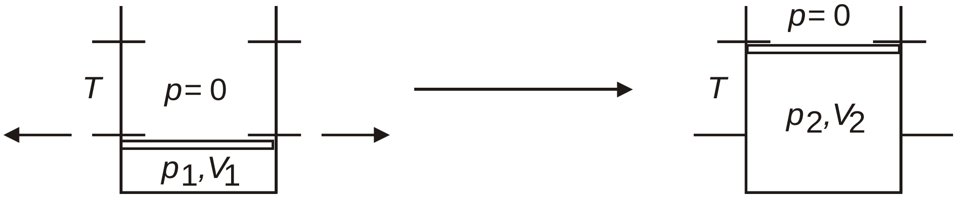
EXPANSIONS, ENERGY, ENTHALPY

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

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

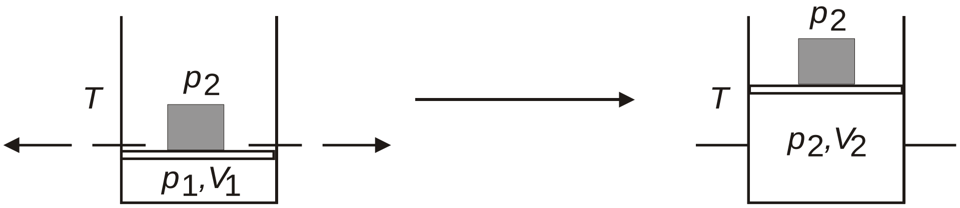
Irreversibly (many ways possible)

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

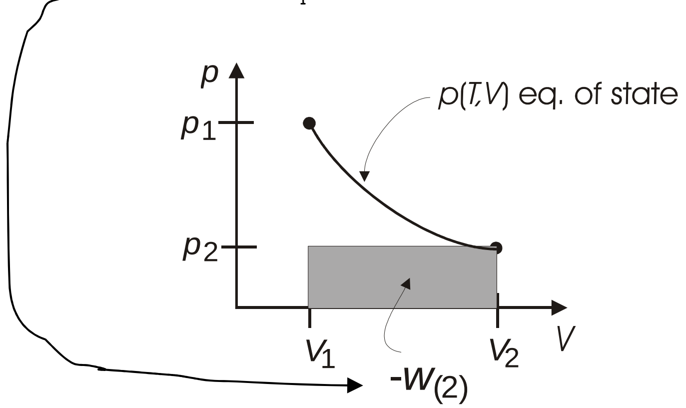


$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext}\,dV = 0$$

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



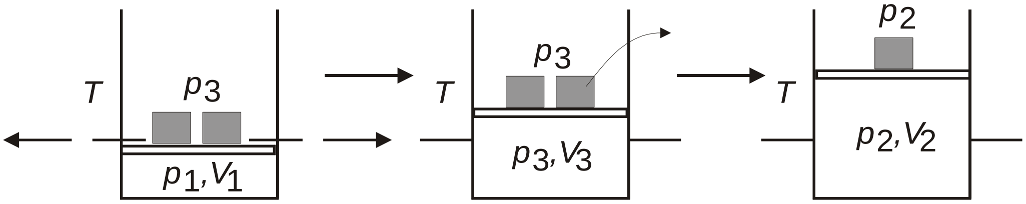
$$w_{(2)} = -\int_{V_1}^{V_2} p_2\,dV = -p_2\left(V_2 - V_1\right)$$



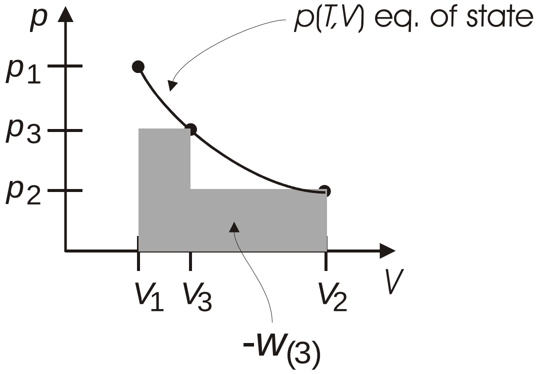
Note, work is negative: system expands against surroundings

(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) $\quad p_1 > p_3 > p_2$

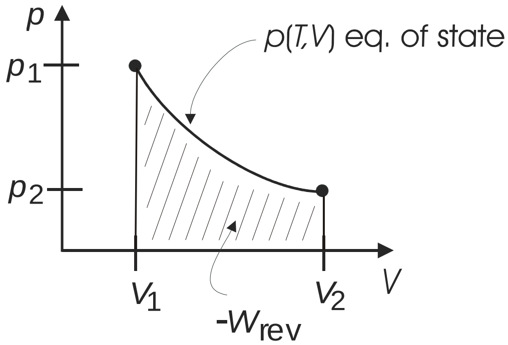


$$w_{(3)} = -\int_{V_1}^{V_3} p_3 dV - \int_{V_3}^{V_2} p_2 dV = -p_3\left(V_3 - V_1\right) - p_2\left(V_2 - V_3\right)$$



More work delivered to surroundings in this case.

