ESO201A

Lecture #12

(Class Lecture)

By

Dr. P. S. Ghoshdastidar

Summary of the basis of van der Waals EOS

$$P v = RT \quad \text{Ideal Gas EOS}$$

or $$P_{ideal}\, v_{ideal} = RT$$

$$P_{van\ der\ Waals} = P_{ideal} - \frac{a}{v^2_{van\ der\ Waals}}$$

$$\Rightarrow \quad P_{ideal} = P_{van\ der\ Waals} + \frac{a}{v^2_{van\ der\ Waals}}$$

$$v_{van\ der\ Waals} = v_{ideal} + b$$

$$\Rightarrow \quad v_{ideal} = v_{van\ der\ Waals} - b$$

P_{ideal} and v_{ideal} in the ideal gas equation are replaced by $P_{van\ der\ Waals} + \frac{a}{v^2_{van\ der\ Waals}}$ and $v_{van\ der\ Waals} - b$ respectively.

Thus,
$$\left(P_{van\ der\ Waals} + \frac{a}{v^2_{van\ der\ Waals}}\right)\left(v_{van\ der\ Waals} - b\right) = RT$$

Example Problem

Predict the pressure of nitrogen gas at $T = 175$ K and $v = 0.00375\ m^3/kg$ on the basis of (a) the ideal gas equation of state, and (b) the van der Waals equation of state. Compare the values obtained with the experimentally determined value of 10,000 kPa. The gas constant of nitrogen gas is 0.2968 kJ/kg K.

Solution

(a) Using the ideal-gas equation of state, the pressure is found to be

$$P = \frac{RT}{v} = \frac{(0.2968)(175)}{0.00375}$$

$$= 13,851 \text{ kPa}$$

~~P. C. Error~~ $= \cancel{\frac{v_{expt} - v_{ideal}}{10,000\, v_{expt}}}$

$$\text{P. C. Error} = \frac{P_{ideal\text{-}gas} - P_{expt}}{P_{expt.}}$$

$$= \frac{13851 - 10,000}{10,000}$$

$$= 0.3851$$

$$= 38.51\%$$

(b) van der Waals EOS

$$a = \frac{27 R^2 T_{cr}^2}{64 P_{cr}} \qquad kJ \cdot m^3/kg^2$$

$$b = \frac{R T_{cr}}{8 P_{cr}} \qquad m^3/kg$$

For Nitrogen

$T_{cr} = 126.2 K$

$P_{cr} = 3.39$ MPa

$$a = \frac{27 (0.2968)^2 (126.2)^2}{64 \times 3.39 \times 10^3}$$

$$= \frac{27 (0.08809024)(15926.44)}{64 \times 3.39 \times 10^3}$$

$$= \frac{37880.02589}{216,960}$$

$$= 0.17459 4514$$

$$= 0.175 \; m^6 \, k\frac{N}{m^2} / kg^2$$

$$= 0.175 \; k m^4 N / kg^2$$

$$= 0.175 \; m^3 . kN\text{-}m / kg^2$$

$$= 0.175 \; m^3 \, kJ / kg^2$$

$$= 0.175 \; m^3$$

$$\frac{(kJ/kg\,K)^2 (K)^2}{kPa}$$

$$= \frac{(kN-m)^2}{kg^2 K^2} K^2 \cdot \frac{1}{k\frac{N}{m^2}}$$

$$= \frac{(kN)^2 m^2}{kg^2} \cdot \frac{1\,m^2}{kN}$$

$$= \frac{kN\,m^4}{kg^2}$$

$$= \frac{kN \cdot m \cdot m^3}{kg^2}$$

$$= \frac{kJ \cdot m^3}{kg^2}$$

$$b = \frac{R\,T_{cr}}{8\,P_{cr}}$$

$$= \frac{(0.2968)(126.2)}{8\,(3.39 \times 10^3)}$$

$$= \frac{37.45616}{27.12 \times 10^3}$$

$$= \frac{37.45616}{27120}$$

$$= 1.38 \times 10^{-3}$$

$$= 0.00138\ m^3/kg$$

$$\cancel{\frac{\frac{m^6 \cdot kPa}{kg^2}}{\frac{m^6}{kg^2}}}$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$= \frac{(0.2968)(\cancel{126.2}\ 175)}{0.00375 - 0.00138} - \frac{0.175}{(0.00375)^2}$$

