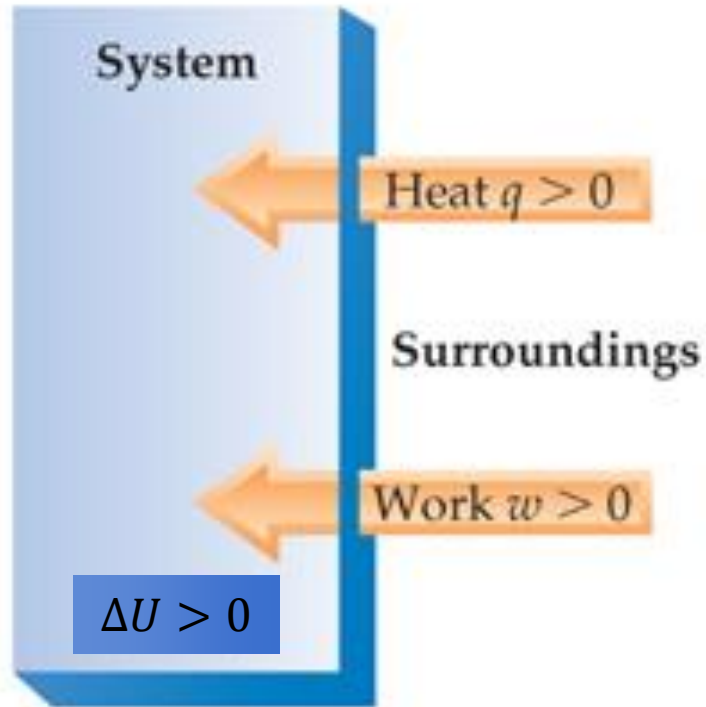


Universidade de São Paulo
Instituto de Química

Prof. Dr. Thiago C. Correra

Primeira lei da termodinâmica e a entalpia

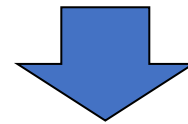
Primeira lei da termodinâmica



▲ **Figure 4.6 Sign conventions for heat and work.** Heat, q , absorbed by a system and work, w , done on a system are both positive quantities. Both increase the internal energy, E , of the system, causing ΔE , which equals $q + w$, to also be a positive quantity.

