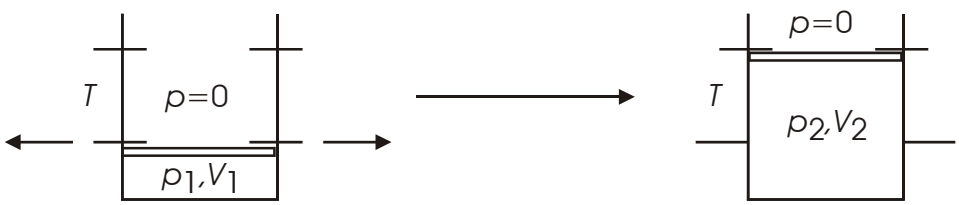
Isothermal Gas Expansion $(\Delta T = 0)$

gas (p_1, V_1, T) = gas (p_2, V_2, T)

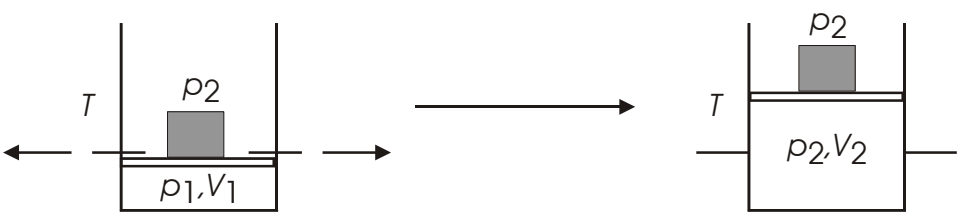
Irreversibly (many ways possible)

(1) Set $p_{ext} = 0$

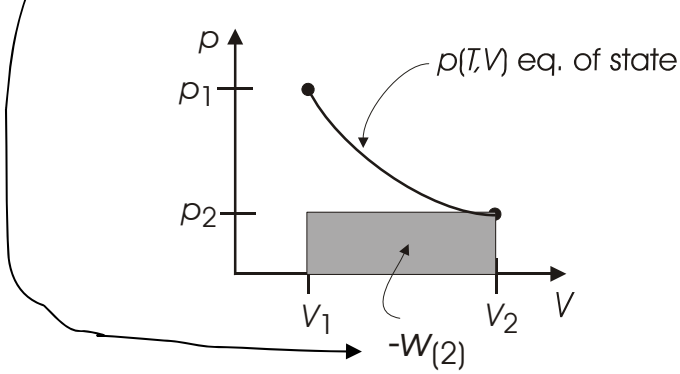


$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext} dV = 0$$

(2) Set $p_{ext} = p_2$



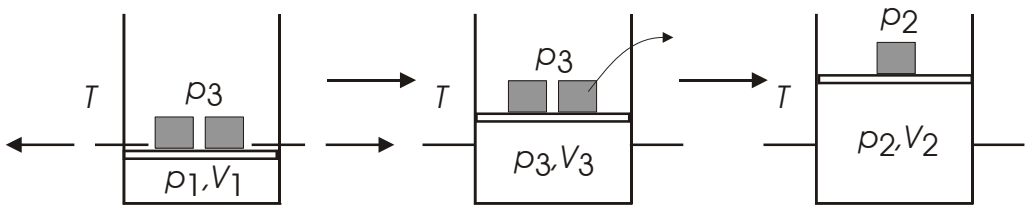
$$w_{(2)} = -\int_{V_1}^{V_2} p_2 dV = -p_2 (V_2 - V_1)$$



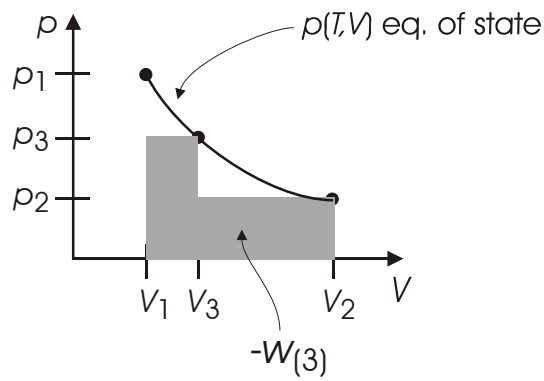
Note, work is negative: system expands against surroundings

