Reversible Adiabatic Expansion (or compression) of an Ideal Gas

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

adiabatic $\Rightarrow$ $đq = 0$ Reversible $\Rightarrow$ $đw = -pdV$

Ideal gas $\Rightarrow$ $dU = C_v dT$

$\therefore$ From 1st Law $dU = -pdV \Rightarrow$ $C_v dT = -pdV$ along path

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

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

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

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

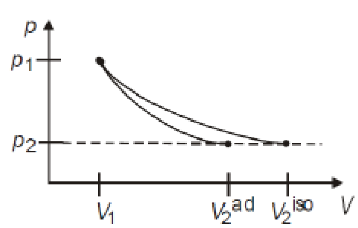
In an adiabatic expansion ($V_2 > V_1$), the gas cools ($T_2 > T_1$).
And in an adiabatic compression ($V_2 < V_1$), the gas heats up.

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

$\boxed{pV^{\gamma} \text{ is constant along a reversible adiabat}}$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

For an isothermal process T = constant $\Rightarrow$ pV = constant



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

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

Whence, $$C_V = \frac{R}{\gamma - 1}$$

Therefore $$W = C_V \Delta T = \frac{R \Delta T}{\gamma - 1}$$

Since $RT_1 = P_1V_1$ and $RT_2 = P_2V_2$, this expression may be written:

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

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

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

adiabatic ⇒ $đq = 0$

Constant $p_{ext} = p_2$ ⇒ $đw = -p_2 dV$

Ideal gas ⇒ $dU = C_v dT$

1st Law ⇒ $dU = -p_2 dV$

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

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

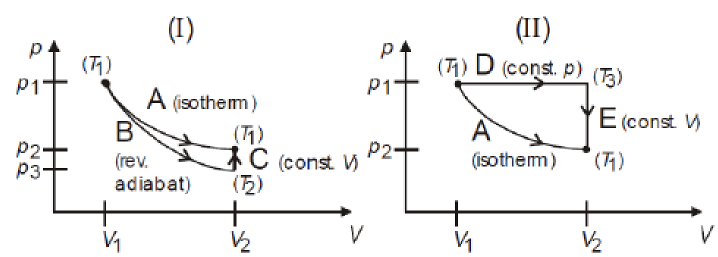
Using $pV = RT$ $$T_2(C_V + R) = T_1\left(C_V + \frac{p_2}{p_1}R\right)$$

Note $p_2 < p_1$ ⇒ $T_2 < T_1$ Again, expansion cools

Note also $(-w_{rev}) > (-w_{irrev})$ Less work is recovered through an irreversible process

Some Thermodynamic Cycles

- Reversible Ideal Gas processes: Find ΔU, ΔH, q, w, $\int \frac{đq}{T}$



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

Ideal gas isotherm: $\boxed{\Delta U_A = 0}$ $\boxed{\Delta H_A = 0}$

$$w_A = -RT_1 \ln\frac{V_2}{V_1} \qquad q_A = RT_1 \ln\frac{V_2}{V_1} \qquad \int\frac{đq}{T} = R\ln\frac{V_2}{V_1}$$

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

Adiabat: $\boxed{q_B = 0}$

Ideal gas:

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

1st Law: $\boxed{w_B = C_V(T_2 - T_1)}$ $\boxed{\int\frac{đq_B}{T} = 0}$

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

Constant V: $\boxed{w_C = 0}$ Ideal gas:

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

1st Law: $\boxed{q_C = C_V(T_1 - T_2)}$

$$\int\frac{đq_C}{T} = C_V \ln\left(\frac{T_1}{T_2}\right)$$

This result suggests that $\left(\int \frac{dq_{rev}}{T}\right)$ is a state function!

[D]

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

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

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

$$\int \frac{dq_D}{T} = C_p \ln\left(\frac{T_3}{T_1}\right)$$

[E]

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

$$w_E = 0$$

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

$$\int \frac{dq_E}{T} = C_V \ln\left(\frac{T_1}{T_3}\right)$$

EX/ One mole of an ideal gas with C_p = (7/2)R and C_v = (5/2) R expands from P_1 = 8 bar and T_1 = 600 K to P_2 = 1 bar by each of the following paths:
(a) Constant volume; (b) Constant temperature; (c) Adiabatically.
Assuming mechanical reversibility, calculate W, Q, ΔU, and ΔH for each process.