$$\Delta U = q + w$$

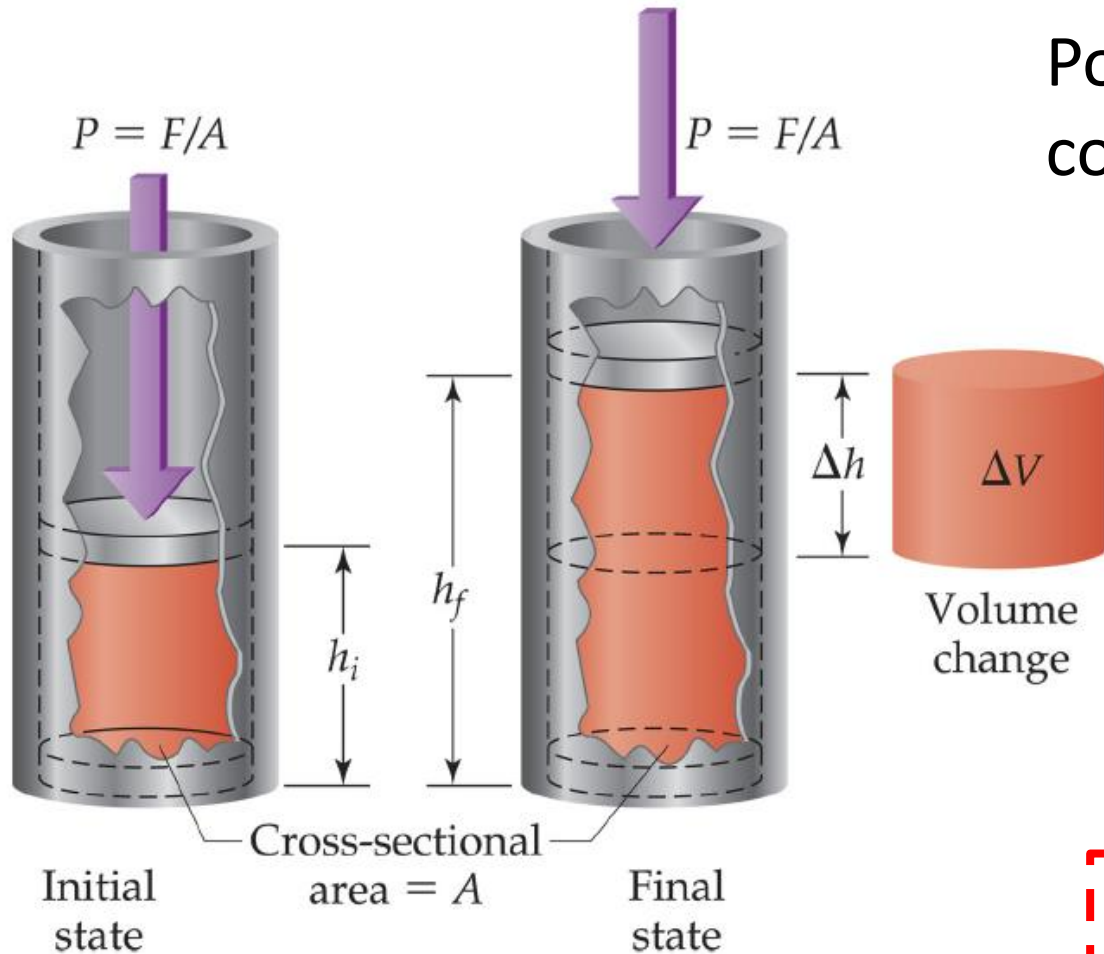
$$dU \equiv dq + dw$$



Descreve a variação de energia interna do sistema em estudo

Calculando w

Trabalho mecânico: Criado por mudança de volume



Pode ser expansão ou compressão

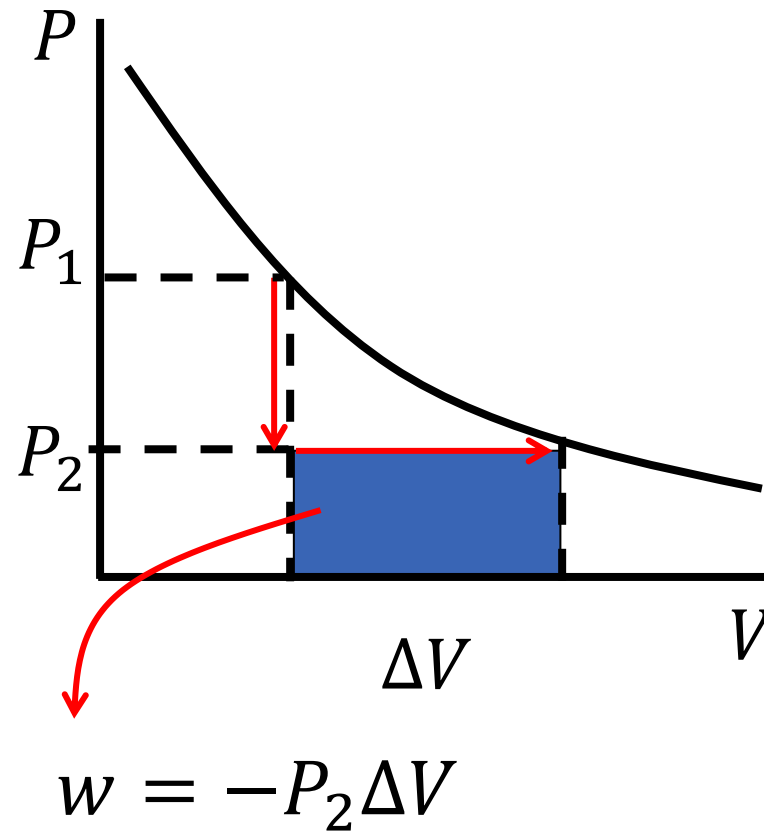
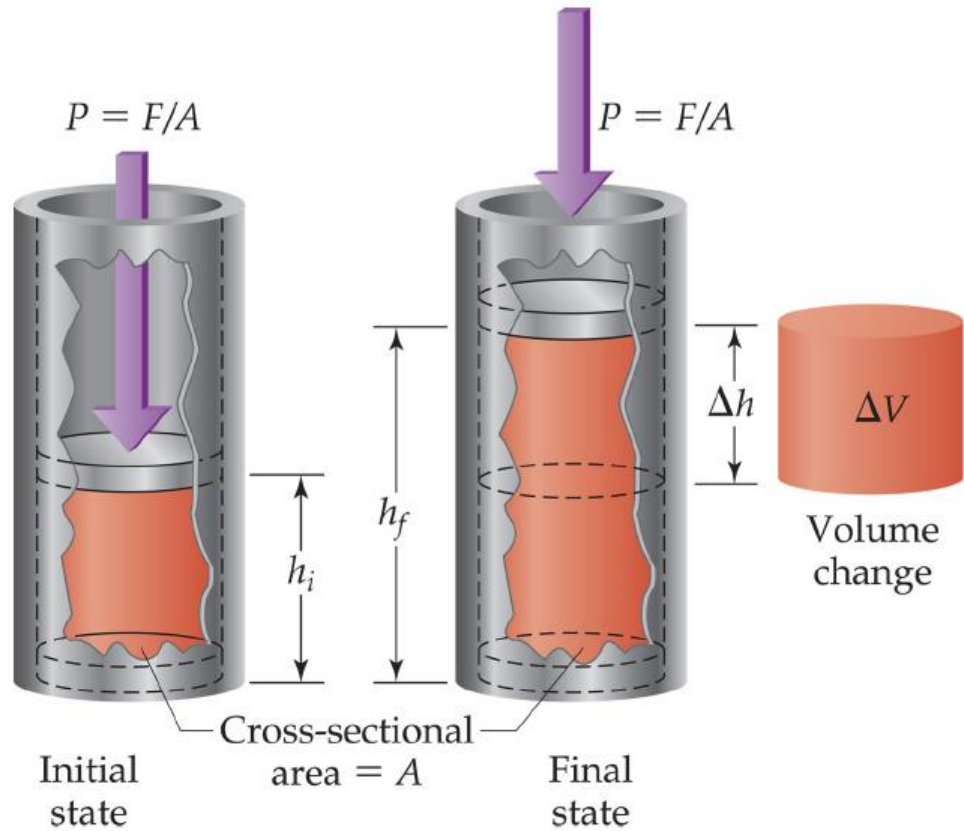
$$dw = -Fdh$$

