Eq. de Estado $PV = nRT$

$$\Delta U = U(T_i) - U(T_f)$$

$\boxed{U(T)}$ $\Delta T \to 0$ gás rarefeito

Demonstração empírica

$U,$ Variáveis de estado
$V,$
$P,$
T

Entalpia: Joule-Thomson

$$\Delta U = U_f - U_i = P_i V_i - P_f V_f = -W_{i \to f}$$

$$\underbrace{U_f + P_f V_f}_{} = \underbrace{U_i + P_i V_i}_{} \quad ; \Delta Q = 0$$

conserva no processo

$H \equiv U + P.V$ → cte. do sistema (Joule-Thomson)

Entalpia: $H = U + P.V$

outros processos $\Rightarrow$ variação de entalpia

$$dH = dU + \left(\frac{\partial}{\partial P}(PV)\right)_V dP + \left(\frac{\partial}{\partial V}(PV)\right)_P \cdot dV$$

$$dH = dU + VdP + PdV$$

definição 1ª lei termodinâmica

$$dU = d'Q - d'W$$
$$= d'Q - P.dV$$

$$dH = d'Q + V.dP$$

Processo isobárico (reações químicas a P cte)

$$dH = d'Q$$

$$f(x,y,z) \therefore df = \left(\frac{\partial}{\partial x}f\right)dx + \left(\frac{\partial f}{\partial y}\right)dy + \left(\frac{\partial f}{\partial z}\right)dz$$

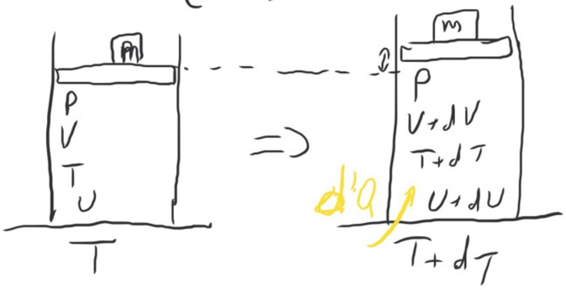
Capacidade Térmica Molar C

$$1 \text{ mol} \Rightarrow d'Q = C\,dT$$

distintos processos

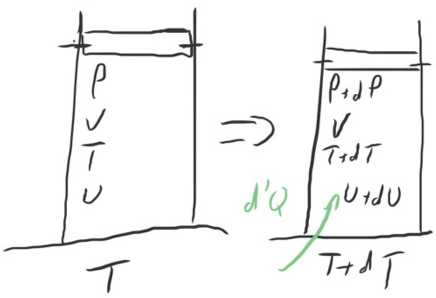
Processo isobárico ($P = cte$)

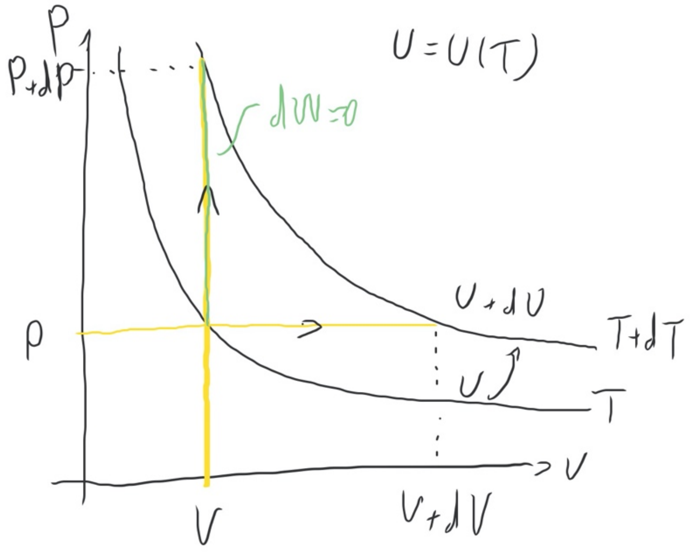
$$d'Q_p = C_p \cdot dT$$



Processo isocórico ($V = cte$)

$$d'Q_v = C_v \cdot dT$$





$U = U(T)$

C_p

$C_V \rightarrow dW = 0$

Isocórico

$dU_V = C_V \cdot dT = d'Q_V$

Isobárica

$dU_p = d'Q_p - d'W$

$= C_p \cdot dT - P \cdot dV$

$U(T) \rightarrow dU_V = dU_p$

$$\boxed{C_V dT = C_p dT - P dV}$$

$C_V dT = C_p dT - P dV \longrightarrow PV = RT \quad (1\,mol)$

$V \cdot \underbrace{dP}_{=0} + P \cdot dV = R \cdot dT$

$C_V dT = C_p dT - R dT$

$R = C_p - C_V \qquad C_p = C_V + R \quad \left(\text{gás ideal} \rightarrow R \simeq 2 \frac{cal}{mol \cdot K}\right)$