Sol/

$P_1 := 8 \cdot bar \qquad P_2 := 1 \cdot bar \qquad T_1 := 600 \cdot K \qquad Cp := \frac{7}{2} \cdot R \qquad Cv := \frac{5}{2} \cdot R$

(a) Constant V: $W = 0$ **and** $\Delta U = Q = Cv \cdot \Delta T$

$T_2 := T_1 \cdot \frac{P_2}{P_1} \qquad \Delta T := T_2 - T_1 \qquad \Delta T = -525\,K$

$\Delta U := Cv \cdot \Delta T$ **Q and** $\Delta U = -10.91 \frac{kJ}{mol}$ **Ans.**

$\Delta H := Cp \cdot \Delta T \qquad \Delta H = -15.28 \frac{kJ}{mol}$ **Ans.**

(b) Constant T: $\Delta U = \Delta H = 0$ **and** $Q = W$

$\text{Work} := R \cdot T_1 \cdot \ln\left(\frac{P_2}{P_1}\right)$ Q **and** $\text{Work} = -10.37 \frac{kJ}{mol}$ **Ans.**

(c) Adiabatic: $Q = 0$ **and** $\Delta U = W = C_V \cdot \Delta T$

$\gamma := \frac{C_P}{C_V}$ $T_2 := T_1 \cdot \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ $T_2 = 331.227\,K$ $\Delta T := T_2 - T_1$

$\Delta U := C_V \cdot \Delta T$ $\Delta H := C_P \cdot \Delta T$

W **and** $\Delta U = -5.586 \frac{kJ}{mol}$ **Ans.** $\Delta H = -7.821 \frac{kJ}{mol}$ **Ans.**

EX/An ideal gas initially at 600 K and 10 bar undergoes a four-step mechanically reversible cycle in a closed system. In step 12, pressure decreases isothermally to 3 bar; in step 23, pressure decreases at constant volume to 2 bar; in step 34, volume decreases at constant pressure; and in step 41, the gas returns adiabatically to its initial state (2 bar). Calculate Q, W, ΔU, and ΔH for each step of the cycle. Cp = (7/2)R and Cv = (5/2)R.

Sol/

$P_4 := 2bar$ $C_P := \frac{7}{2}R$ $C_V := \frac{5}{2}R$

$P_1 := 10bar$ $T_1 := 600K$ $V_1 := \frac{R \cdot T_1}{P_1}$ $V_1 = 4.988 \times 10^{-3} \frac{m^3}{mol}$

Step 41: Adiabatic $T_4 := T_1 \cdot \left(\frac{P_4}{P_1}\right)^{\frac{R}{C_P}}$ $T_4 = 378.831\,K$

$\Delta U_{41} := C_V \cdot (T_1 - T_4)$ $\Delta U_{41} = 4.597 \times 10^3 \frac{J}{mol}$

$\Delta H_{41} := C_P \cdot (T_1 - T_4)$ $\Delta H_{41} = 6.436 \times 10^3 \frac{J}{mol}$

$Q_{41} := 0 \frac{J}{mol}$ $Q_{41} = 0 \frac{J}{mol}$

$W_{41} := \Delta U_{41}$ $W_{41} = 4.597 \times 10^3 \frac{J}{mol}$

$P_2 := 3bar \qquad T_2 := 600K \qquad V_2 := \frac{R \cdot T_2}{P_2} \qquad V_2 = 0.017\frac{m^3}{mol}$

Step 12: Isothermal

$\Delta U_{12} := 0\frac{J}{mol} \qquad \Delta U_{12} = 0\frac{J}{mol}$

$\Delta H_{12} := 0 \cdot \frac{J}{mol} \qquad \Delta H_{12} = 0\frac{J}{mol}$

$Q_{12} := -R \cdot T_1 \cdot \ln\left(\frac{P_2}{P_1}\right) \qquad Q_{12} = 6.006 \times 10^3 \frac{J}{mol}$

$W_{12} := -Q_{12} \qquad W_{12} = -6.006 \times 10^3 \frac{J}{mol}$

$P_3 := 2bar \qquad V_3 := V_2 \qquad T_3 := \frac{P_3 \cdot V_3}{R} \qquad T_3 = 400K$

Step 23: Isochoric

$\Delta U_{23} := C_V \cdot (T_3 - T_2) \qquad \Delta U_{23} = -4.157 \times 10^3 \frac{J}{mol}$

$\Delta H_{23} := C_P \cdot (T_3 - T_2) \qquad \Delta H_{23} = -5.82 \times 10^3 \frac{J}{mol}$

$Q_{23} := C_V \cdot (T_3 - T_2) \qquad Q_{23} = -4.157 \times 10^3 \frac{J}{mol}$

$W_{23} := 0\frac{J}{mol} \qquad W_{23} = 0\frac{J}{mol}$

$P_4 = 2bar \qquad T_4 = 378.831K \qquad V_4 := \frac{R \cdot T_4}{P_4} \qquad V_4 = 0.016\frac{m^3}{mol}$

Step 34: Isobaric

$\Delta U_{34} := C_V \cdot (T_4 - T_3) \qquad \Delta U_{34} = -439.997\frac{J}{mol}$

$\Delta H_{34} := C_P \cdot (T_4 - T_3) \qquad \Delta H_{34} = -615.996\frac{J}{mol}$

$Q_{34} := C_P \cdot (T_4 - T_3) \qquad Q_{34} = -615.996\frac{J}{mol}$

$W_{34} := -R \cdot (T_4 - T_3) \qquad W_{34} = 175.999\frac{J}{mol}$