$$F = P \cdot A$$

$$dw = -PAdh$$

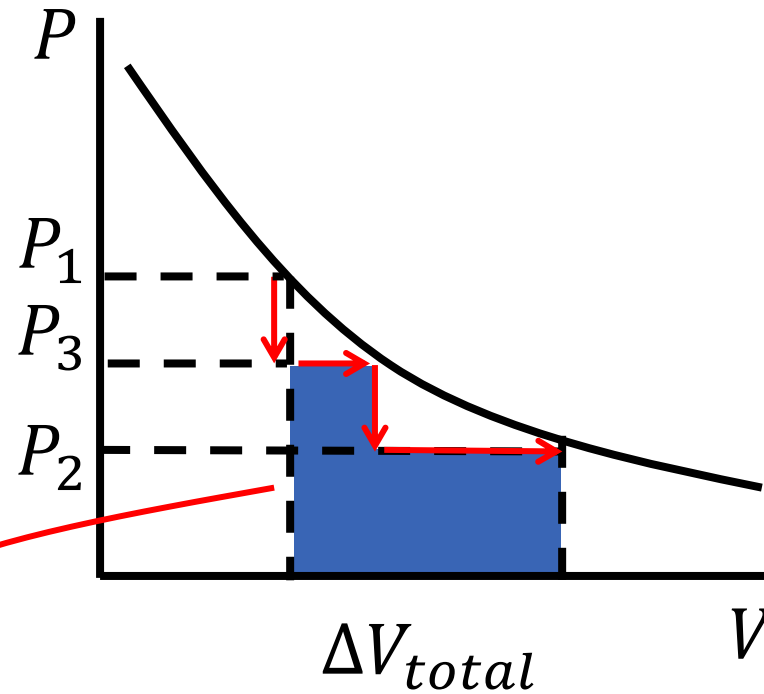
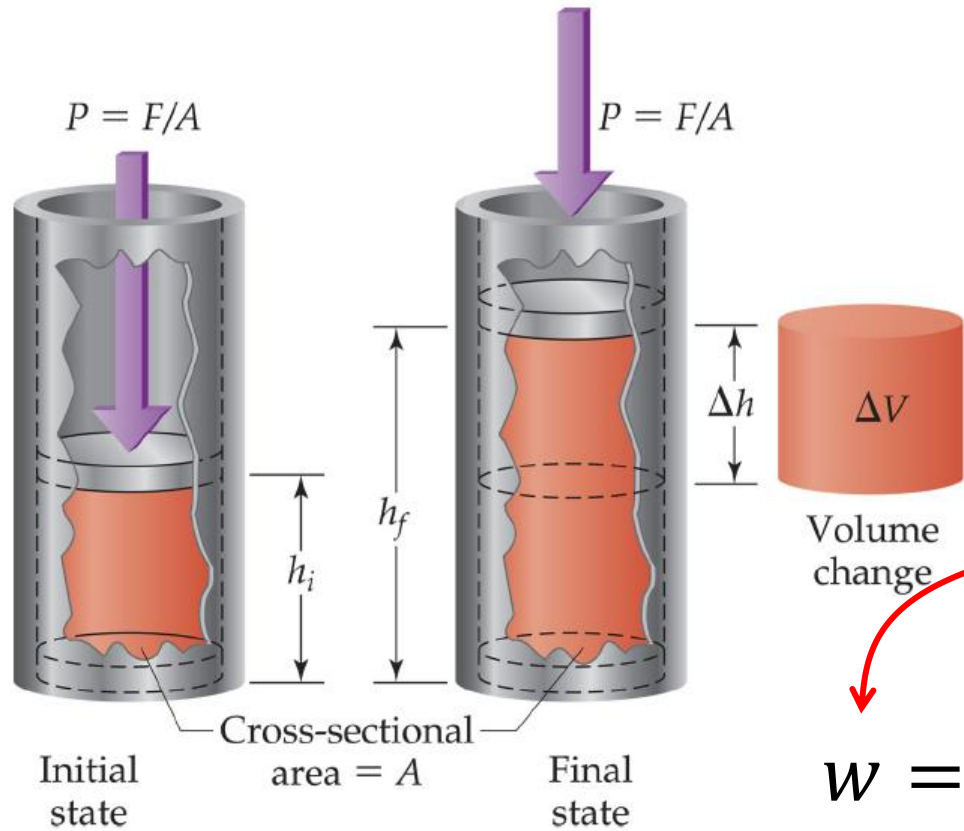
$$dw = -PdV$$

Reversibilidade



Súbita diminuição de pressão
causa a expansão

Reversibilidade

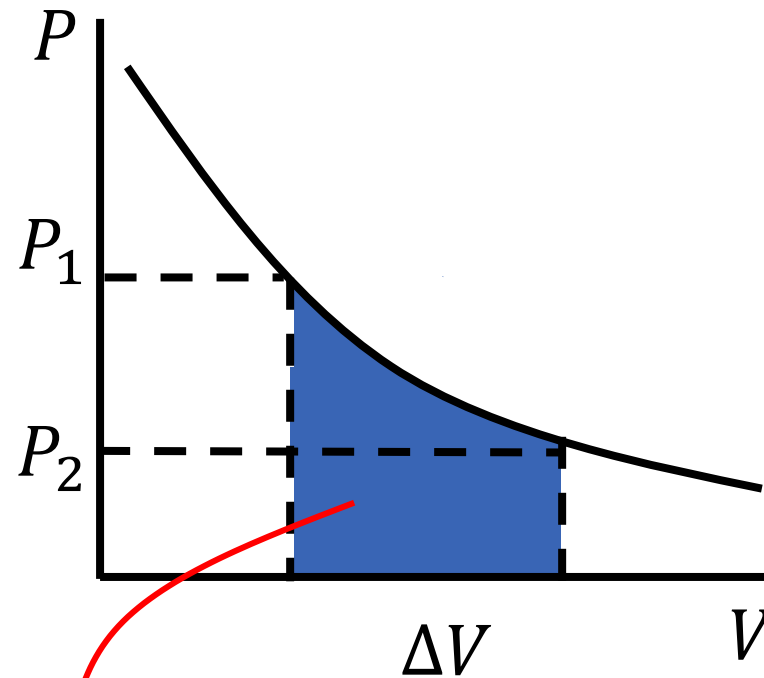
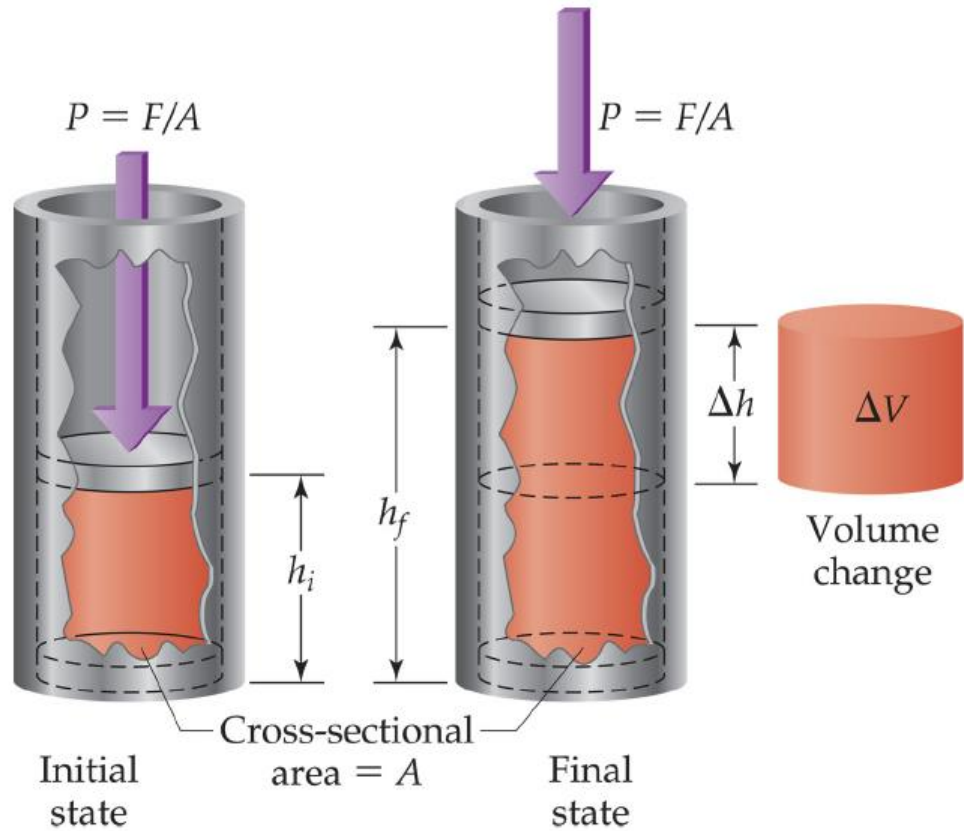


