

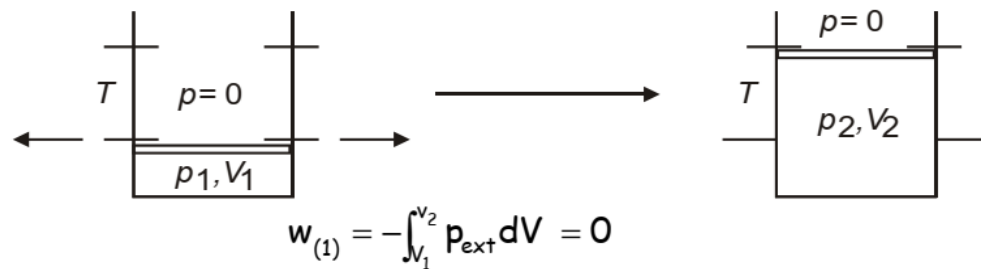
# EXPANSIONS, ENERGY, ENTHALPY

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

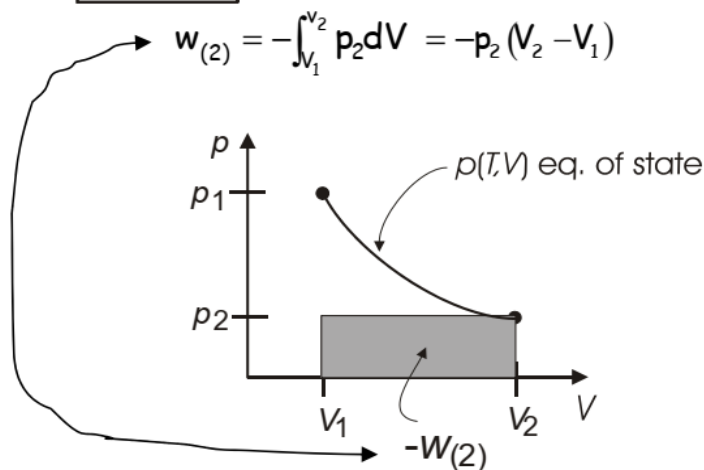
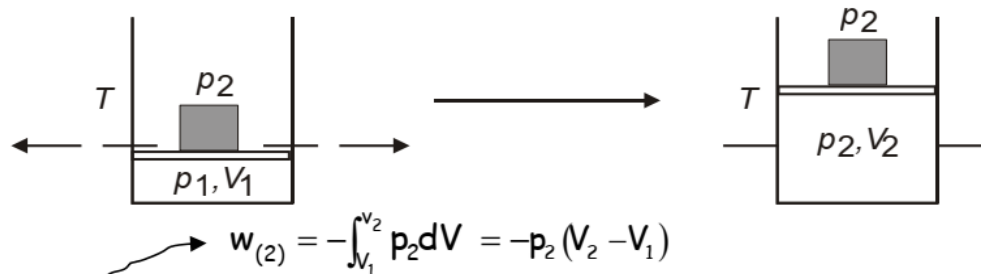
gas ( $p_1, V_1, T$ ) = gas ( $p_2, V_2, T$ )

Irreversibly (many ways possible)

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



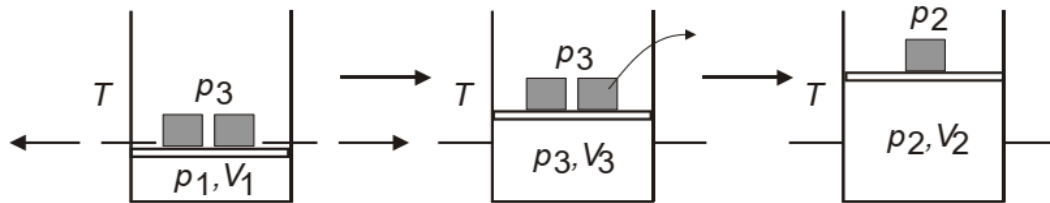
(2) Set  $p_{\text{ext}} = p_2$



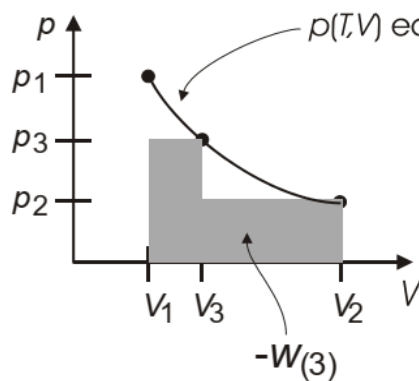
Note, work is negative: system expands against surroundings

