

EXPANSIONS, THERMODYNAMIC CYCLES

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

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

$$\begin{array}{ll} \text{adiabatic} \Rightarrow \quad \delta q = 0 & \text{Reversible} \Rightarrow \quad \delta w = -pdV \\ \text{Ideal gas} \Rightarrow \quad dU = C_V dT & \end{array}$$

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

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

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

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

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

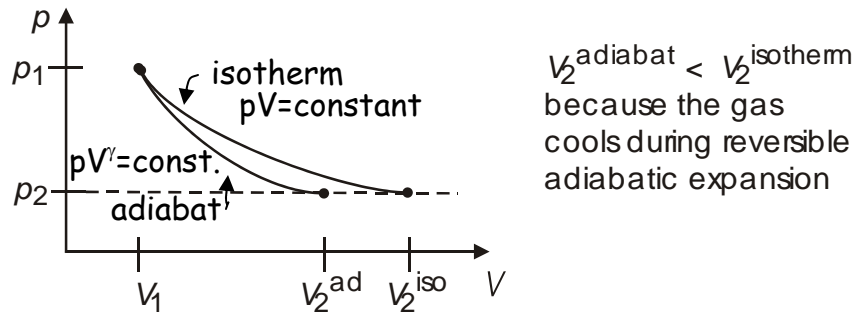
[More generally the heat capacity for a molecular species has a temperature dependence that can be approximated as $C_p(T) = a + bT + cT^2$ with a, b, and c tabulated.]

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^γ is constant along a reversible adiabat

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



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

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

adiabatic $\Rightarrow \delta q = 0$
 Constant $p_{\text{ext}} = p_2 \Rightarrow \delta w = -p_2 dV$
 Ideal gas $\Rightarrow dU = C_v dT$
 1st Law $\Rightarrow dU = -p_2 dV$

$\therefore C_v dT = -p_2 dV$

Integrating: $C_v (T_2 - T_1) = -p_2 (V_2 - V_1)$

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

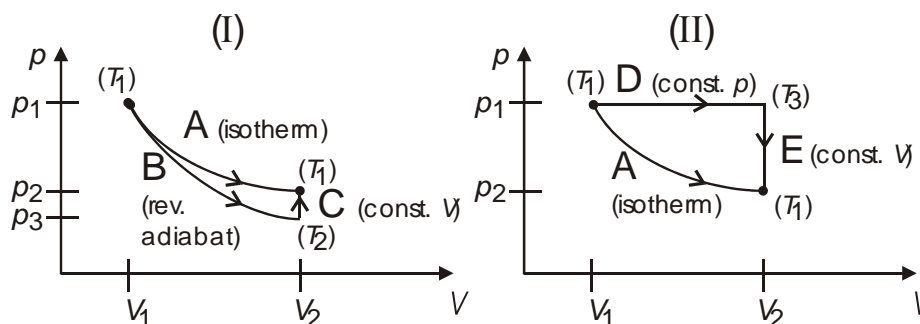
Note $p_2 < p_1 \Rightarrow T_2 < T_1$ Again, expansion cools

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

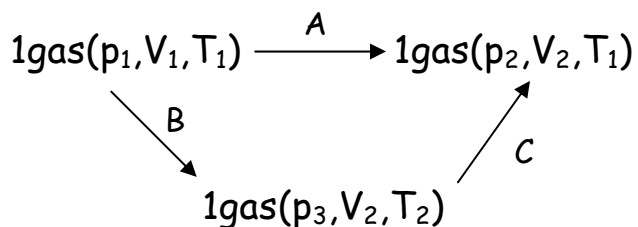
Thermodynamic Cycles

- 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) $\stackrel{\text{const. } T}{=} 1 \text{ mol gas } (p_2, V_2, T_1)$

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) $\stackrel{\text{rev.adiabat}}{=} 1 \text{ mol gas } (p_3, V_3, T_2)$

Adiabat:

$$q_B = 0$$

Ideal gas:

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

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

1st Law:

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

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

Constant V :

$$w_C = 0$$

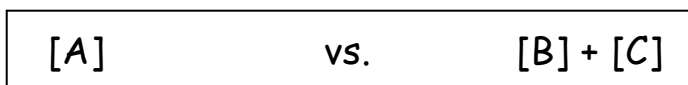
Ideal gas:

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

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

1st Law:

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



$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

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

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

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

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

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

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

[D]

$\Delta U_D = C_V (T_3 - T_1)$
$\Delta H_D = C_p (T_3 - T_1)$

$q_D = C_p (T_3 - T_1)$

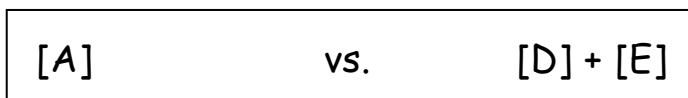
$w_D = -R(T_3 - T_1)$

[E]

$\Delta U_E = C_V (T_1 - T_3)$
$\Delta H_E = C_p (T_1 - T_3)$

$w_E = 0$

$q_E = C_V (T_1 - T_3)$



$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

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

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

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

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

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

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