$$w = -P_2 \Delta V_{total} - \Delta P_{(3-2)} \Delta V_{(3-2)} - \dots$$

Podemos dividir em mais passos cada vez menores

$$w = - \sum_i \Delta P_i \Delta V_i$$

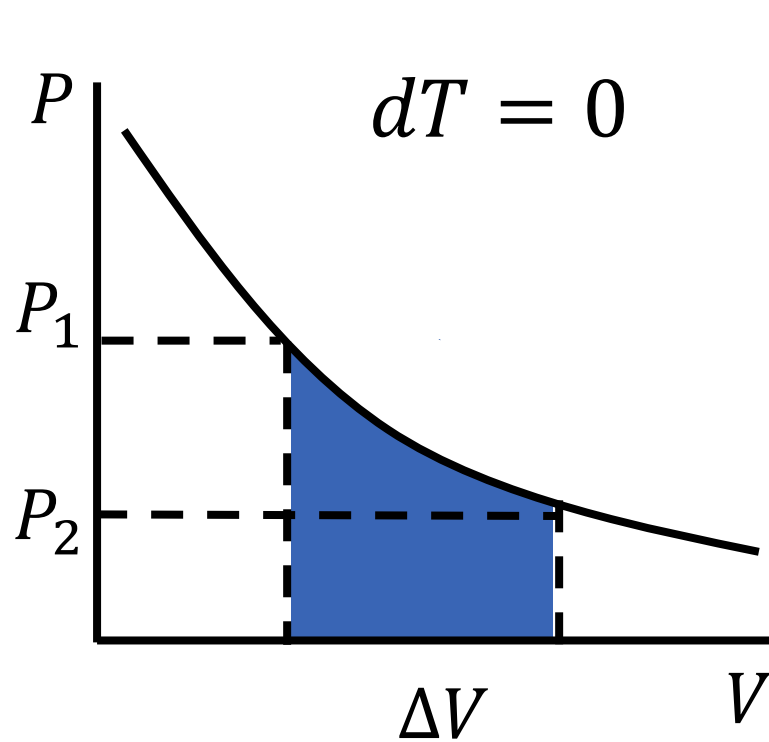
Reversibilidade



Trabalho reversível é o **trabalho máximo** realizado de forma **infinitesimal**

$$w = - \int_{V_i}^{V_f} P dV$$

Expansão isotérmica reversível



$$w = - \int_{V_i}^{V_f} P dV$$

$$PV = nRT$$

$$w = - \int_{V_i}^{V_f} nRT \frac{dV}{V}$$

$$w = -nRT \ln \frac{V_f}{V_i}$$

Calculando q

$$dU = dq + dw_{\text{expansão}} + dw_{\text{outros}}$$

Se o sistema não realiza/recebe trabalho:

$$dV = dw_{\text{exp}} = dw_{\text{outros}} = 0$$



$$dU = dq_{(V \text{ cte, sem } w \text{ adicional})}$$

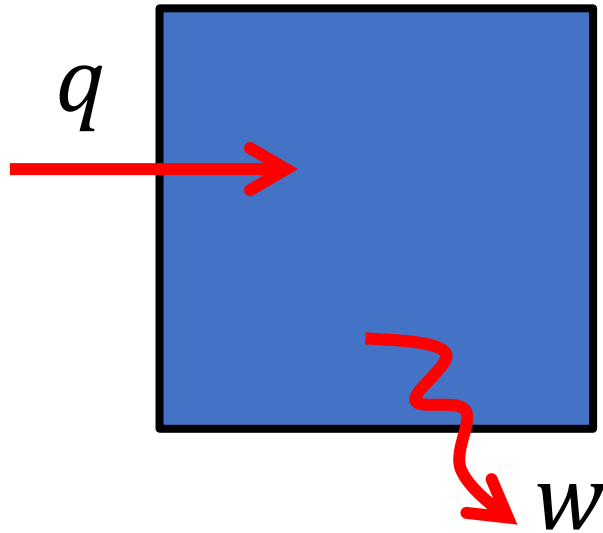


$$dU = dq_r$$

Todo calor é
convertido em
energia interna

Se o sistema pode trocar calor e trabalho

$$dU = dq + dw$$



Nem todo
 q fornecido se
converte em U

$$dq > 0, dw < 0$$

$$dU < dq$$

Energia interna não fornece o total de calor
que pode ser retirado do sistema!