(3) Carry out change in two steps

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

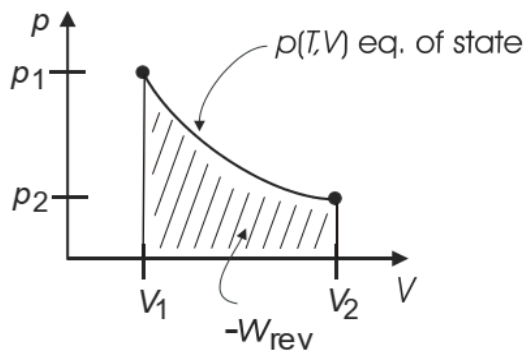


$$w_{(3)} = -\int_{V_1}^{V_3} p_3 dV - \int_{V_3}^{V_2} p_2 dV = -p_3(V_3 - V_1) - p_2(V_2 - V_3)$$



More work delivered to surroundings in this case.

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

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

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

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

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  $\Rightarrow \delta q = 0 \Rightarrow dU = \delta w^{\text{reversible}} = -p dV$
- Constant V  $\Rightarrow w = 0 \Rightarrow dU = \delta q_V$

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

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

But also

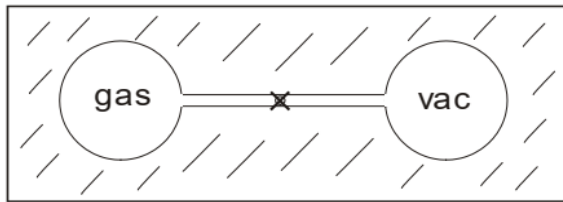
$$\delta q_V = C_V dT \Rightarrow \boxed{\left( \frac{\partial U}{\partial T} \right)_V = C_V} \quad \text{very important result!!}$$

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

← 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.  $w = 0$   
( $p_{\text{ext}}=0$ )

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

Since  $q = w = 0 \Rightarrow dU \text{ or } \Delta U = 0$  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.  $\lim_{\Delta V \rightarrow 0} \left(\frac{\Delta T}{\Delta V}\right)_U = \left(\frac{\partial T}{\partial V}\right)_U \equiv \eta_J \therefore \boxed{dU = C_V dT - C_V \eta_J dV}$

Joule coefficient

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

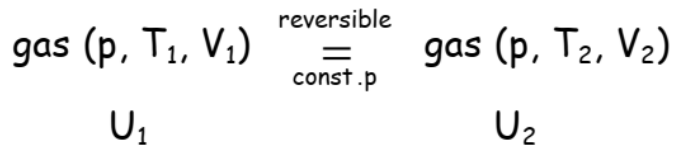
The internal energy of an ideal gas depends only on temperature

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

## 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.



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

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

$$\Delta U + \Delta(pV) = q_p \Rightarrow \Delta(U + pV) = q_p$$

define as H

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

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

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

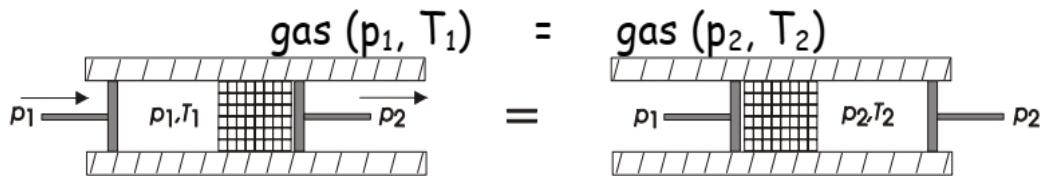
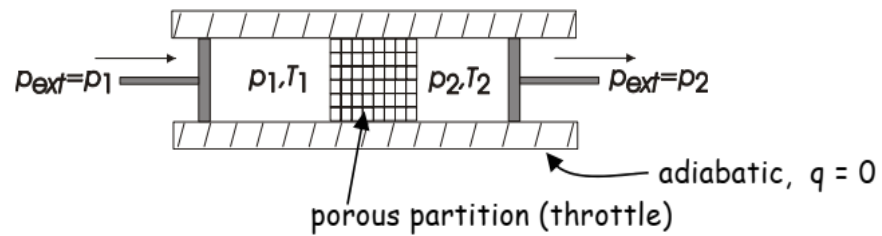
- $\left(\frac{\partial H}{\partial T}\right)_p \Rightarrow$  for a reversible process at constant  $p$  ( $dp = 0$ )

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

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

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

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



$$w = p_1 V_1 - p_2 V_2 \Rightarrow \Delta U = q + w = p_1 V_1 - p_2 V_2 = -\Delta(pV)$$

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

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

Joule-Thomson is a constant Enthalpy process.

