5.60 Thermodynamics & Kinetics
Spring 2008

•   <u>Reversible Adiabatic Expansion (or compression) of an Ideal Gas</u>

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

adiabatic $\Rightarrow$ đ$q = 0$ Reversible $\Rightarrow$ đ$w = -pdV$

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

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

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

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

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

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

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

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

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

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

$V_2^{adiabat} < V_2^{isotherm}$ because the gas cools during reversible adiabatic expansion
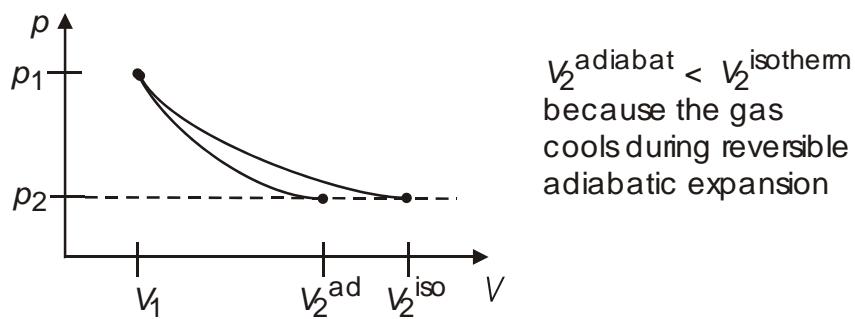
- <u>Irreversible</u> <u>Adiabatic Expansion of an ideal gas against a constant</u> <u>external pressure</u>

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

adiabatic $\Rightarrow$ đq = 0
Constant $p_{ext} = p_2$ $\Rightarrow$ đw = $-p_2 dV$
Ideal gas $\Rightarrow$ $dU = C_v dT$
1st Law $\Rightarrow$ $dU = -p_2 dV$

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

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

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

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

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

Some Thermodynamic Cycles

- Reversible Ideal Gas processes: Find ΔU, ΔH, q, w, $\int \dfrac{\text{d}q}{T}$

(I)

p

p_1 (T_1)

A (isotherm)

B

(T_1)

p_2

p_3 (rev. adiabat)

C (const. V)

(T_2)

V_1　　V_2　　V

(II)

p

p_1 (T_1) D (const. p) (T_3)

E (const. V)

p_2 A (isotherm) (T_1)

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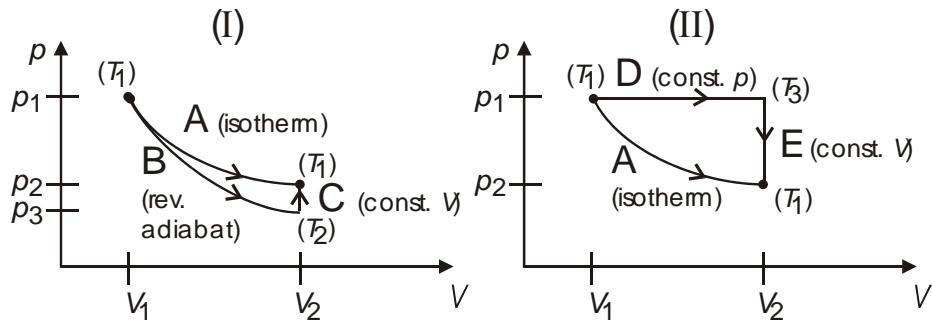
[A]　1 mol gas (p_1, V_1, T_1) $\overset{\text{const. } T}{=}$ 1 mol gas (p_2, V_2, T_1)

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

$$\boxed{w_A = -RT_1 \ln \frac{V_2}{V_1} \qquad q_A = RT_1 \ln \frac{V_2}{V_1} \qquad \int \frac{\text{d}q}{T} = R \ln \frac{V_2}{V_1}}$$

[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:　$\boxed{\begin{array}{l} \Delta U_B = C_V (T_2 - T_1) \\ \Delta H_B = C_p (T_2 - T_1) \end{array}}$

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

[C]   1 mol gas $(p_3, V_2, T_2) \overset{\text{reversible}}{\underset{\text{const. } V}{=}}$ 1 mol gas (p_2, V_2, T_1)
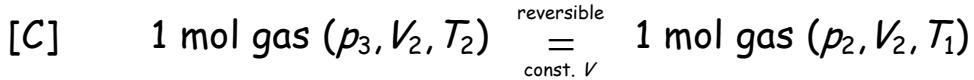
Constant V: $\boxed{w_C = 0}$ Ideal gas: $\boxed{\begin{array}{l} \Delta U_C = C_V (T_1 - T_2) \\ \Delta H_C = C_p (T_1 - T_2) \end{array}}$

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

$$\boxed{\int \frac{\text{d}q_C}{T} = C_V \ln\left(\frac{T_1}{T_2}\right)}$$

$$\boxed{[A] \qquad \text{vs.} \qquad [B] + [C]}$$

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

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

$q_A = R T_1 \ln \dfrac{V_2}{V_1}$ $q_B + q_C = C_V (T_1 - T_2) \neq q_A$

$w_A = -R T_1 \ln \dfrac{V_2}{V_1}$ $w_B + w_C = C_V (T_2 - T_1) \neq w_A$

$\int \dfrac{\text{d}q_A}{T} = R \ln \dfrac{V_2}{V_1}$ $\int \dfrac{\text{d}q_B}{T} + \int \dfrac{\text{d}q_C}{T} = R \ln\left(\dfrac{V_2}{V_1}\right) = \int \dfrac{\text{d}q_A}{T}$

This result suggests that $\left(\int \dfrac{\text{d}q_{rev}}{T}\right)$ is a state function!

[D] $\boxed{\begin{array}{l} \Delta U_D = C_V (T_3 - T_1) \\ \Delta H_D = C_p (T_3 - T_1) \end{array}}$ $\boxed{q_D = C_p (T_3 - T_1)}$

        $\boxed{w_D = -R (T_3 - T_1)}$ $\boxed{\int \dfrac{\text{d}q_D}{T} = C_p \ln\left(\dfrac{T_3}{T_1}\right)}$

[E] $\boxed{\begin{array}{l}\Delta U_E = C_V\left(T_1 - T_3\right) \\ \Delta H_E = C_p\left(T_1 - T_3\right)\end{array}}$ $\boxed{w_E = 0}$ $\boxed{q_E = C_V\left(T_1 - T_3\right)}$

$$\boxed{\int \frac{\text{đ}q_E}{T} = C_V \ln\left(\frac{T_1}{T_3}\right)}$$

$$\boxed{\qquad [A] \qquad\qquad \text{vs.} \qquad\qquad [D] + [E] \qquad}$$

$\Delta U_A = 0$ $\Delta U_D + \Delta U_E = \Delta U_A$

$\Delta H_A = 0$ $\Delta H_D + \Delta H_E = \Delta H_A$

$q_A = R T_1 \ln\dfrac{V_2}{V_1}$ $q_D + q_E = R\left(T_3 - T_1\right) \neq q_A$

$w_A = -R T_1 \ln\dfrac{V_2}{V_1}$ $w_D + w_E = -R\left(T_3 - T_1\right) \neq w_A$

$\displaystyle\int \frac{\text{đ}q_A}{T} = R\ln\frac{V_2}{V_1}$ $\displaystyle\int \frac{\text{đ}q_D}{T} + \int \frac{\text{đ}q_E}{T} = R\ln\left(\frac{V_2}{V_1}\right) = \int \frac{\text{đ}q_A}{T}$

Here again $\left(\displaystyle\int \frac{\text{đ}q_{rev}}{T}\right)$ looks like a state function!