Entalpia

$$H \equiv U + PV \quad \left. \vphantom{H \equiv U + PV} \right\} \text{ Função de estado}$$

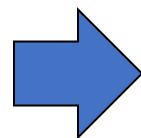
Por consequência, $dH = dq$. Vejamos:

$$dH = dU + d(PV)$$

$$dH = dq + dw + PdV + VdP$$

$$dH = dq + VdP$$

Para um sistema a P cte



$$dH = dq_P$$

Entalpia

$$H \equiv U + PV \quad \left. \vphantom{H \equiv U + PV} \right\} \text{ Função de estado}$$

$$dH = dq + VdP$$

Para um sistema a P cte $\rightarrow dH = dq_P$

Entalpia é o calor a pressão constante



Qual função termodinâmica eu devo usar? U ou H ?



Depende do seu sistema

Derivada total de U e H

$$U = f(T, V, n_1, n_2, \dots, n_k)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \\ + \left(\frac{\partial U}{\partial n_1}\right)_{T,V,n_j} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{T,V,n_j} dn_2 + \dots + \left(\frac{\partial U}{\partial n_k}\right)_{T,V,n_j} dn_k$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i}\right)_{T,V,n_j} dn_i$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_{i=1}^k U_{m_i} dn_i$$

Derivada total de U e H

Se a composição é fixa: $dn_i = 0$

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

Para H: $H = g(T, P, n_1, n_2, \dots, n_k)$

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P,n} dT + \left(\frac{\partial H}{\partial P} \right)_{T,n} dP + \sum_{i=1}^k H_{m_i} dn_i$$

Se a composição é fixa: $dn_i = 0$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

Energia interna e entalpia

$$\left. \begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$

Precisamos obter as taxas de variação parcial

Primeira lei e entalpia

$$\left. \begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$

Precisamos obter as taxas de variação parcial

$$C \equiv \frac{dq}{dT}$$

C: capacidade calorífica
Quanto uma unidade de temperatura fornecida aumenta o fluxo de calor

$$C_V$$

$$dU = dq + dw \quad \Rightarrow \quad dq = dU - dw$$

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

$$C = \frac{dq}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left\{ \left(\frac{\partial U}{\partial V}\right)_T + P \right\} \frac{dV}{dT} \times \frac{1}{dT}$$

Para usarmos U, $dV = 0$

$$C = C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_p$$

$$dH = dq + VdP \quad \Rightarrow \quad dq = dH - VdP$$

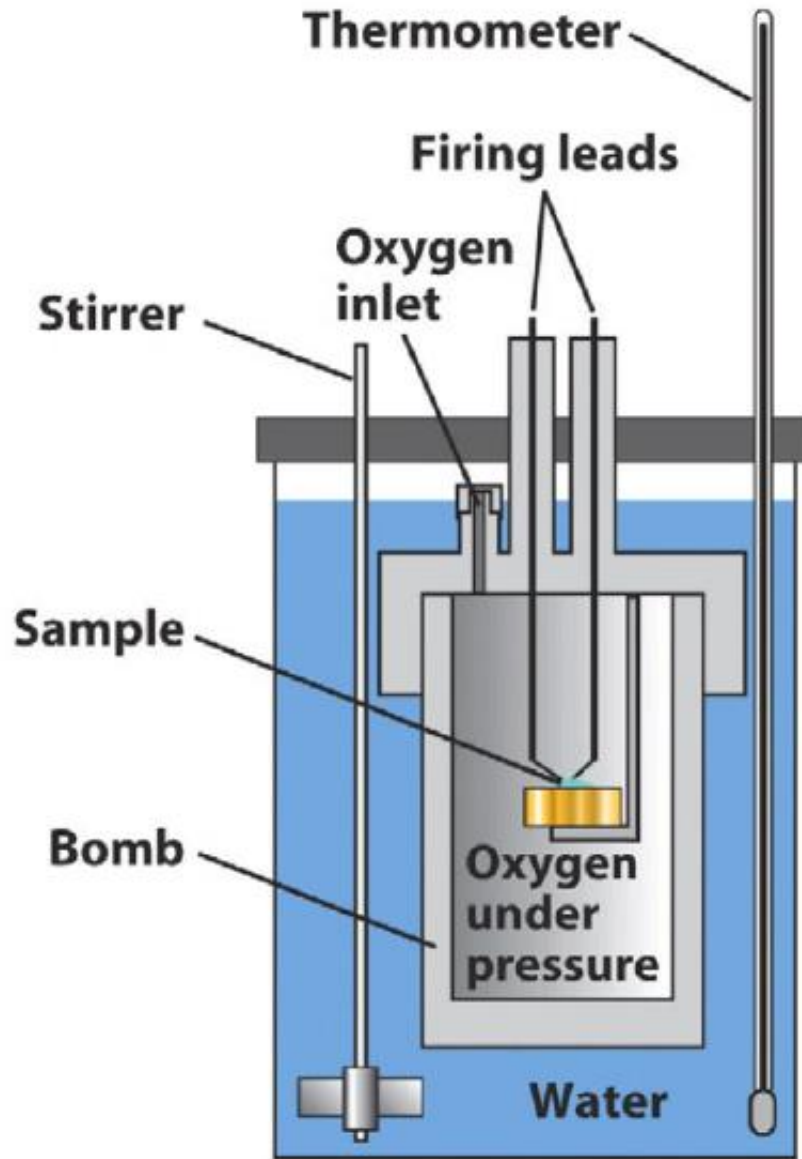
$$dq = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP - VdP$$

$$C = \frac{dq}{dT} = \left(\frac{\partial H}{\partial T} \right)_P + \left\{ \left(\frac{\partial H}{\partial P} \right)_T - V \right\} \frac{dP}{dT} \quad \times \frac{1}{dT}$$