$$P = \frac{51.94}{2.37 \times 10^{-3}} - \frac{0.175}{1.40625 \times 10^{-5}}$$

$$= 21915.61181 - 12444.44444$$

$$= 9471.16737$$

$$= 9471.2 \text{ kPa}$$

$$= 9471 \text{ kPa}$$

$$\text{P. C. Error} = \frac{9471 - 10,000}{10,000}$$

$$= -0.0529$$

$$= -5.29\%$$

$$= -5.3\%$$

Energy Analysis of closed systems

(To be taught)

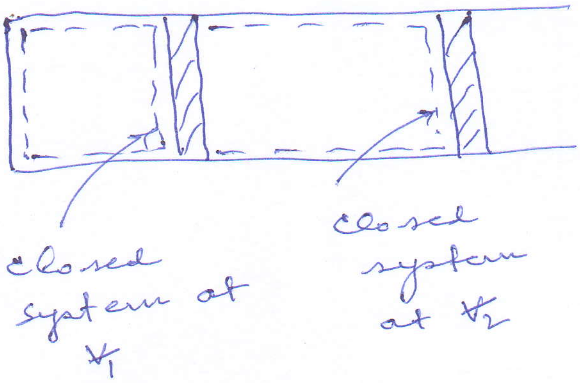
- Moving boundary work
- General energy balance (1st law): $E_{in} - E_{out} = \Delta E_{system}$ applied to pure substances.
- Definition of specific heats
- Obtain relations for u and h of ideal gases in terms of specific heats and temperature changes.
- Perform energy balances on various systems involving ideal gases.
- Repeat this for systems involving solids and liquids, which are approximated as incompressible substances.

Moving Boundary Work

Moving boundary or displacement work occurs when the boundary of the closed system moves.

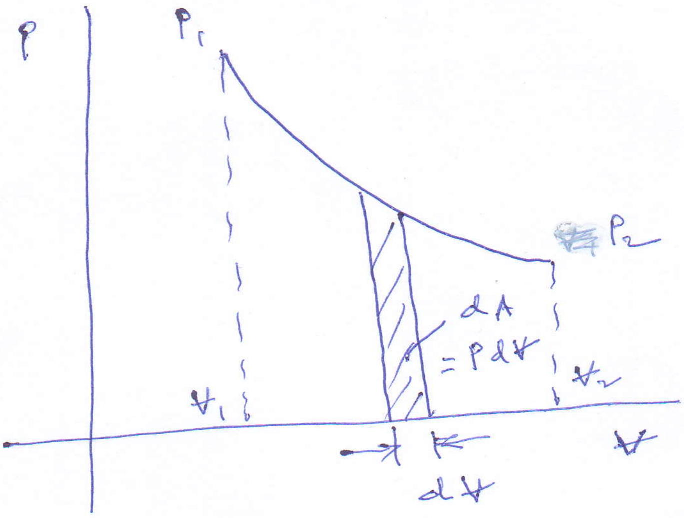
Frequently, only part of the boundary moves, when for example, a gas expands against a piston in a cylinder. On the other hand, the whole boundary could move as in the expansion of a balloon.

Quasi-equilibrium Expansion



Expansion work is positive.

Compression work is negative.



