases :

As seen in a previous lecture, enthalpy is defined as

$$H = U + PV$$

Thus, on a basis of unit mass of substance we have

$$h = u + Pv$$

For an ideal gas, the equation of state is $Pv = RT$.
Substituting this in above equation, we get

$$h = u + RT$$

Taking derivative of both sides with respect to T, we get

$$\boxed{C_P = C_V + R}$$

On a molar basis : $\boxed{\overline{C}_P = \overline{C}_V + R_u}$

Here $\overline{C}_P$ and $\overline{C}_V$ are molar specific heats and R_u is universal gas constant

Another important quantity related to specific heats is the ratio of specific heats, defined as $k = C_P / C_V$

Example :

A piston–cylinder device initially contains 0.5 m³ of nitrogen gas at 400 kPa and 27°C. An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of 2800 J occurs during the process. Determine the final temperature of nitrogen.
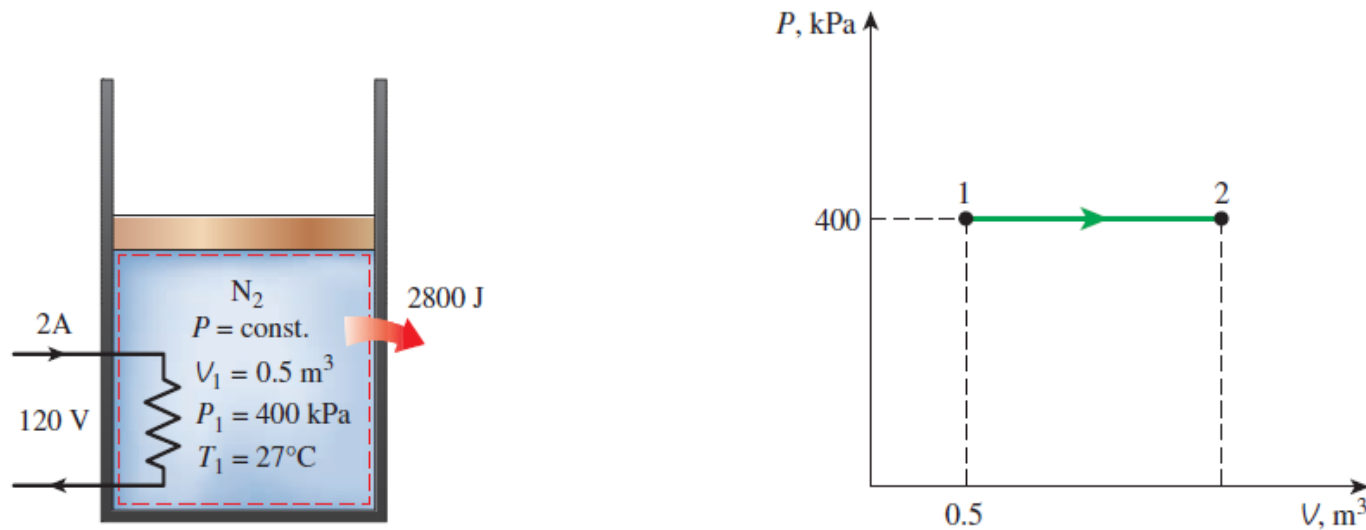
SOLUTION Nitrogen gas in a piston–cylinder device is heated by an electric resistance heater. Nitrogen expands at constant pressure while some heat is lost. The final temperature of nitrogen is to be determined.

Assumptions 1 Nitrogen is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values of −147°C, and 3.39 MPa. 2 The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. 3 The pressure remains constant during the process and thus $P_2 = P_1$. 4 Nitrogen has constant specific heats at room temperature.

Analysis We take the contents of the cylinder as the *system*. This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston–cylinder device typically involves a moving boundary and thus boundary work, W_b. Also, heat is lost from the system and electrical work W_e is done on the system.

First, let us determine the electrical work done on the nitrogen:

$$W_e = VI \, \Delta t = (120 \text{ V})(2 \text{ A})(5 \times 60 \text{ s})\left(\frac{1 \text{ kJ/s}}{1000 \text{ VA}}\right) = 72 \text{ kJ}$$

The mass of nitrogen is determined from the ideal-gas relation:

$$m = \frac{P_1 V_1}{RT_1} = \frac{(400 \text{ kPa})(0.5 \text{ m}^3)}{(0.297 \text{ kPa·m}^3/\text{kg·K})(300 \text{ K})} = 2.245 \text{ kg}$$

$$W_{e,in} - Q_{out} - W_{b,out} = \Delta U$$

$$W_{e,in} - Q_{out} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1)$$

since $\Delta U + W_b = \Delta H$ for a closed system undergoing a quasi-equilibrium expansion or compression process at constant pressure. From Table A–2a, $c_p = 1.039 \text{ kJ/kg·K}$ for nitrogen at room temperature. The only unknown quantity in the previous equation is T_2, and it is found to be

$$72 \text{ kJ} - 2.8 \text{ kJ} = (2.245 \text{ kg})(1.039 \text{ kJ/kg·K})(T_2 - 27°C)$$

$$T_2 = 56.7°C$$

Discussion Note that we could also solve this problem by determining the boundary work and the internal energy change rather than the enthalpy change.

Polytropic process :

Consider a sufficiently slow process of expansion or compression of an ideal gas such that mechanical equilibrium is maintained throughout and that the gas is in a state of internal equilibrium (quasi-static 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 : $X = \dfrac{\delta Q_{in}}{\delta W_{out}}$

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, $dU = (X - 1)P dV$

OR $m\, C_V\, dT = (X - 1)\, P dV$ (A)

(since $dU = m\, C_V\, dT$ for an ideal gas, m = mass of ideal gas)

Polytropic process :

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,

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

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

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

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

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

$$-d(\ln P) = nd(\ln V)$$

Here k = C_P / C_V is the ratio of specific heats

Polytropic process :

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

$$PV^n = C \text{ (constant)}$$

Thus, a polytropic process of an ideal gas is a quasi-static expansion or compression process in which Cp, Cv, and X (energy transfer ratio) are constant. Now we can consider work done by the gas in a polytropic process as follows :

$$W_{out} = \int_1^2 P dV$$

$$= \int_1^2 \frac{C}{V^n} dV$$

$$= C\left(\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} \right) \qquad \text{for } n \neq 1$$

$$= \left(\frac{P_2 V_2^n V_2^{-n+1} - P_1 V_1^n V_1^{-n+1}}{-n+1} \right)$$

$$= \left(\frac{P_2 V_2 - P_1 V_1}{-n+1} \right)$$

Polytropic process :

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) → 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) → $PV^k = C$ (constant)

   The work done is given by (see expression on last slide) $W_{out} = \left(\frac{P_2 V_2 - P_1 V_1}{-k+1}\right)$