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

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

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

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

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

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

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

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

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

$$\bar{H} = \bar{U} + p\bar{V}, \quad p\bar{V} = RT$$

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

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

$$\therefore \bar{C}_p = \bar{C}_v + R$$

## EXPANSIONS, THERMODYNAMIC CYCLES

- Reversible Adiabatic Expansion (or compression) of an Ideal Gas

$$1 \text{ mole gas } (V_1, T_1) = 1 \text{ mole gas } (V_2, T_2)$$

$$\begin{array}{ll} \text{adiabatic} \Rightarrow \dot{dq} = 0 & \text{Reversible} \Rightarrow \dot{dw} = -pdV \\ \text{Ideal gas} \Rightarrow & dU = C_v dT \end{array}$$

$$\therefore \text{From 1}^{\text{st}} \text{ Law} \quad dU = -pdV \Rightarrow C_v dT = -pdV \text{ along path}$$

$$C_v dT = -pdV \quad \xrightarrow{p=\frac{RT}{V}} \quad C_v \frac{dT}{T} = -R \frac{dV}{V}$$

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \quad \Rightarrow \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/C_v} \quad \xrightarrow{C_p - C_v = R \text{ for i.g.}} \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v} - 1}$$

Define  $\gamma \equiv \frac{C_p}{C_v} \Rightarrow \boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}}$

For monatomic ideal gas:  $\left. \begin{array}{l} C_v = \frac{3}{2}R \\ C_p = \frac{5}{2}R \end{array} \right\} \gamma = \frac{5}{3} \text{ (> 1 generally)}$

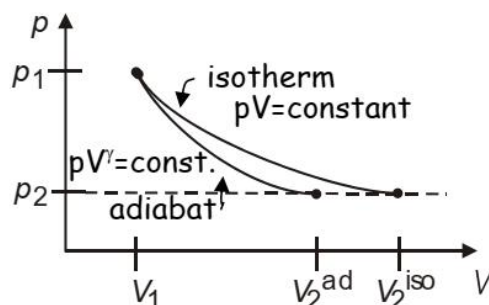
[More generally the heat capacity for a molecular species has a temperature dependence that can be approximated as  $C_p(T) = a + bT + cT^2$  with  $a$ ,  $b$ , and  $c$  tabulated.]

In an adiabatic expansion ( $V_2 > V_1$ ), the gas cools ( $T_2 < T_1$ ).  
And in an adiabatic compression ( $V_2 < V_1$ ), the gas heats up.

For an ideal gas (one mole)  $T = \frac{pV}{R} \Rightarrow \left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^\gamma \Rightarrow \boxed{p_1 V_1^\gamma = p_2 V_2^\gamma}$

$pV^\gamma$  is constant along a reversible adiabat

Recall, for an isothermal process  $T = \text{constant} \Rightarrow pV = \text{constant}$



$V_2^{\text{adiabat}} < V_2^{\text{isotherm}}$   
because the gas  
cools during reversible  
adiabatic expansion

- Irreversible Adiabatic Expansion of an ideal gas against a constant external pressure

$$1 \text{ mol gas } (p_1, T_1) = 1 \text{ mol gas } (p_2, T_2) \quad (p_{\text{ext}}=p_2)$$

$$\begin{aligned} \text{adiabatic} &\Rightarrow dq = 0 \\ \text{Constant } p_{\text{ext}} = p_2 &\Rightarrow dw = -p_2 dV \\ \text{Ideal gas} &\Rightarrow dU = C_v dT \\ \text{1}^{\text{st}} \text{ Law} &\Rightarrow dU = -p_2 dV \end{aligned}$$

$$\therefore C_v dT = -p_2 dV$$

$$\text{Integrating: } C_v (T_2 - T_1) = -p_2 (V_2 - V_1)$$

$$\text{Using } pV = RT \quad T_2 (C_v + R) = T_1 \left( C_v + \frac{p_2 R}{p_1} \right)$$