Para usarmos H, $dP = 0$

$$C = C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Calorímetro de bomba



$$dV = 0, \Delta U = q_r$$

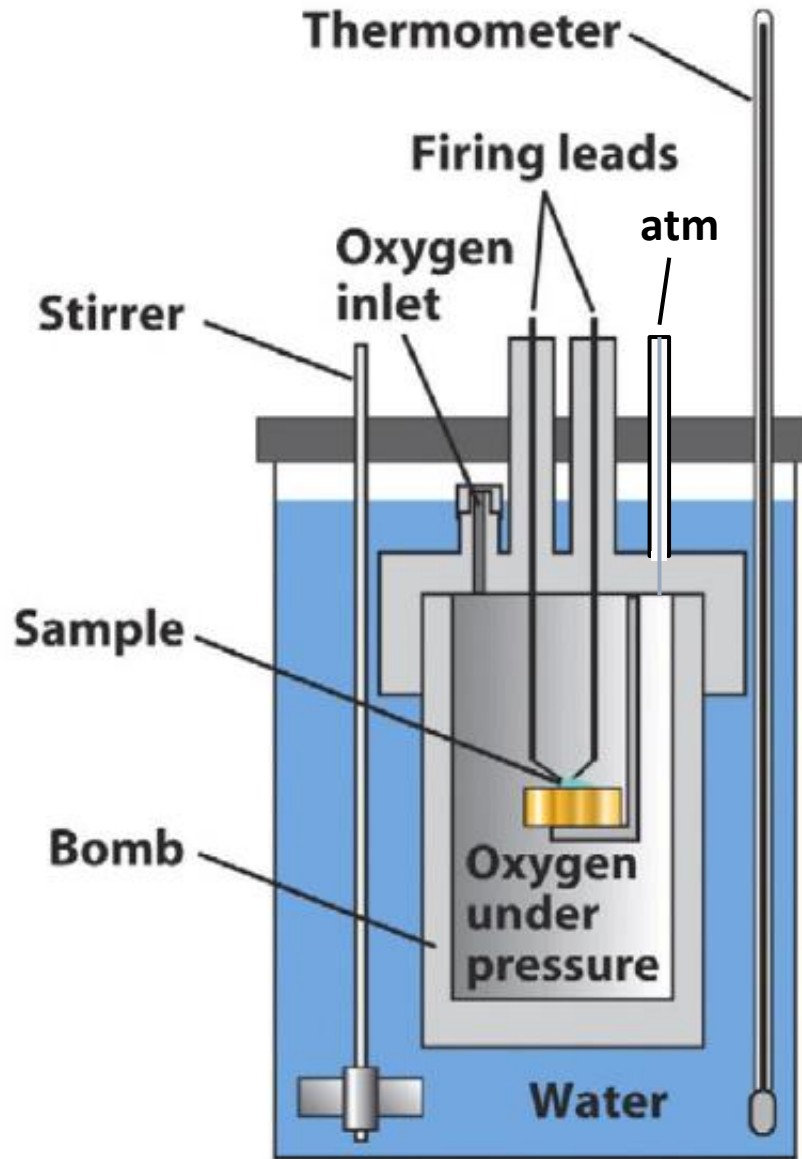
$$q_r \propto \Delta T$$

$$q_r = C_v \Delta T$$

$$\Delta U = C_v \Delta T$$

$$C_V \cong \frac{\Delta U}{\Delta T}$$

Calorímetro a pressão constante



$$dP = 0, \Delta H = q_r$$

$$q_r \propto \Delta T$$

$$q_r = C_p \Delta T$$

$$\Delta H = C_p \Delta T$$

$$C_p \cong \frac{\Delta H}{\Delta T}$$

Calor específico

$$c = C/m$$

TABLE 6.2 Specific and Molar Heat Capacities of Common Materials*

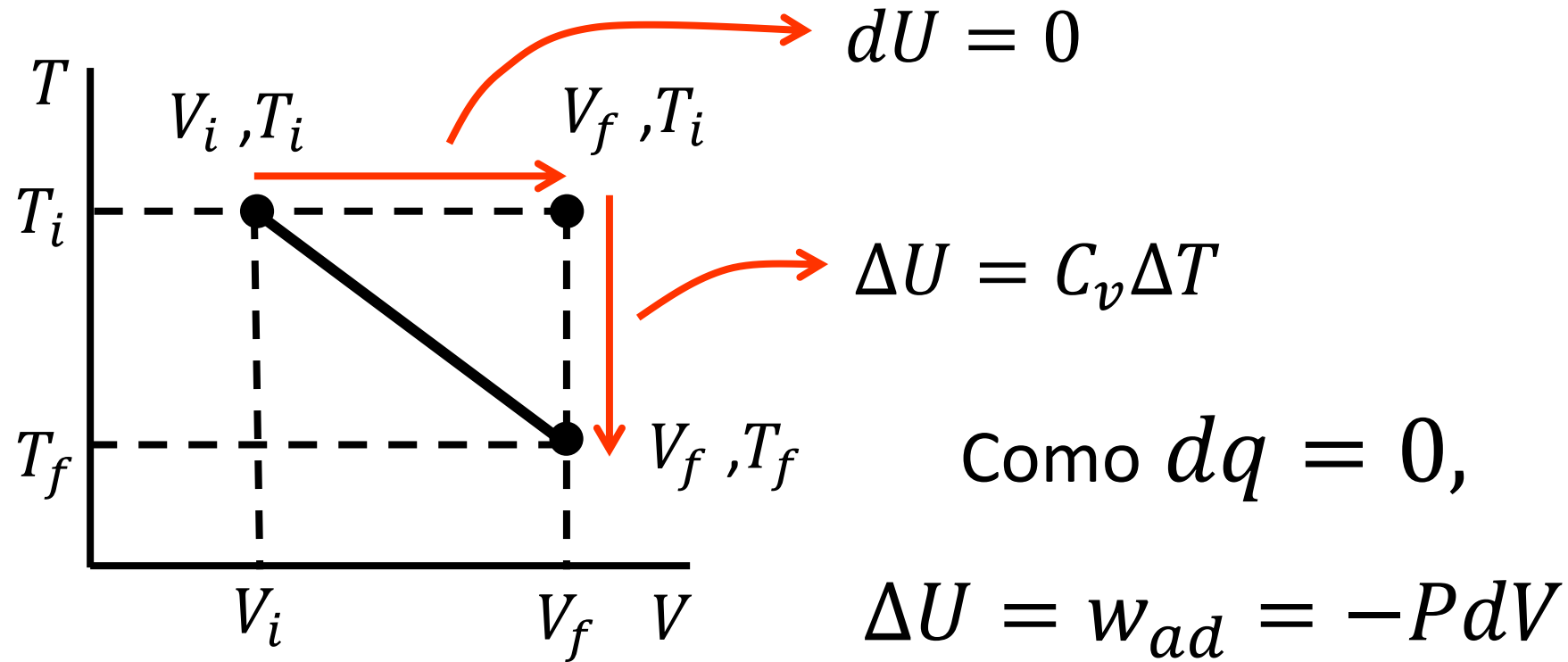
Material	Specific heat capacity (J·(°C) ⁻¹ ·g ⁻¹)	Molar heat capacity (J·K ⁻¹ ·mol ⁻¹)
air	1.01	—
benzene	1.05	136
brass	0.37	—
copper	0.38	33
ethanol	2.42	111
glass (Pyrex)	0.78	—
granite	0.80	—
marble	0.84	—
polyethylene	2.3	—
stainless steel	0.51	—
water: solid	2.03	37
liquid	4.184	75
vapor	2.01	34