(4) Reversible 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 reversible 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** $\Rightarrow$ $w = 0 \Rightarrow dU = đq_V$

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

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

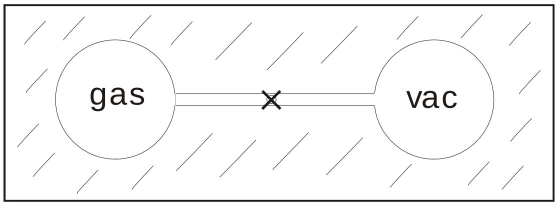
But also

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

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

$\uparrow$ 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

Enthalpy $H(T,p)$ $H \equiv U + pV$

Chemical reactions and biological processes usually take place under constant pressure and with reversible pV work. Enthalpy turns out to be an especially useful function of state under those conditions.

$$\begin{array}{ccc} \text{gas }(p,\ T_1,\ V_1) & \overset{\textit{reversible}}{\underset{\textit{const.p}}{=}} & \text{gas }(p,\ T_2,\ V_2) \\ U_1 & & U_2 \end{array}$$

$$\Delta U = q + w = q_p - p\Delta V$$

$$\Delta U + p\Delta V = q_p$$

$$\Delta U + \Delta(pV) = q_p \quad \Rightarrow \quad \Delta\overbrace{(U + pV)}^{\text{define as } H} = q_p$$

$H \equiv U + pV \quad \Rightarrow \quad \Delta H = q_p$ for a reversible constant p process

Choose $H(T,p) \quad \Rightarrow \quad dH = \left(\dfrac{\partial H}{\partial T}\right)_p dT + \left(\dfrac{\partial H}{\partial p}\right)_T dp$

What are $\left(\dfrac{\partial H}{\partial T}\right)_p$ and $\left(\dfrac{\partial H}{\partial p}\right)_T$?

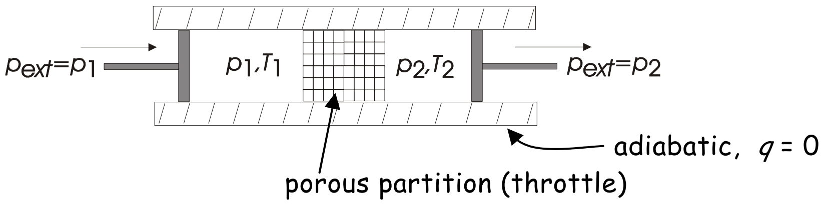
- $\left(\dfrac{\partial H}{\partial T}\right)_p \quad \Rightarrow$ for a reversible process at constant p ($dp = 0$)

$$dH = \text{đ}q_p \quad \text{and} \quad dH = \left(\frac{\partial H}{\partial T}\right)_p dT$$

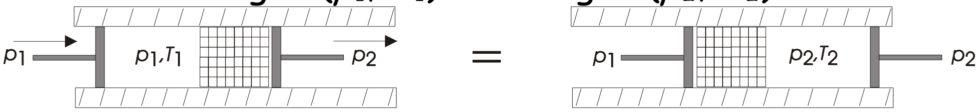
$$\Rightarrow \quad \text{đ}q_p = \left(\frac{\partial H}{\partial T}\right)_p dT \qquad \text{but} \qquad \text{đ}q_p = C_p dT \quad \text{also}$$

$$\therefore \qquad \boxed{\left(\frac{\partial H}{\partial T}\right)_p = C_p}$$

- $\left(\frac{\partial H}{\partial p}\right)_T \quad \Rightarrow$ Joule-Thomson expansion



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



$$w = p_1V_1 - p_2V_2 \quad \Rightarrow \quad \Delta U = q + w = p_1V_1 - p_2V_2 = -\Delta(pV)$$

$$\therefore \quad \Delta U + \Delta(pV) = 0 \quad \Rightarrow \Delta(U + pV) = 0$$

$$\therefore \quad \boxed{\Delta H = 0}$$

Joule-Thomson is a constant Enthalpy process.

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad \Rightarrow \quad C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp_H$$

$$\Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\partial T}{\partial p}\right)_H \quad \leftarrow \text{ can measure this } \quad \left(\frac{\Delta T}{\Delta p}\right)_H$$

Define $\displaystyle \lim_{\Delta p \to 0}\left(\frac{\Delta T}{\Delta p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_H \equiv \mu_{JT}$ ← Joule-Thomson Coefficient

$$\therefore \quad \boxed{\left(\frac{\partial H}{\partial p}\right)_T = -C_p\mu_{JT}} \quad \text{and} \quad \boxed{dH = C_p dT - C_p\mu_{JT} dp}$$

For an ideal gas: $U(T)$, $pV=nRT$

$$H \equiv U(T) + pV = \underbrace{U(T) + nRT}_{\text{only depends on } T,\ \text{no } p \text{ dependence}},$$

$$H(T) \quad \Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = \mu_{JT} = 0 \quad \text{for an ideal gas}$$

For an ideal gas $\bar{C}_p = \bar{C}_V + R$

$$\bar{C}_p = \left(\frac{\partial \bar{H}}{\partial T}\right)_p, \qquad \bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

$$\underbrace{\bar{H} = \bar{U} + p\bar{V}}_{\downarrow}, \qquad p\bar{V} = RT$$

$$\overbrace{\left(\frac{\partial \bar{H}}{\partial T}\right)_p = \left(\frac{\partial \bar{U}}{\partial T}\right)_p + R}^{\uparrow}$$

$$\bar{C}_p = \overbrace{\bar{C}_V + \underbrace{\cancel{\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T}}_{=0 \text{ for ideal gas}} \left(\frac{\partial \bar{V}}{\partial T}\right)_p + R}^{\uparrow}$$

$$\therefore \quad \bar{C}_p = \bar{C}_V + R$$