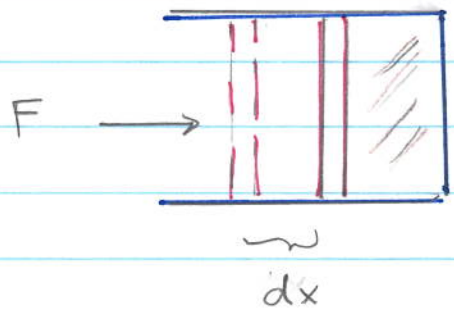
Work

- Consider the compression of a gas



$$đW = F \cdot dx$$

now $A\,dx = -dV$

So since $p = F/A$ we have

$$\boxed{đW = -p(T,V)\,dV}$$

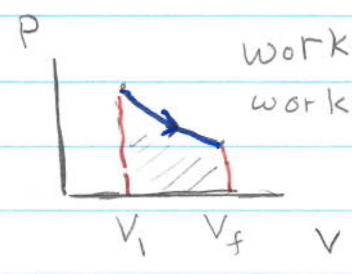
work by me   determined by EOS β_P, κ_T

- This is the work by me on gas. Of course, the work by the gas on me is minus this, $đW_{\substack{by\\gas}} = +p\,dV$.

- So

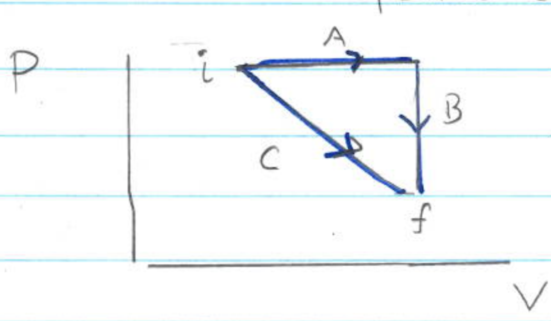
$$W_{if} = -\int_i^f p(T,V)\,dV$$

$$= -\text{Area under curve}$$



work by me <0
work by gas >0

- The work done depends on the path e.g.



- i.e. the work $W_A + W_B \neq W_C$

We say $đW$ is an inexact differential. Meaning it represents a small amount of work, dV is an exact differential and represents a small change in volume V, $dV = V_f - V_i$, it does not depend on the path

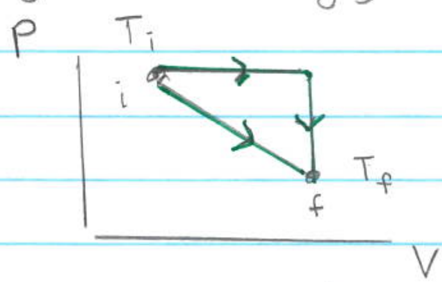
The first Law

- The change in energy of the system is the heat put in and the work done

$$dU = \underbrace{đQ}_{\text{amount of heat put in}} + \underbrace{đW}_{\text{amont of work done}}$$

dU: Change in energy

- The change in energy is independent of the path



- At the initial and final points the temperature is determined by the eos $P = P(T, V)$

And $\Delta U = U_f - U_i$

with e.g. $U_f = U(T_f, V_f)$

Heat Capacity + The First Law

- Consider the energy of the system $U(T, V)$ as a function of volume of the gas and temperature. The number of particles is held fixed (implicitly):

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

~ kinetic and potential terms

So the heat that flows in is:

$$đQ = dU - đW$$

(use $đW = -p\,dV$)

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

(1) So first if volume is held constant:

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

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

So a specific heat measurement tells you about the internal energy changes

we quoted this earlier

So for a MAIG

$$U = \frac{3}{2} N k_B T \quad \text{and} \quad C_V = \frac{3}{2} N k_B$$

(2) Now if pressure is held fixed

☆ $$C_p = \left(\frac{đQ}{dT}\right)_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \underbrace{\left(\frac{dV}{dT}\right)_p}_{V\beta_p}$$

Now recall

$$\frac{1}{V}\left(\frac{dV}{dT}\right)_p \equiv \beta_p \equiv \text{thermal expansion coefficient}$$

- **Remark** Eq. ☆ after small algebra gives

$$\left(\frac{\partial U}{\partial V}\right)_p = \frac{C_p - C_V}{V\beta_p} - p$$

So this gives us an experimental way to determine $\left(\frac{\partial U}{\partial V}\right)_p$. Recall that $\left(\frac{\partial U}{\partial V}\right)_p$ reflects the interactions between the particles, which is reflected in the energy response C_p, C_V and the expansion, β_p.

- **Ideal Gasses** have $\left(\frac{\partial U}{\partial V}\right)_T = 0$,

and, $V = \frac{N k_B T}{p} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{N k_B}{p}$

and so we find as claimed earlier

$$\boxed{C_p = C_V + N k_B} \qquad \text{(ideal gas)}$$

- For ideal mono-atomic / diatomic gasses C_V is $\frac{3}{2} k_B T$ or $\frac{5}{2} k_B T$ respectively and C_p is.

$$C_p = \begin{cases} 5/2\, N k_B & \text{(mono)} \\ 7/2\, N k_B & \text{(dia)} \end{cases} \quad \text{or} \quad C_p^{\text{mol}} = \begin{cases} 5/2\, R \\ 7/2\, R \end{cases}$$

cp per mole

- For later use we define

$$\boxed{\gamma \equiv \frac{C_p}{C_V}} = \frac{C_V + N k_B}{C_V}$$

this is called the adiabatic index because it arises in an adiabatic expansion

For a MAIG we have

$$\gamma = \frac{3/2\, N k_B + N k_B}{\frac{3}{2} N k_B} = \frac{5}{3}$$