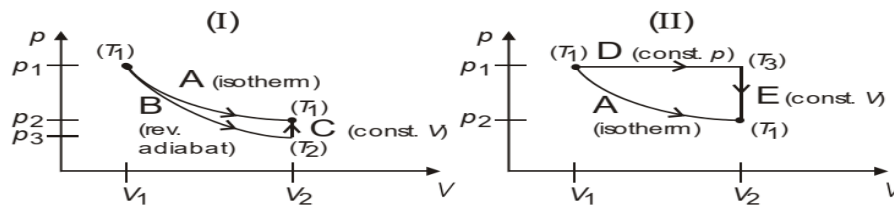
Note  $p_2 < p_1 \Rightarrow T_2 < T_1$  Again, expansion cools

Note also  $(-w_{\text{rev}}) > (-w_{\text{irrev}})$  as expected, less work is recovered through an irreversible process

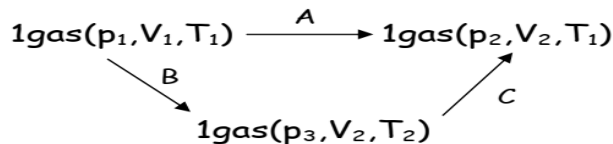
### Thermodynamic Cycles

- Reversible Ideal Gas processes:

Find  $\Delta U, \Delta H, q, w$



For (I)



There are two paths from initial to final states (A) and (B+C). As far as functions of states (e.g. U, H) are concerned it doesn't matter which path is taken.

[A] 1 mol gas ( $p_1, V_1, T_1$ )  $\stackrel{\text{const. } T}{=}$  1 mol gas ( $p_2, V_2, T_1$ )

Ideal gas isotherm:

$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

$$w_A = -RT_1 \ln \frac{V_2}{V_1} \quad q_A = RT_1 \ln \frac{V_2}{V_1}$$

[B] 1 mol gas ( $p_1, V_1, T_1$ )  $\stackrel{\text{rev. adiab.}}{=}$  1 mol gas ( $p_3, V_3, T_2$ )

Adiabatic:

$$q_B = 0$$

Ideal gas:

$$\Delta U_B = C_V (T_2 - T_1)$$

$$\Delta H_B = C_p (T_2 - T_1)$$

1<sup>st</sup> Law:

$$w_B = C_V (T_2 - T_1)$$

[C] 1 mol gas ( $p_3, V_2, T_2$ )  $\stackrel{\text{reversible}}{\stackrel{\text{const. } V}{=}}$  1 mol gas ( $p_2, V_2, T_1$ )

Constant V:

$$w_C = 0$$

Ideal gas:

$$\Delta U_C = C_V (T_1 - T_2)$$

$$\Delta H_C = C_p (T_1 - T_2)$$

1<sup>st</sup> Law:

$$q_C = C_V (T_1 - T_2)$$

[A]

vs.

[B] + [C]

$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

$$\Delta U_B + \Delta U_C = 0 = \Delta U_A$$

$$\Delta H_B + \Delta H_C = 0 = \Delta H_A$$

$$q_A = RT_1 \ln \frac{V_2}{V_1}$$

$$q_B + q_C = C_V (T_1 - T_2) \neq q_A$$

$$w_A = -RT_1 \ln \frac{V_2}{V_1}$$

$$w_B + w_C = C_V (T_2 - T_1) \neq w_A$$

[D]

$$\begin{aligned} \Delta U_D &= C_V (T_3 - T_1) \\ \Delta H_D &= C_p (T_3 - T_1) \end{aligned}$$

$$q_D = C_p (T_3 - T_1)$$

$$w_D = -R (T_3 - T_1)$$

[E]

$$\begin{aligned} \Delta U_E &= C_V (T_1 - T_3) \\ \Delta H_E &= C_p (T_1 - T_3) \end{aligned}$$

$$w_E = 0$$

$$q_E = C_V (T_1 - T_3)$$

[A]

vs.

[D] + [E]

$$\Delta U_A = 0$$

$$\Delta U_D + \Delta U_E = \Delta U_A$$

$$\Delta H_A = 0$$

$$\Delta H_D + \Delta H_E = \Delta H_A$$

$$q_A = RT_1 \ln \frac{V_2}{V_1}$$

$$q_D + q_E = R (T_3 - T_1) \neq q_A$$

$$w_A = -RT_1 \ln \frac{V_2}{V_1}$$

$$w_D + w_E = -R (T_3 - T_1) \neq w_A$$