Force = Pressure × Piston area

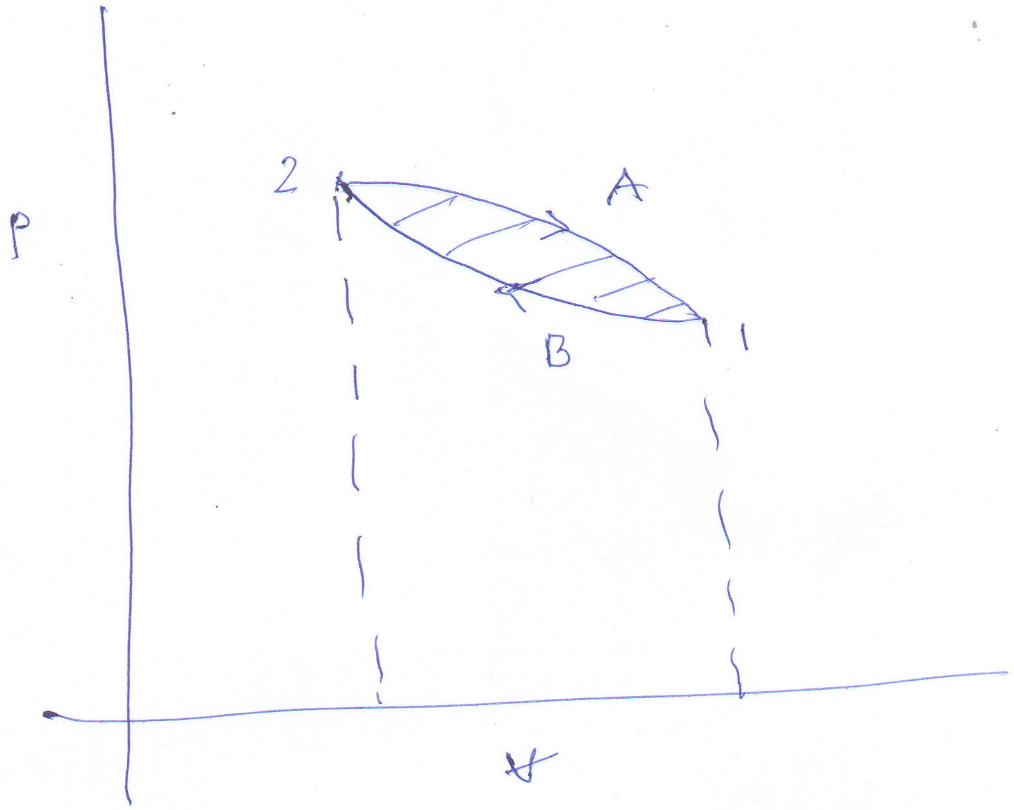
$$\delta W_b = P A \cancel{dx}\, ds$$

$$\Rightarrow \delta W_b = P\, dV$$

$$W_b = \int_1^2 P\, dV$$

The area under the curve is the integral, that is, total work done.

Cycle



Net work in a cycle

$= W_{expansion} - W_{compression}$

$= W_A - W_B$

$= W_{\text{done by the system}} - W_{\text{done on the system}}$

Nonquasi-equilibrium Processes

To calculate the displacement work, we need to know the relation between P and $\forall$.

Strictly speaking, the pressure P in $W_b = \int_1^2 P\,d\forall$ is the pressure at the inner surface of the piston. It becomes equal to the pressure of the gas in the cylinder only if the process is quasi-equilibrium and thus the entire gas in the cylinder is at the same pressure at any given time.

The eq. $W_b = \int_1^2 P\,d\forall$ can also be used for nonquasi-equilibrium processes provided that the pressure at the inner face of the piston is used for P.

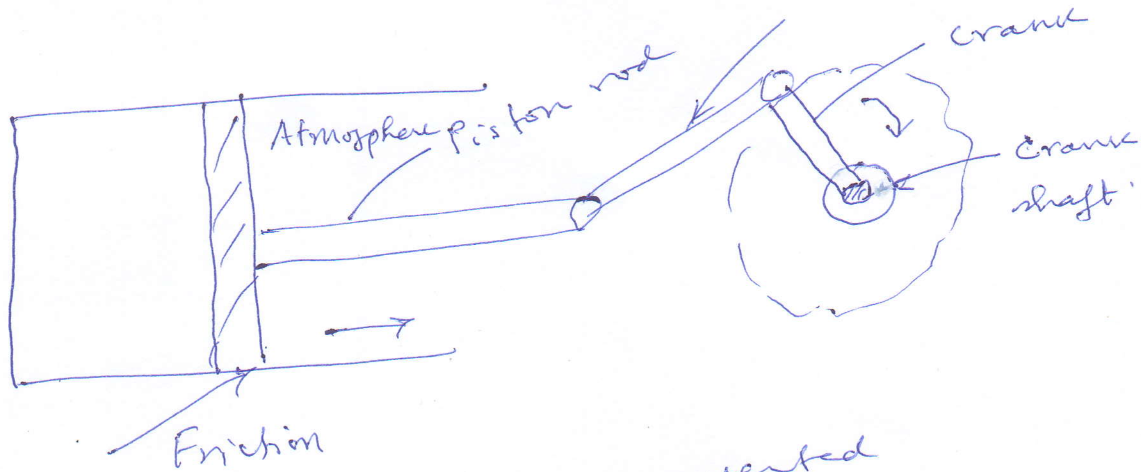
$$W_b = \int_1^2 P_i\,d\forall$$

where P_i is the pressure at the inner face of the piston.