*More values are available in Appendices 2A and 2D; values assume constant pressure. Specific heat capacities commonly use Celsius degrees in their units, whereas molar heat capacities commonly use kelvins. All values except that for ice are for 25°C.

$$C_p \cong \frac{\Delta H}{\Delta T}$$

$$\Delta T C_p \cong q$$

Processos adiabáticos



$$C_v dT = -PdV \quad \Rightarrow \quad \frac{C_v dT}{T} = -\frac{nRdV}{V}$$

Processos adiabáticos

$$\frac{C_v dT}{T} = -\frac{nR dV}{V} \quad \rightarrow \quad C_v \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$c \ln \left(\frac{T_f}{T_i} \right) = \ln \left(\frac{V_i}{V_f} \right), \quad c = \frac{C_{v,m}}{R} \quad T_f = T_i \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}}$$

$$W_{ad} = C_v \Delta T = C_v \left(T_i \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} - T_i \right)$$

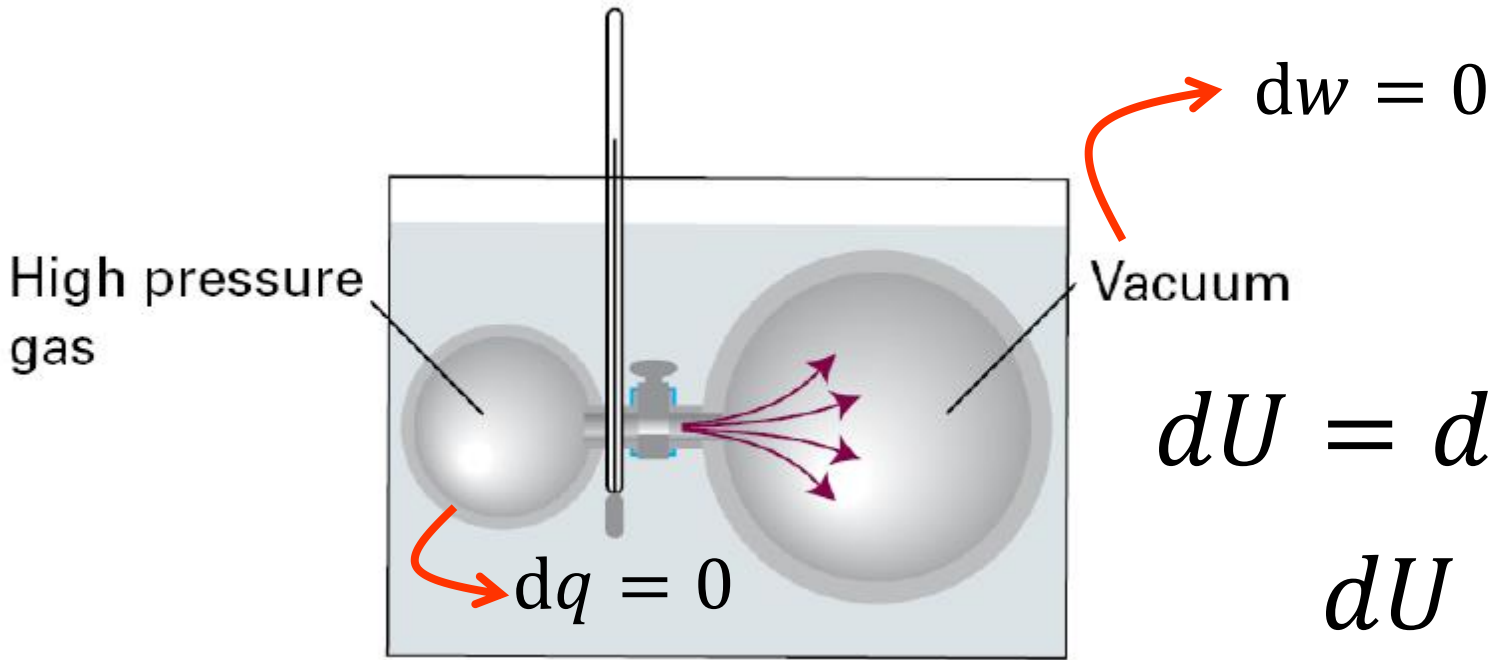
$$\Delta U = C_v T_i \left(\left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} - 1 \right)$$

Energia interna e entalpia

$$\left. \begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$

$$\left. \begin{aligned} dU &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$

