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5.60 Thermodynamics & Kinetics
Spring 2008

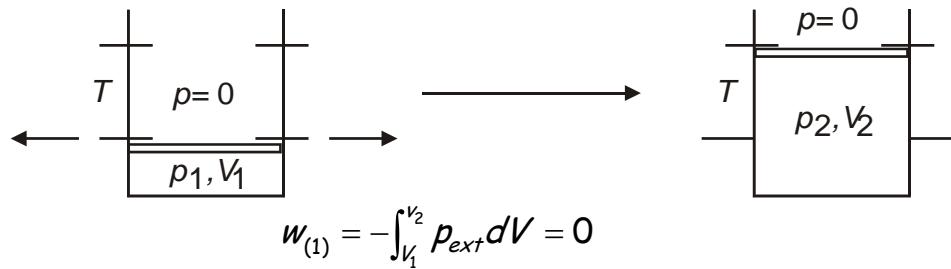
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Isothermal Gas Expansion ($\Delta T = 0$)

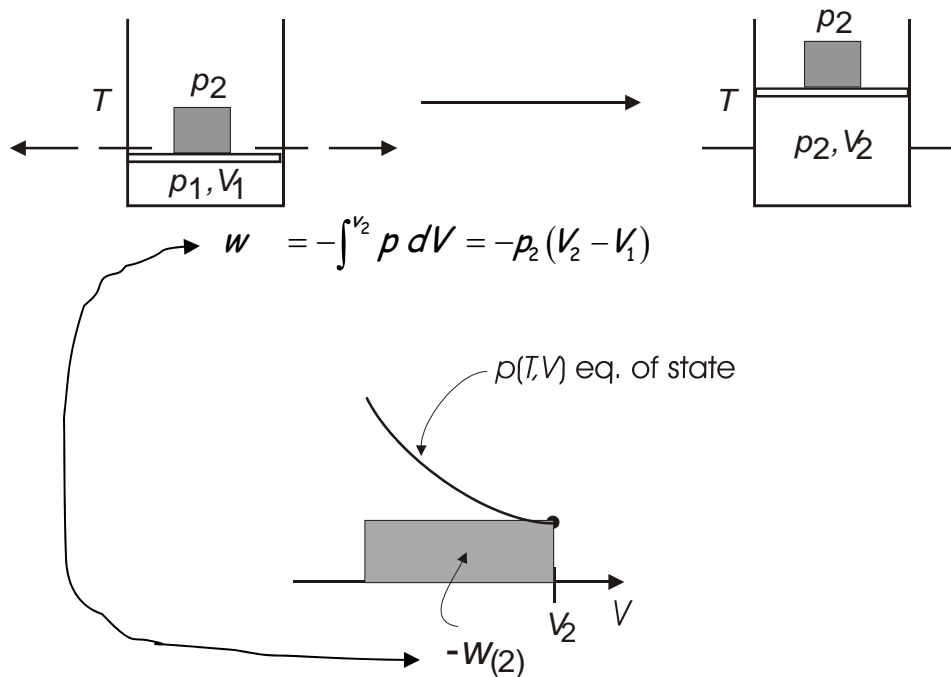
gas (p_1, V_1, T) = gas (p_2, V_2, T)

Irreversibly (many ways possible)

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



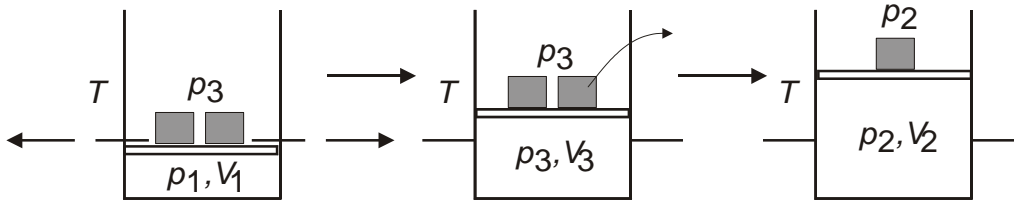
(2) Set $p_{ext} = p_2$



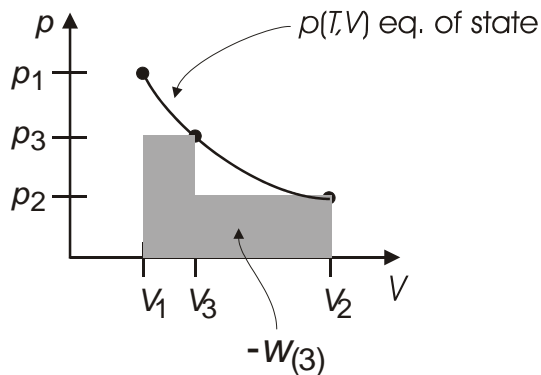
Note, work is negative: system expands against surroundings

(3) Carry out change in two steps

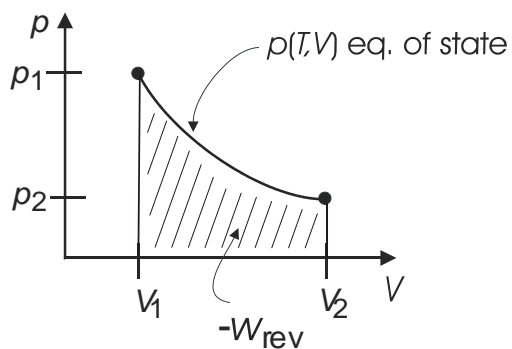
gas (p_1, V_1, T) = gas (p_3, V_3, T) = gas (p_2, V_2, T) $p_1 > p_3 > p_2$



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



More work delivered to surroundings in this case.

(4) Reversible change $p = p_{\text{ext}}$ throughout

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

Maximum work delivered to surroundings for isothermal gas expansion is obtained using a reversible path

For ideal gas:

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

The Internal Energy U

$$dU = \delta q + \delta w \quad (\text{First Law})$$

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

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

Some frequent constraints:

- Reversible $\Rightarrow dU = \delta q_{\text{rev}} + \delta w_{\text{rev}} = \delta q_{\text{rev}} - p dV$
($p = p_{\text{ext}}$)
- Isolated $\Rightarrow \delta q = \delta w = 0$
- Adiabatic $\Rightarrow \delta q = 0 \Rightarrow dU = \delta w \stackrel{\text{reversible}}{=} -p dV$
- Constant V $\Rightarrow w = 0 \Rightarrow dU = \delta q_V$

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

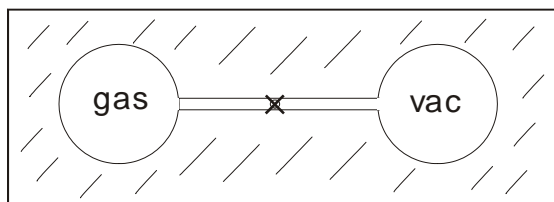
$$\Rightarrow \delta q_V = \left(\frac{\partial U}{\partial T} \right)_V dT$$

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

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

↖ 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. $w = 0$
($p_{\text{ext}} = 0$)

$$\text{gas } (p_1, T_1, V_1) = \text{gas } (p_2, T_2, V_2)$$

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

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

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

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U \quad \text{measure in Joule exp't!} \quad \left(\frac{\Delta T}{\Delta V}\right)_U$$

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

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