(3) Carry out change in two steps

gas (p_1, V_1, T) = gas (p_3, V_3, T) = gas (p_2, V_2, T) $\quad p_1 > p_3 > p_2$

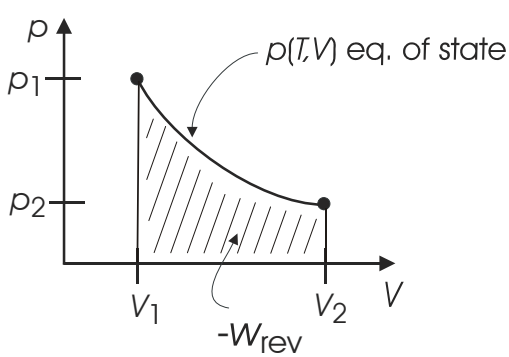


$$w_{(3)} = -\int_{V_1}^{V_3} p_3 dV - \int_{V_3}^{V_2} p_2 dV = -p_3(V_3 - V_1) - p_2(V_2 - V_3)$$



More work delivered to surroundings in this case.

(4) <u>Reversible</u> change $\quad p = p_{ext}$ throughout



$$w_{rev} = -\int_{V_1}^{V_2} p dV$$

Maximum work delivered to surroundings for isothermal gas expansion is obtained using a <u>reversible</u> path

For ideal gas:

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{p_2}{p_1}$$

The Internal Energy U

$$dU = đq + đw \qquad \text{(First Law)}$$

$$dU = C_{path}dT - p_{ext}dV$$

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

Some frequent constraints:

- Reversible $\Rightarrow$ $dU = đq_{rev} + đw_{rev} = đq_{rev} - pdV$ $(p = p_{ext})$
- Isolated $\Rightarrow$ $đq = đw = 0$
- Adiabatic $\Rightarrow$ $đq = 0 \Rightarrow dU = đw \overset{reversible}{=} -pdV$
- Constant V $\Rightarrow$ $w = 0 \Rightarrow dU = đq_V$

but also

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

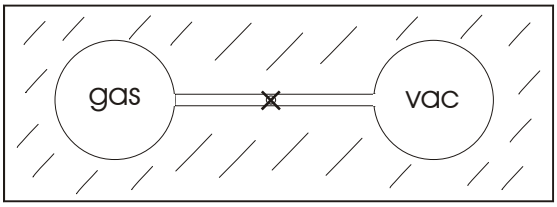
$$\Rightarrow \quad đq_V = \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$đq_V = C_V dT \quad \Rightarrow \quad \boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V}$$ very important result!!

So $\quad dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

what is this?

Joule Free Expansion of a Gas (to get $\left(\frac{\partial U}{\partial V}\right)_T$)



Adiabatic $q = 0$

Expansion into Vac. $w = 0$
(p_{ext}=0)

gas (p_1, T_1, V_1) = gas (p_2, T_2, V_2)

Since $q = w = 0$ $\Rightarrow$ dU or $\Delta U = 0$ Constant U

Recall $$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV_U = -C_V dT_U$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U$$

measure in Joule exp't! $\left(\frac{\Delta T}{\Delta V}\right)_U$

Joule did this. $$\lim_{\Delta V \to 0}\left(\frac{\Delta T}{\Delta V}\right)_U = \left(\frac{\partial T}{\partial V}\right)_U \equiv \eta_J \quad \therefore \quad \boxed{dU = C_V dT - C_V \eta_J dV}$$

Joule coefficient

- For Ideal gas $\Rightarrow$ $\eta_J = 0$ exactly
  $dU = C_V dT$ Always for ideal gas
  $U(T)$ only depends on T

The internal energy of an ideal gas depends only on temperature

Consequences $\Rightarrow$ $\Delta U = 0$ For all isothermal expansions or compressions of ideal gases

$\Rightarrow$ $\Delta U = \int C_V dT$ For any ideal gas change in state