Experimento de Joule



$$dU = dq + dw$$

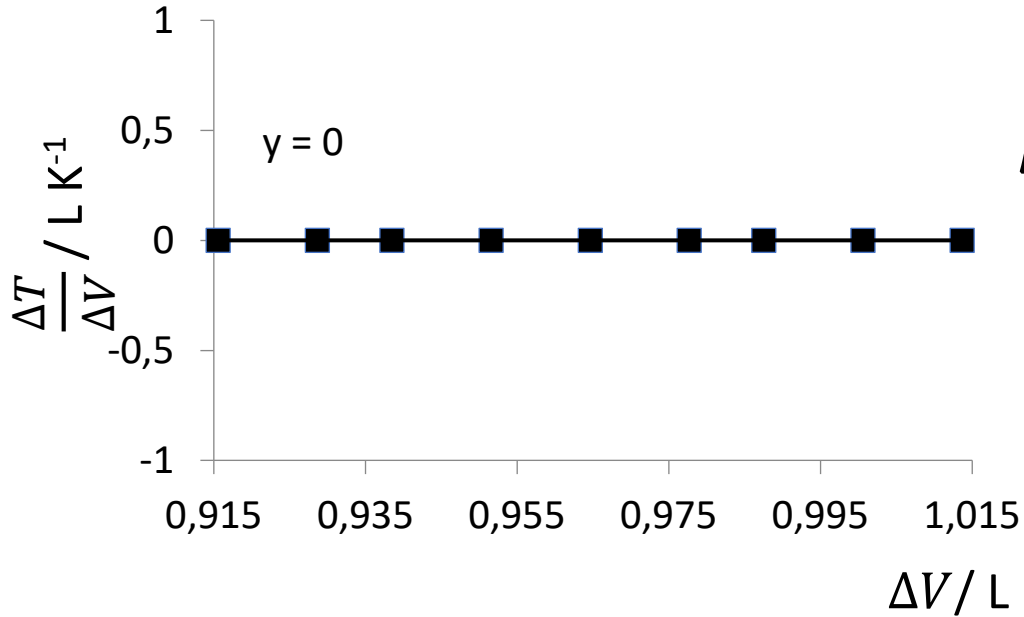
$$dU = 0$$

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad dU = 0$$

$$\left(\frac{\partial U}{\partial V} \right)_T = -C_V \left(\frac{\partial T}{\partial V} \right)_U = -C_V \mu_J$$

Coeficiente de Joule


Coeficiente de Joule



$$\mu_J = \left(\frac{\partial T}{\partial V} \right)_U = \lim_{\Delta V \rightarrow 0} \left(\frac{\Delta T}{\Delta V} \right)_U$$

$$\mu_J = 0$$

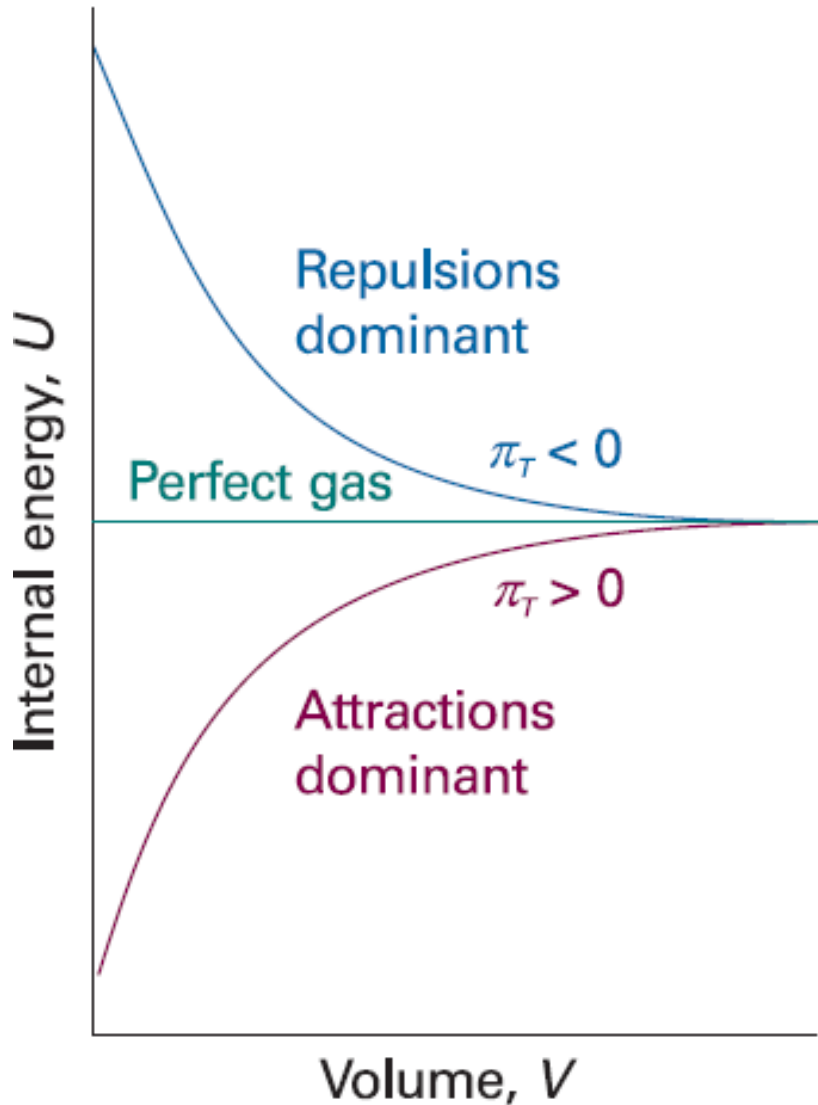
Para gás ideal

Pressão interna 

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = -C_V \mu_J$$

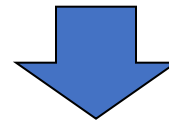
Derivada total: $dU = C_V dT - \mu_J C_V dV$

Pressão interna



$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = -C_V \mu_J$$

Gás ideal não possui interações



Energia interna não depende do volume

Energia interna e entalpia

$$\left. \begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$

$$dU = C_V dT - \mu_J C_V dV$$

$$\left. \begin{aligned} dH &= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned} \right\} dn = 0$$