Boundary Work (Expansion) in real engines

$$W_b = W_{friction} + W_{atm} + W_{crank}$$

$$= \int_1^2 \left(F_{friction} + P_{atm} A + F_{crank} \right) ds$$



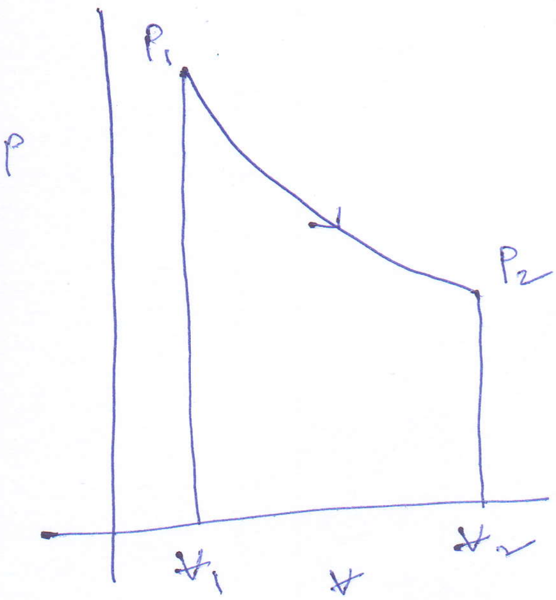
Frictional work is converted to heat.

Energy transmitted through the crankshaft is transmitted to other components (such as wheels).

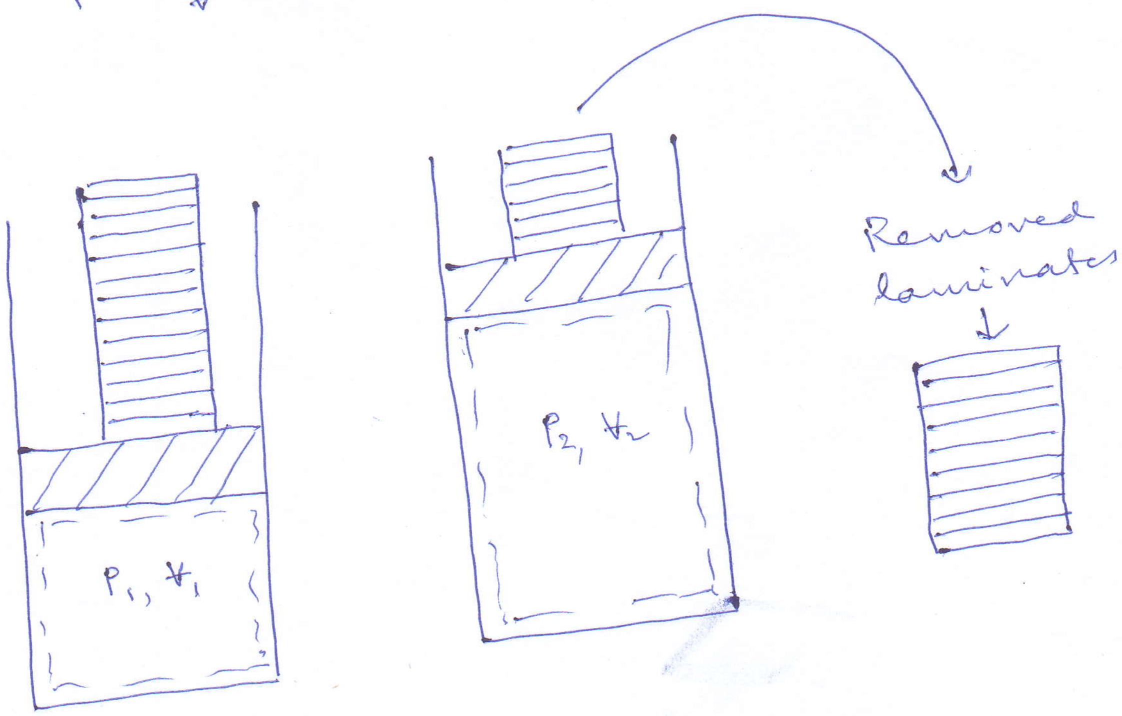
W_b is used to overcome friction b/w the piston and the cylinder, to push the atmospheric air out of ~~the~~ way, and to rotate the crankshaft.