Energia Interna do Gás:

Vol. cte $\Rightarrow d'W = 0$

$dU = C_V \cdot dT$

Capacidade térmica molar a Volume constante

$C_V = \frac{d}{dT} U(T) = C_V(T)$

$$\boxed{dU = n\, C_V(T)\, dT}$$

$$U(T) = U(T_0) + n\int_{T_0}^{T} C_v(T')\,dT'$$

n = nº de moles

$$C_v(T) = C_v \qquad n\,C_v\cdot T_0 \rightarrow U_0 = U$$

$$\boxed{U(T) = U_0 + n\cdot C_v\cdot T}$$

independe de P, V

depende da quantidade de matéria

Processos adiabáticos: Gás Ideal

$PV = nRT$; $U(T)$; $C_v(T) = C_v$

$U(T) = U_0 + nC_v \cdot T$

$d'Q = 0 \Rightarrow dU = -dW = -P \cdot dV$

Processo isobárico $dU = nC_v dT$ $\rightarrow$ $\boxed{P \cdot dV = -nC_v \cdot dT}$

$\rightarrow \quad nR\,dT = P \cdot dV + V \cdot dP$

$nR\,dT = -dU + V \cdot dP$

$nR\,dT = -nC_v dT + V \cdot dP \Rightarrow \boxed{V \cdot dP = n(C_v + R)dT = nC_p dT}$

$P \cdot dV = -nC_v dT$

$V \cdot dP = nC_p \cdot dT \cdot \frac{C_v}{C_v} = nC_v dT \cdot \gamma = -\gamma \cdot P \cdot dV$

$$\frac{dP}{P} = -\gamma \frac{dV}{V} \qquad \gamma = \frac{C_p}{C_v} = \left(1 + \frac{R}{C_v}\right) > 1$$

$dV \rightarrow dP \leftarrow dT \rightarrow dV$

T variável

$$\int_{P_0}^{P} \frac{dP'}{P'} = -\gamma \int_{V_0}^{V} \frac{dV'}{V'}$$

$$\ln P' \Big|_{P_0}^{P} = -\gamma \ln V \Big|_{V_0}^{V} \Rightarrow \ln\left(\frac{P}{P_0}\right) = -\gamma \ln\left(\frac{V}{V_0}\right) = \ln\left(\frac{V}{V_0}\right)^{-\gamma}$$

$$\frac{P}{P_0} = \left(\frac{V_0}{V}\right)^{\gamma} \to P \cdot V^{\gamma} = P_0 V_0^{\gamma} = \underline{cte}$$ no processo adiabático

$$C_p = C_v + R \to C_p - C_v = R$$

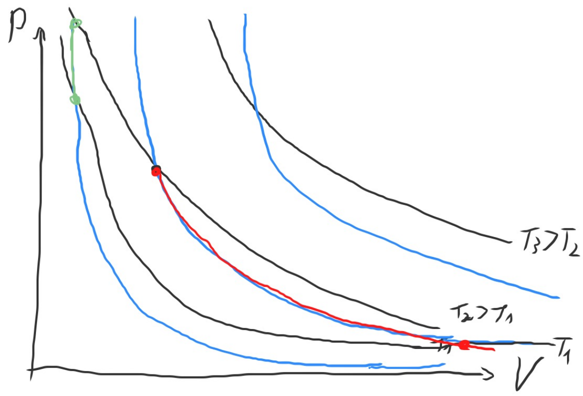
$$\frac{C_p}{C_v} = \gamma \to$$ He, Ar $\to \gamma = \frac{5}{3}$ Monoatômicos

Oxigênio
Hidrogênio $\to \gamma = \frac{7}{5}$ Diatômicos
Nitrogênio
Ar (N+O)