Differences between Reversible and Irreversible Work

Reversible



Weighted piston.
Piston is frictionless.

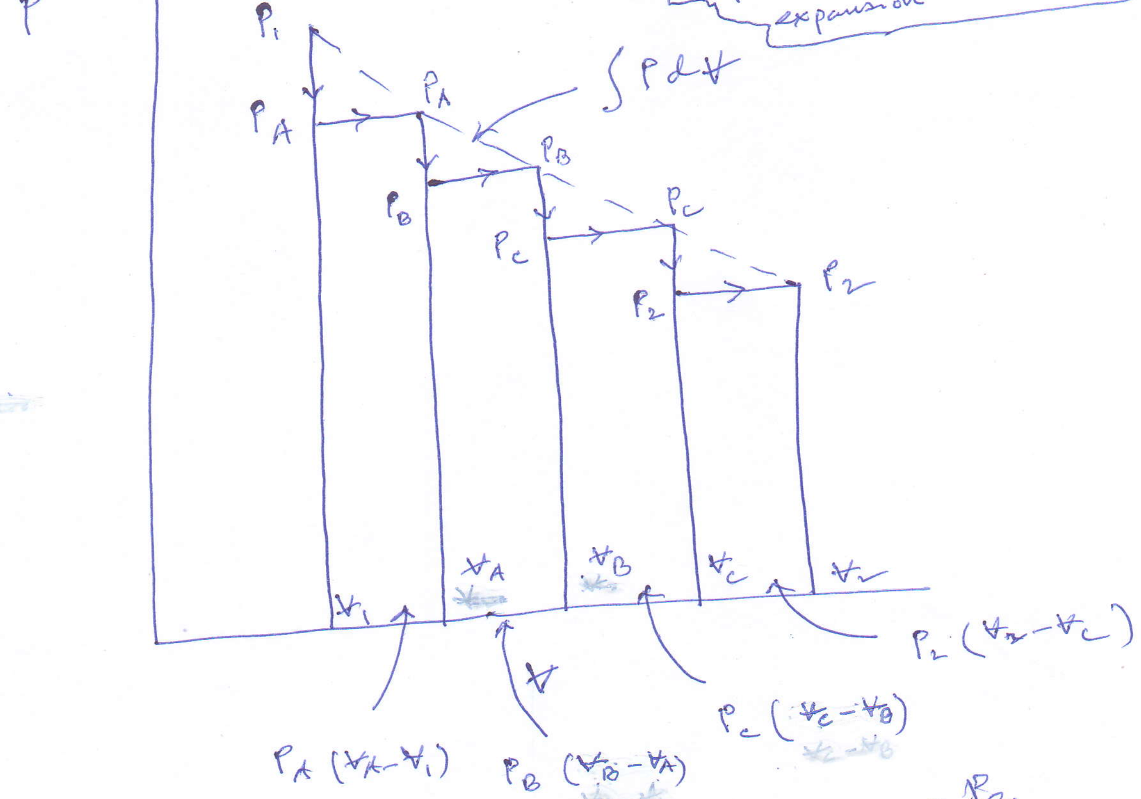


Irreversible Expansion

Laminates are removed in finite steps of equal numbers.

Suppose now that the weights are removed in four equal bundles, instead of one at a time.

$$\boxed{W_{irrev,\ expansion} < \int P\,dV}$$



$$P_1 \rightarrow P_A \rightarrow P_B \rightarrow P_C \rightarrow P_2$$

$$W_{irrev,\ expansion} = P_A(V_A - V_1) + P_B(V_B - V_A) + P_C(V_C - V_B) + P_2(V_2 - V_C)$$

$$= \text{Sum of the areas of four rectangles}$$