Por quê? $\to$ M. Estatístico
$C_p(T)$, $C_v(T) \to$ M. Quântico

Adiabáticas	X	Isotermas
$P = \frac{cte}{V^{\gamma}}$		$P = \frac{cte}{V}$
$\frac{dP}{dV} = -\gamma \frac{P}{V}$		$\frac{dP}{dV} = -\frac{P}{V}$

inclinação acentuada



Variação de Temperatura → Processo Adiabático

$p \propto \frac{T}{V}$

$$P \cdot V^{\gamma} = P_0 V_0^{\gamma}$$

$$\underbrace{(P \cdot V)}_{\propto T} V^{\gamma - 1} = \underbrace{(P_0 V_0)}_{T_0} V_0^{\gamma - 1}$$

$$T \cdot V^{\gamma-1} = cte$$

$$T = \frac{cte}{V^{\gamma - 1}} \qquad \gamma > 1$$

$T \uparrow \quad V \downarrow$

$$-dT = \frac{P}{nC_V} \cdot dV$$

Variação de Pressão

$V \propto \frac{T}{P}$

$$T \cdot V^{\gamma-1} = \left(\frac{T}{V}\right) V^{\gamma} = cte$$

$$\propto P \, / \propto \left(\frac{T}{P}\right)^{\gamma}$$

$$P \cdot \frac{T^{\gamma}}{P^{\gamma}} = \frac{T^{\gamma}}{P^{\gamma - 1}} = cte$$

$\frac{\gamma-1}{\gamma} > 0$

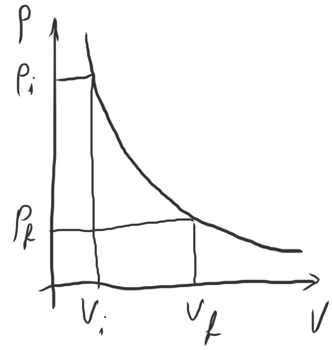
$T \propto P^{\gamma - 1/\gamma}$

$$\frac{T}{P^{\gamma-1/\gamma}} = cte$$

$T \uparrow \quad P \uparrow$

$$dT = \frac{nC_p}{V} \, dP$$

Trabalho: $pV^{\gamma} = P_i V_i^{\gamma} = P_f V_f^{\gamma}$



$$W_{i\to f} = \int_{V_i}^{V_f} p \cdot dV = D \int_{V_i}^{V_f} V^{-\gamma} dV$$

$$p \cdot V^{\gamma} = D \Rightarrow p = D \cdot V^{-\gamma}$$

$$W_{i\to f} = D\left(\frac{V^{1-\gamma}}{1-\gamma}\right)\Bigg|_{V_i}^{V_f} = \frac{V_f \cdot \boxed{\frac{D}{V_f^{\gamma}}} - V_i \cdot \frac{D}{V_i^{\gamma}}}{1-\gamma} = \frac{V_f \cdot P_f - V_i P_i}{1-\gamma}$$

$$W_{i\to f} = -\left(\frac{P_f V_f - P_i V_i}{\gamma - 1}\right)$$

$$= -\frac{(nRT_f - nRT_i)}{\frac{C_p}{C_v} - 1} = -\frac{n\cancel{R} \cdot C_v}{\underbrace{C_p - C_v}_{=\cancel{R}}} \cdot (T_f - T_i) = -nC_vT_f + nC_vT_i$$

$$W_{i\to f} = -(U_f - U_i) \quad \text{Q.E.D.}$$

Trabalho adiabático → muda a energia interna → $\Delta Q = 0$; $W_{i\to f} = -\Delta U$

Trabalho isotérmico → energia interna não varia ⇒ $\Delta Q = W_{i\to f}$

Propagação de ondas sonoras

$$v = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)}$$

$$P \cdot V^{\gamma} = cte \rightarrow P \propto \frac{1}{V^{\gamma}}$$

$$P = b \cdot \rho^{\gamma}$$

$$\frac{\partial P}{\partial \rho} = \gamma \, b \cdot \rho^{\gamma - 1} = \gamma \, \frac{b\rho^{\gamma}}{\rho} = \gamma \cdot \frac{P}{\rho}$$

$$v = \sqrt{\gamma \cdot \frac{P}{\rho}}$$